

# QUALITY AND POLLUTION CONTROL TECHNOLOGIES FOR WATER, AIR, AND SOIL

GUEST EDITORS: JOSIANE NIKIEMA, EVANS M. NKHALAMBAYAUSI-CHIRWA,  
AND YVES ANDRÈS





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# **Quality and Pollution Control Technologies for Water, Air, and Soil**

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**Quality and Pollution Control Technologies  
for Water, Air, and Soil**

Guest Editors:

Josiane Nikiema, Evans M. Nkhalambayausi-Chirwa,  
and Yves Andrès



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## Editorial

# Quality and Pollution Control Technologies for Water, Air, and Soil

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This special issue presents scientific papers originating from 4 continents and addressing important environmental issues. Indeed, environment is today a major issue in several countries. New or stricter regulations on the release of several pollutants or greenhouse gases are being implemented all around the world. Consequently, the followup and control of pollutants being rejected becomes necessary.

The use of plants, microorganisms, or isolated enzymes and other biomaterials in environmental treatment is well known, but many researchers try to understand the involved mechanisms with the goal of optimizing and intensifying the efficiency of pollution removal processes. Three papers were more specifically dedicated to this area. The first paper studies the seasonal and spatial changes of microorganism communities in constructed wetlands, a community level physiological profiling analysis, proposed by Chazarenc et al. The second paper, from Nikiema and Heitz, investigates the use of inorganic packing materials during methane biofiltration. After the microbial involved processes, the third paper presents the production of ligninolytic enzymes by white-rot fungus/*Datronia* sp./KAPI0039 and their application for reactive dye removal, by Vaithanomsat et al.

The use of new or advanced processes to control water pollution with recalcitrant pollutants from various origins is also described in this special edition. The fourth paper proposes the simultaneous use of ozone and oxygen for the reduction of the chemical oxygen demand of an effluent generated by a paper processing plant (Terry). In the fifth paper, a combined AOP/Biological system is tested for the treatment of various recalcitrant organic compounds (Makgato and Chirwa). Advanced processes are also applied, in the sixth paper, to the removal of organic matter from

landfill leachate (Li et al.). Still for landfills, a study by Umar et al., assessing the pollution potential of leachate in Malaysia, is proposed (the seventh paper). In the eighth paper of Qiu et al. gives an overview of the nitrogen and phosphorous removal in municipal wastewater treatment plants in China. All these articles answer to the need to protect the integrity of natural water resources especially in this day and age when clean water is becoming scarce due to extensive pollution and urbanisation.

Accepted papers also include a study conducted by Chazarenc et al. on the movement of pollutants and global water balance of a wetland system (the ninth paper). Finally, the tenth paper was published on the efficiency of treatment of wastewater streams in power generation plants for recirculation using Koch Membranes (Jassim).

The sources of some toxic gaseous pollutants such as dioxins are presented in the eleventh paper (Wielgosinski), and methods to reduce such emission of pollutants to the atmosphere are discussed. On the other hand, the monitoring and modeling of the trends of some air pollution precursors in atmosphere are the subjects of the twelfth paper proposed by Al-Salem and Khan.

Finally, two papers focused on soil/sediments pollution, by studying the nitrate and ammonia nitrogen losses in surface runoff (Zhang et al., the thirteenth paper) and the fate of heavy-metal pollutants in sediments (Martin et al., the fourteenth paper). Overall, the fifteenth paper (Zadnik) reminds us of the importance of protecting the environment since pollution may have a detrimental effect on health.

Worldwide, the environmental market represents around \$800 billion and the global need of for environmental technologies, able to control pollution in air, water and soil,

is in continuous increase. This special edition is therefore a prominent source of reliable scientific information on environment, its protection, and the future challenges that, as a society, we should face to win the battle against air, water, and soil pollution.

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Evans M. Nkhalambayausi-Chirwa  
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## Research Article

# Seasonal and Spatial Changes of Microorganism Communities in Constructed Wetlands: A Community Level Physiological Profiling Analysis

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In constructed wetlands, microorganisms associated with plants are assumed to play a major role. A one-year survey was conducted in five vertical flow constructed wetland systems that had been operating from 2 months to 8 years in small French villages (100–500 People Equivalent) to provide a better understanding of microbiological activity. The objective of our study was to highlight the most important factor generating variability between microorganisms communities compared to treatment performances. Results of community level physiological profiling using Biolog Ecoplates were analyzed using principal component analysis. The greatest microbial activity was observed in the oldest wetland during summer. Profiles of fed and rest bed were differentiated by the nature of the main carbon source metabolized. Whereas carbohydrates and carboxylic acids appeared to be better assimilated with fed beds, it seemed that phosphate compounds as well as amines allowed better growth in the plates inoculated with samples of rest beds. In all fed beds, the most important parameters affecting the diversity were the season and the age of the wetlands. There were only slight profile differences between surface and subsurface samples and between the first and second stage samples.

## 1. Introduction

In constructed wetlands (CWs), it is widely recognized that microorganisms associated with macrophytes play a major role in pollutant removal. Over the last ten years a greater focus has been put on understanding microorganisms diversity and spatial distribution, on characterizing bacterial communities, or on monitoring microbial biomass. A large number of biochemical tools were successfully adapted to monitor microorganisms in CWs, such as epifluorescence, enzymatic activities, protein concentration, flow cytometry, fish probes, PCR, and DGGE [1–6].

In vertical flow constructed wetlands (VFCWs), pollutant removal efficiency (especially TKN removal) can be affected by several factors including season, CW age, and feeding mode (batch loads, periods of rest, etc.). Our

study aimed at verifying whether treatment performance was linked or not to microbial diversity by applying the community-level physiological profiles (CLPPs) method using Biolog EcoPlate for constructed wetlands microorganism communities. The CLPP method using microtiterplates with multiple sole-carbon sources has become a popular tool for the comparison of microbial communities with respect to their functional potential. CLPP was successfully adapted to the study of complex communities [7]. This method was shown to enable rapid assessment of variation in community structure in biological water treatment systems such as mixed liquor [8, 9] or biofilters [10, 11].

We analysed microbial diversity in five VFCWs designed to treat raw wastewater. We inoculated a total of 46 plates during two sampling campaigns. The first campaign (25 plates) was realized in February, April, June, and October

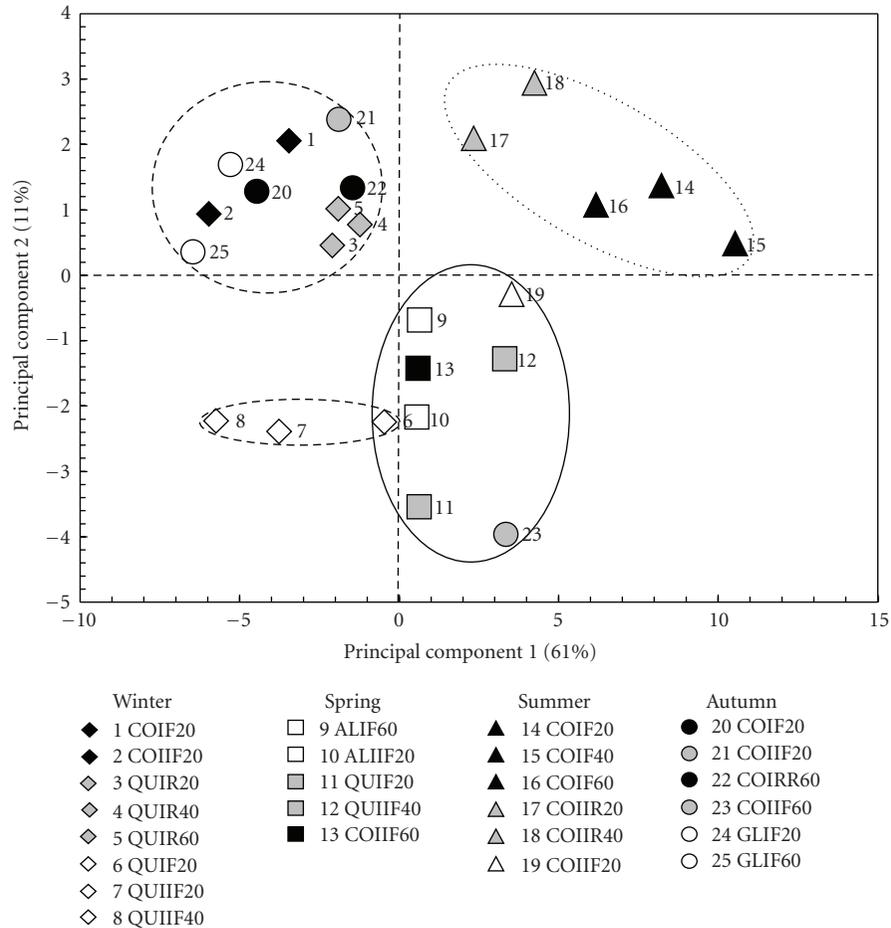


FIGURE 1: PCA of Biolog data of the first sampling campaign. A code identifies each sample: the first two letters refer to the CW name, followed by I for first stage and II for the second; we referred to the depth as 20 for 0–20 cm, 40 for 20–40, cm and 60 for 40–60; the feeding mode was expressed as F for bed fed for 3 days, R for bed in rest for 3 days, and RR for bed in rest for 8 to 10 days. For example, COIF20RR refers to Colomieu, stage I, 0–20 cm layer, in rest for 10 days.

2002 in 5 different sites and enabled to highlight season influence on bacteria community profile. The second campaign (21 plates) was performed in November 2003 in two sites to determine the vertical distribution of microbial activity in relation to CW age and feeding mode (fed and rest rotation).

## 2. Material and Methods

**2.1. Wetlands Systems.** The studied two-stage VFCWs, constructed by the Société d'Ingénieries Nature et Techniques, were designed to treat raw wastewater of small communities in the Rhone-Alpes region of France (Table 1).

Each stage was made of two to four beds fed according to 5–7 days rotation. Beds were 0.7 m. deep and planted with *Phragmites australis*. Average treatment performances observed during the two campaigns for the first stage of all VFCWs except Evieue are available in Table 2.

**2.2. Sampling, Biofilm Solution Extraction, and Biolog Methods.** For the first campaign, samples were taken at Colomieu,

Glandieu, Allèves, and Queige at four different dates, 2002 (March, April, June, October). For the second campaign, samples were taken at Colomieu and Evieue, in November 2003. A 60 cm long core, divided in three 20 cm sections, was taken at 50 cm of an inlet pipe. Between 2 and 15 grams of cores were first washed with a phosphate buffer solution ( $K_2HPO_4$ ,  $9.3 \text{ g L}^{-1}$ ;  $KH_2PO_4$   $1.8 \text{ g L}^{-1}$ ;  $\text{pH} = 7.2$ ) to separate gravel and obtain a final solution concentration having 2% w/w of extracted matter and was screened on a 5 mm filter. This method was effective in normalising the cell number density in the final inoculum for the Biolog EcoPlate. Carbon sources utilization pattern was realized using Biolog EcoPlate (Hayward, CA, USA). Each plate contains 31 of the most useful carbon sources for soil community analysis [12, 13]. Carbon sources are preloaded and dried into 96 wells (Figure 4). Tetrazolium Violet is used as a redox dye to indicate carbon sources use.

The extraction solution was diluted 20 times using phosphate buffer and vortexed for 10 minutes. Finally  $150 \mu\text{L}$  aliquots of supernatant were added in each well. After injection, EcoPlate was incubated at  $20^\circ\text{C}$  in obscurity for

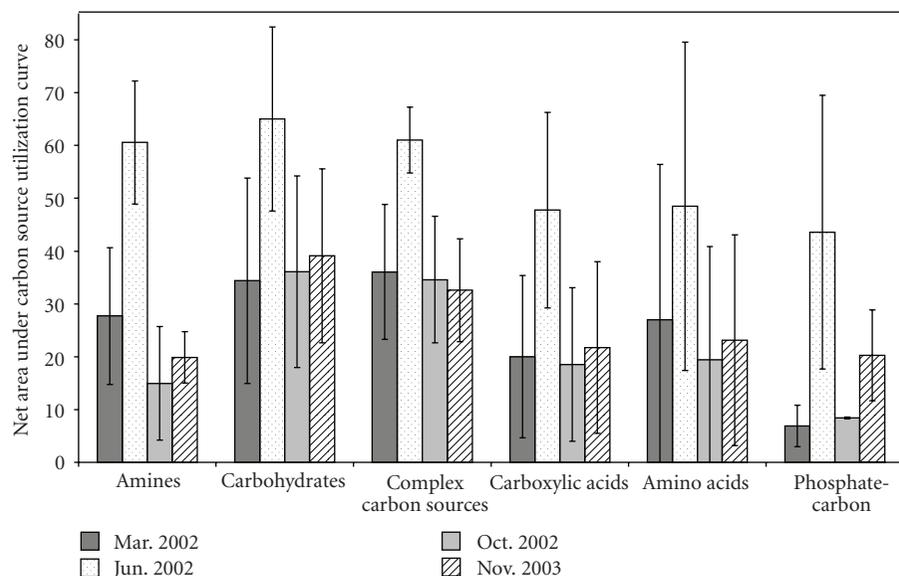


FIGURE 2: Seasonal metabolic response of samples taken in surface of the fed bed, first stage of Colomieu.

TABLE 1: VFCWs characteristics.

	Units	Glandieu	Queige	Allèves	Evieu	Colomieu
People equivalent	Pe	250	500	250	100*	200
First stage area	m <sup>2</sup>	233	850	360	—	300
Second stage area	m <sup>2</sup>	164	750	230	—	225
Initial organic load	g BOD <sub>5</sub> m <sup>-2</sup> d <sup>-1</sup>	64	32	—	—	48
Starting date	year	1999	1998	1999	2003	1993

\* Evieu was only connected to 30 Pe for almost 3 months during the sampling campaign (November 2003).

at least 72 hours, during which coloration development was measured every 12 hours using a Vmax microplate reader (Molecular Device, Sunnyvale, CA, USA). Results (31 curves/sample) were analysed by curve integration and principal component analysis (PCA) according to Guckert et al. [14] and Kaiser et al. [9]. Since the inoculum density was controlled, data were not normalized by average area on each plate thus giving an indication of the global activity. Data were also compared using grouping of carbon sources. To simplify direct comparison, 6 main categories were chosen: amines, carbohydrates, complex carbon sources, carboxylic acids, amino acids, and phosphate-carbon (Figure 4).

### 3. Results and Discussion

**3.1. Carbon Source Utilization.** Microbial communities sampled in CWs were generally able to use all of the 31 carbon sources. The most important growths were observed on L-asparagine, L-serine, lactose, mannitol, acetyl glucosamine, glycogen, and cellobiose sources. As expected, elementary sugars or polymers such as glycogen were greatly metabolised, most probably in Krebs's cycle by oxidative phosphorylation. Complex carbon source and carbohydrates provided the best growth, most probably because they are the

more energetic compounds. The smallest microbial growths were reported on carbon sources containing aromatic cycle.

**3.2. Sampling Campaign 1.** Principal component 1 accounted for 61% of total variability and was mainly associated to carbon source B1, D2, and E2 (Figure 1). Principal component 2 accounted for 11% of total variability and was mainly associated with B4, C4, F4, and H4 (amino acids). There was little influence of sampling depth and CW age, with Biolog ecoplate profiles being mainly differentiated according to season. Samples taken in warm periods (with bed having full active macrophytes) had more positive score value for the first principal component than samples taken in winter or autumn (Figure 1). Less of the variability was explained by the second principal component differentiating between age of CW (all profiles of Queige and Allèves) and most probably spring profiles compared to the others. Similarities between three distinct groups were drawn with summer profiles in dotted line, spring profiles in indented line, and winter and autumn profiles in full line (Figure 1). This pattern could be linked to a decrease in activity of several bacteria species under cold conditions. Sludge accumulation in the first stages in winter [15], by limiting infiltration rate and oxygen renewal, may also affect microbial communities environment and redox. TKN

TABLE 2: Average performances (mass removal in %) observed in the first stage of the different VFCWs (adapted from Chazarenc and Merlin, [4]).

Name	Spring-Summer (average)			Autumn-winter (average)		
	TSS	COD	N-TKN	TSS	COD	N-TKN
Allèves	95.2 ± 5.5	92.3 ± 4.5	84.2 ± 12.4	95*	83.9*	85.6*
Colomieu	96.6 ± 4.5	93,4 ± 6,4	98.4 ± 0.6	96.1 ± 2.2	92.3 ± 4.2	76.7 ± 18.5
Glandieu	99.6*	98.7*	93.3*	98.5*	95.7*	—
Queige	92.5 ± 6.9	91.0 ± 9.4	77.7 ± 26.0	90.1 ± 8.1	83.0 ± 7.9	38.3 ± 14.3

\* only one measurement available.

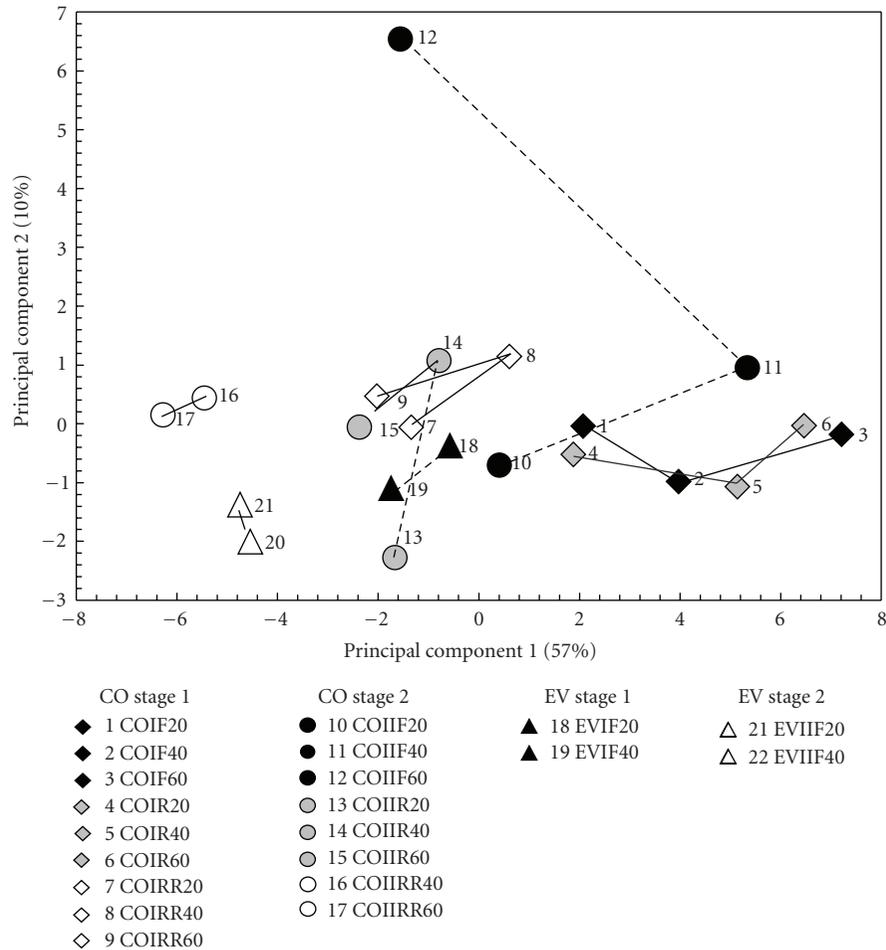


FIGURE 3: Ordination produced from PCA analysis of Biolog profile obtained during the second campaign. Samples connected with lines represent sampling from the same bed at different depths; full line: Colomieu stage 1; indented line: Colomieu stage 2; dotted line: Evieue. See legend in Figure 2 for sample codes.

removal efficiency decreased from 78% in summer to 38% in winter 2002 in Queige and from 98% to 77% in Colomieu (Table 2). To some extent, the spring group (full line in Figure 2) represented a transition between little diversified profiles (winter) and summer profiles.

Seasonal variations of bacterial community response in the upper layer of the fed bed in Colomieu illustrate well the seasonal changes observed in all samples (Figure 2). Net activities follow season temperature, with a maximum in June and lower values in late winter and autumn.

3.3. *Sampling Campaign 2.* Figure 3 shows PCA results obtained when comparing all profiles from the second sampling campaign. Principal component 1 accounted for 57% of total variability and was mainly associated to carbon source E1, F1. Principal component 2 accounted for only 10% of total variability and was mainly associated with E4, D1, and G1.

Profiles distribution along principal component 1 was mostly related to community diversity and activity. Slight differences were observed when comparing profiles for bed

Biolog EcoPlate	1	2	3	4
A	Water	$\beta$ -methyl-D-glucoside	D-galactonic acid $\gamma$ -lactone	L-arginine
B	Pyruvic acid méthyl ester	D-xylose	D-galacturonic acid	L-asparagine
C	Tween 40	i-erythritol	2-hydroxy benzoic acid	l-phenylalanine
D	Tween 80	D-mannitol	4-hydroxy benzoic acid	L-serine
E	$\alpha$ -cyclodextrin	N-acetyl-D-glucosamine	$\gamma$ -hydroxy butyric acid	L-threonine
F	Glycogen	D-glucosamic acid	Itaconic acid	Glycyl-L-glutamic acid
G	D-cellobiose	Glucose-1-phosphate	$\alpha$ -ketobutyric acid	Phenylethyl-amine
H	$\alpha$ -D-lactose	D,l- $\alpha$ -glycerol phosphate	D-malic Acid	Putrescine

	Amines		Carboxylic acids
	Carbohydrates		Amino acids
	Complex carbon sources		Phosphate-carbon

FIGURE 4: Carbon sources in Biolog EcoPlate wells. Codification matrix and groups of carbon source isolated (real configuration is in triplicate).

fed and in rest for 3 days in the first stage of Colomieu (1–3 compared to 4–6) (Figure 3). This suggests that the microbial metabolic response is very similar between the two beds and that the growing conditions (amount of nutrients, humidity, etc.) were the same after few days of rest. On the other hand, a net difference appears after 10 days of rest (7–9) (Figure 3), suggesting that microbes were less active and probably less diversified. Whereas carbohydrates and carboxylic acids appeared to be better assimilated with fed beds, it seemed that phosphate compounds as well as amines allowed better growth in the plates inoculated with samples of rest beds [16]. Thus, a change in microbial communities should also appear between fed and long-period rest beds, predicting development of different purifying mechanisms (e.g. endogenous respiration).

Because the second stages were shown to be mostly efficient for TKN removal [15], we expected more differences in microbial communities between stages. A strong difference is only apparent in the deeper profile of the second

stage in Colomieu (12) (Figure 3). This difference was also apparent in the ACP of the first campaign (23) (Figure 1). Because Colomieu is the oldest CW, accumulation of organic matter in the deeper zone of the filtration matrix, by generating a reduced environment, could explain its distinct microbial composition. Except for this difference, profiles from Evieu were comparable to those of Colomieu. However, considering principal component 1, Evieu profiles of fed beds were similar to those observed in rest for almost 10 days in Colomieu. This could be a consequence of both the very low organic load in Evieu during the sampling period (Table 1) and the absence of a well-established surface layer. This was shown to enhance biological and hydraulic activities in the oldest CW such as Colomieu [4, 15].

One can suppose that wastewater greatly contribute to microbial establishment in CW; it could have been very interesting to compare profiles of influent versus CW effluent to see and study the wetland contribution as showed by Hench et al. [17].

#### 4. Conclusion

Season was the most important parameter generating variability between bacterial community profiles. Small differences between same samples taken at different depth were observed except for the one of Colomieu 40–60 cm. Profile differences between fed beds and bed in rest for almost 10 days suggest that other degradation mechanisms such as endogenous respiration appeared over time (this could explain low sludge production in French VFCWs). Biolog Ecoplates are a quantitative tool for a simple comparison of microbial metabolic pattern in VFCWs. However care must be taken in interpreting results as the statistical analysis highlights mostly relative differences from a sample profile to another. Furthermore a wide range of bacteria such as strict anaerobic ones are not detected using microplates. Finally, this tool enabled us to see clearly differences between samples taken in the same CW and could be useful to optimize batch loading, to identify dead volumes or bypass, or to estimate dysfunction. In the future, wastewater contribution to bacteria communities should be studied.

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## Research Article

# The Use of Inorganic Packing Materials during Methane Biofiltration

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The objective behind this study is to select a suitable inorganic packing material for methane biofiltration. Three packing materials are to be compared: two rock materials (average particles' sizes: 2 and 5 mm) and one porous clay particles (average particle size of 7 mm). The main parameter used to assess the efficiency of the packing material is the methane elimination capacity. The study reveals that the rock material having an average particle size around 2 mm is to be preferred. This result is probably due to its high specific surface area and to its good surface properties as compared to the other 2 tested porous materials. The influence of the nonirrigation with the nutrient solution of the biofilter is also investigated. It has been found that nonirrigation of biofilter causes the biofilter performance to decrease significantly (e.g., 45% decrease in 1 week) even with the humidification of the gas phase prior to its introduction into the biofilter.

## 1. Introduction

Methane ( $\text{CH}_4$ ) is the most important greenhouse gas (GHG) after carbon dioxide ( $\text{CO}_2$ ). Its worldwide contribution to the greenhouse effect is estimated to 15% while for  $\text{CO}_2$ , it is 78%. Methane has a global warming potential of 21, when compared to  $\text{CO}_2$ , for a lifespan in the atmosphere of around 12 years [1]. Methane emissions are encountered in agriculture, in the energy sector, and in landfills with the latter being responsible for 25% of the total  $\text{CH}_4$  emissions in Canada. It is to be noted that around 60% of the total worldwide emissions of  $\text{CH}_4$  are of anthropogenic sources [2].

To avoid direct emissions into the atmosphere of the deleterious  $\text{CH}_4$ , biofiltration can be used. This bioprocess involves microorganisms that biodegrade the target pollutant. The interest given to biofiltration is due to its operational cost, generally considered as lower than other elimination techniques such as the flaring. For a successful operation of a biofilter, a solid phase, also called packing material, on which the microorganisms attach and then grow, is required. Nonoptimized selection of the packing

material generally yields an inefficient biological process [3] while its optimization results in lower footprint requirements.

Packing materials that may be used during  $\text{CH}_4$  biofiltration are grouped into 2 main categories: organic and inorganic materials. Organic materials include composts and soils and are generally considered by several authors as the preferred materials [4]. The main advantages of those materials are that they are easily accessible and can naturally contain methanotrophic bacteria, which exclude the necessity of an inoculation, and may result in lower start-up period (down to 1 week with compost materials and 2 weeks with soils [5]). Another advantage is that they contain nutrients, such as nitrogen and phosphorus, which are necessary for the growth of microorganisms. However, it is important to make sure that the intrinsic concentrations of the bioavailable ammonium and nitrite are minor since both compounds are known to inhibit the  $\text{CH}_4$  biodegradation [6].

Among organic materials, compost materials seem to be the most efficient, as compared to soils (this is due to the higher availability of nutrients in composts rather than

TABLE 1: Characteristics of the tested packing materials.

	PM1 (expanded clay—7 mm)	PM2 (rock—5 mm)	PM3 (rock—2 mm)
Density (kg/m <sup>3</sup> )	750	1200	2850
External specific surface area (m <sup>2</sup> packing external surface/m <sup>3</sup> of biofilter)	470	1250	1360
Void fraction in the biofilter	0.55	0.40	0.37
Water holding capacity (Vol. water/Vol. material)	0.15	0.07	0.10

in soils) [7]. Nevertheless, experiments conducted up till date with composts have revealed their tremendous limit during long-term experiments (the lifetime being in general <6 months), the suspected reasons being the compaction of the packing material, that results in an increase of the pressure drop and the apparition of channelling problems in the biofilter, and the depletion of its nutrients' content with time [8].

The inorganic packing materials have been, up till date, of minor interest during CH<sub>4</sub> biofiltration compared to the organic materials because traditionally they are not used alone. Nevertheless, some authors use them as an additive to improve the mechanical properties of organic materials, which reduces the risks of settlement during CH<sub>4</sub> biofiltration [9]. This group includes natural and manufactured materials such as rocks, ceramics, glass, polyurethane foam, and many others. When used during biological processes, they offer several advantages, such as a good mechanical resistance, as compared to organic materials. Furthermore, their physical properties (e.g., porosity, specific surface area, etc.) can be more easily adjusted according to the requirement of the bioprocess. However, their main disadvantage is that they generally do not contain any nutrient and, in some particular case, have high densities [10].

Very few experiments using these inorganic materials for CH<sub>4</sub> biofiltration, especially when there is no tricking, are presented in the literature. In the first one, reported in 1993, a synthetic material composed of glass tubes 10 mm long and with an 8 mm diameter was tested for biological CH<sub>4</sub> elimination during a biotrickling experiment. For an empty bed retention time in the biofilter of 20 minutes, a 90% CH<sub>4</sub> conversion was reached when CH<sub>4</sub> concentrations were approximately between 1.6 and 6.5 g/m<sup>3</sup> [11]. Also, crushed porous clay was used for CH<sub>4</sub> removal in an open biofilter built on a real landfill site. The CH<sub>4</sub> inlet load varied from 0 to 247 g/m<sup>3</sup>/h (median value = 9.5 g-CH<sub>4</sub>/m<sup>3</sup>/h, arithmetic mean = 19 g-CH<sub>4</sub>/m<sup>3</sup>/h) according to the natural cycle of CH<sub>4</sub> emissions within the landfill. Elimination capacities (ECs) of up to 80 g-CH<sub>4</sub>/m<sup>3</sup>/h were obtained, in spite of a possible oxygen limitation occurring in the biofilter [12]. Finally, Nikiema et al. [13] compared 2 filter materials: an organic (compost) and an inorganic material. Their study revealed that the inorganic material can give elimination capacities 2 times higher than those with the organic material (typically 36 versus 15 g/m<sup>3</sup>/h for the inorganic and the organic materials, resp., for an IL of 75 g/m<sup>3</sup>/h).

Following the previous study, the aim of the present one is therefore to continue the investigation relative to the use of inorganic packing materials in CH<sub>4</sub> biofilters as packing materials. Three commercial inorganic materials are selected and compared to find the one that appears to be the most efficient, when used as a packing material in a CH<sub>4</sub> biofilter. The selection of these 3 materials is made based on their availability. Two of these materials are rocks while the third one is porous clay. Several authors have studied the influence of the gas flow rate and of the interruption of the irrigation for biofilter treating several pollutants, such as the volatile organic compounds [14]. However, to our knowledge, only the work published by Nikiema and Heitz [15] was directly related to CH<sub>4</sub> biofiltration. To improve the knowledge of the influence of these parameters, a study has been performed and the results will be presented in the second part of this paper.

## 2. Material and Methods

The packing material 1 (PM1) is a spherical synthetic material made of expanded porous clay. It has an average particle size of around 7 mm. The packing material 2 (PM2) is a rock material having nearly a diameter of 5 mm. Packing material 3 (PM3) is a rock material having an average particle size of around 2 mm. Additional properties of these 3 materials, such as their densities, water holding capacity, external specific surface area ( $A_s$ ) (i.e., excluding the surface of the microinternal pores which are generally completely covered during the biofiltration) and calculated from a method based on Jorio [16], and void fraction in the biofilter, are available in Table 1. As a pretreatment, all materials were rinsed with water to eliminate possible impurities present at their surfaces.

The flowsheet of the up-flow biofiltration system is presented in Figure 1. Each biofilter is an assembled cylindrical tube comprised of 3 identical components, each being packed with around 33 cm in height of packing material (total height of packing material within each biofilter: around 1 m). The internal diameter of the biofilter is 0.15 m, which led to a total reactive volume around 0.018 m<sup>3</sup>. The provided CH<sub>4</sub> comes from a cylinder filled with almost pure methane (99% V/V) purchased from Praxair Inc. (Sherbrooke, Canada). To generate the polluted gas to be introduced in a biofilter, the pure CH<sub>4</sub> affluence is mixed with a prehumidified ambient air affluence (relative

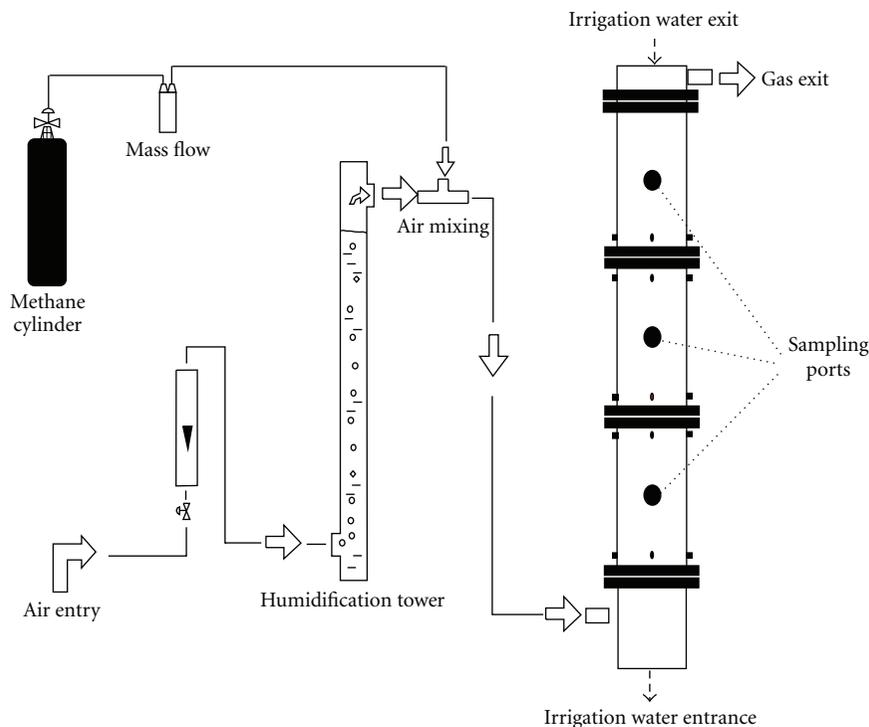


FIGURE 1: Lab-scale biofiltration system.

humidity > 90%). The obtained inlet gas mixture contained approximately  $0.7 \text{ g/m}^3$  of carbon dioxide (the same concentration as in the ambient air).

To maintain sufficient nutrient concentration and humidity in each biofilter, irrigation is performed once a day throughout the entire study with  $0.0015 \text{ m}^3$  of nutrient solution (excess irrigation liquid was collected at the base of the biofilter). The nutrient solution is a nitrate minimal salt solution and its composition was the following:  $\text{NaNO}_3$ :  $4.55 \text{ g/L}$ ;  $\text{Na}_2\text{HPO}_4$ :  $0.86 \text{ g/L}$ ;  $\text{KH}_2\text{PO}_4$ :  $0.53 \text{ g/L}$ ;  $\text{K}_2\text{SO}_4$ :  $0.17 \text{ g/L}$ ;  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ :  $0.037 \text{ g/L}$ ;  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ :  $0.007 \text{ g/L}$ ;  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ :  $0.00112 \text{ g/L}$ ;  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ :  $0.000576 \text{ g/L}$ ;  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ :  $0.000466 \text{ g/L}$ ;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ :  $0.00025 \text{ g/L}$ ;  $\text{KI}$ :  $0.000166 \text{ g/L}$ ;  $\text{H}_3\text{BO}_3$ :  $0.000124 \text{ g/L}$ ;  $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ :  $0.000096 \text{ g/L}$ ;  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ :  $0.000096 \text{ g/L}$  for 1 L of water solution.

The parameters used for the description of the results defined in Table 2 are inlet load (IL), conversion (X), elimination capacity (EC), specific elimination capacity ( $\text{EC}_{\text{sp}}$ ), and  $\text{CO}_2$  production rate ( $P_{\text{CO}_2}$ ). The follow-up of the biofilter performance, that is, concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  at the entry and exit of each stage, is achieved using two analyzers, one of total hydrocarbons from Horiba (Model FIA 510) and the other of  $\text{CO}_2$  from Siemens (Model Ultramat 22P). The pressure drop is monitored through a differential manometer (Air Flow Development Ltd., UK, type 4). A T-type thermocouple, connected to a read-out unit (Omega, model DP465), was also used, to monitor the temperature.

### 3. Results and Discussion

**3.1. Influence of the Packing Material.** Figure 2(a) represents the EC ( $\text{g/m}^3/\text{h}$ ), measured when steady state was reached in the biofilters packed with PM1, PM2, and PM3, as a function of the IL. It is to be recalled that steady state corresponds to a week period during which the variation of the EC with time, for a constant IL, is <5%. To perform the experiment, the flow rate of the polluted air introduced at the base of the biofilter is maintained at  $4.2 \text{ L/min}$  (i.e., an empty bed residence time of around 4.1 min) and the  $\text{CH}_4$  concentration used is between  $0.5$  and  $6.3 \text{ g/m}^3$  (higher  $\text{CH}_4$  concentrations could not be tested for safety reasons).

In Figure 2(a), a continuous increase of the EC with the IL is observed in all 3 packing materials. Further, the present study range highlights 2 main operation domains: firstly, a continuous linear increase of the EC with the IL when it is between 0 and  $50 \text{ g/m}^3/\text{h}$ , and then, secondly, a deceleration favouring lower levels of increase in the EC with the IL when it is superior to  $50 \text{ g/m}^3/\text{h}$ , which is confirmed by the decrease of the slope of the curve presenting the EC as a function of the IL. For example, with PM3, the slope is initially 0.70 when  $\text{IL} \leq 50 \text{ g/m}^3/\text{h}$  (i.e., diffusion limitation) and decreases to 0.35 when  $\text{IL} \geq 50 \text{ g/m}^3/\text{h}$ . This deceleration is probably a consequence of the saturation in the biomass performance (i.e., reaction limitation). The maximum  $\text{CH}_4$  EC values for this experiment, measured at a  $\text{CH}_4$  IL of around  $90 \text{ g/m}^3/\text{h}$ , are 17, 38, and  $50 \text{ g/m}^3/\text{h}$  within PM1, PM2, and PM3, respectively. This leads to the conclusion that PM3 is more

TABLE 2: Determination of the quantitative parameters.

Parameters	Methods of determination
IL: Volumetric inlet load (g/m <sup>3</sup> /h)	$IL = \frac{C_{(CH_4)in} \times Q}{V}$
X: Conversion (%)	$X = \frac{C_{(CH_4)in} - C_{(CH_4)out}}{C_{(CH_4)in}} \times 100$
EC: Elimination capacity (g/m <sup>3</sup> /h)	$EC = IL \times X$
EC <sub>sp</sub> : Specific EC (g/m <sup>2</sup> /h)	$EC_{sp} = \frac{EC}{A_s}$
P <sub>CO<sub>2</sub></sub> : Carbon dioxide production rate (g/m <sup>3</sup> /h)	$P_{CO_2} = \frac{(C_{(CO_2)out} - C_{(CO_2)in}) \times Q}{V}$

C<sub>CH<sub>4</sub></sub>: Methane concentration in g/m<sup>3</sup>; C<sub>CO<sub>2</sub></sub>: Carbon dioxide concentration in g/m<sup>3</sup>; Q = Volumetric flow rate of air mixture in m<sup>3</sup>/h; V: Biofilter volume in m<sup>3</sup>; A<sub>s</sub>: external specific surface area in m<sup>2</sup> of packing surface per m<sup>3</sup> of biofilter.

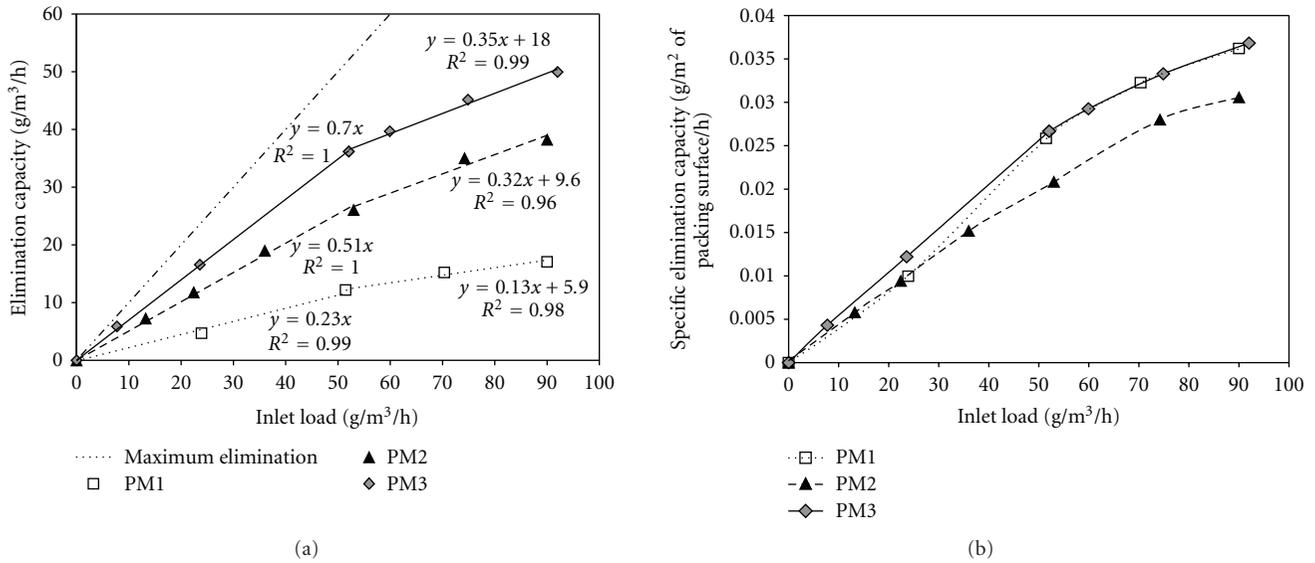


FIGURE 2: (a) EC of CH<sub>4</sub> as a function of the CH<sub>4</sub> IL for the 3 tested packing materials. (b) EC<sub>sp</sub> of CH<sub>4</sub> as a function of the CH<sub>4</sub> IL for the 3 tested packing materials.

efficient than the 2 others, at similar conditions, and seems to be an appropriate packing material for CH<sub>4</sub> biofiltration.

To explain this result, one can think of the fact that the A<sub>s</sub> values are different for the 3 packing materials (A<sub>s</sub> depends mainly on the particle size of the packing material and on its void fraction in the biofilter). For the present study, A<sub>s</sub> (PM3) is around 10% higher than A<sub>s</sub> (PM2) and 190% higher than A<sub>s</sub> (PM1). It is also commonly accepted that high A<sub>s</sub> values are favourable for pollutants' removal by biofiltration because the biofilm surface is increased, which causes an increase of the total amount of pollutant that is transferred from the gas phase to the biofilm. On the other hand, the effect of A<sub>s</sub> value on the biofilter efficiency is more and more obvious, as the IL is increased [9]. Typically, at the IL of around 90 g-CH<sub>4</sub>/m<sup>3</sup>/h (the highest IL tested for this study), EC (PM3) is 190% and 30% higher than EC (PM1) and EC (PM2) (Figure 2(a)). This means that, at this IL, the 190% higher A<sub>s</sub> value of PM3 can explain its superiority, in terms of measured EC, as compared to PM1. However, for PM2

and PM3 (differences of 10% and 30% for the A<sub>s</sub> values and the EC, resp.), there is at least one additional factor (other than A<sub>s</sub>) that also affects the packing material efficiency and accounted for 20% of the difference in the values of EC. This (or these) additional factor(s) can be related to the surface properties of packing materials.

Indeed, according to several authors, the fixation of microorganisms on a solid packing material depends on several parameters (combined herein through the appellation: surface properties), which can include the extracellular polysaccharide (EPS) production of the microorganisms, the roughness of the packing material surface, and also the charge and the hydrophobicity of both the microorganisms' cells and packing material surfaces [17–20]. Therefore, some packing materials' surfaces can appear to be more or less suitable for some methanotrophs, which would result, in the CH<sub>4</sub> biofilter, in high or low densities of biomass per unit of packing surface. Because high CH<sub>4</sub> removal efficiencies are usually associated with high biomass density (except when

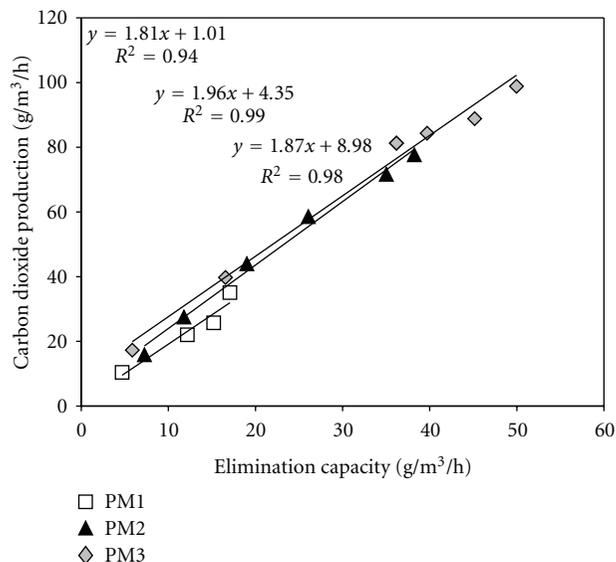


FIGURE 3: CO<sub>2</sub> production as a function of the EC of CH<sub>4</sub> in the biofilters packed with PM1, PM2, or PM3.

clogging occurs, which was not observed in our study), the surface properties of the packing material affect the overall CH<sub>4</sub> elimination process efficiency.

To determine the relative contribution of these surface properties of PM3 to its performance, the graph in Figure 2(b) has been constructed. It represents the specific elimination capacity (EC<sub>sp</sub>), expressed in g CH<sub>4</sub> eliminated per m<sup>2</sup> of packing material surface and per hour, as a function of the methane inlet load (g/m<sup>3</sup>/h) for the 3 tested packing materials. The A<sub>s</sub> remained almost constant because of the low biomass growth rates in the CH<sub>4</sub> biofilter [21]. EC<sub>sp</sub> represents the actual efficiency in CH<sub>4</sub> removal associated with a given external surface of packing materials. Since EC<sub>sp</sub> does not depend on A<sub>s</sub>, it therefore allows the comparison of the performance of the 3 packing materials in terms of their surface properties only. Consequently, high EC<sub>sp</sub> values are associated with good surface properties (favouring the attachment of active methanotrophs and the development of a biofilm).

From Figure 2(b), it appears that, for inlet load <25 g/m<sup>3</sup>/h (i.e., CH<sub>4</sub> concentrations <1.6 g/m<sup>3</sup>), the 3 packing materials are almost equivalent in terms of CH<sub>4</sub> removal per packing surface unit but, as the CH<sub>4</sub> IL increases, PM1 and PM3 reveals to be slightly better than PM2, with EC<sub>sp</sub> reaching values 20% higher than within PM2. For example, at an IL of 90 g/m<sup>3</sup>/h, one obtains EC<sub>sp</sub> of 0.036 and 0.037 g/m<sup>2</sup>/h, for PM1 and PM3, respectively, while for PM2, EC<sub>sp</sub> is 0.031 g/m<sup>2</sup>/h.

As an overall conclusion, if the EC of PM3 is superior to the EC of PM1, it should be mainly because of its high A<sub>s</sub> value. This means that if the A<sub>s</sub> of PM1 was increased (e.g., after reducing the particle size), it could theoretically perform as well as PM3. On the other hand, if PM3 is superior to PM2, it is because of both its high A<sub>s</sub> value (which contributed, in these experiments, to 1/3 of the difference in

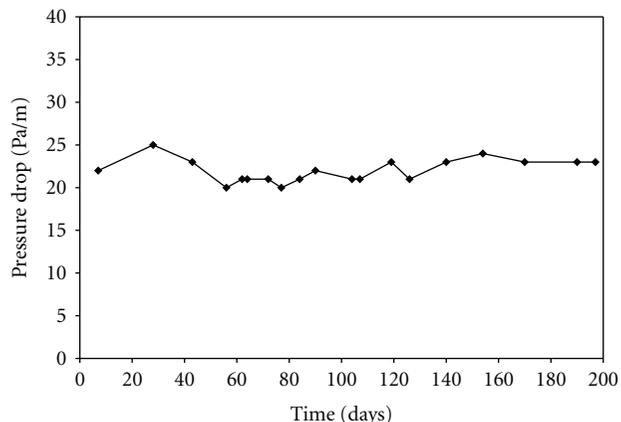


FIGURE 4: Pressure drop as a function of time in the PM3 biofilter.

EC values measured between PM3 and PM2) and its better surface properties (i.e., 2/3 of the difference in ECs observed between PM3 and PM2). Therefore, even after increasing the A<sub>s</sub> of PM2, it should, in theory, remain less efficient than PM3 because it does not have good surface properties.

Throughout this study, the total CO<sub>2</sub> production within the biofilter is monitored. In all 3 packing materials, it can be noted that both the EC and the P<sub>CO<sub>2</sub></sub> follow the same tendency. As a consequence, all trends of the P<sub>CO<sub>2</sub></sub> (g/m<sup>3</sup>/h) displayed as a function of the EC (g-CH<sub>4</sub>/m<sup>3</sup>/h) in the biofilter packed with PM1, PM2, or PM3 are linear (Figure 3). From Figure 3, it appears that 1.8 g to 2 g of CO<sub>2</sub> are produced per g of CH<sub>4</sub> eliminated by each CH<sub>4</sub> biofilter. This also means that no more than 65%–72% of the carbon in CH<sub>4</sub> is converted into CO<sub>2</sub> by the microorganisms during the biodegradation (Table 3)—the remaining part is generally used for synthesis of EPS and new biomass [22]. The biofiltration of CH<sub>4</sub> reveals therefore to be very appealing, as compared to other chemical oxidation processes since it reduces the emissions of greenhouse gas CO<sub>2</sub>. The percentages of CH<sub>4</sub> converted into CO<sub>2</sub> in this study are in the same order of magnitude than those presented in the literature, which are 70% during CH<sub>4</sub> biotrickling and 60% during biofiltration of CH<sub>4</sub> in atmospheric air [11, 23]. The fact that the CO<sub>2</sub> productions are almost similar in all 3 biofilters could suggest that their biomasses were behaving similarly (e.g., similar bacterial growth rate), but microbial analysis has not been performed to confirm this hypothesis.

Figure 4 displays the pressure drop as a function of time in the PM3 biofilter. Because of the particle bed size of PM3 (around 2 mm), as compared to the one of PM1 and PM2 (7 mm and 5 mm, resp.), a pressure drop between 20 Pa/m and 25 Pa/m, higher than the ones measured in biofilters packed with PM1 (<1 Pa/m) and PM2 (<2 Pa/m), is measured in the biofilter packed with PM3. However, there was no increase with time, over more than 6 months, of the pressure drop in all 3 biofilters. Indeed, variation of the pressure drop is usually the result of the excessive biomass growth in the biofilter, which happens not to be the case in this experiment at the tested operating conditions.

TABLE 3: Main results for the 3 tested packing materials.

	PM1 (expanded clay-7 mm)	PM2 (rock—5 mm)	PM3 (rock—2 mm)
Maximum EC ( $\text{g}/\text{m}^3/\text{h}$ )	17	38	50
EC and $P_{\text{CO}_2}$ : Similar tendencies	Yes	Yes	Yes
Average percentage of $\text{CH}_4$ converted into $\text{CO}_2$	65.8	71.2	68.0
Maximum bed temperature ( $^{\circ}\text{C}$ )	27.2	29.1	30.6
Pressure drop (Pa)	<1	<2	20–25

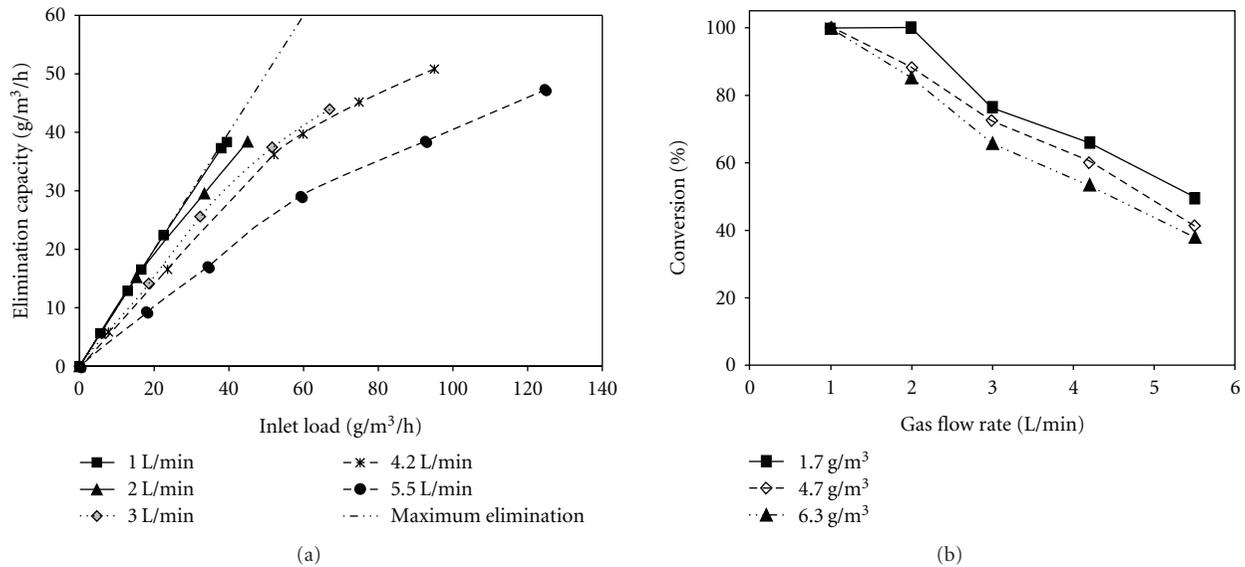


FIGURE 5: (a) EC of  $\text{CH}_4$  within the biofilter packed with PM3 as a function of the IL for GFR comprised between 1 and 5.5 L/min. (b)  $\text{CH}_4$  conversion as a function of the GFR for  $\text{CH}_4$  concentrations of 1.7, 4.7, and 6.3  $\text{g}/\text{m}^3$ .

Moreover, within the PM3-packed bed biofilter, the highest average temperature ( $30.6^{\circ}\text{C}$ ) is obtained for an IL of around  $90 \text{ g}/\text{m}^3/\text{h}$  and was between  $1.5^{\circ}\text{C}$  and  $3.4^{\circ}\text{C}$  higher than those in PM2 and PM1, respectively, under similar operating conditions (Table 3).

**3.2. Influence of the Flow Rate on Packing Material 3.** To determine the impact of gas flow rate variation on the efficiency of PM3, experiments have been conducted. Figure 5(a) shows the EC within the biofilter packed with PM3 as a function of the IL when the gas flow rate is maintained at between 1 L/min and 5.5 L/min. The  $\text{CH}_4$  concentration is generally varied between 0.9 and 6.3  $\text{g}/\text{m}^3$ , except at 1 L/min, for which higher  $\text{CH}_4$  concentrations, that is, reaching 11  $\text{g}/\text{m}^3$ , are also investigated. It is noted that gas flow rates of  $\leq 2 \text{ L}/\text{min}$  are preferable in order to obtain the highest EC. For a similar  $\text{CH}_4$  concentration, the increase of the inlet gas flow rate causes an increase in the IL values and also of the EC. On the other hand, for a similar IL, the higher the GFR is, the lower is the biofilter EC. At a gas flow of 1 L/min, the critical load is  $\geq 40 \text{ g}/\text{m}^3/\text{h}$ . It is to be noted that a similar study has been conducted previously using another inorganic packing material [15] and the same GFR operation range ( $\leq 2 \text{ L}/\text{min}$ ) was identified.

Figure 5(b) depicts, on the other hand, the  $\text{CH}_4$  conversion as a function of the GFR for 3 methane concentrations, that is, 1.7, 4.7, and 6.3  $\text{g}/\text{m}^3$ . It is confirmed from Figure 5(b) that the increase of the GFR from 1 to 5.5 L/min causes the conversion to decrease from 100% to 38%, which corresponds to a 14% decrease in the conversion after a 1 L/min increase in the GFR. For the lower methane concentration level (i.e., 1.7  $\text{g}/\text{m}^3$ ), the decrease in the conversion following the increase in the GFR begins at a GFR above 2 L/min, while for the other  $\text{CH}_4$  concentrations levels, it starts at 1 L/min. This is the consequence of the fact that inhibition occurs more easily at high  $\text{CH}_4$  concentrations than at lower  $\text{CH}_4$  concentrations.

**3.3. Influence of Interrupting Biofilter Irrigation.** Figure 6 illustrates the conversion as a function of time at a GFR of 5.5 L/min and a  $\text{CH}_4$  concentration of 2.3  $\text{g}/\text{m}^3$ . This study aims at measuring the robustness of the biofilter packed with the PM3 packing material. At day 0, the biofilter is irrigated (after measurement of the biofilter performance) and is kept in operation without additional nutrient solution until day 18. It is to be noted that the gas introduced in the biofilter was continuously humidified at a level of around 90% of relative humidity. The nonirrigation of the biofilter causes the biofilter performance to decrease with time. For

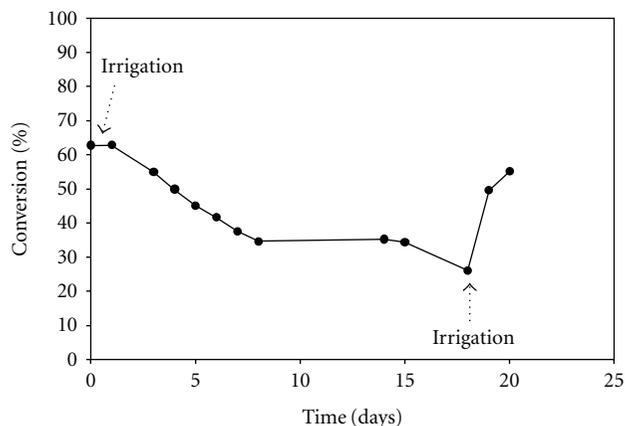


FIGURE 6: Conversion of  $\text{CH}_4$  as a function of time at a GFR of 5.5 L/min and a  $\text{CH}_4$  inlet concentration of 2.3 g/m<sup>3</sup>.

example, it takes 7 days for the conversion to decrease from 63% to 35%. After that period, the conversion of the biofilter remains almost constant for an additional week (from day 8 until day 15). In overall, after 17 days of nonirrigation, the  $\text{CH}_4$  conversion within the biofilter falls to 26% (a 60% decrease in the conversion). This decrease can be mainly attributed to the depletion of nutrients available for  $\text{CH}_4$  elimination within the  $\text{CH}_4$  biofilter. Once the irrigation is started again at day 18, a rapid recovery of the biofilter performance is noted. From day 18 to day 19, the conversion within the biofilter doubles to 50%. The day after, the conversion is only 13% lower than the normal value, that is, the one measured at days 0 and 1 (then the conversion continues to increase until reaching the value of day 0). This confirms that irrigation with a nutrient solution, in the case of inorganic packing materials, is a very important parameter for the effective elimination of  $\text{CH}_4$ .

#### 4. Conclusion

The main objective of this study was to compare 3 inorganic packing materials to identify the most efficient for  $\text{CH}_4$  biofiltration. Of these materials, PM3, the rock material having an average particle size of 2 mm appeared to be the most efficient compared to the 2 others (PM1: porous clay (~7 mm) and PM2: rock (~5 mm)). The reasons of its superiority are linked to the fact that it has the highest surface area and good "surface properties". The highest  $\text{CH}_4$  EC was around 50 g/m<sup>3</sup>/h for an IL of 90 g- $\text{CH}_4$ /m<sup>3</sup>/h. With PM3, the gas flow rate must be kept under or at 2 L/min for best performance. In such conditions, it was noted that the biofilter conversion was at least of 80% for  $\text{CH}_4$  concentrations of up to 6.3 g/m<sup>3</sup>. Also, this study revealed that irrigation of PM3 with a suitable nutrient solution is determinant for biofilter efficiency. Indeed, after 1 week without nutrient solution provision, it was noted that the  $\text{CH}_4$  conversion within the biofilter was reduced by half. With all packing materials, the carbon dioxide production followed a tendency that was similar to the one of the EC. In addition, between 1.8 g and 2 g of  $\text{CO}_2$  were generated in each biofilter per g of eliminated  $\text{CH}_4$ .

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## Research Article

# Production of Ligninolytic Enzymes by White-Rot Fungus *Datronia* sp. KAPI0039 and Their Application for Reactive Dye Removal

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This study focused on decolorization of 2 reactive dyes; Reactive Blue 19 (RBBR) and Reactive Black 5 (RB5), by selected white-rot fungus *Datronia* sp. KAPI0039. The effects of reactive dye concentration, fungal inoculum size as well as pH were studied. Samples were periodically collected for the measurement of color unit, Laccase (Lac), Manganese Peroxidase (MnP), and Lignin Peroxidase (LiP) activity. Eighty-six percent of 1,000 mg L<sup>-1</sup> RBBR decolorization was achieved by 2% (w/v) *Datronia* sp. KAPI0039 at pH 5. The highest Lac activity (759.81 UL<sup>-1</sup>) was detected in the optimal condition. For RB5, *Datronia* sp. KAPI0039 efficiently performed (88.01% decolorization) at 2% (w/v) fungal inoculum size for the reduction of 600 mg L<sup>-1</sup> RB5 under pH 5. The highest Lac activity (178.57 UL<sup>-1</sup>) was detected, whereas the activity of MnP and LiP was absent during this hour. The result, therefore, indicated that *Datronia* sp. KAPI0039 was obviously able to breakdown both reactive dyes, and Lac was considered as a major lignin-degradation enzyme in this reaction.

## 1. Introduction

Large amount of chemical dyes, approximately 10,000 different dyes and pigments per year, are used for various industrial applications such as textile and printing industries. It is estimated that about 10% are lost in industrial effluents [1]. As a result, a significant proportion of these dyes are released to the environment in wastewater. Moreover, these dyes are designed to be resistant to light, water, and oxidizing agents and therefore difficult to naturally degrade once released into aquatic systems [2]. Thus, this can cause the obstruction of sunlight pass through the water resource by synthetic dyes, then leading to the decrease in oxygen dissolved in water, the photosynthesis of water plants, and the biodegradation of organic matters. At present, the biotechnological approaches were proven to be potentially

effective in treatment of this pollution source in an eco-efficient manner [2]. The possibility to use ligninolytic fungi for the removal of synthetic dyes is one approach that attracts considerable attention. This is due to their production of ligninolytic enzymes—most frequently laccase and manganese peroxidase—that enable these microorganisms to oxidize a broad range of substrates including synthetic dyes [3].

Many reports so far have demonstrated that white-rot fungi, such as *Phanerochaete chrysosporium*, *Trametes versicolor*, *Pleurotus ostreatus*, *Ganoderma* spp., *Irpex lacteus*, *Dichomitus squalens*, and *Ischnoderma resinotum*, in Basidiomycete class, were efficiently capable of decolorization of pulping effluent and dye solution by lignin-degrading enzymes (Lignin Peroxidase (LiP), Laccase (Lac), and Manganese Peroxidase (MnP)) through the oxidation of phenolic

group in dyes [4–8]. They have been also widely researched for their ability in degradation and adsorption of dyes and some toxic chemicals such as PAHs or chlorophenol compounds [9, 10]. It was assumed that the color disappeared only after the chromophore structure of dye molecule was destroyed by many attack of lignin-degrading enzymes [11]. Attempts have still been made to screen for new strains with these capabilities. In 2006, Apiwattanapiwat et al. reported the efficiency of *Datronia* sp. KAPI0039 and *Trichaptum* sp. KAPI0025, isolated from rotten woods in Thailand, for 54.9% and 54.4% decolorization of pulp and paper mill effluent, respectively. In 2009, Chedchant et al. showed that *Datronia* sp. KAPI0039 that was cultivated on solid agar containing sawdust or rice straw released extracellular Lac and MnP. However, no research is conducted whether the decolorization capability of this strain is related to lignin-degrading enzymes. The knowledge obtained from this research is not only important to the use of enzymes or microorganisms in control either synthetic dyes removal or lignin degradation, but also to the understanding as alternatives to the conventional treatments.

The present study aimed at enhancing the knowledge of white-rot fungus *Datronia* sp. KAPI0039 involved in the bio-oxidation of different reactive dyes. To this purpose, the relationship between ligninolytic enzymes production and decolorization of reactive dye solution by *Datronia* sp. KAPI0039 was assessed. Furthermore, its degradation efficiency for azo-based and anthraquinone-based reactive was compared.

## 2. Materials and Methods

**2.1. Microorganism and Culture Conditions.** A culture of white-rot fungus, *Datronia* sp. KAPI0039, obtained from Apiwattanapiwat et al. [12], was used in this study. The fungal stock culture was maintained through periodic transfer on Potato Dextrose Agar (PDA) at 4°C until use. To prepare the inoculum, the fungus was transferred onto a fresh PDA plate and incubated at 30°C for 7 days. This was ready to be used for further experiments.

**2.2. Dyes.** The reactive dyes used in this study were obtained from DyStar Thai Company Limited in Thailand. They were Reactive Blue 19 (RBBR) and Reactive Black 5 (RB5). RBBR is a synthetic anthraquinone-based reactive dye. RB5 is a tetrasulphonated disazo reactive dye.

**2.3. Bio-Oxidation of the Reactive Dye Solution by *Datronia* sp. KAPI0039 (Adapted from [13]).** Decolorization experiments were carried out in flasks. The dye solutions were prepared with the supplement of (g/L): glucose 10.0; K<sub>2</sub>HPO<sub>4</sub> 1.0; MgSO<sub>4</sub>·7H<sub>2</sub>O 0.5; KCl 0.5; FeSO<sub>4</sub>·7H<sub>2</sub>O 0.01; NH<sub>4</sub>NO<sub>3</sub> 1.75; and pH 5.5. To prepare inocula for liquid cultures, 20 agar plugs ( $\phi$ 7 mm from the edge of a 7-day-old agar culture) of *Datronia* sp. KAPI0039 growing mycelia were inoculated into 250 mL Glucose Yeast Extract (GYE) medium and then incubated with 150 rpm shaking at 30°C for 6 days [12]. After that, they were filtered through

cheese cloth to obtain fungal pellets. The bio-oxidation experiment was carried out in 500-mL flasks containing 300 mL dye solution. These were inoculated with 2.5% (w/v) wet *Datronia* sp. fungal pellets and incubated with 150 rpm shaking at 30°C for 7 days. The color units and lignin-degrading enzymes production were monitored periodically in order to evaluate the performance of fungal cells in decolorization. All treatments were run in triplicates. The related parameters, including the concentration of reactive dyes (200, 400, 600, 800, and 1,000 mg/L), fungal inoculum size (1, 2, and 3 g), and pH (3, 5, 7, and 9) were studied.

**2.4. Enzyme Activities.** Laccase (Lac) activity was measured by monitoring the oxidation of 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) at 420 nm (molar extinction coefficient = 36,000 M<sup>-1</sup> cm<sup>-1</sup>) according to Eggert et al., 1996. One unit of laccase activity was defined as the amount of enzyme that oxidizes one 1  $\mu$ mol ABTS in 1 minute.

Lignin peroxidase (LiP) activity was measured by monitoring the oxidation of veratryl alcohol in the presence of H<sub>2</sub>O<sub>2</sub> at 310 nm (molar extinction coefficient = 9,300 M<sup>-1</sup> cm<sup>-1</sup>) according to Tien and Kirk [14]. One unit of LiP activity was defined as the amount of enzyme catalyzing the formation of 1  $\mu$ mol of veratraldehyde per minute.

Determination of Manganese peroxidase (MnP) activity using MBTH and DMAB was based on Castillo et al., 1994. MBTH and DMAB were oxidatively coupled by the action of the enzyme in the presence of added H<sub>2</sub>O<sub>2</sub> and Mn<sup>2+</sup> ions to give a purple indamine dye product. One unit of MnP activity was defined as an amount catalyzing the production of 1  $\mu$ mol of green or purple product per ml per min.

**2.5. Color Unit.** The samples were filtered through 0.45  $\mu$ m cellulose acetate membrane to remove suspended solids. The intensity of color, before and after treatment, was spectrophotometrically determined (HUCH DR/2010) at 592 nm [3].

## 3. Results and Discussion

**3.1. Activities of Lac, LiP, and MnP.** The results showed the consistent result with Chedchant et al. [15] that *Datronia* sp. KAPI0039 produced Lac and MnP but not LiP. The activity of the enzymes, however, differed significantly (data not shown). Lac was detectable in the early growth period and reached maximum (4,502.2 U/g substrate) after 4 days of cultivation. Unlikely, MnP activity was maximum (471.7 U/g substrate) after 8 day cultivations. However, none of LiP was detected.

**3.2. Biodegradation of the Reactive Dye Solution by *Datronia* sp. KAPI0039**

**3.2.1. The Effect of Reactive Dyes Concentrations.** The effects of reactive RBBR and RB5 concentrations on %decolorization, Lac and MnP activities by *Datronia* sp.

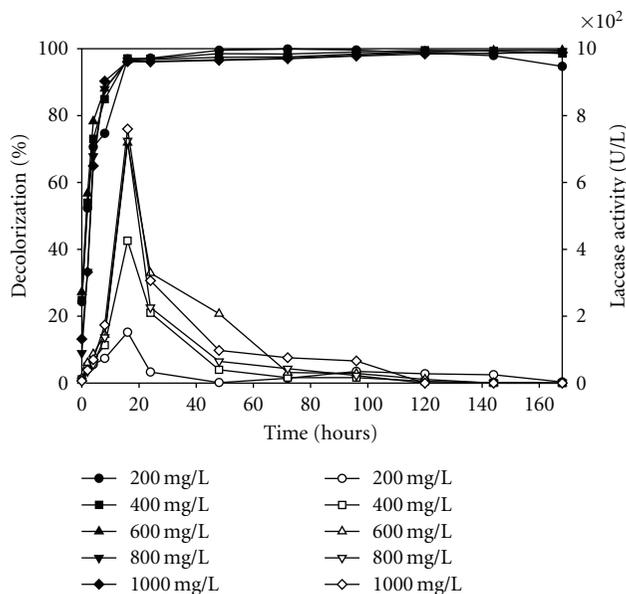


FIGURE 1: The effect of reactive RBBR dye concentrations on %decolorization and Lac activity after cultivation with *Datronia* sp. KAPI0039; close symbol = %decolorization; open symbol = Laccase activity.

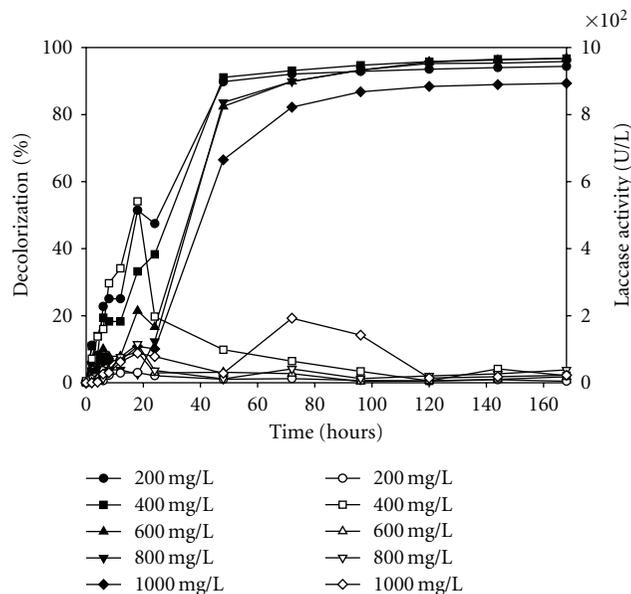


FIGURE 2: The effect of reactive RB5 dye concentrations on %decolorization and Lac activity after cultivation with *Datronia* sp. KAPI0039; close symbol = %decolorization; open symbol = Laccase activity.

KAPI0039 were experimented. Dye solutions were varied at 200, 400, 600, 800, and 1,000 mg/L concentrations. The results indicated a dramatic decrease (>90%) in color reduction of both RBBR and RB5 solutions at every concentration (Figures 1 and 2, respectively). The results (99.6% decolorization in 72 hours) also indicated the rate and extent of decolorization of RBBR compared favourably with those by other white-rot fungi such as *P. chrysosporium* (83% decolorization in 264 hours; [16]), *Bjerkandera* sp. BOS55 (65% decolorization in 480 hours; [16]), and *Trametes trogii* (85% decolorization in 72 hours; Mechichi et al., 2006 [17]). Furthermore, the result demonstrated that dye concentration did affect the time period to reach maximum decolorization for both RBBR and RB5 solutions. A general tendency was that more concentrated dye solution caused slower rate and longer time period for decolorization [11]. For example, *Datronia* sp. KAPI0039 reached maximum 99.86% color reduction from 200 mg L<sup>-1</sup> RBBR solution within only 72 hours of treatment, whereas maximum 98.87% decolorization from 1,000 mg L<sup>-1</sup> RBBR solution was achieved after 168 hours of treatment (Figure 1). This was consistent with the study by Aksu et al. (2007) [18] that the white-rot *T. versicolor* took 8 days to reach maximum 95% color reduction from 58.4 mg L<sup>-1</sup> RB5 starting solution, whereas maximum 77% color reduction from 358.6 mg L<sup>-1</sup> RB5 starting solution was achieved within 14 days. Interestingly, RBBR seemed to be degraded much better than RB5 as observed by higher %decolorization (Figures 1 and 2). Revankar and Lele [19] reported azo dyes were recalcitrant to decolorization and could be decolorized to a limited extent. However, Eichlerová et al. [20] stated that the difference between decolorization of structurally different dyes was

not easy to explain. This was because that this process required the destruction of the chromophore, thus, the slow decolorization rate of some dyes could be attributed to the complexity of their chromophores, but the overall complexity alone was not an indicator of the difficulty of decolorization of a particular dye.

During the course of dye decolorization, maximum Lac activities at 759.81 UL<sup>-1</sup> and 178.57 UL<sup>-1</sup> were detected in the fungal-treated RBBR and RB5 solutions (Figures 1 and 2, respectively). A little MnP and none of LiP activities (data not shown) was detected. The results also indicated the corresponding increase in Lac activity with an increased %decolorization, with the enzyme activity peaking at the time of maximum color reduction (16-h cultivation). Thus, only Lac seemed to be correlated with the dye decolorization as also supported by Rodríguez study [1]. Moreover, the highest Lac activity and %decolorization were obtained when 1,000 mg L<sup>-1</sup> RBBR and RB5 solutions were applied. Thus, the higher dye concentration induced more Lac production and then resulting in more decolorization [2, 3]. This could also imply that decolorization of reactive dyes partially depended on Lac activity in the liquid cultures, but not on MnP and LiP activities. In addition, Lac activity in the liquid culture with RBBR was also much higher than that with RB5 (Figures 1 and 2) even though the similar %decolorization was observed. This could be associated with the specificity of ligninolytic enzymes on different dye structures [1], thus, different dye structures led to the induction of different ligninolytic enzymes. The important role of purified LiP in color reduction of several azo-, triphenyl methane, heterocyclic, and polymeric dyes has been clearly demonstrated [1, 11, 21]. In this experiment,

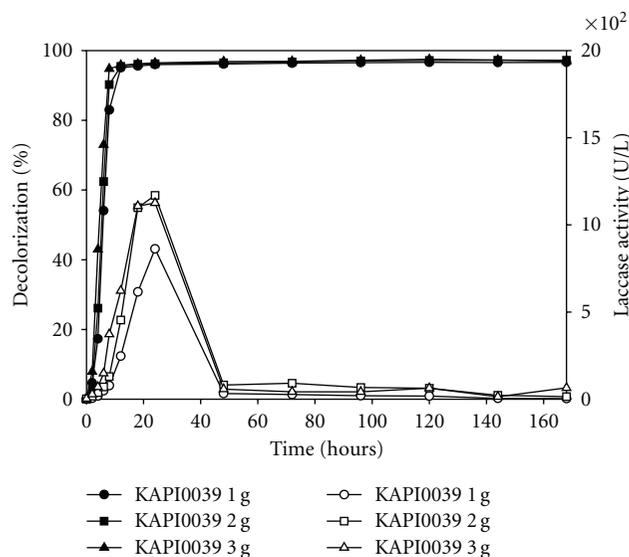


FIGURE 3: The effect of fungal inoculum size on %decolorization of RBBR dye solution and Lac activity after cultivation with *Datronia* sp. KAPI0039; close symbol = %decolorization; open symbol = Laccase activity.

none of LiP was detected, therefore, high %decolorization of RB5 solution was thought to be involved in other mechanisms. One approach was attributed to the sorption of the dye on the fungal mycelium [3, 8]. Thus, it could be assumed that the mechanism of synthetic dye degradation by *Datronia* sp. KAPI0039 was shared by the extracellular enzymes activity and biosorption on fungal cells. However, the relative contributions of ligninolytic enzymes to the decolorization of dyes might be different for each fungal strain and each dye [22].

**3.2.2. The Effect of Fungal Inoculum Size.** The effect of fungal inoculum size on %decolorization, and Lac and MnP activities by *Datronia* sp. KAPI0039 was investigated (Figures 3 and 4). The inoculum sizes used in this study were varied at 1, 2, and 3% (w/v). This strain decolorized both dyes tested, but RBBR decolorization was faster and started earlier than that of RB5. Over ninety percent of RBBR was decolorized as early as in the first 24 hours of cultivation, but only 20% of RB5 was removed within the same period and continuously removed to maximum 90% after 100 hours of cultivation. The fungal inoculum size was found to slightly affect the decolorization of both dyes. The production of Lac and MnP was also studied under the same conditions as in the decolorization experiments. The high activity of Lac was detected whereas low amount of MnP was detected. The results showed that Lac activity was affected partially by the fungal inoculum size as observed by the similar Lac activity in every fungal inoculum size used in the study. Usually, lower inoculum size requires longer time for the cells to multiply to sufficient number to utilize the substrate and produce enzyme. An increase in the inoculum size would ensure a rapid proliferation and biomass synthesis. However, after a certain limit, enzyme production could decrease because

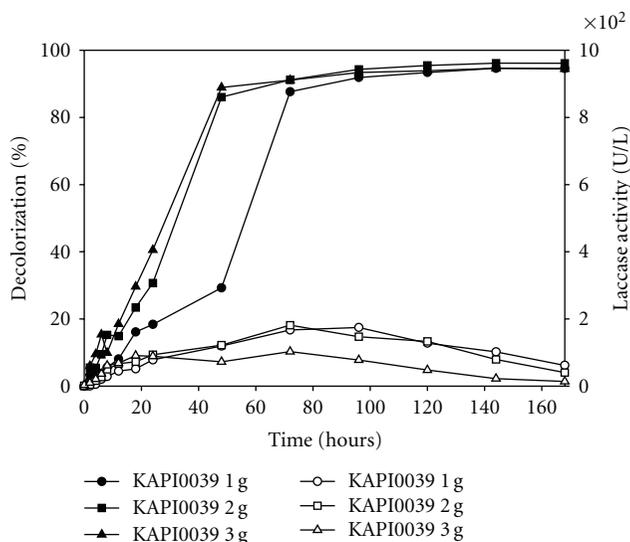


FIGURE 4: The effect of fungal inoculum size on %decolorization of RB5 dye solution and Lac activity after cultivation with *Datronia* sp. KAPI0039; close symbol = %decolorization; open symbol = Laccase activity.

of depletion of nutrients due to the enhanced biomass, which would result in a decrease in metabolic activity [23]. Furthermore, the results demonstrated direct relationship between Lac activity and dye decolorization as shown by the highest Lac activity and dye decolorization at the same period. The study of Baldrian and Šnajdr [3] was also consistent showing that RBBR was more efficiently degraded than RB5 by the litter-decomposing fungi, as well as that Lac was the major ligninolytic enzyme found in that condition.

**3.2.3. The Effect of Reaction pH.** The effect of pH on dye decolorization was investigated at 4 pH (3, 5, 7, and 9). The results were shown in Figures 5 and 6. Although the decolorization of individual dye (RBBR and RB5) was affected by pH to different extent, a better decolorization was observed for RBBR. The results also indicated that a better decolorization of RBBR was achieved under the neutral to basic conditions whereas RB5 was decolorized better under an acidic condition. This was consistent with the study by Young and Yu [11] that the azo-based dye was more effectively degraded by white-rot fungi under an acidic condition. During the decolorization experiment, the production of Lac and MnP by the fungus was determined as a function of time (Figures 5 and 6). Of the two enzymes studied, Lac activity was found in larger amount in the crude extract of both RBBR and RB5. The pH clearly affected Lac production (Figure 5). This is consistent with the research by Tavares et al. [24] that low pH values of the culture medium are not favorable for Lac production by *Trametes versicolor*. There could be 2 explanations for this: (1) either the metabolism of Lac synthesis is repressed at low pH values; or (2) conformational changes in the enzyme's three-dimensional structure are promoted by low pH, affecting the active site, not allowing biocatalytic reactions. Several

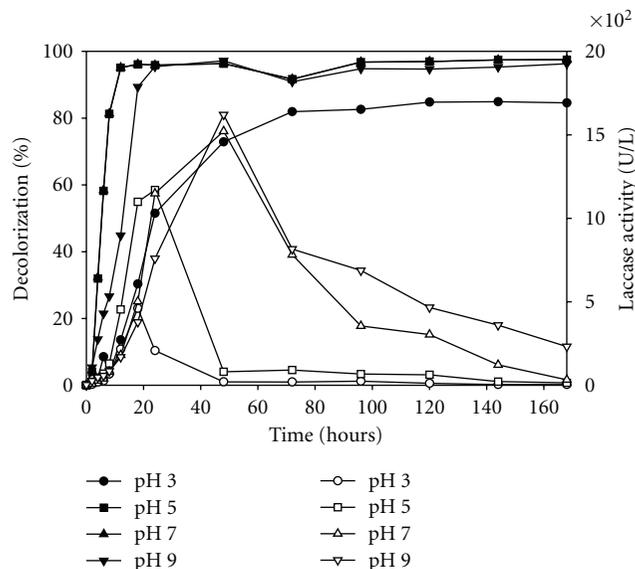


FIGURE 5: The effect of pH on %decolorization of RBBR dye solution and Lac activity after cultivation with *Datronia* sp. KAPI0039; close symbol = %decolorization; open symbol = Laccase activity.

studies also show that Lac stability was very dependent on pH and temperature. Nyanhongo et al. [25] reported that Lac stability from *T. modesta* was significantly affected by pH <4.5. Another study by Jönsson et al. [26] showed that pH less than 4 was detrimental for Lac production and suggested that a possible explanation for this was Lac's susceptibility to acidic proteases. Furthermore, the results indicated the relationship between time course of Lac production and the ability of *Datronia* sp. KAPI0039 to decolorize the two dyes.

#### 4. Conclusion

Recently, there has been a growing interest in studying the lignin-degrading enzymes with the expectation to find more effective systems for the application in various biotechnological approaches. Previous studies demonstrated the presence of ligninolytic enzymes; Lac, MnP, and LiP; in several species of white-rot fungi, especially in *P. chrysosporium* and *T. versicolor*, but none has reported those enzymes in Genus *Datronia*. This is the first evident to report the decolorization capability and the production of ligninolytic enzymes, mainly Lac and MnP, by the Genus *Datronia* in the reactive dye solution. This study supports the different extent of fungal ability to degrade synthetic dyes of diverse structures. Although high concentration of dyes might have toxic effect on fungi, it was found that even a concentration of 1,000 mg/L of reactive dyes was tolerated by the tested specie. Interestingly, none was reported for the decolorization of such high dye concentrations by any white-rot fungi, except that studied by Eichlerová et al. [20]. This study suggests the possibility to decolorize a high concentration of commercial dyes. This could be a great advance in the treatment of dye-containing wastewater and the method may have a potential application for dye decolorization, especially

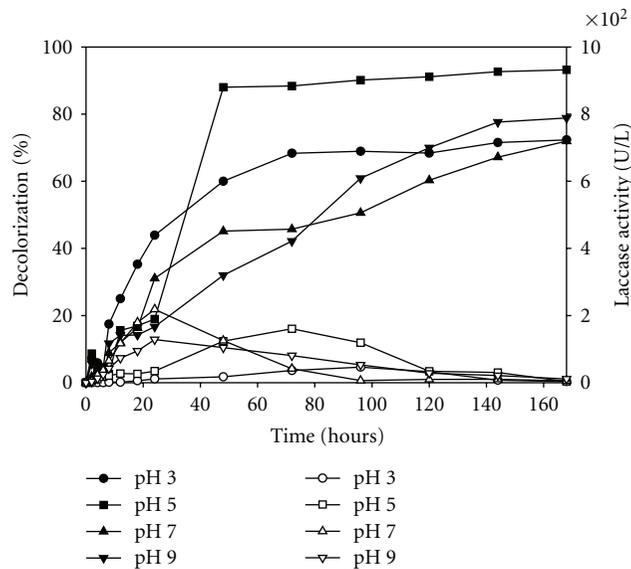


FIGURE 6: The effect of pH on %decolorization of RB5 dye solution and Lac activity after cultivation with *Datronia* sp. KAPI0039; close symbol = %decolorization; open symbol = Laccase activity.

in textile industry. The results also seem to indicate that Lac is the major ligninolytic enzymes involved in the breakdown of the dye in the solution. The crude extract from *Datronia* sp. KAPI0039 cultures showed the highest Lac activity and %decolorization. Thus, Lac from *Datronia* sp. KAPI0039 will be purified and their kinetics constants determined with ABTS, RBBR, and RB5 as substrates in order to elucidate the specificity of Lac on these reactive dye structures. Moreover, the performance of Lac on decolorization reaction should be studied *in vitro*.

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## Research Article

# Application of Ozone and Oxygen to Reduce Chemical Oxygen Demand and Hydrogen Sulfide from a Recovered Paper Processing Plant

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A pilot study was performed at the Fox River Fiber recovered paper processing company in DePere, Wisconsin, to determine the extent to which injection of oxygen and ozone could reduce the high chemical oxygen demand, COD, in the effluent and the effectiveness of the ozone/oxygen stream in suppressing production of hydrogen sulfide gas in downstream sewage lines. Adaptive Ozone Solutions, LLC, supplied the oxygen/ozone generation and injection system. Samples were analyzed both before and after oxygen/ozone injection. Hydrogen sulfide gas was continuously monitored at sewer stations downstream of Fox River Fiber. Results showed that with a very short contact time, effluent COD was reduced by over 15%. A simple kinetic model predicts that a contact time of fewer than 30 minutes could reduce COD by as much as 60%. In addition, downstream hydrogen sulfide gas production in the sewage mains was also better controlled, such that costly Biocide applications could be reduced.

## 1. Introduction and Literature Review

In a growing world, it is increasingly more necessary to treat municipal and industrial wastewaters using environmentally green technologies. Current technologies often employ man-made chemicals as the primary treatment agent, but there are growing concerns and problems associated with the residual effects of putting more chemicals in wastewater. Displacing these chemicals with economic, environmentally friendly processes offers a significant market opportunity [1].

Among primary manufacturing industries, paper manufacturing is the fourth largest user of energy and the largest generator of wastes, measured by weight. Water is the basic medium of pulp and paper manufacturing; it carries fibers through each treatment step and separates spent pulping chemicals and the complete mixture of organic residues from the pulp [2]. The process of pulp and paper processing involves production of effluent water streams with high chemical oxygen demand, COD, loads. COD is a measure of the oxygen requirement of the organic matter susceptible to oxidation by a strong chemical oxidant. It is used to define

the organic strength of industrial wastes and polluted waters. COD wastes usually are not readily biodegradable and often contain compounds that inhibit biological activity [3] in wastewater treatment facilities.

In addition, one of the challenges faced by wastewater treatment facilities is hydrogen sulfide,  $H_2S$ , gas production in sewer lines, especially in warmer weather. High biological and chemical oxygen demand loads combined with low dissolved oxygen content of sewage water and effluents from paper processing facilities create anaerobic septic conditions in sewage lines. Hydrogen sulfide gas, produced as a result of these conditions, is the most common odorous gas found in municipal wastewater collection and treatment systems. It emits a characteristic smell of rotten eggs and is both toxic to humans and corrosive to steel and concrete. Condensation moisture on the side walls and crowns of sewer pipes absorbs  $H_2S$  and oxygen from the atmosphere in the sewer and sulfur-oxidizing bacteria, *Thiobacillus*, then forms  $H_2SO_4$ . The sulfuric acid reacts with lime in concrete sewers causing crown corrosion and compromising the structural integrity of sewer lines [3, 4].

The best protection for sanitary sewers is to use corrosion resistant pipe, such as vitrified clay or plastic, but this may be economically prohibitive in large systems. In these systems crown corrosion can be retarded by ventilation to control build-up of  $H_2S$  gas. Another treatment option is Bioxide, an aqueous solution of calcium nitrate, produced by Siemens Water Technologies, Inc. Bioxide creates a biological process that both removes dissolved  $H_2S$  and prevents its formation through the addition of nitrate oxygen. It reduces sewage treatment biological oxygen demand (BOD) loads while preventing corrosion of concrete or metal collection systems. The biggest drawbacks to Bioxide is that it adds a new chemical, calcium nitrate, to a process. Because it is still under patent protection, the biggest drawback of Bioxide is its cost, which many facilities find to be prohibitive [5].

Fox River Fiber Company, FRF, is a small recovered fiber paper manufacturing facility located in DePere, Wisconsin. The process of recovering recycled paper involves deinking by either chemical or mechanical means and creating market pulp ready for conversion to paper products. The paper-making process uses on average between 10 to 19 liters of water per kilogram of product, which includes deinking and pulping chemicals, inks, coatings, adhesives, and cellulosic and lignin paper fibers.

The Green Bay Metropolitan Sewerage District (GBMSD) wastewater treatment plant recently began accepting effluent wastewater from FRF to its DePere, WI, facility. In order to control the introduction of pollutants into the sewerage system and, ultimately, its facility, GBMSD has implemented an industrial pretreatment program to regulate certain industries called Significant Industrial Users (SIUs). SIUs must comply with federal, state, and local requirements through a permit system that includes self monitoring and compliance. GBMSD also inspects SIUs annually to review operations and promote pollution prevention. FRF because of its high effluent COD levels has been designated as an SIU.

Unlike larger paper manufacturers, Fox River Fiber Company does not pretreat its effluent water prior to discharge to the GBMSD system and, hence, must pay the sewerage district to compensate for the load associated with such high COD levels. Fox River Fiber's effluent water stream has between 5000 to 6000 mg/L CODs depending on the variety of recovered paper being processed. At its current COD release level, Fox River Fiber pays GBMSD \$1.4 million per year, \$200,000 of which is fixed and \$1.2 million of which is a linear function of the plant's effluent COD level.

In addition to high COD loads, to suppress production of hydrogen sulfide gas in sewage mains, Fox River Fiber applies as much as 1710 liters per day of Bioxide to their effluent during warm summer months when  $H_2S$  production is at its worst. Lower quantities are applied during colder months. GBMSD requires that effluent from Fox River Fiber does not lead to  $H_2S$  gas levels in the air space of the downstream sewage system that exceed a maximum peak of 40 ppm and an average of 20 ppm over a twenty-four hour period. The plant's normal operating temperature is about 40° Celsius, which contributes to  $H_2S$  gas production and makes COD reduction more difficult.

Previous studies have considered applications of ozone to water treatment, but primarily as a disinfectant, where ozone's effectiveness is well documented [1, 3]. Ozone is shown to reduce cryptosporidium and control taste and odor problems in surface water treatment systems [6]. Recent studies [7, 8] investigated ozonation to increase the biodegradation of resistant textile wastewaters containing dyes and detergents. Many commercial laundering systems have used ozone successfully and its microbiological benefits have been observed [9]. Another recent study [10] summarized potential options for improvement of wastewater treatment plant effluents using ozone and integration of ozone technology to existing and conventional plants. Preozonation has also been considered to enhance the biodegradability of recalcitrant compounds prior to biological treatment of wastewater [11]. In addition, the applicability of ozone to treatment and mass reduction of wastewater sludge has been studied [12].

A pilot study was performed on the Fox River Fiber effluent to determine to what extent COD reduction could be achieved through addition of high pressure oxygen and ozone. In addition, suppression of  $H_2S$  gas production in sewage lines was monitored. The study included reduction of Bioxide application during oxygen/ozone injection. To determine the project's success, COD was monitored in the FRF's effluent before and after oxygen/ozone injection as well as dissolved oxygen (DO), pH, and temperature. Due to the pilot study's limitation that the ozone injection system be completely with Fox River Fiber's plant and that pre- and postinjection samples be drawn from within Fox River Fiber's facility, the contact time between injected ozone and wastewater stream was considerably less than optimal. Experiments were performed to model the kinetics of the oxygen COD degradation reaction and estimate the overall potential of the process for a longer contact time that would be included in a permanent system. A third oxygen/ozone experiment was conducted to quantify the effect of increasing ozone levels on COD removal. In addition,  $H_2S$  gas was monitored at several gravity sewage mains downstream of Fox River Fiber. While other effluent streams join the water flow to GBMSD, the temperature and COD load associated with Fox River Fiber's effluent make it the greatest contributor to low DO levels and  $H_2S$  gas production in sewage lines.

One potential concern with the use of high pressure ozone is that it is known to be corrosive to some gasket materials that are prevalent in water collection systems. Uni-Bell PVC Pipe Association [13] has published information on resistance of natural and synthetic rubber gasket materials to ozone exposure. A number of factors must be present before ozone degradation of synthetic rubbers forms cracks that grow and lead to material failure. First, elongation must be present for crack formation. Unstretched rubber reacts with ozone until all of the surface double bonds are consumed, and then the reaction ceases. In the process, a gray film, or frosting, appears on the surface of the rubber, but no cracks form. Ozone will continue to react with rubber only if the surface of ozonized products is moved aside to expose underlying unsaturation. Consequently, cracks only form and grow if the rubber is stretched to expose underlying unsaturation.

Because rubber gaskets in service are under a compressive load, they do not experience elongation and, hence, it is not likely that they will degrade via ozone attack past the initial inner surface of the gasket that contacts the ozonated water. The gray film, or frosting, associated with surface attack should appear, but the compressive forces holding the gasket in place should prevent the critical elongation required to expose underlying saturation. Selection of an EPDM, neoprene or Viton gasket material will also protect against loss of service due to gasket failure [14–16].

## 2. Experimental Methods and Results

Adaptive Ozone Solutions, AO<sub>3</sub>, LLC, designed and installed the ozone system used in all pilot studies and experiments. The company, located in Lenexa, Kansas, manufactures and sells oxygen and ozone systems for municipal and industrial applications. Their patented technology uses electrochemical cells to generate ozone and supplies concentrated oxygen and ozone feed streams to wastewaters via aerosol diffusers.

Dissolved oxygen, pH, and temperature were measured using a Hach HQ40d Intellical™ portable field kit. COD was measured using Hach standard method 8000 photometric analysis with a Hach DRD200 reactor, Hach DR890 colorimeter, and Hach high range (0 to 15,000 ppm) plus reagent tubes. All tests were performed in triplicate with averages presented. Dissolved ozone concentration was measured with a model Q45H portable dissolved ozone analyzer from Analytical Technology, Inc. The analyzer has capability to measure dissolved ozone in the low range of 0–200 ppb and also the range of 0–2 ppm, typical of water bottling or municipal water treatment applications.

**2.1. Ozone Corrosivity.** Because of the potentially corrosive nature of ozone to synthetic rubber gasket materials, tests were performed to determine how long after injection into a pipe system ozone maintains a residual. A model experimental apparatus was constructed at the Green Bay Metropolitan Sewerage District, Green Bay, Wisconsin, to measure ozone residual following injection into a stream of incoming wastewater. The system consisted of an ozone generator, ozone diffuser, and four inch PVC piping system designed by Adaptive Ozone Solutions, LLC. The generator fed ozone in an oxygen stream into the system at a rate of 18 grams/hour ozone. To measure ozone residual, nine test ports were installed into the piping system. Each of these was connected to a dissolved ozone monitor and cell. The sample ports were located at 1.5, 4.5, 10.7, 16.8, 22.9, 29.0, 50.3, 53.3, and 59.4 meters, respectively, from the diffuser.

Wastewater flow through the system was 76 liters/minute. Ozone measurements taken at the first sample port, 1.5 meters from injection, showed no residual ozone. Tests were performed multiple times to verify the zero reading. The same was the case for all downstream sample ports. For 9-centimeter outer diameter PVC pipe, a 76 liter/minute flow gives a water velocity of about 17.7 cm/second and a residence time of 8.6 seconds to reach the 1.5 meter sample port. Therefore, the ozone residual in the water was less

TABLE 1: Pre- and post-O<sub>2</sub>/O<sub>3</sub> injection measurements (O<sub>3</sub> loading rate of 0.053 g/min/liter water and O<sub>2</sub> loading rate of 0.53 g/min/liter water).

	Temperature (°C)	pH	DO (mg/L)	COD (mg/L)	Standard deviation
Pre injection	40.6	7.47	0.12	5244	352
Postinjection	40.8	7.31	18.56	4422	256

than 8.6 seconds. This is similar to a result found by a study of ozone disinfection of water [1] who measured ozone residuals following disinfection with contact times of 10, 18, 50, and 93 seconds and found that, in some cases, ozone residual decayed too rapidly to be measurable.

**2.2. Effect of Ozone and Oxygen on COD Effluent from Fox River Fiber.** For seven weeks during June through July 2009, an AO<sub>3</sub> installed ozone generator injected 4 grams/minute of ozone, in addition to high pressure oxygen, into the approximately 76 liters/min effluent water stream of Fox River Fiber Paper Company. The ozone loading rate was 0.053 grams/min/liter water and that for oxygen was 0.53 grams/min/liter water. During this time, Bioxide addition was reduced incrementally from its peak application rate of 1520 liters per day to 1330 liters per day, 950 liters per day, and finally 570 liters per day. Dissolved oxygen, pH, temperature, and COD were measured both at a sample point upstream of the injection point and one downstream of the injection point, but prior to entering the GBMSD sewage lines. Process limitations required that the post-ozone injection sampling point be located within the plant, such that the contact time of the oxygen/ozone stream in the system prior to the second sample point was limited to approximately two minutes. Table 1 shows the pre- and postinjection point averages for triplicate samples collected bi-weekly during the nine week pilot run.

COD in Fox River Fiber's effluent averaged 5244 mg/L, while that post-oxygen/ozone injection averaged 4422 mg/L for an average reduction of 15.7%. The water pH was not significantly affected by addition of oxygen/ozone. While Bioxide addition rates were reduced during this period, COD measurements were not affected by these changes. Because of the chemicals used in the recovered paper manufacturing process, plant effluent DO was very low, but Adaptive Ozone Solution, LLC's, generator raised values to approximately 25 mg/L at the injection point and almost 20 mg/L as measured at the second sample point. Based on an average 15.7% reduction in COD and a linear relationship between the \$1.2 million per year payment made to GBMSD for excessive COD, AO<sub>3</sub>'s system could save Fox River Fiber \$188,400 per year.

**2.3. Kinetic Study.** Because of the limitations associated with the existing piping system at Fox River Fiber, the previous COD and DO measurements were taken after a contact time of only approximately two minutes. Given an almost 16% reduction in COD for such a short reaction time,

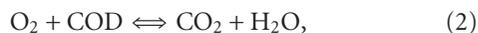
FIGURE 1: O<sub>3</sub>/O<sub>2</sub> aerosol bubble injection contact chamber.TABLE 2: Kinetics of first-order reaction with  $k = 0.12/\text{min}$ .

Time (min)	$C/C_o$	% Unreacted O <sub>2</sub>
1	0.89	89%
2	0.79	79%
5	0.55	55%
10	0.30	30%
20	0.09	9%

experiments were performed to estimate the kinetics of the reaction of oxygen with COD waste and, hence, estimate the effectiveness of oxygen and ozone to continue to reduce COD in Fox River Fiber's effluent. Dissolved oxygen was measured as a function of time in postinjection samples to estimate how rapidly oxygen is consumed by COD waste. First-order kinetics

$$\ln\left(\frac{C}{C_o}\right) = -kt, \quad (1)$$

with respect to oxygen degradation, were assumed for the reaction



where  $C_o$  is initial recorded DO at the postinjection sample point,  $C$  is DO remaining in water after time  $t$ ,  $t$  is reaction, or contact time of oxygen with COD waste, and  $k$  is reaction rate constant ( $\text{min}^{-1}$ ).

The first-order reaction rate constant was conservatively 0.12/min. Based upon this and a reaction time between injection and the postinjection sample point of approximately two minutes, only 21% of injected oxygen was consumed prior to sampling. The COD was reduced 15.7% based upon this. Table 2 shows the percent of oxygen that would be consumed as a function of time, which would lead to lower COD



FIGURE 2: Close-up of aerosol bubble mass transfer.

TABLE 3: DO and COD as a function of Ozone/Oxygen injection rate.

O <sub>3</sub> loading rate (g/min/liter)	DO (mg/L)	COD (mg/L)	% COD reduced
No O <sub>2</sub> or O <sub>3</sub>	0.14	5907	
0.53 O <sub>2</sub>	67.1	5440	7.9
0.053 O <sub>3</sub>	61.6	4970	15.8
0.105 O <sub>3</sub>	58.5	5043	14.6
0.158 O <sub>3</sub>	59.9	5040	14.7
0.212 O <sub>3</sub>	62.0	5053	14.5
0.318 O <sub>3</sub>	68.4	5033	14.8

levels if the sampling point was further downstream of the injection point. While the exact reduction cannot be exactly quantified without more information about the nature of the COD waste, it is clear that actual reduction in COD sent to GBMSD would be considerably lower than that recorded from the postinjection sample point at Fox River Fiber. If a constant stoichiometric ratio of O<sub>2</sub> to COD was assumed, a reaction time adequate to deplete 80% of injected oxygen could potentially remove up to 60% of COD with a reaction time of less than 20 minutes. At a linear rate of reduction in the fee paid to GBMet for excessive COD, Fox River Fiber could save \$720,000 per year.

2.4. COD as a Function of O<sub>3</sub>. A final experiment was performed to quantify the effect of increasing the ozone injection rate on effluent COD. A 9.5 liter/min side stream of Fox River Fiber's effluent stream was diverted and dosed with increasing quantities of ozone under the same water flow velocity and contact time as tests performed on the total effluent stream. Ozone was generated and injected with oxygen as aerosol bubbles using an AO<sub>3</sub> system as shown in Figures 1 and 2. Initially just oxygen was added, after which both oxygen and ozone were added with the oxygen amount approximately constant at 0.53 grams/min/liter water. At

TABLE 4: Peak hydrogen sulfide gas as a function of Bioxide addition at sample sites downstream of Fox River Fiber.

Sample site	Peak H <sub>2</sub> S: no O <sub>3</sub>	Peak H <sub>2</sub> S (ppm) for each bioxide application rate with O <sub>3</sub>			
	1520 L/day	1520 L/day	1330 L/day	950 L/day	570 L/day
NSI035	3	3	2.5	4	4
NSI028	7	6	4	3	12
NSI013	6	1	0	9	22
ASC020	20	0	0	22	68
ASC013	17	1	2	11	25
ASC008	30	2	4	22	47
ASC005	9.5	1	1	9	25

each ozone level, samples were drawn and analyzed for DO and COD. Table 3 summarizes the results.

The average percent reduction in COD due to ozone addition was 14.9%, but increasing ozone above a loading rate of 0.053 grams/min/liter water did not improve COD reduction. Addition of both oxygen and ozone did improve COD removal compared to just oxygen addition.

**2.5. Hydrogen Sulfide Suppression.** In addition to COD reduction, another concern of GBMSD with the high COD released by Fox River Fiber is the production of H<sub>2</sub>S gas in gravity sewer lines between GBMSD and FRF. Both prior to and following installation of the oxygen/ozone system, continuous measurements of H<sub>2</sub>S gas at a number of sample locations in the air space of the sewage lines were performed using Odalog gas loggers, Detection Instruments Corporation, in the 0 to 200 ppm range. The first set of data was collected between 6/2/2009 to 6/25/2009. During the first week of June, 2009, Green Bay experienced record high temperatures which would increase H<sub>2</sub>S gas production. Table 4 summarizes the results. Dissolved sulfides in the liquid phase were also measured and varied between 0 and 0.5 ppm.

At the beginning of the study Bioxide was added to the system by FRF at a rate of 1520 liters per day. Almost immediately Bioxide was reduced to 1330 liters per day. Within 24 hours, it was reduced to 950 liters per day. After eight days Bioxide was further reduced to 570 liters per day. For all tests, the O<sub>3</sub> loading rate was 0.053 grams/min/liter water, and the O<sub>2</sub> loading rate was 0.53 grams/min/liter water.

A comparison of peak H<sub>2</sub>S data in Table 4 for the cases of just 1520 liters/day Bioxide and 1520 liters/day Bioxide with ozone/oxygen generation shows that additional of ozone/oxygen to the FRF effluent did reduce the peak H<sub>2</sub>S. Reducing the Bioxide addition to 1330 liters/day and 950 liters/day did not result in increased H<sub>2</sub>S peak values, and average values were consistently below 20 ppm. For all sample sites, peak H<sub>2</sub>S remained below the maximum acceptable upper limit of 40 ppm. In addition, average H<sub>2</sub>S remained below the required 20 ppm for all but one measurement. Further reducing Bioxide to 150 gal/day resulted in two H<sub>2</sub>S peaks that exceeded the acceptable upper limit and many averages above 20 ppm. The optimal Bioxide dose could be as low as 780 liters/day, which would save FRF up

to 780 liters/day during warmer summer months. Even at a reduced dose of 950 liters/day, 150 gal/day of Bioxide could be saved. At a cost of \$0.695 per liter, \$396/day could be saved.

### 3. Conclusions

Addition of a high pressure oxygen/ozone stream to the effluent discharged by Fox River Fiber Company to the GBMSD system reduced COD sent to GBMSD by FRF by over 15% despite a very small contact time. A first-order kinetic model of the degradation reaction between oxygen and COD predicts as great as a 60% COD reduction if the contact time was increased via additional piping to as few as 30 minutes. Dissolved oxygen in the system was greatly increased by the Adaptive Ozone Solutions process. FRF currently pays a fee of \$1.2 million per year to GBMSD to handle their high COD stream, but this fee is linearly proportional to average COD. A 15.7% reduction, therefore, could save FRF \$188,400 annually. A 60% reduction in effluent COD could save the plant as much as \$720,000 annually. While this analysis did not include the electrical cost of the ozone generator, this amount would be small (on the order of several hundred dollars per month) compared to the potential savings.

Hydrogen sulfide gas monitoring during the study showed that the Adaptive Ozone Solutions, LLC, process could suppress H<sub>2</sub>S gas production in the air space of the sewage mains to below peaks of 40 ppm, the maximum acceptable value, under reduced Bioxide applications. Data showed that reducing Bioxide to 950 liters per day maintained sufficiently low hydrogen sulfide production, but that further decreasing the Bioxide addition rate to 570 liters per day caused two peaks above 40 ppm. Additional experimentation would be required to determine the exact point between 570 and 950 liters per day at which hydrogen sulfide peaks would become unacceptably high. This particular sewage system used gravity mains, which allows discharge of residual injected oxygen. It is anticipated that hydrogen sulfide production would be even more effectively suppressed in a force main, which operates under pressure. A reduction of 150 gallons per day would save FRF \$144,540 per year based on 365 days per year operation. A reduction to as little as 780 liters per day could save \$192,720 annually. Hence, at the experimental conditions employed during the summer

trial, FRF could save as much as \$332,940 in cost of high CODs and reduced Bioxide. If the contact time between injected oxygen and COD was increased prior to the effluent leaving the plant Bioxide could be reduced by as much as 950 gallons per day, a maximum potential savings of \$960,900 annually.

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## Research Article

# Performance Evaluation of AOP/Biological Hybrid System for Treatment of Recalcitrant Organic Compounds

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Process water from nuclear fuel recovery unit operations contains a variety of toxic organic compounds. The use of decontamination reagents such as  $\text{CCl}_4$  together with phenolic tar results in wastewater with a high content of chlorophenols. In this study, the extent of dehalogenation of toxic aromatic compounds was evaluated using a photolytic advanced oxidation process (AOP) followed by biodegradation in the second stage. A hard-to-degrade toxic pollutant, 4-chlorophenol (4-CP), was used to represent a variety of recalcitrant aromatic pollutants in effluent from the nuclear industry. A UV-assisted AOP/bioreactor system demonstrated a great potential in treatment of nuclear process wastewater and this was indicated by high removal efficiency (> 98%) under various 4-CP concentrations. Adding hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as a liquid catalyst further improved biodegradation rate but the effect was limited by the scavenging of  $\text{OH}^\bullet$  radicals under high concentrations of  $\text{H}_2\text{O}_2$ .

## 1. Introduction

Process water from nuclear fuel recovery unit operations contains a variety of toxic organic compounds. The use of decontamination reagents such as  $\text{CCl}_4$  together with phenolic tar results in wastewater with a high content of chlorophenols. Chlorophenols are compounds of serious environmental concern due to their toxic impacts and discharge from a wide range of industrial sources. A large number of chlorophenol derivatives are refractory in nature rendering them resistant to biological degradation. The recalcitrance of these compounds results from the carbon-hydrogen bond, which is cleaved with great difficulty [1]. Due to their stability, halogenated phenols tend to accumulate in higher-order organisms. In summary, a large component of nuclear waste contains organic waste consisting of alcohols and phenolics.

Current treatment processes for the removal of halogenated organic compounds involve dehalogenation using salts followed by chemical oxidation of the unhalogenated form [2]. The chemical process results in the production of harmful byproducts that require further disposal [3]. Among

the alternative methods to the chemical treatment processes are the biological processes using specialized species of chlorophenol degrading organisms, oxidative reaction using AOP and photocatalysis [4]. However, when used alone AOPs still produce harmful byproducts and may be energy intensive.

Lately, more interest has been directed towards finding solutions that involve the use of cultures of microorganisms to treat contaminated sediments and water impacted by nuclear waste [5]. The biological technology is the most cost effective alternative when compared to the other conventional treatment options as it has the potential to treat organic pollutants without leaving undesirable toxic byproducts. However, biological processes tend to be slow. A promising alternative is to use photoassisted AOP as a pre-treatment step to convert initially toxic organic compounds to more readily biodegradable intermediates followed by the biological oxidation of these intermediates to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [3].

An example of an AOP/biological hybrid system is illustrated by Vogelpohl and Kim [6] in an experiment where naturally toxic compounds were detoxified in an AOP

thereby forming easily degradable compounds for further degradation in the biological process. In this study, the latter concept was evaluated for the treatment of nuclear process water using 4-CP as a primary carbon sources for a local mixed culture.

## 2. Materials and Methods

**2.1. Microorganisms, Media, and Chemicals.** A mixed culture of activated sludge bacteria was originally collected from sand drying beds at a nearby Wastewater Treatment Plant (WWTP) (Brits, Northwest Province). The start up culture was prepared by growing overnight in Luria-Bettani (LB) broth at 32°C. This culture was used to inoculate the biological reactor (2nd stage). The feed solution, basal mineral medium (BMM) was prepared by dissolving (in 1 L distilled water): 0.535 g  $\text{NH}_4\text{Cl}$ ; 10.744 g  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ; 2.722 g  $\text{K}_2\text{HPO}_4$ ; 0.0493 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; 0.0114 g  $\text{NaSO}_4 \cdot 2\text{H}_2\text{O}$ ; and 0.0493 g  $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ . During the startup, 2 g  $\text{L}^{-1}$  of glucose was added to the feed solution in order to start the experiment with a healthy culture. The 4-CP used in this experiment was obtained at purities higher than 99% from MERCK Chemicals. LB agar was prepared by adding 20 g of agar powders in 1 L of distilled water. Plate Count Agar (PC) was prepared similarly. Both the LB Agar and PC Agar were autoclaved for 15 min and allowed to cool to 45°C before use.

**2.2. Experimental Apparatus.** The two-stage system used in this study consisted of a 22.8 L photoreaction chamber (Reactor 1) in Figure 1 followed by a 32.7 L biological reactor (Reactor 2) in Figure 1 both made from Perspex glass, 9 Watts UV-lamp, feed pump, and UV-recycle pump. The dimensions of the photoreactor were 300 × 295 × 295 mm (L × B × H) whereas the biological reactor were 447 × 348 × 246 mm (L × B × H). The two reactors were operated as CSTRs connected in series. Reactor 2 was expected to utilize byproducts of the degradation of phenolic compounds as carbon sources.

**2.3. Culture Characterization.** Phylogenetic characterization of cells was performed on individual colonies of bacteria from the 8th-10th tube in the tenfold serial dilution preparation. LB and Plate Count (PC) agar was used for colony development. In preparation for the 16S rRNA sequence identification, the colonies were first classified based on morphology. A 16S rRNA fingerprinting method was used to obtain DNA sequences of pure isolates from the sludge. Genomic DNA was extracted from the pure cultures using a DN easy tissue kit (QIAGEN Ltd, West Sussex, UK). 16S rRNA genes of the isolates were then amplified by reverse transcriptase-polymerase chain reaction (RT-PCR) using primers pA and pH1. The primer pA corresponds to position 8–27 and primer pH1 corresponds to position 1541–1522 of the 16S gene [7]. The PCR products were then sent to Inqaba Biotech facility (in Pretoria) for sequencing where an internal primer pD was used. Primer pD corresponds to position 519–536 of the 16S gene. The sequence relationships to known bacteria were determined by searching known

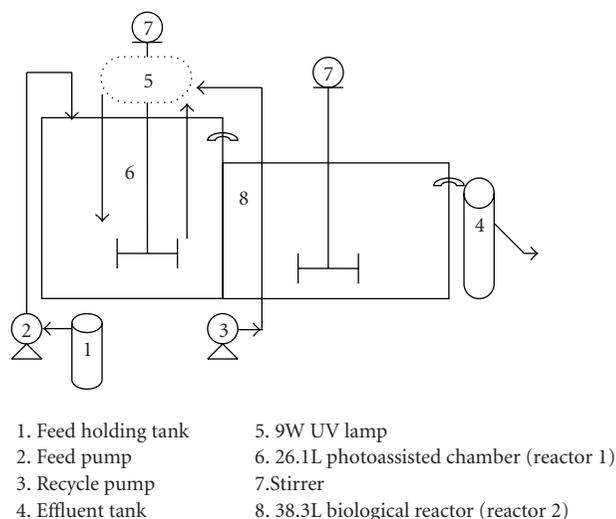


FIGURE 1: Apparatus set-up for photoassisted biodegradation process design.

sequences in GenBank using a basic BLAST search of the National Center for Biotechnology Information (NCBI) gene library.

### 2.4. Analytical Methods

**2.4.1. Chlorophenol Determination.** 4-CP concentration was measured in a Waters Alliance 2695 High-Performance Liquid Chromatography (HPLC) (Meadows Instrumentation Inc, Illinois, USA). The HPLC system consisted of the Waters 626 LC System, 717 Plus Autosampler, and the 996 Photodiode Array Detector. A Waters PAH  $\text{C}_{18}$  Symmetry Column (4.6 mm × 250 mm, 5  $\mu\text{m}$ ) was used. The samples were first filtered through a 5 mL syringe filter (0.4 5  $\mu\text{m}$  pore size). The injection volume was 10  $\mu\text{L}$  and the detector wavelength was 254 nm. The mobile phase used, A: B, 1% acetic acid in water: 1% acetic acid in acetonitrile. Data was interpreted by the Millennium 2010 Chromatography Manager.

**2.4.2. Characterization of Intermediates.** Degradation products were identified using gas chromatography coupled to mass spectrometry detector (GC-MS) (Clarus 600T, PerkinElmer, Massachusetts, USA) GC system with 5973N Mass Selective Detector, 7683 Series Injector Autosampler and G1701DA MSD Chem Station data acquisition software was used for GC-MS analysis. The GC separation was performed on a fused silica capillary column (30 m × 0.25 mm × 0.25  $\mu\text{m}$  HP-5MS). The helium carrier gas flow rate was 1.0  $\text{mL min}^{-1}$ ; the injector temperature was 250°C; the detector temperature was 280°C; and the transfer line temperature was set at 280°C. The column temperature was programmed to rise at a rate of 10°C  $\text{min}^{-1}$  first from 50 to 260°C, and then kept isothermal for 3 min at 260°C. 70 eV EI was used as the ionization voltage in the mass spectrometric analysis.

2.4.3. *Gravimetric Analysis of Biomass.* 2 mL of solution was drawn from the reactor and placed in preweighed centrifuged tube and centrifuged on Mini Spin (Eppendorf) for 10 min at 10,000 rpm. After decanting the supernatant, the wet centrifuged tube was weighed and placed into an oven at 50°C for 24 h. The resulting change in weight from dried centrifuged tube with biomass and without was used to determine the cell weight. The mass and the volume filtered were used to calculate suspended cells concentration in  $\text{mg L}^{-1}$ .

### 3. Reaction Rate Kinetics

A general mass balance of 4-CP around a completely mixed photoreactor is as follows [8]:

$$V \frac{dC}{dt} = Q(C_{\text{in}} - C) + r_s V, \quad (1)$$

where  $C_{\text{in}}$  = influent substrate concentration ( $\text{ML}^{-3}$ ),  $C$  = effluent substrate concentration ( $\text{ML}^{-3}$ ), reaction rate ( $\text{ML}^{-3}\text{T}^{-1}$ ),  $Q$  is flow rate across the reactor ( $\text{L}^3\text{T}^{-1}$ ), and  $V$  = operating volume of the reactor ( $\text{L}^3$ ). During steady state operation, the left-hand derivative approaches zero, that is,  $V \cdot dS/dt \Rightarrow 0$ . Thus, (1) is simplified to.

$$-r_s = \left(\frac{Q}{V}\right)(C_{\text{in}} - C). \quad (2)$$

For the single reactant kinetics in the photochemical reaction chamber, we assume first-order rate kinetics,  $-r_s = k_s \cdot C$ , such that, the rate constant can be estimated during steady-state operation from the influent and effluent concentration as follows:

$$\frac{C}{C_{\text{in}}} = \frac{1}{1 + k_s \cdot \tau}, \quad (3)$$

where  $\tau$  = the hydraulic retention time  $V/Q$  ( $T$ ) and  $k_s$  = the first-order maximum reaction rate coefficient ( $T^{-1}$ ).

For the biological reactor, two reaction rate models were evaluated—the reaction without inhibition as described by the Michaelis-Menten substrate utilization rate kinetics [9]:

$$-r_s = \frac{k_{ms}CX}{K_s + C} \quad (4)$$

and the reaction with substrate level inhibition as described by Briggs and Haldane [10]:

$$-r_s = \frac{k_{ms}CX}{K_s + C + C^2/K_I}, \quad (5)$$

where  $k_{ms}$  = maximum specific reaction rate coefficient ( $T^{-1}$ ),  $K_s$  = half velocity concentration ( $\text{ML}^{-3}$ ),  $K_I$  = coefficient of inhibition ( $\text{ML}^{-3}$ ), and  $X$  = the viable cell concentration in the reactor ( $\text{ML}^{-3}$ ). The reaction rate is substituted into the reactor mass balance as shown in (6) for example,

$$V \frac{dC}{dt} = Q(C_{\text{in}} - C) + \left(-\frac{k_{ms}C \cdot X}{K_s + C}\right)V \quad (6)$$

which resolves to

$$\frac{X\tau}{C_{\text{in}} - C} = \left(\frac{K_s}{k_{ms}}\right)\frac{1}{C} + \frac{1}{k_{ms}}. \quad (7)$$

Equation (7) determined from the cell mass balance across the reactor shows that the cell yield in the reactor is proportional to substrate utilized by bacteria in the reactor, that is,  $Y$  = mass of cells per mass of substrate utilized. The above expression is only true when the HRT is short enough such that cell death within the reactor is insignificant. Two operation conditions were required to yield two equations that were solved simultaneously for the parameters  $k_{ms}$  and  $K_s$ . The mass balance equation resulting from the substitution of the inhibition kinetics (5) is more complex

$$V \frac{dC}{dt} = Q(C_{\text{in}} - C) + \left(-\frac{k_{ms}C \cdot X}{K_s + C + C^2/K_I}\right)V \quad (8)$$

which resolves to

$$C_{\text{in}} - C = \left(\frac{V}{Q}\right)\left(-\frac{k_{ms}C \cdot X}{K_s + C + C^2/K_I}\right). \quad (9)$$

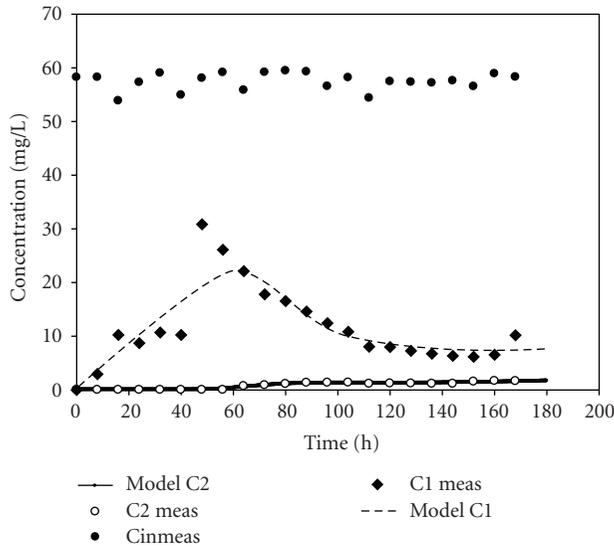
The above equation was solved numerically.

## 4. Results and Discussion

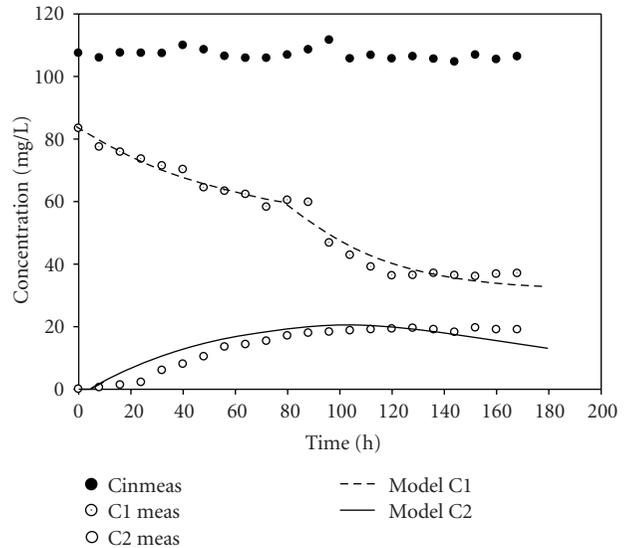
4.1. *Effect of 4-Chlorophenol Influent Loading.* A series of experiments were carried out at different feed 4-CP concentrations (50 to 1000  $\text{mg L}^{-1}$ ). The reactor was operated continuously until effluent conditions stabilized in a *quasi-steady* state. True steady-state conditions are expected after operation for 3 to 4 times the HRT (space times). This was shortened to two space times at a value of 6 days HRT. Operation at 50  $\text{mg L}^{-1}$  yielded *quasi-steady* state conditions with observed effluent concentrations of 6.24  $\text{mg 4-CP L}^{-1}$  in the chemical reactor and 1.13  $\text{mg 4-CP L}^{-1}$  in the biological reactors (Figure 2(a)). Operation at 100  $\text{mg L}^{-1}$  yielded *quasi* steady-state conditions with observed effluent concentrations of 36.3  $\text{mg 4-CP L}^{-1}$  in the chemical reactor and 19.2  $\text{mg 4-CP L}^{-1}$  in the biological reactor (Figure 3(a)).

The system was further challenged to 4-CP concentration of 200  $\text{mg L}^{-1}$ . At the latter concentration, no *quasi-steady* state was attained and was characterized by significant viable biomass losses. The system was further challenged with an influent of 1000  $\text{mg L}^{-1}$ . No *quasi-steady* state was attained under this loading due to high toxicity and loss of biomass (Figure 4). The results show that it was necessary to keep the 4-CP influent to the second stage very low for the biological system to function properly.

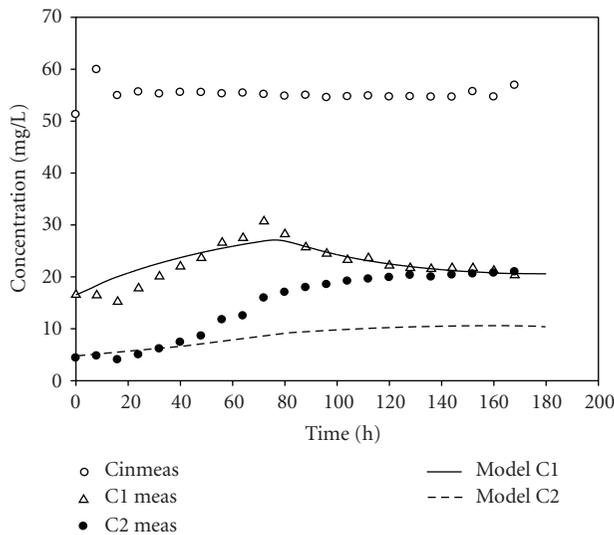
4.2. *Effect of  $\text{H}_2\text{O}_2$  in the Influent Concentration.* Another important parameter to consider in the combined AOPs with biological treatment process is the amount of  $\text{H}_2\text{O}_2$  required to obtain the best efficiency in the treatment. The impact of adding the chemical catalyst  $\text{H}_2\text{O}_2$  was investigated within the loading range (50 to 300  $\text{mg L}^{-1}$ ) using an  $\text{H}_2\text{O}_2$  dose of 0.1  $\text{mL L}^{-1}$ . The effect of  $\text{H}_2\text{O}_2$  on the removal of 4-CP is shown in Figures 2(b), 3(b) and 5.



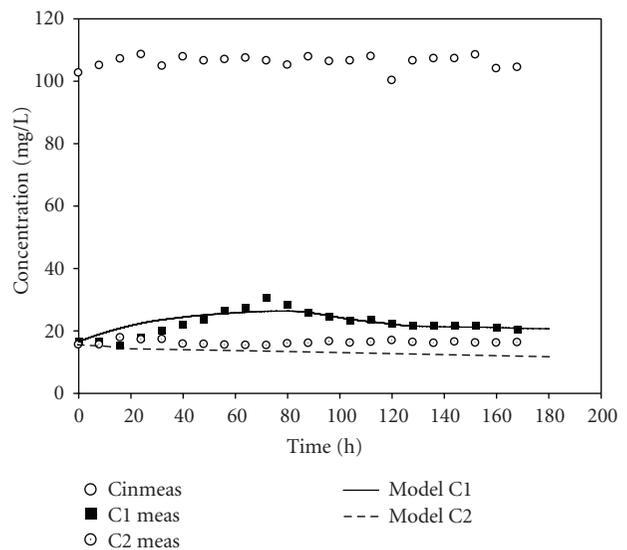
(a)



(a)



(b)



(b)

FIGURE 2: Photodegradation and biodegradation of 4-CP at an influent of  $50 \text{ mg L}^{-1}$  (a) Without  $\text{H}_2\text{O}_2$ , (b) With  $\text{H}_2\text{O}_2$ .

FIGURE 3: Photodegradation and biodegradation of 4-CP at an influent of  $100 \text{ mg L}^{-1}$  (a) Without  $\text{H}_2\text{O}_2$ , (b) With  $\text{H}_2\text{O}_2$ .

When  $0.1 \text{ mL H}_2\text{O}_2 \text{ L}^{-1}$  was added into  $50 \text{ mg 4-CP L}^{-1}$  influent, *quasi-steady state* was attained for both the chemical reactor ( $21.6 \text{ mg 4-CP L}^{-1}$ ) and biological reactor ( $19.8 \text{ mg 4-CP L}^{-1}$ ) resulting in effluent concentration of  $21.72$ . Operation with added  $\text{H}_2\text{O}_2$  under an influent 4-CP concentration of  $100 \text{ mg 4-CP L}^{-1}$  resulted in *quasi-steady state* conditions at effluent concentrations of  $21.3 \text{ mg 4-CP L}^{-1}$  in the chemical chamber and  $16.9 \text{ mg 4-CP L}^{-1}$  in the biological reactor.

At  $200 \text{ mg 4-CP L}^{-1}$  the system reached *quasi-steady-state* conditions with  $10.1 \text{ mg L}^{-1}$  in the chemical reactor and  $6.6 \text{ mg L}^{-1}$  in the biological reactor (Figure 5). These results show that, adding the chemical catalyst ( $\text{H}_2\text{O}_2$ ) improved the performance of the system with much lower concentrations observed in both the chemical and biological reactors. This

is in comparison with performance at  $200 \text{ mg 4-CP L}^{-1}$  influent concentration whereby there was significant viable biomass loss before *quasi-steady-state* conditions could be reached. The results agree with the reported results by Wen et al. [11] in which 4-CP concentration was tested at initial concentrations higher than  $300 \text{ mg L}^{-1}$  in bioreactors operated under aerobic and anaerobic conditions.

The system was further challenged with 4-CP influent concentration of  $300 \text{ mg L}^{-1}$  in the presence of  $0.1 \text{ mL H}_2\text{O}_2 \text{ L}^{-1}$ . The system did not attain *quasi-steady-state* condition. This was accompanied by excessive loss of viable biomass.

The above data in the peroxide experiment show that, 4-CP degradation in the photoreactor was highest at  $200 \text{ mg L}^{-1}$  indicating an optimum operation condition at this concentration. The suggestions by Pera-Titus et al.

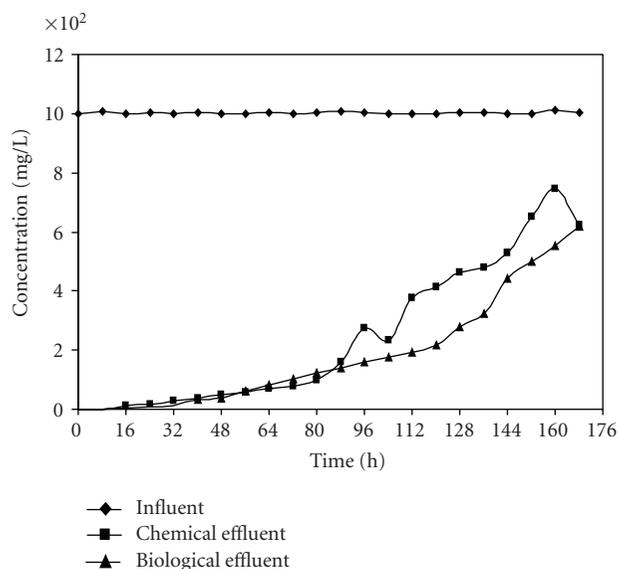


FIGURE 4: Photodegradation and biodegradation of 4-CP at an influent of  $1000 \text{ mg L}^{-1}$  without  $\text{H}_2\text{O}_2$ .

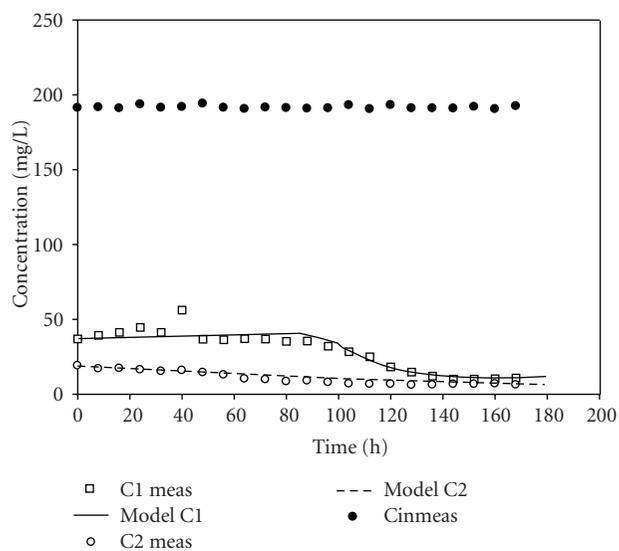
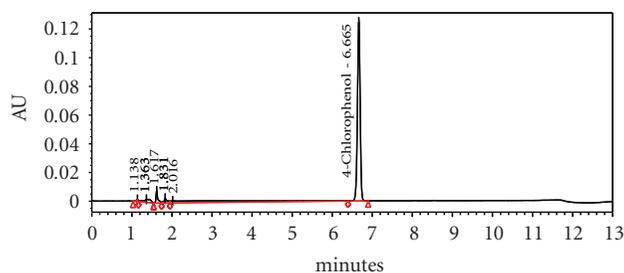


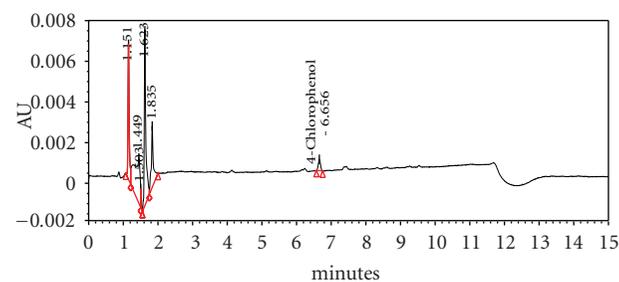
FIGURE 5: Photodegradation and biodegradation of 4-CP at an influent of  $200 \text{ mg L}^{-1}$  with  $\text{H}_2\text{O}_2$ .

[12] that the existence of an excessive amount of non-reacted  $\text{OH}^\bullet$  radicals under a low organic feed results in the recombination of the radicals to form water without useful reaction with the organics was confirmed.

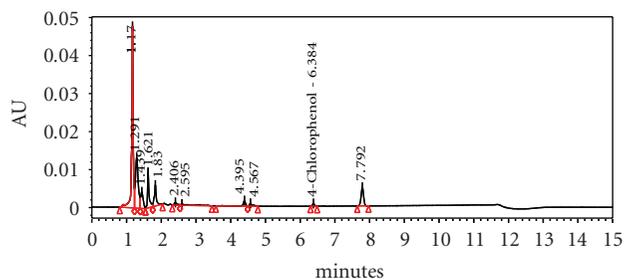
The above is supported by another case reported by Xu et al. [13] where the enhancement of degradation by addition of  $\text{H}_2\text{O}_2$  was due to the increase in the  $(\text{OH}^\bullet)$  radical concentration. Our results are in good agreement with Wen et al. [11] findings who reported that direct photolysis appears to be less effective than other processes where radiation is combined with  $\text{H}_2\text{O}_2$  or  $\text{O}_3$ , or where homogeneous, heterogeneous catalysis or photocatalysis are employed.



(a)



(b)



(c)

FIGURE 6: Chromatographic showing residual (a) 4-chlorophenol (b) Intermediates, (c) Metabolites [16].

**4.3. 4-Chlorophenol Removal Efficiency.** The removal efficiency of 4-CP was calculated from experimental data and the results were recorded over a range of concentration as indicated in Table 1. These results agree with cited results by various literature reports [14, 15] where authors examined the efficiency of the combined photochemical and biological treatment process. When the influent concentration was doubled without changing any of the process parameters to  $100 \text{ mg L}^{-1}$ , the overall percentage degradation of 82% was observed. Sahinkaya and Dilek [15] obtained 98% when using  $100 \text{ mg L}^{-1}$  with added  $\text{TiO}_2$  as a catalyst. When combine UV assisted AOP with biological treatment process was challenged to  $200 \text{ mg L}^{-1}$ , no *quasi*-steady-state was obtained in the biological reactor due to significant loss of viable biomass. It could be seen from the observed results that the degradation efficiency was affected by increase in influent concentration.

In another example, Suryaman [14] used combined biological-photocatalytic treatment process to treat wastewater containing phenol at  $50 \text{ mg L}^{-1}$ . The results from the latter study indicated that phenol was removed to the concentration of  $6.8 \text{ mg L}^{-1}$ . It can therefore be deduced that

TABLE 1: Summary of combined photoassisted AOPs with biological treatment process performance.

No	Influent (4-CP) concentration	UV-AOP removal (%)	Biological removal (%)	Combined process (%)
1	50 mg L <sup>-1</sup>	89.2	83.1	98
2	100 mg L <sup>-1</sup>	65.2	48.6	82.2
3	200 mg L <sup>-1</sup>	—	—	—
4	1000 mg L <sup>-1</sup>	—	—	—
5	50 mg L <sup>-1</sup> with 0.1 ml H <sub>2</sub> O <sub>2</sub> L <sup>-1</sup>	62.5	2.2	63
6	100 mg L <sup>-1</sup> with 0.1 ml H <sub>2</sub> O <sub>2</sub> L <sup>-1</sup>	79.9	25.3	85
7	200 mg L <sup>-1</sup> with 0.1 ml H <sub>2</sub> O <sub>2</sub> L <sup>-1</sup>	94.6	33.9	96.4
8	300 mg L <sup>-1</sup> with 0.1 ml H <sub>2</sub> O <sub>2</sub> L <sup>-1</sup>	—	—	—

“—” means no *quasi*-steady-state was reached.

TABLE 2: Characterized activated sludge cultures.

No	Blast result	Max ID	Further down on list (same max ID)
1	Uncultured bacterium, <i>Delftia</i> spp	99%	<i>Delftia tsuruhatensis</i>
2	<i>Staphylococcus pasteurii</i>	99%	<i>Deinococcus</i> spp.
3	<i>Bacillales</i> bacterium, <i>S. pasteurii</i>	99%	
4	<i>Pseudomonas stutzeri</i>	100%	Other <i>Pseudomonas</i> spp. (99%)
5	<i>Stenotrophomonas maltophilia</i>	100%	<i>P. aeruginosa</i> (99%)
6	<i>B. cereus</i>	100%	<i>B. thuringiensis</i> (99%)
7	<i>Pseudomonas mendocina</i>	100%	Other <i>Pseudomonas</i> spp. (99%)
8	<i>Pseudomonas lubricans</i>	99%	Other <i>Pseudomonas</i> spp.
9	Uncultured Caulobacteraceae	100%	<i>Brevundimonas</i> spp.
10	<i>P. aeruginosa</i>	99%	Other <i>Pseudomonas</i> spp.

the removal rate in the current culture is much higher both with and without chemical catalyst (H<sub>2</sub>O<sub>2</sub>). In this study, the highest removal efficiencies of 4-CP were obtained at 50 mg L<sup>-1</sup> and 200 mg L<sup>-1</sup> with added H<sub>2</sub>O<sub>2</sub> (98.0% and 96.4%, resp.) (Table 1). The lowest 4-CP removal efficiency was obtained at 50 mg L<sup>-1</sup> with added H<sub>2</sub>O<sub>2</sub>. In all cases, 4-CP was not completely removed in the bioreactor meaning that concentration of 4-CP could still be detected in low concentrations.

**4.4. Identification of Intermediates and Metabolites.** Figure 6 is a chromatogram showing residual 4-chlorophenol (a), intermediates (b) and metabolites (c) as shown by HPLC, [16]. It could be seen from the figure how the 4-CP disappears from chemical reactor to biological reactor. Ten different intermediates were detected by GC-MS.

In various studies, different authors [17–20] examined the reaction pathway for the 4-CP oxidation. The results of extensive research conducted by various researchers listed the main intermediates products of 4-CP as: benzoquinone, hydroquinone, 4-chlorocatechol; and chlorohydroxyquinol. The main intermediates found in this study are not in agreement with these reported primary oxidation products of 4-CP. However, 1,2 benzenedicarboxylic acid, propanoic acid, hexadecanoic acid in Table 2 agrees with the results reported by [21–23]. Various authors, [24, 25] also confirmed that more organic acids could be formed as more 4-CP degraded. In a separate report, Ying et al. [26] also agreed that organic acids such as formic, acetic, oxalic, propanoic and maleic

acid were generated in 4-CP degradation process. 2-(3,5-dichloro-4-methoxymethylphenyl) also agrees with results reported by Theurich et al. [27] where biphenyl derivatives were reported as 4-CP degradation products.

Different types of photoproducts and metabolites have been identified both in this study and in the literature. According to Arslan-Alaton et al. [28], the major concerns of organic pollutants degradation by AOPs is the nature of oxidation intermediates and end products. Equally important, Lipczynska-Kochany and Bolton [29] mentioned that treatment products might be more toxic or recalcitrant than the original pollutants after being subjected to advanced oxidation. As a result, it was of paramount importance to qualitatively identify degradation products in order to suggest a reaction mechanism.

In order to avoid high energy consumption which represents about 60% of the total operational cost because of the electric light sources, the photolytic treatment time must be reasonably short. However, if the fixed pretreatment time is too short, the intermediates remaining in the solution could still be structurally similar to the initial biorecalcitrant compounds and therefore non-biodegradable, [3].

**4.5. Culture Characterization.** Using 16S rRNA fingerprint, ten species of bacteria including *Staphylococcus pasteurii*, *Bacillales* bacterium, *Pseudomonas stutzeri*, *Stenotrophomonas maltophilia*, *Bacillus cereus*, *Delftia* spp., *Pseudomonas mendocina*, *Pseudomonas lubricans*, *Caulobacteraceae* spp., and *Pseudomonas aeruginosa* were characterized as shown in

TABLE 3: Chemical reactor reaction rate coefficients

Targeted concentration (mg L <sup>-1</sup> )	50	100	200	50 + H <sub>2</sub> O <sub>2</sub>	100 + H <sub>2</sub> O <sub>2</sub>	200 + H <sub>2</sub> O <sub>2</sub>
Observed concentration (mg L <sup>-1</sup> )	55	107	205	55	106	191
Steady-state concentration (mg L <sup>-1</sup> )	6.24	36.2	—	21.6	21.3	10.1
$k_s$ (h <sup>-1</sup> )	0.070	0.017	—	0.014	0.035	0.157

“—” means no quasi-steady-state was reached.

TABLE 4: Operating conditions for 2nd stage biological reactor.

Parameter	50 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>	200 mg L <sup>-1</sup>
	With 0.1 ml H <sub>2</sub> O <sub>2</sub>	With 0.1 ml H <sub>2</sub> O <sub>2</sub>	With 0.1 ml H <sub>2</sub> O <sub>2</sub>
$C_{in}$ (mg L <sup>-1</sup> )	21	36	10
$C$ (mg L <sup>-1</sup> )	20	19	6
$V$ (L)	32.7	32.7	32.7
$Q$ (L h <sup>-1</sup> )	0.20	0.20	0.20
$X_0$ (g m <sup>-3</sup> )	52	44	37
Weight of 1 ml of cells (g)	$45 \times 10^{-4}$	$45 \times 10^{-4}$	$45 \times 10^{-4}$

Table 2. Among the identified species, the two *Pseudomonas* species, *P. aeruginosa* and *P. mendocina* are well known aromatic compound degraders. *P. mendocina* has been demonstrated to degrade toluene at the laboratory scale where as *P. aeruginosa* has been extensively studied in the degradation of chlorophenols and other polynuclear aromatic compounds, [30]. Other species such as *P. stutzeri* are capable of degrading aliphatic chlorinated compounds such as carbon tetrachloride, [30]. These species could serve as house keeping organisms by degrading halogenated byproducts of chlorophenol degradation in the biological reactor. These results are in good agreement with Field and Sierra-Alvarez [31] who also reported that *Pseudomonas sp B-13* are capable of growing on 4-CP as a source of carbon and energy.

## 5. Parameter Evaluation

**5.1. Parameter Evaluation in the Chemical Reactor.** The photochemical reactor reaction rate coefficient was calculated using (3) and the values are recorded as indicated in Table 3. From Table 3 above, it could be concluded that increasing the influent concentration of 4-CP while maintaining H<sub>2</sub>O<sub>2</sub> concentration negatively affected the first-order reaction rate constant,  $k$ . The findings published by Catalkaya et al. [32] were compared with the calculated  $k_s$  values in this study. Catalkaya et al. [32] reported  $k_s$  values as 0.0997, 0.0480 and 0.0307 for 50, 100 and 200 mg L<sup>-1</sup> with added H<sub>2</sub>O<sub>2</sub>, respectively. The difference between the literature values and the values obtained in this study are attributed to the difference in experimental conditions employed. The pseudo-first order rate constants ( $k_s$ ) of 4-CP with (OH<sup>•</sup>) radicals was also reported in another case by Ghaly et al. [33] as 0.15 min<sup>-1</sup>. The result of Ghaly et al. [33] appears to be too high in comparison to our observed  $k$  values partly due to the fact

that Ghaly et al. [33] used the light intensity of 60 W, seven times higher than the 9 W used in this study.

**5.2. Steady-State Estimation of Biological Parameters.** The values of the kinetic parameters,  $K_s$ ,  $k_{ms}$  and  $K_I$  in the continuous flow process were determined from the experimental data under quasi-steady-state conditions as shown in Table 4 using (7) and (9). The values are recorded in Table 5. The degradation rate coefficient,  $k_{ms}$ , was determined to be very low compared to first-order maximum reaction rate coefficients,  $k$  as shown in Table 3. The low value of  $k_{ms}$  is a result of the low 4-CP loading at the HRT of 6 days. Maximum specific reaction rate coefficient in the biological reactor,  $k_{ms}$  is lower than the chemical reactor first-order maximum reaction rate coefficient,  $k_s$ . This indicates that 4-CP was degraded faster in the chemical reactor than in the biological reactor. In addition, the inhibition effects ( $K_I$ ) of 4-CP biodegradation was found to be 25.0 mg L<sup>-1</sup>. The  $K_I$  value is in good range reported by Konya et al. [34] as shown in Table 5. The high value of  $K_I$  also implies that the inhibition was very high which means that the bacteria were probably growing predominantly on the 4-CP intermediates.

**5.3. Parameter Estimation Using Transient State Model.** Since the reactor were operated 2-3 HRTs each, true steady state conditions could not have been reached. For a more realistic modeling effort, the reaction rates kinetics were evaluated under transient state using the Aquatic systems Simulation software (AQUASIM 2.0). In AQUASIM 2.0, the mass balance (2) and (6) were evaluated numerically by fourth order Runge-Kutta method (RK-4). The parameters were obtained by minimizing the Chi-square ( $\chi^2$ ) values between the model data and the actual data using a simplex method built within AQUASIM, [35].

The parameters derived from the steady-state assumptions for the chemical reactor did not fit the experimental data because it did not take into consideration the accumulation of the H<sub>2</sub>O<sub>2</sub>, catalyst in the system. During photolytic degradation, the amount of (OH<sup>•</sup>) radical formation is the driving force for 4-CP removal. The (OH<sup>•</sup>) radical started accumulating in Reactor 1 only after the UV light was switched on. At the beginning of each run, the (OH<sup>•</sup>) radical was not sufficient to facilitate 4-CP removal. This resulted in the characteristic rise and deep in the 4-CP concentration in Reactor 1. In order to capture this trend, changes are proposed in the following model:

- (1) Since the (OH<sup>•</sup>) radical is the second reactant, the reaction is adjusted to the second order with respect to 4-CP and (OH<sup>•</sup>) radical.

TABLE 5: Parameter estimation in biological reactor using numerical methods.

Parameter	Units	Experimental results		Results from literature	
		(Michaelis-Menten model) Value	(Haldane Model) Value	Konya et al. [34]	Jiang et al. [36]
Microorganisms used		Activated sludge	Activated sludge	Activated sludge	<i>Candida tropicalis</i>
$K_s$	mg L <sup>-1</sup>	18.95	4.59	25.7	1.11 × 10 <sup>3</sup>
$k_{ms}$	h <sup>-1</sup>	6.091 × 10 <sup>-6</sup>	3.43 × 10 <sup>-6</sup>	0.06	4.79
$K_I$	mg L <sup>-1</sup>	—	25.0	17.0	4.33

—: means not applicable.

- (2) Logistic accumulation of the (OH•) radical is suggested to capture the rising trend in the reaction rate.
- (3) The occurrence of the (OH•) radical in solution is transitional.

The revising of the first-order rate kinetics  $-r_s = k_s \cdot C$  with consideration for the concentration of the (OH•) radical required for initial 4-CP removal followed second-order rate kinetics, (10).

$$r_1 = kC_1C_{oh}, \quad (10)$$

where:

$$C_{oh} = C_{ohmax} + \frac{a}{[1 + e^{-(t-t_0)/b}]} c, \quad (11)$$

$$X = X_0 e^{(Yk_{ms}C_2/K_s - k_d)t}.$$

**5.3.1. Chemical Reactor Parameters.** Estimated kinetic parameters for the chemical reactor are presented over a range of influent concentration as:  $a = 648.78 \text{ mg L}^{-1}$ ,  $b = 14.27 \text{ h}^{-1}$ ,  $c = 249.39$ ,  $t_0 = 10.13 \text{ h}$ ,  $k = 1.97 \times 10^{-5} \text{ L}^{-3} \text{ mg}^{-1} \text{ h}^{-1}$ ,  $C_{ohmax} = 534.82 \text{ mg L}^{-1}$  and  $\chi^2 = 1046.55$ . These kinetic parameters were determined by means of optimization.

**5.3.2. Biological Reactor Parameters.** The average kinetic parameters in the biological reactor were determined for both inhibited and non-inhibited conditions:  $k_d = 2.02 \times 10^{14} \text{ (h}^{-1}\text{)}$ ,  $K_s = 3.24 \times 10^{-4} \text{ mg L}^{-1}$ ,  $X_0 = 1740 \text{ mg L}^{-1}$  and  $\chi^2 = 921.52$  and with inhibition:  $k_d = 2.00 \times 10^{14} \text{ (h}^{-1}\text{)}$ ,  $K_I = 259.01 \text{ mg L}^{-1}$ ,  $k_{ms} = 1.96 \times 10^{-5} \text{ h}^{-1}$ ,  $K_s = 3.24 \times 10^{-4} \text{ mg L}^{-1}$ ,  $X_0 = 908 \text{ mg L}^{-1}$ , and  $\chi^2 = 921.52$ . These parameters values were adjusted by reoptimization against measured data.

**5.4. Model Validation.** Model predictions were in good agreement with the experimental data indicating the validity of the model (Figures 2(a), 3(a), 3(b), and 4). However, in Figure 2(b), the proposed model could not track the 4-CP concentration profiles. The effluent concentrations of  $21 \text{ mg L}^{-1}$  in the chemical reactor and  $20.5 \text{ mg L}^{-1}$  in the biological reactor were recorded at quasi-steady-state resulting in poor biodegradation efficiency of 2.2%, (Table 1). The difference between these values is insignificant and thus makes the model to not work well because of poor degradation efficiency. Therefore low efficiency limits

applicability of the model on photoassisted AOPs with biological treatment process.

The estimated parameters may be valid for the wastewater containing 4-CP and other chlorinated mono-nuclear phenols. Obtained results in this study are sufficient to promote combined photoassisted AOPs with biological treatment process for treatment of organic pollutants in nuclear industry applications.

## 6. Conclusion

In this study, a combined AOP with biological treatment process (hybrid reaction process) was applied to treat halogenated breakdown products from nuclear fuel recovery process water. Based on the experimental results, the following conclusions can be drawn: (1) a mixed culture of microorganism isolated from sand drying beds at a nearby wastewater treatment plant (Brits, Northwest Province) completely degraded 4-CP to a maximum concentration of  $100 \text{ mg L}^{-1}$ ; (2) adding hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as a liquid catalyst further improved biodegradation rate but the effect was limited by the scavenging of OH• radicals under high concentrations of  $\text{H}_2\text{O}_2$ . In fact the AOP step was able to enhance the capacity of removing 4-CP and practically mineralizing the organic matter in the biological treatment stage. A combined Advanced Oxidation Processes with biological treatment and UV/ $\text{H}_2\text{O}_2$  processes were thus demonstrated to be a feasible method to efficiently remove 4-CP from the aqueous phase.

## Nomenclature

- $a$ : kinetic parameter for accumulation of hydroxide radical ( $\text{ML}^{-3}$ )
- $b$ : kinetic parameter for accumulation of hydroxide radical (T)
- $c$ : kinetic parameter for accumulation of hydroxide radical
- $C$ : concentration at steady-state ( $\text{ML}^{-3}$ )
- $C_1$ : chemical reactor calculated effluent concentration ( $\text{ML}^{-3}$ )
- $C_{1\text{meas}}$ : chemical reactor measured effluent concentration ( $\text{ML}^{-3}$ )
- $C_2$ : biological reactor calculated effluent concentration ( $\text{ML}^{-3}$ )
- $C_{2\text{meas}}$ : biological reactor measured effluent concentration ( $\text{ML}^{-3}$ )

$C_{in}$ :	influent substrate concentration ( $ML^{-3}$ )
$C_{inmeas}$ :	influent measured substrate concentration ( $ML^{-3}$ )
$C_{oh}$ :	calculated concentration of hydroxyl radical ( $ML^{-3}$ )
$C_{ohmax}$ :	initial concentration of hydroxyl radical ( $ML^{-3}$ )
$C_{ohmeas}$ :	concentration of hydroxyl radical from literature ( $ML^{-3}$ )
$k_s$ :	the first-order maximum reaction rate coefficient ( $T^{-1}$ )
$k$ :	the second-order maximum reaction rate coefficient ( $L^3M^{-1}T^{-1}$ )
$k_d$ :	endogenous decay coefficient ( $T^{-1}$ )
$K_i$ :	coefficient of inhibition ( $ML^3$ )
$k_{ms}$ :	maximum specific reaction rate coefficient ( $T^{-1}$ )
$K_s$ :	half velocity concentration ( $ML^{-3}$ )
$Q$ :	flow rate across the reactor ( $L^3T^{-1}$ )
$r_1$ :	the rate of 4-CP degradation in chemical reactor ( $T^{-1}$ )
$r_2$ :	the rate of 4-CP biodegradation in biological reactor ( $T^{-1}$ )
$r_s$ :	reaction rate for substrate s ( $T^{-1}ML^{-3}$ )
$\tau$ :	the hydraulic retention time (T)
$t$ :	time (T)
$t_0$ :	initial boundary value for accumulation of hydroxide radicals (T)
$V$ :	reactor volume ( $L^3$ )
$X$ :	viable cells concentration in the reactor ( $ML^{-3}$ )
$X_0$ :	initial viable cells concentration in the reactor ( $ML^{-3}$ )
$\chi^2$ :	chi squared
$X_s$ :	cell concentration in reactor at steady-state ( $ML^{-3}$ )

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## Review Article

# Removal of Organic Matter from Landfill Leachate by Advanced Oxidation Processes: A Review

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In most countries, sanitary landfill is nowadays the most common way to eliminate municipal solid wastes (MSWs). However, sanitary landfill generates large quantity of heavily polluted leachate, which can induce ecological risk and potential hazards towards public health and ecosystems. The application of advanced oxidation processes (AOPs) including ozone-based oxidation, Fenton oxidation, electrochemical oxidation, and other AOPs to treatment of landfill leachate was reviewed. The treatment efficiency in term of chemical oxygen demand (COD) of various AOPs was presented. Advantages and drawbacks of various AOPs were discussed. Among the AOPs reviewed, Fenton process should be the best choice, not only because it can achieve about 49~89% of COD removal with COD ranging from 837 to 8894 mg/L, but also because the process is cost-effective and simple in technological aspect, there is no mass transfer limitation (homogeneous nature) and both iron and hydrogen peroxide are nontoxic.

## 1. Introduction

Due to rapid economic development in recent years, the excessive generation of municipal solid wastes (MSWs) has been identified as one of the most serious environmental problems in the world which needs to be addressed urgently for environmental protection. Up to 95% total MSW collected worldwide is disposed using the landfilling method [1]. After landfilling, solid waste undergoes a series of physicochemical and biological changes. Consequently, the degradation of the organic fraction of the wastes in combination with percolating rainwater leads to the generation of a highly contaminated liquid called "leachate". Leachate may contain large amount of organic matter (biodegradable, but also refractory to be biodegraded), ammonia-nitrogen, heavy metals, and chlorinated organic compounds and inorganic salts.

The characteristics of landfill leachate are affected by many factors, such as age, precipitation, weather variation, and waste types and compositions. In particular, the composition of landfill leachate varies greatly depending on the age

of the landfill [2]. According to the landfill age, the leachate can be classified into three types: young, intermediate, and old, and the relationship of the characteristics of landfill leachate versus the age of landfill is summarized in Table 1 [3, 4]. The young landfill leachate is commonly characterized by high biochemical oxygen demand (BOD) (4000–13,000 mg/L) and chemical oxygen demand (COD) (30,000–60,000 mg/L), moderately high content of ammonium nitrogen (500–2000 mg/L), high ratio of BOD/COD (ranging from 0.4 to 0.7), and low pH values (as low as 4.0), with biodegradable volatile fatty acids (VFAs) appear to be its major constituents [5]. With an increase in the landfill age and decomposing of VFAs in the landfill leachate by anaerobic bacteria over a period of 10 years, the old leachates are catalogued as stabilized and characterized by a relatively low COD (<4000 mg/L), slightly basic pH (7.5–8.5), low biodegradability ( $BOD_5/COD < 0.1$ ), and high molecular weight compounds (humic substances) [6].

Toxicity analysis carried out using various test organisms such as *Vibrio fischeri*, *Daphnia similis*, *Artemia salina*, and *Brachydanio rerio* has confirmed that the potential dangers

TABLE 1: Landfill leachate classification versus age [3, 4].

Type of leachate	Young	Intermediate	Old
Age (years)	<5	5–10	>10
pH	<6.5	6.5–7.5	>7.5
COD (mg/L)	>10,000	4000–10,000	<4000
BOD <sub>5</sub> /COD	0.5–1.0	0.1–0.5	<0.1
Organic compounds	80% volatile fatty acids (VFA)	5%–30% VFA + humic and fulvic acid	Humic and fulvic acids
Ammonia nitrogen (mg/L)	<400	N.A	>400
TOC/COD	<0.3	0.3–0.5	>0.5
Kjeldahl nitrogen (g/L)	0.1–0.2	N.A	N.A
Heavy metals (mg/L)	Low to medium	Low	Low
Biodegradability	Important	Medium	Low

of landfill leachate [7–10] and the necessity to treat is so as to meet the standards for discharge in receiving waters. Laboratory studies to determine the effectiveness of various biological, physical, and chemical treatment processes on landfill leachate have been investigated since the early 1970s. Biological treatment processes, including anaerobic and aerobic processes, are quite effective for leachate generated in the early stage with a high BOD<sub>5</sub>/COD. However, they generally fail to treat a leachate with a rather low BOD<sub>5</sub>/COD, or high concentration of toxic metals [11]. Hence, physical-chemical processes are mostly used for pretreatment or full treatment for this type of landfill leachate.

Among the various types of physical-chemical treatments, advanced oxidation processes (AOPs) has been reported as one of the most effective method to degrade a variety of refractory compounds in landfill leachate [12]. This can be attributed to the role of a highly reactive radical intermediate such as hydroxyl radical ( $\bullet\text{OH}$ ) as an oxidant. The radicals can be produced in ozone oxidation, Fenton oxidation, and electrochemical oxidation systems.

With an oxidation potential ( $E^0$ ) of 2.80 V (Table 2), the  $\bullet\text{OH}$  radical can rapidly degrade recalcitrant organics such as aromatic, chlorinated, and phenolic compounds [13]. Once a reaction of the free radical is initiated by ozone or  $\text{H}_2\text{O}_2$ , a series of oxidation reactions occurs in the solution and the radicals rapidly react with most of the target compounds. The kinetic rate of AOPs depends on the concentration of radicals and pollutants, temperature as well as the presence of scavengers such as bicarbonate ion [14].

## 2. Treatment of Landfill Leachate via AOPs

**2.1. Ozone-Based Oxidation Processes.** Ozonation processes are attractive means for the treatment of landfill leachates due to the high oxidative power that ozone possesses [15]. As one of the most powerful oxidants with an oxidation potential ( $E^0$ ) of 2.08 V (Table 2), ozonation alters the molecular structure of refractory organic compounds in landfill leachate, turning them into compounds that are easily assimilated biologically [16].

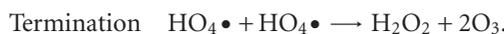
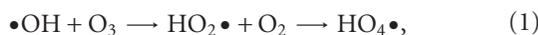
Depending on the pH values, which play major roles in the ozone decomposition, ozone oxidation follows the two

TABLE 2: Oxidizing potential of some oxidizing agents [13].

Type of oxidizing agents	Oxidation potential ( $E^0$ ) (V)
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hypochlorite	1.49
Hydrogen peroxide	1.78
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

main pathways: either a direct electrophilic attack of the ozone molecule to the recalcitrant pollutants or a generation of  $\bullet\text{OH}$  radicals due to the ozone decomposition process and followed by a subsequent attack of the radicals on the pollutants [17].

At an acidic pH range, ozone undergoes selective electrophilic attack on the specific part of the organic compounds that have C=C bonds and/or aromatic ring [18] and decomposes them into carboxylic acid and aldehydes as the end products [19]. When exposed to the pH values ranging from 8.0 to 9.0, in the presence of  $\text{OH}^-$  ions, the hydroxide ion reacts with ozone to yield superoxide anion radicals ( $\bullet\text{O}_2^-$ ), which in their turn are involved in a series of reactions as follows:

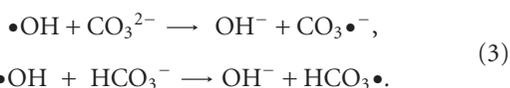


Overall, 1 mol of  $\text{O}_3$  yields 1 mol of  $\bullet\text{OH}$ .

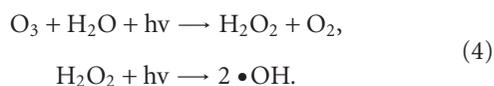
When pH is higher than 9.0, oxidation through the formation of  $\bullet\text{OH}$  radical is limited by the presence of ozone-resistant compounds or  $\bullet\text{OH}$  radical scavengers. Under such condition, bicarbonate ions are converted to carbonate ions, which are the scavengers for  $\bullet\text{OH}$  radicals that slow down the kinetic rate of the oxidation reaction [17]. The corresponding equation is listed as follows:



where P represents the scavenger of hydroxyl radicals such as  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . Some examples of the reactions are presented as follows:



As a single process, oxidation with ozone is not considered as very effective due to the complexity of leachate composition, high ozone doses are often required and the respective reaction may take longer time, rendering this process economically unfavorable [20]. Ozone processes can be made more effective by employing UV irradiation ( $\text{O}_3/\text{UV}$ ) or the addition of hydrogen peroxide ( $\text{O}_3/\text{H}_2\text{O}_2$ ). UV and  $\text{H}_2\text{O}_2$  initiate a series of radical reactions that enhance ozone decomposition to yield  $\bullet\text{OH}$  [21]. In the  $\text{O}_3/\text{UV}$  process, UV irradiation not only activates the ozone molecules by absorbing the UV light at 254 nm, but also makes other organic molecules susceptible to the oxidation process [22]. The initial step of the radical mechanism in this process is the direct photolysis of the ozone to produce  $\bullet\text{OH}$ , as shown in the following reactions [23]:



And the net reaction is



On the other hand, in the  $\text{O}_3/\text{H}_2\text{O}_2$  system, the addition of  $\text{H}_2\text{O}_2$  can accelerate the decomposition of ozone and subsequently enhance the production of  $\bullet\text{OH}$  radicals, as (6):



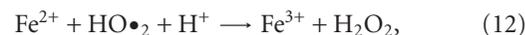
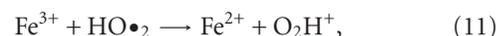
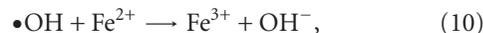
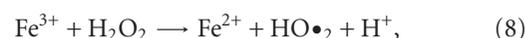
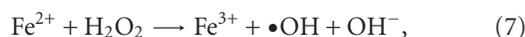
The reactions involved are very complex in the systems, since the organic compounds can be degraded either by direct ozonation, photolysis reaction, or  $\bullet\text{OH}$  oxidation [17].

Performance of  $\text{O}_3$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ , and  $\text{O}_3/\text{UV}$  process can be evaluated thanks to key parameters (COD, BOD, BOD/COD, and oxidant dose) summarized in Table 3. As previously mentioned, ozonation as a single process was not considered as very effective (COD reduction is about 15–50%) [15, 16, 24–29]. Thus, most researchers used ozonation process as pretreatment before biological treatment or tertiary treatment prior to discharge in the environment. COD reduction can be greatly enhanced via combining oxidants ( $\text{H}_2\text{O}_2/\text{O}_3$ ) (Table 3). Wable et al. [28] and Schulte et al. [30] reported the

efficiency of organic matter removal can be up to 95% and 97%, respectively. However, adding an irradiation system ( $\text{UV}/\text{H}_2\text{O}_2$ ) was not as efficient as  $\text{H}_2\text{O}_2/\text{O}_3$  system, with COD reduction at a range between 40% and 63%.

The common drawback of ozone-based oxidation is the high demand of oxidant ( $\text{O}_3$  or  $\text{H}_2\text{O}_2$ ) and the electrical energy used by UV lamps, which results in rather high treatment costs. However, ozone-based oxidation can improve the biodegradability of landfill leachate (Table 3). Using ozone-based oxidation as pretreatment of biological treatment can lower the cost.

**2.2. Fenton Oxidation.** Fenton process has been extensively studied in recent years, and analyses indicate Fenton process to be one of the most cost-effective alternatives for this application [37]. In the Fenton process, hydrogen peroxide is added to wastewater in presence of ferrous salts, generating species that are strongly oxidative with respect to organic compounds.  $\bullet\text{OH}$  is traditionally regarded as the key oxidizing species in the Fenton processes. The classical Fenton free radical mechanism in the absence of organic compounds mainly involves the sequence of reactions below [38]:



$\bullet\text{OH}$  radicals are rapidly generated through (7). In the above reactions, iron cycles between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and plays the role of catalyst. The net reaction of (7)–(13) is the decomposition of  $\text{H}_2\text{O}_2$  into water and  $\text{O}_2$  catalyzed by iron as follows:



Generally speaking, Fenton's oxidation process is composed of four stages including pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. The organic substances are removed at two stages of oxidation and coagulation [39].  $\bullet\text{OH}$  radicals are responsible for oxidation, and coagulation is ascribed to the formation of ferric hydroxo complexes [40]. The relative importance of oxidation and coagulation depends primarily on the  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio. Chemical coagulation predominates at a lower  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio, whereas chemical oxidation is dominant at higher  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratios [41]. Wang et al. [42] and Lau et al. [43] reported that oxidation and coagulation were responsible for approximately 20 and 80% of overall COD removal respectively, in Fenton treatment of biologically stabilized leachate.

TABLE 3: O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, and O<sub>3</sub>/UV treatments of leachates (updated from Renou et al. [2]).

Initial characteristics of the leachate				BOD/COD	Removal efficiency (%)		O <sub>3</sub> (a.g/l) or (b.gO <sub>3</sub> /g COD)	H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> (g/g)	UV(W)	Reference
COD (mg/L)	BOD (mg/L)	pH	Color (mgP tCo/l)	After treatment	COD	Color				
O <sub>3</sub>										
6500	500	8.1	12,000	0.5	15	90	1.2 <sup>a</sup>			[15]
3096	130	8.2	5759	0.2-0.3	25-50	—	3.0 <sup>a</sup>			[16]
3460	150	8.2	5300	—	48	87	3.0 <sup>a</sup>			[24]
4850 ± 100	520 ± 30	8.2	—	0.25	30	—	1.3-1.5 <sup>b</sup>			[25]
5000	20	—	8300	0.015	33	100	1.7 <sup>b</sup>			[26]
5230	500	8.7	—	0.1	27	—	—			[27]
4850	10	—	—	0.1	33	—	—			[29]
895	43	8.2	—	0.14	28	—	0.76 <sup>b</sup>			[31]
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>										
5230	500	8.7	—	0.7	48	94	—	H <sub>2</sub> O <sub>2</sub> :2 g/L		[27]
2000	—	—	—	—	95	—	3.5 <sup>b</sup>	0.4		[28]
600	—	—	—	—	92	—	3.3 <sup>b</sup>	0.4		
2000	160	8.4	—	0.13	92	—	1.5 <sup>b</sup>	0.3		[32]
—	—	8	—	—	97	—	2.5 <sup>a</sup>	2		[30]
—	—	8	—	—	70	—	—	0.5		
1360	<5	8.4	—	0.32	93	—	1.5 <sup>b</sup>	0.3		[31]
480	25	7.7	—	0.13	40	—	0.05-0.5 <sup>b</sup>	0.25-1		[33]
O <sub>3</sub> /UV										
1280	100	2	—	—	54	—	—	—	100	[34]
1280	100	2	—	—	47	—	—	—	500	
2300	210	8	—	—	40	—	1 <sup>b</sup>	—	15	[32]
430TOC	—	—	—	—	51TOC	—	0.1 <sup>a</sup>	—	300	[35]
26,000	2920	7.8	—	63	0.32	—	3.5 <sup>b</sup>	—	1500	[36]
26,000	2920	7.8	—	61	0.35	—	4.7 <sup>b</sup>	—	1500	

The introduction of UV irradiation into the Fenton process as well as electro-Fenton process may be able to improve the removal of COD. Many researchers studied the treatment efficiency of Fenton, photo-Fenton and electro-Fenton processes and the performances are summarized in Table 4. It indicated that leachate quality in terms of COD, odor, and color can be greatly improved following Fenton treatment.

The treatment efficiency of Fenton process depends on pH and the dosage of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>. According to Table 4, the optimal pH was in a range 2.0-4.0. The pH value affects the activity of both the oxidant and the substrate, the speciation of iron, and hydrogen peroxide decomposition [44]. Higher •OH radical product yields in the pH range of 2.0-4.0 by a reaction involving in the organometallic complex where either hydrogen peroxide is regenerated or reaction rates are increased [45]. The dosage of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> are major operational cost items for wastewater treatment. The removal of organic contaminants is improved as the concentration of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> increases. However, the extent of increase becomes negligible when the dosage is increased above a certain threshold level. Most researches

indicated that the optimal molar ratio of H<sub>2</sub>O<sub>2</sub> to Fe<sup>2+</sup> was from 1.5 to 3.0 [44, 46-48].

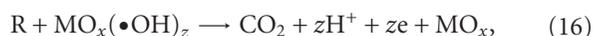
Fenton process can significantly remove recalcitrant and toxic organic compounds, and increase the biodegradability of organic compounds [49, 50, 52, 56]. There are four advantages of the Fenton's reagent: (i) both iron and hydrogen peroxide are relative cheap and nontoxic; (ii) there is no mass transfer limitation due to its homogeneous catalytic nature; (iii) there is no form of energy involved as catalyst; (iv) the process is technologically simple. However, Fenton process also shows drawback that large amounts of iron sludge may form, because Fe<sup>3+</sup> is converted to ferric-hydroxo complexes.

**2.3. Electrochemical Oxidation Processes.** Electrochemical oxidation of pollutants in wastewater is fulfilled through two different approaches, as shown in Figure 1: indirect oxidation, where a mediator is electrochemically generated to carry out oxidation, and direct anodic oxidation, where pollutants are destroyed on the anode surface [57]. During indirect oxidation, the agents generated anodically, which are responsible for oxidation of inorganic and organic

TABLE 4: Fenton, photo-Fenton, and electro-Fenton treatments of leachates.

Initial characteristic of leachate			COD	BOD/COD	Optimal condition	Reference
COD (mg/L)	BOD (mg/L)	pH	Removal (%)	after treatment		
Fenton						
1300	30	8.7	—	—	pH: 3.5, Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> : 500 mg/L, H <sub>2</sub> O <sub>2</sub> : 1650 mg/L	[39]
8298–8894	—	6.65–6.69	—	—	pH: 2.5, H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> (molar ratio): 1.5, reaction time: 30 min	[44]
10540	2300	8.2	60	0.5	pH: 3, Fe <sup>2+</sup> : 275 mg/L, H <sub>2</sub> O <sub>2</sub> : 3300 mg/L, reaction time: 2h	[49]
837–6119	42.50–620.00	8.09–8.47	80 (young leachate) 60~70 (old leachate)	—	pH: 2.5, H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> (molar ratio): 1.5, [H <sub>2</sub> O <sub>2</sub> ]: 0.075 M	[46]
1100–1300	—	8.18	61	—	pH: 3, [H <sub>2</sub> O <sub>2</sub> ]: 0.24 M, H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> (molar ratio): 3	[47]
8894	—	6.65–6.69	89	—	pH: 2.5, [H <sub>2</sub> O <sub>2</sub> ]: 0.15 M, H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> (molar ratio): 3	[48]
5700 ± 300	3600 ± 200	7.8 ± 0.3	66	0.88	pH: 3.5, H <sub>2</sub> O <sub>2</sub> : 650 mg/L, H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> (molar ratio): 1 : 19	[50]
Photo-Fenton						
3824	680	7.94	86	—	Fe <sup>2+</sup> : 2000 mg/L, H <sub>2</sub> O <sub>2</sub> : 10000 mg/L	[51]
5200 ± 27	720 ± 81	8.4 ± 0.1	49	0.4	pH: 2.8, Fe <sup>2+</sup> : 10 mg/L, H <sub>2</sub> O <sub>2</sub> : 2000 mg/L	[52]
1150	4.6		70		pH: 3, Fe <sup>2+</sup> : 56 mg/L, H <sub>2</sub> O <sub>2</sub> : 34 mg/L, UV: 80 KW/m <sup>3</sup>	[53]
Electro-Fenton						
5000	—	6.4	83.4	—	pH: 3, H <sub>2</sub> O <sub>2</sub> : 0.34 mol/L, Fe <sup>2+</sup> : 0.038 mol/L, I: 2 A, d = 2.1 cm	[54]
2350	—	2.36	72	—	pH: 3, H <sub>2</sub> O <sub>2</sub> : 2000 mg/L, I: 2 A, reaction time: 20 min	[55]
1941	195	8.1	69	0.29	pH: 4, H <sub>2</sub> O <sub>2</sub> : 750 mg/L	[56]

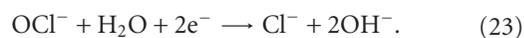
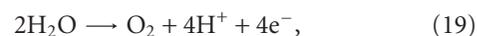
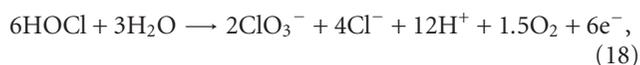
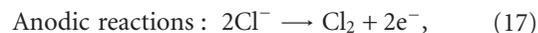
pollutants may be chlorine and hypochlorite, hydrogen peroxide, ozone and metal mediators such as Ag<sup>2+</sup>. Direct anodic oxidation is achieved through two different pathways: electrochemical conversion and electrochemical combustion [58]. During electrolysis, two species of active oxygen can be electrochemically generated on oxide anodes (MO<sub>x</sub>). One is the chemisorbed “active oxygen” (oxygen in the oxide lattice, MO<sub>x+1</sub>), responsible for the electrochemical conversion through (15). While the other is the physisorbed “active oxygen” (adsorbed hydroxyl radicals, •OH), responsible for electrochemical combustion through (16):



where R represents organic compounds; z represents the number of adsorbed •OH on anode.

During the electrochemical oxidation of landfill leachate, the removal of pollutants may be primarily attributed to

indirect oxidation, utilizing chlorine/hypochlorite formed by anodic oxidation of chlorine originally existing or added in the leachate [59]. However, direct anodic oxidation may to some extent destroy pollutants adsorbed on the anode surface [60]. A series of reactions involving indirect oxidation during electro-oxidation are shown in (17)–(23)



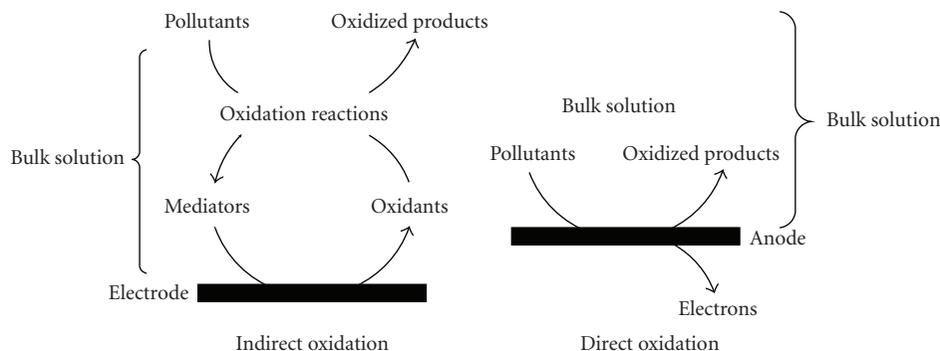


FIGURE 1: Pollutant removal pathways in electrochemical oxidation (indirect and direct oxidation) [57].

Hypochlorite ( $\text{OCl}^-$ ) generated in (20) and (21) is a strong oxidant that can oxidize aqueous organic compounds. So, it can oxidize the organic matters in the leachate.

Some researchers have investigated the treatment efficiency of electrochemical oxidation in treating landfill leachate [59–63]. The pollutant removal efficiency was influenced by a number of operating factors, including anode materials, pH, current density,  $\text{Cl}^-$  concentration, and electrolytes added (Table 5). The common anode materials are ternary Sn-Pd-Ru oxide-coated titanium (SPR), binary oxide-coated titanium Ru-Ti oxide (DSA),  $\text{PbO}_2$ -coated titanium ( $\text{PbO}_2/\text{Ti}$ ), graphite,  $\text{SnO}_2$ -coated titanium ( $\text{SnO}_2/\text{Ti}$ ), iron (Fe) and aluminum (Al), and the COD removal efficiency when using the anode material followed the order of  $\text{SPR} > \text{DSA} > \text{PbO}_2/\text{Ti} > \text{graphite}$  [59]. Moraes and Bertazzoli [61] found that the removal rates achieved were 73% for COD, 57% for TOC, 86% for color and 49% for ammonium at a current density of  $116.0 \text{ mA/cm}^2$ , using oxide-coated titanium anode. Bashir et al. [63] used graphite carbon and got 70% BOD removal, 68% COD removal, and 84% color removal when the current density was  $79.9 \text{ mA/cm}^2$  and reaction time was 2 hours.

Electrochemical oxidation of landfill leachate under appropriate conditions can remove most COD and significantly remove color. The important advantage of electrochemical oxidization is to oxidize organic pollutants into  $\text{CO}_2$  and water to avoid a problem of contaminants shifting from one phase to another. Also, the operation at room temperature and atmospheric pressure prevents volatilization and discharge of unreacted wastes, and the reaction can be simply terminated in seconds by cutting off the power [64]. However, there are two drawbacks of electro-oxidation which may limit its wide application for landfill leachate treatment, one is high energy consumption, and the other is potential for formation of chlorinated organics. Especially because of its expensive operating costs compared with other available technologies (for example, biological processes), electro-oxidation will be favored as a finishing step in a combined process or an auxiliary unit in emergency situations, instead of a full treatment for landfill leachate [65].

**2.4. Other AOP Processes.** Wet air oxidation (WAO) is a useful treatment method for reduction of aqueous pollution

bound to heavily contaminated wastewater, in particular when it is necessary to treat low volumes. This process consists in the oxidation of dissolved or suspended aqueous solution of organic and inorganic substances by means of oxygen, at elevated temperature (450–590 K) and pressure (2–15 MPa), assuring wet conditions of reaction. Under these conditions organic waste streams too dilute to incinerate and too concentrated for biological treatment can be degraded to simpler, frequently more biodegradable, organic compounds or completely converted to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [66]. Typically, WAO process has shown promising results (80%–99% of COD removal) for a complete mineralization of organic compounds or for their degradation into a less complex structure, which is more biodegradable [67]. This process is cost-effective for leachate treatment with COD concentrations ranging from 10,000 to 100,000 mg/L. If complete COD removal is not required, the operating conditions such as the air flow rate, temperature, and pressure can be lowered to reduce the operational cost [68]. Although WAO offers some advantages such as a small plant for operations and its ability to deal with varying flow rates and composition of the effluent, this process is not cost-effective for leachate treatment with a COD concentration of less than 5000 mg/L.

Ultrasonic process is considered as a possibility in wastewater treatment for several decades. It is able to remove pollutants through the production of radicals in the bubble of cavitation that can react with refractory compounds [69]. Ultrasonic irradiation is an effective method for the removal of organic matters and ammonia nitrogen from landfill leachate. After 180 minutes ultrasound irradiation (ultrasonic power input: 150 W, pH: 11) up to 96% ammonia nitrogen removal efficiency can be obtained [70]. Due to the high cost of ultrasonic, it is always used as pre- or posttreatment of the biological treatment. Ultrasound pretreatment of raw leachate can significantly improve the removal rates of COD and nitrogen compound (frequency: 20 kHz and amplitude:  $12 \mu\text{m}$ ) [71].

It is obvious that WAO and ultrasonic show a better treatment efficiency of the landfill leachate. However, there are two drawbacks of the two AOPs. One is high energy consumption, and the other is the operation mode restrain its practical application. They are suitable for small quantity and high strength wastewater.

TABLE 5: Influence of operating factors in electro-oxidation of leachate [57].

Operating factor	Influence
Anode materials	Anode materials with high electrocatalytic activity and high anodic oxygen evolution potential cause a high COD and NH <sub>3</sub> -N removal efficiency; usage of metal anode such as Fe and Al causes simultaneous electro-oxidation and electro-coagulation
pH	The influence of pH is unclear. Reported results are inconsistent
Current density	Increase in current density causes increase in removal efficiencies of COD and color
Chloride ion concentration	Increase in Cl <sup>-</sup> concentration improves removal of pollutants, but increase the hazard of formation of chlorinated organics
Additional electrolytes	Effects of additional electrolytes depend on their species and properties

TABLE 6: Summary of the highest reported COD removal of some AOPs.

AOPs	Optimal condition	Initial COD (mg/L)	COD removal efficiency (%)	Reference
O <sub>3</sub>	3 g/L	3460	48	[24]
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> : 3.5 g/gCOD H <sub>2</sub> O <sub>2</sub> g/g O <sub>3</sub>	2000	95	[28]
O <sub>3</sub> /UV	O <sub>3</sub> : 3.5 g/gCODUV:1500 W	26,000	63	[36]
Fenton	pH: 2.5, [H <sub>2</sub> O <sub>2</sub> ]: 0.15 M, H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> (molar ratio): 3	8894	89	[48]
Photo-Fenton	Fe <sup>2+</sup> : 2000 mg/L, H <sub>2</sub> O <sub>2</sub> : 10000 mg/L	3823.8	86	[51]
Electro-Fenton	pH: 3, H <sub>2</sub> O <sub>2</sub> : 0.34 mol/L, Fe <sup>2+</sup> : 0.038 mol/L, I: 2 A, d = 2.1 cm	5000	83	[54]
Electrochemical oxidation	Current density: 116.0 mA/cm <sup>2</sup>	1855	73	[61]

### 3. Comparison of Various AOP's Performance

The outcomes of AOPs applied to treat the landfill leachate can be classified into two types: (i) oxidize organics substances to their highest stable oxidation states being carbon dioxide and water (i.e., to reach complete mineralization); (ii) improve the biodegradability of recalcitrant organic pollutants up to a value compatible with subsequent economical biological treatment. Thus, the comparison of various AOP's performance was evaluated from these two aspects.

Table 6 presents the outstanding treatment performance and optimum operate condition of various AOPs for COD removal from landfill leachate. The ozone-based process can achieve 40–95% of COD removal with COD concentration ranging from 2000 to 26,000 mg/L, while electrochemical oxidation process and Fenton process can achieve 70–90% of COD removal with COD concentration ranging from 1855 to 8894 mg/L. It should be noted that the treatment efficiency of Fenton process is better than ozone-based process and electrochemical oxidation. In term of biodegradability improvement, BOD/COD ratios are 0.29–0.88 [49, 50, 52, 56] and 0.1–0.5 (Table 3) were reported after oxidation by Fenton process and ozone-based oxidation, respectively.

Concerning the cost of various AOPs, electrochemical oxidation, wet air oxidation, and ultrasound oxidation are more expensive due to the high demand of electrical energy

for devices ozonizers, UV lamps, ultrasounds. The only exception is the Fenton's process. In such a process, in fact, under acidic condition, a Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> mixture produces •OH radicals in a very effective way [49]. Tizaoui et al. [27] estimated the treatment cost of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system was about 2.3 US\$/kg COD. Kurniawan et al. [17] showed that the treatment cost of leachate using ozone-GAC adsorption varies between US\$ 2 and 4 per m<sup>3</sup> of the treatment effluent. While Rivas et al. [72] estimated the operational cost for Fenton treatment of leachate was 8.0 × 10<sup>-3</sup> US\$ per m<sup>3</sup> of leachate and ppm of COD removed. Based on the analysis and Lopez et al. [49], Fenton process seems to be the best compromise because the process is technologically simple, there is no mass transfer limitation (homogeneous mature) and both iron and hydrogen peroxide are relatively cheap and nontoxic. But Fenton's process required low pH and a modification of this parameter is necessary.

### 4. Conclusions

The application of AOPs including ozone-based oxidation, Fenton oxidation, electrochemical oxidation, wet air oxidation, and ultrasound oxidation to treatment of landfill leachate was reviewed. Among the AOPs reviewed, ozone-based oxidation and Fenton oxidation are the most frequently studied and widely applied methods for the

treatment of landfill leachate. Both techniques can achieve about 15~95% of COD removal with COD concentration ranging from 600 to 26,000 mg/L. In particular, Fenton process can improve BOD/COD ratio to close 0.5. Fenton process seems to be the best compromise because the process is technologically simple, there is no mass transfer limitation (homogeneous mature) and both iron and hydrogen peroxide are cheap and nontoxic. From the economic point of view, using Fenton process as the pretreatment of biological treatment can lower the cost and improve the treatment efficiency.

In the past, most of works were focused on the removal efficiency of organic matters from landfill leachate. Only a few researches considering the toxicity reduction were involved. However, the toxicity assessment of landfill leachate is very important, which determines the effect of the subsequent biological treatment or the influence on the environment. So, the toxicity reduction of AOPs should be evaluated in the future research.

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## Research Article

# Variability of Parameters Involved in Leachate Pollution Index and Determination of LPI from Four Landfills in Malaysia

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Landfill sites are potential sources of human and environmental hazards. Leachate produced from these waste dumping sites is heterogeneous and exhibits huge temporal and seasonal variations. Leachate pollution index (LPI) provides an overall pollution potential of a landfill site. The parameters required to calculate LPI from a landfill site are discussed in terms of their variations over time, and their significance has been highlighted in the context of LPI. The LPI values of two semiaerobic and two anaerobic landfill sites in Malaysia have been calculated in this study. Pulau Burung Landfill Site (PBL) was found to have the highest LPI score while Ampang Jajar Landfill Site (AJLS) showed the lowest LPI as compared to other landfills. It is concluded that LPI value can be used as a tool to assess the leachate pollution potential from landfill sites particularly at places where there is a high risk of leachate migration and pollution of groundwater.

## 1. Introduction

Landfills are the primary means of municipal solid waste (MSW) disposal in many countries worldwide because they offer dumping high quantities of MSW at economical costs in comparison to other disposal methods such as incineration. Landfill leachate produced from MSW landfill sites is generally heavily contaminated and consists of complex wastewater that is very difficult to deal with [1–4]. The generation of leachate is a result of percolation of precipitation through open landfill or through cap of the completed site [5]. Leachate is characterized by high concentration of organic matter (biodegradable and non-biodegradable), ammonia nitrogen, heavy metals, and chlorinated organic and inorganic salts [6]. The characteristics of leachate are highly variable [7] depending on the waste composition [2], amount of precipitation, site hydrology, waste compaction, cover design, sampling procedures, and interaction of leachate with the environment, landfill design and operation [8]. Organic content of leachate pollution is generally measured in terms of biological oxygen demand (BOD<sub>5</sub>) and chemical oxygen demand (COD). The concentrations of leachate contaminants may range over several orders of magnitude

[9]. A combination of pollutants (BOD<sub>5</sub>, COD, ammonia, inorganic salts, etc.) in higher concentrations renders landfill leachate as a potential source of contamination both to ground and surface waters, hence necessitates its treatment prior to discharge to water resources [10]. The management of leachate is among the most important factors to be considered in planning, designing, operation, and long-term management of an MSW landfill [11]. Leachate can contaminate groundwater where landfills are not provided with liners and surface water if it is not collected and treated prior to its discharge. The overall pollution potential of landfill leachate can be calculated in terms of leachate pollution index (LPI) as proposed by Kumar and Alappatt [12]. Because identification and quantification of pollutants in landfill leachate is the major limitation for its successful treatment [13], LPI can be used as a mean to determine whether a landfill requires immediate attention in terms of introducing remediation measures. Most of the landfills in developing countries including Malaysia are not designed with proper leachate collection mechanism. There are 230 landfills in Malaysia recognized officially [14]. Most of these landfills do not come under sanitary landfill classification because there are no facilities for collection and/or treatment

of leachate and there is no infrastructure to collect landfill gas [14]. Many of these landfill sites are located near rivers and streams which are a major source of agriculture and productivity, industrial and domestic water supply. The present study was carried out to determine and compare the LPI for leachate collected from four landfill sites, that is, semiaerobic Pulau Burung Landfill Site (PBLs), anaerobic Kulim Landfill Site (KLS), semiaerobic Ampang Jajar Landfill Site (AJLS) and improved anaerobic Kuala Sepetang Landfill Site (KSLS).

## 2. Significance and Variations of LPI Parameters

**2.1. PH.** Leachate is generally found to have pH between 4.5 and 9 [15]. The pH of young leachate is less than 6.5 while old landfill leachate has pH higher than 7.5 [16]. Initial low pH is due to high concentration of volatile fatty acids (VFAs) [17]. Stabilized leachate shows fairly constant pH with little variations and it may range between 7.5 and 9. Kulikowska and klimiuk [7] and Tatsi and Zouboulis [18] reported similar range of pH from old landfill sites, that is, 7.46–8.61 and 7.3–8.8, respectively.

**2.2. TDS.** TDS comprises mainly of inorganic salts and dissolved organics. TDS is one of the parameters taken into consideration for licensing discharge of landfill leachate in many countries such as the U.K. [19]. The amount of TDS reflects the extent of mineralization and a higher TDS concentration can change the physical and chemical characteristics of the receiving water [20]. The increase in salinity due to increase in TDS concentration also increases toxicity by changing the ionic composition of water.

**2.3. BOD<sub>5</sub> and COD.** In the initial acidogenic biodegradation stage, the leachate is characterized by high BOD<sub>5</sub> and COD [21]. Young landfill leachate is characterized by high BOD<sub>5</sub> (4000–13,000 mg/L) and COD (30,000–60,000 mg/L) [22]. According to Tatsi et al. [23], young leachate may have BOD<sub>5</sub> as high as 81,000 mg/L. A much higher value of COD (70,900 mg/L) is reported in leachate obtained from the Thessaloniki Greater Area (Greece) by Tatsi and Zouboulis [18]. A decrease in BOD<sub>5</sub> and COD is often reported with the increase in age of the landfill. For stabilized leachates, COD generally ranges between 5000–20,000 mg/L [24]. The BOD<sub>5</sub>/COD ratio provides a good estimate of the state of the leachate and this ration for young leachate is generally between 0.4–0.5 [25]. During the methanogenic phase, the organic strength of the leachate is reduced by methanogenic bacteria such as *methanogenic archaea* and the concentration of VFAs also declines which results in a ratio of BOD<sub>5</sub>/COD less than 0.1 [25, 26].

**2.4. Total Nitrogen.** Ammonium represents the major proportion of total nitrogen. In comparison to soluble organics, the release of soluble nitrogen from waste into leachate continues over longer period [7]. As a result, the concentration of ammonia nitrogen increases with the increase in age of the landfill which is due to hydrolysis and fermentation of nitrogenous fractions of biodegradable refuse substrates

[16]. Ammonia is considered as a major long-term pollutant because of its stability under anaerobic conditions. Ammonia concentration differs highly in leachates from different landfills from tens or hundreds of mg N<sub>NH4</sub>/L to couple of thousands (2000 mg N<sub>NH4</sub>/L) to several thousands (>10000 mg N<sub>NH4</sub>/L) [7, 18, 27, 28]. The mean concentration of ammonia in leachate ranges between 500–1500 mg/L after a period of 3–8 years of waste placement and continues to be within this range over 50 years [7]. According to Li and Zhao [24], ammonia nitrogen in stabilized leachate might range between 3000–5000 mg/L. Ammonia nitrogen is ranked as a major toxicant to living organisms, as established by various toxicity analyses using bioassays and various test organisms such as *Salmo gairdneri* and *Oncorhynchus nerka* [25]. Higher concentrations of ammonia are also known to enhance algal growth, promote eutrophication due to decreased dissolved oxygen [25]. Due to its toxicity it can also disrupt biological leachate treatment operations [29].

**2.5. Heavy Metals.** In general, the concentration of heavy metals in landfill leachate is fairly low [15]. Concentration of heavy metals in a landfill is generally higher at earlier stages because of higher metal solubility as a result of low pH caused by production of organic acids [7]. As a result of decreased pH at later stages, a decrease in metal solubility occurs resulting in rapid decrease in concentration of heavy metals except lead because lead is known to produce very heavy complex with humic acids [30]. A lower concentration of Cd (0.006 mg/L), Ni (0.13 mg/L), Zn (0.61 mg/L), Cu (0.07 mg/L), Pb (0.07 mg/L), and Cr (0.08 mg/L) were found in 106 Danish landfills by Christensen et al. [15] and Kjeldsen and Christophersen [31]. The high dissolved organic carbon (DOC) concentration in leachate renders the metals nontoxic because only the free metals are known to exhibit toxicity [32, 33]. However, the solubility and mobility of metals may increase in the presence of natural and synthetic complexing ligands such as EDTA and humic substances [21]. Further, colloids have great affinity for heavy metals and a significant but highly variable fraction of heavy metals is associated with colloidal matter [15, 34]. According to Baun and Christensen [35], less than 30%, typically less than 10% of the total metal concentration is present in free metal ion forms and the rest is present in colloidal or organic complexes. Jensen and Christensen [34] found that 10–60% of Ni, 30–100% Cu and 0–95% Zn were constituted in colloidal fractions. The solubility of the metals can also increase because of the reducing condition of the leachate which changes the ionic state of the metals (i.e., Cr (VI) → Cr (III), and As (V) → As (III) [21, 36–38].

**2.6. Phenol.** Christensen et al. [15] reports the concentration of phenolic compounds in a landfill between 1–2100 µg/L. Phenolic compounds are readily degradable under aerobic conditions while their degradation under anaerobic conditions is uncertain [15].

**2.7. Chlorides.** According to Deng and Englehardt [29], the concentration of chlorides may range between 200–3000 mg/L for a 1–2 year- old landfill and the concentration

decreases to 100–400 for a landfill greater than 5–10 years old. Bowman et al. [39] found chlorides as high as 8000 mg/L in Newington landfill leachate in Sydney. Because chlorides are usually not attenuated by soil and are extremely mobile under all conditions, they have a special significance as the tracer element of leachate plume linking the groundwater [40].

### 3. Materials and Methods

Leachate samples were collected from four landfill sites; the Pulau Burung landfills (PBLs), Ampang Jajar Landfill Site (AJLS), Kuala Sepetang Landfill Site (KSLS) and Kulim Landfill Site (KLS).

PBLs is a semiaerobic landfill situated within Byram Forest Reserve at 5°24' N, 100° 24' E and encompasses an area of 23.7 ha. This site is contained by a natural marine clay liner [41]. In 1991, it was upgraded to sanitary landfill level II by a controlled tipping technique and was further upgraded to a sanitary landfill level III through leachate recirculation and controlled tipping in 2001 [42].

AJLS is a semiaerobic closed landfill site situated at 5.24'.0''N and 100.24'.22''E with a total surface area of 17 acres. Receiving both municipal and industrial wastes, this landfill was started as a dump in the early eighties and it had neither any leachate collection system nor defined space for waste dumping. During operation the landfill received approximately 650 tons of solid waste per day. The landfill possesses no base liner which resulted in heavy pollution of nearby river and groundwater in its early stages.

Kuala Sepetang landfill site is located at 4.49'.20.08''N and 100.40'.44.08''E. The landfill receives about 300 tons of solid waste daily and is classified as improved anaerobic landfill. The landfill is around 12 years old. Natural marine clay and local soil are used as cover material for dumped waste. Leachate produced is collected in a collection pond and is not provided any treatment.

The samples were carefully collected from the landfill site and temperature and pH were measured onsite. The samples were then transferred to the laboratory in an ice cooler and stored in a cold room at 4°C. Prior to analysis, the samples were allowed to return to room temperature and measurements for leachate parameters were carried out. The parameters measured for each landfill are given in Tables 1 and 2. pH was measured on site using a portable pH meter (Hach, sens ion 1, USA). All the parameters were measured according to the standard methods for the examination of water and wastewater [43]. After measuring the laboratory parameters, the LPI was calculated according to.

$$LPI = \frac{\sum_{i=1}^m w_i p_i}{\sum_{i=1}^m w_i}, \quad (1)$$

where LPI is the weighted additive leachate pollution index,  $m$  is the number of leachate pollutant parameters for which data is available,  $w_i$  is the weight for  $i$ th pollutant variable,  $p_i$  is the sub index score of the  $i$ th leachate pollutant variable.

When all the leachate parameters are unknown,  $m < 18$  and

$$\sum_{i=1}^m w_i < 1. \quad (2)$$

### 4. Results and Discussion

Table 1 shows the PBLs and KLS leachate characteristics and LPI obtained for these landfill sites. Since the data for all the parameters required for LPI was not available, the LPI has been calculated on the basis of the available data. The concentration of TDS, COD, TKN, and NH<sub>3</sub>-N was higher in PBLs leachate while KLS contained relatively higher value of BOD<sub>5</sub> as seen in Table 1. A significant difference between individual pollution ratings of TKN and NH<sub>3</sub>-N for both landfill sites was observed due to the distinct difference in TKN and NH<sub>3</sub>-N concentrations. Although the concentration of COD in PBLs leachate was higher than KLS leachate, the difference was insignificant in terms of individual and consequently cumulative pollution ratings. The concentration of heavy metals was fairly similar for both the landfills except for Pb where PBLs almost has twice higher concentration than KLS (Table 1). The two sites also exhibited notable differences for chlorides and total coliforms. However, the difference in the concentrations of chlorides for PBLs and KLS had insignificant influence on individual and cumulative pollution ratings. But, the concentration of total coliforms in KLS leachate was much higher than PBLs which resulted in significantly higher cumulative pollution rating in comparison to PBLs. It is clear from Table 1 that the higher concentrations of TKN, NH<sub>3</sub>-N, total coliform and to some extent Pb significantly influenced the cumulative pollution ratings of PBLs. Because the individual pollution ratings of TKN and NH<sub>3</sub>-N were lower for the case of KLS, the cumulative pollution rating of KLS was consequently lower in comparison to PBLs.

The characteristics of leachate from AJLS and KSLS and the resulting LPI from these landfill sites are given in Table 2. As can be seen from Table 2, the concentrations of TDS, BOD<sub>5</sub>, COD, TKN and NH<sub>3</sub>-N represent a significant difference between AJLS and KSLS leachate. The higher concentrations of TDS, COD, TKN and NH<sub>3</sub>-N for KSLS leachate imply higher individual and cumulative pollution rating and consequently higher LPI value. Although the concentration of heavy metals showed slight variations, it has no effect on individual pollution ratings (Table 2). The concentration of total coliforms was higher for AJLS but this difference was not as significant as was in the case of PBLs and KLS (Table 1), hence the difference in LPI values of AJLS and KSLS is little influenced by the difference in the concentrations of total coliforms (Table 2). The concentration of chlorides in KSLS leachate was more than five times higher than AJLS, but the cumulative pollution rating for chlorides in KSLS was only 1.4 times higher than AJLS (Table 2).

Figure 1 gives graphical representation of LPI values for each landfill site. The comparison of LPI values for four landfill sites shows that semiaerobic PBLs has the highest LPI value, while the LPI value for closed semiaerobic AJLS

TABLE 1: Characteristics and LPI of leachate from PBLS and KLS\*.

Parameter	Value		Individual pollution rating ( $p_i$ )		weights ( $w_i$ )		Cumulative pollution rating ( $p_i w_i$ )	
	PBLS	KLS	PBLS	KLS	PBLS	KLS	PBLS	KLS
pH	8.3	7.8	5	5	0.055	0.055	0.275	0.275
TDS	9693	6900	19	15	0.050	0.050	0.95	0.75
BOD <sub>5</sub>	358	515	11	15	0.061	0.061	0.671	0.915
COD	1788	1593	47	42	0.062	0.062	2.914	2.604
TKN	1685	612	60	20	0.053	0.053	3.18	1.06
NH <sub>3</sub> -N	1380	503	100	55	0.051	0.051	5.1	2.8
Total iron	3.6	6	5	5	0.045	0.045	0.225	0.225
Cu	0.01	0.2	5	6	0.050	0.050	0.25	0.3
Ni	0.1	0.2	6	6	0.052	0.052	0.312	0.312
Zn	0.3	0.3	6	6	0.056	0.056	0.336	0.336
Pb	3	1.6	27	11	0.063	0.063	1.7	0.693
Cr	0.2	0.1	5	5	0.064	0.064	0.32	0.32
Hg	—	—	—	—	—	—	—	—
As	—	—	—	—	—	—	—	—
Phenol	6	3	10	8	0.057	0.057	0.57	0.456
Chlorides	622	290	7	5	0.048	0.048	0.336	0.24
Cyanide	—	—	—	—	—	—	—	—
Total coliform	50	$0.81 \times 10^4$	40	90	0.052	0.052	2.08	4.68
<b>Total</b>					<b>0.819</b>	<b>0.819</b>	<b>19.21</b>	<b>15.97</b>
<b>LPI</b>							<b>23.45</b>	<b>19.50</b>

\* All values in mg/L except pH and total coliform; total coliform unit (CFU/100 mL).

TABLE 2: Characteristics and LPI of leachate from AJLS and KSLS\*.

Parameter	Value		Individual pollution rating ( $p_i$ )		weights ( $w_i$ )		Cumulative pollution rating ( $p_i w_i$ )	
	AJLS	KSLS	AJLS	KSLS	AJLS	KSLS	AJLS	KSLS
pH	7.5	8.1	5	5	0.055	0.055	0.275	0.275
TDS	2543	12568	7	26	0.050	0.050	0.35	1.3
BOD <sub>5</sub>	48	85	7	26	0.061	0.061	0.427	0.488
COD	599	990	20	35	0.062	0.062	1.24	2.17
TKN	822	1176	25	39	0.053	0.053	1.235	2.06
NH <sub>3</sub> -N	566	996	60	100	0.051	0.051	3.06	5.1
Total iron	3	5	5	5	0.045	0.045	0.225	0.225
Cu	0	0.7	5	5	0.050	0.050	0.25	0.25
Ni	0	0.3	5	5	0.052	0.052	0.26	0.26
Zn	0.01	0.2	5	5	0.056	0.056	0.28	0.28
Pb	0.3	0.4	5	5	0.063	0.063	0.31	0.31
Cr	0	0.05	5	5	0.064	0.064	0.32	0.32
Hg	—	—	—	—	—	—	—	—
As	—	—	—	—	—	—	—	—
Phenol	2	4	7	9	0.057	0.057	0.39	0.51
Chlorides	124	655	5	7	0.048	0.048	0.24	0.336
Cyanide	—	—	—	—	—	—	—	—
Total coliform	$0.66 \times 10^4$	$0.16 \times 10^4$	87	76	0.052	0.052	4.52	3.95
<b>Total</b>					<b>0.819</b>	<b>0.819</b>	<b>13.47</b>	<b>17.83</b>
<b>LPI</b>							<b>16.44</b>	<b>21.77</b>

\* All values in mg/L except pH and total coliform; total coliform unit (CFU/100 mL).

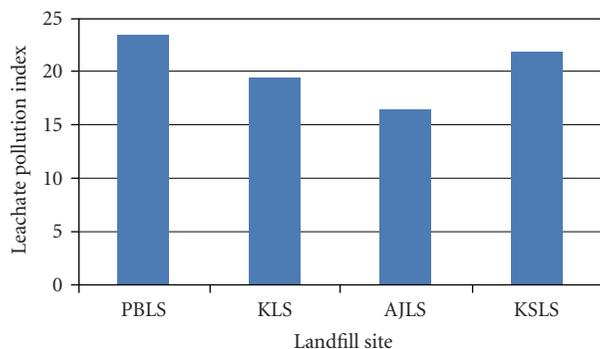


FIGURE 1: Leachate pollution index for four landfill sites.

is the lowest. The LPI value of anaerobic KSLs is slightly higher than anaerobic KLS but both these anaerobic landfill sites have lower LPI value than semiaerobic PBLs. Kumar and Alappat [12] calculated LPI values for two active landfill sites and reported higher LPI (36.4 and 39) than PBLs (23.45), KLS (19.50) and KSLs (21.77). This can be ascribed to the lower individual pollution ratings of PBLs, KLS and KSLs due to the relatively lower concentrations of BOD<sub>5</sub>, COD, TKN, NH<sub>3</sub>-N and to some extent the chlorides than the landfill sites studied by Kumar and Alappat [12]. The lower LPI value for AJLS suggests that the landfill leachate is stabilized which is also indicated by the BOD<sub>5</sub> and COD values given in Table 2. The lower LPI value for a closed landfill site has also been reported by Kumar and Alappat [12]. The authors reported LPI value of 15.97 for Nagu Chi Wan (NCW) landfill site which is almost similar to the LPI value reported for AJLS (16.44) in this study. The similarity of LPI value for these two sites is worth mentioning because the NCW landfill site studied by Kumar and Alappat [12] and AJLS in this study were of similar age. The fact that PBLs is currently operational and is receiving domestic and industrial wastes, higher LPI value shows that the leachate produced from PBLs should be attended first if the local management has to choose among the four landfill sites for leachate management and treatment. Because the characteristics of landfill leachate changes over time, the LPI value will also differ from one sampling period to another, hence the LPI value would correspond to the leachate samples analysed at a particular time for a specific landfill site.

## 5. Conclusion

Leachate characteristics demonstrate high variations and which range of physical, chemical, and biological parameters may vary over several order magnitude. LPI is a good tool to compare pollution potential of landfill sites. Among the four sites, semiaerobic PBLs has the highest LPI value while semiaerobic AJLS has the lowest LPI. It is interesting to note that the semiaerobic PBLs is better comparable with KSLs anaerobic landfill in terms of LPI value. In the similar manner semiaerobic AJLS is comparable to anaerobic KLS based on the value obtained for LPI. Although LPI of the

four studied landfill sites is not very high, the leachate shall be treated prior to discharge for individual pollution parameters such as BOD<sub>5</sub>, COD, and ammonia to meet individual standards. The landfill sites requiring immediate attention can also be prioritized based on the value of LPI to avoid big pollution incident. Because changes in individual quality parameters alter the value of LPI, it can be used as a reliable tool to report seasonal and site specific variations in quality of landfill leachate.

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## Review Article

# Nitrogen and Phosphorous Removal in Municipal Wastewater Treatment Plants in China: A Review

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Surface water environment in China was degraded rapidly in the last two decades, resulting in increasingly tighten criteria issued for municipal wastewater treatment plants (WWTPs). This paper reviewed the recent advances of process design and operational optimization for nutrients removal. Three major processes, as anaerobic-anoxic-oxic (AAO) process, oxidation ditch (OD), and sequencing batch reactor (SBR) occupied 65% of WWTPs amounts and 54% of treatment volumes of China in 2006. However conservative process designs and operational faults often impaired the process performances and energy efficiency. Therefore, typical processes were modified, combined, and innovated to meet the requirements of the diverse influent characteristics and lower energy consumptions. Furthermore, operational optimization techniques by modeling, simulation, and real-time control were also developed and applied in China to improve the process operation. Although great efforts had been contributed to improve the WWTPs performances in China, attentions should be continuously paid to the introduction, instruction, and implementation of advanced techniques. At last, the technical demands and appropriated techniques of WWTPs in China were briefly discussed.

## 1. Introduction

In the last two decades, surface water environment in China was rapidly degraded by the booming industrialization and fast urbanization. The first large scale municipal wastewater treatment plant (WWTP) in China was constructed and operated 25 years ago [1]. In recent ten years, the construction of municipal WWTPs was catalyzed by the serious deterioration of surface water around cities, as shown in Figure 1. The reduction of ammonia nitrogen ( $\text{NH}_3\text{-N}$ ) and total phosphorous (TP) are also shown in the figure [2] in the unit of part per million (ppm) and also mg/L in water. The ammonia reduction was only 13.2 to 18.3 mgN/L and the phosphorous reduction was almost constant at 2.5 mgP/L from 2001 to 2007 [1], implying unsatisfied process performances in current WWTPs.

The rapid development of municipal WWTPs and their unsatisfied performances promoted the engineering innovations, as well as the academic studies. In this paper, the recent progresses of nitrogen and phosphorous removal in municipal WWTPs were reviewed in the aspects of

process design and operational optimization, the advances in academic studies, and the practices in engineering fields in China.

## 2. WWTP Processes in China

### 2.1. Features of Processes in WWTPs in China

2.1.1. *Composition of WWTPs Processes.* Biological nutrients removal (BNR) processes apply alternative aerated and unaerated environments to remove nitrogen and phosphorous from water by the growth and metabolism of specific bacteria. Typical BNR processes include conventional activated sludge (CAS) process, anaerobic-anoxic-oxic (AAO) process, anaerobic/anoxic-oxic (AO) process, oxidation ditch (OD), sequencing batch reactor (SBR), membrane bioreactor (MBR), biofilm reactor, and lagoon [3].

Figure 2 shows the WWTPs amounts and the treatment wastewater volumes for BNR processes in China in 2006. The statistic data covered 74% and 77% of the total ranges of

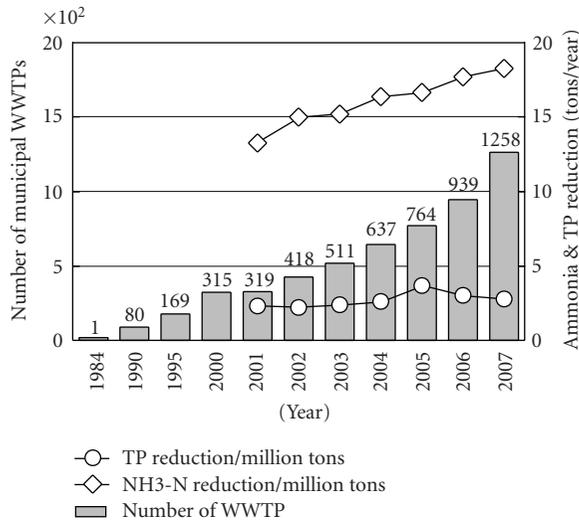


FIGURE 1: Nutrients reduction in municipal WWTPs based on treated wastewater in China.

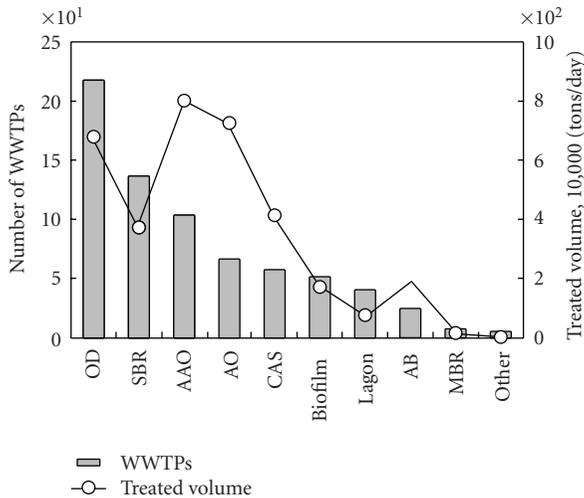


FIGURE 2: Composition of processes in municipal WWTPs in China.

TABLE 1: Capacities of WWTP processes in geographic zones of China in 2006<sup>a</sup>.

	North	East	Northeast	Middle	South	Southwest	Northwest
OD	110	280	0	140	40	60	50
SBR	30	120	70	10	50	80	30
AAO	220	370	10	20	120	60	20
AO	120	290	120	110	40	60	1
CAS <sup>b</sup>	60	110	50	50	130	10	10

<sup>a</sup>Statistic data covers 75% of the total WWTPs, and the data are approx. total capacities for each process. Capacity is in the unit of 10,000 tons/day;

<sup>b</sup>Conventional activated sludge processes including primary treatment processes.

WWTPs amounts and treated volumes, respectively. Among the investigated processes, OD, SBR, and AAO were the three major processes, which together occupied 65% of WWTPs amounts and 54% of treated volumes. The different

occupations among the investigated processes were related with their distinct features, for example, easiness of operation and maintenance, instrumental requirements, and energy consumptions, and also of great importance, related with the process reformation and upgrade. It could be expected that WWTPs numbers and treated wastewater volumes of AAO process would be continuously increased by the strong potential of the reformation of CAS process.

**2.1.2. Spatial Distributions of WWTPs Processes.** Table 1 shows the spatial distributions of the major processes in the seven geographic zones of China. The amounts of wastewater were usually determined by the population densities and economic levels, therefore larger volumes of wastewater were treated in the North, South, and East China than other zones. The process design of WWTPs was often affected by comprehensive factors in China, such as distinct features of different processes, natural conditions like temperature and water resources, social situations like population and economics, and the orientations of process designers. For example, OD process has never been applied in the Northeast China because of the very low ambient temperature there. However, it was popularly adapted in the East and Middle China because of the less production of excessive sludge and the designers' favorites.

**2.1.3. Performances of WWTPs Processes.** Table 2 shows the different performances of the major processes in 2006, including the influent concentrations and average removal rates of pollutants. The major processes showed similar performances on the removal of COD, NH<sub>3</sub>-N, TN, and TP according to the table. The better performance of phosphorous removal over nitrogen removal was partially related with the chemical precipitation processes optionally adapted in municipal WWTPs.

**2.2. Developing Criteria for Nutrient Removal.** Table 3 lists the historical discharging standards for municipal WWTPs in China, which reflects the development trace of municipal wastewater treatment [1]. Only the criteria of nutrients were shown in the table because the complete contents were too much to be included. According to the table, NH<sub>3</sub>-N and TP were firstly included in the national criteria in 1998 and TN was additionally included in 2003. During the process reformations and upgrades, current active I-A level became the ambition of municipal WWTPs because it was the limits to WWTP effluents for water reuse and recycling. At the areas with serious pollution of surface water, for example, around Taihu Lake, more tightened criteria than national I-A level were issued to control the eutrophication. The criteria in the future were expected to be close to the surface water quality standards, as shown in the table, to meet the requirements of wastewater reclamation due to the crisis of water shortage in municipal cities.

**2.3. Difficulties for Successful BNR Processes.** Performances of BNR processes were often impaired by the improper design and operation, which often occurred in municipal WWTPs

TABLE 2: Performance of major WWTP processes in China in 2006 (unit, mg/L).

	COD			NH <sub>3</sub> -N			TN			TP		
	mean <sup>a</sup>	range <sup>b</sup>	% <sup>c</sup>	mean <sup>a</sup>	range <sup>b</sup>	% <sup>c</sup>	mean <sup>a</sup>	range <sup>b</sup>	% <sup>c</sup>	mean <sup>a</sup>	range <sup>b</sup>	% <sup>c</sup>
OD	320	125–550	84%	28	12–46	68%	34	18–58	59%	4.2	1.2–7	71%
SBR	300	120–500	83%	27	10–48	66%	34	15–57	58%	4.0	1.2–6	71%
AAO	390	150–700	85%	32	14–54	75%	39	16–68	55%	5.4	2.0–10	78%
AO	460	140–860	80%	31	11–49	64%	46	19–74	58%	5.3	1.0–9	70%
CAS <sup>d</sup>	440	175–790	88%	34	14–58	50%	40	6–86	42%	4.9	1.7–10	66%

<sup>a</sup>Average concentrations of pollutants in raw influent to WWTPs; <sup>b</sup>10 and 90 percentiles in the distribution of pollutant concentrations; <sup>c</sup>Removal rates based on average values of WWTP influent and effluent; <sup>d</sup>Conventional activated sludge processes with primary and secondary treatment.

TABLE 3: National discharge criteria of municipal WWTPs in China.

Standards	Levels	COD <sub>Cr</sub>	BOD <sub>5</sub>	SS	NH <sub>3</sub> -N	TP	TN	Active time
GB-73		100	60	500				1973
GB8978-88		120	30	30				1989.1.1
GB8978-96	II level	120	30	30	15	1		1998.1.1
	I level	60	20	20	15	0.5		
GB18918-2002	II level	100	30	30	25 (30) <sup>a</sup>	3		2003.1.1
	I-B level	60	20	20	8 (15)	1	20	
	I-A level	50	10	10	5 (8)	0.5	15	
Expectation		20 <sup>b</sup>	3	3	1	0.1 <sup>c</sup>	5	future

<sup>a</sup>Criteria for chilly weather lower than 12 Celsius degree; <sup>b</sup>COD<sub>Mn</sub> in surface water instead of COD<sub>Cr</sub> in wastewater; <sup>c</sup>Standards only for lake water and reservoirs.

in China. Typical problems in process design and operation were usually derived from diverse influent characteristics, inevitable design defects, and undeveloped operation levels.

**2.3.1. Inadequate Studies on Influent Characteristics.** The design and operation of WWTP processes in China were based on experiences of engineers rather than scientific conclusion. There are very few investigations on the components in the influent of municipal WWTPs, as well as the spatial and seasonal variations of influent concentrations in China, resulting in inadequate knowledge on the diverse influent characteristics. The studies on influent characterization were affected by the greatly varied natural and social conditions all over the country, for example, developing industries and constructing sewer systems may intensively change the influent components in short period. Furthermore, the difficulties of continuous monitoring, the lack of data accumulation, and the negative wills of managers in WWTPs hindered the optimization of BNR processes.

**2.3.2. Defects in Process Designs.** Process designers in China often followed the similar influent characteristics to start the design without careful investigations on the actual concentrations of pollutants. Except of the uncertainty of influent characteristics, process designers might face more complicated situations like the absence of sewer system data, inaccurate prediction of population, uncontrolled industrial wastewater discharge, and so forth, limiting their possibility to design the configuration with satisfied flexibility. Therefore big variation coefficients, large volumes

of tanks, and very long hydraulic retention times were utilized in the designs to ensure the security of process operation. This situation produced conservative and rigid processes and resulted in operational difficulties, for example, very few designs allowed engineers to change the return flows of mixed liquor along with the influent flows.

**2.3.3. Undeveloped ICA Levels.** The WWTPs were almost tripled in the last seven years as shown in Figure 1, requesting not only the huge amount of infrastructural investments but also a number of skilled and experienced operational engineers which could not be cultured in short time. Instrumentation, control, and automation (ICA) techniques could alleviate this human resource crisis, which had been developed and successfully applied in municipal WWTPs in Europe [4]. In this field, the researchers in China made rapid progresses in the theoretical studies, control algorithms, optimization strategies, and supervisory systems. However, the application of ICA techniques in actual processes was still very limited due to the expensive online instruments and the current huge amount of employees.

### 3. Advances in Process Design and Innovation

#### 3.1. Process Design and Augmentation

**3.1.1. Process Design for Municipal WWTPs.** After 25 years of practices on large-scale municipal WWTPs, the process design has been gradually improved in China. Table 4 shows the processes and performances of several example

TABLE 4: Typical processes applied in municipal WWTPs and their performances in 2006.

Group	Process	WWTPs	From <sup>m</sup>	Capacity 10 <sup>4</sup> m <sup>3</sup> /d	Removal by WWTP, % <sup>n</sup>			
					COD	NH <sub>3</sub> -N	TN	TP
AAO	r-AAO <sup>a</sup>	Gaobeidian in Beijing	1993	100	90	90	50	20
	AAO	Xiaohongmen in Beijing	2005	60	90	90	60	60
	AO	Jizhuangzi in Tianjin	2005	54	90	70	55	90
	A-AAO <sup>b</sup>	Tangjiatuo in Chongqing	2006	30	85	85	60	50
	VIP <sup>c</sup>	Licunhe in Qingdao	1998	8	95	90		80
SBR	CAST <sup>d</sup>	Zhengrun in Zhenjiang	2003	10	80	20	10	90
	DAT-IAT <sup>e</sup>	Diyi in Benxi	2004	23	70	80	50	70
	UNITANK <sup>f</sup>	Chengbei in Nanjing	2003	30	80	75	55	80
	ICEAS <sup>g</sup>	Disan in Kunming	1997	15	80	80	40	55
OD	Orbal	Chengbei in Wuxi	2001	10	90	90		90
	Carrousel	Yangli in Fuzhou	2003	20	85	90	40	55
	T-OD <sup>h</sup>	Luofang in Shenzhen	2001	25	90	85		60
	DE-OD <sup>i</sup>	Beishiqiao in Xi'an	1998	15	95	90	70	90
	A+OD <sup>j</sup>	Dongjiang in Dongguan	2002	20	90	90		50
Biofilm	BAF <sup>k</sup>	Xiannvhe in Shenyang	2003	40	85	35		85
	BioLak <sup>l</sup>	Binzhoushi in Shandong	2002	10	80	70		50

<sup>a</sup>reverse AAO; <sup>b</sup>AAO with preanoxic zone; <sup>c</sup>VIP process; <sup>d</sup>Cyclic activated sludge technology; <sup>e</sup>UNITANK process; <sup>f</sup>Demand aeration tank-intermittent tank; <sup>g</sup>Intermittent cycle extended aeration; <sup>h</sup>Triple channel oxidation ditch; <sup>i</sup>Dual channel oxidation ditch; <sup>j</sup>Anaerobic zone before Carrousel oxidation ditch; <sup>k</sup>Biological aeration filter; <sup>l</sup>BioLak is a process developed by a German Company; <sup>m</sup>The time of operation started; <sup>n</sup>Removal rates calculated approximately by values in 2006.

WWTPs in 2006 [3]. AAO process group in China usually included conventional AAO, reverse AAO, AO, AAO with preanoxic zone (A-AAO), and UCT/VIP processes. SBR process group consisted of CAST, DAT-IAT, UNITANK, and ICEAS processes. OD process groups adapted in China were Orbal, Carrousel, T-OD, DE-OD, and other modifications like Carrousel with preanaerobic zones (A+OD) [5].

The scheme diagrams of above processes were shown in Figure 3. The more candidate processes gave designers more possibilities to configure good processes with lower cost and higher efficiency. For example, in order to deal with the distinct conflicts between nitrogen removal and phosphorous removal in AAO process, designers may adapt reverse AAO (r-AAO) or A-AAO process to enhance the nitrogen removal with the price of unsatisfied phosphorous reduction [6], and other designers may prefer simple AO process coupled with chemical precipitation. Furthermore, decision-making tools for complicated multicriteria, such as capital and operation cost, land area, nutrient removal, and sludge disposal, were developed to obtain scientific and reasonable process among municipal wastewater treatment alternatives [7].

Local enterprises in China had integrated or modified the imported processes in their engineering practices as shown in Figure 4, such as CSBR (continuous flow/constant level SBR) modified by THUNIP Company, DF-MBR (dual filtration membrane bioreactor) integrated by NEPRI (national electricity environmental protection institute of China), modified Carrousel OD developed by Anhui Guozhen Corp., and HSCBR (high efficient separation composite biological fluidized reactor) owned by Jiangsu Yihuan Corp [8].

*3.1.2. BNR Augmentation Attempts.* Bioaugmentation was often applied to enhance the nutrients removal in conventional processes in China. The most popular solution was to introduce specially designed porous media into the aeration tanks to augment biofilm reactions [9]. The total biomass concentrations could be augmented from 3.2 g/L to 4.3–5.8 g/L with the carriers in 15%–30% of volumetric portion [10]. The media characteristics of surface areas and hydrophobic properties were important for the performance of biofilm and its startup.

In South China, domestic wastewater is always low in strength due to the high water level of groundwater and setting of septic tank at the beginning of wastewater collection system [6]. The bioaugument process, which installed polyurethane foams as carriers and inoculated specialized bacteria on the media, was found more easily started up in lower DO concentrations [11]. Zeolite was also used to enhance conventional contact stabilization activated sludge process and improved nitrogen removal for 27%, by the mechanism of preferential ion exchange of zeolite to ammonium [12].

*3.2. Process Innovation for Municipal WWTPs.* Some innovated processes have been demonstrated to achieve good nutrients removal in China, such as (1) natural purification system, for example, various infiltrations and wetlands, (2) anaerobic biological treatment processes, for example, upflow anaerobic sludge blanket reactor, anaerobic filters, and anaerobic baffled reactor, (3) biofilm reactors, for example, three-phase fluidized reactor, and (4) wastewater reclamation techniques with the core of membrane separation [8, 13].

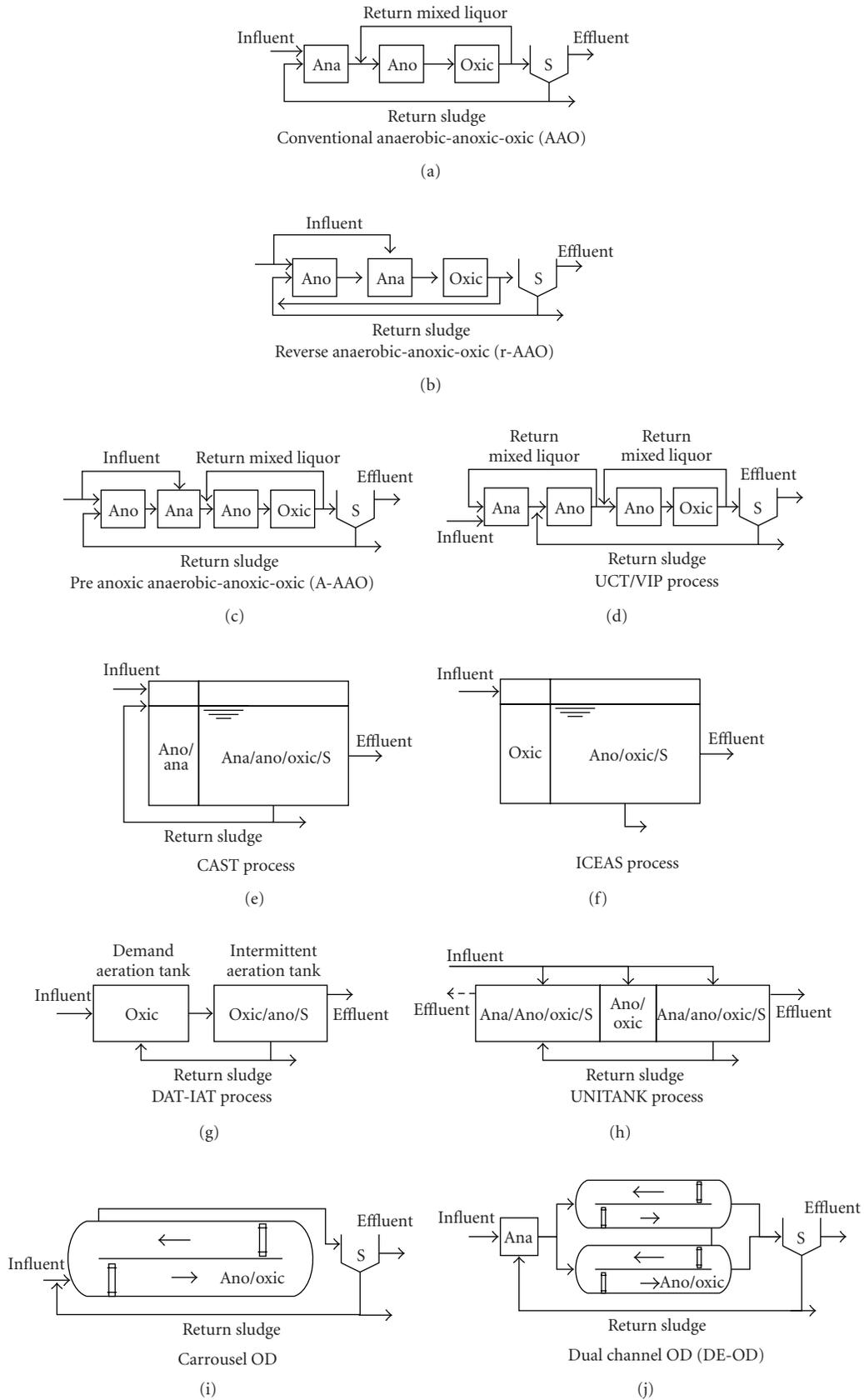


FIGURE 3: Continued.

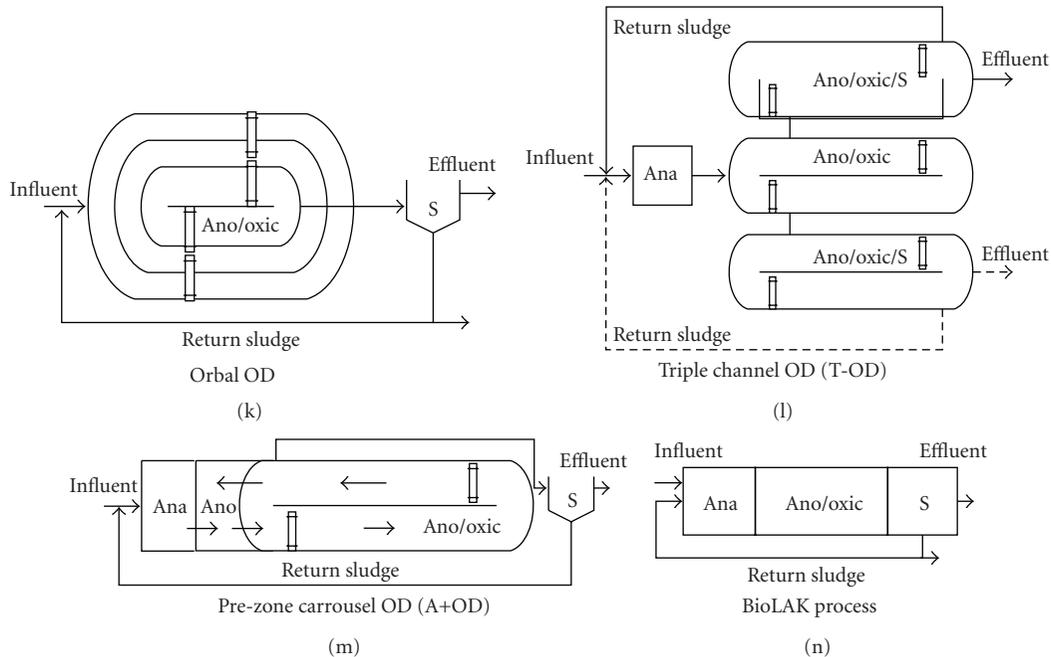


FIGURE 3: Scheme diagrams of major processes in WWTPs in China.

**3.2.1. Innovation for Critic Environmental Conditions.** Municipal wastewater treatment encountered some critic conditions such as high salinity in coasts, and frozen temperature in chilly zones. An integrated process (SANI, see Figure 4) consisting of sulfate reduction, autotrophic denitrification and nitrification was developed in Hongkong and applied in coastal areas of China to reclaim saline water without any excessive sludge discharge [14]. SBR was found also capable of removing nitrogen in saline wastewater by short-cut nitrification [15]. In chilly seasons, an internal circulation compound bioreactor worked well by isolation and immobilization of cold-adapted microorganisms onto soft polyurethane foams, with COD removal of 86% in the conditions of 4–10°C [16].

**3.2.2. Innovation for Low Concentration Wastewater Treatment.** The TN removal was often limited by the low concentrations of influent organics in South China. There were several techniques developed to deal with the lack of carbon sources, for example, a primary treatment process enhanced by composite flocculant which combined bioflocculants Pullulan and poly-aluminum-chloride (PAC) could achieve 91% and 15% of TP and NH<sub>3</sub>-N removal, respectively [17]. Biological contact oxidation process and biological aerated filter (BAF) process were also capable to enhance the nutrients removal by careful selection of the media [18]. The limited carbon source could be effectively utilized by optimized feeding methods, for example, four-stage step-feeding AO process [19]. Another option was to utilize short-chain fatty acids generated during waste activated sludge fermentation in alkaline conditions as internal carbon sources [20].

**3.2.3. Innovation for Lower Cost and Energy Consumption.** Some techniques were innovated or optimized to save the land use and investments. Anaerobic-anoxic-nitrification (A2N, see Figure 4) process with two stages of return sludge flow utilizes denitrifying phosphorous removing bacteria (DPB) to removal nitrate and phosphorous simultaneously [21], which is more promising than UCT/VIP processes (see Figure 3) [22]. By simple modification of the flow lines, the DPB could be isolated and accumulated in the system to achieve better performance of denitrification [23]. Simultaneous nitrification and denitrification (SND) process via nitrite could obviously reduce the aeration and thus save the energy consumption, which could be achieved in SBR [15] and hybrid SBR systems [24]. The airlift oxidation ditch (AOD, see Figure 4), using underwater aeration to achieve simultaneous aeration and agitation, was operated in lower cost and higher efficiency than other oxidation ditches. The land use and energy consumption could be saved for 25% and 55%, respectively, according to the pilot-scale experiments [25]. After integrating a transverse flow membrane module and a MBR in an innovative configuration, the system gained the advantages of lower energy consumption and more resistance to membrane fouling [26].

## 4. Advances in Process Optimization

Nutrients removal was often harmed by inadequate denitrification, inhibition of phosphorous removal by nitrate, over aeration, over dosage of chemicals, and improper operation of settling pretreatment tanks. In the last decade, attempts from both academic and engineering sides in China were contributed to improve the process operation in municipal WWTPs.

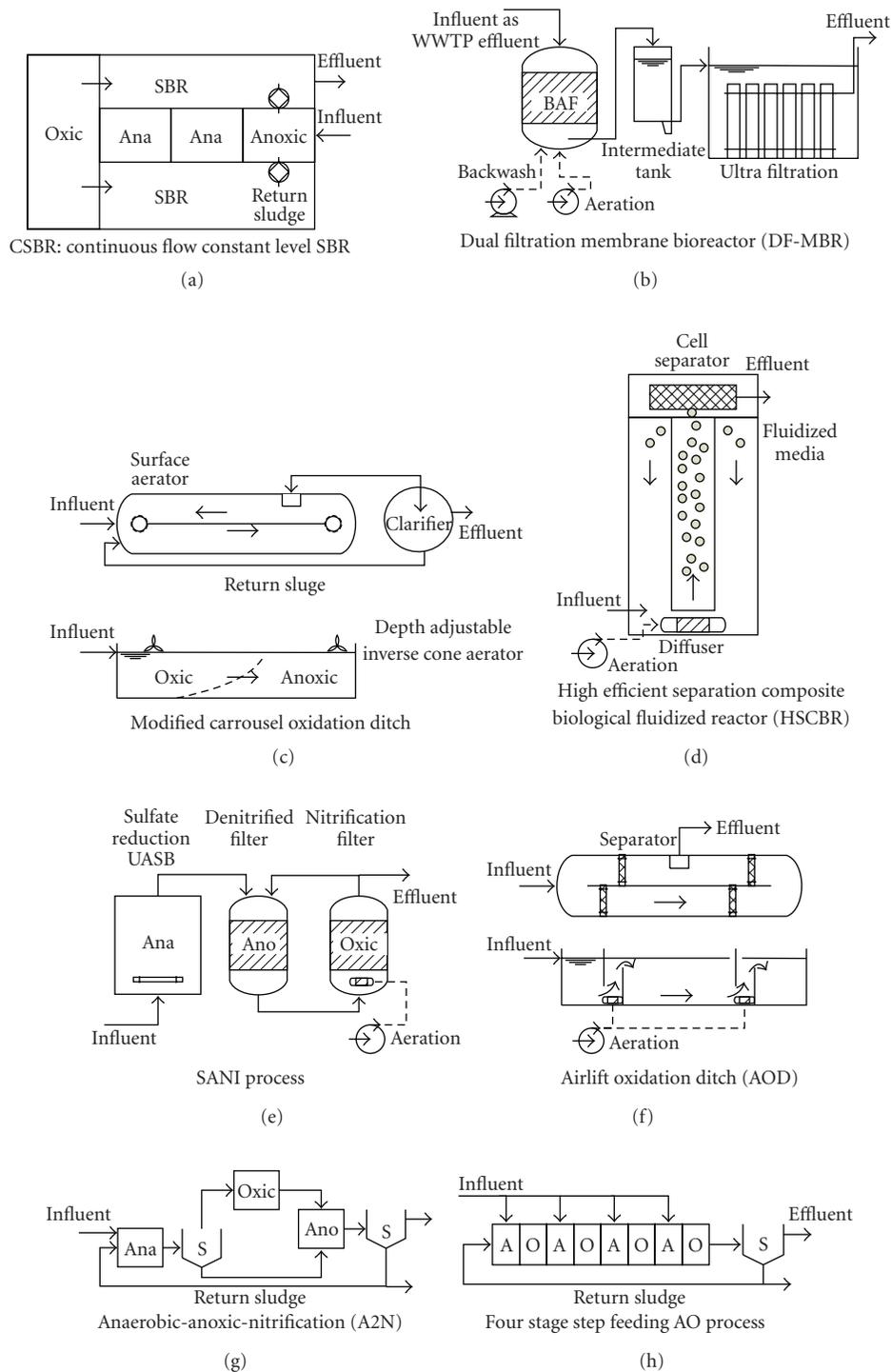


FIGURE 4: Innovated or modified processes in WWTPs in China.

4.1. Modeling, Simulation, and Optimization of Process. Modeling and simulation based on activated sludge models (ASMs) were useful to screen optimization strategies for process operation by an effective and economic method. The manipulative variables in actual AAO process, such as dissolve oxygen (DO), volumetric portions for denitrification, return flow rates, and excessive sludge flow rate, could be

refined by the systematic procedure of modeling, simulation, and optimization [4]. Benchmarking simulation models (BSMs) were intensively studied for real-time control in last decades in China, helping to accumulate knowledge and testify the novel control methods like model predictive control strategies and sophisticated feedback control systems [27].

New models based on ASMs were developed in China for scientific studies and engineering feasibility. An integral model named fully coupled activated sludge model (FCASM) described the interactions of eight functional microorganisms involved in BNR processes [28], while a simplified model based on carbon oxidation steps in ASM1 was successfully applied in Jizhuangzi WWTP at Tianjing City [29].

Sedimentation tanks play important role for guarding the effluent with good quality. By using computational fluid dynamics (CFDs), the distribution of suspended solids in secondary sedimentation tanks could be simulated by the three-dimensional two-fluid model, resulting in useful information for process design [30]. Particle image velocimeter was useful to study the settling of activated sludge flocs under turbulent flow conditions, indicating that the settling velocity was correlated to the particle size, turbulence intensity, and solid concentrations [31]. Whatever, conventional models, such as Vesilind model and double exponential model, were still feasible for simulation of compression settling process by careful model calibration [32].

CFD technique was systematically applied in the field simulation, optimization of aerators and shapes of oxidation ditches. Particle dynamic analyzer (PDA) and CFD simulation were found useful to optimize the designs of Carrousel OD [33]. Nitrogen removal could be improved in Carrousel OD by controlling the return sludge flow, dissolved oxygen (DO), and influent sites according to the influent loadings and temperature [34]. The promotion of DO distribution to nitrogen removal was also observed in a fluidized bed reactor, which was affected by the vertical stratification of active sludge populations [35].

**4.2. Real-Time Controlling for BNR Process.** Operational optimization of process requires high levels of ICA techniques in municipal WWTPs. Unfortunately, the studies of real-time controlling system and relative strategies were very few in China, and mainly focused on SBR systems. In SBR process, even single variant control by DO level could achieve better biological nitrogen removal and sludge population optimization [36]. The control strategies utilized pH and oxidation reduction potential (ORP) as on-line control parameters could remove TN as high as 98% with very low influent carbon/nitrogen ratio (C:N=3.5) [37]. By a real-time aeration control strategy based on DO, pH, and ORP, the short-cut nitrogen removal could be achieved by nitrification and denitrification via nitrite [38]. Furthermore, the performance and benefits of the real-time controlling system were validated in a pilot-scale SBR [39]. Fuzzy control strategies were applied in scientific studies for the real-time control of activated sludge process. For example, AO process could be optimized by using on-line sensors DO, pH, and ORP and fuzzy inference system to control aeration, nitrate recirculation flow, and external carbon dosage [40].

**4.3. Implementation of ICA Techniques.** Although current ICA techniques are in state-of-art, application of ICA

in municipal WWTPs in China was obstructed by the expensive instruments and controllers, rare and ineffective maintenance, easily broken actuators, lack of knowledge, and absence of consultancies. Although automatic control was utilized in most of SBR systems, it was limited in unit operations instead of process optimal operation. The first application of feed-forward control by ICA techniques, in its original meaning, might be the reformation project of Bailonggang WWTP in Shanghai City in 2008, in which a bioprocess intelligent optimization system (BIOS, BioChem Company, USA) [41] was installed to control the aeration based on the online signals of ammonia and nitrate.

## 5. Future Perspectives

The appropriated processes or technologies for municipal WWTPs in China have the features of high efficiency and stability, lower energy consumption and operational cost, easy operation and maintenance, and lower specific footprint to reduce the occupied land area and the investment [13]. Additionally, suitable technologies for wastewater handling in small communities were necessary for the purpose of scattering treatment instead of centralizing sewer systems [42].

Although a lot of attempts have been contributed for nutrients removal, more attentions should be paid to the introduction, instruction, and implementation of advanced techniques in municipal WWTPs by considering the urgent crisis of surface water contamination and water resource shortage. The Major Projects on Control and Rectification of Water Body Pollution (2005–2020), which are supported by the central and local governments and enterprises, has covered the most topics of municipal wastewater treatment and will greatly promote the development and application of new techniques.

## 6. Conclusions

This paper reviewed the advances of nitrogen and phosphorous removal in municipal WWTPs in China. The construction of municipal WWTPs was gradually increased in last decade. AAO, SBR, and OD processes were major candidates for process design, but their performances were unsatisfied according to the more strict discharge criteria. Typical problems in process design and operation were summarized as inadequate knowledge of influent, design defect, and undeveloped ICA techniques. Great efforts had been made by researchers and industries to deal with the problems, including process design innovated for critic conditions, low concentration of influents, and saving energy consumption, and process optimization achieved by modeling and simulation, real-time control, and implementation of ICA techniques. Despite of all those efforts, more attentions should be paid to the implementation of advanced techniques in municipal WWTPs. Finally, the appropriate techniques and future perspectives were briefly discussed.

## Nomenclature

AAO:	Anaerobic-anoxic-oxic process
A-AAO:	AAO process with preanoxic zone
AO:	Anoxic-oxic or anaerobic-oxic process
CAS:	Conventional activated sludge process
ASMs:	Activated sludge models
A+OD:	Carrousel-OD with preanaerobic zones
BAF:	Biological aeration filter
BNR:	Biological nutrient removal process
BSMs:	Benchmarking simulation models
Carrousel-OD:	Carrousel type oxidation ditch
CAST:	Cyclic activated sludge technology, a type of SBR
CFD:	Computational fluid dynamics
COD:	Chemical oxygen demand
DAT-IAT:	Demand aeration tank and intermittent aeration tank, a type of SBR
DE-OD:	Dual channels oxidation ditch
DF-MBR:	Dual filtration membrane bioreactor
DO:	Dissolved oxygen
DPB:	Dionitrification phosphorous bacteria
HSCBR:	High efficient separation composite biological fluidized reactor
ICA:	Instrumentation, control and automation
ICEAS:	Intermittent cycle extended aeration system, a type of SBR
NH <sub>3</sub> -N:	Ammonia nitrogen
MBR:	Membrane biological reactor
OD:	Oxidation ditch process
Orbal-OD:	Orbal type oxidation ditch
ORP:	Oxidation and reduction potential
PDA:	Particle dynamic analyzer
r-AAO:	Anoxic-anaerobic-oxic process
SBR:	Sequencing batch reactor
SND:	Simultaneous nitrification and denitrification
T-OD:	Triple channels oxidation ditch
TP:	Total phosphorous
TN:	Total nitrogen
UASB:	Upflow anaerobic sludge blanket reactor
UCT/VIP:	University of Campton Tank/VIP
UNITANK:	A type of SBR
WWTP:	Wastewater treatment plant.

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## Research Article

# Modeling the Effect of Plants and Peat on Evapotranspiration in Constructed Wetlands

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Evapotranspiration (ET) in constructed wetlands (CWs) represents a major factor affecting hydrodynamics and treatment performances. The presence of high ET was shown to improve global treatment performances, however ET is affected by a wide range of parameters including plant development and CWs age. Our study aimed at modelling the effect of plants and peat on ET in CWs; since we hypothesized peat could behave like the presence of accumulated organic matter in old CWs. Treatment performances, hydraulic behaviour, and ET rates were measured in eight 1 m<sup>2</sup> CWs mesocosm (1 unplanted, 1 unplanted with peat, 2 planted with *Phragmites australis*, 2 planted with *Typha latifolia* and 2 planted with *Phragmites australis* with peat). Two models were built using first order kinetics to simulate COD and TKN removal with ET as an input. The effect of peat was positive on ET and was related to the better growth conditions it offered to macrophytes. Removal efficiency in pilot units with larger ET was higher for TKN. On average, results show for COD a  $k_{20}$  value of 0.88 d<sup>-1</sup> and 0.36 d<sup>-1</sup> for TKN. We hypothesized that the main effect of ET was to concentrate effluent, thus enhancing degradation rates.

## 1. Introduction

In constructed wetlands (CWs) for wastewater treatment, evapotranspiration (ET) may represent a major factor increasing the hydraulic residence time (HRT) during summer months in temperate countries. In horizontal subsurface flow constructed wetlands (HSSFCWs), ET ranges between 0 and 50 mm/d [1] and can reach up to 200 mm/d in favorable periods [2]. High ET may improve global treatment performances [3] and modify water flow [4]. ET follows a diurnal cycle and is affected by a wide range of parameters such as plant development, CW design (surface, subsurface or vertical flow), and CW age [5].

Simulations were used to predict the performance of CWs using a direct plug flow reactor model [1], a plug flow with axial dispersion model (PFD) [4, 6–8], a stirred tank in series model [9] or a combination of these models [10]. One of the most limiting factors in predicting CWs efficiency was identified as the hydraulic behavior governed

by environmental conditions [11, 12]. Furthermore, in modeling or design equations, ET can be taken into account as an input to the model [8].

The aim of our work was first to determine (1) the effect of peat and of plant species on ET, since we hypothesized peat could behave like presence of accumulated organic matter in old CWs and (2) the importance of ET on treatment performances in an experimental constructed wetland system. The hydraulic behavior of pilot scale CWs was modeled during high ET rate periods and with ET values as an input of the hydraulics and performance models.

## 2. Material and Methods

Eight 1 m<sup>2</sup> wetland mesocosms (1.2 m long × 0.8 m wide × 0.3 m deep) were used in this study. Each mesocosm (Figure 1) was fed with 30 L/d (two batches per day) of a reconstituted fish farm effluent (187 mg TSS/L, 373 mg

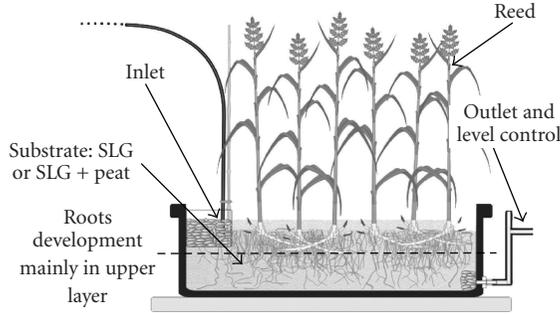


FIGURE 1: Section view of a mesocosm.

TABLE 1: Description of mesocosms, pulse input tracer, evapotranspiration, and aboveground biomass.

Pilot ID <sup>1</sup>	Plant	Peat	Tracer recovered	$\tau^2$	$ts^3$	Average ET rates	Above ground biomass
			%	$d$	$d$	mm/d	kg/m <sup>2</sup>
U1	no	no	75.5	3.6	5.4	0.3	—
U2	no	yes	85.1	4.1	9.9	0.2	—
R1	Reed	no	65.1	4.4	7.0	8.0	1.2
R2	Reed	no	61.2	4.2	5.9	6.3	0.9
C1	Cattail	no	67.4	3.9	5.9	3.8	0.2
C2	Cattail	no	61.8	4.3	6.1	7.3	0.6
R3	Reed	yes	27.2	6.0	7.7	16.7	2.3
R4	Reed	yes	41.0	5.9	9.2	16.4	2.2

<sup>1</sup>Adapted from Naylor et al. [13].

<sup>2</sup>Theoretical HRT ( $\tau$ ) was calculated following the method described in Chazarenc et al. [8].

<sup>3</sup>Experimental HRT ( $ts$ ) was determined using integration of response curves.

COD/L and 12.4 mg TKN/L). All mesocosms were filled with a combination of rock media (Table 1) and in four of them 60 L of peat was added and mixed (initially to reduce alkalinity caused by steel slag). The substrate was composed by mass of 25% 5–10 mm electric arc furnace EAF-steel slag, 20% 2.5–10 mm limestone, and 55% of 2.5–10 mm granite gravel. Four mesocosms were planted with *Phragmites australis*, two with *Typha latifolia* and two were left unplanted (Table 1). Planting was done one year prior to the experiment, during the summer of 2000, to allow adequate establishment. More details on the experimental setup are provided by [13].

Experiments were conducted between July and August 2001 in a greenhouse at the Botanical Garden of Montreal. Concentration of TSS, COD, and TKN were measured daily at the inlet and outlet of each mesocosms according to standards methods [14]. Pulse input tracer studies were conducted using lithium chloride (LiCl) simultaneously in all eight mesocosms operating at the same inflow. HRT was estimated by injecting 15 L of tracer (33 mg Li<sup>+</sup>/L) over a period of 5 minutes in each mesocosm and outlet concentrations were measured daily during 30 days. Lithium concentrations were determined by atomic

absorption spectrophotometry. The amount of daily water lost by ET was estimated as the difference between inflow and outflow. Treatment performances ( $P$ ) were calculated based on pollutant mass flow removal

$$P = 100 \cdot \left(1 - \frac{Q_i \cdot C_i}{Q_o \cdot C_o}\right), \quad (1)$$

where  $Q$  = flow,  $C$  = pollutant concentration,  $i$  = inlet,  $o$  = outlet.

**2.1. Hydraulic Models.** The plug flow with axial dispersion model (PFD) [15] was preferred to the classical plug flow model with a background concentration (see [16]). This choice was made in order to achieve the objective of estimating the effect of plant presence and activity on dispersion inside the mesocosm.

A second model was built (using the object oriented Visim software), based on the hypothesis of a two layers flows: (1) the surface layer modeling the rhizomial part of the mesocosm, with a time delay block taking into account ET, and (2) a bottom layer. The two-layer model (TLM) was built by associating several basic blocks (continuous stirred tank, plug flow and gain) specified using Laplace transforms (Figure 4).

**2.2. Performance Models.** COD and TKN treatment performances were predicted by using an integrated form of the two hydraulics models. Volumetric first order kinetics ( $k$ ) were assumed for COD and TKN degradation rate. The integrated forms of the PFD model [17] and of the TLM are presented respectively in

$$\frac{C_s}{C_o} = \frac{4 \cdot a \cdot e^{(Pe/2)}}{(1+a)^2 e^{(a \cdot Pe/2)} - (1-a)^2 e^{(-a \cdot Pe/2)}} \quad (2)$$

with  $a = \sqrt{1 + \frac{4 \cdot k \cdot \tau}{Pe}}$

$$\frac{C_s}{C_o} = G \cdot \frac{1}{(1+2 \cdot k)^2} \cdot e^{(-k \cdot td)} + (1-G) \cdot \frac{1}{(1+2 \cdot k)^2},$$

with  $C_s, C_o$ : outlet and inlet COD and TKN concentration, respectively, [mg/L],  $Pe$ : Péclet number according to PFD model.  $Pe = 1/D$  with  $D$  System dispersion number [–],  $\tau$ : HRT estimated with PFD model [d],  $td$ : time delay in first layer of the conceptualized model [d],  $k$ : first-order volumetric kinetic constant [d<sup>-1</sup>],  $k = k_{20}(\theta)(T^{-20})$  with  $T$  effective temperature.  $\theta$  constant (1.06).  $k_{20}$  first-order volumetric kinetic constant at 20°C, determined for COD and TKN [d<sup>-1</sup>].  $G$ : ratio in the first layer of the TLM model [–]

Those two models have been used to simulate treatment performances on COD and TKN removal during the 30 days of test.

### 3. Results And Discussion

**3.1. Influence of Peat on ET Rates and Hydraulic.** On average, ET was highest in planted peat mesocosms (16.7 mm/d

TABLE 2: Simulation results of hydraulic models (\*Pearson correlation).

	PFD model			TLM Visim model		
	D (-)	$\tau_{\text{PFD}}$ (day)	$R^{2*}$	Ratio in layer 1 (G)	Time delay	$R^{2*}$
U1	0.21	3	99.6	0.5	0	98.1
U2	0.36	3.6	97.8	—	—	—
R1	0.14	4.4	97.1	0.7	1.7	95.1
R2	0.25	3.4	98.7	0.6	0.8	97
C1	0.3	3	97.8	0.6	0.4	94.8
C2	0.27	3.2	95.4	0.6	0.4	95.3

in R3) and lowest in the unplanted control without peat (0.1 mm/d in U1). Maximal daily values were estimated at 20 mm/d in R3 and R4, which are in accordance with values proposed in the literature [1, 3, 4].

Association between reed and peat generated the most important ET rates (Table 2). The positive effect of peat on ET can be explained on the one hand by the better growth conditions it offered to plants (presence of more plant biomass). On the other, the effect of peat on mesocosms hydraulic behavior was hypothesized to be similar to accumulated organic matter appearing in constructed wetlands over time [18]. As observed between the two unplanted units, peat enhanced the retention by acting as a sponge. In absence of peat, while the HRT remained fairly close to the theoretical value in U1, it was up to 30% greater than the theoretical hydraulic residence time value in pilot units with high ET (those with large active macrophytes). Experimental HRT, determined using response curves (Figure 2), were always greater than theoretical values (Table 2). This was a possible consequence of the non-ideal flow in the different reactors.

**3.2. Influence of Plant Presence and Species on ET Rates and Hydraulic.** Effects of *Phragmites* and *Typha* on ET rates were similar (Table 2). The relationship between ET and plants seemed mostly related to plant biomass irrespective of plant species.

The ratio of tracer collected at outlets was sufficient for a more detailed analysis in all cases except for the R3 and R4 mesocosms where less than 45% of the tracer was recovered (Table 1). In the response curves of the R3 and R4 mesocosms, a small tracer peak was observed after which lithium concentrations never returned to background levels, even after 30 days (not shown). This was most probably the consequence of the sorption of lithium by peat (also observed in a minor extend in unplanted U2) followed by slow release back into solution [19] associated to ET cumulative effects. Results from R3 and R4 were not further analyzed.

The PFD and the TLM models (Figure 4) were used to fit the experimental response curve. System dispersion numbers ( $D$ ), estimated by fitting experimental data with PFD model, were in the range of 0.14 to 0.36 (Figure 3) which is in the observed range of 0.009 to 0.48 for  $D$  values in HSSFCWs [1]. In HSSFCWs it was shown that presence of high rates of ET generally leads to a decrease of  $D$  values [4, 8]. In our study,

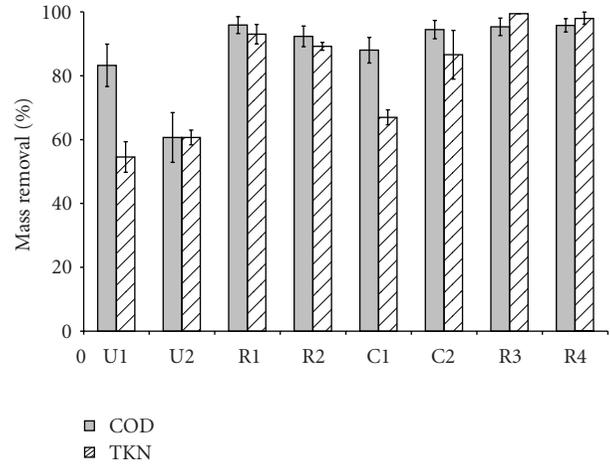


FIGURE 2: Treatment performances during the 30-day test.

there was little variation in  $D$  values between mesocosms. This was probably due to the small size of the mesocosms which led to a permanent bypass along the wall.

**3.3. Effect of ET Rates on COD and TKN Removal, Modeling.** No TSS removal differences were found between the different mesocosms (results not shown). COD removal was higher in U1 than in U2, and this was likely due to the release of organic carbon by the peat. This difference was less pronounced between R1 and R2 (planted with reed) and R3 and R4 (planted with reed and with peat). Overall, there were slight differences between performances of all the planted mesocosms for COD degradation (Figure 1), irrespective of ET and plant species.

Removal efficiency in pilot units with higher ET (more than 50% of inflow) was greater for TKN (Figure 1). In R3 and R4 mesocosms, average net rate of N mineralization values of  $0.36 \text{ g m}^{-2} \text{ d}^{-1}$  were reported (which represented almost all of the input) until in unplanted units it was about  $0.15 \text{ g m}^{-2} \text{ d}^{-1}$ . In similar pilot units and experimental conditions, rates of 0.22 to  $0.53 \text{ g m}^{-2} \text{ d}^{-1}$  have been reported [20]. Nitrification should have been enhanced by the presence of well established plant biomass associated to high ET rates, furthermore the contact time between plants shoots (the principal oxygen supplier in HSSFCWs) and effluent was extended.

Performance models (2) were used to predict treatment performances of pilots U1, R1, R2, C1, C2. The first step was to determine the best  $k_{20}$  value for COD and TKN, to fit the model with experimental data. On average, results show a  $k_{20}$  value of 0.88 for COD removal and 0.36 for TKN removal. Large ranges of annual average values, from 0.06 to 6.11 for  $\text{BOD}_5$  and from 0.06 to 0.16 for TKN are reported for CWs [16]. Our results are on the same order for COD (while assuming a ratio of 0.25 for  $\text{BOD}_5/\text{COD}$ ). High values obtained for TKN kinetics are probably a consequence of the favourable conditions (high temperatures, plant activities) during the experiment.

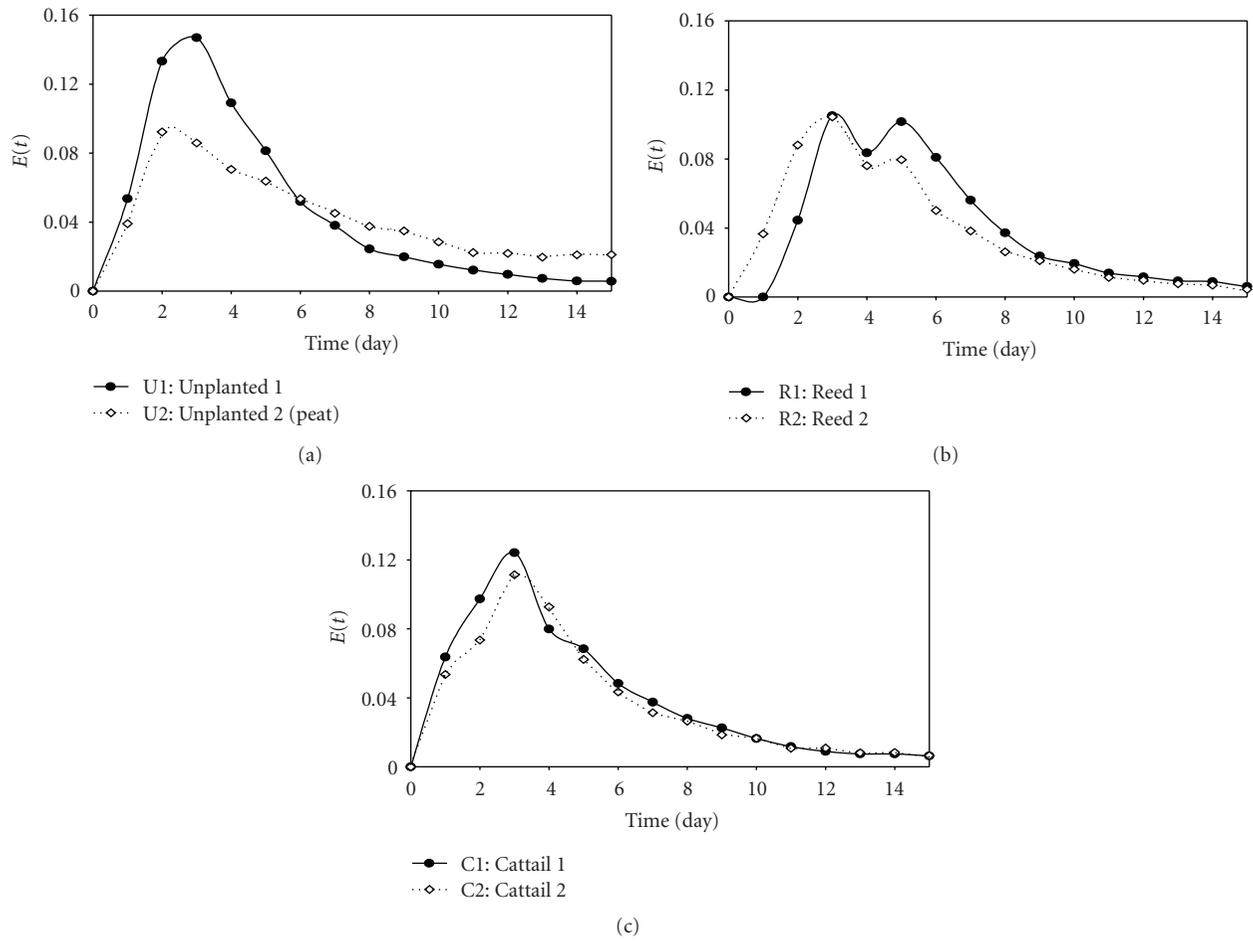


FIGURE 3: Response curves of the different pilots.

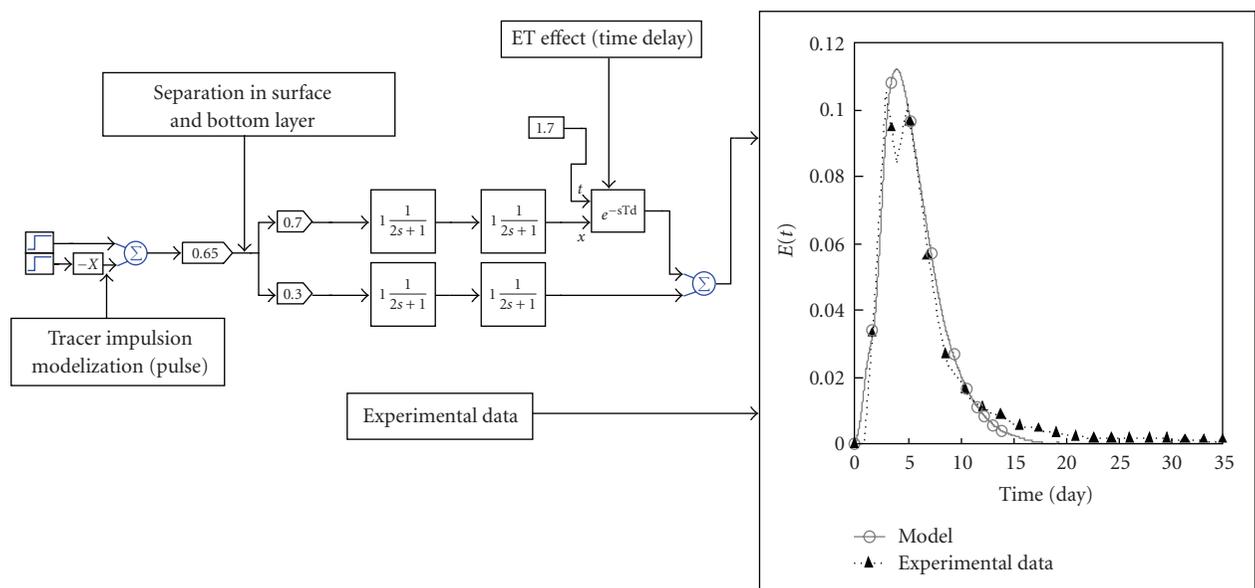


FIGURE 4: Conceptualized two-layer model (TLM) with results from R1.

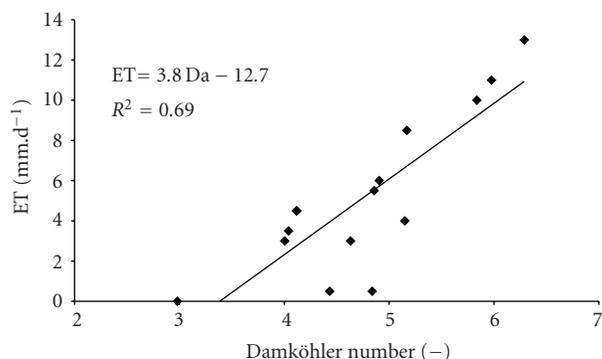


FIGURE 5: Relationship between Damköhler number and ET for TKN degradation (except for R3 and R4).

Simulation results were closer to experimental data when using the TLM, but care should be taken when interpreting the correlation coefficients obtained. Simulation with PDF model ( $R^2 = 0.46$  for COD and  $0.33$  for TKN) seemed to give inferior results than simulation with TLM model ( $R^2 = 0.94$  for COD and  $0.71$  for TKN). The only input in the PFD model was the Peclet number while the TLM model counted two inputs, the  $G$  ratio and the total delay ( $T_d$ ), which led to a more accurate determination of performances. On the other hand, the TLM enabled a better comprehension of flow and removal gradient in mesocosms. The ratio " $G$ " used in the TLM model was proportional to ET magnitude and the time delay increased with high ET (Table 2).

The Damköhler number ( $Da = k \cdot \tau$ ) is the normalised first order reaction rate constant and is defined as the ratio of the degradation rate to the mass transfer rate. A correlation between ET and  $Da$  values for TKN removal was underlined for all cases except pilots R3 and R4 (Figure 5). This suggested that ET enhanced the degradation rates. We hypothesised that the first effect of ET was to concentrate effluent, thus enhancing degradation rates (especially for TKN). Another contribution of ET could have been the amplification of gas transfer in aerenchyma, thus enhancing oxygen supply in the rhizosphere.

#### 4. Conclusion

A positive contribution of peat on plant biomass development and consequently ET rates was observed. Effects of peat can also be related to those of large amounts of accumulated organic matter that can be found in old constructed wetlands. Thus adding peat in young CWs represents a clear improvement for plant establishment and can increase treatment performances for TKN.

In our study, the effects of ET were not clearly observed in hydraulic behavior by modeling the different mesocosms. No effect of ET on the dispersion coefficient was observed when using the plug flow with axial dispersion model. This was probably due to the small size of the mesocosms which led to a permanent bypass along the wall.

There was no clear difference between Phragmites and Typha effect on ET rates. The major factor increasing the

ET was most likely the amount of plant biomass. Effect of ET was beneficial to TKN removal by increasing HRT. In temperate countries, favoring ET (building CWs well exposed to sun light) represents a clear increase on treatment performances, especially TKN. Effects of peat and of large ET on hydrodynamics of full scale CWs have to be measured to confirm those results.

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## Research Article

# Assessment of the Performance of Membranes Type Koch in Hartha Power Plant

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This paper deals with the assessment of the performance of reverse osmosis membranes type (TFC-Koch) model (8822XR-365) which are used in water desalination unit in Hartha power plant, one of the electrical power plant in the south Iraq. This unit has a capacity of 100 m<sup>3</sup>/h withdraws water from Shat Al-Arab River as a raw water having total dissolved solid (TDS) > 3000 ppm, and consists of two stages with total recovery and salt rejection of about 60% and 95%, respectively. The first array contains twelve vessels and the second six vessels. Each vessel contains six elements, 8 inches in diameter and 40 inches in length. The performance of the reverse osmosis (RO) membranes is based on surveying the chemical analysis of different ions present in water for both permeate and rejected streams from the unit log book, and only those readings where the overall recovery was 60% were selected. The results depicted that the reduction of membrane efficiency is attributed to the membrane blockage due to scaling and fouling. Under high fouling conditions the permeate flow rate is reduced and accordingly a high feed pressure is required to produce the design flow rate of permeate or percent recovery. A simulation of the behavior of RO membranes was conducted using standard Saehane software and compared with predicted model that was developed by the same authors. The results revealed that the reduction in water flow in both elements one and two in each vessel in the first array is attributed to the high permeate water flux through these two elements beyond the operation limits. Accordingly it is necessary to replace these two elements or change their position relative to other elements periodically.

## 1. Introduction

Membrane technology has become of great interest for treatment of different feeds. Depending on the membrane types, materials in the feed and process conditions, the membrane loses its performance with time. A reverse osmosis (RO) desalination system has many advantages in point of saving energy and less installation spaces and has become a favored technology for the production of fresh water.

In Basrah, one of the major industrial cities in the southern Iraq, RO is predominately utilized for the production of desalted water both for drinking and industry including Hartha power plant. This plant has RO unit of capacity 100 m<sup>3</sup>/h and withdraws water from Shat AL-Arab River with TDS>3000 ppm.

It is well known that RO system of recoveries higher than 50% requires more than one stage in order not to exceed

the single element recovery limit. Usually two arrays will suffice for recoveries up to 75% [1], however, three arrays must be used for higher recoveries up to 87.5%. The rejected water from the first stage is fed to the second stage, while the permeates from all vessels are combined to form the product. Recently, most of RO units use double-pass systems rather than single pass, the advantage of this arrangement is as follows[2].

- (1) Production cost for fresh water is reduced by around 15%.
- (2) Unit installation space is reduced.
- (3) Unit capacity can be easily expanded up to around 15% by only adding a second stage array.
- (4) Disposal of brine water is reduced to about two thirds.

TABLE 1: General properties of Koch membrane type TFC-8822XR-365ft<sup>2</sup>.

Permeate flow rate (m <sup>3</sup> /d)	34.1
Chloride rejection %	99.7
Membrane area (m <sup>2</sup> )	33.9
Maximum operation pressure (kpa)	4140
Maximum operation temperature (°C)	45
Maximum continuous feed chlorine (ppm)	<0.1
Maximum differential pressure per element (kpa)	69
Maximum differential pressure per vessel (kpa)	414
Maximum feed turbidity NTU	1
Maximum feed SDI	5
Construction	Spiral wound with fiberglass outer warp
Application	Extra high rejection for brackish water treatment

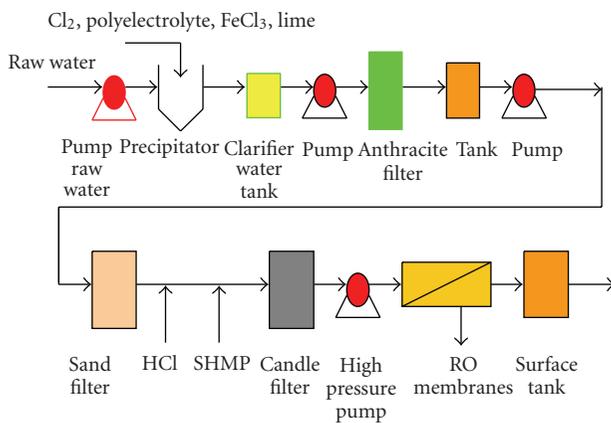


FIGURE 1: Flow Diagram of RO Plant.

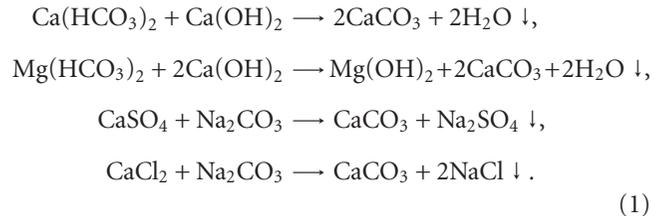
The performance of RO system is influenced by feed pressure, feed water composition, temperature, and percent recovery. For example, a feed temperature drop of 4°C will cause a decrease of permeates flow of about 10% [2].

AbdulSattar et al. [3] studied the effect of applied pressure on the performance of two types of membranes; Koch type (8822-XR) and Saehane type (RE8040BE). They showed that the amount of permeate for Saehane membranes is larger than that for Koch membranes by about 26%. Abdul Sattar et al. [4] developed a mathematical model for evaluating the performance of RO unit using various types of membranes. El-Manharawy and Hafez [5] studied the effect of percent recovery and feed concentration on the design of RO units.

In this work the effect of operation time on the performance of Koch membranes type (8822-XR) was studied. The assessments of membranes performance based on water analysis of different ions concentration in both permeate and rejected water with 60% recovery were considered. The study covered two years of plant operation. A complete set of operating data including permeate flow rates for each array, permeate flux, permeate TDS, and feed pressure for each element were made available from the unit log books.

## 2. Plant Process Description

Feed water is pumped from Shat Al-Arab River to the sedimentation tank to precipitate the large suspended particles by the addition of ferric chloride FeCl<sub>3</sub> and polyelectrolyte as a coagulant. The water is then pumped to the precipitator of the lime-soda ash process to remove carbonate hardness as shown by the following equations [6].



The lime-soda ash process can also reduce the silica concentration, due to the formation of aluminum and iron silicate calcium carbonate when ferric chloride is added as a coagulant [1]. Hypochlorite is added to remove the biological matter. The clarified water is collected in a tank having a capacity of about 50 m<sup>3</sup>. A booster pump (capacity of 180 m<sup>3</sup>/h and pressure of 5 bars) which draws water from the clarifier tank pumps it through an anthracite filter to remove any dissolved organics and chlorine in water. The output stream from the anthracite filter is collected in a special tank having a capacity of 500 m<sup>3</sup>. A centrifugal booster pump (capacity 165 m<sup>3</sup>/h and 5 bar pressure) draws water from the water tank and sends it to the polishing filter vessel (sand filter) to remove turbidity and any other impurities. Hydrochloric acid is added to the clarified water to adjust the pH so as to reduce the risk of precipitating soluble carbonate salts. Sodium hexametaphosphate (SHMP) is also added to the feed water prior to RO system to provide a further safety against scaling of the membrane by gypsum and other soluble salts. The treated water is passed through a microfilter (5 μm) to remove small particles prior to pumping. The treated water to the RO membrane vessels utilizes a high pressure pump (capacity 165 m<sup>3</sup>/h and pressure 35 bars). Desalted water or permeate is collected in a service tank (capacity about 150 m<sup>3</sup>) while the waste or rejected water is treated prior to being discharged to the river. A process flow diagram is shown in Figure 1.

Al-Hartha RO unit consists of two stages, the first stage comprises of 12 vessels and the second 6 vessels where each vessel contains six elements (40 inches in length and 8 inches in diameter). The raw water is divided into 12 branches, one for each vessel. The first array of these vessels has a percent recovery of about 40%. The rejected water of the first array is fed to the second array which contains six vessels in parallel arrangement with a recovery of about 20%, which means that the total recovery of the unit is around 60%.

## 3. Results and Discussion

The aim of this work is to assess the performance of Koch membranes type (8822XR-365Koch) of USA origin, which is used in the reverse osmosis unit at the Hartha power plant.

TABLE 2: Theoretical and experimental values of ions in the rejected stream for fourteen samples.

Ions concentration ppm											
Theoretical values						Experimental values					
Ca <sup>+2</sup>	Mg <sup>+2</sup>	SO <sub>4</sub> <sup>-2</sup>	Cl <sup>-1</sup>	TH	TDS	Ca <sup>+2</sup>	Mg <sup>+2</sup>	SO <sub>4</sub> <sup>-2</sup>	Cl <sup>-1</sup>	TH	TDS
347.4	302.6	1186	1876	650	7121	444	337	1649	2111	781	7418
386.8	321	1813	2250	707	6860	435	361	990	1288	796	7590
405.3	342.1	1813	2813	723	8476	401	333	1182	2681	734	8280
407.9	339.5	1931	2939	747	8984	401	540	1436	3041	941	8316
365.8	294.7	1786	2239	660	6966	340	291	1318	2146	631	6158
326.3	255.3	1439	1739	581	5210	364	211	1065	1671	575	4488
439.5	373.7	2131	2834	813	8631	359	309	1418	2079	663	6679
489.5	426.3	2018	3105	916	9186	582	302	1156	3017	902	8659
610.5	434.2	1713	3158	1021	10531	489	361	872	1263	850	6389
531.6	471.1	1745	3126	1002	11342	464	368	1053	2574	832	8560
415.8	310.5	1700	2053	7,26	7015	318	265	993	1928	583	5227
510.5	386.8	1602	2355	907	7676	420	276	1120	1386	696	5841
518.4	352.6	1839	2552	871	8094	436	330	992	2265	766	6668
360.5	278.9	1792	1979	660	6305	396	285	1102	1386	679	6060

TABLE 3: General properties for production in array 1 and 2.

Array	Pressure bar	Permeate flow rate m <sup>3</sup> /h	Concentrate flow m <sup>3</sup> /h	Permeate TDS (ppm)	Concentrate TDS (ppm)
1	14.8	77.2	82.8	19.21	4507
2	12.3	22.8	60.4	50.72	6164

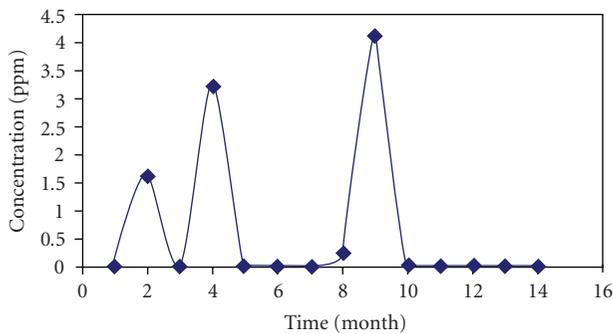


FIGURE 2: Ca ion concentration in the permeate.

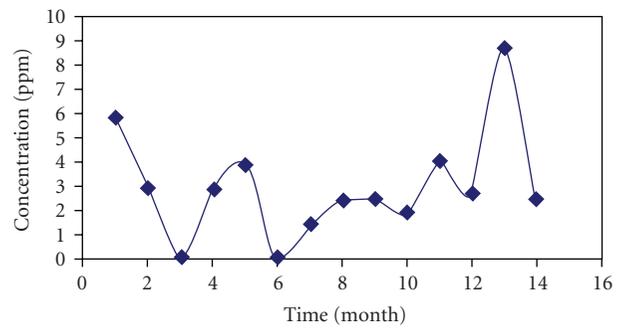


FIGURE 3: Mg ion concentration in the permeate.

The chemical analyses were derived from the log book of the unit, all having recoveries of 60%. Chemical analysis for (14) samples was collected from permeates and rejected streams.

The chemical compositions of the concentrated streams (rejected water) can be estimated from the material balance based on the composition of various ions in the feed water and the percent recovery. The Concentration factors as follows [1]:

$$CF = \frac{1}{(1 - R)}, \quad (2)$$

where  $R$  is the percent recovery.

Table 1 shows the properties of Koch membranes type TFC-8822XR. Membrane efficiency depends on the variation of the ions concentration through the permeate stream

which reflects membrane fouling and scaling problems, due to the deposition of such ions on the membrane surface.

Figures 2–7 show the concentration of profiles Ca<sup>+2</sup>, Mg<sup>+2</sup>, SO<sub>4</sub><sup>-2</sup>, Cl<sup>-</sup>, TH (Total Hardness), and TDS (Total Dissolved Solids) in mg/l for the permeate stream as a function of operation time in months. It can be seen that the concentrations of these various ions increase with time and they decrease and reach zero value after chemical cleaning.

The increase in the ions concentration in the permeate stream with operation time may be attributed to the membrane blocking by both calcium sulphate and organic substances. The effect of concentration polarization could be another reason for increased salinity in the permeate flow rate.

The effect of concentration polarization is specifically felt near the membrane surface and is considered as a major

TABLE 4: Total results in details for the theoretical properties of each element in arrays 1 and 2.

Array	El. No.	Feed Pressure bar	Feed m <sup>3</sup> /h	Permeate m <sup>3</sup> /h	Recovery	Feed TDS (ppm)	Permeate TDS (ppm)
1	1	14.8	13.3	1.2	0.093	2342	12.4
	2	14.3	12.1	1.2	0.096	2580	14.6
	3	13.8	10.9	1.1	0.101	2853	17.2
	4	13.4	9.8	1.0	0.106	3170	20.4
	5	13.1	8.8	1.0	0.111	3542	24.5
	6	12.9	7.8	0.9	0.117	3982	29.6
2	1	12.3	13.8	0.8	0.058	4507	34.7
	2	11.8	13	0.7	0.056	4782	40.6
	3	11.3	12.3	0.7	0.053	5061	47.5
	4	10.8	11.6	0.6	0.950	5342	55.6
	5	10.4	11	0.5	0.047	5621	65.1
	6	10	10.5	0.5	0.044	5897	76.5

TABLE 5: Total results in details for the theoretical properties of each element in arrays 1 and 2 using Saehane software.

Array	El. No.	Feed Pressure bar	Feed m <sup>3</sup> /h	Permeate m <sup>3</sup> /h	Recovery	Feed TDS (ppm)	Permeate TDS (ppm)
1	1	15.5	13.9	1.2	0.09	3282.8	15.7
	2	14.9	12.6	1.2	0.093	3605.6	18.5
	3	14.5	11.5	1.1	0.096	3972.4	21.8
	4	14.1	10.4	1.0	0.1	4392.5	25.8
	5	13.7	9.3	1.0	0.104	4877.1	30.8
	6	13.4	8.4	0.9	0.108	5440.0	37.0
2	1	12.9	14.9	0.8	0.053	6097.5	42.8
	2	12.2	14.1	0.7	0.051	6439.4	50.1
	3	11.6	13.4	0.7	0.048	6780.1	58.8
	4	11.1	12.8	0.6	0.044	7116.0	69.0
	5	10.6	12.2	0.5	0.41	7443.2	81.1
	6	10.2	11.7	0.4	0.037	7757.9	95.6

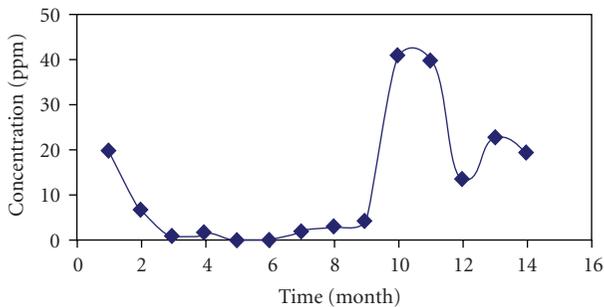
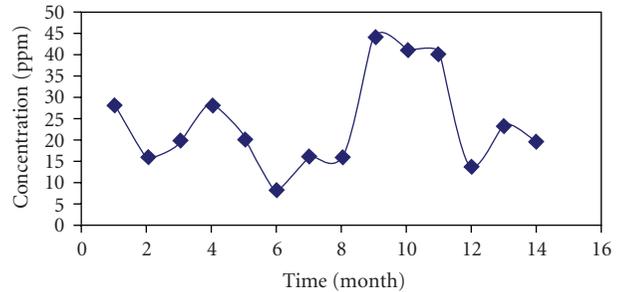
FIGURE 4: SO<sub>4</sub> ion concentration in the permeate.

FIGURE 5: Cl ion concentration in the permeate.

reason for the increased ions concentration in the permeate stream. The effect of concentration polarization increases osmotic pressure, leading to a reduction of net driving pressure differential across the membrane and hence reducing the product flow rate and increasing the scale potential. In order to compensate for such adverse effects, higher pressure should be applied. Table 2 shows the ions concentrations in the rejected stream, both experimentally and theoretically.

A simulation run using Saehane software was conducted in order to investigate the performance of each individual element. It was observed that during the unit operation history, the performance of some membrane modules started to deteriorate with time due to scale formation and fouling deposition on the surface of the membranes. Cleaning therefore became necessary to improve the performance of the membranes. Cleaning gives a great improvement in both the quality and quantity of the permeate stream. This is

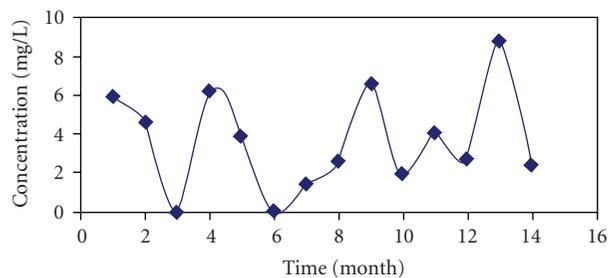


FIGURE 6: Total hardness concentration in the permeate.

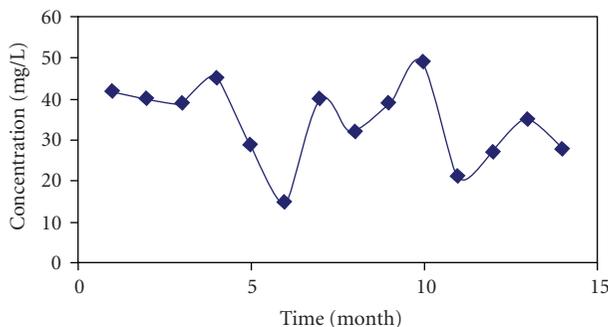


FIGURE 7: Total dissolved solids concentration in the permeate.

evident from Figures 2, 3, 4, 5, 6, and 7 which show the improvement of membrane efficiency after chemical cleaning especially after three and six months of operation.

The cleaning agent, composed of 0.1% Sodium Triphosphate, 1%  $\text{Na}_4\text{EDTA}$ ,s and 2% Citric Acid, was used for chemical cleaning to remove both organic and inorganic salts. Table 3 shows the overall properties for the influent streams from the arrays one and two, while Table 4 shows the theoretical results for each element using the program that was developed previously by the same authors [4]. Table 5 revealed the theoretical values for each element using Saehane software.

The degradation of elements one and two for each vessel in the first array of the RO unit in Hartha power plant is attributed to the mechanical damage. This is due to the increasing of the permeate flux relative to the standard flux. Accordingly, the replacement of elements one and two or change of position relative to other elements is required to improve the permeate quality.

#### 4. Conclusions

A simulation of the behavior of RO membranes was conducted using standard Saehane software and compared with predicted model that was developed by the authors. The results revealed that the reduction in water flow in both elements one and two in each vessel in the first array is attributed to the high permeate water flux through these two elements beyond the operation limits. Accordingly it is necessary to replace these two elements or change their position relative to other elements periodically.

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## Review Article

# The Possibilities of Reduction of Polychlorinated Dibenzo-P-Dioxins and Polychlorinated Dibenzofurans Emission

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In the study the most important and known polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) emission sources are presented and known methods of reduction of dioxin emission to the atmosphere are discussed in detail. It is indicated that the most relevant emission source is a combustion process. The mechanism of dioxin formation in thermal processes is presented in brief. The author characterized primary methods of reduction of PCDDs/PCDFs emission encompassing the interference into the combustion process to minimize their formation and discussed known secondary methods aimed at their removal from the stream of waste gases. It was attempted to make a critical assessment of PCDD/Fs reduction methods described in literature.

## 1. Introduction

On 23 May, 2001 in Stockholm there was signed the Convention concerning persistent organic pollutants (POPs). The reason for the convention was the necessity to regulate the issues connected with the production and utilization of certain organic substances—the so-called persistent organic pollutants. The convention introduced relevant limitations in the production, application, export, and import of POPs, as well as strict requirements concerning the record and monitoring. One of the most important decisions of Convention was the commitment to the continuous minimization or the final elimination of the release of such substances as dioxins and furan (PCDD/Fs), hexachlorobenzene (HCB) (as a precursor of dioxin synthesis) as well as polychlorinated biphenyls (PCBs)—as compounds with similar toxicity to dioxins, to the environment. This indicates the necessity of the implementation of the best available techniques (BAT) to the industrial practice in the following fields: waste incineration, paper-mills using chlorine for whitening, steel mills and copper, aluminum and zinc mills, refineries utilizing waste oils, crematories, power plants, and thermal-electric power plants as well as the other activities.

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans are categorized as the so-called endocrine disrupters—the substances disturbing the activity of the endocrine system. Since 1970s PCDD/Fs have been thought to belong to the group of the strongest poisons among the known chemical compounds so far. Nevertheless, in spite of very high toxicity of certain dioxins and furans with regard to some animal organisms, one may find it difficult to compare PCDD/Fs with the other strong toxins present in the environment. This is because their activity is not instantaneous in the concentrations one encounters every day. According to the toxicological data it is difficult to acknowledge that they exhibit the so-called acute toxicity [1, 2]. The harmful activity of PCDD/Fs concerns the fact that they disturb the endocrine functions of an organism, resulting in the fertility disorders, the problems with pregnancy, or even infertility (the chemical structure of dioxins bears a strong resemblance to the steroid hormones, including sex hormones). This is connected with disorders in progesterone release, the hormone being indispensable to hold pregnancy and to the appropriate course of pregnancy [3, 4]. In contrast, the results concerning the carcinogenic activity of dioxins were not confirmed [5, 6]. De facto, one should not neglect the

way dioxins and furans affect a human organism. Hence, all activities aimed at the restriction of the emission of dioxins to the atmosphere are fully justified.

## 2. Dioxins Emission Sources

Based on the known results of investigations carried out for over twenty years it is known today that dioxins (polychlorinated dibenzo-p-dioxins –PCDDs) and furans (polychlorinated dibenzo-furans –PCDFs) form as an undesirable side product in practically all combustion processes (including incineration processes of waste: municipal, industrial and medicinal waste or sewage sludge as well as during combustion of fossil fuels, particularly hard coal, brown coal and biomass). Furthermore, dioxins form during certain industrial production processes such as pesticide, paper and cellulose production and in iron and steel industry and in nonferrous metallurgy. Even in the 70s and 80s waste incineration plants were the main source of PCDD/Fs emission in the vast majority of countries all over the world. At present, as a result of restriction of emission norms and due to the development of new incineration technologies and the application of efficient systems of flue gases treatment, the situation has changed. Consequently, contemporary waste incineration plants emit flue gases containing dioxins and furans in such a concentration that is usually present in the polluted city air. The fact that chloroorganic pesticides have been withdrawn from production and that paper whitening with chlorine has been stopped has contributed to a considerable decrease of dioxin and furan emission in those processes as well. Nowadays, a significant dioxin emission source is metallurgy industry both in Poland and in many European countries comprising ferrous and nonferrous industry as well as secondary scrap processing. However, to very serious problems one may account noncontrollable incineration of household waste in domestic furnaces and combustion of solid fuels of low quality, including hard and brown coal in small local boiler rooms being obsolete and exploited. The incineration conditions are there very bad considering thermodynamics and chemistry of incineration. At the moment these are the main sources of dioxin emission to the atmosphere in the vast majority of European countries and in Poland [7].

Presently, the basic and the most important dioxin emission source in the vast majority of industrialized countries of the European Union is municipal heating sector being usually equipped with obsolete energy boilers of small in which there takes place the combustion of fuels of low quality under bad conditions (high concentrations of carbon monoxide) and equipped with individual heating systems frequently incinerating wood waste [8].

As mentioned above, humanity has been accompanied with dioxin emission since time immemorial. Investigations carried out in recent years indicate that it is possible to identify dioxins in high concentrations in many environmental samples. This also concerns samples originating from the period before industrial boom in the 19th century [9–11].

The first information about dioxins originating from the combustion process appeared in 1977–1978. Olie [12] found dioxins in flue gases from Dutch waste incineration plants and, subsequently, Buser [13] also confirmed the presence of dioxins in fly ashes from Swiss waste incineration plants.

Then the theory appeared that polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-furans originate from combustion processes- and it was termed *trace chemistry of fire* from the title of the article being published in the respected and prestigious journal “Science” in 1980 [14]. According to the theory, the basic sources of dioxin emission to the atmosphere and, particularly, to the environment, there may be as follows: waste incineration plants, power plants heated with mineral fuels, car engines (petrol and diesel), fire places, barbecues and cigarettes. To summarize, in 1992, the first decade of intensive investigations concerning dioxins, Rappe [15] concluded that environmental pollution due to dioxins may result from emission from the following sources.

- (i) *Chemical Reactions*. This is the result of side reactions occurring in the processes of chemical synthesis, for example, the production of chlorinated pesticides, chloro-phenoxy-herbicides, chlorophenols, and PCB. Another relevant source is also the production and chemical utilization of chlorine, particularly electrolysis combined with chlorine production, cellulose pulp whitening with chlorine, and so forth.
- (ii) *Thermal Processes*. This concerns first and foremost municipal, medicinal, and chemical waste incineration as well as iron, steel, magnesium, and nickel production. Moreover, the sources of dioxin emission to the environment are flue gases.
- (iii) *Photochemical Reactions*. One may account here photochemical dechlorination of higher chlorinated dioxins—generation of more toxic congeners—lower chlorinated, photochemical o-phenoxy-phenol cyclization or photochemical chlorophenol dimerization.
- (iv) *Enzymatic Reactions*. This is the process of PCDD/F formation from chloro-phenols under an influence of peroxidases which may occur under the natural conditions, for example, in bioslurry, sewage sludge or bottoms of rivers, and lakes.

In 2000 Baker [16] asked a fundamental question whether incineration is the main source of dioxin emission to the environment. He formulated the thesis that dioxin emission is a fundamental feature of economical development and the quantity of dioxin emission in a given country depends mainly on GDP and it is proportional to CO<sub>2</sub> emission as well.

Today, analyzing the available plentiful subject literature it may be recognized that the main sources of dioxin emission to the environment are first and foremost thermal processes, both incineration and others, for instance, metallurgic, chemical, photochemical, and biological ones [17]:

- (i) waste incineration: municipal, medicinal and hazardous waste, and incineration of sewage sludge,
  - (ii) cement production and waste co-incineration in cement plants,
  - (iii) energetic combustion of fuels and waste co-incineration in power plants,
  - (iv) wood incineration in industrial and household devices,
  - (v) fuel combustion in small household furnaces,
  - (vi) illegal waste incineration,
  - (vii) fuel combustion in car engines,
  - (viii) crematories,
  - (ix) paper industry,
  - (x) metallurgy,
  - (xi) chemical and textile industry,
  - (xii) fires, including forest fires,
  - (xiii) volcano eruption,
  - (xiv) cigarette smoking,
  - (xv) biological and photochemical processes.
- (iii) synthesis from various types of organic precursors such as chlorophenols, polychlorinated diphenyl-ethers, polychlorinated biphenyls, and other products of incomplete combustion which may react with themselves both in gaseous phase and on the surface of metals being present in the composition of volatile ash [22].

In the light of results of the investigations it follows that the most important mechanism resulting in the highest production of dioxins is the third mechanism, then the second one and the lowest production of dioxins may be observed as for the first mechanism [23].

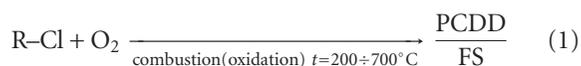
In the combustion process, at the temperatures higher than 900°C carbohydrate radicals and flammable gases are released from incinerated waste and other solid and liquid fuels. Subsequently, they participate in many complex synthesis reactions (halogenations, oxy-halogenation, oxidation, recombination and disproportionation) [24–27] resulting in the production of the so-called products of incomplete combustion. To the category of incomplete combustion products one may account phenols and chlorophenols, chlorobenzenes, alkylbenzenes, simple aliphatic carbohydrates, aldehydes and ketones, alcohols and simple carboxyl acids [28–31].

Chlorophenols, chlorobenzenes or polychlorinated biphenyls and polychlorinated naphthalenes constitute a group of dioxin precursors which at the temperature of 500–700°C may combine giving polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-furans. Those precursors may react with themselves both at the temperature 500–700°C in gaseous phase [20] and on the surface of volatile ash at the temperature of 200–500°C [32, 33].

De novo synthesis occurs at the temperature of 200–500°C from molecules of carbon contained in volatile ash reacting with oxygen and chlorine on the surface of a catalyst [21, 34, 35]. The carbon source in de novo synthesis is the most frequently the so-called elementary carbon contained in the molecules of volatile ash as the remaining part after the processes of thermal decomposition and oxidation in the combustion process. In practice it is not possible to attain complete burn-up of carbon contained in fuel and small amounts of carbon which is only partially burnt up occur in waste gases in the form of soot. The key for molecules chlorination in de novo synthesis is Deacon's reaction [36] of catalytic oxidation of hydrogen chloride (formed during combustion) to molecular chlorine, being capable of carrying out the reaction of chlorination. The reaction is catalyzed by copper compounds (Cu, CuCl, CuCl<sub>2</sub>, CuO, Cu<sub>2</sub>O i CuSO<sub>4</sub>) [37]. In reality, numerous metals are located on the surface of volatile ash having a various influence on the process of dioxin synthesis—certain metals catalyze the process of de novo synthesis or catalyze the process of chlorination of low chlorinated dioxins formed earlier (in the synthesis in a gaseous phase). To exemplify, one may account here copper, zinc, molybdenum, manganese, iron, aluminium, magnesium and other metals catalyze decomposition of the remaining dioxins or relatively their dechlorination, for instance, chromium, vanadium, tungsten, cobalt and nickel [38]. De novo synthesis is a

### 3. Dioxins Formation Mechanisms

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-furans form practically in each combustion process [14, 18] of solid and liquid fuels (more seldom gaseous fuels) if chlorine, oxygen and organic matter appear in the zone of the appropriate temperatures. The thesis is valid not only for combustion processes but also for the majority of thermal processes taking place at the temperatures of 200–700°C. The general course of the reaction is as follows:



In case of waste incineration plant a given range of temperatures indicates unequivocally that dioxin synthesis occurs beyond the incineration zone. The investigations carried out by Hunsinger [19] proved among others that temperature above 900°C and deficiency of oxygen cause a complete dioxin decomposition. This means that dioxin synthesis may occur only after final air supply to the process and at the temperatures below 900°C.

Based on numerous results of investigations of dioxin formation process three possible ways of dioxin formation have been proposed:

- (i) the reaction in gaseous phase at the temperature of 500–700°C [20],
- (ii) dioxin formation from molecular and organic carbon or inorganic chlorine in the presence of volatile ash at the temperature of 250–350°C called de novo synthesis [21],

slow, frequently very slow, reaction and the reaction of dioxin formation for instance from chlorophenols is about  $10^2$ – $10^5$  times faster [39]. Therefore, *de novo* synthesis occurs in combustion installation (not only but also in other thermal processes, e.g., metallurgic ones) beyond the combustion zone at the temperature of 200–400°C, on molecules of deposited volatile ash. According to Goldfarb, the majority of dioxins generated in waste incineration plants is formed in accordance with this mechanism [40].

#### 4. Methods of Dioxins Emission Reduction

The methods limiting the emission of dioxins from technological processes may be divided into two groups: the primary and secondary methods. The primary methods may be defined as the interference into a technological process and creation of such conditions of its course that the amount of dioxins is possibly the smallest [41]. Secondary methods are the so-called “end-of-pipe technologies” allowing to decrease their emission to the atmosphere.

Among the primary methods, the problem of crucial importance is to avoid the presence of chlorine in thermal processes. The processes of dioxins formation are nonequilibrium processes and even the trace amount of chlorine and organic material in the elevated temperature zone (200–700°C) must result in the production of dioxins. Unfortunately, the presence of chlorine is frequently unavoidable.

The next factor one shall attach importance to is the temperature—dioxins are not so persistent chemical compounds as they are widely considered to be and they are decomposed at the temperature of 700°C [42]. Unfortunately, the vast majority of dioxins in thermal processes are produced as a result of the so-called “*de novo*” synthesis and the optimal range of the temperatures used in “*de novo*” synthesis is 300–350°C. Analogously, one may observe the production of dioxins during the process of gas cooling from the temperature of 700°C to 200°C. The amount of dioxins produced as a consequence of “*de novo*” synthesis is inversely proportional to the rate of gas cooling (taking away the heat); thus, it is essential that one aims at the building of very efficient systems of heat recovery (heat exchangers) and the eventual cooling of gases by quenching [43]. Furthermore, the presence of carbon monoxide and soot as well as dust (particulates) containing metals (for example, copper, iron, nickel, aluminum or zinc) favors “*de novo*” synthesis [42]. That is why, to the primary methods of the emission limitation one may account flue gases afterburning (so as to minimize the presence of carbon monoxide and soot) as well as hot gas scrubbing or such adjustment of the flow rate by the systems of heat recovery that the gas which is contained in those systems is not deposited on them. The formation of zones in the system of heat recovery, on which one may observe the process of dust and soot deposition, brings about an increase in the amount of dioxins as a result of “*de novo*” synthesis” [17]. What allows to decrease the emission of dioxins formed as a result of *de-novo* synthesis is to apply a quick and effective cooling

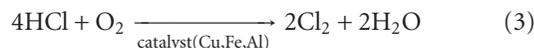
of flue gases from the temperature of about 400°C to the temperature below 200°C. The flue gases cooling rate has an important meaning for the quantity of dioxins formed. From the data contained in the subject literature [44] one may infer that in case of cooling of flue gases in a typical heat exchanger with the normal rate of the order 100–200°C/s dioxin concentration at outlet is equal to about 5 ng TEQ/m<sup>3</sup> whereas to achieve dioxin concentration equal to about 1 ng TEQ/m<sup>3</sup> it would be necessary to attain the cooling rate of the order 500–1000°C/s.

In the processes of combustion the issue of utmost importance is the appropriate control of combustion so that it is so similar to the process of complete combustion as it is possible [43]. The research of combustion and formation of organic micro-pollutants (e.g., the products of incomplete combustion) in this process led to the conclusion [45] that one of the most important parameters determining their emission, including dioxins, is the concentration of carbon monoxide in flue gases, in other words the quality of combustion. Those observations were confirmed by Seeker [46]. According to his research the concentration of carbon monoxide, in other words the conditions of combustion, considerably influences the amount and emission of dioxins generated in this process.

To the primary methods of the restriction of dioxins emission one may account the presence of sulphur dioxide in flue gases due to its inhibition of the dioxins synthesis. During the extensive research into waste combustion processes, it was concluded that the presence of sulphur dioxide in the combustion zone decreases to a large extent the amount of dioxins. Indeed, in the gas phase one may observe [47, 48] the reaction between chlorine and sulphur dioxide:



The reaction has become an argument in the debates concerning the possibility of waste cocombustion in power stations and thermal-electric power stations. The results of the research carried out by US EPA and the confirmation of dioxins emission from combustion processes have made it possible to perceive the problem in a different way. It is essential to remember that at the elevated temperature one may notice the competitive Deacon’s reaction—the catalytic decomposition of HCl [49]:



Hence, it is obvious that no chance of the complete elimination of dioxins in the combustion process exists. Further research concerning an impact of sulphur dioxide on the emission of dioxins indicates that the inhibitive influence of sulphur dioxide is not so high and strongly dependent on its excess. On the other hand, Deacon’s reaction possesses its own optimum being dependent on the temperature and concentration of HCl.

It must be underlined that good results in the scope of the limitation of dioxins production are obtained using

inhibitors. To the most frequently encountered inhibitors there belong nitrogen and sulphur compounds which bring about the blocking of the metallic active centers in the particles of volatile dust, on the surface of which one may notice “de novo” synthesis [50–54].

To summarize, one shall state that the aforementioned primary methods of the restriction of dioxins emission have a chance to substantially decrease the amount of dioxins but it is not possible to completely eliminate their production. Moreover, in practice, one may observe that it is not possible to reduce the concentration of dioxins in flue gases below the required level  $0.1 \text{ ng TEQ/m}^3$  using only the primary methods.

As regards the secondary methods of the reduction of dioxins emission, the methods of utmost importance are the following:

- (i) adsorption on the activated carbon (on solid medium or the stream method)
- (ii) catalytic decomposition of dioxins in the vanadium catalyst,
- (iii) the filtrating-catalytic method “REMEDIA”,
- (iv) the absorbing-adsorbing method “ADIOX”,
- (v) the radiation method (using an electron beam),
- (vi) the corona discharge method,
- (vii) adsorption on carbon nanotubes,
- (viii) nanocatalysis.

Dioxins, analogously to the majority of chemical substances are well adsorbed on active carbon [55]. Two variants of the adsorption process are known: the adsorption on the solid bed [56–58] and the so-called stream adsorption. In the first case great adsorbers filled with active carbon are the most frequently used. Active carbon should be replaced at the regular time intervals. The variations of those devices are the adsorbers with a moving bed of active carbon, which operate in the flowing manner [59–61]. The carbon used is the most frequently directed to combustion taking place in waste incineration plant. Another variation may be the application of adsorbers with fluidized bed [62] or with monolithic static, packed bed [63]. The stream adsorption is connected with the introduction of certain amounts of powdered active carbon (sometimes in the mixture with powdery calcium oxide known as Sorbalit, Sorbacal, Spongiacal, etc.) to the stream of flowing gases and, then, gas scrubbing on a fabric filter [64]. The method of adsorption on the solid or moving bed of active carbon has found its application to municipal waste incineration plants—such a solution was used in the modern (accepted to the public use in 1998) waste incineration plant in Cologne, in the hazardous waste and sewage sludge incineration plant EBS Simmering in Vienna and in the only one Polish waste incineration plant in Warsaw. In medical waste incineration plants there is a widely used method of stream adsorption combined with dry desulphurization using Sorbalit as a sorbent. It must be added that the stream adsorption method of dioxins elimination has been used with success in one of the Belgian

steel plants recently. The efficacy of dioxins elimination usually attains the value of 95%. The adsorption methods also present some disadvantages such as the problem of the used adsorbent management which comprises considerable amounts of dioxins as well as heavy metals (Hg in particular). The method with the application of active carbon (most of all, the adsorption on the solid bed) has one important flaw, namely the possibility of spontaneous carbon ignition at the elevated temperature (above  $200^\circ\text{C}$ ) and fire of the installation. Therefore, the application of the method of the reduction of dioxins emission is gradually diminished.

It must be highlighted that the catalytic method is deprived of this disadvantage. During the exploitation of the catalytic systems of NOx removing from flue gases it was noticed that dioxins in waste gas are subject to the efficacious decomposition. The research done by Hagenmeier [65] indicates that the vanadium-tungsten catalyst on the titanium oxide carrier effectively decomposes PCDD/Fs with the release of carbon dioxide, water and HCl. Such a catalyst is widely used in the catalytic reduction of nitrogen oxide (with the addition of ammonia) in the process of selective catalytic reduction known as SCR (Selective Catalytic Reduction). Further research [66–76] indicated that it is feasible to effectively reduce the emission of both nitrogen oxides and PCDD/Fs on the appropriately prepared catalyst  $\text{V}_2\text{O}_5\text{--WO}_3/\text{TiO}_2$  in the presence of ammonia. Today it is known that on the tungsten or platinum catalyst one may observe dechlorination and oxidation of dioxins (the partition of those processes—dechlorination and oxidation—is dependent on the composition of the catalyst) [77].

The products of those reactions are carbon dioxide, water and HCl. The temperature of the process is in the range of  $250\text{--}300^\circ\text{C}$ . The efficacy of dioxins elimination using the catalytic methods is 95–99% [78]. The numerous industrial applications confirm the high efficacy of the method [79]. It must be added that a lot of research was conducted using the other catalysts such as the platinum or perovskite catalysts. Yet those trials with platinum catalyst were completed with no success due to the secondary synthesis of dioxins on the catalyst [80–83]. To the disadvantages of the catalytic method one may account its high price, almost double as high when compared to the systems with the sorbent injection and a fabric filter and slightly higher than the systems with a moving bed of active carbon.

It is quite recently that a new method of dioxins elimination from waste gases has appeared. The method has been developed in the GORE Associates Company under the name “REMEDIA” [84–87] and it comprises such methods as the adsorption, dedusting and catalytic decomposition. The main part constitutes the membranes produced from teflon and glass fibers, specially modified with the layer of vanadium compounds. The membranes operate at the temperatures  $180\text{--}250^\circ\text{C}$ . On the layer of dust separated on the filtrating membranes the preliminary adsorption of dioxins occurs (those which are in the solid form). On the other hand, those dioxins which were not absorbed are subject to dechlorination and oxidation using vanadium salts deposited on the membrane. The efficacy of dioxins

elimination is equal to 95%. According to the scientists who developed the method it is slightly cheaper than the method with the injection of the sorbent and fabric filter and 60% cheaper than the catalytic systems. The experiments in using the filtering—catalytic method in the IVRO municipal waste incineration plant in Roeselare (the capacity of 2 lines 47 000 Mg/a) in Belgium are positive though [88, 89]. As a result of the observations lasting 42 months it was confirmed that 99.95% of the restriction of dioxins emission and the systematic maintenance of the dioxins concentration in waste gases is in the range of 0.008–0.037 ng TEQ/m<sup>3</sup>. It must be added that recently a similar installation has been used in the municipal waste incineration plant in Liberec in the Czech Republic [90].

The absorbing-adsorbing method (ADIOX) has been recently developed by the Swedish company Götaverken Miljö. The method applies the so-called “memory effect” [91] being observed in waste incineration plants. The effect is based on the absorption of dioxins in the elements of the flue gases cleaning systems made of plastics (i.e., polypropylene) and their subsequent desorption from the packing elements to the stream of flue gases in the case of the relevant decrease of their concentration in the flue gas stream as a result of, for instance, the application of the primary methods of the reduction of emission.

The solution of ADIOX encompasses the introduction of activated carbon into polypropylene applied to the process of the elements of flue gases wet purification (mainly packing elements). The molecules of dioxins, which have been absorbed in polypropylene, are additionally adsorbed on the surface of activated carbon and, efficaciously, eliminated from the flue gas stream in a persistent manner. The used elements, saturated with dioxins, are, after the replacement, burnt in waste incineration plant. Due to the fact that the process of dioxins production is a nonequilibrium process it does not influence an increase in PCDD/Fc emission from the emitter of incineration plant. The method was applied in several municipal and hazardous waste incineration plants (i.e., Kloding, Thisted, Fasan, Glostrup in Denmark, Umeå, Holstebro and Malmö in Sweden, Tredi Salaise in France and Trondheim in Norway) with a good result [92–98].

The search for the new methods of the reduction of dioxins emission is being continued. The promising effects provides the application of a radiation method (with a beam of electrons) [99–105] used till now to the simultaneous elimination of sulphur dioxide and nitrogen oxides in power plants. Furthermore, it is reported that the application of corona discharge permits one to reduce the emission of dioxins [106, 107]. There has also appeared the proposition of using the XXI—century technique—nanotechnology to remove dioxins. One of the variations is using the unique adsorbing abilities of carbon nanotubes [108–112], another is using the nanoparticles of transition metals (e.g., titanium, vanadium) introduced to flue gases the presence of which causes the catalytic decomposition of dioxins [113–116]. Nonetheless, this research is being carried out on a laboratory scale, analogously to the first examinations using ionic liquids in the selective absorption of dioxins and furans [117].

## 5. Recommendations

The problem of dioxin emission is identified the most frequently with waste incineration and it has been solved in the most satisfactory way in waste incineration plants. A considerable number of municipal waste incineration plants and big hazardous waste incineration plants have been equipped with the systems of catalytic reduction of nitrogen oxides being as well reactors of PCDD/Fs catalytic decomposition. Certain installations have been equipped with huge adsorbers with moving activated coke bed. More and more installations apply today a filtration-catalytic method (REMEDIA) or an adsorbing-adsorbing method (ADIOX). In case of small medicinal waste or other hazardous waste incineration installations a basic method is the use of calcium reagent (lime) for acidic gas removal (e.g., Sorbalit, Sorbacal, Spongiacal, etc.) provided with ca. 5–10% addition of powder activated carbon. In combination with fabric filter the efficiency of dioxin removal using this method is very high. Part of those small installations are equipped with a catalytic reactor SCR in which PCDD/Fs decomposition also takes place. However, waste incineration plants are not the only sources of dioxin emission from industry. The Stockholm Convention imposes the reduction of their emission from all sources. Seemingly, the problem of dioxin emission from large combustion plants i.e. electric power stations and thermal-electric power stations, constitutes no problem. Numerous research results published in literature [118–121] indicate that for hard coal combustion PCDD/Fs concentrations do not usually exceed 0.01 ng TEQ/m<sup>3</sup> and, hence, they are at least 10-times lower than the values allowed for waste incineration. A similar situation takes place in case of lignite [122] or oil combustion [123]. This is the result of sulfur content in fuel and fixation of chlorine capable of taking part in chlorination reaction during de novo synthesis. The most recent investigations performed by Koniecznyński and Grochowalski [124] proved that there is a visible dependence between dioxin concentration in flue gases and the size of installation for coal combustion—in case of small boilers dioxin concentrations in flue gases applied in households may slightly exceed 0.1 ng TEQ/m<sup>3</sup>. Great possibilities of reduction of dioxin emission from power plants are connected with the application of technology of simultaneous SO<sub>2</sub> and NO<sub>x</sub> removal utilizing electron beam technology [104, 105]. Apart from reduction of those two pollutants there also occurs decomposition and oxidation of PCDD/Fs with good efficiency.

A relevant source of dioxin emission to the environment is metallurgy sector. There are a lot of data proving that dioxin concentrations in waste gases may reach the level of 50–1200 ng TEQ/m<sup>3</sup> [125–129]. In this sector there are no regulations reducing dioxin concentrations in waste gases at present (with the exception of Belgium and Canada). Nevertheless, in many countries installations reducing dioxin emission using a filtration-catalytic method (REMEDIA) [84, 85] have appeared in the recent years. The second method used in metallurgy sector is the application of inhibitors based on chemical compounds containing nitrogen and sulfur in a molecule, for example, urea, ammonium

sulfate, and so forth, [50–54]. Seemingly, the method has great perspectives in metallurgy sector due to a relatively low cost.

In conclusion, amongst the secondary methods of dioxin emission reduction one may recommend the catalytic method as the most important and the most efficacious one allowing to decrease simultaneously and considerably the emission of PCDD/Fs and reduce the emission of nitrogen oxides (SCR). Very good results are also attained by the application of filtration-catalytic method. Numerous installations give a chance to disseminate the technology in industry as well. The obstacle may be a high price of filtrating sacks applied in this method. However, it seems to be that the utilization of adsorption technologies using active carbon has only slight chances to be implemented. The utilization of radiation method (with an electron beam) may also be promising as it is an effective method of reduction of sulphur dioxide and nitrogen oxide emission being implemented on a commercial scale of production. The application of adsorption to carbon nanotubes seems to be very intriguing; however, the actual state of technique does not give a chance to implement the method on a large scale.

## 6. Conclusions

The problem of dioxin emission from combustion processes really exists. The intensity of this emission is the resultant of combustion conditions and the effectiveness of flue gases treatment system. However, it must be remembered that even the most novel and the greatest system of flue gases treatment is not able to dispose of all pollutants, particularly in case of unstable installation operation and changing parameters of gases subjected to treatment. The key here is continuous, stable installation work, combustion of low emissivity and the appropriate conservation. These are the conditions to be obeyed so that the properly designed installations with an efficient system of flue gases treatment have the emission in accordance with the regulations [130]. All oscillations of work parameters, particularly carbon dioxide concentration oscillations will always result in the increased dioxin emission.

However, seemingly, after 30 years of investigations concerning dioxin formation and methods of reduction of their emission we may say that we have been acquainted with the process so thoroughly to prevent effectively dioxin formation and to reduce their emission to the level which is not hazardous to the environment and human health.

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## Review Article

# Monitoring and Modelling the Trends of Primary and Secondary Air Pollution Precursors: The Case of the State of Kuwait

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Since the beginning of the industrial revolution, processes of different scales have contributed greatly to the pollution and waste load on the environment. More specifically, airborne pollutants associated with chemical processes have contributed greatly to the ecosystem and populations health. In this communication, we review recent activities and trends of primary and secondary air pollutants in the state of Kuwait, a country associated with petroleum, petrochemical, and other industrial pollution. Trends of pollutants and impact on human health have been studied and categorized based on recent literature. More attention was paid to areas known to researchers as either precursor sensitive (i.e., nitrogen oxides (NO<sub>x</sub>), volatile organic compounds (VOCs)) or adjacent to upstream- or downstream-related activities. Environmental monitoring and modelling techniques relevant to this study are also reviewed. Two case studies that link recent data with models associated with industrial sectors are also demonstrated, focusing mainly on chemical mass balance (CMB) and Gaussian line source modelling. It is concluded that a number of the monitoring stations and regulations placed by the Kuwait Environment Public Authority (KUEPA) need up-to-date revisions and better network placement, in agreement with previous findings.

## 1. Introduction

It is of paramount importance to monitor and study the behaviour of primary and secondary precursors of air pollution, to establish a better understanding of their trends and impact on the surrounding environment. Human-related activities result in a number of airborne chemicals (i.e., primary pollutants), which include methane (CH<sub>4</sub>) and nonmethane hydrocarbons (collectively known as total hydrocarbons-THC), total sulphur, nitrogen oxides and hydrogen sulphide (SO<sub>x</sub>, NO<sub>x</sub>, H<sub>2</sub>S), carbon mono- and dioxide (CO and CO<sub>2</sub>), BTEX (C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>), and other heavy metals (e.g., Hg, Pb, etc.). The interaction of such chemicals with the surrounding environment and the effect of photochemical reactions in the atmosphere results in what is known as secondary pollutants, a valid example of which is ozone (O<sub>3</sub>).

Urban air pollution photochemistry is somewhat unique, and has been a matter of debate for a number of years amongst researchers [1–6]. One of the main characteristics of urban air pollution is the oxidation of SO<sub>2</sub> and NO<sub>2</sub> and their conversion to particulate sulphate (SO<sub>4</sub><sup>2-</sup>) and gaseous and particulate nitrates (NO<sub>3</sub>). Moreover, the rate of the conversion of NO<sub>x</sub> to NO<sub>3</sub> affects ozone formation and the fate of the NO<sub>x</sub> in the atmosphere. NO<sub>x</sub> is oxidized to nitric acid (HNO<sub>3</sub>) in the atmosphere, which in turn forms NO<sub>3</sub> particles [7].

Acidification of precipitation, visibility reduction, and deleterious effects on human health and plants are all effects associated with these secondary pollutants. Nonetheless, one of the main worries with regards to urban air pollution is the substitution of a pollutant with another in a reversible reaction. This could be witnessed in many Asian and European countries via the following nitric oxide reaction

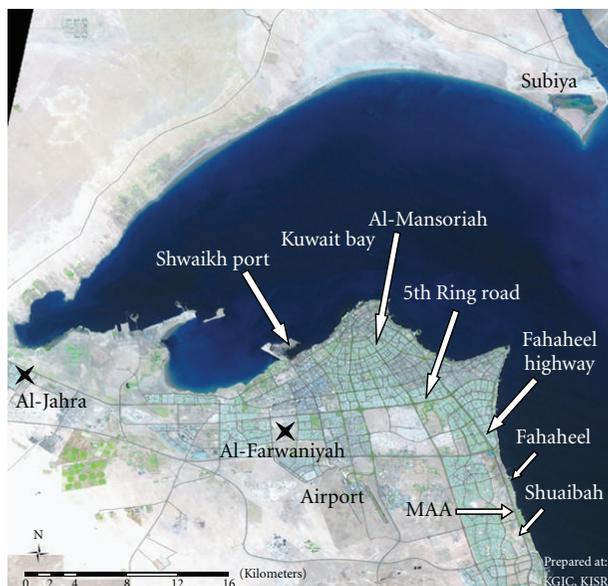


FIGURE 1: Urban Kuwait map showing main locations in the stat. Image courtesy of satellite archives at the Kuwait Institute of Scientific Research.

with ozone



Hence, one pollutant ( $\text{O}_3$ ) is substituted by another in the lower atmosphere (i.e.,  $\text{NO}_2$ ) [5]. In this paper, we review recent developments and trends associated with air pollution precursors, in terms of increase and diurnal patterns in the state of Kuwait and the surrounding region, mainly the Arabian Gulf peninsula. Environmental measuring techniques and modelling methods are reviewed within the scope of this paper.

**1.1. Major Pollution Sources and Activities within the State of Kuwait.** Kuwait is a principality state in the North-Eastern corner of the Arabian Gulf peninsula, currently with an estimated population of 2.8 million. Kuwait is characterized by a typical *desert climate* with long harsh summers, in which ambient temperatures exceed  $55^\circ\text{C}$  and mild winters. It is also a major exporter of crude oil (ranking forth in OPEC's producers list), where the 2.6 million barrels per day (mmbld) mark was crossed back in 2007 [8], with plans to increase production to 4 mmbld in 2020 [9]. Three major refineries process over 935,000 bbl/d, situated in the southern part of the country, collectively referred to as the *refineries belt* [10].

Such characteristics make Kuwait a country with air pollution associated with down/upstream processes, namely, in southern parts of the country. In addition, petrochemical processing lines and conversion industries are all located, somewhat, in the vicinity of Al-Shuibah industrial area (Figure 1). Border lines of the city, stretching to the fifth ring road, make Kuwait City an area cornered by the bay. The city area harbours both traffic-related airborne pollutants and southern sources emissions. In addition, activities within city

limits and harbour pollution from the northern stretch also contribute to the pollution load. Moreover, Kuwait has the largest and oldest power plant and desalination network in the region, dating back to the 1960s. The capacity of which is estimated at 16,095 MW and  $2 \times 10^6 \text{ m}^3/\text{day}$ , respectively [11].

Traffic congestion and rush hours within city limits and along major highways (i.e., King Abdulaziz (Fahaheel), 5th and 6th ring road) contribute mainly to the  $\text{CO}$ ,  $\text{NO}_x$  and VOCs levels in the air. For every 33 residents in Kuwait, there are 100 cars registered [11]. Such estimates makes airborne pollution studies a must for concerned parties, namely, the Kuwait Environment Public Authority (KUEPA), which since 2001 is recognized as an independent government body with legal powers.

**1.2. Primary Pollutants Monitoring.** Compared to its neighbouring countries, Kuwait suffers from primary pollutants effects. This is witnessed clearly on the number of pollutants recorded in the KUEPA stations, which operate a number of fixed monitoring stations around the country. A previous study by Al-Rashidi et al. [12] stated that the stations were not appropriately distributed around the city limits, and there is a need to relocate them within residential areas to measure the actual impact of a number of primary pollutants (e.g.,  $\text{SO}_2$ ). Abdul-Wahab [13] compared two areas in the Gulf Council Countries (GCC), namely Al-Khalidiya (Kuwait) and Qalhat (Oman), in terms of air pollutants and their load. Results showed higher levels of pollution in the urban residential area of Kuwait than in the suburban industrial area in Oman. The data recorded in Al-Khalidiya showed that both nonmethane hydrocarbons (NMHC) and  $\text{NO}_2$  have exceeded the Kuwait standards for residential areas. Furthermore, the results showed that the hourly distribution of NMHC,  $\text{CO}$ , and  $\text{NO}_x$  in Khaldiya was characterized by three peaks which were associated with the traffic loads on the main streets. The data recorded in the urban area of Kuwait showed marked day-of-week dependence also.

**1.3. Secondary Pollutants.** The major concern with secondary airborne pollutants is ground level ozone ( $\text{O}_3$ ), namely, in a country with high ambient temperatures that induce (alongside radiation energy, volatile organic compounds (VOCs), and  $\text{NO}_x$ ) ozone formation. In essence, controlling precursor emissions (i.e., VOCs and  $\text{NO}_x$ ) coming from anthropogenic sources can minimize ozone formation [14]. The main contributor of such sources is combustion processes (local industries including power stations, gasoline and diesel operated vehicles, etc.). Transportation emissions control is hence considered crucial to ozone reduction.

Ground level ozone ( $\text{O}_3$ ) formation is a continuous physical-chemical accumulation/destruction process [15]. Therefore, a diurnal ozone cycle/curve reflects the effects of all those underlying factors on ozone dynamics, which underlines the importance of monitoring such a chemical. Abdul-Wahab et al. [16–18] have used a mobile laboratory to study and analyse air pollution in Kuwait. Data analysis

TABLE 1: Standard USEPA methodology for annual population risk (APR) and hazard index (HI) calculations used by Al-Salem and Bouhamrah [27]; Al-Salem and Al-Fadhlee [28].

Equation/correlation	Notes
$OX = C_{O_3} + C_{NO_x} - C_{NO}$	Used for data filtration, where OX is the concentration of oxides in the ambient (ppb), $C_{O_3}$ , $C_{NO_x}$ and $C_{NO}$ are the concentrations in ppb of ozone, NO <sub>x</sub> and nitric oxide, respectively.
$E = \frac{C \cdot CR \cdot EF \cdot ED}{BW \cdot AT}$	Where $C$ is the contaminant concentration ( $mg \cdot m^{-3}$ ); CR is the contact rate in $m^3 \cdot day^{-1}$ ; EF is the exposure frequency in days per year; ED exposure duration (year); BW is the average human body weight (kg); AT is the averaging time in hours/year.
APR = Risk factor $\times$ Population/lifetime	APR is the annual population risk
$HI = \Sigma (C_i/PEL_i)$	Where $C_i$ is the concentration of $i$ in $mg/m^3$ ; $PEL_i$ is the permissible exposure limit for $i$ in $mg/m^3$ .

showed that ozone concentration exhibited a maximum at 27°C as a function of ambient temperature. Increase in the ambient temperature above 27°C resulted in a decrease in the ozone concentration. Increase in power consumption in the summer, due to the increased use of indoor air conditioning, resulted in increase in emission rates of various pollutants.

It is also known that stratosphere ozone layer acts as a shield against all ultraviolet radiation approaching the planet Earth through absorption. Al-Jeran and Khan [19] analyzed data of ozone layer thickness obtained from Abu-Dhabi (UAE) station and detailed measurement of air pollution levels in Kuwait. The ozone layer thickness in stratosphere had been correlated with the measured pollution levels in the State of Kuwait. The influence of import of ozone depletion substances (CFCs) for the last decade had been evaluated. Other factor that strongly affects the ozone layer thickness in stratosphere is local pollution levels of primary pollutants such as total hydrocarbon compounds and nitrogen oxides. The dependency of ozone layer thickness on ambient pollutant levels presented in detail reflecting negative relation of both nonmethane hydrocarbon and nitrogen oxide concentrations in ambient air. The ozone thickness related to the ground level concentration of nonmethane hydrocarbon and can be used as an indicator of the health of ozone layer thickness in the stratosphere. The thinning of ozone layer on the poles was alarming that resulted into different protocols while near equatorial regions this phenomenon is not that much pronounced. The maximum thinning occurred in the month of June and the least in the month of December based on five years data from Abu-Dhabi monitoring station.

**1.4. Health Impact.** Increased levels of primary and secondary pollutants are known to have adverse effects on human health [20], to cause injury to plants [21], to reduce crops yield [22], and to negatively affect ecosystems [23]. Natural ecosystems adjacent to urban areas are exposed increasingly to air pollutants of urban origin. Air pollutants, particularly SO<sub>2</sub>, NO<sub>2</sub> and the major secondary photochemical oxidant O<sub>3</sub>, OH, and SO<sub>4</sub> are important threats to plants. Their effects comprise many physiological and biochemical changes in plants, which may result in growth reduction and yield loss, even at low levels chronic exposure. Concerning human health, tropospheric O<sub>3</sub> measured in urban regions and across regional airsheds are known to affect human health [24].

Air pollution in Kuwait is a major contributor to a number of health effects associated with many age groups in the city and around urban suburbia [25]. Local health reports show that 40% of the patients in one of the main hospitals in Kuwait during the period of August–October 1991 suffered from respiratory problems, baring first Gulf War effects and oil fields fires by retreating Iraqi troops. Statistical analysis showed that there was a highly significant correlation between the increased concentration of specific pollutants and symptoms of reactive and nonreactive airway diseases [26].

Al-Salem and Bouhamrah [27] studied a number of carcinogens and other primary pollutants in an industrial area in Kuwait. The main focus was on calculating the annual population risk (APR) to establish a better cancer risk assessment study by calculating APRs and hazard indices (HIs). Benzene (C<sub>6</sub>H<sub>6</sub>), di bromo-chloro methane, bromoform, chloroform, and methylene chloride were all measured using diffusive passive sampling techniques. Using the standardized USEPA methodology (Table 1), APR was increasing within winter months (mainly January) and had a proportional relationship with benzene levels in the atmosphere, wind direction, and location of site. On average, the industrial site in Kuwait exceeded the US average, city of St. Louis (US) and Modena (Italy), levelling at 6 cases on a 70 year average in population much less than the rest. Cases associated with leukaemia are attributed to benzene levels in the lower atmosphere. In a followup study investigating the south regions of Kuwait, Al-Salem and Al-Fadhlee [28] studied the APR and HI associated with benzene levels in the atmosphere in a residential area over the period of 3 years (2004–2006). The HI calculations were based on SO<sub>2</sub>, NO<sub>2</sub>, and NH<sub>3</sub> levels, which resulted in a value of 0.03, that is, fit for living conditions. Khan and Al-Salem [29] studied the effects of NO<sub>x</sub> and NO on birth and still birth rates in Al-Ahamdi governorate in Kuwait. A relationship was proved based on statistical analysis performed using one and two way ANOVA. Based on the five years data collected, the still births in the area increased from 153 cases (2000) to 196 (2004), corresponding to an increase in the NO level.

The State of Kuwait oil fires and military operations associated with the 1991 Gulf War resulted in substantially increased levels of airborne particulate matter (PM) in the region around it, namely, the GCC. White et al. [30] used a quantitative risk assessment methodology to estimate

TABLE 2: Summary of recent studies conducted in the state of Kuwait focused on primary pollutants monitoring and source determination.

Reference	Primary pollutants studied	Notes
Al-Salem and Khan [10]	NO <sub>x</sub> , NO, SO <sub>2</sub> , CO, H <sub>2</sub> S, NH <sub>3</sub>	Monitoring the trends and diurnal patterns of Al-Riqa and Fahaheel areas. A number of exceedences were recorded in violation of KUEPA rules and regulations.
Sebzali and Al-Salem [32]	NMHC, NO <sub>x</sub> , SO <sub>2</sub> , CO, H <sub>2</sub> S, NH <sub>3</sub>	A neural network was developed based on multilayer processor modeling in Al-Mansoriah area. The study was used to estimate primary pollutants with a high accuracy.
Khan and Al-Salem [33]	C <sub>6</sub> H <sub>6</sub> , Cl <sub>2</sub> , NO <sub>2</sub> , NO <sub>x</sub> , H <sub>2</sub> S, CH <sub>4</sub>	Three years of data were assessed and filtered to execute concentration roses around a receptor point. Combustion and downstream activities were determined to be the major source.
Al-Salem [34]	CH <sub>4</sub> , CO	A series of wind and concentration roses were executed to investigate the source of the two pollutants around Fahaheel. Patterns and shapes determined that the refineries belt side was the major contributor to the load.
Al-Salem et al. [35]	NO <sub>x</sub> , NO, SO <sub>2</sub> , CO, H <sub>2</sub> S, NH <sub>3</sub>	Al-Mansoriah area was investigated and levels of NH <sub>3</sub> were exceeding threshold limits. The area was determined to be a NO <sub>x</sub> sensitive area in the state of Kuwait.
Albassam et al. [36]	CO, NO <sub>x</sub> , NMHC	An assessment of air quality in the vicinity of a school was carried out, NMHC was above permissible limits. Statistical analysis was used to predict a number of primary pollutant.
Khan and Al-Salem [37]	C <sub>6</sub> H <sub>6</sub> , CO, NO <sub>x</sub>	Seasonal variations and metrological conditions were affecting primary pollutants dispersion and fate in the atmosphere based on this study. Using executed roses around a receptor point and analysis the authors determined the effect.
Al-Adwani et al. [38]	CO, NO <sub>x</sub> , THC	An intersection was monitored for automobile primary pollutants at the switch period of MTBE unleaded gasoline in Kuwait. CO and THC emissions increase as volatility increases.

the increase in premature deaths in citizens of Saudi Arabia associated with the Gulf War. Meta-analysis of daily time-series studies of nonaccidental mortality associated with increased PM<sub>10</sub> levels using two alternative methodologies yielded exposure response relative risk functions of 2.7% and 3.5% per 50 µg/m<sup>3</sup> increase in PM<sub>10</sub> concentration. Combining these exposure-response functions with estimates of the magnitude and duration of the increased PM<sub>10</sub> exposure, the size of the exposed population and baseline mortality rates provided an estimate of approximately 1,080 to 1,370 excess nonaccidental deaths of Saudi citizens during 1991-1992 associated with the Gulf War-related increase in PM levels. Lange et al. [31] examined relationships between symptoms of respiratory illness present 5 years after the war and both self-reported and modeled exposures to oil-fire smoke that occurred during deployment of troops. Modeled exposures were exhaustively developed using a geographic information system to integrate spatial and temporal records of smoke concentrations with troop movements ascertained from global positioning systems records. Approximately 94% of the study cohort were still in the gulf theater during the time of the oil-well fires, and 21% remained there more than 100 days during the fires. There was modest correlation between self-reported and modeled exposures ( $r = 0.48$ ,  $P < .05$ ). Odds ratios for asthma, bronchitis, and major depression increased with increasing self-reported exposure. In contrast, there was no association between the modeled

exposure and any of the outcomes. These findings do not support speculation that exposures to oil-fire smoke caused respiratory symptoms among veterans.

## 2. Monitoring, Trends, and Diurnal Patterns

*2.1. Pollutants Monitoring and Major Contributing Sources.* In a country that is dominated by petroleum upstream/downstream industries, primary pollutants are of major concern, with regards to air quality. Other sources of primary pollutants in Kuwait include power stations (operating on fossil fuels) and road traffic. A recent study by Ramadan [39] was concerned with measurements of fortnightly average concentrations of a number of primary pollutants, namely: NO, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, and VOCs. The study location was in southern Kuwait (Al-Zour); an area influenced by petroleum refining and electrical generation activities. No violations of KUEPA standards were reported, but consistency of the results allowed the production of spatial distribution maps of the pollutants measured and consequently the comparison between levels of air pollution at different locations. A comparison between the measured concentrations and the applicable air quality standards promulgated by KUEPA showed that those compounds had low concentrations compared to both industrial and residential KUEPA standards. Table 2

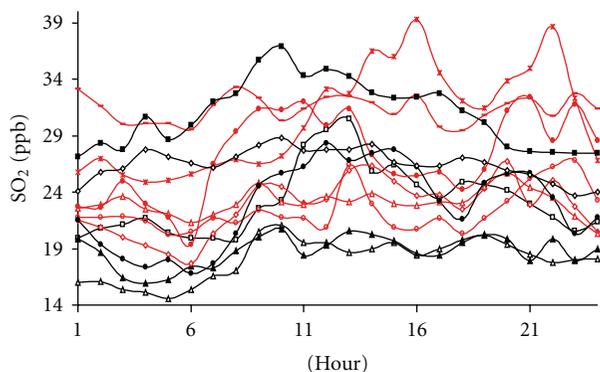


FIGURE 2: Diurnal pattern of  $\text{SO}_2$  recorded over the period 2000-2004 in Al-Mansorih. Source: Al-Salem et al. [35].

summarizes a number of studies conducted in the state of Kuwait in the last decade, focused on primary pollutants monitoring.

A number of reasons drive researchers to study  $\text{PM}_{10}$  in an arid country like Kuwait, mainly for the abundance of surrounding sources around the city limits. Road traffic and frequent dust storm are proposed to be essential contributors to the total  $\text{PM}_{10}$  ambient load in urban areas [40]. Other sources include burning fuels (i.e., gasoline, oil, diesel, or wood) and blown dust. In a compiled study of seven European cities, Querol et al. [41] show that mineral dust, combustion, and secondary aerosols were important  $\text{PM}_{10}$  sources. They also show that  $\text{PM}_{10}$  levels were enriched at kerbsides relative to urban background, a fact that must be attributed to road traffic emissions. The same area (Fahaheel) was studied by Al-Salem and Khan [10] for its diurnal patterns of major primary and secondary pollutants. Al-Mansorih residential area was monitored by Al-Salem et al. [35] for the same purpose (Figure 2). Similarities were found in typical airborne pollutants associated with both residential and industry adjacent sites.  $\text{NO}$  peaks were in contrast to ozone (titration effect) concentrations. And  $\text{THC}$  were associated with industrial sources at emissions strength hours. Heal et al. [42] point out traffic, combustion, and crustal material as the major sources in urban background. Studies on  $\text{PM}_{10}$  have been very limited in the state of Kuwait. A study by Al-Salem [43] over the period of two years considered  $\text{PM}_{10}$  data (January 2004–December 2005) and analyzed for Fahaheel urban area. The annual mean values exceeded (both years of continuous monitoring) the KUEPA permissible limit ( $90 \mu\text{g m}^{-3}$ ), recording 291 in 2004 and  $289 \mu\text{g m}^{-3}$  in 2005. 14 exceedances were recorded in 2004 based on daily rolling averages, while in 2005 15 exceedances were recorded. Engelbrecht et al. [44] initiated a study around Kuwait and other neighbouring countries, including UAE, Qatar and others. The study focused on providing information on the chemical and physical properties of dust collected over a period of approximately a year. By comparison, average  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  mass and chemical concentration levels from the Middle East deployment sites areas many as 10 times greater than those from five rural

(IMPROVE) and five urban (CSN) sites in the southwestern US.

$\text{CO}_2$  is another important pollutant that has been a concern in the state for the last somewhat 20 years. The  $\text{CO}_2$  concentrations also show a strong diurnal pattern with lowest values in the mid-afternoon when the local atmosphere is most unstable and highest concentrations in the early evening when the atmosphere becomes more stable and vehicular traffic is high. A secondary peak occurs in the early morning when traffic increases and the atmosphere is most stable [45]. In a study by Nasrallah et al. [46], measurements of an urban area in Kuwait were compared to the city of Phoenix (Arizona, USA). Analysis of this record reveals (a) an annual cycle with highest values in February and lowest values in September reflecting the growth and decay of vegetation in the Northern Hemisphere as well as fluctuations in motor traffic, (b) a weekly cycle with highest values during the weekdays and lowest values during weekends, and (c) a diurnal cycle with highest values after sunset when the local atmosphere becomes more stable following vehicular emission of  $\text{CO}_2$  throughout the day and lowest values in late afternoon following several hours of relatively unstable conditions. During the daytime,  $\text{CO}_2$  concentrations are related to wind direction, with westerly winds (coming from the desert) promoting lowest  $\text{CO}_2$  concentrations. At night, lowest  $\text{CO}_2$  levels are associated with higher wind speeds and winds from the north. Asia and more specifically the Middle East has become the largest contributor to mercury (Hg) in the atmosphere, responsible for over half the global emissions. A number of sources contribute to the Hg levels, such as Hg mining, gold mining, chemical industry, metal smelting, coal/crude oil combustion, natural, and agriculture resources. With the probable effects of a unique combination of climatic (e.g., subtropical climate), environmental (e.g., acid rain), economic (e.g., swift growth) and social factors (e.g., high population density), more effort is still needed to understand the biogeochemistry cycle of Hg and associated health effects in Asia. Li et al. [47] reviewed the Hg levels and sources in Asia. They have concluded that Kuwait was over contaminated by Hg due to chemical processing around the bay area due to salt and chlorine processing. BuTayban and Preston [48] conducted Hg pollution investigation in sediments in Kuwait Bay, which received wastewater from a Salt and Chlorine Plant (SCP) and untreated sewage. Highest T-Hg concentrations ( $36,500 \pm 34,930 \text{ ng/gm}$ ) were observed around previous industrial outfall, where sediments were disturbed by shipping activities. T-Hg concentrations were lower in Shuwaikh Port area ( $650 \pm 210 \text{ ng/gm}$ ) and decreased towards northern coastline of Kuwait Bay (wider Bay region,  $50 \pm 30 \text{ ng/gm}$ ). These values were still above background concentrations of  $15\text{--}20 \text{ ng/g}$ . Calculation of T-Hg inventory in surface sediments indicated that 22.5 tons Hg was present which was similar to estimated industrial discharges of 20 tons, suggesting that the contamination is largely confined to the Bay. The distributions of Me-Hg were similar to those of T-Hg and represented ranges between 0.23% and 0.5% of T-Hg, indicating that surface sediments within Kuwait Bay contained 80 kg Me-Hg.

TABLE 3: Exceedences against KUEPA rules and regulations reported in Fahaheel and Al-Riqa over the period between 2004-2005. Source: Al-Salem and Khan [10].

Pollutant	KUEPA hourly limit (ppb)	#Exceedences (year, area)	Reference
SO <sub>2</sub>	170	4 (2004, Fahaheel)	KUEPA [49]
		2 (2004, Al-Riqa)	
		18 (2005, Fahaheel)	
		12 (2005, Al-Riqa)	
H <sub>2</sub> S	140	6 (2004, Fahaheel)	KUEPA [49]
		2 (2004, Al-Riqa)	
		25 (2005, Fahaheel)	
		9 (2005, Al-Riqa)	
O <sub>3</sub>	80	416 (2004, Fahaheel)	KUEPA [49]
		122 (2004, Al-Riqa)	
		154 (2005, Fahaheel)	
		55 (2005, Al-Riqa)	
NH <sub>3</sub>	800	None (2004, Fahaheel)	KUEPA [49]
		None (2004, Al-Riqa)	
		1 (2005, Fahaheel)	
		None (2005, Al-Riqa)	

**2.2. Rules and Regulations.** Rules and regulations that govern the emissions and concentration of airborne pollutants in the state of Kuwait are proposed and governed by Kuwait Environment Public Authority (KUEPA). In 2001, KUEPA was recognized as a separate entity with holding and legal power. It was previously considered as a division of the Ministry of Health in Kuwait. Residential and industrial areas are governed by threshold limits that regulate the emissions and sources strengths of all major primary and secondary precursors. A number of studies in Kuwait took place with the aim of recording exceedences against limits of certain airborne pollutants. Al-Salem and Khan [10] studied the outdoor air quality of two areas adjacent to upstream/downstream facilities in Kuwait. Table 3 shows the main findings of the study in terms of exceedences against KUEPA standards. In a residential area in mid-city borders, Al-Salem et al. [35] studied the exceedences of Al-Mansoriah area. Findings could be seen in Table 4.

### 3. Modelling Section

**3.1. Related Studies, Principles, and Parameters.** Ettouney et al. [11] used the ISCST (Industrial Source Complex Short Term) model to generate a numeric datasheet of an emission inventory in Kuwait. The model uses the steady-state Gaussian plume equation for a continuous elevated source, with the downwind hourly average concentration given in the following equation adapted from Wark et al. [2] and previously used by Al-Salem [50]:

$$C(x, y, z) = \frac{Q}{(2\pi)\sigma_y\sigma_z u} \cdot \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \times \left\{ \exp\left[\frac{-(z-H)^2}{2\sigma_z^2}\right] + \exp\left[\frac{-(z+H)^2}{2\sigma_z^2}\right] \right\}. \quad (2)$$

Comparison of the ISCST model predictions and the data base showed reasonable agreement for the hourly averages. The ISCST model was also used by Abdul-Wahab et al. [51] to study SO<sub>2</sub> pollution pattern in the Al-Shuibah (southern Kuwait) industrial area in Kuwait. Some discrepancies were found, however, in the measured and predicted SO<sub>2</sub> concentrations at ground level. A similar approach was applied by Abdul-Wahab et al. [52] to study SO<sub>2</sub> pollution generated in an oil refinery in Oman over a 21 day period in January 2000. A model for the input of PM<sub>10</sub> dust has been constructed by Draxler et al. [53]. An assumption of the omnipresence of particles having sizes between 88 and 125 μm was verified by analyses of sampled desert sediments and published data. A well-tested function-related horizontal flux of all aeolian mass to friction velocity and threshold friction velocity. Finally, the ratio of vertical flux of PM<sub>10</sub> dust to the horizontal flux of all aeolian mass as a function of surface sediment texture was used to express the vertical flux of PM<sub>10</sub> dust. Textures of all sampled soils were quite close to "sand" texture and consequently only one ratio was used for all soils in the source areas of the area. The model domain is for Kuwait, part of Syria, Saudi Arabia, the United Arab Emirates, and Oman.

**3.2. Chemical Mass Balance (CMB) Modelling.** The chemical mass balance (CMB) model for source allocation based on receptor point measurements is a tool applied to (mainly) determine the contribution of sources surrounding a data collection point or site. To use CMB analysis, the researcher must assume that all sources affecting the airshed are identifiable, and that the pollution source profile associated with each source can be speciated. Back calculations are typically involved employing chemical fingerprinting of sources, that is, concentrations of certain pollutants associated with source strength or activity. A number of studies have been carried out in the past using CMB. Christensen and Gunst [54] have determined errors associated with CMB employed in a number of cases in air quality data. CMB equations have been used to apportion observed pollutant concentrations to their various pollution sources. Typical analyses incorporate estimated pollution source profiles, estimated source profile error variances, and error variances associated with the ambient measurement process. Often the CMB model is fit to the data using an iteratively reweighted least-squares algorithm to obtain the effective variance solution. CMB model was considered within the framework of the statistical measurement error model to minimize reported errors. Christensen [55] considered the performance of several solutions to the CMB equations for cases in which one or more solutions affecting the airshed are unknown. It was demonstrated that the presence of unknown sources in the airshed can lead to substantial (and sometimes surprising) errors when estimating the known source contributions. A simple illustration of the effect of unknown sources on the problem is given and the vulnerability of iterative estimators (such as the effective variance estimator) in the presence of unknown sources is explained. Six sediment cores were collected from Green Bay, Wisconsin, in order to identify

TABLE 4: Exceedences against KUEPA rules and regulations reported in Al-Mansoriah over the period between 2000-2004. Source: Al-Salem et al. [35].

Pollutant	Averaging period	Permissible limit (ppb)	#Exceedences/year	Reference
Ozone	8 hrs	60	6/2000 1/2004	KUEPA [49]
Ozone	Hourly	80	6/2000 5/2001 1/2002 1/2003 3/2004	KUEPA [49]
NO <sub>2</sub>	Daily	50	95/2000 48/2001 41/2002 93/2003 73/2004	KUEPA [49]
NO <sub>2</sub>	Hourly	100	234/2000 237/2001 342/2002 259/2003 323/2004	KUEPA [49]
NO <sub>2</sub>	Annual	30	5/(2000–2004)	KUEPA [49]
SO <sub>2</sub>	Hourly	170	5/2000 8/2002 12/2003 17/2004	KUEPA [49]
SO <sub>2</sub>	Annual	30	1/2003	KUEPA [49]
SO <sub>2</sub>	Daily	60	5/2003	KUEPA [49]
CO	Daily	8000	6/2004	KUEPA [49]

possible sources of polycyclic aromatic hydrocarbons (PAHs) using CMB model by Su et al. [56]. The cores had total PAH concentrations between 8.04 and 0.460 ppm. The results show that coke burning, highway dust, and wood burning are likely sources of PAHs to Green Bay. The contribution of coke oven emissions (CB) for the Green Bay cores is in the range of 5% to 90%. The overall highway dust (HWY) contribution is between 5% and 70%. Daily average PM<sub>10</sub>, TSP (total suspended particulate matter) and their chemical species mass concentrations were measured at residential and industrial sites of an urban region of Kolkata during November 2003 through November 2004 by Gupta et al. [57]. Source apportionment using CMB model revealed that the most dominant source throughout the study period at the residential site was coal combustion (42%), while vehicular emission (47%) dominates at the industrial site to PM<sub>10</sub>. Paved road, field burning, and wood combustion contributed 21%, 7%, and 1% at the residential site, while coal combustion, metal industry, and soil dust contributed 34%, 1%, and 1% at industrial site, respectively, to PM<sub>10</sub> during the study period. The contributors to TSP included coal combustion (37%), soil dust (19%), road dust (17%),

and diesel combustion (15%) at residential site, while soil dust (36%), coal combustion (17%), solid waste (17%), road dust (16%), and tyre wear (7%) at industrial site.

In light of the previously stated review, and importance of such methods in the execution of source allocation, the following section will demonstrate case studies of modelling nature performed in Kuwait. The first will be on the CMB model execution and the second is of a line source emission strength determination, all performed within state limits over the past 5 years, with the latter being of importance to industrial sectors concerned with green oil processing.

*3.3. Case Study No. 1: On the Execution of CMB around Urban/Industry Adjacent Sites.* The following work was carried out in two adjacent areas in Kuwait to a number of upstream and downstream facilities, alongside other medium-scale industries. Both urban areas are situated in Al-Ahmadi governorate (Figure 3). Fahaheel area (inhabited with about 100,000 residents) is considered one of five major areas in the state of Kuwait. The location of the area makes it a major point in work commuting and real estate ventures. The overly populated Fahaheel is adjacent to the largest in capacity oil refinery in the state (Mina Al-Ahamdi -MAA- refinery). Petrochemical industries; such as ammonia, urea, polyethylene, and polypropylene plants, as well as the newly proposed polystyrene and both of the aromatics project and the Olefins II project and other private small cottage industries also exist on the south side of the area. Background concentrations are associated with the second largest oil field in the world (The Greater Burgan Field) which on the other hand is located somewhat on the west end of Fahaheel. However, Al-Riqa area (inhabited with about 40,000 inhabitants) is less populated than Fahaheel. The residential area of Al-Riqa host Kuwaiti residents of mid and working classes. It is situated to the north side of Fahaheel and is dominated by inner roads that lead to the downtown of the area. To the south of Al-Riqa, the three refineries belt and Fahaheel area exist and the north eastern part is occupied by the downtown area of Al-Riqa. Data were secured from KUEPA monitoring stations in both areas located on the roof of the main polyclinics.

The source allocation was ascertained by analyzing the data points collected and observing the wind directions of peak pollutants concentration values. Many researchers in their investigations have used CMB models to identify the predominant sources with respect to wind direction and their impact on to the ambient air quality. Various major airborne pollutants were present in the current pool of data. Sectors around each data collection point (receptor point) were divided to ease the analysis part of the constructed CMB model. Al-Riqa sectors were as follows: (1) downtown area, (2) refineries, petroleum, and petrochemical industries, and (3) traffic line sources (Fahaheel highway), gas stations, and sports clubs. Table 5 shows the distribution of these three sectors with respect to data collection point in Al-Riqa (Polyclinic). As for Fahaheel, the primary pollution sources and each corresponding sector is shown in Table 6 [10, 58–60].

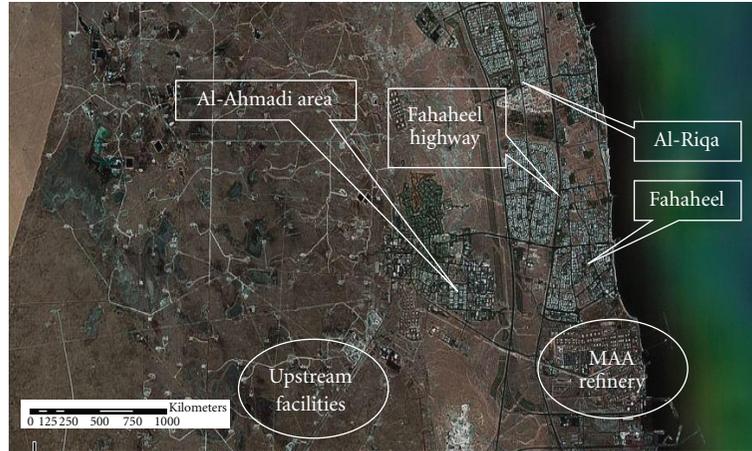


FIGURE 3: Satellite image showing both areas under investigation (Fahaheel and Al-Riqa) with respect to the main petroleum downstream, namely MAA refinery and upstream facilities in the state of Kuwait. Source: image adapted from KISR satellite archives (Kuwait). Source: Al-Salem and Khan [10].

TABLE 5: Position distribution around outdoor data collection point in Al-Riqa urban area.

Position in degrees	Potential air pollution source
300–130	Downtown area
131–260	Refineries, petroleum and petrochemical industries
261–299	Traffic line sources (Highway), gas stations, and sports clubs

Based on the initial analysis and collected data, the CMB model was setup in Microsoft Office 2003 in an EXCEL program. Nonmethane hydrocarbons (NMHC), methane, carbon monoxide (CO), total hydrocarbons (HCT), and O<sub>3</sub> concentrations were also used in execution of CMB model. The standard approach was applied for apportioning observed pollutant concentrations to their sources. The model implements a least-square solution to a set of linear equations, expressing each source as a linear sum product of the source percent contribution with predominant wind sector.

The CMB equations were based on the assumption that the observed ambient quantity of a chemical species is the simple sum of the product of pollutants contributions affecting the airshed and fraction of the wind sector. CMB model uses the chemical and physical characteristics of gases and particulate at a given receptor point to identify the presence of and/or quantify source contributions. Equation (3) is the basic relation corresponding to the selected receptor point. This equation expresses the relation between the concentrations of the chemical species measured at the receptor point (Main health center of Al-Riqa) and the chemicals emitted from the source.

$$\Delta C_i = \sum F_{ij} - S_i, \quad (3)$$

TABLE 6: Position distribution around outdoor data collection point in Fahaheel urban area.

Position in degrees	Source
0–135	Downtown area
136–255	Refineries, petroleum, and petrochemical industries
256–300	Oil production facilities (Burgan)
301–360	Traffic line sources (Highway), gas stations, and sports clubs

where  $\Delta C_i$  is the difference in concentration of a chemical compound  $i$  at the receptor point,  $F_{ij}$  is the fraction of concentration of the species  $i$  starting from the source  $j$  &  $S_i$  is the concentration of pollutant  $i$  at the receptor point.

The total wind speed contribution must be calculated in order to get the percent wind speed contribution with respect to the desired range of wind directions; that is, the source. Equation (4) was used to calculate the wind speed contribution with respect to each source.

$$\%WS_i = \left( \frac{k_i}{K} \right) \times 100, \quad (4)$$

where  $\%WS_i$  is the percent contribution of wind speed with respect to source  $i$ ,  $k_i$  is the summation of wind speed points collected with respect to source  $i$  in (m/s) &  $K$  is the total summation of wind speed points in (m/s) excluding calm period.

In order to match the concentrations at the receptor point, predefined linear functions were solved with an objective function. The objective function which is defined as the sum of squares of difference between measured and the sum of fractional concentrations of different sources chemical fingerprints including the influence of wind sector, is minimized. The chemical fingerprints were average readings of concentrations reflecting the recorded inventories of the sources [61, 62]. Equation (5) is the one set to solve

TABLE 7: source contribution in Al-Riqa and Fahaheel urban areas based on CMB model results averaged over the period of the study.

Source	Fahaheel (%SC)	Al-Riqa (%SC)
Petroleum downstream facilities	70	10
Petroleum upstream facilities	2	—
Fahaheel highway	18	70
Area's downtown	10	20

for the least linear square root. The linear function was introduced for the four major sources studied as well as, the receptor point, which represents the total cumulative concentration of a pollutant to be matched.

$$LF = \sum_{j=1}^m \sum_{i=1}^n C_i \cdot WS_i \cdot SC_i - \sum_{i=1}^n C_i \cdot WS_i \cdot SC_i, \quad (5)$$

where LF is the linear function set to match the percent contribution of each source,  $C_i$  is the concentration of airborne chemical  $i$  at a certain source or receptor point,  $\%WS_i$  is the percent wind speed contribution at a certain wind direction range for source  $i$ ,  $\%SC_i$  is the percent source contribution for a source  $i$  &  $i$  represent pollutants, and  $j$  sources.

The CMB model developed in this study was based on the values obtained in the months of January and July, since both months recorded variations of many airborne pollutants and had many maximum readings of the concentrations resulting from the sources under study for major pollutants. These two months were chosen to represent the two longest seasons in Kuwait, summer and winter for being severe in their metrological conditions. Fahaheel and Al-Riqa areas average contribution of the its four primary sources of air pollution over the period of study are shown in Table 7.

It can be noticed from the above stated results that in the case of Fahaheel, being more close to the three refineries belt, the downstream facilities were more dominant on the area ambient air quality were it had contributed 70% of its total pollution load. The least affective air pollution source was the upstream facilities of the Greater Burgan area (2%). The distance and winds are the strong influencing parameters to dispersing gaseous pollutants away from the two urban areas. Comparing the two downtown areas, Al-Riqa's was almost contributing 20% to the total ambient load where Fahaheel was exactly half of that percentage. Al-Riqa downtown (Although smaller in size than Fahaheel) is more populated and is occupied by all sorts of human related pollution activities that too contribute to the load. The effect of the downstream facilities was least effective in the case of Al-Riqa area.

**3.4. Case Study No. 2: Line Source Modelling around Fahaheel Urban Area.** To assess a better outdoor air quality an area, namely Fahaheel urban area, the second primary air pollution source around it (Fahaheel highway) was modelled



FIGURE 4: Imaginary axis lines for point source modelling around Fahaheel highway showing corresponding coordinates at:  $X = 14.5$  cm and  $Y = 2.1$  cm. The blue dot represents the source at the refinery (Tank farm) and the red and black circles represent, respectively, the receptor point and the point of calculation for the line source.

for its primary emission source ( $\text{NO}_2$ ) due to its significant in contributing to the ambient load of pollution pool and assessing the air quality of it too. The highway was previously demonstrated to be the second most contributing source on the area's pollution levels [50]. Fahaheel highway (Figures 3 and 4) contribution was estimated to be 18% of the total concentration of all primary airborne pollutants. The primary source of  $\text{NO}_2$ ,  $\text{NO}_x$ , and CO is always considered to be urban traffic terrains and motorways.

In the case of the main highway, a continuous model was chosen for the dispersion of  $\text{NO}_2$ . Assuming a northwest wind direction with respect to the receptor point. Equation (6) relates the concentration of a line source to the variables in hand [2]

$$C(x, 0) = \left[ \frac{2q}{(2\pi)^{0.5} u \sigma_z} \right] \exp\left(-0.5 \left(\frac{H}{\sigma_z}\right)^2\right), \quad (6)$$

where  $q$  is the source strength of pollutant emissions (i.e.,  $\text{SO}_2$ ) downwind per unit distance,  $C$  is the ground level concentration of the source (with respect to terrain) in ppb,  $H$  is the receptor point elevation (m).

The line source model described above, gives a wide range of application. The modification came in excluding the effective height and using the half full height at the tank farm [50]. The refinery side gave a  $2 \text{ ngm/s} \cdot \text{m}^2$   $\text{NO}_2$  emission rate or strength, taking in perspective the total area of the refinery (MAA refinery total area =  $10\,533\,400 \text{ m}^2$ ). This result combined with the line sources one, which is  $0.15 \mu\text{gm}/\text{sm}^2$  per unit scale can give a clear view of the rate of  $\text{NO}_2$  alone that is being emitted to the area. The calculations were based on the month of May 2004 with measurements taken from KUEPA Fahaheel monitoring station original 5 minutes data.

#### 4. Final Remarks

After reviewing the subject matter, a number of conclusions could be withdrawn with regards to the monitoring of primary and secondary pollutants in the state of Kuwait.

- (i) Monitoring stations situated in residential and industrial areas by KUEPA, should incorporate better receptor point placement and modern prediction techniques that can aid in the data gathering.
- (ii) Metrological data gathered (as literature reviewed suggest) must be coherent with pollutants sources designed to be monitored.
- (iii) A number of pollutants are not being recorded when it comes to industrial sites, associated with health effect, which should be in the future plans of the state.
- (iv) A number of monitoring cases in Kuwait reveal different data than gathered by KUEPA, due to the lack of attention paid in placing mobile stations.

Modelling cases carried out reveal that Kuwait is a country influenced not only by chemical industries pollutants, but by traffic and other sources which should be regulated according to international rules and regulations. Concerned parties should start within the next few years in seriously revising state rules with regard to outdoor air quality, to provide better and healthier living conditions to the population. Airborne NO<sub>2</sub> was studied from a line source (2 ngm/s·m<sup>2</sup>) taking in perspective the total area of the refinery considered. This result combined with the line sources one, which is 0.15 μgm/sm<sup>2</sup> per unit scale can give a clear view of the rate of NO<sub>2</sub> alone that is being emitted to the area. Furthermore, chemical mass balance modelling (CMB) revealed that the three refineries belt of Kuwait was associated with higher contribution (70%) than other sources of pollution. This is particular to one case of a southern area in Kuwait. Whilst in the case of another part of the same Governorate, the contribution was mainly due to the Highway pollution load. Associated health impacts are also demonstrated by this study. In conclusion, findings in literature surveys and other aspects of air pollution modelling, lead to industrial sources and human factors as the main polluting source in the state of Kuwait.

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## Research Article

# Effect of Saturated Near Surface on Nitrate and Ammonia Nitrogen Losses in Surface Runoff at the Loess Soil Hillslope

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Water pollution from agricultural fields is a global problem and cause of eutrophication of surface waters. A laboratory study was designed to evaluate the effects of near-surface hydraulic gradients on  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  losses in surface runoff from soil boxes at 27% slope undersimulated rainfall of a loess soil hillslope. Experimental treatments included two near-surface hydraulic gradients (free drainage, FD; saturation, SA), three fertilizer application rates (control, no fertilizer input; low,  $120 \text{ kg N ha}^{-1}$ ; high,  $240 \text{ kg N ha}^{-1}$ ), and simulated rainfall of  $100 \text{ mm h}^{-1}$  was applied for 70 min. The results showed that saturated near-surface soil moisture had dramatic effects on  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  losses and water quality. Under the low fertilizer treatment, average  $\text{NO}_3\text{-N}$  concentrations in runoff water of SA averaged 2.2 times greater than that of FD, 1.6 times greater for  $\text{NH}_4\text{-N}$ . Under the high fertilizer treatment,  $\text{NO}_3\text{-N}$  concentrations in runoff water from SA averaged 5.7 times greater than that of FD, 4.3 times greater for  $\text{NH}_4\text{-N}$ . Nitrogen loss formed with  $\text{NO}_3\text{-N}$  is dominant during the event, but not  $\text{NH}_4\text{-N}$ . Under the SA condition, the total loss of  $\text{NO}_3\text{-N}$  from low fertilizer treatment was 34.2 to 42.3% of applied nitrogen, while under the FD treatment that was 3.9 to 6.9%. However, the total loss of  $\text{NH}_4\text{-N}$  was less than 1% of applied nitrogen. These results showed that saturated condition could make significant contribution to water quality problems.

## 1. Introduction

Water pollution is a major global problem that amounts for more than 14,000 deaths daily [1]. The national environmental statistic bulletin of China reported that total discharge amount of ammonia nitrogen was  $127.0 \times 10^4 \text{ t}$  in waste water in 2008 [2]. In the most recent national report on water quality in the United States, 45 percent of assessed streammiles, 47 percent of assessed lake acres, and 32 percent of assessed bay and estuarine square miles were classified as polluted [3].

Phosphorous (P) and nitrogen (N) in runoff from agricultural fields are key components of nonpoint source pollution and can accelerate eutrophication of surface waters [4, 5]. Most mineral forms of nitrogen are quite soluble in water and may be easily lost from soils through leaching and volatilization. In most freshwater (lakes and streams), P is

the nutrient that can set off eutrophication, and N is the nutrient most likely to cause eutrophication for saltier waters (estuaries and costal areas) [6].

The transport of agricultural chemicals from the field to groundwater or to surface-water bodies is most commonly facilitated by water movement, and it is affected by rainfall characteristics, underlying surface conditions, and the properties of the soil solute. Hydrogeology, climate, and agricultural management practices can have important influences on the movement of water and chemicals [7, 8].

Spatially and temporally variations may affect the dominant erosion processes occurring on the hillslope. During rainfall events, different hydraulic gradients, especially due to seepage or drainage, at different locations on a hillslope profile may have a profound effect on the dominant erosion processes. Recent laboratory studies showed that near-surface hydraulic gradient had a profound effect in the

dominant erosion process and total sediment delivery [9, 10]. Gburek et al. [11, 12] studied results showed that most in-stream P came from soils within 60 m of the stream, and Zheng et al. [10] studied results showed that artesian seepage could make important contribution to water quality problems.

Nevertheless, interactions among hydrologic, surface runoff, sediment regimes and N & P losses, and how they are affected by changes in rainfall intensities have not been evaluated extensively in China [13–15]. Based on those studies, the purpose of this study was to examine nitrate and ammonia nitrogen loss of the loess soil in runoff under saturated soil that occurs at  $100 \text{ mm h}^{-1}$  rainfall intensity. Results of this study will further the understanding of how saturated soil water content impacts the losses of  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  in surface runoff of the loess soil at the hillslope of China.

## 2. Materials and Methods

**2.1. Soil Sample Collection.** The soil used in this study was a loess soil collected from the surface to a 40 cm depth at Ansai Country near Yan'an city, Shaanxi province, China. The collected soil was air dried and sieved through a 10-mm-opening sieve and stored in covered concrete floor until used in this experiment.

**2.2. Soil Properties.** The collected loess soil consists of 64.9% sand, 23.2% clay and 11.9% silt. The soil contains 5.3 mg/kg organic matter, 0.4 g/kg total N, 0.6 g/kg total P, and 18.2 g/kg total K. The content of alkali-hydrolyzable nitrogen is  $32 \text{ mg kg}^{-1}$ , while the content of rapidly available phosphorus and potassium is  $4 \text{ mg kg}^{-1}$  and  $114 \text{ mg kg}^{-1}$ , respectively. The water pH is 8.5 (water/soil ration is 5:1) and the cation exchange capacity (CEC) is  $6.01 \text{ cmol (+) / kg}$ .

**2.3. Experimental Setup.** The study was conducted on three soil boxes that were 100 cm long, 50 cm wide, and 40 cm deep. Each soil box had 18 watering/drainage holes at the bottom. A water supply system was designed to supply water to the soil box from the bottom of the soil box to create the near-surface hydraulic gradient (Figure 1), especially the saturated condition, as described by Zheng et al. [10], and the free drainage condition was created by rainfall.

Two groups of rainfall simulation nozzles, each group with four nozzles, spaced 12 m apart, were used in this study. The nozzles were approximately 16 m above the soil surface. During the rainfall simulation, the nozzle pressure was kept at  $2.5 \text{ kg/cm}^2$ . This rainfall simulator could be set to any pre-selected rainfall intensities, ranging from 20 to  $300 \text{ mm h}^{-1}$ , by programming the compounding of the nozzles [16].

Experimental treatments in this study included 2 near-surface hydraulic gradient treatments: saturated condition, and free drainage, and three fertilizer input treatments were subjected to the two soil moisture treatments: control (no fertilizer input, NF), low input ( $120 \text{ kg N ha}^{-1}$ , LF), and high

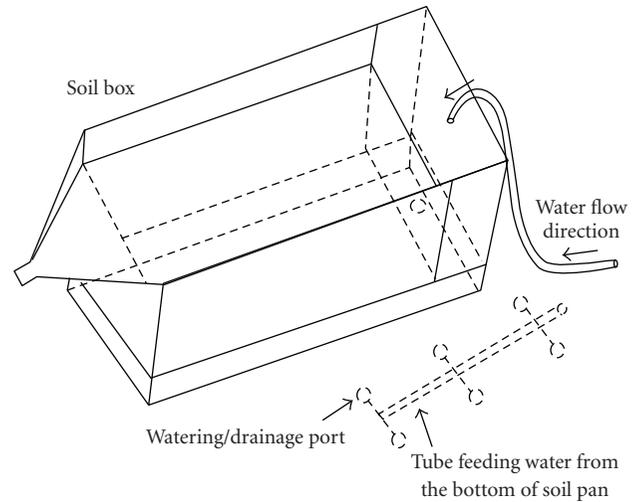


FIGURE 1: Experiment setup.

TABLE 1: List of experiment treatments.

Soil moisture treatment	Fertilizer treatment	Fertilizer inputs
		N $\text{Kg hm}^{-2}$
Saturation (SA)	Control (NF)	0
	Low input (LF)	120
	High input (HF)	240
Free Drainage (FD)	NF	0
	LF	120
	HF	240

NF, no fertilizer input; LF, low fertilizer treatment/input ( $120 \text{ kg N ha}^{-1}$ ); HF, high fertilizer treatment/input ( $240 \text{ kg N ha}^{-1}$ ). FD, free drainage hydraulic gradient; SA, saturated hydraulic gradient.

input ( $240 \text{ kg N ha}^{-1}$ , HF). The detailed experimental treatments appeared in Table 1. For each near-surface hydraulic gradient, three replicates were made for rainfall simulation.

**2.4. Preparation of Soil Boxes.** Each soil box was packed with a 5 cm layer of sand at the bottom and a 35 cm depth layer with the air-dried test soil. Moisture content of the test soil was determined prior to packing of the soil box to calculate the amount of soil needed to obtain a bulk density of  $1.3 \text{ g cm}^{-3}$ . The moisture content of the air-dried test soil used for packing soil box ranged from 3% to 5% by weight. To ensure uniformity, the soil box was packed in individual 5 cm layers, and the upmost 5 cm soil was divided into 3 cm (below) and 2 cm (top), and the top 2 cm soil was thoroughly mixed with  $\text{KNO}_3$  (AR) as designed [17].

For each layer of soil boxes, the weight of packaged wet soil was calculated by the following equation

$$W = \rho \times l \times w \times h \times \frac{1 + \theta}{100}, \quad (1)$$

where,  $W$  is the wet soil weight for packaging in kg,  $\rho$  is soil bulk density in  $1.3 \text{ g cm}^{-3}$ ,  $l$  is length of soil boxes in 100 cm,

$w$  is width of soil boxes in 50 cm,  $h$  is deepness of each layer in soil boxes in cm,  $\theta$  is soil moisture content in %.

After soil box preparation, to further avoid water-drop-induced splash and surface sealing, two layers of gauze were placed over the soil surface. This step was applied to obtain the correct hydraulic gradient, create a uniform surface soil moisture condition prior to the experiment, and reduce surface variability from preparation. After the water supplying, the soil box was covered with a plastic sheet and allowed to equilibrate under each hydraulic condition for 24 hrs.

**2.5. Rainfall Experiments.** After the water supplying, soil boxes were set to  $15^\circ$  (approximately 27%) slope steepness and subjected to the experimental hydraulic gradients. And a simulated rainstorm of  $100 \text{ mm h}^{-1}$  for 70 min was applied to all treatments based on the result of the basic erosive rainfall standard on the Loess Plateau is  $5.8 \text{ mm}/5 \text{ min}$  [18, 19]. During rainfall simulation runs, runoff samples were collected every 6 min. During each event, the rainfall amount was measured at least twice with two hyetometers around soil boxes to calibrate the rainfall intensity.

Immediately after each run, runoff samples were weighted and set for 24 hrs. Water was stored in the plastic buckets in 100 ml and then was analyzed for the contents of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N.

**2.6. Calculation of Near-Surface Hydraulic Gradient.** Soil moisture of the test soil was measured before packed into the soil boxes, preparing for calculating supply water volumes of each near-surface hydraulic gradient, and the volumes were calculated by (2) to control the used-water volumes and save excess water:

$$W_s = W \times 7 \times \frac{M - \theta}{(1 + \theta/100)/100}, \quad (2)$$

where,  $W_s$  is water volume of complementarities in kg,  $W$  is wet soil weight for packing in kg, 7 is the layers of soil packaged,  $M$  is near-surface hydraulic gradient to control in %,  $\theta$  is soil moisture content of packing soil in %.

**2.7. Analysis of  $\text{NO}_3^-$ -N and  $\text{NH}_4^{3+}$ -N in Surface Runoff Water.** The collected surface runoff water was set for 24 hrs, centrifuged for 10 min with 8000 r/min by high speed refrigerated centrifuge (CR21G, Hitachi, Japan), and filtered to test the concentration of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N, then all samples were determined by automated chemistry analyzer (Auto analyzer 3-AA3, Bran+Luebbe, Germany).

**2.8. Calculation of  $\text{NO}_3^-$ -N and  $\text{NH}_4^-$ -N in Surface Runoff Water.** For each simulated precipitation,  $\text{NO}_3^-$ -N or  $\text{NH}_4^-$ -N loss in surface runoff water for the event,  $L$  (mg), was calculated by [10]

$$L = \sum_{i=1}^n C_i R_i, \quad (3)$$

where  $L$  is  $\text{NO}_3^-$ -N or  $\text{NH}_4^-$ -N loss in surface runoff water for the event at time increment  $i$ , mg;  $C_i$  is concentration in

surface runoff water at time  $i$ , mg/L;  $R_i$  is runoff volume at time  $i$ , L;  $n$  is the total number of collected samples.

For each run, the average  $\text{NO}_3^-$ -N or  $\text{NH}_4^-$ -N concentration in surface runoff water,  $C_n$  (mg/L), was calculated as [10]

$$C_n = \frac{L}{V}, \quad (4)$$

where,  $L$  is  $\text{NO}_3^-$ -N or  $\text{NH}_4^-$ -N loss, mg; and  $V$  is total runoff volume, L.

For each soil water content treatment under the same fertilizer treatment, the average  $\text{NO}_3^-$ -N or  $\text{NH}_4^-$ -N concentration in surface runoff water,  $C_m$  (mg/L), was calculated as [10]

$$C_m = \frac{\sum_{j=1}^p L_j}{\sum_{j=1}^p V_j}, \quad (5)$$

where,  $p$  is the number of replications in each soil water content treatment,  $p = 3$ ,  $L_j$  is  $\text{NO}_3^-$ -N and  $\text{NH}_4^-$ -N loss for the event times  $j$ , mg, and  $V_j$  is total runoff volume, L.

**2.9. Statistical Analysis.** The LSD test was performed using SAS (SAS Institute Inc., Cary, NC, USA). Means of each  $\text{NO}_3^-$ -N and  $\text{NH}_4^-$ -N concentration and amount of loss resulting from different treatments were compared for significant difference ( $P < .05$ ) using Duncan's procedure. In all statistical analyses, a probability level of .05 or less ( $P \leq .05$ ) was used for significance.

### 3. Results and Discussions

**3.1. Concentration of  $\text{NO}_3^-$ -N and  $\text{NH}_4^-$ -N in Surface Runoff Water.** The average concentrations of  $\text{NO}_3^-$ -N in surface runoff water were significantly greater than that of  $\text{NH}_4^-$ -N (Table 2). The average concentrations of  $\text{NO}_3^-$ -N and  $\text{NH}_4^-$ -N in surface runoff water of the FD treatments were less than  $12.0 \text{ mg L}^{-1}$  and  $0.5 \text{ mg L}^{-1}$ , respectively, regardless of the fertilizer treatments. When the near-surface hydraulic gradients shifted from FD to SA, concentrations of  $\text{NO}_3^-$ -N and  $\text{NH}_4^-$ -N in surface runoff water increased significantly.

For the control treatment,  $\text{NO}_3^-$ -N concentrations in runoff water of SA averaged 1.8 times greater than that of FD, but it was not statistically significantly difference. Under the low fertilizer treatment,  $\text{NO}_3^-$ -N concentrations in runoff water of SA averaged 2.2 times greater than that of FD. Under the high fertilizer treatment,  $\text{NO}_3^-$ -N concentrations in runoff water of SA averaged 5.7 times greater than that of FD. These results were similar to those reported by Zheng et al. [10]. Under the FD treatment, although  $\text{NO}_3^-$ -N concentrations in the runoff water of the low fertilizer treatment were numerically larger than that of the high fertilizer treatment, concentrations were not significantly different. This is probably the result of less water runoff and better infiltration into the soil.

Concentrations of  $\text{NH}_4^-$ -N in surface runoff water of SA were statistically lower than that of FD, those trends similar to  $\text{NO}_3^-$ -N concentrations in runoff water. For the control treatment,  $\text{NH}_4^-$ -N concentrations in runoff water of SA

TABLE 2: Means of nutrient concentration with runoff under different near-surface soil moisture conditions.

Treatment <sup>†</sup>	Concentration in surface runoff			Losses in surface runoff		
	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	Loss as a percentage of N input	NH <sub>4</sub> <sup>+</sup> -N	Loss as a percentage of N input
	mg/L		kg ha <sup>-1</sup>		kg ha <sup>-1</sup>	
CFD	7.94c <sup>‡</sup>	0.45b	7.27d		0.42c	
CSA	14.14c	0.76a	21.11c		1.14b	
LFD	11.9c	0.46b	8.28d	6.9	0.32d	0.27
LSA	26.36b	0.73a	41.02b	34.2	1.14b	0.95
HFD	11.02c	0.17c	9.36d	3.9	0.15e	0.06
HSA	63.22a	0.73a	101.56a	42.3	1.18a	0.49

<sup>†</sup> C, control fertilizer treatment (no fertilizer input); L, low fertilizer treatment/input (120 kg N ha<sup>-1</sup>); H, high fertilizer treatment/input (240 kg N ha<sup>-1</sup>). FD, free drainage hydraulic gradient; SA, saturated hydraulic gradient.

<sup>‡</sup> Mean values with a fertilizer treatment followed by any identical letters are not statistically different at the 95% confidence level according to LSD tests.

averaged 1.7 times greater than that of FD. Under the low fertilizer treatment, NH<sub>4</sub>-N concentrations in runoff water of SA averaged 1.6 times greater than that of FD. Under the high fertilizer treatment, NH<sub>4</sub>-N concentrations in runoff water of SA averaged 4.3 times greater than that of FD.

Fertilizer application rates influenced NO<sub>3</sub>-N concentrations under the saturation treatment, and the NH<sub>4</sub>-N concentrations in surface runoff water under the FD treatment. Under the SA treatment, both the high and low fertilizer treatments resulted in significantly higher NO<sub>3</sub>-N concentrations than that of the control, increasing by 347.1% and 139.8%, respectively. NH<sub>4</sub>-N concentrations in the runoff water of the control input to low and high fertilizer treatment were not statistically different. Under the FD treatment, NH<sub>4</sub>-N concentrations in runoff water from control input to low fertilizer input were not statistically different, but that of high fertilizer input was statistically smaller than that of control input and low fertilizer input. It is an interesting question for the results as described above, and no research results could explain the reason, because there were no fertilizers formed with NH<sub>4</sub>-N to soil, and the whole conditions were similar between each soil box and each run, so it is necessary to have a deep research on that. Maybe the fertilizer application rate of KNO<sub>3</sub> was the key point for that, and NH<sub>4</sub>-N loss with sediment was the other way for the results above because nutrients formed with NH<sub>4</sub>-N in eroded sediment were enriched compared with topsoil [20, 21]. The results above indicated that denitrification had less effect on loss of NH<sub>4</sub>-N in surface runoff water in SA treatment in this study.

**3.2. NO<sub>3</sub>-N and NH<sub>4</sub>-N Losses.** Average losses of NO<sub>3</sub>-N and NH<sub>4</sub>-N displayed similar trends as their concentrations (Table 2). Average NO<sub>3</sub>-N and NH<sub>4</sub>-N losses of the SA treatment were statistically significantly greater than that of FD. NO<sub>3</sub>-N loss in the surface runoff water of CSA was 2.9 times greater than that of CFD. NO<sub>3</sub>-N loss in the surface runoff water of LSA was 5.0 times greater than that of LFD. NO<sub>3</sub>-N loss in the surface runoff water of HSA was 10.9 times greater than that of HFD. Compared to the CSA treatment, NO<sub>3</sub>-N losses in surface runoff

water of the LSA and HSA treatment were 1.9 and 4.8 times greater, respectively. However, under the FD treatment, NO<sub>3</sub>-N losses in the surface runoff water among control, low fertilizer, and high fertilizer input treatment were not significantly different.

Average NH<sub>4</sub>-N loss in surface runoff water from CSA was 2.7 times greater than that of CFD. Under the low fertilizer treatment, average NH<sub>4</sub>-N loss in surface runoff water of SA was 3.6 times greater than that of FD. Average NH<sub>4</sub>-N loss in surface runoff water from HSA was 7.9 times greater than that of LFD. However, under the SA treatment, average NH<sub>4</sub>-N losses of CSA and LSA were not statistically different, although it was statistically different from HSA to LSA and CSA. Under the FD treatment, average NH<sub>4</sub>-N loss of control treatment was statistically greater than that of low and high fertilizer treatments, and it was 1.3 and 2.8 times greater, respectively. The change trend was similar to that as described on concentrations of the part of NO<sub>3</sub>-N and NH<sub>4</sub>-N in Surface Runoff Water in this study.

Under low and high fertilizer treatments, NO<sub>3</sub>-N loss accounted from 3.9 to 42.3% of the applied N (Table 2). And NO<sub>3</sub>-N loss as a percentage of N input of SA treatment was statistically greater than that of FD. However, NH<sub>4</sub>-N loss accounted from 0.06 to 0.95% of the applied N, those were less than 1%.

These results showed that the saturated flow could make an important contribution to total chemical transport, which was similar to the results of P loss of Gburek and Sharpley studied in 1998 [11], and Zheng et al. [10]. However, it was opposite to the results of Fisher and Healy [8], which showed that the time of the year at which chemicals are applied may be important for chemical transport through the unsaturated zone. And the results of this study also showed that NO<sub>3</sub>-N loss could be more important for contribution to nitrogen loss than that of NH<sub>4</sub>-N.

**3.3. Temporal Trends of NO<sub>3</sub>-N and NH<sub>4</sub>-N Concentrations.** Under the FD treatment, the NO<sub>3</sub>-N concentrations in runoff changed little as time progressed for all fertilizer treatments tested, and it was less pronounced than that

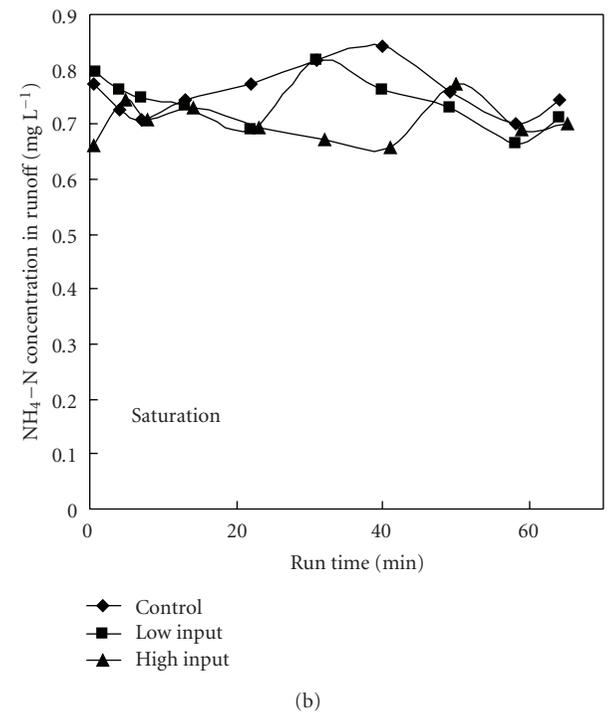
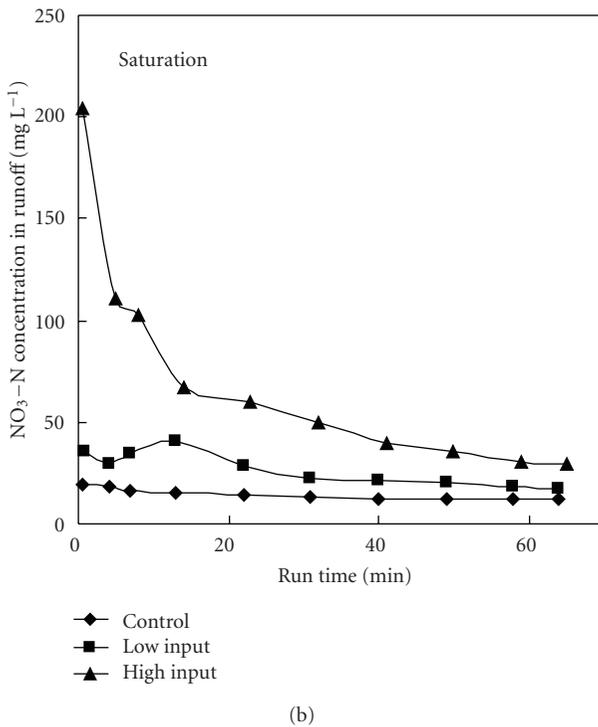
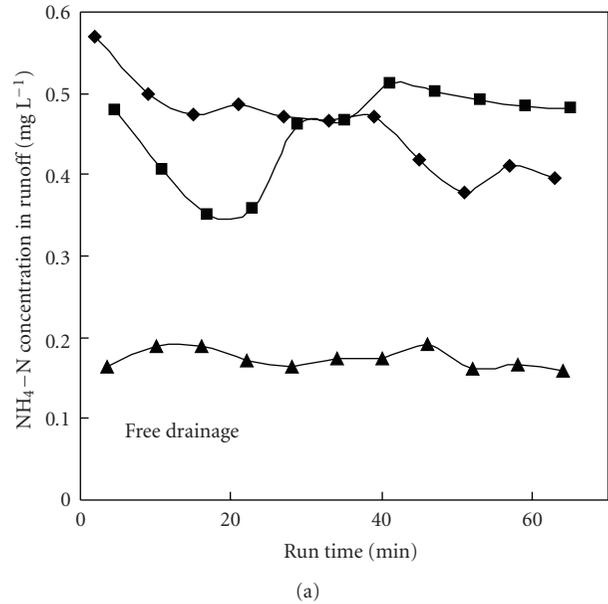
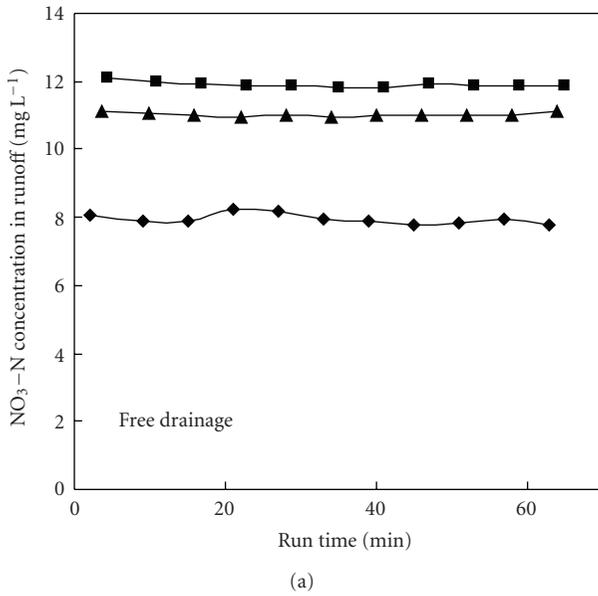


FIGURE 2: The NO<sub>3</sub>-N concentration in runoff under different hydraulic gradients.

FIGURE 3: The NH<sub>4</sub>-N concentration in runoff under different hydraulic gradients

of the SA treatments (Figure 2). And the trends of NO<sub>3</sub>-N concentrations in runoff during the run were similar to the means of NO<sub>3</sub>-N concentrations (Table 2). Under the SA treatment, although the temporal trend showed that NO<sub>3</sub>-N concentrations in runoff were greatest in the initial runoff and decreased gradually during the run of high fertilizer input, NO<sub>3</sub>-N concentrations of control and low fertilizer input treatments showed little change. And the total temporal trends of NO<sub>3</sub>-N concentrations in surface runoff

were similar to the results of saturated condition of Zheng et al. [10].

Under the FD treatment, NH<sub>4</sub>-N concentrations in runoff were greatest in the initial runoff and decreased gradually during the run of control treatment, while NH<sub>4</sub>-N concentrations in runoff of the low fertilizer treatment were greatest in the initial runoff and decreased, then increased gradually (Figure 3). But the NH<sub>4</sub>-N concentrations in runoff of high fertilizer treatment changed little. May be

those were influenced by runoff progress. Under the SA treatment, the  $\text{NH}_4\text{-N}$  concentrations in runoff changed little in waves with the entire three fertilizer application rate.

The results of this study indicated that a saturated condition event could cause a severe water quality problem, which is similar to the results reported on P loss by Gburek and Sharpley [11], and  $\text{NO}_3\text{-N}$  and P losses by Zheng et al. [10]. And in the saturated condition, compared to control treatment, the concentrations and amount of  $\text{NH}_4\text{-N}$  of low and high fertilizer treatment were similar; may be the fertilizer rates and denitrification have less effect on loss of  $\text{NH}_4\text{-N}$  in surface runoff water. While in free drainage condition, compared to topsoil, rapidly available P and  $\text{NH}_4\text{-N}$  in eroded sediment were enriched in the Loess Plateau of China [21], and artificial rainfall experiment results also showed that the amount of  $\text{NH}_4\text{-N}$  losses in surface runoff water increased with the fertilizer rate increasing [14]. So it would be necessary to study extensively on  $\text{NH}_4\text{-N}$  loss in surface runoff and sediment.

#### 4. Conclusions

This paper presents a laboratory study of near-surface hydraulic gradient effects on losses of  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  in surface water under a simulated rainstorm. The results showed a significant increase of  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  transport or losses in surface runoff water under the saturated condition. These results demonstrate the importance of understanding watershed hydrology and its temporal patterns in predicting areas of high chemical loading potential and also showed that the saturated condition can cause greater chemical transport than that of the free drainage condition. The results show that  $\text{NO}_3\text{-N}$  losses in saturated condition could make a significant contribution to water quality problems.

The results of this study also showed that nitrogen loss formed with  $\text{NO}_3\text{-N}$  is dominant during the event, but not  $\text{NH}_4\text{-N}$ . However, under FD treatment,  $\text{NH}_4\text{-N}$  concentrations in runoff water from high fertilizer input were statistically smaller than those from control input and low fertilizer input without  $\text{NH}_4\text{-N}$  fertilizer input, and it also showed denitrification had less effect on loss of  $\text{NH}_4\text{-N}$  in surface runoff water in SA treatment. The trend of  $\text{NH}_4\text{-N}$  loss should be studied more and deeply in the future because of its toxicity to fish, and the rates of fertilizer formed with  $\text{NH}_4\text{-N}$  should be determined for agriculture during rain season.

Although many studies have been made to determine factors contributing to N loss, especially the effects of near-surface hydraulic gradient have been quantified. Incorporating the basic understanding of hydraulic factors and  $\text{NH}_4\text{-N}$  transport may contribute to control chemical transport to water and minimize water quality problems.

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## Research Article

# Toxicity Assessment of Sediments with Natural Anomalous Concentrations in Heavy Metals by the Use of Bioassay

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The potential toxicity in riverbed sediments was assessed with a bioassay using the bioluminescent bacteria *Vibrio fischeri*. The selected area was characterized by the presence of ultramafic rocks (peridotites), and the sediments had high values in Ni, Cr, and Co. For the toxicity bioassay with *Vibrio fischeri*, water-soluble forms were used. The results indicated that most of the samples had a very low degree of toxicity, with 10% of reduction in luminescence in relation to the control; meanwhile 25% of the samples had a moderate degree of toxicity with a reduction in luminescence between 13 and 21% in relation to the control. The toxicity index correlated significantly with the concentrations of Ni and Cr in the water extracts. This toxicity bioassay was proved to be a sensitive and useful tool to detect potential toxicity in solutions, even with anomalous concentrations in heavy metals of natural origin.

## 1. Introduction

Today, in Ecological Risk Assessment (ERA), soil and sediment contamination studies are increasingly important. ERA processes involve several predictive and descriptive phases [1, 2] with special emphasis placed on the toxicity characterization of the contaminated media. In this field, many toxicity assays are applied in the study of contaminated soils [3–6], and for ecosystem protection, toxicity bioassays are key to support the regulation framework in the declaration of contaminated soils [7].

Most bioassays applied to contaminated soils and sediments are based on the evaluation of the toxic effect of the solution extracted from the solid phase or by the solid phase itself over a living organism (animals, algae, plants, and bacterial bioassays) [8]. In this way, bacterial bioassays are commonly used because they are quick, cost effective, and reproducible [9]. Particularly, the bioassay using *Vibrio fischeri* relates the presence of contaminants to the inhibition in light emission from these luminescent bacteria. This test is defined as sensitive and has a high correlation with the

response of other toxicity tests [10]; in addition, it has been used in the toxicity assessment of soils contaminated by heavy metals [11, 12].

Rivers distribute heavy metals in the ecosystem by mobilizing pollutants and thus spreading the affected area, with potential toxicity risk to aquatic organisms as well as to human health through the food chain. Heavy metals can reach aquatic ecosystems by anthropic activities or by natural processes, and in such circumstances, the contaminants can be distributed as water-soluble species, colloids, suspended forms, or sedimentary phases [13]. According to Jain [14], heavy metal pollution in aquatic ecosystems has received increased scientific attention in the recent years because the contaminants tend to accumulate and progressively raise the toxicity risk to the living organisms [15]. In this sense, many studies have demonstrated that heavy metal concentration in river bed sediments can be good indicators of pollution in hydrological systems [16].

The different forms of heavy metals in the sediments of an aquatic medium determine their bioavailability and toxicity. Thus, the study of the different fractions of the

elements in sediments is vital, because the total concentrations are not representative of the real degree of the potential contamination. Heavy metals can be bound to or occluded in amorphous materials, adsorbed on clay surfaces or iron/manganese oxyhydroxides, coprecipitated in secondary minerals such as carbonates, sulphates, or oxides, complexed with organic matter, or included in the lattice of primary minerals such as silicates [13]. The fractionation techniques of heavy metals in the river sediments have been used by different authors [14, 17–20] to assess the mobility and bioavailability of pollutants in this media.

The Verde River basin is located in the Province of Malaga (southern Spain), and its catchment area receives many streams flowing over peridotitic materials, characterized by high concentrations of Mn, Cr, Co, and Ni. In this basin lies La Concepción Reservoir, which contributes with more than 24% of the drinking water used in the western Costa del Sol (dominated by the city of Marbella), one of the main tourist areas in Spain and in southern Europe. The above-mentioned scenario prompted the examination of the riverbed sediments of this area.

In this study, we analyse the concentration in the riverbed sediments of heavy metals, both total as well as water-soluble forms, to characterize the potential mobility of these elements in the Verde River basin. The potential toxicity of heavy metals was studied using bioassay of bioluminescent bacteria in order to assess the potential risk of contamination in the area.

## 2. Material and Methods

Verde River is approximately 36 km long, originating in the Sierra de Las Nieves mountains (2000 m.a.s.l.) and sharply descending to 400 m to reach the Mediterranean Sea. This abrupt change in altitude in a short distance involves many different slopes, with the steeper ones predominating (25%–55%). The lithology is dominated by peridotite and serpentine rocks and with carbonate and metamorphic rocks in lesser proportion (Figure 1). The catchment area is comprised of the main channel of the Verde River and 11 tributaries, including La Concepción reservoir, holding 44,515 hm<sup>3</sup>/year.

Sediments of the Verde River and main tributaries were collected in the bottom part of each stream (Figure 1). At each sampling point, composite samples were taken by mixing 250 g of sediments from each corner and center of a square 0.5 m per side. Samples were taken from the river bed to 0–20 cm depth. In the laboratory, samples were air dried, and the fine fraction (<50 μm) of the sediments [19, 21] was used to characterize the main properties for the toxicity bioassay.

The total heavy metals were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) in a PE SCIEX ELAN-500A spectrophotometer. The analyses were made after acid digestion (HNO<sub>3</sub> + HF; ratio 2:3) at a high temperature and pressure in a Teflon-lined vessel. The spectrometer was equipped with quartz torch, nickel sampler, and skimmer cones, a cross-flow type pneumatic nebulizer, and a double-pass Scott-type spray chamber.

Instrumental drift was monitored by regularly running standard element solutions between samples. The water-soluble forms were obtained from sediment-water extract in a ratio of 1:5 [22, 23], and the heavy metals solubilized were also determined by ICP-MS. All ICP-MS standards were prepared from ICP single-element standard solutions (Merck quality) after appropriate dilution with 10% HNO<sub>3</sub>. For calibration, two sets of multielement standards containing all the analytes of interest at five concentrations were prepared using rhodium as an internal standard. Procedural blanks for estimating the detection limits ( $3\sigma$ ;  $n = 6$ ) were <0.96 ppb for Mn, <2.73 ppb for Cr, <0.24 ppb for Co, <0.42 ppb for Ni, <0.12 ppb for Cu, <2.68 ppb for Zn, <0.21 ppb for As, and <0.23 ppb for Pb. The analytical precision was better than ±5% in all cases.

The toxicity bioassay was made with the water extract of the sediment. Prior to the assay, pH was measured potentiometrically in a 1:5 soil:water suspension in a CRISON 501 instrument, and electric conductivity (EC) was measured at 25°C in a CRISON 522 instrument. The toxicity bioassay was made with bacterium (*Vibrio fischeri*), which diminishes its bioluminescence capacity in the presence of toxic elements. The freeze-dried luminescent bacteria (NRLLB-11177) and the reconstitution solution were supplied by AZUR Environmental. The test was performed in a Microtox 500 analyser from Microbics Corporation, according to a modification of Microtox Basic Test for Aqueous Extracts Protocol [24], in which the water-sediment extracts and a control sample (distilled water) were used, with three replicates per sample. The luminescence was measured before the mixture with the extracts (0 min). The inhibition of bioluminescence was measured at 5 (Inh5) and 15 minutes (Inh15) after the mixture with the extracts of the samples. Afterwards, these measurements were used to calculate two Toxicity Indexes:

- (i) normalized Inhibition of luminescence at 5 min (I5), calculated by:

$$I5 = \frac{-(\text{Inh}5_{\text{sample}} - \text{Inh}5_{\text{control}})}{100 - \text{Inh}5_{\text{control}}}, \quad (1)$$

where  $\text{Inh}5_{\text{sample}}$  is the percentage of luminescence reduction in the samples at 5 min, and  $\text{Inh}5_{\text{control}}$  is percentage of luminescence reduction of control at 5 min.

- (ii) normalized inhibition at 15 min (I15), calculated by:

$$I15 = \frac{-(\text{Inh}15_{\text{sample}} - \text{Inh}15_{\text{control}})}{100 - \text{Inh}15_{\text{control}}}, \quad (2)$$

where  $\text{Inh}15_{\text{sample}}$  is the percentage of reduction of the sample at 15 min, and  $\text{Inh}15_{\text{control}}$  is the percentage of reduction of control at 15 min;

The values of I5 and I15 can range from –1 (maximum toxicity) to >0, and the following classes can be established: (a) 0 to –0.25 low, (b) –0.25 to –0.5 moderate, (c) –0.5 to –0.75 high, and (d) –0.75 to –1 very high toxicity. Values >0 would indicate stimulation of the luminescence (hormesis).

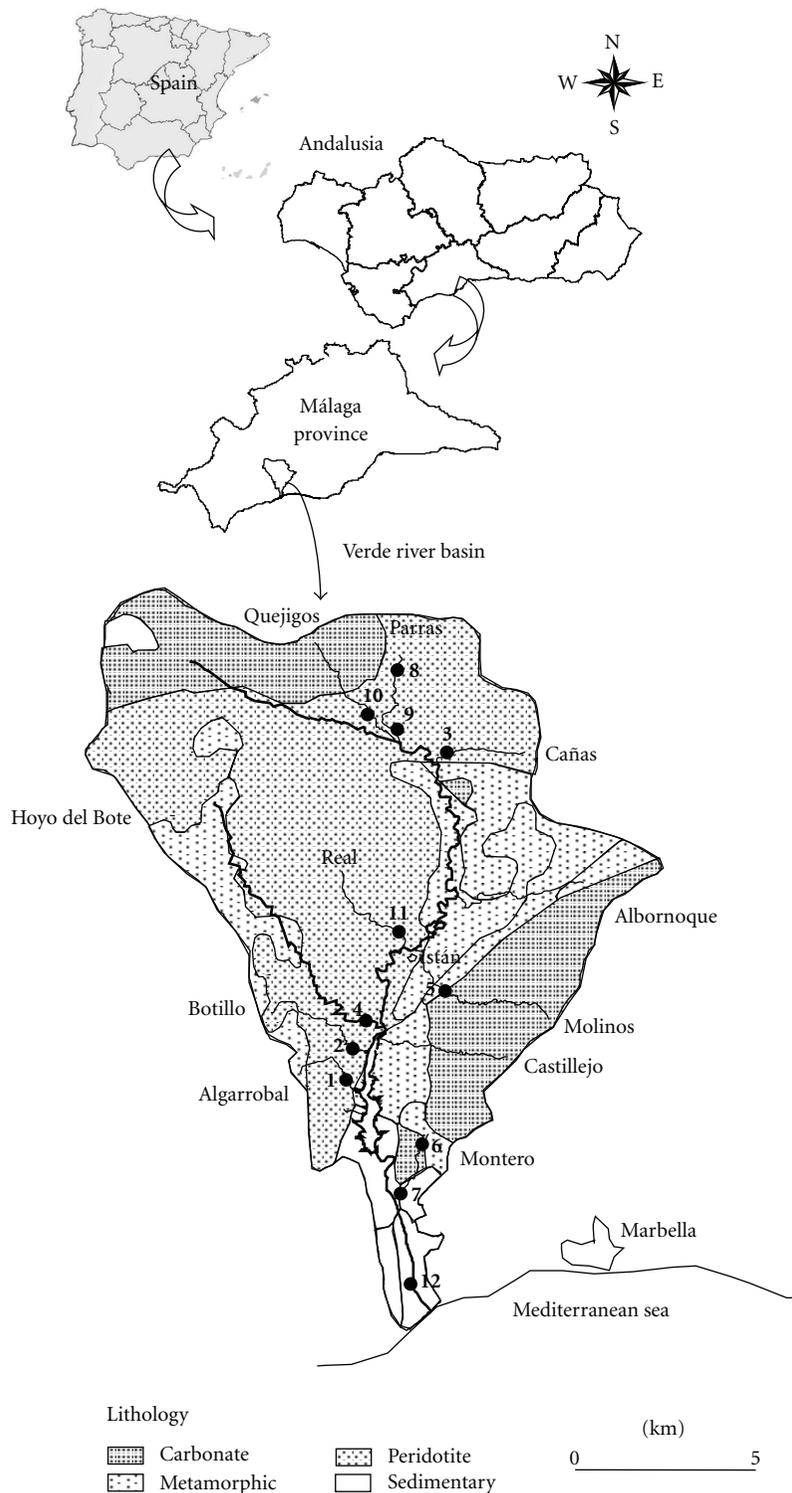


FIGURE 1: Location of the study area, sampling points, and lithological scheme of the River Verde basin.

### 3. Results and Discussion

The total concentrations of heavy metals in the sediments (Table 1) indicate that the peridotite materials have very high concentrations in Cr, Ni, Mn, and Co while in the other

materials (carbonate and metamorphic rocks) the values of these elements are low, and the concentrations in Zn and As are higher than in the peridotite area; the differences in Pb are not statistically significant between the two types of materials. Therefore, the total concentrations in heavy metals

TABLE 1: Total heavy-metal concentrations ( $\text{mg kg}^{-1}$ ) in sediments from peridotite materials and from other materials in the Verde River basin.

	Peridotite	Other materials
Mn	$1244.95 \pm 81.92$	$708.07 \pm 165.37$
Cr	$1040.79 \pm 131.15$	$236.00 \pm 125.62$
Co	$114.86 \pm 14.21$	$34.00 \pm 13.49$
Ni	$1833.26 \pm 232.46$	$372.78 \pm 273.77$
Cu	$23.93 \pm 1.45$	$32.50 \pm 4.09$
Zn	$69.40 \pm 6.10$	$166.64 \pm 67.25$
As	$4.94 \pm 0.80$	$26.41 \pm 13.30$
Pb	$19.43 \pm 4.09$	$21.75 \pm 6.97$

TABLE 2: Water-soluble heavy-metal concentrations ( $\text{mg kg}^{-1}$ ) in sediments from peridotite and from other materials in the Verde River basin.

	Peridotite	Other materials
Mn	$0.497 \pm 0.245$	$0.280 \pm 0.151$
Cr	$0.013 \pm 0.004$	$0.002 \pm 0.001$
Co	$0.015 \pm 0.006$	$0.003 \pm 0.001$
Ni	$0.153 \pm 0.048$	$0.008 \pm 0.002$
Cu	$0.009 \pm 0.002$	$0.008 \pm 0.002$
Zn	$0.019 \pm 0.006$	$0.011 \pm 0.006$
As	$0.005 \pm 0.001$	$0.004 \pm 0.002$
Pb	$0.0004 \pm 0.0003$	$0.0004 \pm 0.0003$

in the sediments of the Verde River are directly related to the different parent materials present in the area.

The highest heavy-metal concentrations were for Ni and Cr, with maximum values of  $2552 \text{ mg kg}^{-1}$  and  $1514 \text{ mg kg}^{-1}$ , respectively. According to the geochemical background of the trace elements in soils of Andalusia [25], the sediments of the study area have anomalous values only for Ni, Cr, and Co in the peridotite materials, with concentrations exceeding, respectively, 36-, 10-, and 2-fold the reference values for the region. The concentrations of the other elements were within the normal range in all cases.

For the assessment of the potential toxicity of the samples, water extracts of the sediments were obtained to make the toxicity bioassay using luminescent bacteria. The main variables affecting the measurement in the bioassay were pH and electric conductivity (EC); these properties should be determined to assess their influence in the test results. The water extract of the samples had a pH value of  $8.03 \pm 0.13$ , and the mean value of EC was  $1.36 \pm 0.12$ . These values are within the recommended range for this toxicity bioassay [26]. The concentration of soluble heavy metals in the water extracts are presented in Table 2. The sediments coming from the peridotite area had significantly higher concentrations in soluble Ni, Cr, and Co than the sediments coming from other materials. The other elements analysed had no significant differences in their soluble concentration between the different materials considered.

According to the toxicity bioassay with *Vibrio fischeri*, most samples showed a decrease in the luminescence in

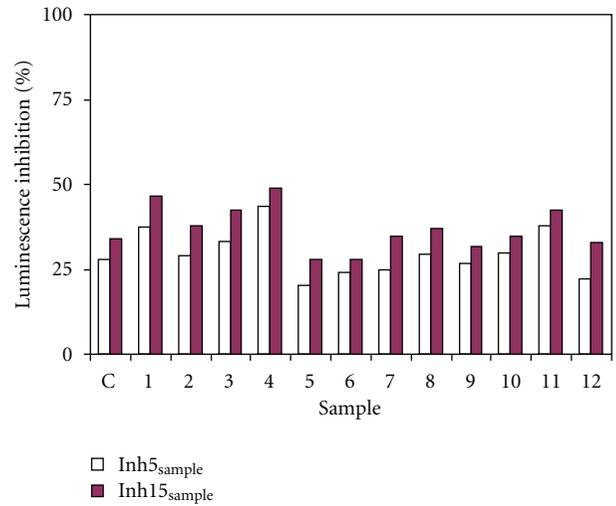


FIGURE 2: Luminescence inhibition (%) of the water extract in the sediment analysed (C = control sample).

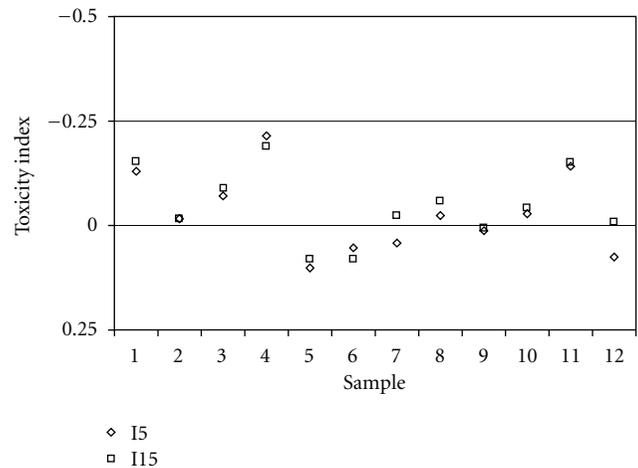


FIGURE 3: Toxicity index of the water extract in the sediment analysed.

relation to the initial value (Figure 2). Because this bacterium is from a marine environment, the control samples (distilled water) had also a luminescence reduction of between 27 and 34%. The water extract of the samples showed a reduction at 5 min ( $\text{Inh}_{5\text{sample}}$ ) and 15 min ( $\text{Inh}_{15\text{sample}}$ ) below 50% in relation to the initial value in all cases although these values were normalized to calculate the inhibition in relation to the control. The lower inhibition of luminescence was found in the sediments belonging to the nonperidotite area (samples 5, 6, and 7) and in sample 12, which received a mixture of sediment both from the peridotite materials as well as from the metamorphic carbonate area.

The water extracts of the sediments had a very low toxicity index in most cases (Figure 3), with values below  $-0.1$  (representing a 10% luminescence reduction in relation to control) in 75% of the samples. Values of the toxicity index at 5 and 15 min had a good correlation in the dataset studied.

TABLE 3: Toxicity index of the water extract at 5 min (I5) and 15 min (I15). (M: mean; SD: standard deviation; a, b: significant differences ( $P < .05$ ) in Tukey test).

Sample		1	2	3	4	5	6	7	8	9	10	11	12
I5	M	-0.13a	-0.01b	-0.07b	-0.21a	0.10b	0.05b	0.04b	-0.03b	0.01b	-0.03b	-0.14a	0.08b
	SD	0.02	0.07	0.08	0.05	0.10	0.03	0.02	0.01	0.08	0.03	0.03	0.10
I15	M	-0.15a	-0.02b	-0.09b	-0.19a	0.08b	0.08b	-0.03b	-0.06b	0.00b	-0.04b	-0.15a	-0.01b
	SD	0.02	0.09	0.05	0.03	0.09	0.05	0.02	0.04	0.08	0.05	0.01	0.05

In the case of the sediments coming from the non-peridotite area or from a mixture of different parent materials (samples 5, 6, 7, and 12), the toxicity index had values higher than zero, indicating the occurrence of hormesis phenomena related to the stimulation of the bacterial activity. Only one sample (4) had values of the toxicity index close to  $-0.25$  (representing a 25% reduction in luminescence with respect to the control), indicating a moderate degree of toxicity. The ANOVA of the toxicity index indicated that samples 1, 4, and 11 (located in the lower part of the peridotite area) significantly differed in relation to the other samples analysed (Table 3), with a toxicity index ranging from  $-0.13$  to  $-0.21$ ; therefore, these three samples had a luminescence reduction of more than 10% but less than 25%, which could be related to the heavy-metal concentrations in the water extracts used in the bioassay. To correlate the heavy metal concentration in the water extracts with the toxicity index based on the reduction of luminescence, we used the Spearman correlation coefficient. In the studied dataset, we found a negative and significant correlation ( $P < .05$ ) between the toxicity index and the Ni and Cr concentration in the solutions. For I5, the coefficients were  $-0.636$  with Ni and  $-0.622$  with Cr, and for I15 the coefficients were  $-0.650$  with Ni and  $-0.580$  with Cr. The comparison with the toxic levels in the literature [27] indicates that the only elements exceeding these limits were Ni and Cr, for which the toxic levels in water solutions surpassed 3- and 10-fold, respectively. No significant correlations were detected for other heavy metals in the water extract, indicating the influence of the peridotite materials in the toxicity of the samples analysed.

#### 4. Conclusions

The study area is dominated by peridotite materials, and the riverbed sediments in the basin have high concentrations of Ni, Mn, Cr, and Co. The soluble forms were from the water extract of the sediments of the main river and tributaries in the basin. The toxicity bioassay with *Vibrio fischeri* used the water extract of these sediments to assess the bioluminescence reduction in these bacteria. The toxicity degree was very low in 75% of the samples, with values of luminescence reduction below 10% in relation to the control. A moderate-to-low degree of toxicity was found in 25% of the samples (all belonging to the non-peridotite area), with a luminescence reduction between 13 and 21% in relation to the control. The correlation coefficient (Spearman) indicated a negative and significant relation between the toxicity index and the concentrations in Ni and Cr in the water extracts

of the sediments. This toxicity bioassay was proved to be a sensitive and useful tool for detecting the potential toxicity of solutions, even in samples with anomalous concentrations in heavy metals of natural origin.

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## Review Article

# Monitoring of Lead in Topsoil, Forage, Blood, Liver, and Kidneys in Cows in a Lead-Polluted Area in Slovenia (1975–2002) and a Case of Lead Poisoning (1993)

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The paper presents the results of a prolonged research in a lead-polluted area. Extensive systematic studies of lead concentrations in topsoil, forage, blood, liver, and kidney in cows on farms within 1–10 km around the lead mine and smelter were carried out. After installation of a filter in 1978, lead concentrations began to decrease. However, when toxic levels of lead were within normal reference values, the authorities stopped to finance the project. In 2002, the research was concluded. A review of studies showed that the protective filter was effective; during the period 1975–2002 mean lead in forage dropped from  $584.0 \pm 324.0$  to  $5.5 \pm 2.9$  mg/kg, and the mean blood lead levels dropped from  $1.251 \pm 0.580$  to  $0.069 \pm 0.041$  mg/kg. Three years after the filter was installed the amount of lead in the liver and kidneys had normalized. Closely related to our research was also a case of cow lead poisoning.

## 1. Introduction

Lead is a bluish white to gray heavy metal that was probably the first toxic element recognized by man. Lead is ubiquitous in the manmade environment, because of its numerous uses and yet still has great relevance today [1]. Very frequent and potential source of lead content in animal tissues are forage produced on agricultural surface or cattle grazing on pastures contaminated by airborne emissions from nearby smelters [2–5]. Chronic and nonapparent poisoning due to ingesting smaller quantities of lead contaminated forage over a longer period of time is characterized by nonspecific signs which may be expressed as loss of appetite, weight loss, reproduction disorders, anemia, osteoporosis and immunosuppression [6–9]. Environmental pollution in the vicinity of lead-ore processing factories can result in varying degrees of poisoning with lead [2, 10–12]. Cows blood lead levels is a good bioindicator of environmental contamination [2, 7, 13]. Concentration of lead in whole blood and milk resulting from the daily exposure to lead does not produce any clinical evidence of disease [13]. In dead and slaughtered animals lead was usually analyzed in the liver, kidneys, and muscles [13–15].

The contamination of food of animal origin with lead in some areas of Slovenia was presented in amounts higher ( $>0.500$  mg/kg WW) than the levels allowed by national guidelines [16]. One of these areas is the Upper Meža Valley. From the point of polluted environment and emissions of lead gasses and dust, the valley is ranked into the 4th class of national classification for environmental pollution [17]. It is an area with stationary contamination of upper layers of soil and with very limited air self-cleansing possibilities [17, 18]. Lead content in tissues and blood of animals that live in polluted areas is usually elevated and risk of acute or chronic poisoning is increased [2, 3, 19–21]. Lead has a particular affinity for bones and causes osteoporosis; it also enters the liver and kidney. It interferes with iron metabolism and may cause anemia. Most of the symptoms relate to the neurotoxicity of lead. Affected cattle may charge around, press their heads against a wall, and later they develop ataxia [1, 7].

Lead mining in the Meža River Valley (Slovenia) dates from 1424. The year 1893 can be considered the beginning of mining-metallurgic activity in the area [2]. In 1962, a factory of storage batteries became an integral part of the plant. In 1989, technology changed and the primary raw material,

lead sulphide ore (galenite), was replaced by secondary raw material (old lead storage batteries) [2, 18]. Today, the lead mine is closed but the smelter and big recycling plant is in full use. Vegetation and soil in Upper Meža Valley has been contaminated by mining and smelter operations for more than a century [18, 22].

Prpić-Majić [2] reported that in 1976, 1982, 1984, and 1988 the characteristic indicators of lead absorption (lead in blood,  $\delta$ -ALA-D) were determined in a representative number of cows ( $n = 120$ ) from pasture in Upper Meža Valley and from one pasture in the control area. Lead in blood and  $\delta$ -ALA-D showed a trend towards normal values after the bag filter installation. But even ten years later the differences in lead in blood and  $\delta$ -ALA-D in cows from exposed and control areas were still highly significant indicating that the environment of Meža Valley was still contaminated by lead [2, 23].

At our Clinic, the first investigation was performed in 1975 [6]. From 1979 to 2002, lead effects on health condition and fertility in cows from farms in this area were studied systematically. The study in cows was initiated to verify the hypothesis that lead absorption in cows was in direct relationship with the environmental pollution of air, water, soil, and lead contaminated of forage [2, 24, 25]. There were endless arguments among cattle breeders and mine management because of economic losses in spite of the installation of an expensive bag filter system in 1978 to prevent further lead pollution from the smelter [2, 3, 26]. Before 1990, there were numerous complaints and reimbursements for the animals that were slaughtered for salvage and those that were clinically normal, yet at slaughter showed elevated lead contents in the liver and kidneys which could mean a nonapparent poisoning of animals that adversely affected production and reproduction [19, 27]. Via a 25-year-long systematic investigation on lead concentration in topsoil, forage, liver, kidneys and blood of cows we gathered valuable data on lead contamination of the environment [2, 3, 19].

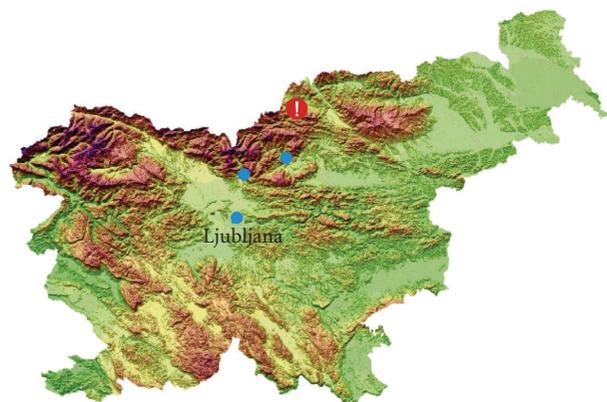
Via a systematic, several years lasting investigation on lead concentrations, we gathered valuable data on contamination rate of hay and silage and lead absorption in the organism of the animals [28–30].

The aim of this review was to determine the dynamics of yearly lead content in the topsoil, forage (hay, silage), liver, kidneys, and blood of cows on exposed farms after emission was put under control.

Reported is also yet a source of environmental contamination associated with the improvement of marshy pastures on a farm with gravel and dump material from mine and smelter which caused acute lead poisoning of cows.

## 2. Material and Methods

**2.1. Location of the Research Area.** Farms under the investigation are located in the Upper Meža Valley, which is a steep mountain valley with poor ventilation. It is situated in the Northern part of Slovenia, bordering on Austria (Figure 1). For over 100 years mining operations had been going on,



- ❗ Location of research area (Upper Meža Valley)
- Control area

FIGURE 1: Map of Slovenia with the research area and the three areas of the control groups.

and in 1989 the mine was closed for the lack of primary raw ore material and replaced by a big smelting plant for old car batteries.

On these traditional Alpine farms, the feeding of animals was based on exclusively home produced forage. The cattle had been chronically exposed to ingesting vegetation and soil contaminated by atmospheric fallout until 1978, when a modern bag filter system was installed to decrease the emission of lead gasses and dust to the environment.

**2.2. Sampling Procedure and Laboratory Analyses.** The first investigation on lead content in the hay and blood of cows was carried out in 1975. During 1976 the systematic work continued. Between 1977 and 1978, our Clinic did not take part in the research activities. Questioning, registering of clinical data, and collecting biological material were done each year at the end of April or first day of May. From the year 1979 to 2002, with the exception of 1988, the workers of the Clinic visited the exposed farms each year.

Topsoil ( $n = 116$ ), hay ( $n = 259$ ), silage ( $n = 35$ ), liver ( $n = 23$ ), kidney ( $n = 23$ ), and blood ( $n = 1,279$ ) samples were taken, depending on yearly financial support, from 1 to 14 of the most exposed farms, 1 to 10 km around a lead mine and smelter area.

Most of cows were Simmental breed and were during the winter season kept in classic tied-housing systems with hay bedding. All cows received exclusively home-produced forage twice a day. Because of the highly polluted environment the grazing of animals on farms near the mine and smelter was banned until 1982. After 1982, the farmers on some farms started of with grazing because of high availability of pasture.

Liver ( $n = 23$ ) and kidney ( $n = 23$ ) samples were collected individually from 1979 to 1985. Each year the samples were collected at slaughter houses. The owners sent for slaughter the cows that were in poor condition

TABLE 1: The examined biological material, total number of samples ( $n = 1,734$ ), and measurements units from 1975 to 2002 on farms ( $n = 1$  to 14) around the mine area and smelter in the Upper Meža Valley.

Samples of biological materials	Samples ( $n$ )	Measurement units(mg/kg)
Topsoil to 10 cm	116	mg of lead/kg
Hay samples	259	mg of lead/kg DM
Silage samples	35	mg of lead/kg DM
Liver samples	23	mg of lead/kg WW
Kidney samples	23	mg of lead/kg WW
Whole blood of cows samples	1,279	mg of lead/kg WW
Total number	1,735	

TABLE 2: Mean  $\pm$  SD lead concentrations in the blood of 32 cows from the three control areas in Slovenia.

Year of research	Area of research	Number of cows	Mean lead concentration in the blood of cows (mg/kg)
1976	Ljubno ob Savinji	22	0.0600 $\pm$ 0.002
1995	Below Krvavec Mountain	6	0.0390 $\pm$ 0.001
2002	Moste heating plant in Ljubljana	4	0.0375 $\pm$ 0.004
Total		32	0.0455 $\pm$ 0.012

and losing weight. Afterwards, the fresh liver and kidneys were sent to our laboratory for analyses. If the lead content exceeded the normal values the owners were reimbursed for the slaughtered animals.

Blood was taken from the jugular vein. Thirty mL (3 tubes/10 mL) of whole blood was obtained by venipuncture in Pb-free heparinized tubes. The blood was cooled to 4°C for 24 h, frozen, and stored for 2 months at -20°C. All samples were analyzed on the same day. On each farm, blood samples were collected from 2 to 5 cows ( $n = 1,279$ ; mean age =  $6.7 \pm 2.3$  years).

The biological material, total number of samples, and measurement units are given in Table 1.

Lead analysis was performed using flame Atomic Absorption Spectrophotometry (Varian, Australia) [31]. To control the contamination at the sampling, along the contaminated samples, blank samples of all investigated materials containing nondetectable amount of lead were analyzed. Analytical procedure was controlled using samples spiked with appropriate amount of lead.

**2.3. Control Group of Cows.** During the research period (1975–2002), the blood samples for comparative lead concentrations were taken from 32 control cows from three areas in Slovenia: The Savinja Valley (1976), below the Mount Krvavec (1995), and the surroundings of the heating plant Moste in Ljubljana (2002).

**2.4. Statistical Analysis.** All data was statistically analyzed with SPSS STATISTICS 17.0 (One-Way ANOVA).

### 3. Results

Table 3 presents the results of mean lead concentrations in topsoil, hay, silage, liver, and kidney of cows from farms near former lead mine and current big smelter operating plant.

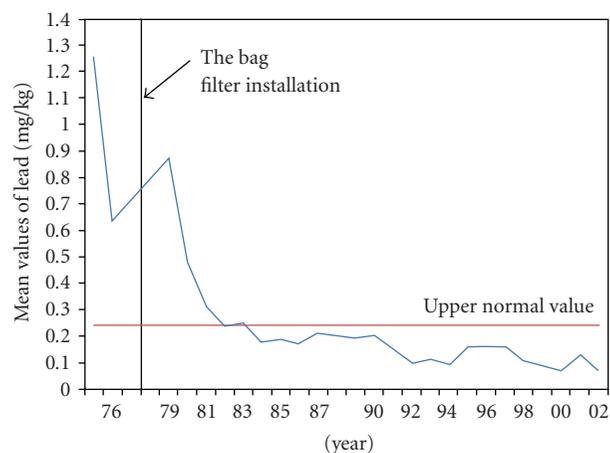


FIGURE 2: Mean concentration of lead in the blood of cows before (1975–1976) and after the installation of bag filter system.

Table 4 and Figure 2 present the dynamics of lead concentration in the blood of cows. Table 2 presents mean lead concentrations in control groups of cows. Table 5 presents results of lead concentrations on blood, liver, kidney, and feces in one of the cows dead on pastures with typical clinical signs for acute lead poisoning. On the farm with the lead poisoning incident, we also took soil and water samples to establish concentration of lead. Two months after poisoning, blood samples from all cows ( $n = 27$ ) on farm were taken (Table 4, year 1993). Of the 27 animals, three had concentration of 0.710, 0.310, and 0.280 mg of lead/kg blood, respectively.

**3.1. A Case of Lead Poisoning in Cows.** Until 1985, the veterinary service registered several cases in the acute, subacute and chronic of lead poisoning in cows on monitored farms. In 1993, it was reported that on the farm that was not

TABLE 3: Mean lead concentrations in topsoil, hay, silage, liver, and kidney of cows from farms near the lead mine and smelter before the installation of bag filter system in 1975/1976 and after the installation from 1979 to 2002.

Year of research	Topsoil* (min-max or mean mg/kg)	Hay (mg/kg DM)	Silage (mg/kg DM)	Liver (mg/kg WW)	Kidney (mg/kg WW)
1975	192 to 1,558 ( $n = 33$ )	$584.0 \pm 324.0$ ( $n = 4$ )	—	—	—
1976	—	821.0 ( $n = 1$ )	—	—	—
1979	—	$69.10 \pm 61.3$ ( $n = 13$ )	—	$5.23 \pm 2.3$ ( $n = 3$ )	$8.12 \pm 3.1$ ( $n = 5$ )
1980	—	$48.9 \pm 28.2$ ( $n = 13$ )	—	$3.06 \pm 1.9$ ( $n = 7$ )	$6.23 \pm 1.9$ ( $n = 6$ )
1981	—	$34.5 \pm 29.6$ ( $n = 13$ )	—	$1.74 \pm 0.7$ ( $n = 8$ )	$6.49 \pm 1.4$ ( $n = 5$ )
1982	$350.4 \pm 331.3$ ( $n = 9$ )	$13.6 \pm 3.8$ ( $n = 13$ )	—	0.44 ( $n = 1$ )	$5.93 \pm 0.9$ ( $n = 4$ )
1983	$320.6 \pm 198.8$ ( $n = 9$ )	$22.2 \pm 8.1$ ( $n = 13$ )	—	$6.67 \pm 0.8$ ( $n = 2$ )	1.20 ( $n = 1$ )
1984	$370.2 \pm 278.3$ ( $n = 9$ )	$34.1 \pm 18.2$ ( $n = 13$ )	—	8.00 ( $n = 1$ )	5.62 ( $n = 1$ )
1985	51.3 – 310.5 ( $n = 9$ )	$23.3 \pm 12.6$ ( $n = 13$ )	—	0.85 ( $n = 1$ )	1.21 ( $n = 1$ )
1986	42.5 – 720.4 ( $n = 5$ )	$17.8 \pm 13.0$ ( $n = 11$ )	—	—	—
1987	$390.4 \pm 281.3$ ( $n = 9$ )	$18.5 \pm 11.1$ ( $n = 10$ )	—	—	—
1989	$400.4 \pm 239.1$ ( $n = 9$ )	$18.0 \pm 8.3$ ( $n = 12$ )	—	—	—
1990	—	$17.2 \pm 9.7$ ( $n = 12$ )	—	—	—
1991	—	$18.1 \pm 10.4$ ( $n = 12$ )	—	—	—
1992	—	$13.6 \pm 7.4$ ( $n = 12$ )	—	—	—
1993	—	$8.0 \pm 2.4$ ( $n = 2$ )	—	—	—
1994	—	$3.4 \pm 2.1$ ( $n = 4$ )	—	—	—
1995	—	$11.4 \pm 4.2$ ( $n = 4$ )	—	—	—
1996	—	$6.9 \pm 3.1$ ( $n = 6$ )	$12.5 \pm 3.6$ ( $n = 4$ )	—	—
1997	—	$6.5 \pm 3.8$ ( $n = 14$ )	$12.8 \pm 1.2$ ( $n = 10$ )	—	—
1998	—	$8.3 \pm 4.2$ ( $n = 12$ )	3.5 ( $n = 1$ )	—	—
1999	$619.1 \pm 321.9$ ( $n = 3$ )	$10.3 \pm 3.9$ ( $n = 13$ )	$15.0 \pm 3.6$ ( $n = 3$ )	—	—
2000	$454.8 \pm 278.2$ ( $n = 3$ )	$7.2 \pm 4.6$ ( $n = 14$ )	$7.3 \pm 2.6$ ( $n = 6$ )	—	—
2001	$283.6 \pm 189.2$ ( $n = 8$ )	$6.5 \pm 3.7$ ( $n = 12$ )	$4.7 \pm 1.8$ ( $n = 6$ )	—	—
2002	$347.5 \pm 300.1$ ( $n = 10$ )	$5.6 \pm 3.3$ ( $n = 12$ )	$8.8 \pm 2.2$ ( $n = 5$ )	—	—

\*Research of topsoil samples encompassed the farms nearby the smelter [2, 3, 22].

included in systematic monitoring, four cows showed clinical signs of plumbism (neurological signs) during the first week of pasture. One cow survived and three died. Tissue samples were collected from one of these animals. Samples were also taken and lead content was measured where cows licked soil along with samples from the drinking water (Table 5).

## 4. Discussion

**4.1. Lead in Topsoil.** Almost 3 decades lasting measurements of total lead in the topsoil on farms in the vicinity of the mine and smelter enabled an insight into prolonged soil contamination with this heavy metal. Because of the careless attitude of the smelter management towards the environment, lead intensively accumulated in the vegetation and soil until 1978. The main source of contamination was the emission of gasses and dust from the mine and smelter operations. Data gathered from the local farmers confirmed that the emission was extremely high, especially around the smelter plant in Upper Meža Valley until 1978 when the bag filter system had been installed [2, 12, 18, 24, 33]. The consequences are still visible today; nature around the



FIGURE 3: Upper Meža Valley is ranked into the 4th class of environmental pollution (dead valley). It is an area with stationary lead contamination of upper layers of soil and with very limited air self-cleansing possibilities [17].

smelter is devastated and called the “dead valley” (Figure 3). The studies show that lead concentration depended on the distance from the main source of emission (vicinity of the smelter). In the Upper Meža Valley, the first research

TABLE 4: Mean, standard deviation (SD), and minimal-maximal concentrations of lead in the blood of cows before (1975-1976) and after the installation of bag filter system.

Year of research	Number of farms	Number of cows	Mean lead concentration in blood (mg/kg)	± SD of lead in blood (mg /kg)	Min. – max. of lead in blood (mg /kg)
1975*	2	9	1.251	0.580	0.501–2.301
1976*	5	28	0.645	0.239	0.251–1.130
1979	13	43	0.870	0.410	0.351–1.890
1980	13	57	0.478	0.290	0.180–2.080
1981	13	60	0.320	0.062	0.140–0.450
1982	13	53	0.241	0.127	0.080–0.660
1983	13	58	0.248	0.134	0.103–0.960
1984	13	60	0.179	0.048	0.094–0.311
1985	13	58	0.191	0.065	0.100–0.410
1986	12	57	0.173	0.051	0.070–0.270
1987	10	44	0.213	0.087	0.110–0.430
1989	12	60	0.195	0.041	0.120–0.320
1990	12	59	0.202	0.073	0.060–0.380
1991	12	60	0.150	0.034	0.061–0.230
1992	12	60	0.098	0.072	0.040–0.320
1993	1	27	0.112	0.138	0.050–0.710
1994	2	15	0.095	0.013	0.070–0.113
1995	6	106	0.158	0.052	0.070–0.280
1996	6	30	0.164	0.039	0.095–0.238
1997	14	59	0.161	0.028	0.021–0.580
1998	14	59	0.109	0.022	0.010–0.267
1999	14	58	0.087	0.019	0.015–0.129
2000	14	57	0.073	0.011	0.024–0.160
2001	12	51	0.131	0.143	0.002–0.581
2002	12	51	0.069	0.041	0.004–0.174

\*Time before the installation of bag filter system.

TABLE 5: Lead concentration in soil of pasture, drinking water, blood, liver, kidney, and feces of one dead cow, and mean ±SD ( $n = 27$ ) and min-max blood lead concentration in cows from the farm with acute lead poisoning two months after incident.

Samples ( $n = 1$ )	Lead concentration mg/kg	Lead concentration in the blood of cows two months after poisoning ( $n = 27$ )
Blood	0.350 †	Mean = 0.112 ±SD = 0.138 Min – max = 0.050 – 0.710
Liver	6.32 (WW) †	
Kidney	11.28 (WW) †	
Feces	14.71 (DM) †	
Pasture soil where cows licked it	295 †	
Drinking water	<0.050 mg/L	

† Increase concentration [7, 32].

activities began already in 1968 and 1969. Lead was measured in 184 soil samples at 33 locations. Samples were taken from different altitudes and arranged in accordance with the direction of the wind and distance (from 979 m to 7,250 m) from the source of dust emission. In the topsoil, from 191 mg/kg to 1,558 mg/kg of lead was measured [2, 22, 33]. The same authors carried out research also in the years

1970 and 1971. Table 3 presents the results of the analyses of the topsoil samples to the depth of 10 cm. A comparison of mean lead concentration in soil from 1982 to 1989 and concentrations during 1968/69 revealed that, on most farms for many years after the filters had been installed, no decline of lead concentration in the upper layers of soil occurred [2, 33, 34]. The measured high lead content in

the topsoil is the result of prolonged direct emission of lead gasses and dust, which accumulated in vegetation and soil. Lead is changed into insoluble form that may remain in the soil practically indefinitely [34]. Prpić-Majić et al. [35] and Prpić-Majić [2] reported that lead content in the soil significantly depends on the distance of the farm from the source of emission, direction of the wind, configuration of terrain, altitude, meteorological conditions, and cultivation of the soil. We conclude that persistency of lead in soil is a risk for contamination of other areas when the soil is exposed and moved to be used at other locations.

**4.2. Lead in Hay and Silage.** Several epidemics of lead poisoning in domestic animals have been recorded throughout the world [7, 32]. From Table 3, it is evident that mean lead content ( $584 \pm 324$  mg/kg DM) in four hay samples (1975) and in one (1976) was 23- to 32-times higher than in two control hay samples (20.0 and 29.0 mg/kg DM) in the Upper Savinja Valley [27]. Also other authors reported on high lead concentrations in contaminated grass (12.3 to 886.4 mg/kg DM) and hay (5.4 to 409.6 mg/kg DM) from the Meža Valley [2, 30, 34]. According to older people, trees in the area around the smelter were silvery-bluish from the dust from the chimneys. An interesting monitor for veterinary service and people were cats, especially the young ones that licked their hair after the night hunt and frequently died in spasms from acute plumbism. Besides cattle and horses also sheep were affected, especially the young ones [2, 27]. Table 3 also shows that after the installation of filters mean lead concentrations in hay progressively declined until 1992. Up to 2002 mean values were within the reference range ( $<10,0$  mg lead/kg DM). After 1990, we did not detect any acute lead poisoning in cows. However, cattle reared in the vicinity of the smelter are at present still exposed to the risk of acute and especially chronic lead poisoning. As it is known from the literature, acute plumbism most commonly occurs in cattle if lead content in silage is above 140.0 mg/kg DM [7, 13, 36] and in hay above 150.0 mg of lead/kg DM [7, 35]. The established dynamics of mean lead hay concentrations can be explained by somewhere lower and somewhere higher contamination of grass from the upper layers of soil. It is well known that grazing cattle commonly have up to 10% soil in their diet [36]. The results of forage analyses showed high mean ash content ( $10.52 \pm 1.21\%$ ) therefore we may claim that fodder was contaminated via the soil especially during pasture and hay/silage making [3]. According to the literature, the lead amount in the soil is in weak correlation to the lead amount in the above ground parts of the plants because roots inhibit the transport of lead into shoots [37, 38].

**4.3. Lead in Cow Liver and Kidney.** Literature reported that tissue lead levels in cattle from industrial areas are significantly higher (liver 0.230 mg/kg WW, kidney 0.420 mg/kg WW) than in cattle from clear air zone (liver and kidney less than 0.100 mg/kg WW) [7, 14, 15, 32].

The first liver samples from cows that died or were slaughtered because of suspect lead poisoning were examined

in 1979, a year after the modern filter system was installed. All samples contained over 2.0 mg of lead/kg WW. This is the amount that may cause clinically manifested lead poisoning [7, 11, 32]. In all such cases, owners of animals were reimbursed for the loss of the cows. In 1980, five of seven delaminated samples of liver contained over 2.0 mg of lead/kg WW (2.73–4.82 mg of lead/kg WW). A year later, the amount of the examined lead in all samples ( $n = 8$ ) was below 2.0 mg of lead/kg WW (0.81–1.99 mg of lead/kg WW). In 1982, only one sample of liver was delivered; the lead content was only (0.44 mg of lead/kg WW) [26].

The samples of kidneys, which were delivered from 1979 to 1982 lead concentrations, did not exceed the critical level of 10 mg of lead/kg WW, the amount that according to Rosenberger [32] may cause clinical signs of plumbism. The majority of samples contained less than 5.0 mg of lead/kg WW.

From the data, it may be concluded that lead concentration in the internal organs of affected or slaughtered animals decreased linearly with the lead amount in hay, silage, and blood [26].

After 1985, no samples of liver or kidney were delivered for examination, so lead content in the blood of cows became the major indicator of plumbism.

**4.4. Lead in Blood.** Lead levels in the blood provide a reliable indicator of cattle exposure to the lead-contaminated environment [39]. Lead is usually absorbed via intestines and respiratory system [7, 32, 40]. Whole blood levels of lead in normal ruminants are usually below 0.05–0.250 mg/kg; poisoned animals usually have levels above 0.350 mg/kg and deaths begin at 1.0 mg/kg [7, 40]. Table 4 and Figure 2 present the dynamics of lead in the blood of cows. It is evident that mean lead concentrations in 1975/76 were  $1.251 \pm 0.580$ , respectively,  $0.645 \pm 0.239$  mg/kg. After 1978, these high lead concentrations gradually dropped. In 1982, mean concentration reached the level that most researches claim to be within the reference values (0.050 to 0.250 mg of lead/kg of the blood) [7, 27]. For comparison of concentrations between polluted and unpolluted areas, lead content was measured in the blood of 32 cows from 3 control areas. Mean lead concentration was  $0.047 \pm 0.012$  mg of lead/kg of blood. For example, Villegas-Navarro et al. [11] established mean values  $0.035 \pm 0.013$  mg of lead/kg in the blood of cattle from an unpolluted area. After 1982, mean lead concentrations of lead in the blood of cows were within normal reference values. However, the lowest mean concentration ( $0.069 \pm 0.041$  mg/kg) in 2002 was still 2-times higher compared to the concentrations in unpolluted areas in Slovenia. It was established that lead concentration in the blood of cows dropped simultaneously with the concentrations in hay and silage.

**4.5. A Case of Lead Poisoning.** In the literature, similar reports on lead poisoning in cattle are numerous [41–44]. Lead poisoning occurs most commonly in cattle at pasture, particularly if the pasture is poor and the animals are allowed to forage in unusual places. Cattle on lush pasture may also



FIGURE 4: Part of pasture where  $>300\text{ m}^3$  of gravel from the mine was temporarily stored in 1992; on this location (behind the tractor) is also the drinking place for animal.



FIGURE 5: Waste material ( $>30\text{ m}^3$ ), parts of asphalt, gravel, lead plates which was used for building the road to the pasture, and drinking water; the photo shows a lead plate  $20\times 60\text{ cm}$  and weighing about 3 kg.

seek out foreign material to chew [7, 32]. In many countries the incidence of plumbism is highest in cattle in the spring of the year a few days after the animals have been turned out onto pasture [7].

We diagnosed accidental lead poisoning as a consequence of melioration works (pasture, road) on that farm in 1992 where greater amounts of gravel ( $>300\text{ m}^3$ ) were used from the near lead mine as well as some dross ( $30\text{ m}^3$ ) from the smelter mixed with lead chips (Figures 4 and 5). A sample of soil contained  $295\text{ mg}$  of lead/kg. A sample of drinking water contained less than  $0.050\text{ mg}$  of lead/L. From Table 5, it is evident that lead concentration in soil, blood, liver and kidney of dead animal without signs of lead poisoning exceeded the allowed recommended lead levels [7, 32].

Licking and ingestion of dross caused clinical poisoning and death of three out of 27 cows as well as increased lead concentration ( $0.710$ ;  $0.310$ ;  $0.280\text{ mg}$  of lead/kg) in blood samples of three cows on that farm, collected two months after the incidence. Our finding is confirmed also by hay analysis containing  $10.7\text{ mg}$  of lead/kg DM that is slightly above the normal value. According to Rosenberger [32], poisoning does not occur if hay or silage contain between  $2\text{--}8\text{ mg}$  of lead/kg DM.

In our case, poisoning was caused also by factors associated with early spring pasture (deficiency of roughage and energy, protein surplus, pica, and postpartum period).

## 5. Conclusion

The mine, big smelter, and lead recycling plant in Upper Meža Valley has been operating over a hundred years. The investigation of lead concentration in topsoil, forage, blood, and tissues of cows began in 1975 and lasted till 2002. Until 1978, when protective filters were installed in the plant chimneys, the farms around plant had been exposed to heavy industrial-metallurgic effluent.

Early measurements (1968 to 1975) of high lead ( $>600.0\text{ mg}$  of lead/kg) in the topsoil and continuing investigations (1981 to 2002) showed no significantly decreased lead after the installation of filters.

Mean lead in hay and silage samples gradually decreased. In 1975, lead concentrations in 4 samples of hay were  $227.0$  to  $953.0\text{ mg/kg DM}$ . In 2002 ( $n = 12$ ), mean lead concentrations were about 100-fold lower ( $5.6 \pm 3.3\text{ mg}$  of lead/kg DM).

A similar trend of decreasing lead concentration occurred also in the blood and tissues (liver, kidney) of cows. After 1982, mean cow lead blood concentration were within normal reference values ( $<0.250\text{ mg}$  of lead/kg). Mean lead contents in the blood of cows dropped (1975–2002) from  $1.251\text{ mg/kg}$  to  $0.069\text{ mg}$  of lead/kg of blood. However, during 1992 to 2002, mean lead concentrations have still been 1- to 2-fold above the values measured in blood of animals ( $n = 32$ ) from 3 control nonpolluted areas in Slovenia.

After 1985, no samples of liver ( $n = 23$ ) and kidney ( $n = 23$ ) showed increased values ( $>2.0$  or  $>10.0\text{ mg}$  of lead/kg WW).

Blood lead levels in cows proved a good bioindicator of environmental contamination.

Today, twenty-five years after filters were installed, we are of the opinion that the major source of forage contamination was high lead content in the topsoil, which contaminated grass especially after heavy rains and haymaking.

The established lead concentrations in the blood of cows were the result of prolonged ingestion of the lead contaminated grass, hay, and silage as well as mobilization of lead from the bones. Because lead may persist in the soil practically indefinitely, we are of the opinion that, under certain circumstances, cattle in this area is still at risk to develop subclinical and even clinical manifestations of plumbism.

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