Pollutants Source Control and Health Effects

Guest Editors: Roya Kelishadi, Mohammad Mehdi Amin, Ali Akbar Haghdoost, Ajay K. Gupta, and Tuula Anneli Tuhkanen



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Editorial **Pollutants Source Control and Health Effects**

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Received 1 October 2013; Accepted 1 October 2013

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In the current special issue, different aspects of controlling pollutants and their health effects are being discussed.

Considering the vicious cycle of rapid urbanization and increasing levels of air pollution, public health and regulatory policies for environmental protection and controlling pollutants from their sources should be integrated into the main priorities of the primary health care system and into the educational curriculum of health professionals [1, 2].

Discovery of the environmental exposures is of crucial importance. It may contribute to or protect against injuries, illnesses, developmental conditions, disabilities, and deaths and the identification of public health and health care actions to avoid, prepare for, and effectively manage the risks associated with harmful exposures. Control of emissions and effluents into air, water, or soil has several beneficial effects at global level [3]. Environmental pollution influences human's health before conception and continues during pregnancy, childhood, and adolescence to adult life [4–6].

It is suggested that such health hazards may represent the greatest public health challenge humanity has faced till now. Studying the effects of environmental factors on the early stages of chronic diseases can serve for future studies and offer strategies for primary preventive interventions [7].

The current special issue seeks to define source control of pollutants and the articles which are related to interaction between environmental pollutants and their effects on health. Its potential topics include recent developments in source control of pollutants, advances in environmental epidemiology, evaluation of mechanisms for action of environmental exposures, the influence of environmental pollutants on human health, and identification of public health and health care policies and measures for risk management.

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Research Article

Relationship between Lighting and Noise Levels and Productivity of the Occupants in Automotive Assembly Industry

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Received 28 February 2013; Revised 7 September 2013; Accepted 9 September 2013

Academic Editor: Mohammad Mehdi Amin

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Work environment affects human productivity and his performance. The aims of this study were to investigate the effects of lighting and noise levels on human productivity in the automotive assembly industry. *Method*. Subjects were 181 workers from different parts of an automobile assembly industry. Illuminance (Lx) at the height of 30 inches from the surface of work station and noise (dBA) were locally measured. Also human productivity by the Goldsmith and Hersey scale (1980) was measured. Data were analyzed by using SPSS v20 Pearson correlation coefficient. *Results*. The results showed that the relationship between noise level and human productivity is negative and significant (P < 0.05, r = -0.178), but there was no significant relationship between lighting and human productivity (P > 0.05). *Conclusion*. Based on the results, in assembly tasks, noise has a negative impact on human productivity, and lighting does not affect this. So, in order to increase employee productivity, noise control and reduction to less than the standard values (less than 85 dB) is necessary.

1. Introduction

Human productivity is optimized utilization of human talent, power, and skill to obtain maximum benefits along other factors in organizations and companies [1]. This issue is related to personal, organizational, social, and environmental (noise, lighting, temperature, etc.) factors [2]. In order to increase human productivity, the first step is always creating healthy working environment [3]. Besides having negative effect on human health like desire to increase resting time during working hours, reduction in human concentration, tiredness, and absence from work for being monotonous [4, 5], inappropriate inner environment has also a negative effect on human performance and their comfort during working hours. It has been estimated that inappropriate working environment causes millions of dollars losses [6]. So keeping work environment safe and healthy along with providing human health and comfort and increasing their productivity and performance will increase organization productivity and also will increase quality and quantity of its products and services.

Physical condition of the workplace in terms of environmental ergonomics, occupational health, and work psychology includes lighting, noise, temperature, relative humidity, and air flow rate [7–9]. Exposure to noise because of work is in connection with negative effect on human health, and its connection with being deaf has been truly approved. In industrial environment, exposure to the noise is in connection with a vast range of physical effects on health, in this regard we can mention heart disease and absence due to work illness and tiredness [10]. Moreover, some studies have shown the connection of response dose of noise exposure and outbreak of psychological distress in industrial workers [11]. So noise has negative effect on job satisfaction of workers [10] and as a result has negative effect on workers' productivity and performance [12]. In addition to direct influences, exposure to the noise in work environment has negative effect on human performance by causing psychological stress [13]. Also the studies have shown that noise exposure in work environment has negative effect on tasks needing concentration [14], performance in investigating and mental tasks needing high mental power [15], and measuring performance in detecting the number of repetitive tasks functions [16].

The direct and indirect influences of lighting intensity on human productivity and capacity as another environmental factor have been examined in various studies, such as improvement of lighting condition which will decrease vision disturbance and neck and shoulder pains [17]. Also improving lighting system causes decrease in eye fatigue and headache [18]. Also negative effect of lighting quality and its efficiency on occupational performance, human temper, health, job satisfaction, and comfort has been studyied. Energetic and high quality lighting provides more adjustment between the person and its work environment [19, 20].

Given the above, levels of noise and light by directly and indirectly affecting physical and mental aspects, impact human productivity and performance. So improving its condition will have positive effect on humans and their productivity. Because of assembling vehicles parts with different size and shape, automotive assembly industries require special physical and mental needs and making different aspects of work healthy, like controlling noise and improving lighting system which is an important and effective task. In most of the industries in Iran, noise is considered as a fundamental issue because of not observing controlling issues, which will influence human health and performance. Beside this, task nature in Iran is different from that of other countries, and this difference is because of occupational security, management, and labor law, amount of payment, and social, economic, and cultural conditions which will influence human productivity. So this study aims to investigate whether noise level and lighting intensity can have influence on human productivity regardless of the above-mentioned issues and if it is effective, how much it is, so we can improve the changes of this two parameters for improving human productivity.

2. Material and Methods

2.1. Subjects. This cross-sectional study has been done on 181 employees from different units of Farman Khodro Sepahan Co. (Isfahan, Iran) in August–November 2012. Different units in this study include administrative, commercial (buying and selling), assembly units of Nissan and Paykan, drilling, production, machining, welding, warehouse, and technoengineering. At first, demographic information including age, sex, height, weight, job experiment, level of education, job, and the related unit of each person has been gathered. Having at least one year of occupational background in related unit was the criterion for entering the test. Other factors include not having heart disease, severe muscular disorder, and diabetes. The factor for discluding the person from the study was his/her reluctance to cooperate and delivery of incomplete questionnaire.

2.2. Noise Level Measurement. For measuring noise level, Noise Level Meter TES-1358 model (TES Electrical Electronic Corp., Taiwan) was located near the stations of the persons to be studied for measuring noise level. Exposure to equivalent noise level (Leq) in each station was 8 hours of daily exposure and 40 hours of weekly exposure. Average level (Leq) was considered for each station. As operator station was fixed, local measurement of noise around the worker was used. Noise level gauges were calibrated by special calibrator, Lutron. Finally, for comparing achieved results by the Standard measurements, standard measurements of Iran noise level (1381, 2nd edition, technical committee of occupational health, Iran management office of work and environment health) were used which are according to the standards of ACGIH.

2.3. Lighting Measurement. To measure lighting in work environment, Light Meter TES-1336 model (TES Electrical Electronic Corp., Taiwan) was used in different units. This device was calibrated in reference laboratory of hygiene center of Isfahan province. Also it was calibrated by zero point calibration method before measuring in units. Measuring total lighting intensity (natural and artificial lighting) by lux was done in workers stations at the height of 30 inches. For comparing the amount of measured lighting intensity to the standard amounts, the standards announced by, 1381, 2nd edition, technical committee of occupational health, Iran management office of work and environment health were used which are according to the Standards of Lighting Engineering Association of North America (IESNA). The amount of lighting defined in this standard for each location has been defined as two amounts, the minimum amount and the recommended amount. The amount of needed lighting by LUX (luman/m²) should be according to the recommended amount of lighting.

2.4. Human Productivity Assessment. For determining the amount of productivity, 26-questionnaire of Goldsmith and Hersey [21] was used. In compilation of this model, these two researchers tried to determine the issues key factors that can have influence on human performance and also determine these issues in such a way that a manager can use them [21]. According to this, the variable related to effective performance of human will be defined like "ACHIEVE" model. And seven variables including ability, clarity and confidence, help (or support), incentive (or motivation), evaluation, validity, and environment were examined. Scoring this scale will be according to the 5-choice scale of Likert. Validity and stability of this scale were achieved by Kronbakh Alfa coefficient 0.81% by Ashkan Nasirpour et al. (2009) [22].

2.5. Statistics. All data were analyzed by using SPSS software (Chicago, IL, USA, version 20.0, SPSS Inc.). Descriptive statistics was used for examining the average and deviation of measured amounts criterion in the statistical group of the studied people. The relation between noise, lighting, and human productivity was examined by Pearson correlation coefficient test.

3. Results

The average of age, experience, height, weight, and BMI (standard deviation) in subjects were 34/11 (1.87) year, 1/7 (0/78) year, 172/6 (2/99) m, 72/17 (5/41) kg, and 24/25 (1/47) kg/m², respectively. The average amount of noise (standard deviation) in a network for all work stations according to dB (standard deviation) was 83/41 (8/46) dB (the range is between 64 and 102 dB). The average amount of lighting in all stations was 310/44, (177/48) (range is between 1310 and 75). Also for the purpose of examining lighting amount in two different seasons, this parameter was measured in August

TABLE 1: Average of noise, lighting, and productivity.

| Unit | Noise (dBA) | | Lighting (L | Productivity | |
|---------|---------------|--------|-------------|--------------|--------------|
| om | rtoise (ubri) | Actual | Minimum | Proposed | Troductivity |
| Tech-en | 71.87 | 195.25 | 300 | 500 | 72.42 |
| Mac | 86.00 | 321.55 | 300 | 500 | 58.07 |
| Ni-as | 85.62 | 275.75 | 300 | 500 | 69.07 |
| War | 69.57 | 164.57 | 300 | 500 | 52.16 |
| Pro | 92.50 | 289.10 | 300 | 500 | 65.88 |
| Pr-as | 88.70 | 305.36 | 200 | 300 | 63.88 |
| Off | 70.24 | 382.55 | 200 | 500 | 72.61 |
| Com | 77.57 | 466.42 | 300 | 500 | 81.25 |
| Dri | 89.66 | 510.66 | 300 | 500 | 56.00 |
| Wel | 90.00 | 203.88 | 200 | 300 | 58.20 |
| Total | 83.41 | 310.44 | _ | _ | 64.75 |

Actual, average measured, minimum, and proposed are standard values; lighting requirements (Lx) must be equal proposed values. Units: Tech-en: technical-engineering, Mac: machining, Ni-as: Nissan assembly, War: ware-house, Pro: production, Pr-as: pride assembly, Off: office, Com: commercial, Dri: drilling, Wel: welding.



FIGURE 1: Relationship between noise level (dBA) and human productivity in automotive assembly industry.

and November 2012, and its average was 320/35 (182/73) and 302/77(173/83), respectively. The average of productivity (standard deviation) was 64/75(15/33) (the range is between 26 and 112). The average of noise, lighting, and human productivity according to the units has been listed in Table 1.

The results gained from Pearson correlation coefficient between noise level and productivity level showed that productivity has a significant relationship with noise (P = 0.935, r = -0.178) (Figure 1). Analysis of data related to lighting and productivity by Pearson correlation coefficient showed that productivity does not have significant relationship with lighting intensity (P = 0.753, r = 0.027) (Figure 2).

The result of Pearson correlation coefficient between demographic factors and productivity showed that only age has a significant relationship with human productivity (P = 0.035, r = 0.177) (Figure 3). Other variables like occupational background, sex, BMI, height, and weight do not have a significant relationship.



FIGURE 2: Relationship between lighting (Lux) and human productivity in automotive assembly industry.



FIGURE 3: Relationship between age (year) and human productivity in automotive assembly industry.

4. Discussion

Automotive assembly industry by its own nature needs special mental and physical charges. Material handling, sitting at work stations, inappropriate postures and long-time sittings, locating small and big parts, repeated works, and and so forth are risk factors that influence mental and physical health of the human. From the point of view of macroergonomics, one of the most important relations along machine-human relation, system-human relation, and organization-human relation in work environment is the relation of environment and human [23, 24]. Making working environment parameters like noise, lighting, thermal stresses, ergonomics problems, and so on healthy and according to the standards is very important for providing health for workers and increasing their productivity and performance.

In this study, relationship between noise and lighting level with human productivity in automotive assembly industry was examined. The results have shown that in machining, production, Pride assembly, Nissan assembly, drilling, and welding units, the amount of noise level was more than national or international standards (>85 dBA). Also total lighting including natural and artificial lightings was less than the standard amounts in production, warehouse, Nissan assembly, and technoengineering units. The results gained from analysis of Pearson correlation coefficient have shown that there is a significant relationship. This relationship was reverse between noise level and human productivity. The results of this study are aligning with the results of other studies [25–27]. Nowier reports decrease in productivity due to increase of noise (1984-1985). Bergs (2002) reported meaningful difference between noise level and productivity. Also Tafalla and Evans (1997) reported the decrease of productivity due to noise increasing.

The achieved results of Pearson correlation coefficient did not report any significant relationship between influence of lighting (Lx) and human productivity. Therefore, it has been made clear that lighting amount does not have any influence on human productivity of automobile parts assembly unit and also its changes do not have any influence on productivity of other people in other units. Despite this, most studies have reported improvement of productivity due to improvement of lighting condition. Juslén et al. (2007) have made a research on examining the influence of lighting on the working speed and work quality of electrical devices assembly unit and have reported that production speed in working environment having 1200 lux is 2/9% more than 800 lux and in winter, with higher amount of light, was 3.1% more [28]. Also Niemelä et al. (2002) have reported an increase in productivity due to improvement of lighting condition, aligning with other factors in working environment [29]. According to Hedge (2004), too much luminosity and dazzling in working stations cause a decrease in human performance and productivity. He believes that according to the task the person does and his age, need to lighting will be different [30].

The result of Pearson correlation coefficient has shown that there is a meaningful relationship between personal variables, age, with productivity, and by aging, human productivity will increase. Of course this study was done among the persons of 30/8 to 39/4 years old. Schwab and Heneman have informed that elderly workers are of more productivity than youngers [31]. Skirbekk (2008) has announced that in tasks which need solving a problem, learning, and also speed, aging will decrease productivity while in tasks that experience and verbal ability are important, productivity will slightly decrease or maybe will not at all [32].

5. Conclusion

The aim of this study was examining relationship between lighting and noise level on human productivity in automotive assembly industry. Noise level in workplace has negative effect on human productivity which leads to decrease in organization productivity and decrease in quality and quantity of services and products. Therefore, it is recommended to control noise level of workplace and decrease it to standard level (less than 85 dB) to increase comfort and human productivity. Nevertheless, lighting as another environmental factor did not have effect on human productivity, and changes in lighting did not have a relationship with changes of human productivity.

Among young workers, by aging, the productivity will increase till middle age period. In this case, the skills and experience of working and learning more about the processes and tasks increase human productivity in the workplace. But more study is needed for examining human productivity in different age groups and also determining effective factors of human productivity.

Acknowledgments

This paper is the result of a research project approved in the School of Health, Isfahan University of Medical Sciences. The authors sincerely thank the Farman Khodro Sepahan company (F.K.S) and its employees.

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Research Article

Efficiency of Constructed Wetland Vegetated with *Cyperus alternifolius* Applied for Municipal Wastewater Treatment

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Received 1 March 2013; Revised 10 July 2013; Accepted 10 July 2013

Academic Editor: Mohammad Mehdi Amin

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The treatment of municipal wastewater from Yazd city (center of Iran) by constructed wetland vegetated with *Cyperus alternifolius* was assessed. Two identical wetlands with a total working volume of 60 L and 10 cm sandy layer at the bottom were used. First wetland (W1) was control and had no *Cyperus alternifolius* plant. Second wetland (W2) had 100 *Cyperus alternifolius* shrubs with 40 cm height. Influent wastewater was provided from Yazd's septic tanks effluents and after a 4-day retention time in wetlands, reactors effluent was sampled for parameters analysis. Results show that chemical oxygen demand (COD), NO⁻₃-N, NH⁺₄-N, and PO⁻³₄-P in W1 were reduced to 72%, 88%, 32%, and 0.8%, and in W2, these parameters were removed in values of 83%, 81%, 47%, and 10%, respectively. In both wetlands, the highest and lowest removal efficiencies were related to COD and phosphorus, respectively. Also, the removed phosphorus can be released to stream when the soil saturated or influent phosphorus decreased and when the plant died. After a 4-day-retention time, the W2 wetland showed a statistically significantly lower COD and NH⁺₄-N in comparison with W2 wetland.

1. Introduction

As the word suggests, a natural wetland is an area of ground that is saturated with water, at least periodically. Plants that grow in wetlands, which are often called wetland plants or saprophyte, have to be capable of adapting to the growth in saturated soil [1]. Wetland plants are an important component of wetlands, and the plants have several roles in relation to the wastewater treatment processes. The ability of wetlands to transform and store organic matter and nutrients has resulted in a widespread use of wetland for wastewater treatment worldwide [2]. Wetlands can be used for primary, secondary, and tertiary treatments of domestic wastewater, storm wastewater, combined sewer overflows (CSF), overland runoff, and industrial wastewater such as landfill leachate and petrochemical industries wastewater [3, 4].

Moreover, the use of constructed wetlands is now recognized as an accepted ecotechnology especially beneficial to small towns or industries that cannot afford expensive conventional treatment systems [5, 6]. The most common systems are designed with horizontal subsurface flow (HF CWs) but vertical flow (VF CWs) systems are getting more popular at present. Constructed wetlands with free water surface (FWS CWs) are not used as much as the HF or VF systems despite being one of the oldest designs in Europe [1, 7]. Constructed wetlands (CWs) for wastewater treatment are potentially a good solution for treating domestic and industrial wastewaters in less-developed countries with warm and tropical climates [8]. The selection of plants is an important matter regarding wetlands. Selected plants must be tolerant to toxicity and the changes in the entering wastewater characters. In Europe, most plants used in wetlands are *Phragmites australis.* However, other species such as *Typha* spp., Scirpus spp., and Phalaris arundinacea are also used in wetlands. In Portugal, such species as P. australis, Iris pseudacorus, and Cyperus spp. are used as macrophytes in wetlands [4]. Umbrella sedge or umbrella palm whose scientific name is Cyperus alternifolius is a multi-year-old plant that can be grown in humid soil or in marshy areas. The plant has strong underground root and erect aerial stem which does not have any branches. Cyperus alternifolius can be easily multiplied using seeds and pieces of the plant [9]. It has been used in different studies as a wetland plant. Cyperus alternifolius' advantage compared with other plants like Miscanthidium violaceumis is that it eliminates nutrients of the wastewater [10].

Yazd with the area of $131,551 \text{ km}^2$ is situated at an oasis where the Dasht-e Kavir desert and the Dasht-e Lut desert meet. The city itself is located at 1203 m. above sea-level, and it covers $16,000 \text{ km}^2$. The population of the Yazd city was 550,000 at the 2011 census.

Yazd is the driest major city in Iran with an average annual rainfall of only 60 mm, and it is also the hottest north of the persian gulf coast with summer temperatures very frequently above 40° C in blazing sunshine with no humidity.

Given the cost-effectiveness of the wetlands for the purpose of wastewaters treatment and easy planting of *Cyperus alternifolius*, the present research studies this plant as wetland macrophyte under the weather conditions of Yazd, in Iran, for municipal wastewater treatment. In addition, the nutrient removal efficiencies by constructed wetland vegetated with *Cyperus alternifolius* were studied and discussed.

2. Materials and Methods

2.1. Chemicals and Instrumentation. All the chemicals in this study were of extra pure or analytical grade and prepared from Merck Co. COD, nitrate, ammonia, and phosphorus concentrations in influent and effluent wastewater solutions were measured using a Dr/2000 HACH spectrophotometer (Germany).

2.2. Wetland Setup and Tests Procedure. The present research is an interventional study and surveys the efficiency of the *Cyperus alternifolius* in eliminating the parameters such as COD, nitrate (NO_3^--N) , ammonia (NH_4^+-N) , and phosphorus $(PO_4^{-3}-P)$ in the winter of 2011 in Yazd. Two identical wetlands with a length of 50, a width of 40, and a depth of 30 cm with a total working volume of 60 L were operated in parallel and fed with Yazd municipal wastewater. Sandy layer with a height of 10 cm by various diameters was put at the bottom of the reactor. Larger sands were put near the reactor's tap and the medium and small size sands were put on the middle and the end of the reactor, respectively. Some clay was also added to the reactors. In the main reactor (W2), 100 *Cyperus alternifolius* with an average size of 40 cm were planted. Figure 1 shows the design and setup of wetland with *Cyperus alternifolius* in a laboratory.

In control wetland (W1), the *Cyperus alternifolius* plants were not cultivated inside W1. The wastewater entering in both reactors was derived from Yazd's septic tank. Average pH and temperature of the incoming wastewater were 8.6 and 16.5° C during the project. At first, 8 L of wastewater was poured to each reactor and the variation of wastewater parameters in outlet after 4 days was examined. The efficiency of *Cyperus alternifolius* in wastewater treatment was studied by comparing the level of parameters in the inlet and outlet of the reactor.

The nominal hydraulic retention time (HRT) is defined as the ratio of the useable wetland water volume to the average flow rate (Q_{ave}). The theoretical HRT can be calculated as follows:

$$t = \frac{V_W \times \epsilon}{Q_{\text{ave}}},\tag{1}$$

where V_W is the volume constructed wetland and ϵ is the porosity of a wetland. The wetland porosity values have ranged from 0.65 to 0.75 for fully vegetated wetlands and for dense to less-mature wetlands, respectively [11, 12].

2.3. Analysis of Samples. Wastewater samples were analyzed for NO_3^--N , NH_4^+-N and $PO_4^{-3}-P$ contents by a spectrophotometer. COD was measured according to the Standard Methods [13].

2.4. Statistical Analyses. Tests for significant differences between treatments (various influent parameters and reactors) were determined by a two-sample *t*-test (or Mann-Whitney). Pearson correlation coefficients were used to examine the relationship between the initial concentration of each parameter and related removal efficiency. The results were considered significant when P < 0.05. All calculations were performed through the version 18 of SPSS for windows.

3. Results

3.1. Effect of Cyperus alternifolius on COD Removal. The municipal wastewater from Yazd city (Iran) was treated in two identical wetlands as main and control (W2 and W1). The performance of Cyperus alternifolius was assessed and analyzed for COD removal in COD concentration of 432, 462, 464, 437, 484, and 420 mg/L corresponding to COD loading of 2.16, 2.31, 2.32, 2.19, 2.42, and 2.1 g/m².d, respectively. Figure 2 shows the wastewater COD in the different COD concentration and COD loading.

In general, the main reactor exhibited significant (P value < 0.05) higher values for the COD removal compared to the control reactor (Table 1). Relatively high correlation was not observed between initial COD concentration and the removal percentage of COD (r: 0.28, P value > 0.38).

3.2. Variation of NO_3^- -N Concentration by Cyperus alternifolius. To determine the variation of NO_3^- -N concentration by Cyperus alternifolius, the NO_3^- -N removal with



FIGURE 1: Design of constructed wetland vegetated with *Cyperus alternifolius*.



FIGURE 2: Effect of initial COD concentration on effluent and removal percentage of COD in W1 and W2 (HRT: 42 d and 16.5° C).

TABLE 1: Comparison of effluent concentration and removal efficiency of COD by each reactor.

| Peactor | Effluent | | | Removal | | |
|---------|----------|-------|----------------|---------|------|----------------|
| Reactor | Mean | SD | <i>t</i> -test | Mean | SD | <i>t</i> -test |
| W1 | 124.67 | 27.23 | 0.004 | 72.15 | 6.72 | 0.007 |
| W2 | 75.5 | 18.33 | | 83.15 | 4.45 | 0.007 |

initial NO_3^- -N concentration of 11, 13.8, 13.9, 14.7, 22.3, and 29.4 mg/L was investigated over NO_3^- -N loading of 0.055, 0.069, 0.07, 0.074, 0.112, and 0.147 g/m².d, respectively.

Figure 3 illustrates the changes of nitrate concentrations by considering influent concentration, loading rate, and reactor type. Over all, Figure 3 shows that the nitrate removal percentage was higher in reactor *by Cyperus alternifolius* (W2) than that without *Cyperus alternifolius* (W1) under the conditions evaluated. The results are depicted in Figure 3, which shows an increase in the nitrate removal efficiency over time with increasing initial nitrate concentration. In W1 and W2, the highest nitrate removal efficiency was obtained at 29.4 mg/L initial nitrate concentration and corresponding to nitrate removal efficiency of 94 and 93%, respectively.

The effluent concentration and removal of NO_3^--N by W1 and W2 were statistically compared using the Mann–Whitney U tests (Table 2). The NO_3^--N effluent concentration from *Cyperus alternifolius* wetland (W2) was not



FIGURE 3: Variation of effluent NO_3^- –N concentration in W1 and W2 (HRT: 42 d and 16.5°C).

TABLE 2: Comparison of effluent concentration and removal efficiency of NO_3^- -N by each reactor.

| Ponctor | Effluent | | | Removal | | |
|---------|----------|------|----------------|---------|-------|----------------|
| Reactor | Mean | SD | <i>t</i> -test | Mean | SD | <i>t</i> -test |
| W1 | 2.15 | 0.58 | 0.52 | 86.22 | 5.68 | 0.75 |
| W2 | 3.27 | 2.57 | 0.32 | 76.15 | 26.22 | 0.75 |
| | | | | | | |

significantly higher in comparison with the nitrate effluent concentration from control reactor (P value > 0.05). Relatively high correlation was not observed between initial NO₃⁻-N concentration and NO₃⁻-N removal (r: 0.52, P value > 0.08).

3.3. Influence of $PO_4^{-3}-P$ Concentration in the Phosphorus Removal. The effect of Cyperus alternifolius on the phosphorus removal was studied using different initial $PO_4^{-3}-P$ concentrations 4.38, 3.62, 5.25, 5.38, 6.5, and 6.88 mg/L and $PO_4^{-3}-P$ loading of 0.022, 0.018, 0.026, 0.027, 0.033, and 0.034 g/m².d, respectively. The variation of influent and effluent $PO_4^{-3}-P$ concentration and $PO_4^{-3}-P$ removal efficiencies using W1 and W2 are illustrated in Figure 4. As seen in Figure 4, $PO_4^{-3}-P$ removal decreased almost linearly by mounting influent $PO_4^{-3}-P$ concentration increased from 4.4 to 6.8 mg/L, the removal efficiency fluctuated from 17 and 23% to -2 and 2%, respectively.

Table 3 presents the results of average and standard deviation of effluent $PO_4^{-3}-P$ concentration and $PO_4^{-3}-P$ removal efficiency. W1 and W2 were statistically compared using the independent samples *t*-test (Table 3). For each effluent $PO_4^{-3}-P$ concentration and $PO_4^{-3}-P$ removal efficiency, no significant differences between the W1 and W2 were observed (*P* value > 0.05). Relatively high correlation was not observed between initial $PO_4^{-3}-P$ concentration and their removal efficiency (*r*: -0.46, *P* value > 0.13).

3.4. NH_4^+ -N Removal Function of Initial NH_4^+ -N Concentration. The efficiency of Cyperus alternifolius for NH_4^+ -N



FIGURE 4: Effluent concentration and removal efficiency of $PO_4^{-3}-P$ as functions of initial concentration (HRT: 42 d and 16.5°C).

TABLE 3: Comparison of effluent concentration and removal efficiency of PO_4^{-3} -P by each reactor.

| Reactor | Effluent | | | Removal | | |
|---------|----------|------|----------------|---------|-------|----------------|
| | Mean | SD | <i>t</i> -test | Mean | SD | <i>t</i> -test |
| W1 | 5.29 | 1.38 | 0.59 | 1.17 | 9.29 | 0.11 |
| W2 | 4.81 | 1.55 | | 11.41 | 10.91 | |

removal was assessed in NH_4^+-N concentration of 62.3, 58.3, 52, 56, 5, 62, and 67.5 mg/L corresponding to NH_4^+-N loading of 0.31, 0.29, 0.26, 0.28, 0.31, and 0.34 g/m².d, respectively. Figure 5 gives the NH_4^+-N removal percentage in both reactors function of initial NH_4^+-N concentration. The results are depicted in Figure 5, which shows a decline in the NH_4^+-N removal efficiency with rising initial NH_4^+-N concentration. It was found that the NH_4^+-N removal efficiency by W1 and W2 diminished from 43% and 71% to 28% and 45% when the NH_4^+-N concentration was amplified from 62 to 68 mg/L, respectively.

As seen in Table 4, in the initial NH_4^+-N concentration 62 to 68 mg/L, the W2 showed a low effluent NH_4^+-N concentration in comparison with the W1; however, the difference was statistically significant (*P* value > 0.05). Relatively high correlation was not observed between initial NH_4^+-N concentration and removal percentage of NH_4^+-N (*r*: -0.026, *P* value > 0.93).

4. Discussion

The study found that the highest efficiency of wetland in wastewater treatment was related to the elimination of COD, which increased at the presence of *Cyperus alternifolius*. The lowest efficiency was seen for Phosphorus elimination which did not show a significant change at the presence of *Cyperus alternifolius* (9.8%). The cause of little elimination of phosphorus in the control reactor is phosphorus absorption by the soil, biological elimination by existing bacteria, and complex formation and sediment at the presence of calcium, iron, and magnesium [10, 14]. The amount of phosphorus removal in similar systems that used *Cyperus alternifolius*



FIGURE 5: Influence of initial NH_4^+ –N concentration on effluent and removal efficiency of NH_4^+ –N in W1 and W2 (HRT: 42 d and 16.5°C).

was reported as 83.2% and in another study was less than 20% [10, 14, 15]. As shown in Figure 4, in some points, the amount of outlet phosphorus is more than the inlet phosphorus (negative elimination efficiency), which is caused by the release of phosphorus. In some other studies, the release of phosphorus was reported during the saturation of soil or during the reduction of incoming phosphorus. Another reason behind the increase in the outlet phosphorus in the main reactor in this study could be the death of Cyperus alternifolius and the release of the phosphorus from the pieces of the plant [14]. The amount of eliminated ammonium (NH_4^+-N) in the main reactor is 43%, which had 10% rise compared to that of the control reactor. An elimination amount of 75.3%, 70%, and less than 20% has been reported for ammonium $(NH_4^+ - N)$ [10, 15]. The processes helping the elimination of ammonium are the absorption by the plant and bacterial nitrification/de-nitrification [10]. In various studies, the efficiency of wetlands in the elimination of ammonium (NH_4^+-N) has been reported differently, even as little as 1% [14]. One mechanism for ammonium (NH_4^+-N) removal is volatilization, that happened in pH > 9; thus this mechanism effect is minimal in this study (pH in this study: 8.5) [10]. Cui et al. (2009) found that in China Cyperus alternifolius played a considerable role in eliminating TN (total nitrogen) from the domestic wastewater in artificial wetland with a vertical current [16]. Liao et al. studied the ability of Cyperus alternifolius and Vetiver in treating the pig farm wastewater. The efficiency of the BOD, COD, NH₄⁺-N, and TP (total phosphorus) removal in this study was 68%, 64%, 20%, and 18%, respectively [9]. In another study, the ability of Cyperus alternifolius in elimination of nutrients including nitrogen, phosphorus, copper, and zinc from wastewater was reported to be from 4 to 7 times more than that of Vetiveria zizanioides plant [17]. The COD removal in the main reactor was very high. This high level was maintained during the study and only a small decrease was observed near the end of the study. The decrease may have been caused by the death of the plants. This was going to decrease with phosphorus rise in outlet samples, which supported the death of the plant at this stage [14].

TABLE 4: Comparison of effluent concentration and removal efficiency of NH_4^+ -N by each reactor.

| Reactor | Effluent | | | Removal | | |
|---------|----------|------|----------------|---------|-------|--------|
| | Mean | SD | <i>t</i> -test | Mean | SD | t-test |
| W1 | 40.5 | 6.42 | 0.068 | 32.36 | 7.22 | 0.039 |
| W2 | 31.5 | 8.65 | | 47.19 | 13.53 | |

5. Conclusion

As a matter of fact, using Cyperus alternifolius is capable of eliminating such parameters as COD properly. When primary treatment of wastewater is essential, application of this plant is very helpful and produce good results. However, the same system is not appropriate for advanced wastewater treatments; that is, this system is not helpful for tertiary purposes and nutrients removal such asphosphorus. This could be because of local conditions. Therefore, it is recommended to use Cyperus alternifolius with another plant that is well capable of phosphorus elimination. It is also suggested that outgoing wastewater be treated in a separate stage through chemical techniques for phosphorus eliminating. Overall, Cyperus alternifolius has been widely used in wetlands because of its cost-effectiveness; it can also be used as forage for livestock and aquaculture, and it is costeffective due to fast growing.

Acknowledgment

The present study is part of the research project approved by the Research Department of the Faculty of Health at Shahid Sadouqi Medical University of Yazd, to which the authors express their gratitude.

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Research Article

Do US Ambient Air Lead Levels Have a Significant Impact on Childhood Blood Lead Levels: Results of a National Study

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Received 10 December 2012; Accepted 6 June 2013

Academic Editor: Mohammad Mehdi Amin

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Introduction. Although lead paint and leaded gasoline have not been used in the US for thirty years, thousands of US children continue to have blood lead levels (BLLs) of concern. *Methods.* We investigated the potential association of modeled air lead levels and BLLs $\geq 10 \,\mu$ g/dL using a large CDC database with BLLs on children aged 0–3 years. Percent of children with BLLs $\geq 10 \,\mu$ g/dL (2000–2007) by county and proportion of pre-50 housing and SES variables were merged with the US EPA's National Air Toxics Assessment (NATA) modeled air lead data. *Results.* The proportion with BLL $\geq 10 \,\mu$ g/dL was 1.24% in the highest air lead counties, and the proportion with BLL $\geq 10 \,\mu$ g/dL was 0.36% in the lowest air lead counties, resulting in a crude prevalence ratio of 3.4. Further analysis using multivariate negative binomial regression revealed that NATA lead was a significant predictor of % BLL $\geq 10 \,\mu$ g/dL after controlling for percent pre-1950 housing, percent rural, and percent black. A geospatial regression revealed that air lead, percent older housing, and poverty were all significant predictors of % BLL $\geq 10 \,\mu$ g/dL. *Conclusions.* More emphasis should be given to potential sources of ambient air lead near residential areas.

1. Introduction

Although blood lead levels (BLL) in US children have been dramatically reduced over the past 40 years [1], lead poisoning events continue to occur. The Lead-Based Paint Poisoning Prevention Act legislation was passed in 1971, and by 1978 the use of lead-based paint in residential housing was banned [2]. Regulations phasing out lead in gasoline were implemented in 1973. The elimination of lead from these two sources has resulted in a dramatic reduction in BLLs. However, there are still subgroups of children in both urban and rural areas with high BLLs. Data evaluated from 26 states that are part of the Centers for Disease Control (CDC) Childhood Lead Poisoning Prevention Program (CLPPP) and have data available on the CDC Environmental Public Health Tracking Network (Tracking Network) revealed that almost 95,000 children between 0 and 3 years of age had confirmed blood lead $\geq 10 \ \mu g/dL$ from 2000 to 2007 with an estimated 7,000 children in 2006 alone.

In 2002, over 9,000 industrial sites reported lead releases to the US Environmental Protection Agency (EPA) Toxic Release Inventory (TRI) [3]. Lead is one of the EPA [4] Criteria Air Pollutants that have been established as harmful to either human health or the environment. The current National Ambient Air Quality Standards for lead are $0.15 \,\mu g/m^3$ for a rolling 3-month average and $1.5 \,\mu g/m^3$ for

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a quarterly average. The contribution of industrial sources to BLLs has been studied in select industrial communities [5–8]; however, a rigorous systematic evaluation of ambient air lead and its possible contribution to blood lead in US children has not been done at the county level or census tract level.

Aside from many occupational studies [9–12] that link air and dust lead from lead smelters, battery reclamation, and mining jobs with high BLLs among workers, there have been very few studies that specifically examined the contributions of lead in air and lead in soil to childhood BLLs [13–20]. Although a great deal has been accomplished to minimize the exposure to lead paint in the US, little research has been done to quantify the modest but consistently higher childhood BLLs among those living in areas near industrial sources emitting lead.

A review article by Levin et al. [19] estimates that lead paint and dust from household sources account for up to 70% of BLL $\geq 10 \,\mu g/dL$ in US children, but more than 30% of these children do not have exposure to lead paint in their home. Most recently, Miranda et al. [20] evaluated children's BLLs by proximity to airports with planes using avgas, a leaded fuel used in small aircraft. The highest BLLs were in children within 500 m of an airport, but there was an impact within 1000 m. The US EPA [21] has determined that exposure to lead from avgas may be through inhalation directly from air or ingestion from soil after the lead has deposited.

Although BLLs in the US have fallen considerably with the removal of lead in gasoline and the considerable efforts of the Healthy Homes and Lead Poisoning Prevention Branch (HHLPPB) at CDC, Housing and Urban Development (HUD), and state and local health departments, there are counties in the US where as many as 10% of screened children have a BLL $\ge 10 \,\mu g/dL$. Clusters of higher BLLs raise considerable concern that we have not completed the task. The Tracking Network houses over five million childhood blood lead results by county and the proportion of children per county who have confirmed BLLs $\geq 10 \,\mu g/dL$. Given the availability of these data and the information on air lead levels by census tract and county from the USEPA National-Scale Air Toxics Assessment (NATA), we evaluated the linkage of these two comprehensive databases to determine the overall relationship at the ecological level as the first step in understanding the role of ambient air lead to childhood blood lead poisoning. The purpose of this investigation is to utilize air lead exposure and biomonitoring data on childhood blood lead screening available on the Tracking Network to develop methods to characterize populations who may be at higher risk of lead poisoning.

2. Methods

The Tracking Network uses data collected by state and local childhood lead poisoning prevention programs to track childhood BLL. It is recommended that high-risk children are screened for blood lead between the ages of 0–3. The results of these tests are provided to state and local public health programs, funded in part by HHLPPB. The state and local departments then share information with the HHLPPB

to compile a national database. To conduct a comprehensive nation-wide evaluation of the impact of air lead on children's BLLs, the University of Pittsburgh requested childhood blood lead data from the HHLPPB for 1644 (52%) of the 3220 US counties.

Some states mandatorily test all children aged 0-3, while others test only a "targeted" population most at risk for lead poisoning, usually those who receive Medicaid or live in older housing. Data included the number of children ages 0-3 found to have BLL $\geq 10 \,\mu g/dL$ and the number of children who had blood lead testing for each year 2000-2007 by county. Summary information, including the total number of children tested per county for all years available, was calculated using SPSS version 18. For the following analysis, only those counties with at least 50 children tested over the eight year period were selected (n = 1508 counties). The excluded counties tested an average of four children per year and had an average population of 29,372. For 2007, only 77 of the 1508 (5%) had reported lead data at the time of the data request. Therefore, 2007 data is also not presented. Annual percent high and a summary total $\geq 10 \,\mu g/dL$, total tested, and percent $\geq 10 \,\mu g/dL$ per county were calculated using SPSS.

2.1. NATA Data (2002 and 2005). Every three years since 1996, EPA has compiled a national-scale air toxics assessment (NATA). The assessment is a state-of-the-science tool that provides estimates of the concentrations, exposures, and broad estimates of the risk from breathing air toxics. In 2002, NATA evaluated 180 of the 187 Air Toxics, including lead and lead compounds. The 2005 NATA estimated 177 of the 187 air toxics. The NATA assessment involves compiling a national air toxics emissions inventory of outdoor stationary and mobile sources (National Emissions Inventory, NEI). These sources include major stationary sources, for example, large waste incinerators and factories; area and other sources, for example, dry cleaners, small manufacturers, and wildfires; and both on road and nonroad mobile sources, for example, cars, trucks, planes, and boats.

We conducted a sensitivity analysis of the validity of NATA estimates. The EPA monitors to which we compared the NATA estimates exist for these regulatory purposes. Under the Clean Air Act, EPA sets and reviews national air quality standards for lead. We compared the average yearly measurement from these lead monitors to the NATA concentration estimate in the census tract in which the monitor sits. The over 200 lead monitors measure concentrations of lead throughout the country. Quartiles of NATA concentrations and quartiles of monitor readings were compared using weighted Kappa statistics.

We used modeled ambient concentrations of lead and lead compounds at the county level for the 2005 National-Scale Air Toxic Assessment (NATA downloaded from the EPA website) [22]. There were notable improvements from the 2002 to 2005 NATA estimates, which include inclusion of 19,000 airports as point sources, onroad and nonroad inventories were updated, and the state-of-the-art Community Multi-Scale Air Modeling (CMAQ) model was used. Because of these improvements, the 2005 model was used. These air lead levels were merged by FIPS code to the county of interest and its corresponding blood lead testing data.

2.2. 2000 Census Data. Additional county-level census variables that were downloaded to explore their predictive value for childhood BLLs include percentage of older (pre-1950) housing, percent living in poverty, and racial makeup of the county. The three types of data (health, EPA NATA, and Census) were merged by FIPS code using SPSS.

In addition, counties were classified into the following based upon the NCHS Urban Rural Classification Scheme Methodology [23]. They were classified into (1) Central counties of a metro area with more than a million people, (2) fringe counties of a metro area of more than a million people, (3) counties in a metro area of 250,000 to 999,999 people, (4) counties in a metro area of 50,000 to 24,999 people, (5) micropolitan counties (20,000 to 49,999, adjacent to a metro area), and (6) noncore counties, with a population between 20,000 and 49,999 and not adjacent to a metro area or a population under 20,000 whether or not they are adjacent to a metro area. For this analysis, classification no. 1 is "Urban," no. 2–5 are "Suburban," and no. 6 is "Rural."

2.3. Data Analysis. First, we compared the mean proportion of children with high BLL who reside in the top 10% (highest decile) of high air lead counties with the proportion with high BLL who reside in the counties with the lowest air lead (lowest decile). Second, a nonparametric correlation matrix was created and analyzed to determine the degree of interrelationship between percent pre-1950 housing, poverty, race, rural (as defined by the National Center for Health Statistics), and percent of children with BLL \geq 10 µg/dL.

In order to utilize the relationship between the proportion of children with high BLL and demographic/census variables such as NATA air lead estimate in 2005, percent pre-1950 housing, rural, African Americans, and percent of population at less than 185% of poverty, we first applied multiple linear regression. However, our response variable and model did not meet the assumptions of normality and linearity. Therefore, we used Box-Cox transformation with parameter 0.297 (indicating a cube root transformation) to improve normality and linearity. The Box-Cox generalizes power transformations as

$$y_i^{\theta} = \frac{\left(y_i^{\theta} - 1\right)}{\theta}, \quad \text{where } \theta \neq 0,$$

$$y_i^{\theta} = \ln\left(y_i\right), \quad \text{where } \theta = 0$$
(1)

- θ = 2 square transformation
- $\theta = 1$ (no transformation)
- $\theta = 1/2$ square root transformation
- $\theta = 1/3$ cube root transformation
- $\theta = 0 \log \text{transformation}$
- $\theta = -1$ reciprocal transformation.

2.4. Negative Binomial Regression. As an alternative to using the proportion of children with high BLL as the dependent variable, we modeled the counts of children with high BLL among total number of children tested per county from 2000 to 2007 (offsetting the number of children tested) using Poisson regression. Because the Poisson regression models indicated overdispersion (variance exceeding the mean) our final models were based on negative binomial regression. These models were used to investigate the dependence of counts of children with high blood levels on the NATA air lead estimates without and with adjustment for the demographic and census variables noted above.

The negative binomial log linear regression for the rate is

$$\log\left(\frac{\mu}{n}\right) = \alpha + \beta x,$$

$$\log\left(\mu\right) - \log\left(n\right) = \alpha + \beta x,$$

$$\mu = n e^{\alpha + \beta x},$$
(2)

where μ is the expected value of counts (ex: the expected value of children with high BLLs), *n* is index of the time or space (ex: total number of children tested per county), and $-\log(n)$ is an adjustment term which is referred to as an offset, and each subject may have a different value of *n*.

2.5. Spatial Linear Regression. Counties in our sample are spatially related to each other by virtue of being spatial neighbor and therefore subject to common underlying exposures. Spatial autocorrelation (or dependence) is measured in terms of first-order (i.e., only adjacent counties) contiguity where the dependent variable or error term for each county is correlated with observations for the dependent variable or error term at contiguous locations. Aspatial forms of regression are applied to all of the data within a county, quantifying global relationships between variables, assuming no spatial correlation. These results serve as our baseline analysis. If the relationship across space between the independent variable(s) and dependent variables does not change, and error terms are independent between counties, the aspatial regression would provide our final results.

However, as we detected significant spatial correlation among residuals from the aspatial regression, we next considered spatial regression allowing correlated residual terms. However, as the dependent variable did not approximate the normal distribution, the cube root of the term percent $\geq 10 \,\mu$ g/dL was taken, as spatial regression uses a multiple linear regression. We begin with general formulation of spatial regression model defined as a spatial lag model and also referred to as the spatial autoregressive model. The spatial lag model is expressed as follows:

$$Y = \rho W y + X \beta + \varepsilon,$$

$$\varepsilon \sim N \left(0, \sigma^2 I_n \right),$$
(3)

where *Y* is an *n* by 1 vector of observations on the dependent variable (percent with BLL $\ge 10 \,\mu\text{g/dL}$), *X* is the matrix of county characteristics, W_v is the row-standardized spatial



FIGURE 1: Mean concentrations of Pb from criteria air pollutant lead monitors by NATA percentile.

weight matrix, and the parameter ρ is a coefficient on the spatial lag of the dependent variable. "*Wy*" captures the extent to which BLLs are affected by levels in contiguous counties. β denotes the vector of coefficients associated with the independent variables and ε denotes the error terms (25). The blood level data by county is only available for selected counties in the US, and as such the boundary file has "islands" where no data are available for BLL. We therefore cannot calculate a contiguity matrix that expresses the neighborhood structure. We are therefore limited to using a distance matrix for a spatial weight matrix using the centroids of each county with BLL data. This avoids problems of "islands" in the data.

ArcGIS version 10 provides the polygons representing all the counties in our sample. GeoDa (a freely downloadable software package) version 0.9.5-i by Luc Anselin was used to develop and estimate the spatial lag.

3. Results

The sensitivity analysis of lead monitor readings and NATA air lead estimates indicated a correlation of R = 0.91 (P < .001) and a Kappa of 0.424, which indicates good agreement (26). See Figure 1.

In 2000, the proportion of children <36 months of age with BLL $\geq 10 \,\mu$ g/dL ranged from 8.89% (IL) to 0.42% (KY, WA). In 2006, this ranged from 2.45% (CT) to 0.42% (LA). The proportion of children with BLL $\geq 10 \,\mu$ g/dL in general fell from 2000 to 2006, among most states for example, Michigan from 4.06% in 2000 to 0.98% in 2006 and Ohio from 3.5% in 2000 to 1.21% in 2006 and among those tested in Illinois 8.89% were over 10 μ g/dL in 2000 and 3.52% in 2004. Clearly, pockets of children at high risk for childhood lead poisoning remain across the country. See Table 1.

When the counties that were included in the sample were stratified into highest and lowest deciles of air lead, we found that the highest ten percent of air lead included those counties with total concentrations greater than $0.00297 \,\mu\text{g/m}^3$ while the counties with the lowest decile of air lead had concentrations below $0.000526 \,\mu\text{g/m}^3$. The proportion with



FIGURE 2: Cumulative percentage of children with BLL $\ge 10 \ \mu g/dL$ by county, 2000–2007.

BLL $\ge 10 \,\mu$ g/dL was 1.24% in the highest air lead counties, and the proportion with BLL $\ge 10 \,\mu$ g/dL was 0.36% in the lowest air lead counties, resulting in a crude prevalence ratio of 3.4. See Figure 2.

The counties included in this analysis had a range of poverty (from 2.6 to 41.1%), minority (from 0.3 to 86.5% Black), and older housing (from 0.8 to 66.7%). Population within a county ranged from less than 2000 to over five million. As these have been established as important independent predictors of lead burden, these were controlled for in the analysis. See Table 2.

BLL $\geq 10 \,\mu$ g/dL by county were moderately correlated with NATA lead (r = 0.15, P < .001) and older housing (r = 0.37, P < .001) by county. The census covariates (poverty, rural, Black) were all highly correlated with NATA exposure estimates (P < .001).

A negative binomial regression was considered with blood lead data as the dependent (predicted) variable and air lead, percent pre-1950 housing, and percent rural as the

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TABLE 1: Percentage of children with BLL $\geq 10 \,\mu g/dL$ by state and year, 2000–2006.*

| State | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 | 2006 | Universal testing |
|-------|------|------|------|------|------|------|------|-------------------|
| US | 1.55 | 1.39 | 1.32 | 1.07 | 0.97 | 0.75 | 0.70 | |
| AZ | 2.29 | 2.13 | 4.95 | 1.25 | 0.47 | _ | — | Targeted |
| CO | — | _ | _ | _ | — | _ | _ | Mandatory |
| СТ | 4.50 | 4.20 | 3.95 | 3.90 | 3.27 | 2.99 | 2.45 | Mandatory |
| FL | 0.96 | 0.86 | 0.50 | 0.36 | 0.30 | _ | _ | Targeted |
| GA | 0.76 | 0.62 | 0.53 | 0.31 | 0.22 | 0.18 | | Targeted |
| IA | 2.21 | 1.98 | 1.87 | 1.69 | 1.53 | 1.12 | 0.89 | Mandatory |
| IL | 8.89 | 6.75 | 5.00 | 4.26 | 3.52 | | | Targeted |
| KS | 2.50 | 1.64 | 1.10 | 1.03 | 1.21 | 0.62 | 0.46 | Mandatory |
| KY | 0.42 | 0.57 | 0.59 | 0.39 | 0.41 | 0.30 | 0.53 | Targeted |
| LA | _ | — | 1.09 | 0.78 | 0.46 | 0.37 | 0.42 | Mandatory |
| MD | 1.98 | 1.20 | 0.98 | 0.77 | 0.54 | 0.32 | 0.23 | Targeted |
| ME | 2.13 | 1.91 | 1.74 | 1.62 | 1.80 | 1.30 | | Targeted |
| MA | _ | — | 1.13 | 1.05 | 0.92 | 0.83 | 0.66 | Mandatory |
| MI | 4.06 | 2.91 | 2.27 | 1.89 | 1.65 | 1.16 | 0.98 | Targeted |
| MS | 1.88 | 1.21 | 0.93 | 0.78 | 0.67 | 0.59 | 0.54 | Targeted |
| MO | 2.27 | 1.92 | 1.64 | 1.40 | 1.08 | 0.92 | 0.89 | Targeted |
| NH | 2.10 | 2.27 | 2.18 | 1.91 | 1.38 | 1.45 | | Targeted |
| NJ | 0.90 | 1.25 | 1.59 | 1.47 | 1.19 | 1.03 | 0.84 | Mandatory |
| OH | 3.53 | 2.72 | 2.21 | 1.98 | 1.65 | 1.37 | 1.21 | Targeted |
| OK | 1.13 | 0.94 | 0.96 | 0.75 | 0.80 | 0.73 | | Targeted |
| PA | 7.04 | 6.52 | 4.99 | 3.38 | 2.63 | 2.52 | 1.95 | Targeted |
| RI | 5.27 | 3.56 | 3.07 | 2.71 | 2.14 | | | Mandatory |
| UT | 0.36 | 0.23 | 0.19 | 0.66 | 0.61 | 0.58 | 0.76 | Targeted |
| VA | 1.06 | 0.73 | 0.71 | 0.83 | 0.77 | 0.64 | 0.44 | Targeted |
| WA | 0.42 | 0.49 | 0.41 | 0.49 | 0.29 | 0.23 | 0.17 | Targeted |
| WI | 2.64 | 2.47 | 2.12 | 1.91 | 1.60 | 1.25 | 1.20 | Targeted |

—: Data not available.

* Data provided by CDC Tracking (2/2011).

 TABLE 2: Descriptive statistics of 1508 counties with 50 or more children tested for blood lead.

| | Percent below poverty | Percent rural | Percent Black | Percent pre-50 | Population | NATA 2005 |
|------|-----------------------------|------------------|------------------|-------------------|------------|--------------|
| Mean | 13.6 | 56.8 | 10.6 | 25.7 | 97366 | 0.0013 |
| Min | 2.6 | 0 | 0.26 | 0.78 | 1844 | 0.0005 |
| Max | 41.13 | 100 | 86.5 | 66.7 | 5376741 | 0.0149 |

predictive/independent variables. The advantage of a negative binomial regression is that it weights each county by number of children tested. The result of univariate binomial regression analysis shows that county-level NATA for 2002, NATA for 2005, percentage of pre-1950 housing per county, rural classification of the county, and county-specific percentage below poverty are statistically significant while percentage black is borderline significant (P = 0.074). See Table 3. The correlation among these explanatory variables has been examined and percent black and percent below poverty have a positive, significant correlation (0.54) whereas others appear to have a relatively weak relationship. In addition,

TABLE 3: Results of univariate negative binomial regressions predicting number of children with BLL $\ge 10 \ \mu g/dL$ by county.

| Univariate negative binomial regression | | | | | |
|---|--------------|--------------------|--|--|--|
| | Coef. | 95% CI | | | |
| NATA02 | 66.897* | (35.0818, 98.7209) | | | |
| NATA05 | 99.736* | (56.7037, 142.768) | | | |
| % pre50 housing | 0.035^{*} | (0.0320, 0.0385) | | | |
| Urban (ref) | — | | | | |
| Suburban | -0.689^{*} | (-1.0317, -0.3466) | | | |
| Rural | -0.803^{*} | (-1.1508, -0.4551) | | | |
| % Black | -0.003 | (-0.0063, 0.00029) | | | |
| Targeted/mandatory | 0.033 | (-0.1035, 0.1697) | | | |
| % below poverty | -0.019^{*} | (-0.0268, -0.0098) | | | |
| * D : 0.0001 | | | | | |

P < 0.0001.

the collinearity diagnostics indicates that none of explanatory variables in a multiple regression model are highly correlated.

In the *univariate* negative binomial regression, proportion black and mandatory or targeted testing in a county were not significant. In *multivariate* negative binomial regression, NATA modeled air lead was a significant predictor of childhood blood lead ($\% \ge 10 \ \mu g/dL$) after adjusting for % pre-1950 housing, rural classification, and percent of black children by county. Because NATA 2005 was a slightly better predictor in the univariate model, these NATA estimates were entered into the multivariate model. Percent below poverty was not significant in *multivariate* analysis.

The negative binomial loglinear regression for the rate is

$$\log\left(\frac{\mu}{n}\right) = \alpha + \beta x,$$
$$\log\left(\mu\right) - \log\left(n\right) = \alpha + \beta x,$$
$$\mu = ne^{\alpha + \beta x},$$

 $\log(\mu) = \beta_0 + \beta_1 * \text{NATA05} + \beta_2 * \text{pre50} + \beta_3 * \text{suburban}$

+
$$\beta_4 * \text{rural} + \beta_5 * \text{black} + \log (\text{tottest})$$
. (4)

The percent change in the relative risk of total number of BLL $\geq 10 \,\mu$ g/dL increases 36% for every 0.01 μ g/m³ increase in NATA air lead value, 5% for every unit increase in % pre-1950 housing, and 1% for every unit increase in % black people per county. Children living in suburban and rural areas decrease their relative risk by 14% and 34% relative to those living in the urban areas. Children living in mandatory counties are 36% less likely to have BLL $\geq 10 \,\mu$ g/dL than those living in targeted counties. See Table 4.

Finally, the results of a geospatial regression further solidified the relationship between childhood blood lead and air lead and older housing. The cube root transformation of the proportion of children with a BLL $\geq 10 \,\mu$ g/dL was chosen as the dependent variable to satisfy normality. The analysis revealed that poverty, pre-1950 housing, and air lead levels were all significant predictors of BLL $\geq 10 \,\mu$ g/dL (Table 5). The R^2 value was 0.420 (P < .001), and air lead, percent older housing, percent black, and urban/suburban were all significant predictors (P < .001). The coefficient of NATA05 indicates that the cube root of percent elevated is predicted to increase 72.8 when NATA05 is increased by one and decrease by 0.23 when urban/suburban/rural jumps to the next category. See Table 5.

After accounting for spatial autocorrelation of the residuals, R-squared increased to 0.39. All independent variables remain statistically significant. The likelihood ratio test of spatial error dependence is significant. Therefore, we conclude that a spatial lag model is fitted better than the OLS model using cube-root transformation of percent elevated BLLs.

4. Discussion

It is well known that a child's home environment has the clearest relationship with a child's BLL [1]. Childhood BLL have decreased with the removal of lead from paint and gasoline. There remain, however, 250,000 US children annually who exhibit BLL $\geq 10 \,\mu g/dL$ which can affect their mental and physical health. This study was the first to use

TABLE 4: Multivariate negative binomial regression using robust variance estimation predicting number of children with BLL \geq 10 μ g/dL per US county.

| Negative binomial regression | | | | | | |
|------------------------------|---------------|-----------|---------|--------------|--|--|
| Variables | Relative risk | Robust SE | P value | 95% CI | | |
| NATA* | 1.36 | 0.176 | 0.017 | (1.06, 1.75) | | |
| % pre50 housing | 1.05 | 0.002 | 0.000 | (1.04, 1.05) | | |
| Urban-rural | | | | | | |
| Urban | (reference) | | | | | |
| Suburban | 0.86 | 0.135 | 0.337 | (0.63, 1.17) | | |
| Rural | 0.66 | 0.110 | 0.013 | (0.48, 0.92) | | |
| % Black | 1.01 | 0.002 | 0.000 | (1.00, 1.01) | | |
| Targeted/mandato: testing | ry 0.64 | 0.041 | 0.000 | (0.56, 0.72) | | |

Note: the predictor of NATA05 air lead was scaled to 100^{\ast} (the original NATA05 air lead).

TABLE 5: Results of spatial lag regression.

| Spatia | l lag regres | ssion | | |
|-------------------------------|--------------|---------|------------------------|---------|
| Variables | β | SE | \boldsymbol{Z} value | P value |
| NATA05 | 50.83515 | 10.4221 | 4.8776 | < 0.001 |
| % pre50 housing | 0.0125 | 0.00113 | 11.0852 | < 0.001 |
| Urban-rural | 0.0972 | 0.0293 | 3.3193 | < 0.001 |
| % below poverty | 0.0107 | 0.0022 | 4.9392 | < 0.001 |
| Targeted/mandatory testing | -0.2067 | 0.0347 | -5.953 | < 0.001 |
| <i>R</i> -squared: 0.386367 | | | | |
| Sq. Correlation: — | | | | |
| Sigma-square: 0.219 | | | | |
| S.E of regression: 0.4681 | | | | |
| Log likelihood: –1010.7 | | | | |
| Akaike info criterion: 2035.4 | | | | |
| Schwarz criterion: 2072.62 | | | | |
| | | | | |

a national data base on childhood BLL over an eight-year period to link proportion children with a BLL $\geq 10 \,\mu g/dL$ in children with NATA 2005-modeled air lead as well as percent pre-1950 housing, race, and poverty. While many of the primary risks have been removed from our environment, the task of eliminating childhood lead poisoning [19] has not been completed. Air lead has been identified [13–20] as a contributor to childhood BLL in smaller scale studies. These studies were conducted in distinct metro areas and near significant sources of air lead and soil lead such as nearby smelters and lead producing areas. This national assessment of the contribution of air lead to childhood BLLs, controlling for known risk factors such as older housing and poverty levels, will help to quantify the increase in BLL that may be attributed to differences in air lead throughout the US.

Our research group recognizes that there are limitations to epidemiologic methods. While ecologic studies are generally quicker and less cumbersome to conduct, they are prone to the ecologic fallacy and other forms of bias, which can arise from the absence of detailed information on the joint distribution of exposure and outcome within the groups under study. As such, ecologic studies are most useful as hypothesis generating and not hypothesis testing investigations, often providing important clues to occupational and environmental determinants of disease. For example, in the mid-1970s a series of ecologic studies conducted by the US National Cancer Institute implicated industrial factors in the development of various malignant diseases [24].

There are differences in childhood blood lead testing frequency that may influence this study as well. Differences exist between states-even counties within the same stateregarding blood lead testing policies. Typically, there are targeted and mandatory testing policies. We applied "targeted" or "mandatory" to each county within a state based upon the state's policies as stated in 2010. However, these policies may change annually, as public health funding dictates. In addition, some counties may have targeted towns or neighborhoods with known housing or lead industry issues, elevating the likelihood of a child having a high level, thereby increasing the proportion of children with BLL $\geq 10 \, \mu g/dL$. A sensitivity analysis of proportion tested in a sample of targeted and mandatory counties showed that the proportion tested in mandatory counties was double that tested in targeted counties. However, a full complement of data was not available due to privacy concerns. Targeted testing typically focuses on high-risk children, often identified as those on Medicaid or through additional screening questions. Mandatory testing policies indicate that all children should be tested before age three. However, the consistency of the findings among the univariate and multivariate negative binomial as well as the linear spatial regression model results which predict percent BLL $\geq 10 \,\mu g/dL$ (Tables 3–5) strengthens the conclusion that there is a relationship between ambient air lead levels and percent BLL $\geq 10 \,\mu g/dL$ in younger children.

In addition, many of the modest effects we observed were deemed statistically significant due to large sample size. Our exposure estimates are static points in time (NATA 2005 and census 2000). For the pollutant of interest for this investigation (lead), NATA average concentrations for 2002 and 2005 were similar [25]. The degree of concordance between NATA and CAPs improved from 2002 to 2005. The average difference between county-level NATA 2002 and NATA 2005 estimates of air lead is 0.0002, indicating that the overall difference is estimates of concentration of air lead that is small. The NATA county-level correlation coefficient for the 2002 and 2005 assessment years was 0.91 (P < .0001). However, NATA lead estimates are known to be an underestimation of air lead levels.

The results of our evaluation of the relationship of air lead and BLLs at the county level for the US indicate that there may remain a significant relationship between ambient air lead and childhood BLL. The proportion with BLL $\ge 10 \,\mu$ g/dL was 1.24% in the highest air lead counties, and the proportion with BLL $\ge 10 \,\mu$ g/dL was 0.36% in the lowest air lead counties, resulting in a crude prevalence ratio of 3.4. This combined with the fact that the percent change in the relative risk of total number of BLL $\ge 10 \,\mu$ g/dL increases 36% for every 0.01 μ g/m³ increase in NATA air lead value, after controlling for older housing, and rural indicates that there is a significant association between modeled air lead concentration and proportion of children with BLL $\geq 10 \ \mu g/dL$ among those screened in US counties. Further work should be carried out at a more refined geographic level with individual level data to the extent possible to more fully understand the potential contribution of ambient air lead and its concomitant risk from dust inhalation of lead in small children. Proximity to sources of lead emissions should be evaluated as a possible factor to include when identifying children for targeted testing and when evaluating the home environment of a child with BLL $\geq 10 \ \mu g/dL$.

Abbreviations

| BLL: | Blood lead level |
|---------|--|
| CDC: | Centers for Disease Control |
| CLPP: | Childhood lead prevention program |
| EPA: | Environmental Protection Agency |
| EPHTN: | Environmental Public Health Tracking Network |
| FIPS: | Federal information processing standard |
| HHLPPB: | Healthy Homes and Lead Poisoning Prevention |
| | Branch |
| NATA: | National Scale Air Toxics Assessment |
| NEI: | National Emissions Inventory |
| TRI: | Toxic Release Inventory |
| US: | United States. |
| | |

Disclaimer

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the views of the Centers for Disease Control and Prevention.

Funding

This work was funded by the Centers for Disease Control Contract 200-2010-37444.

Conflict of Interests

The authors disclose no competing financial interests.

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Research Article

Municipal Leachate Treatment by Fenton Process: Effect of Some Variable and Kinetics

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Received 1 January 2013; Revised 18 April 2013; Accepted 19 April 2013

Academic Editor: Mohammad Mehdi Amin

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Due to complex composition of leachate, the comprehensive leachate treatment methods have been not demonstrated. Moreover, the improper management of leachate can lead to many environmental problems. The aim of this study was application of Fenton process for decreasing the major pollutants of landfill leachate on Kermanshah city. The leachate was collected from Kermanshah landfill site and treated by Fenton process. The effect of various parameters including solution pH, Fe^{2+} and H_2O_2 dosage, Fe^{2+}/H_2O_2 molar ratio, and reaction time was investigated. The result showed that with increasing Fe^{2+} and H_2O_2 dosage, Fe^{2+}/H_2O_2 molar ratio, and reaction time, the COD, TOC, TSS, and color removal increased. The maximum COD, TOC, TSS, and color removal were obtained at low pH (pH: 3). The kinetic data were analyzed in term of zero-order, first-order, and second-order expressions. First-order kinetic model described the removal of COD, TOC, TSS, and color from leachate better than two other kinetic models. In spite of extremely difficulty of leachate treatment, the previous results seem rather encouraging on the application of Fenton's oxidation.

1. Introduction

In the past decades, industrial growth and technology development lead to the increasing solid waste production [1]. According to the World Health Organization studies, in the many countries such as France, Canada, America, Norway, England, Spain, and Italy, sanitary landfilling had been recognized as the common, economic and acceptable method for solid waste disposal [2–4]. Landfill leachate is a complex waste matter, which usually causes adverse effects in the environment [5, 6]. The leachate characteristics are depended on the type of solid waste, soil properties, rainfall patterns, and age of landfill site. The concentration of nonbiodegradable and resistant materials with high molecular weight such as humic and fulvic acid arises with increase of the landfill site age [7].

Due to variable characteristic of landfill leachate, the coherent method for leachate treatment was not developed [8]. The concerning of solid waste leachate may be related to presence of heavy metals and nonbiodegradable organic materials in solid waste leachate and its adverse effects on human and the environment [3]. Application of biological treatment processes (as dominant treatment) cannot remove nonbiodegradable organic materials and additional treatments are required for leachate treatment [9]. Biological treatment processes are suitable for fresh leachate with high ratio of BOD₅/COD but cannot be applied in the treatment

of aged leachate in which biological treatment occurred, and ratio of BOD_5/COD is low [10].

Chemical treatment methods based on production of hydroxyl radical (OH[•]) are known as advanced oxidation processes (AOP_s) [11, 12]. Oxidation of organic compounds by Fenton solution called the Fenton reaction which is one of the advanced oxidation processes [13]. Fenton reaction is able to destroyed large number of organic compounds without producing toxic byproducts. Another main advantage of Fenton process is that the oxidation and flocculation occur simultaneously that result in removing more organic matters [14].

Fenton process is done according to the following mechanism [3]:

(1)
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\circ}OH + OH^-,$$

(2) $Fe^{2+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+,$
(3) ${}^{\circ}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O,$
(4) ${}^{\circ}OH + Fe^{2+} \rightarrow OH^- + Fe^{3+},$
(5) $Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2H^+,$
(6) $Fe^{2+} + HO_2^{\bullet} + H^+ \rightarrow Fe^{3+} + H_2O_2,$
(7) $2OH_2^{\bullet} \rightarrow H_2O_2 + O_2.$

Oxidation potential of hydroxyl radical (OH^{*}) is greater than ozone, one of the strongest oxidizing materials [15]. Hydrogen peroxide alone is not a strong factor in oxygen transfer, and oxidation of organic materials is better performed in the presence of Fe^{2+} ions [16]. The most important role of Fenton process is removing refractory and toxic organic compounds and increasing the degradability of resistant organic compounds. Fenton processes have been successfully used for treatment of the slaughterhouse, food, olive oil wastewater, and 2,4,6-trichlorophenol from industrial wastewater and landfill leachate [15, 17–22]. This method compared to other advanced oxidation processes is relatively less expensive and requires less time [23].

The aim of this study was to investigate the effect of Fenton process for solid waste leachate treatment from Kermanshah landfill (Iran).

2. Experimental

2.1. Leachate Characteristics. The Leachate sample was collected from the municipal solid waste landfill in Kermanshah city (Iran). The main characteristics of leachate were summarized in Table 1.

2.2. Chemicals. All chemicals were of analytical grade (Merck, Germany), and doubly distilled water was used throughout this study. The hydrogen peroxide (35% w/w) and ferrous sulphate (FeSO₄·7H₂O) were used for all experiment. The FeSO₄ solution was prepared daily. H₂SO₄ and NaOH (1 N) were used for pH adjustment.

2.3. Experimental Procedure. In this study, the effect of Fenton process of leachate treatment was conducted in

TABLE 1: Main characteristics of Kermanshah leachate.

| Parameter | Value | Unit |
|------------------|----------------|-------|
| Color | Dark brown | _ |
| BOD ₅ | 800 | mg/L |
| COD | 3895 ± 180 | mg/L |
| TOC | 1438 ± 95 | mg/L |
| TSS | 1460 ± 80 | mg/L |
| Alkalinity | 2154 ± 130 | mg/L |
| Color | 3045 ± 45 | Pt-Co |
| pН | 7.8 ± 0.1 | — |

environment temperature in glass reactor using jar apparatus as a batch reactor. At first, rapid mix (120 rpm) was applied for 30 s, and then mixers were adjusted for 80 rpm for long time. The effect of various parameters including solution pH, Fe^{2+} and H_2O_2 concentrations, Fe^{2+}/H_2O_2 molar ratio, and reaction time was investigated. All experiments were carried out with 1L beakers, and the beakers were charged with 500 mL leachate [24].

2.4. Analytical Methods. The amounts of pH, COD, TOC, TSS, color, and alkalinity were analyzed in the laboratory by following the standard methods [25]. The pH, TOC, color, and alkalinity measurements were performed by using the WTW Multiparameter 340i, Shimadzu model TOC-CSH, spectrophotometer, and titration method, respectively. Closed reflux colorimetric method was used for COD analysis. For COD measurement of the supernatant, supernatant was put in the water bath at 50°C for 30 min for removal of remaining H_2O_2 in Fenton process experiments [3]. The removal efficiency was calculated by the following equations:

$$R = \left[\frac{C_0 - C_e}{C_0}\right] \times 100. \tag{1}$$

3. Results

3.1. Effect of Solution pH. The Fenton process efficiency for COD, TOC, TSS, and color removal as a function of solution pH was investigated (Figure 1). According to Figure 1, at low pH, the COD, TOC, TSS, and color removal efficiency are low, and with increasing pH up to 3, removal efficiency increased. After this point, COD, TOC, TSS, and color removal were decreased.

The solution pH plays an important role in Fenton process. Figure 1 is evident that with increasing the initial pH from 1 to 3, the removal efficiency quickly increases and at pH > 3 decreases. The results from this experiment are in line with those studies reported by the researchers [6, 23, 26, 27]. They found that pH near 3 is usually optimum for Fenton oxidation. The low efficiency of Fenton process at pH < 3 is due to the formation of $[Fe(II)(H_2O)_6]^{2+}$ complex, which reacts more slowly with H_2O_2 than $[Fe(II)(OH)(H_2O)_5]^+$ and therefore produces lower OH radical [28]. Also, if the solution pH is too high, the iron precipitates as $Fe(OH)_3$ and H_2O_2

TABLE 2: Equations and linear forms and results of kinetics model.

| Kinetic model | Equation | Linear form | Parameter | COD | TOC | TSS | Color |
|---------------|-----------------------------------|--|-----------|--------------------|--------------------|--------------------|--------------------|
| Zero-order | $r_c = \frac{dC}{dt} = k_0$ | $C - C_0 = -k_0 t$ | K_0 | 27.93 | 4.48 | 9.04 | 18.58 |
| | | | R^2 | 0.93 | 0.88 | 0.94 | 0.76 |
| First-order | dC bC | $ln \frac{C}{dt} = -k t$ | K_1 | 0.012 | 0.004 | 0.009 | 0.013 |
| | $r_c = \frac{1}{dt} = \kappa_1 C$ | $\lim \frac{1}{C_0} = -\kappa_1 \iota$ | R^2 | 0.98 | 0.92 | 0.99 | 0.91 |
| Second-order | $dC = 1 C^2$ | $\frac{1}{2} - \frac{1}{2} - k t$ | K_2 | 6×10^{-6} | 4×10^{-6} | 1×10^{-5} | 1×10^{-5} |
| | $r_c = \frac{1}{dt} = \kappa_2 C$ | $C C_0 = \kappa_2 \iota$ | R^2 | 0.97 | 0.91 | 0.95 | 0.94 |



FIGURE 1: Influence of solution pH on COD, TOC, TSS, and color removal $(H_2O_2/Fe^{2+};$ fixed and 90 min reaction time).



FIGURE 2: Effect of reaction time in Fenton process on COD, TOC, TSS, and color removal (H_2O_2/Fe^{2+}) : fixed and pH: 3).

decompose to oxygen and that will reduce its concentration in the solution [29, 30].

3.2. Effect of Reaction Time. The effect of reaction time on COD, TOC, TSS, and color removal during Fenton process is presented in Figure 2. The result showed that with rising reaction time, the COD, TOC, TSS, and color removal increased. The equilibrium time for COD, TOC, TSS, and color removal was obtained, 105 min. After the equilibrium time, the COD, TOC, TSS, and color removal did not change significantly.

Reaction time is an important factor in Fenton process. Different reaction time was reported in various studies. The reaction time for Fenton process in various studies has been



FIGURE 3: Effect of Fe²⁺ concentration on COD, TOC, TSS, and color removal (H_2O_2 : 2500 mg/L, pH: 3, and 105 min reaction time).



FIGURE 4: Influence of H_2O_2 dose on COD, TOC, TSS, and color removal (Fe²⁺: 1800 mg/L, pH: 3, and 105 min reaction time).



FIGURE 5: Effect of Fe^{2+}/H_2O_2 molar ratio on COD, TOC, TSS, and color removal (pH: 3 and 105 min reaction time).



FIGURE 6: The results of kinetic study: zero-order (a), first-order (b), and second-order (c).

fluctuated between 30 min and 3 h [6, 23, 27]. In some studies, based on electro-Fenton process, optimum reaction time has been reported less than 30 min [1].

3.3. Effect of Fe^{2+} Concentration. Figure 3 shows the effect of Fe^{2+} concentration on the COD, TOC, TSS, and color removal during Fenton process. It can be seen that the Fenton efficiency of COD, TOC, TSS, and color removal increases with augmenting Fe^{2+} concentration. The optimum Fe^{2+} concentration for maximum COD, TOC, TSS, and color removal was 1.6 g/L. Further increase of Fe^{2+} concentration results in decrease in COD, TOC, TSS, and color removal efficiency.

Based on operational costs and organic material removal efficiency, dosage of Fenton reagents will be determined. Generally, removal of organic matters improves with increasing concentration of iron salt. However, the removal increment may be marginal when the concentration of iron salt is high. Many studies have revealed that the use of a much higher concentration of Fe²⁺ could lead to the self-inhibition of OH radical by Fe²⁺ ions and decreasing the degradation rate of pollutants: $OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-$ [30].

3.4. Effect of H_2O_2 Dose. The influence of H_2O_2 dose on COD, TOC, TSS, and color removal is shown in Figure 4. The results showed that removal efficiency of COD, TOC, TSS, and color gradually increases as the H_2O_2 concentration

is fluctuated from 500 mg/L to 3000 mg/L and then slowly decreased. It was observed that maximum COD, TOC, TSS, and color removal were obtained at H_2O_2 concentration of 3000 mg/L.

Landfill leachate is composed of a complex mixture of organic matter. During the oxidation process, more decomposition of organic matter causes more pollutant removal. This continues until formation of the end byproducts of oxidation reactions that mainly are short chain organic acids and are difficult to be further oxidized [13]. The presence of H_2O_2 in a high quantity can act as a scavenger for the OH radicals, thus reducing the kinetic rate of Fenton process [31]. In addition, due to decomposition of H_2O_2 and producing hydrogen gas, application of H_2O_2 more than the optimum value are caused flotation of generated iron sludge. Also, additional H_2O_2 causes problems in downstream processes and will prevent wastewater biological treatment [3, 32].

3.5. Effect of Fe^{2+}/H_2O_2 Molar Ratio. The effect of Fe^{2+}/H_2O_2 molar ratio on the COD, TOC, TSS, and color removal with different Fe^{2+}/H_2O_2 molar ratios within a range of 1 to 2 is presented in Figure 5. It can be seen that COD, TOC, TSS, and color removal increase with the rise in Fe^{2+}/H_2O_2 molar ratio up to 1.88 and after this ratio decrease.

In Fenton process, iron and hydrogen peroxide are two major chemicals that determining operation costs as well as efficiency. Determination of the favorable amount of Fenton's reagent is highly important. The results showed that removal efficiencies increased with the increase of H_2O_2/Fe^{2+} molar ratio, and further increase in H_2O_2/Fe^{2+} molar ratio produced less efficient improvement in removals. This fact is due to Fenton's reaction mechanisms proposed by other researchers [27]. If H_2O_2/Fe^{2+} molar ratio is low, the reaction rate follows second pseudoorder up to the stoichiometry ratio of 2Fe(II) \cong H_2O_2 . But, when the H_2O_2/Fe^{2+} molar ratio increases, the reaction kinetics approache toward zero order. However, at high H_2O_2/Fe^{2+} molar ratios, the mechanism changed, and the reaction became independent of hydrogen peroxide [29].

3.6. Kinetic Study of Leachate Treatment by Fenton Process. Reaction rates in the reactor must be specially determined to complete description and design of a reactor system and its direct effect on reactor size. Therefore, the study of reaction kinetics to prediction of pollutant removal rates is very important in designing and modeling of treatment process [33].

Determination of the kinetics of the Fenton on COD, TSS, TOC, and color removal reaction is needed to estimate the time required for COD, TSS, TOC, and color removal. A kinetic analysis was conducted by fitting the time-course performance data with zero-, first-, and pseudo-second-order kinetic equations as shown in Table 2.

Where r_c is the rate of conversion, k_0 , k_1 , and k_2 are reaction rate coefficients, t is time, and C_0 and C are the initial and final concentration of the constituent in the liquid, respectively. The data were appropriately explained with first-order kinetic model (higher R^2), that presented that the model can successfully simulate COD, TSS, TOC, and color removal in the Fenton process. This results show high relationship between COD, TSS, TOC, and color removal efficiency and its initial concentration. In studies carried out by Guedes et al. and Yasar et al, in removal of synthetic dye by Fenton process, reaction rate is described with first-order kinetic model [17, 34]. The effects of COD, TSS, TOC, and color removal in the Fenton process are shown in Figure 6.

According to Figure 6, the linear relation for each pollutant removal confirms the fact that the kinetics of COD, TSS, TOC and color removal adherents of the exponential law with time.

Results showed that application of Fenton process is inadequate for landfill leachate treatment of Kermanshah city, but leachate characteristics could be greatly improved by Fenton process. The most important role of Fenton process is removing organic and toxic organic compounds and increasing the degradability of resistant organic compounds. Thus this process can be used as pretreatment for biological treatment. The main disadvantage of the Fenton process is that it requires disposal of excess sludge production.

Acknowledgments

Financial support for this study was provided by Kermanshah University of Medical Science under research project. Also appreciation is due to Social Development & Health Promotion Research Center to support approval of this research.

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Review Article

Role of Environmental Chemicals in Obesity: A Systematic Review on the Current Evidence

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Received 27 March 2013; Accepted 7 May 2013

Academic Editor: Mohammad Mehdi Amin

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The purpose of this paper is to systematically review the experimental and human studies on obesogenic chemicals and their mechanisms of action to provide a comprehensive view on the multifactorial aspects of obesity. The literatures were searched in available databases. The relevant papers were selected in three phases. After quality assessment, two reviewers extracted the data while another checked their extracted data. In this review, we summarized information regarding environmental chemicals that can be associated with obesity. Most evidence comes from experimental and laboratory studies; however a growing number of human studies also support the role of obesogenic chemicals. The current evidence proposes that the systemic responses to exposure to environmental factors could potentially increase the risk of excess weight. The effects of exposure to these chemicals are of crucial importance during developmental phases of life, when preprogramming for an adipogenic outcome may occur. By considering the adverse transgenerational effects of obesogen chemicals on human health, the global obesity epidemic should be considered as a multifactorial complex disorder necessitating the emphasis of public health interventions for environmental protection.

1. Introduction

Obesity is becoming a human health crisis at individual and public health levels. It has numerous adverse health effects and is considered as one of the main predisposing factors for the emerging epidemic of noncommunicable diseases [1]. Nowadays, overweight and obesity are growing in populations with different levels of economic situation. It is estimated that by continuing the actual trend, the global prevalence rate of 33.0% for overweight and obesity among adult population (1.3 billion people) in 2005 would reach up to 57.8% (3.3 billion people) by 2030 [2]. The World Health Organization included excess weight, with a prevalence higher than undernutrition, as one of the top 10 health risks worldwide [3].

The rise in the incidence in obesity matches the rise in the use and distribution of industrial chemicals that may have a role in development of obesity. In her interesting review in 2002, Baillie-Hamilton postulated a role for chemical toxins in the etiology of obesity by presenting the coincidence of the obesity epidemic with the noticeable increase of industrial chemicals in the environment over the past four decades. An accumulating body of evidence suggests that substances as endocrine-disrupting chemicals (EDCs) may be linked to the obesity epidemic [4]. EDCs are chemicals that alter the normal functioning of hormones and other signaling molecules in the body [5]. Additional studies proposed the existence of chemicals termed "obesogens," molecules with adverse effects on lipid metabolism and adipogenesis, and in turn resulting in obesity [6, 7].

The environmental obesogen hypothesis suggests that prenatal or early-life exposure to certain substances as EDCs may predispose exposed individuals to increased fat mass and excess weight. It is suggested that exposure to obesogens can modify the epigenome of multipotent stromal stem cells, biasing them to the adipocyte lineage at the expense of bone. Hence, humans exposed to obesogens during early life might have an altered stem cell compartment, already preprogrammed for an adipogenic outcome [8]. The list of chemicals studied as possible obesogens continues to grow and includes diethylstilbestrol (DES), bisphenol A (BPA), phthalates, organotins, polybrominated diphenyl ethers (PBDEs), polyfluoroalkyl chemicals (PFCs), organochlorine (OC) pesticides, and polychlorinated biphenyls (PCBs) and some solvents caused weight gain, and it is proposed that these chemicals were interfering with weight homeostasis by changing weight-controlling hormones, modifying sensitivity to neurotransmitters, or altering the sympathetic nervous system activity [9].

The purpose of this paper is to systematically review the experimental and human studies on obesogenic chemicals and their mechanisms of action to provide a comprehensive view on underlying mechanisms and the multifactorial aspects of obesity for clinicians and public health stakeholders.

2. Methods

2.1. Literature Search Strategy. Relevant literature reporting the environmental obesogens was identified through electronic search of MEDLINE, PubMed, ISI Web of Science, and Scopus/Embase with no time or language restrictions. The literature search was conducted during January and February 2013. We searched the databases using the following strategy: for Scopus/Embase we used the Emtree Thesaurus terms; for PubMed search, we considered Medical Subheading (MeSH) words, and for other databases we used keywords (text words). For PubMed search, we used ("endocrine disruptors" [MeSH] OR "endocrine disrupting chemicals" OR "obesogen" [mh] OR "Polychlorinated Biphenyls" [MeSH] OR "Hydrocarbons, Chlorinated" [MeSH] OR "Dioxins" [MeSH] OR "Polybrominated Biphenyls" [MeSH] OR "Carbon Tetrachloride" [MeSH] OR "Organothiophosphorus Compounds" [MeSH] OR "phthalic acid" [Substance Name] OR "Phthalic Acids" [MeSH] OR "Organotin Compounds" [MeSH] OR "bisphenol A" [Substance Name] AND (("obesity" [mh] OR "overweight" [mh] OR "excess weight" [mh] OR "body mass index" [mh] OR "weight gain" [mh] OR "adipogenesis" [mh] OR "adipose tissue" [mh] OR "fat deposition" [mh]) AND (publisher[sb] OR "in process" [sb]).

2.2. Study Selection and Eligibility Criteria. Duplicates were removed; the relevant papers were selected in three phases. In the first and second phases, titles and abstracts of papers were screened and irrelevant papers were excluded. In the last phase, the full text of recruited papers was explored intensely to select only relevant papers. For any additional pertinent studies, the reference list of all reviews and relevant papers was screened as well. All these three screening phases were done by two independent reviewers (FJ and PP). In the next step, the eligibility of relevant papers was checked. Discrepancies were resolved by consultation and consensus.

2.3. Quality Assessment. Identification of main findings of studies was conducted on a case-by-case basis and included consideration of any statistical analyses that might have been conducted, consistency of the general pattern across exposure groups.



FIGURE 1: Flowchart of study selection.

2.4. Data Extraction and Abstraction. The required information that was extracted from all eligible papers was as follows: (i) general characteristics of the study (first author's name, publication year, study year, study design) (ii) characteristics of the chemical, (iii) reason for using the chemical, (iv) suggested obesogen mechanism, and (v) adverse effects on humans or animals.

Two reviewers (FJ and PP) extracted the data while another (RK) checked their extracted data.

3. Results

The flowchart of our study selection is presented in Figure 1. We found that actually many environmental obesogens are identified; they are mainly classified as chemical simulators of metabolic hormones or brain neurotransmitters [10, 11]. Several experimental studies reported the association of exposure to some environmental chemicals with obesity. Bisphenol A [12–15], tributyltin (TBT) [16, 17], nonylphenol [18, 19] and genistein [20, 21], phatalate [22], perfluoroalkyl compounds (PFCs) [23], and perfluorooctanoic acid (PFOA) [24] are some of the obesogen chemicals described by experimental studies. The major environmental obesogen chemicals are presented in Table 1.

Diverse mechanisms are explained for obesogen chemicals; mainly they have disruptive effects on homeostasis of energy balance, glucose and lipid metabolism, and control of adipogenesis. A summary of the underlying mechanisms of these substances is reported in Table 2.

Conflicting results are reported about the effects of obesogen chemicals in human studies. The concentrations of many industrial obesogen chemicals are found to be high in general population [25]. For instance, some studies examined the obesogenic effects of phthalates, which are esters mainly added to plastics to increase their flexibility, transparency, durability, and longevity. Cross-sectional data from the National Health and Nutrition Examination Survey (NHANES) in the USA found significant associations between several phthalates metabolites (monobenzyl phthalate (MBzP), mono-(2-ethyl-5-hydroxyhexyl) phthalate (MEHHP), and mono-(2-ethyl-5-oxohexyl) phthalate (MEOHP)) and measures of abdominal obesity and insulin resistance in men but not in women [26]. A cross-sectional study on 90 girls aged 6-8 years found slightly higher concentrations of some phthalate metabolites as monoethyl phthalate (MEP), mono-(2-ethyl-5-hydroxyhexyl) phthalate (MEHHP), and mono-n-butyl phthalate (MBP) among overweight girls than in their other counterparts; however the difference was not statistically significant [27]. Some epidemiologic studies documented the obesogenic effects of some environmental chemicals, as PCB [28] and BPA [29], whereas such effects are conflicting for some other chemicals as organochlorine pesticides [30-32].

Phytoestrogens, notably soy products, have beneficial health effects and are added to several food and food supplements. However some studies suggested that they may act as obesogen chemicals. Genistein is one the mostly used phytoestrogens in the human diet, and by its estrogenic activity, it has favorable effects for regulating the homeostasis of lipids and carbohydrates [33]. Though its beneficial effects in inhibiting fat deposition in the adipose tissue are considered to be obtained at high pharmacological doses, its low doses in foods are found to increase adiposity and mild peripheral insulin resistance particularly in males [34].

4. Discussion

In this review, we summarized information regarding environmental chemicals that can be associated with obesity. Most evidence comes from experimental and laboratory studies; however a growing number of human studies also support the role of obesogen chemicals.

Chemicals as heavy metals, some solvents, pesticides, BPA, organophosphates, phthalates, PCB, PBBs, and many other substances are documented to cause weight gain. These chemicals interfere with weight and lipid homeostasis by various mechanisms related to weight-controlling hormones, activity of the sympathetic nervous system, and sensitivity to neurotransmitters.

Exposure to these chemicals varies in different age groups; their effects during fetal and infancy periods may be irreversible and long-lasting for adulthood. Even exposure to low doses of EDCs during critical times of differentiation can change the developmental programming and may result in obesity [35]. Barker's hypothesis on the effects of intrauterine growth on fetal programming and fetal origins of adult diseases is well documented [36, 37]; however, other characteristics as later growth spurt and environmental factors are considered to influence this programming. Exposure to environmental chemicals with endocrine-disrupting activities in early life may result in everlasting adverse health effects [38]. Such health consequences may become apparent not only in childhood, but also in adulthood [5], and even in succeeding generations [39]. Transgenerational effects may be because of mutations as well as because of factors regulating gene expression [5]. Our findings support the role of obesogens, as chemicals with disruptive effects on fat homeostasis and various weight controlling mechanisms, in programming the development of excess weight from early life. Although all obesogen chemicals are not yet identified, and their detailed mechanisms of action remain to be explored, generally it is assumed that exposure to different doses of these environmental chemicals in various periods of life from fetal to adult period interacts with some endocrine signaling mechanisms and in turn leads to obesity.

EDCs act by diverse mechanisms; accumulating body of evidence supports that these chemicals disrupt some epigenetic, structural, and functional mechanisms, which control energy homeostasis, lipid metabolism, appetite regulation, and adipogenesis [40–44].

Chemical obesogens are considered to function through various factors as leptin, ghrelin, melanocyte-stimulating hormones, neuropeptide Y, amphetamine-regulated transcript, agouti-related protein, and cocaine, as well as through inhibiting aromatases as the P450 family members (CYP19 and CYP3A1) [42–44] or through modifying the expression of various receptors for steroid hormones, retinoic X, peroxisome proliferator-activated, and glucocorticoids [45]. The exposure to obesogen chemicals may influence the steroid hormone receptors or may change serum levels of metabolic hormones or may influence nuclear receptor signaling pathways in preadipocytes, which would result in adipocyte differentiation and a tendency to excess weight [44, 45].

The systemic reactions to exposure to environmental chemical factors can potentially increase the risk for obesity-related health effects, as metabolic syndrome, insulin resistance [46], prediabetes, diabetes, oxidative stress [47], pre-hypertension [48], hypertension, and nonalcoholic fatty liver diseases [49] even in the pediatric age group.

Even in the pediatric age group, environmental chemicals can influence oxidative stress and proinflammatory cytokines [46, 47, 50], which in turn would initiate the second hit suggested in the "two-hit hypothesis" [51, 52] for the progression of fatty liver to metabolic syndrome and diabetes.

The other aspect of the influences of environmental factors on obesity and its health consequences can be the impact of these chemicals on intrauterine growth retardation,
| | | | | | | in num amattivita itagocana itini | | | |
|---|--|-----------|--------|----------------------|---------------------|--|---|-----------------------------|----|
| Chemicals | 1st author | St.yr | Ge.Loc | Sample size | Study population | Characteristics Uses | Mechanisms | Human effects Animal effect | ts |
| Phytoestrogens (genistein and daidzein) | Miriam J. J. de Kleijn [21] 2002 | 1761 | USA | 5209 | 30–59 y | Included in various food and food supplements, in particular soy product | High doses inhibited adipose deposition but at low doses similar to those found in Western and Eastern diets, in soy milk, or in food supplements containing soy, it induced adipose tissue deposition especially in males | | |
| Perfluorooctanoic acid (PFOA) | Frank D. Gilliland [24] | 1985–1989 | USA | 115 | | | Perfluorooctanoic acid (PFOA) increases PPAR-dependent lipid mobilization, fatty acid oxidation, and adipose tissue and adipose tissue atrophy during periods of experimental exposure. PFOA probably exerts anorexigenic effects through a central hypothalamic hypothalamic hypothalamic nechanism that triggers a decrease in food intake in adult rodents | | |
| Perfluoroalkyl compounds (PFCs) | Sakr,CarineJ [23] 2007 | 2007 | | 1025 | | | Agonists for one or more of the PPARs, providing a mechanistic link to disturbed lipid and steroid metabolism | | |
| Phtalates | Elizabeth E Hatch [22] 2008 | 1999–2002 | USA | 4369 participants | 6-80 y | As plasticizers and stabilizers in a variety of plastics. They are found in industrial paints and solvents but also in cosmetics, perfumes, and | PPARα, PPARγ, ER, and peptidergic hormones | | |

TABLE 1: Summary of main obesogen chemicals and their health effects.

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| | Animal effects | | In-utero studies, showed TBT to accumulate lipids in adipose, testis, and liver tissues in neonate mice. and increasing epididymal adipose mass in adult mice | Mice treated with low doses of E2 or BPA showed rapid increases in insulin release and reduced plasma glucose. High dose for 15 d reduction in body weight. 3 m did not alter body weight and fat depot |
|---------------|---------------------|--|---|---|
| | Human effects | | | There has been no information on BPA effects on human adipocytes |
| | Mechanisms | | PPARg and RXR have been shown to disrupt normal development and homeostatic controls over controls over adipogenesis and energy balance. suggested an inhibition of adipogenesis in the 3T3-L1 cells(1) TBT stimulates adipocytes differentiation in vitro and increases adipose mass in vivo in the 3T3-L1 cells | BPA mimics the actions of E2 on blood glucose homeostasis via two pathways: a rapid pathway involving ncmER and a prolonged pathway involving ER. It inhibits adiponectin release and stimulates release of IL-6 and TNF α . mouse triggers 3T3-L1 cells (fibroblasts that can differentiate into adipocytes) to differentiate into adiporectin and increased IL-6 and TNF α |
| tinued. | Uses | | Antifouling agents in paints for marine for a variety of other uses | Used in food and water containers blaby bottles, lining of food and beverage metal cans, medical tubing, epoxy resins, and dental fillings |
| TABLE 1: Cont | Characteristics | | Tetravalent tin compounds with a variety of mono-, di-, tri-, or tetra- subsituted functional groups | BPA is a small (228 Da) molecule which is used as a monomer in polymeriza- tion reaction to produce polycarbonate plastics |
| | Study population | Primary and junior high schools | Mice, aged 21 days and weighing 10.5–13.5 g | 8–15 y |
| | Sample size | 960 | 32 mice | 360 |
| | Ge.Loc | Taiwan | China | China |
| | St.yr | 2008 | 2009 | 2011 |
| | lst author | Mei-Lien Chen [19] 2009 | Zhenghong Zuo [17] 2011 | He-xing Wangl [15] 2012 |
| | Chemicals | Nonylphenol | Organotins, as tributyltin chloride (TBT) and bis (triphenyltin) oxide | Bisphenol A (BPA) |

TABLE 2: Summary of mechanisms suggested for main obesogen chemicals.

| Mechanism | Acting by | Chemicals |
|---|-----------------------------------|---|
| Metabolic sensors | PPAR, RXR, TR | TBT, TPT, PFCs, phthalate |
| Sex steroid dysregulations | CYP19, ER, AR | TBT, TPT, phthalate, BPA, alkylphenol, phytoestrogen, DES |
| Central integration of energy balance | PH, HPA, EC, NE | TBT, TPT, phthalate, BPA, alkylphenol, phytoestrogen, SSRI, typical antidepressant, atypical antipsychotic |
| Metabolic point | GR signal- ing(11_HSD), HPT | TBT, TPT, PBDEs, Dithiocarbamates, Glycyrrhetinic acid,TZD |

TBT: tributyltin; TPT: triphenyltin; BPA: bisphenol A; PFCs: perfluoroalkyl compounds; PBDEs: polybrominated diphenyl ethers; DES: diethylstilbestrol; SSRI: selective serotoninreuptake inhibitor; TZD: thiazolidinediones; NE: neuroendocrine effects; PH: peptidergic hormones; EC: endocannabinoid; HPT: hypothalamus-pituitary-thyroid; HPA: hypothalamus-pituitaryadrenal.; TR: thyroid hormone receptor; PPAR: peroxisome proliferator activated receptors; RXR: 9-cis retinoic acid receptor; ER: estrogen receptors; AR: androgen receptors.

low birth weight, and prematurity [53–55], which are documented as predisposing factors for obesity and adult chronic diseases.

Whether the results of laboratory models can be generalized to health hazards in humans remain to be determined, but a growing number of epidemiologic studies also suggest a link between exposure to environmental chemicals with obesity. However, it should be considered that in many human studies, weight gain has not been an endpoint in the original proposal, and excess weight has been reported as an adverse effect.

Environmental factors have diverse health effects [47–50, 56–58]. Although rapid changes in lifestyle habits, along with increased energy intake and decreased energy expenditure, are considered as the main causes of excess weight, but by considering the rapid escalating trend of obesity in various age groups and in populations with different lifestyle habits and diverse socioeconomic levels, it is obvious that it is simple-minded to consider only these two factors responsible for this expanding global problem; the role of other environmental determinants as obesogen chemicals is being proposed in this regard.

4.1. Study Limitations. Most studies included in this review have been observational and cross-sectional. Large-scale longitudinal studies with long-term followup are necessary to document the clinical importance of exposure to environmental chemicals.

5. Conclusion

The current evidence proposes that the systemic responses to exposure to environmental factors, notably during developmental phases of life, could potentially increase the risk of excess weight. By taking into account the current knowledge on the adverse transgenerational effects of obesogen chemicals on human health, the global obesity epidemic should be considered as a multifactorial complex disorder necessitating the emphasis of public health interventions for environmental protection.

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Research Article

Investigation of the Effect of Occupational Noise Exposure on Blood Pressure and Heart Rate of Steel Industry Workers

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Received 24 October 2012; Accepted 19 May 2013

Academic Editor: Roya Kelishadi

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Background and Objectives. This study aimed to investigate the effect of noise exposure on blood pressure and heart rate of steel industry workers. *Materials and Methods.* In the present cross-sectional study, 50 workers were selected from a steel company in Fars province, Iran, and exposed to 85, 95, and 105 dB noise levels for 5 minutes. The participants' blood pressure and heart rate were measured using Beurer BC16 pulse meter both before and after the exposure. *Results.* The study results showed no significant difference in blood pressure and heart rate before and after the exposure. However, the workers' systolic blood pressure had increased compared to before the exposure; of course, the difference was not statistically significant (P > 0.05). Besides, although the subjects' heart rate had reduced in comparison to before the exposure, the difference was not statistically significant (P > 0.05). *Conclusion.* No significant change was observed in blood pressure and heart rate after acute exposure to 85, 95, and 105 dB noise levels.

1. Introduction

Noise is one of the physical factors in industries, and, today, more attention is being paid to its harmful effects. After smoking and air pollution, noise pollution is considered as the third cause of heart attack among the residents of Berlin [1]. World Health Organization (WHO) also considers noise as the third dangerous pollutant of megacities [2]. Moreover, damage to the hearing system, interference in conversation, effects on the organs of vision, effects on balance system, social disorders, psychological as well as nervous effects, impacts on electrolytes, physiological effects, and mental effects are among the noise health effects on human body [2].

Almost two thousand years ago, Pliney stated that the individuals living near noisy waterfalls tend to suffer from hearing loss sooner than other people. Also, Ramazzini reported several cases of occupational deafness in 1700 [3]. The results of a study which was conducted in 2000 showed hearing loss as the main harmful effect of long

exposure to occupational noise [4]. Furthermore, Neghab et al. performed a study on the workers of petrochemical complex and revealed that noise had led to an increase in blood pressure and hearing loss in the exposed workers [5]. In the same line, Smith et al. investigated the body's physiological responses when being exposed to high-noise levels and showed that exposure to repeated, continuous noise caused the incidence of physiological as well as psychological responses and resulted in changes in heart rate as well as blood pressure [6, 7]. Moreover, according to the study by Motamedzade and Ghazaiee, exposure to higher than 85 dB noise levels increased both systolic and diastolic blood pressure, affected the working efficiency, and led to interference in conversation [8]. Ising and Michalak compared the effects of noise in both field and laboratory conditions and showed that exposure to 97 dB noise level had resulted in physiological as well as psychological changes in half of the study subjects [9].

Overall, according to the report by WHO, noise causes 4 million dollars health damage every day [10, 11], and

| Variable | Mean (SD) | Range | Number = n |
|-------------|---------------|-------------|--------------|
| Height (cm) | 174 (6.14) | 160–189 | 50 |
| Weight (kg) | 71.78 (12.16) | 49–110 | 50 |
| BMI | 23.42 (3.28) | 16.95-32.14 | 50 |
| Age (years) | 28.92 (5.40) | 19–42 | 50 |

TABLE 1: Demographic and occupational characteristics of the study subjects [mean (SD) and range].

TABLE 2: Systolic and diastolic blood pressure and heart rate before and after the exposure to different noise levels.

| Variable | Mean (SD) before exposure | Mean (SD) after exposure | P-value [*] |
|---------------------------------|---|--|---|
| Systolic blood pressure (mmHg) | 117.38 (12.32) | 115.75 (11.09) | 0.564 |
| Diastolic blood pressure (mmHg) | 73.87 (10.78) | 74.12 (8.69) | 0.925 |
| Heart rate (bpm) | 74.5 (8.33) | 71.5 (13.06) | 0.200 |
| Systolic blood pressure (mmHg) | 111.88 (7.52) | 112.12 (5.81) | 0.889 |
| Diastolic blood pressure (mmHg) | 69.37 (4.68) | 69.75 (4.97) | 0.623 |
| Heart rate (bpm) | 74.5 (9.85) | 71.75 (9.43) | 0.147 |
| Systolic blood pressure (mmHg) | 109.37 (12.51) | 111.87 (9.81) | 0.445 |
| Diastolic blood pressure (mmHg) | 69 (6.5) | 71.5 (6.54) | 0.308 |
| Heart rate (bpm) | 71.12 (9.26) | 70.87 (11.03) | 0.895 |
| | VariableSystolic blood pressure (mmHg)Diastolic blood pressure (mmHg)Heart rate (bpm)Systolic blood pressure (mmHg)Diastolic blood pressure (mmHg)Heart rate (bpm)Systolic blood pressure (mmHg)Diastolic blood pressure (mmHg)Heart rate (bpm)Systolic blood pressure (mmHg)Heart rate (bpm)Heart rate (bpm) | VariableMean (SD) before exposureSystolic blood pressure (mmHg)117.38 (12.32)Diastolic blood pressure (mmHg)73.87 (10.78)Heart rate (bpm)74.5 (8.33)Systolic blood pressure (mmHg)111.88 (7.52)Diastolic blood pressure (mmHg)69.37 (4.68)Heart rate (bpm)74.5 (9.85)Systolic blood pressure (mmHg)109.37 (12.51)Diastolic blood pressure (mmHg)69 (6.5)Heart rate (bpm)71.12 (9.26) | Variable Mean (SD) before exposure Mean (SD) after exposure Systolic blood pressure (mmHg) 117.38 (12.32) 115.75 (11.09) Diastolic blood pressure (mmHg) 73.87 (10.78) 74.12 (8.69) Heart rate (bpm) 74.5 (8.33) 71.5 (13.06) Systolic blood pressure (mmHg) 111.88 (7.52) 112.12 (5.81) Diastolic blood pressure (mmHg) 69.37 (4.68) 69.75 (4.97) Heart rate (bpm) 74.5 (9.85) 71.75 (9.43) Systolic blood pressure (mmHg) 109.37 (12.51) 111.87 (9.81) Diastolic blood pressure (mmHg) 69 (6.5) 71.5 (6.54) Heart rate (bpm) 71.12 (9.26) 70.87 (11.03) |

* Paired *t*-test.

occupational noise can put the industrial workers' health at a high risk [12].

Based on what was mentioned above and since noise can have both physiological and psychological effects on humans, the present study was conducted in order to investigate the effects of noise exposure on blood pressure and heart rate in steel industry.

2. Materials and Methods

The present cross-sectional study aimed to investigate the effect of occupational noise exposure on heart rate and systolic as well as diastolic blood pressure. Considering CI = 95% and power of 90%, the sample size of the study was determined as 50 subjects who were selected through simple random sampling. The inclusion criteria of the study were being physically and psychologically healthy, not smoking, not using alcohol, not taking hypnotic drugs, and not working in shifts.

The participants' demographic information was gathered through a questionnaire, and their systolic as well as diastolic blood pressure and heart rate were measured using Beurer BC16 pulse meter. In addition to assessing the workplace noise, a sample of the devices' noise was also obtained. In doing so, a microphone was attached to a worker's collar near his ear and the device's noise was recorded for 10 minutes.

Considering the features of steel industry, this study was conducted with exposure to 85, 95, and 105 dB noise levels in controlled experimental conditions for 3 consecutive days. At first, the subjects were placed in a quiet room with the background noise level of 40 dB and their systolic as well as diastolic blood pressure and heart rate was measured. Then, they were exposed to the noise recorded from the workplace at 85, 95, and 105 dB levels for 5 minutes and systolic as well as diastolic blood pressure and heart rate was measured again. In order to eliminate the sequence effect, the experiments were performed with 24 h intervals. Finally, the data were entered into the SPSS statistical software, and paired *t*-test was used in order to compare the means of the variables before and after noise exposure.

3. Results

The demographic characteristics of the study subjects are presented in Table 1. In this study, age, weight, height, systolic and diastolic blood pressure, and heart rate followed normal distribution.

Overall, devices were there in 38% of the workplace space. Moreover, the results of workplace noise analysis showed that, among the 60 areas under study, 13 (23%) had over 85 dB noise level and 23 (39%) had caution range noise level, that is, 65–85 dB.

Table 2 presents the subjects' systolic as well as diastolic blood pressure and heart rate before and after noise exposure in the controlled experimental conditions.

As the table depicts, the mean of systolic blood pressure has increased at all noise levels except for 85 dB; however, the changes were not statistically significant (P > 0.05). On the other hand, diastolic blood pressure increased a little at all the three noise levels. Besides, a decrease was observed in the mean of heart rate at all the noise levels; nevertheless, the changes were not statistically significant (P > 0.05).

4. Discussion

Up to now, the mechanism noise that affects blood pressure has not been identified. Nevertheless, several studies have shown high secretion of vasoconstrictors in urine as a result of being exposed to higher than 90 dB noise levels, which might represent the biological effects of noise exposure on blood pressure [5]. In the study by Ising and Michalak no significant difference was observed in the subjects' heart rate after acute noise exposure [9]. In general, acute exposure to 90-100 dB noise levels increases the catecholamines [5, 13] which might have led to an increase in systolic as well as diastolic blood pressure. However, the changes in blood pressure were not statistically significant, which is consistent with the findings of the present study. On the other hand, Motamedzade and Ghazaiee showed that exposure to higher than 85 dB noise levels resulted in an increase in both systolic and diastolic blood pressure, affected the working efficiency, and led to interference in conversation [8], which is in line with the results of the current study. In the study by Neghab et al., a significant difference was found between the exposed and the reference groups' mean blood pressure, which might be due to the industry under investigation as well as the study design. Moreover, the exposed and the reference groups were similar in the present study, while Neghab et al. selected two separate groups (control and exposed) in order to investigate the effects of noise.

Overall, since blood pressure and heart rate might be affected by various factors, the results obtained regarding the effects of noise exposure on these parameters must be interpreted with caution.

5. Conclusion

The findings of the present study were in agreement with those of the previous studies conducted on the issue. According to the results, no significant difference was observed in blood pressure and heart rate before and after acute exposure to 85, 95, and 105 dB noise levels.

Acknowledgments

The present work was financially supported by Shiraz University of Medical Sciences, Shiraz, Iran (Contract no. 90-5940). Hereby, the authors would like to thank the workers of Pasargad industrial complex for their cooperation in the study.

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Research Article

Association of Blood Cadmium Level with Cardiometabolic Risk Factors and Liver Enzymes in a Nationally Representative Sample of Adolescents: The CASPIAN-III Study

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Received 22 March 2013; Accepted 27 April 2013

Academic Editor: Mohammad Mehdi Amin

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Introduction. This study aimed to determine the association of blood cadmium level with cardiometabolic risk factors and liver enzymes in adolescents. *Methods.* This case control study comprised 320 Iranian adolescents, 160 with metabolic syndrome and an equal number of controls. They were selected from participants of a nationwide survey entitled the CASPIAN-III study. Cadmium was measured by atomic absorption method. *Results.* The mean age of the case and control groups was not significantly different (15.3 \pm 2.6 versus 14.63 \pm 2.5 years, resp., P > 0.05). The mean cadmium level was near double-fold higher than the standards of the World Health Organization, without significant difference between the MetS and control groups (10.09 \pm 2.21, 9.97 \pm 2.38 μ g/L, resp., P > 0.05). Cadmium level had positive but nonsignificant correlations with diastolic blood pressure, serum triglycerides, fasting blood glucose, LDL-C, and liver enzymes. *Conclusion.* Cadmium level had positive but nonsignificant level, and this may be because of the high levels of cadmium in both groups studied or because of the young age group of participants. Controlling environmental pollutants shall be a priority for the prevention of chronic diseases.

1. Introduction

Metabolic syndrome (MetS) is an emerging health problem at global level and increases the risk of most chronic diseases. It origins from early life and consists of various components including obesity, elevated blood pressure, elevated serum glucose, and dyslipidemia in terms of increased triglycerides and reduced high-density lipoprotein cholesterol (HDL cholesterol) levels [1]. It is no more limited to the western countries and adult populations [2, 3]. Asians have an ethnic predisposition to MetS, and it is one of health concerns in Iran [4, 5].

MetS is a multifactorial condition, and in addition to genetic and lifestyle factors, environment influences the development of this disorder [6]. Heavy metals are one of the environmental factors that may have a role in this regard.

Heavy metals or toxic metals such as mercury, lead, and cadmium have no biological function in human system and are potentially toxic even at trace concentrations. Cadmium can enter into blood stream by eating and drinking cadmium-contaminated food or water and/or by breathing cadmium-contaminated air [7–9]. Lee and Kim reported for the first time that blood cadmium level is a risk factor for MetS [9]. Various studies showed that urinary cadmium levels are significantly and dose dependently associated with both impaired fasting glucose and diabetes and even can lead to diabetic nephropathy [10, 11]. A study in Pakistan revealed that high cadmium levels in biological samples of diabetic women may play a role in the pathogenesis of diabetes mellitus and may also impact on their neonates [12]. With the advent of large-scale metal mining and smelting, as well as fossil fuel combustion in the industrial countries, the emission rate of heavy metals has increased dramatically [13].

Both MetS and cadmium exposure and accumulation in the body start at young age [14, 15]. Therefore, a relationship may exist between cadmium and MetS from childhood.

This study aimed to compare the serum cadmium level, cardiometabolic risk factors, and liver function tests in adolescents with and without MetS.

2. Methods

This case control study was conducted as a substudy of the third survey of the national school-based surveillance system entitled Childhood and Adolescence Surveillance and PreventIon of Adult Noncommunicable disease (CASPIAN-III) (Caspian is the name of the world's largest lake, located in Northern Iran) study. The main study was approved by the institutional review boards at national and provincial levels. Written consent and oral assent were obtained from students and their parents, respectively. The current substudy was conducted on blood samples collected in the main study and was approved by the Ethics Committee of Isfahan University of Medical Sciences. This study was performed in accordance with the ethical standards of the Helsinki Declaration.

The main study was conducted as a school-based nationwide health survey among 5570 students aged 10–18 years, who were recruited by multistage random cluster sampling from urban and rural areas of 27 provincial counties in Iran. Those students with history of any acute or chronic diseases and any medication use were not included in the study [16].

A trained team of health professionals conducted the physical examination under standard protocols by using calibrated instruments. Weight, height, and waist circumference (WC) were measured. Body mass index (BMI) was calculated as weight (Kg) divided by height squared (m²). Blood pressure was measured under standard protocol [17].

For blood sampling, students were invited to the nearest health center to the school. Fasting venous blood samples were centrifuged, and fresh sera were analyzed for fasting blood glucose (FBG), lipid profile, and liver function tests, that is, alanine aminotransaminase (ALT) and aspartate aminotransaminase (AST) by using Pars Azmoon reagent kits (Tehran, Iran). For measuring cadmium, frozen sera of 160 participants with MetS and an equal number of healthy controls were used. Cadmium levels were determined by atomic absorption spectrophotometer by using hollow cathode lamps. Similar to the first survey of CASPIAN study [18], we used the definition provided by Cook et al. [19]. This definition is based on criteria analogous to that of the National Cholesterol Education Program Expert Panel on Detection, Evaluation, and Treatment of High Blood Cholesterol in Adults Adult Treatment Panel III (ATP III) [20]. It defines the MetS as having at least three of the following criteria: WC was at or above the 90th percentile value for age and sex; SBP and DBP were at or above the 90th percentile for age, sex, and height; the midpoint value for HDL-C (\leq 40 mg/dL) was used as a 10th percentile value; the midpoint value for TG (\geq 110 mg/dL) was taken as the 90th percentile value for age. FBG levels of \geq 100 mg/dL were considered to be high [21].

2.1. Statistical Analyses. Statistical analyses were performed using SPSS statistical package version 18 for Windows. Chisquare and independent sample *t*-tests were used to compare categorical and quantitative data, respectively. Correlation models were used to assess the relationships between the diagnostic components of MetS and cadmium concentration. *P* values of <0.05 were considered as statistically significant.

3. Results

The study population consisted of 320 adolescents (160 with MetS and 160 healthy controls). The mean age of the case and control groups was not significantly different (15.3 ± 2.6 versus 14.96±2.51 years, resp., P > 0.05). The mean cadmium level was near double fold higher than the standards of the World Health Organization [22], without significant difference between the MetS and control groups (10.09±2.21, 9.97 ± 2.38 µg/L, resp., P > 0.05).

Table 1 presents the characteristics of the study population. BMI, total cholesterol (TC), TG, FBG, ALT, SBP, and DBP were significantly higher in the MetS group than in controls. The corresponding figure was not significantly different for AST, HDL-C, and low density lipoprotein cholesterol (LDL-C).

According to the regression analysis, cadmium level had positive but nonsignificant relationship with LDL-C, TG, FBG, ALT, AST, and DBP (Table 2).

4. Discussion

We investigated the association of cadmium level with cardiometabolic risk factors, MetS, and liver function tests in a nationally representative sample of Iranian adolescents. To the best of our knowledge, this study is the first of its kind in the pediatric age group. Cadmium level was near twofold higher than standard levels [22] in all of the population studied. However, cadmium level was not significantly different among adolescents with and without MetS. Likewise, cadmium had positive, but nonsignificant association with liver function tests and most cardiometabolic risk factors. This nonsignificant association may be because of high levels of cadmium in both groups with and without MetS. In addition, it is suggested that the adverse health effects of

| | Metabolic syndrome group | Control group | P value |
|-----------------------------------|--------------------------|--------------------|----------|
| Age (years) | 15.3 ± 2.6 | 14.96 ± 2.51 | 0.13 |
| Cadmium (µg/L) | 9.97 ± 2.38 | 10.09 ± 2.21 | 0.65 |
| Systolic blood pressure (mm Hg) | 122 ± 11.03 | 101.64 ± 14.57 | < 0.0001 |
| Diastolic blood pressure (mm Hg) | 79.32 ± 6.85 | 64.52 ± 11.08 | < 0.0001 |
| Total Cholesterol (mg/dL) | 162.9 ± 40 | 147.45 ± 24.26 | < 0.0001 |
| HDL-C (mg/dL) | 41.56 ± 15.65 | 41.45 ± 9.82 | 0.939 |
| LDL-C (mg/dL) | 91.56 ± 24.14 | 90.65 ± 20.31 | 0.71 |
| Triglycerides (mg/dL) | 130.9 ± 67 | 79.81 ± 20.42 | < 0.0001 |
| Fasting blood glucose (mg/dL) | 97.4 ± 16.95 | 81.3 ± 6.3 | < 0.0001 |
| Alanine aminotransaminase (U/L) | 23.38 ± 5.17 | 16.84 ± 5.88 | < 0.0001 |
| Aspartate aminotransaminase (U/L) | 24.9 ± 5.11 | 23.31 ± 5.24 | 0.2 |

TABLE 1: Characteristics of adolescents with and without metabolic syndrome: the CASPIAN-III Study.

TABLE 2: Linear regression analysis of cadmium with cardiometabolic risk factors and liver enzymes: the CASPIAN-III Study.

| | Cadmi | um level |
|-----------------------------|-------|----------|
| | Beta | P value |
| Body mass index | 0.006 | 0.92 |
| Systolic blood pressure | -0.05 | 0.52 |
| Diastolic blood pressure | 0.10 | 0.24 |
| Total Cholesterol | 0.65 | 0.47 |
| HDL-C | -0.03 | 0.56 |
| LDL-C | 0.04 | 0.62 |
| Triglycerides | 0.02 | 0.78 |
| Fasting blood glucose | 0.042 | 0.58 |
| Aspartate aminotransaminase | 0.06 | 0.92 |
| Alanine aminotransaminase | 0.08 | 0.82 |

cadmium on cardiometabolic risk factors would develop over time and may be nonsignificant in adolescence.

Children can be exposed to cadmium through contaminated air, water, soil, food, consumer products, and secondhand smoke [23]. The estimated half-life of cadmium is about 10 to 30 years, and over time, it accumulates in different organs as kidney, liver, bone marrow, and muscles, and these organs could be a source of cadmium continuously released into the bloodstream [24, 25].

Contrary to our results, a study in Korea revealed that blood cadmium levels increased the risk of MetS in adults [9]. It is well documented that chronic cadmium exposure may cause impaired fasting glucose and diabetes in humans [26, 27]. Heme oxygenase-2 (HO-2) acts as a protective factor against type-2 diabetes and obesity; cadmium has the propensity to alter its catabolism and may increase the risk of diabetes [28]. We did not find any significant association of cadmium with MetS and FBG; this may be because of the young age group studied; such association may develop over time.

Some studies have reported blood cadmium level as a risk factor for prehypertension in both women and men [29]. Cadmium concentrates in the kidney and may induce proteinuria and renal dysfunction; in turn it may cause hypertension. Moreover, renal cadmium reduces CYP4A11 and PPARs, which may be related to hypertension and sodium retention [30, 31]. We found positive association between cadmium and blood pressure, but the weak and nonsignificant correlation may be because of the young age of the study participants, and longitudinal studies are necessary to assess the long-term effects of cadmium on blood pressure.

In our study, the association of cadmium level with serum lipid profile was weakly positive, but nonsignificant; this may be because in both groups with and without MetS, cadmium level was considerably high without significant difference between the two groups. Experimental studies have shown that cadmium exposure induces alterations in lipid profiles [32–34]. No epidemiological study has been performed in this regard. However, some studies showed that cadmium levels in blood and urine are independent factors associated with the development of atherosclerotic plaques by the influence on selected lipid metabolism parameters [35–37].

Environmental factors have various health impacts on risk factors of noncommunicable diseases [38] even in children and adolescents [39, 40]. Different sources of pollutants should be controlled to prevent their short-term and longterm adverse health effects.

4.1. Study Limitations and Strengths. The main limitation of this study is its cross-sectional nature, so the associations of different variables should be considered with caution. The study strengths are the novelty of studying the association of cadmium with cardiometabolic risk factors and liver enzymes in the pediatric age group and using data of a nationally representative group of adolescents, which would increase the generalizability of the study findings.

5. Conclusion

Cadmium level was considerably high in both groups of adolescents with and without MetS. It had positive but nonsignificant association with cardiometabolic risk factors and liver enzymes. This finding may be because of the high levels of cadmium in both groups studied or because of the young age group of participants. Controlling environmental pollutants shall be considered as a health priority for primordial/primary prevention of noncommunicable diseases.

Conflict of Interests

The authors declare that they have no conflict of interests.

Acknowledgment

This project was conducted as a substudy of a national surveillance program. This research project was conducted as a thesis funded by Isfahan University of Medical Sciences.

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Research Article

Nitrogen Removal in a Full-Scale Domestic Wastewater Treatment Plant with Activated Sludge and Trickling Filter

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Received 13 November 2012; Revised 27 February 2013; Accepted 13 March 2013

Academic Editor: Mohammad Mehdi Amin

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During the last decade, more stringent effluent requirements concerning the nutrients effluent values have been imposed by legislation and social concern. In this study, efficiency of total nitrogen removal in activated sludge and trickling filter processes (AS/TF) was investigated in Tehran North wastewater treatment plant. Biological system in this site was included, anoxic selector tank, aeration tank, final sedimentation, and trickling filter. A part of treated wastewater before chlorination was mixed with supernatant of dewatered sludge and fed to the trickling filter. Supernatant of dewatered sludge with high concentration of NH_4 -N was diluted by treated wastewater to provide complete nitrification in trickling filter Produced nitrate in trickling filter was arrived to the anoxic tank and converted to nitrogen gas by denitrification. According to the study result, low concentration of organic carbone and high concentration of NH_4 -N led to nitrification in TF, then nitrate denitrification to nitrogen gas occurred in selector area. NH_4 -N concentration decreased from 26.8 mg/L to 0.29 mg/L in TF, and NO_3 -N concentration increased from 8.8 mg/L to 27 mg/L in TF. Consequently, the total nitrogen decreased approximately to 50% in biological process. This efficiency has been observed in returned flow around 24% from final sedimentation into TF. It was concluded that, in comparison with biological nutrient removal processes, this process is very efficient and simple.

1. Introduction

Many industrial effluents, agricultural wastes, or other human activities generate high strength ammonium wastewater [1]. Water pollution represents one of the most serious environmental problems due to the discharge of nutrients into receiving waters. Hence, stricter standards for the operation of wastewater treatment plants (WWTPs) have been imposed by authorities. In order to meet these standards, improved control of WWTPs is needed. WWTPs should be controlled in such a way that plant operating costs are minimized, while effluent standards are still maintained. Different control algorithms for WWTPs have been introduced over the years [2]. Approximately 25% of all water body impairments are due to nutrient-related causes (e.g., nutrients, oxygen depletion, algal growth, ammonia, harmful algal blooms, biological integrity, and turbidity). Total effluent nitrogen comprises ammonia, nitrate, particulate organic nitrogen, and soluble organic nitrogen. The biological processes that primarily remove nitrogen are nitrification and denitrification [3]. Advances in secondary wastewater treatment processes and increased implementation of regulations on discharged effluents over the last few decades have led to variations in wastewater treatment ranging from simple organic carbon oxidation to the removal of nitrogen (N) and phosphorus (P) [4]. Nitrogen removal is normally realized by sequentially alternating between oxic and anoxic conditions or by the creation of separated zones with suitable conditions for nitrification and denitrification, respectively. Alternatively, high rates of simultaneous nitrification and denitrification (SND) can be achieved, in activated sludge and biofilm type systems alike, at operational conditions where both oxic and anoxic microenvironments are present. Nitrification can occur at the liquid/biomass interface, while denitrification of nitrate (or nitrite) may be found in deeper subsurface biomass zones [5].

Organic matter and nutrient removal from wastewater improves the environmental conditions as well as provides health and well-being to the citizens [6]. Activated sludge process is one of the most widely used biological treatments of wastewaters containing carbon and nitrogen pollutants [7]. Conventional nitrogen removal from wastewater by activated sludge is most often achieved by sequential aerobic and anoxic processes. There is a tremendous need to develop reliable technologies for the treatment of domestic wastewater in developing countries. Such treatment systems must fulfill many requirements, such as simple design, use of nonsophisticated equipment, high treatment efficiency, and low operating and capital costs. In addition, consonant with population growth and increase in urbanization, the cost and availability of land are becoming a limiting factor, and "footprint size" is increasingly becoming important in the choice of a treatment system [8]. There are a number of BNR process configurations available. Some BNR systems are designed to remove only TN or TP, while others remove both. For BNR systems to result in low TN and TP effluent concentrations, proper operation and control of the systems are essential. Operators should be trained to understand how temperature, dissolved oxygen (DO) levels, pH, filamentous growth, and recycle loads affect system performance. BNR costs differ for new plants and retrofits. New plant BNR costs are based on estimated influent quality, target effluent quality, and available funding [9]. One of the key design parameters for any biological nutrient removal system is the influent C, N, and P ratios [1]. The COD/N ratio influences the population of microorganisms. Since an increase in this parameter results in a decrease in nitrification efficiency and an improvement of denitrification efficiency [10]. The control of DO concentration is also crucial as it determines the dominant processes in the reactor. A high DO inhibits denitrification, whereas a low DO causes a limitation of ammonia oxidation [11]. DO is easily controlled by manipulating the air supply, and it strongly influences the cost of wastewater treatment resulting from aeration. A low COD/N ratio and a low DO promote partial nitrification, and this diminishes the oxygen demand by 25% and the COD requirement for denitrification by 40% [12]. The most important factors affecting SND are organic carbon, DO concentration, and floc size [13]. Simultaneous growth of nitrifiers (autotrophs) and heterotrophs in a single reactor with a high COD/N ratio causes low nitrification efficiency due to competition between these two bacterial groups [14]. The optimal DO concentration for effective nitrogen removal via SND equals $0.5 \text{ mg O}_2/\text{L}$ [15]. The aim of this study is survey of efficiency of total nitrogen removal in activated sludge and trickling filter processes (AS/TF) in Tehran North wastewater treatment plant.

2. Materials and Methods

2.1. Description of TWWTP. Tehran wastewater treatment plant (TWWTP) will consist of 4 modules, designed for 2,100,000 person and an average daily inflow of $5.2 \text{ m}^3/\text{s}$. This plant is located within the latitude and longitude of 35.569098 and 51.439877. The two wastewater streams are combined down flow of separate flow measurements and treated together by mechanical and biological treatment steps supplemented with sludge treatment units.

Aeration tanks are employed for biological removal of pollutants using the activated sludge process. Each of the four aeration tanks consists of a selector cascade and two additional cascades. The basins are designed as plug flow reactors of rectangular shape. The outlet of the trickling filters will also be transferred into the inlet channels of the aeration tanks. During normal operation, each of the four trickling filters, will discharge its outlet in one inlet channel of the aeration tanks. Thus, equal distribution of nitrate to the four lines is provided. However, in case of maintenance work in either an aeration tank or a trickling filter it will also be possible to combine the trickling filter outlets in a combined collection/distribution structure and to distribute the flow to all lines (which are in operation) by gravity flow. The aeration tanks represent the very location in which the biological treatment of wastewater takes place by adopting the medium-loaded activated sludge process. Due to the treatment target and the system chosen, mainly degradation of BOD₅ (organic pollutants) will be performed. The required denitrification will mainly be achieved in the anoxic selector cascade and by simultaneous denitrification in anoxic zones of the aerated part of the tank and within the sludge flocks. During periods with low wastewater temperature the predenitrification and simultaneous denitrification will provide a nitrate-free effluent. During periods with high wastewater temperature, some nitrate might remain in the effluent, which is not affecting the effluent quality as long as severe denitrification in the final sedimentation tanks is prevented. To prevent this "wild" denitrification, it will be possible to reduce the sludge retention time in the final sedimentation tanks to below 1 hour by control of the return sludge flow. A selector is employed to prevent and to control filamentous bacteria growth. Air or mechanical mixers can be used for sufficient mixing within the selector compartment. In this case, the selector will mainly provide anoxic conditions due to the inlet of nitrate from trickling filter effluent. Some air supply is foreseen for mixing purposes only. With regard to denitrification capacity, the introduced air is considered in the design as shown below. Generally, the air supply will only have a limited effect on denitrification due to the high respiration rate in this initial compartment of the aeration tank (up to 4 times higher than average respiration rate). Effluent transfers the treated water to agricultural network, in case of noncompliance of the treated water quality with the stipulated treatment standard.

2.2. WWTP Measurements

2.2.1. Full-Scale Experiments. A year monitoring campaign was set up in one of the beds (March, 2011, and March, 2012),



FIGURE 1: The TWWTP schematic and sampling points.



FIGURE 2: BOD₅ in influent and effluent.

including the measurement of flow rate (in flow and out flow of the plant, tricking filter inflow) and the collection of weekly samples (one single sample by week, during 57 weeks) in four points: influent and effluent and two samples in inlet and outlet of trickling filter to determine the total nitrogen (TN), ammonia nitrogen (NH₄-N), and nitrate nitrogen (NO₃-N). For determination of COD/N in this study, COD sample in influent was taken. Figure 1 shows the WWTP processes schematic and location of sampling. The COD was determined with cuvette tests LCK 314 (15– 150 mg COD/L) and LCK 514 (100–2,000 mg COD/L), following DIN 38049-4, and a CADAS 50 spectrometer (Hach Lange, Germany). Total nitrogen, ammonia nitrogen, and nitrate nitrogen were obtained using the cuvette tests LCK 238 (5–40 mg N/L), LCK 303 (2–47 mg NH₄-N/L), LCK 342 (0.6–6 mg NO₂-N L21), and LCK 339(0.23–13.50 mg NO₃-N/L), following standards DIN38406-E 5-1 and DIN 38402-A51 and the same spectrometer. BOD was determined according to the standard methods for the examination of water and wastewater [16]. The experimental apparatus consisted of three parallel module with electrodes for a continuous monitoring of pH, temperature and dissolved oxygen (DO), and computer control system to maintain DO concentration and temperature around set points.

3. Result and Discussion

Sewer system which transfers sewerage to Tehran North wastewater treatment plant is too long and reaches to more than 30 kilometers in some branch. Height deference between the highest and lowest levels in above mention system is more than 700 meters. This matter causes the BOD₅ concentrating in sewer to decrease by reaeration. Average concentrations of BOD₅ in influent and effluent of the plant were, respectively, 255 mg/L and 8.2 mg/L per studied duration. In such condition, ammonification also happens (see Figure 2). Between NH₄-N, NO₃-N, and TN in raw wastewater is shown in Figure 3.

Due to the importance of COD/TN, this factor and its trend was calculated. In NH4-N was analyzed in inlet and outlet of trickling filter, and that removal efficiency was



ΤF

FIGURE 3: NO₃-N, NH₄-N, and total nitrogen in AS and TF.



FIGURE 4: COD/TN and TN removal efficiency in influent.

98%. Between TN removal efficiency and COD/TN shows that these parameters are not related directly, and this trend implies the effective parameters on the total nitrogen removal efficiency. The proof which approves the above result is the stable removal of BOD₅ and unstable removal efficiency of total nitrogen as shown in Figure 4.

Concentration of NH₄-N before trickling filter and after aeration tank has shown that nitrification was well done. NH₄-N concentration decreased from 26.8 mg/L to 0.29 mg/L in TF (see Figure 5), and NO₃-N concentration increased from 8.8 mg/L to 27 mg/L in TF.

Since, the main inflow of trickling filter is supplied by effluent, absorbed oxygen in this unit is used for converting NH₄-N to NO₃-N, and there is no requirement to consume oxygen for organic carbon oxidation. Base on Figure 7, average ratio for TF inflow to total plant flow was 24% and data approves that this ratio is desirable for 50% of TN removal.

Average concentration of total nitrogen of Tehran wastewater treatment plant was analyzed and was shown to be



FIGURE 5: NH₄-N in before and after TF.



FIGURE 6: NO₃-N in before and after TF.

55 mg/L of which 35 mg/L is related to NH_4 -N and 0.8 mg/L for NO₃-N as in Figure 6.

Relation between tricking filter flow to total plant flow ratio and total nitrogen removal efficiency has been demonstrated in Figure 7, in which the average of $Q_{\rm TF}/Q_{\rm in}$ reaches to 24%. This figure shows that nitrification and denitrification have been done well, and dissolve oxygen has been available and enough for nitrification in trickling filter. In order to evaluate TN removal efficiency, this parameter is measured in before and after biological units Based on the plant design, at least 50% of TN must be removed. Therefore, trickling filter was used, and the same time, the power consumption also decreased. Reduction of energy consumption was related to lower dissolve oxygen in aeration tanks; the concentration of dissolve oxygen in aeration tank is set to 0.9 mg/L, and under this condition, BOD₅ and TN diminished to the defined



FIGURE 7: Removal efficiency of TN, $Q_{\rm TF}/Q_{\rm in}$, and TN out.

limit. Also trickling filters are employed for the nitrification of ammonia contained in the highly concentrated filtrate from sludge dewatering Figure 8 illustrates BOD and TN removal efficiency. Additionally, a part of the effluent of the activated sludge stage is returned via the trickling filters for nitrification. Due to subsequent denitrification of the produced nitrate in the activated sludge stage, the effluent requirement of $N_{total} \leq 30 \text{ mg/L}$ will be achieved. Beside the transfer of ammonia to the trickling filters, the recirculation of final clarifier effluent also serves for dilution of the sludge dewatering filtrate in order to provide sufficient alkalinity in the trickling filters. Differing from the original design, it is now foreseen to transfer only filtrate from sludge dewatering to the trickling filters. All other sludge waters and wash waters will be transferred to the primary sedimentation or to the activated sludge stage. Due to this process adaptation, the BOD₅ load and suspended solids (SSs) load to the trickling filters will be very low.

Albuquerque et al. reported that ammonia removal rates reached higher values (from $172 \text{ g N/m}^3 \text{ d}$ to $564 \text{ g N/m}^3 \text{ d}$) for C/N = 2 and lower values (from $13.6 \text{ g N/m}^3 \text{ d}$ to $34.6 \text{ g N/m}^3 \text{ d}$) for C/N = 20. Between 50% and 70% of the ammonia was removed in the upper section of the filter [17].

In Ryu et al. study, NH₄-N removal performance was stable with the removal efficiency of 95-96% on average, regardless of HRT applied. At the TCOD- to TKN-ratio of 3:6 of four-stage biological aerated filter system, the effluent NO₃-N concentration of denitrification column was 2.7 mg/L which was excellent in nitrogen removal performance by employing four columns functioning as sorption, nitrification, denitrification, and purification, respectively [18].

Based on Timothy et al. study, in various operating condition, the TFs removed an average of 2.4×10^{-4} kg N/(dm²), and the NTFs removed an average of 1.5×10^{-5} kg N/(dm²) because of low loading [19].



FIGURE 8: BOD₅ and TN removal efficiency.

In the full-scale bioreactor for treating an average leachate flow of $304 \text{ m}^3 \text{ d}^{-1}$ with a SRT range of 12 and 18 d, the average COD, NH_4^+ -N, and NO_3^- -N concentrations at the upstream end of the bioreactor, that is, influent, were 554, 634, and 3 mg L^{-1} , respectively, whereas no NO_2^- -N was detected in the influent [20].

The resulting independence of the trickling filter from possible fluctuations of the quality of other process streams is a further advantage. Due to the low BOD_5 and SS load, it is evident that the main target of this treatment step is the oxidation of ammonia only. Some degradation of organic pollutants can be seen as side-effect, and it should be stressed that with the low organic load figures TF clogging is definitely prevented. The biologically active biomass will adhere to the filter material and will create a biological lawn mainly consisting of nitrifying bacteria (*Nitrosomonas* and *Nitrobacter*), which will accomplish the oxidation of ammonia to nitrate and further to nitrate. After passing the filter material, the nitrified water is collected and transferred to the inlet of the aeration tank by gravity.

During normal operation, each trickling filter will be directly connected with the inlet channel of one aeration tank. For redundancy reasons, it will also be possible to combine all trickling filter outlet flows before distribution to the aeration tanks. The recycle of the trickling filter effluent to the activated sludge stage contributes to an overall low energy demand of the biological treatment stage.

4. Conclusion

In AS/TF system, low concentration of organic carbone and high concentration of NH_4 -N led to nitrification in TF part, then nitrate denitrification to nitrogen gas occurred in selector area. So, these advantages in TF part causes a better performance than for TN removal in TF and AS separately. NH_4 -N concentration decreased from 26.8 mg/L to 0.29 mg/L in TF, and NO_3 -N concentration increased from 8.8 mg/L to 27 mg/L in TF. Consequently, total nitrogen decreased approximately to 50% in biological process. This efficiency has been observed in returned flow around 24% from final sedimentation into TF. It was concluded that, in comparison with biological nutrient removal processes, this process is very efficient and simple.

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Research Article

Phenol Photocatalytic Degradation by Advanced Oxidation Process under Ultraviolet Radiation Using Titanium Dioxide

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Received 19 October 2012; Accepted 4 March 2013

Academic Editor: Roya Kelishadi

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Background. The main objective of this study was to examine the photocatalytic degradation of phenol from laboratory samples and petrochemical industries wastewater under UV radiation by using nanoparticles of titanium dioxide coated on the inner and outer quartz glass tubes. *Method.* The first stage of this study was conducted to stabilize the titanium dioxide nanoparticles in anatase crystal phase, using dip-coating sol-gel method on the inner and outer surfaces of quartz glass tubes. The effect of important parameters including initial phenol concentration, TiO_2 catalyst dose, duration of UV radiation, pH of solution, and contact time was investigated. *Results.* In the dip-coat lining stage, the produced nanoparticles with anatase crystalline structure have the average particle size of 30 nm and are uniformly distributed over the tube surface. The removal efficiency of phenol was increased with the descending of the solution pH and initial phenol concentration and rising of the contact time. *Conclusion.* Results showed that the light easily passes through four layers of coating (about 105 nm). The highest removal efficiency of phenol with photocatalytic UV/TiO₂ process was 50% at initial phenol concentration of 30 mg/L, solution pH of 3, and 300 min contact time. The comparison of synthetic solution and petrochemical wastewater showed that at same conditions the phenol removal efficiency was equal.

1. Introduction

The most important problem that can threaten the water ecology and public health is the toxic and resistant compounds that can release to the environment through industrial wastewater [1]. Among the chemical compounds that are present in industrial wastewaters, the phenol and its derivatives are prevalent in industrial effluent; in addition, they can be released to water resources through natural ways (degradation of algae or of organic vegetation). Also, due to the physical structure, phenol was found in chemical solutions and even in the municipal wastewater. Due to relatively stability in environment, solubility in water, high toxicity, and associated health problems, phenol removal from industrial wastewater is important [2].

The phenol compounds can be released to environment through some industrial wastewater including coal industry, resin industries, paint industries, pesticides, medicine and cosmetic products, oil refinery, petrochemical, coal mines, aluminum and steel industries, compost, car production, and chemical industry, which can lead to water resources contamination. Phenol is also found in cleaning materials and disinfectants, cigarettes, car exhausts, and some pesticides [3, 4].

Phenol is involved in toxic pollutants, and the US Environmental Protection Agency reported that phenol is a priority among pollutants group [5]. Due to human health effect of phenol, the restrict standards was passed. World Health Organization (WHO) recommended that phenol concentration in water resources entering conventional water treatment must be $<2 \mu g/L$. Furthermore, the concentration of phenol, chlorophenols, 2, 4, 6 trichlorophenol in drinking water must be $<0.1 \mu g/L$ [6]. According to USEPA standard, and the permitted levels of phenol in water resources for human use and for fisheries are 0.3 and 2.6 mg/L, respectively. Furthermore, based on the standards of Japan, the permitted level in industrial wastewater effluent is 5 mg/L [7].

Some methods were used in the treatment of wastewaters containing resistant organic matters such as phenol. Degradation of phenol usually takes place by physicochemical methods including adsorption using activated carbon [8, 9], biological treatment [10], emulsion liquid membrane [11], ion exchanges, advanced oxidation processes (AOPs) (including cavitation, Fenton, and photocatalyst) [10, 12], chemical oxidation (methods in which ozone and water are used), photochemical and electrochemical, and ultrasound waves such as sonochemical, photochemical, photosonochemical [13], and hybrid of mentioned methods.

The hydrothermal oxidation process consists of wet air oxidation and oxidation in subcritical, critical, and supercritical water and was used for phenol degradation, but due to their high cost and energy consuming, they are used in special conditions.

Biological degradation usually takes longer time and is often affected by temperature variations and phenomenon of toxic pollutants [2, 14]. The ion exchanging and adsorption processes are very expensive [2]. However, advanced oxidation processes (AOPs) are among the most effective processes in degradation of resistant compounds.

Generally, AOPs include processes in which active hydroxyl radicals (OH[•]) as a strong oxidant for degradation and destruction of polluting materials are produced using different methods. Due to high oxidation capacity of hydroxyl radicals (2.8 V), most of the AOPs are based on this active radical [15, 16]. One of the most effective methods of advanced oxidation is the use of UV ray and oxidant such as H₂O₂, O₃, and TiO₂ [4, 17]. In recent years, common processes were used in the removal of organic matter including Fenton, photofenton, UV/TiO₂, and UV/H₂O₂/O₃. In photocatalytic degradation, the pollutants are degraded under the UV radiation in the presence of particles of metallic oxides such as ZnO and TiO₂ [8, 14, 18]. Titanium dioxide is a metallic oxide well known for degradation of organic matters [19] and is of relatively low cost, nontoxic, and insoluble in water [20, 21].

 UV/TiO_2 process is one of the latest and most effective methods for the treatment of these pollutants. In this process, titanium dioxide nanoparticles were extensively used in photocatalytic reactions as a catalyst. The small particle size of this metallic oxide can lead to the increase of special surface of catalyst and the improvement of the photocatalytic activity. In recent research, titanium dioxide nanoparticles in anatase crystalline phase are used and in order to description of produced, XRD spectrum and their SEM images was used [22, 23]. When titanium dioxide was used as suspension form, nanoparticles separation from liquid needed in which separation needed to high investment and operational costs. Also, in this method, the designing and operation at continuous system were impossible. Thus, stabilizing titanium dioxide on a solid film caused the removal of the above difficulties and made the industrial application of these processes possible. The improvement of AOP and its application in the industrial projects necessitate the stabilization of photocatalyst on a solid film.

Various methods were applied for the synthesis of titanium dioxide photocatalyst. These methods are divided into two main groups: (1) wet chemistry methods such as solgel method and (2) dry method such as aerosol [24, 25]. Also, different methods are used for the preparation of titanium dioxide films such as chemical vapor deposition, hot oxidation, electron beam evaporation, sol-gel method with rotating coating, and dip coating of titanium dioxide compound [26, 27].

In recent year, sol-gel technique is a new method that is used for the synthesis of mineral oxide materials in low temperatures and in nanoscale. In fact, sol-gel is an efficient physical/chemical method for producing materials in form of powder, ceramic coating, fibers, thin layers, and porous materials. In this method, hydrolysis and repetitive condensation reactions of an alkoxide in presence of humidity can produce mineral oxides with particle size that is adjustable from nanometer to the micron:

Precursors
$$\xrightarrow{\text{Hydrolysis}}$$
 Sol $\xrightarrow{\text{Condensation}}$ Gel. (1)

In photocatalytic degradation, light energy was used in photon form with wavelength less than 387.5 nm as ultraviolet radiation or sunlight. The exposure of electrons surface of titanium atoms with light was caused exciting the surface electron and moving from valance layer to transition layer (e_{CB} -). The changing in energy level can form the free electron in form of OH[•] or other radicals that they can oxidize organic matters and reduced of metals [2, 8, 14, 28]. Photocatalytic destruction of phenol follows the first-order reaction (Figure 1).

The advantages of AOP were including the low cost, stability, and high efficiency [16, 28].

This study was attempts to coating layers of titanium dioxide on the inner and outer surface of quartz tubes and application of AOP (UV/TiO₂) for phenol remove from industrial and petrochemical wastewater.

2. Materials and Methods

2.1. Fixation of TiO_2 on Surfaces of Quartz Tubes. For production of photocatalytic coatings, a solution from nanoparticles of TiO_2 with 1% (w/w) was prepared. The TiO_2 nanoparticles were purchased from Nanosav Co. with specification of SAV2104. The TiO_2 has an oval shape with diameter of >30 nm, and the anatase crystalline phase is formed in water. The TEM image of TiO_2 nanoparticles and XRD spectrum of anatase TiO_2 nanoparticles are shown in Figures 2 and 3.



FIGURE 1: Schematic of photocatalytic mechanism of TiO₂.



FIGURE 2: TEM image of titanium dioxide nanoparticles.

2.2. Preparation of Underlayer. For proper coating of nano layers on surface, there should be no presence of any contamination on the underlayer as it can affect the quality of the coats and create nonuniform layers. Underlayers are comprised of quartz tubes with 20 cm lengths. Cleaning method of underlayers is follows as.

- (1) Washing up with soap and water to remove the contaminants and fats.
- (2) Acetone washing.
- (3) Heating up in a kiln to 500°C for 30 min.
- (4) Placing underlayers in $H_2O_2: H_2SO_4$ solution at 3:7 ratio (w/w) for 1 h. For this purpose, H_2O_2 was slowly added to sulfuric acid to prevent bubbles formation. This solution was called piranha solution (strong oxidant) and was able to produce hydroxyl groups on the surface and create them in a hydrophilic way.
- (5) After washing underlayers with deionized water, were remained in NH₄OH:H₂O₂:H₂O solution (1:1:5 w/w) for 1 h washed, with deionized water, and dried. After this, glass underlayers are ready for coating.



FIGURE 3: XRD spectrum related to anatase TiO₂ nanoparticles.

2.3. Coating. The used coating method was a dip coating. In this method, coat layers are formed by dipping the under layer into solution and extracting them at constant speed. Thickness of coat was determined by speed of extracting and solution viscosity. Dip coating is an efficient and quick method, but it was suffering from some disadvantages including difference between thickness-coated layers. The thickness of top layers is slightly less than bottom layer. Figure 4 shows the system used for coating. The cleaned glass under layer was connected to mechanical hoist, and under layer was vertically dipped into nanoparticle cell and kept for 1 min till the solution becomes undistributed. So, the under layer was extracted at a constant speed, and layer thickness was controlled by variation of speed of hoisting up. Figures 4, 5, and 6 showed stages of dip coating, schematic of dipcoating set up method, and quartz tubes coated with TiO₂ nanoparticle, respectively. To perform the coating of quartz tubes dip-coating method, 180 mL of TiO₂ nanoparticle solution was used to create coating layer with thickness \approx 400 nm on the surfaces of tubes.

2.4. Photocatalysis Reactor Set Up. The photocatalysis reactor consisted of 8 coated quartz tubes with TiO_2 nanoparticles with 30 mm inside diameter as parallel arrangement and contact tank. The contact tank was constructed of plexiglass with dimensions of 50 : 10 : 15 cm and 3.5 L working volume. The quartz tubs were immersed in open top water bath. The feed solution was introduced to system by means of two peristaltic pumps and flowed inside/outside tubes at uniform constant speed. In photocatalysis reactor, in order to provide UV radiation, four UV lamps with maximum wavelengths of 365 nm and 250 w were used on top of reactor. The schematic of photocatalysis reactor and applied UV lamps is shown if Figure 7.

2.5. Operational Conditions. An investigation program comprising 5 different phases was performed. Each phase corresponded to certain intensity of light and distance from UV source (15, 30, 50, 100, and 150 cm), initial phenol



FIGURE 4: Stages of dip-coating method.



FIGURE 5: The schematic of dip-coating set up.

concentrations (30, 40, 60, 80, and 100 mg/L), solution pH (3, 6.5, 9, and 11) contact time (from 0 to 300 min), and phenol removal of Bandar Abbas oil refinery wastewater. All experiments were performed at 25° C.

2.6. Chemicals and Instrument. All chemical substances were purchased from Merck Co. The amounts of phenol were analyzed using the standard methods [29]. The spectrophotometer was used for phenol analysis at wavelength of 670 mm.

3. Results

3.1. Optical Properties of TiO_2 Layers. After coating glass underlayers, their optical transmission spectrum was determined by spectrophotometer UV-Vis at wavelength range



FIGURE 6: The quartz tubes coated with TiO₂ nanoparticle.



FIGURE 7: Photocatalysis laboratory-scale plant.

of 200 to 1100 nm accuracy of 1 nm and scanning speed of 400 nm/min and air as reference.

The TiO₂ (1% wt) cell was used for coating with 3 mm/sec for speed of coating layers. As shown in Figure 8, after first layer coating, the edge of TiO₂ film adsorption has slightly moved from glass position which indicated that coating process successfully performed. This slight movement showed that TiO₂ film deposit on glass was low and thin. TiO₂ is a semiconductor with indirect energy in range of 3–3.2 ev, and it could not properly absorb light in the range of UVA (320– 380 nm) which includes sun UV rays. For this reason, edge of adsorption could not clearly appear at thin film of TiO₂, and oscillations could not be observe due to interference effect. Therefore, only a thin film of TiO₂ was produced.

To increase layers thickness, coating was repeated few times. Optical transmission spectrum of TiO_2 film after coating layers was depicted in Figure 9. For preventing the removal of TiO_2 film of tube surface and for confident estimating of TiO_2 film thickness, after each coating, layers were placed in a kiln at 200°C for 10 min. In this way, the layers were made dry and hard.

According to Figure 9, at first coating, the transmittance of visible light was 85%, and the transmittance of visible light was reduced with the increasing number of coat layers (thickness of TiO_2 film). This reduction in transmittance may be related to interference effects and light scattering. In this stage, the coating speed was 3 mm/sec, and after each layer, layers were placed in a kiln at 200°C for 10 min.

In a thicknesses less than 100 nm, optical transmission spectrum was not indicating oscillations due to interference



FIGURE 8: Optical transmission spectrum through glass only and a thin TiO_2 layer (coating speed: 3 mm/sec).



FIGURE 9: Optical transmission spectrum through some layers of TiO_2 after each coating.

effects. For this, the optical transmission spectrum could not be done for the first and second layer. As the thickness of TiO_2 film was increased, the effect of oscillations clearly appeared. Figure 10 showed the results of optical transmittance for the third and fourth layers of TiO_2 film.

As seen in Figure 10, the experimental and calculated transmitted spectrum in wavelengths of 400–1100 nm was agreed to large extent. Results showed that in monolayer coating, 30 nm of TiO_2 film was adsorbed on under layer, and after dozen coating, the TiO_2 film thickness reached to 360 nm.

3.2. Effects of Intensity of Light and Distance from UV Source. Distance of UV lamps from phenol solution and water was adjusted to 15, 30, 50, 100, and 150 cm. The results of the effects of intensity of UV source are shown in Figure 11. The phenol removal by photocatalysis was straight line decreased with the rising of UV lamps from reactor.

As in Figure 11, it appeared that optimum distance in which concentration reduction occurs most rapidly was 15 cm from surface of phenol solution. The reason for this may



FIGURE 10: Experimental and calculated optical transmission spectrum of TiO₂ layers: (a) third layer and (b) fourth layer.



FIGURE 11: Effect of various intensities of UV lamps on (a) effluent phenol concentration and (b) removal efficiency of phenol (C_0 : 40 mg/L, solution pH: 6.5, and contact time: 0–300 min).

be due to lower light intensity and reduction of surface photocatalytic activities.

the increase in the duration of photocatalysis process for over 5 h led to further diminishment in phenol concentration.

3.3. Effect of Initial Phenol Concentrations and Contact Time. To assess the effect of initial phenol concentrations, the solutions with concentrations of 30, 40, 60, 80, and 100 mg/L were provided and were fed to reactor. Figure 12 showed the results related to of effect of initial phenol concentrations on photocatalysis phenol removal efficiency. In terms of Figure 12, the phenol removal at initial concentration of 25, 30, and 40 mg/L by photocatalysis laboratory-scale plant was about 50% at 300 min contact time.

The percentage of phenol removal (Figure 12) decreases with the mounting of the initial concentration of phenol from 50% to 20%. This could be due to the saturation of the surface coat of photocatalyst with by-product that resulted from degradation of phenol. As clearly seen from Figure 12, 3.4. Effect of pH. The reduction of phenol was studied from the aqueous solution at different pH values. The solution with phenol concentration of 45 mg/L was provided, and HCl and NH_4OH were used in order to adjust solution pH at values of 3, 6.5, 9, and 11. The results obtained are shown in Figure 13 which shows the effect of solution pH on the phenol removal from the aqueous solution by photocatalysis process expressed in terms of the effluent phenol concentration and phenol removed percent. It is clear that phenol was effectively removed at solution pH: 3.

3.5. Phenol Removal from Bandar Abbas Oil Refinery Wastewater. This study was performed in which a pilot scale photocatalysis system was fed from Bandar Abbas oil refinery wastewater. The composition of the Bandar Abbas oil refinery wastewater varied as follows: phenol concentration (45 mg/L)



FIGURE 12: Influence of initial phenol concentration and contact time (a) effluent phenol concentration and (b) phenol removal efficiency (C_0 : 25–100 mg/L, solution pH: 6.5, distance of UV source: 15 cm, and contact time 0–300 min).



FIGURE 13: Effect of solution pH on (a) effluent phenol concentration and (b) phenol reduction (C_0 : 40 mg/L, distance of UV source: 15, contact time 0–300 min, and various solution pH).

and pH (5.5). Figure 14 shows the evolution of phenol removal from Bandar Abbas oil refinery wastewater.

4. Discussion

Photocatalytic degradation of phenol with TiO_2 as catalyst and UV radiation is the newest process. In this research, photocatalytic degradation of phenol with emphasis on contact time, solution pH variations, UV radiation, and initial phenol concentration was assessed.

4.1. TiO_2 Coating Layers. In the first stage of this research, solution of the cell containing TiO_2 nanoparticles with anatase crystalline was prepared. So, coating of solution of cell containing crystallized nanoparticles inside/outside quartz tubes using dip-coating (sol-gel) method was induced. The

particles size, crystalline structure of coated surface with X-ray tests, and SEM were assessed. Results indicated that the obtained nanoparticles had anatase crystalline structure with average particles size of 30 nm and were uniformly distributed over tube surface. Also, results showed that in monolayer coating, 30 nm of TiO₂ film was adsorbed on under layer, and after dozen coating, the TiO₂ film thickness reached to 360 nm. It was clear that light could easily pass through the four layers of coating (1.5 mm).

4.2. Photocatalytic Degradation of Phenol. These results indicated that increasing contact time and reducing initial phenol concentration led to improvement in the removal percentage of phenol. Results of the experiment showed that in this process, removal efficiency was higher in low solution pH. So, with rising the solution pH from 3 to 11, phenol removal efficiency varied from 60% to 30%.



FIGURE 14: Phenol removal from Bandar Abbas oil refinery wastewater with phenol concentration of 45 mg/L.

As mentioned previously, from assessment of initial phenol concentration and with regard to contact time and solution pH, it could be deducted that for lower concentration of phenol in wastewater, removal efficiency is higher. The effect of solution pH showed that pH is an important variable and plays an important role in the equilibrium of acid and alkalinity, thereby, affected on degraded and nondegraded concentration of phenol. The maximum phenol efficiency was related to solution pH of 3 at phenol concentration of 30 mg/L. At constant amount of TiO₂ film on tubes, increasing initial phenol concentration resulted in low phenol removal efficiency and greater contact time needed. It can be predicted that by the increasing TiO₂ contact surface, the removal of higher concentrations will be possible. Comparison obtained results of phenol degradation from laboratory sample and industrial wastewater showed that at similar conditions, the phenol removal was equal.

Photocatalysis laboratory scale studies showed that this process could be suggested as an applicable method for removing phenol as toxic and dangerous matter from effluent and wastewater by degradation and converting it into safe matter. Application of these studies on laboratory scale could provide proper information for using this process as full scale.

It can be expected that AOP including UV/TiO₂ with advantages such as nonproduction of by-products, production of nondangerous by-products, environment friendly, and high efficiency in comparison to the biological methods will have a suitable layout in water and wastewater industries. Photocatalytic UV/TiO₂ process in conjunction with other processes such as membrane process, application of fixed TiO₂ film (present research), and changing of semiconductor TiO₂ surfaces and replacing of visible light in lieu UV radiation could be one of the most effective methods for the removal of organic solutions including phenol and its compounds. In addition, we suggested that other studies should be performed to test this method for some resistance and toxic compounds.

Conflict of Interests

The authors declare that there is no conflict of interests.

Acknowledgment

The authors would like to thank Islamic Azad University, Bandar Abbas Branch, Hormozgan, Bandar Abbas, Iran for its support.

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Research Article

Association of Nitrate, Nitrite, and Total Organic Carbon (TOC) in Drinking Water and Gastrointestinal Disease

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Received 12 February 2013; Accepted 19 March 2013

Academic Editor: Roya Kelishadi

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Objective. We aimed to investigate the amounts of nitrate, nitrite, and total organic carbon (TOC) in two drinking water sources and their relationship with some gastrointestinal diseases. *Methods.* This cross-sectional study was conducted in 2012 in Iran. Two wells located in residential areas were selected for sampling and measuring the TOC, nitrate (NO3⁻), and nitrite (NO2⁻). This water is used for drinking as well as for industrial and agricultural consumption. Nitrate and nitrite concentrations of water samples were analyzed using DR 5000 spectrophotometer. The information of patients was collected from the records of the main referral hospital of the region for gastrointestinal diseases. *Results.* In both areas under study, the mean water nitrate and nitrite concentrations were higher in July than in other months. The mean TOC concentrations in areas 1 and 2 were 2.29 ± 0.012 and 2.03 ± 0.309 , respectively. Pollutant concentration and gastrointestinal disease did not show any significant relationship (P > 0.05). *Conclusion.* Although we did not document significant association of nitrite, nitrate, and TOC content of water with gastrointestinal diseases, it should be considered that such health hazards may develop over time, and the quality of water content should be controlled to prevent different diseases.

1. Introduction

Nitrate is considered as the most prevalent chemical contaminant in the world's groundwater. Organic and inorganic sources of nitrogen are converted to nitrate. After reducing, nitrate can be biologically transformed to nitrogen gas. The growing contamination of public and private well drinking water by nitrate is mostly because of the widespread use of commercial fertilizers and waste [1].

Groundwater is used for agricultural and industrial consumption as well as for drinking water. Humans have altered the nitrogen cycle dramatically over the last decades, and as a result, nitrate is increasingly accumulating in water resources. Globally, human nitrogen production has increased significantly since 1950 due to the use of nitrogen fertilizers. In agricultural areas, groundwater and private and low depth wells have higher levels of nitrate. Fertilizers are most important contributing factor in agricultural areas; however, nitrogen from human waste seems to be an essential source in urban areas with deficient centralized water and sanitation systems [2].

Nitrate is in solution form and is mobile. It could become spread in groundwater and is one of the most common pollutant and concern for human health. It may have several health hazards. Drinking water contamination with nitrate could increase cancer risk, because nitrate could reduce to nitrite and the following nitrosation reactions give rise to N-nitroso compounds, which are especially carcinogenic and can act systemically. The suggested regulatory limit for nitrate is too conservative. A symposium in 2004 on drinking water nitrate and health assessed nitrate exposures and related health effects about the current regulatory limit. The contribution of drinking water nitrate toward endogenous formation of N-nitroso compounds was evaluated with a focus toward identifying subpopulations with increased rates of nitrosation [3, 4].

Drinking nitrate and nitrite under conditions likely to form N-nitroso compounds (NOCs), called endogenous nitrosation, is considered possibly carcinogenic to humans. Nitrate in drinking water is completely related to urine nitrate levels as well as excretion of nitrosoproline, a biomarker of endogenous nitrosation [4].

Water with high nitrate concentration is not suitable for human consumption, especially when its concentration exceeded the threshold limit (50 mg/L) recommended by the health authorities such as the World Health Organization (WHO) [5].

Human alteration of the nitrogen cycle has resulted in continuing accumulation of nitrate in the water resources. According to recent studies, a significant relationship exists between nitrate in drinking water and cancer types [3, 5–7].

Chemical analysis of a study in Iran showed that groundwater and water supply have considerably high levels of nitrate (from 52.3 mg/L to 52.69 mg/L). Nitrate level in some underground water wells in the landfill area was over the drinking water standard (50 mg per liter) [8, 9].

Growing body of evidence proposes the relationship between nitrate level in drinking water and gastric cancer [10–12].

This study aimed to investigate the amounts of nitrate, nitrite, and TOC in two drinking water sources and the relationship of nitrate and nitrite levels with some gastrointestinal diseases.

2. Materials and Methods

This cross-sectional study was conducted from Feb to June 2012 in Shahrekord city in central part of Iran. We selected this city because the level of nitrate in drinking water wells is high in this area with many underground water sources including approximately 493 deep wells, 321 wells, 171 deep semisubterranean, and 93 springs.

Two wells located in residential areas were selected for sampling and measuring TOC, nitrate (NO3⁻), and nitrite (NO2⁻). This water is used for drinking as well as for industrial and agricultural consumption.

Since the concentration of nitrate is usually constant yearround, we limited our study time to 5 months to save time and costs.

To determine the amount of nitrate and nitrite from these two wells, we collected a total of 18 samples (9 samples per well) and six samples (three samples per well) for TOC test.

2.1. Water Sampling. For sampling, we used one-liter plastic containers and filled each bottle with water of wells; then we emptied out their contents and once more about 900 mL of water was filled up to provide enough space for better shaking and mixing.

Samples were delivered to the Chemistry Laboratory of Health Faculty, Isfahan University of Medical Sciences, in less than 3 hours, and then they were analyzed after 24 hours.

Nitrate and nitrite concentrations of samples were read and analyzed using DR 5000 spectrophotometer with a wavelength of 220–275 nm. Experiments were repeated two times for each sample.

2.2. Using Spectrophotometer. The spectrophotometer uses indicator compounds to determine the concentration of nitrate in samples. The HACH Test kit was used; it involves mixing a premeasured amount of the indicator compound with a 50 mL of sample water; then the absorption in a particular wavelength was measured. After mixing and a delay for reaction, a color appeared (for nitrogen it is amber color), the darkness of which was measured in the spectrophotometer. The sample was introduced to the spectrophotometer via a pour-through-cell apparatus to minimize optical interferences from sample handling.

The program offered by the company (HACH 357 N Nitrate UV) was selected from the menu on the device. The device can be calibrated with distilled water. 50 mL of sample prepared with 1 mL of 1 N hydrochloric acid and the prepared sample was transferred to the quartz cell. Thereafter, the absorbance was displayed and we read it.

2.3. *Measuring Nitrite*. Measuring nitrite schedule was provided by the spectrophotometer (371 N Nitrite LR PP). This device was calibrated with samples of water, then we added a package of NitriVer 3 Nitrite reagent to 10 mL water samples, and after 20 minutes we read the absorption rate.

2.4. Measuring TOC. For measuring TOC, samples were transferred to laboratory of Isfahan Water and Sewage Company.

2.5. Gastrointestinal Diseases Hospital Records. The information of patients was collected from the Medical Records Department of Gastroenterology of Al-Zahra Hospital, Isfahan University of Medical Sciences. Patients with gastrointestinal diseases were referred from Shahrekord to this hospital. We selected this hospital because it is the main referral hospital of the region for gastrointestinal diseases, and patients of neighbor cities, including Shahrekord, are referred to this center.

2.6. Statistical Analysis. For statistical analysis, we categorized diseases to the following four groups: (1) bile duct diseases; (2) gastric diseases; (3) intestinal diseases; (4) other gastrointestinal diseases.

Data were analyzed by the Statistical Package for Social Sciences software version 20.0 (SPSS Inc, Chicago, IL, USA). Data are presented as mean and standard deviation. Comparison of values in various groups was assessed by One-Sample *t*- and Kruskall Wallis tests. The significance level was set at P < 0.05.

TABLE 1: Nitrate and nitrite levels in wells of the two areas under study in 2012.

| | | | N | itrate con | centration | ns in diffe | rent mont | hs | | | | | | |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|---------|---------|----------|---------|
| Place of sampling | Febr | ruary | Ma | rch | Ap | oril | Ju | ne | Ju | ly | Me | ean | Std. dev | viation |
| sumpting | Nitrate (mg/L) | Nitrite (mg/L) | Nitrate | Nitrite | Nitrate | Nitrite |
| Area 1 | 30.5 | 0.02 | 31.45 | 0.02 | 31.63 | 0.015 | 32.2 | 0.017 | 32.2 | 0.013 | 31.738 | 0.0166 | 0.74405 | 0.0045 |
| Area 2 | 22.7 | 0.026 | 23 | 0.01 | 22.86 | 0.014 | 22.86 | 0.016 | 24.4 | 0.022 | 23.033 | | 0.59582 | |

3. Results

The results of the analysis of water samples for nitrate, nitrite and TOC measurements are presented in Table 1. Results of descriptive analysis showed that the mean of nitrate and nitrite concentrations obtained in two areas was higher in July 2012 than in other months.

The mean of TOC concentrations in areas 1 and 2 was 2.29 ± 0.012 and 2.03 ± 0.309 , respectively (P > 0.05).

The frequency of abovementioned diseases according to the codes ((1) bile duct diseases; (2) gastric diseases; (3) intestinal diseases; (4) other gastrointestinal diseases) was as follows: 47.6%, 19%, 19%, and 14.3%.

The corresponding numbers in two sampling areas were as follows:

area 1: 0.25%, 0 %, 50%, and 25%,

area 2: 52.9%, 23.5%, 11.8%, and 11.8%.

Evaluation of the relationship between pollutant concentration and gastrointestinal disease did not show any significant relationship in two cities (P > 0.05).

4. Discussion

This study aimed to evaluate the association of nitrite, nitrate, and TOC in water of two areas with the frequency of some common gastrointestinal diseases. We did not find any significant association between the nitrate content of public water supplies and gastrointestinal diseases. The evidence for nitrate as a cause of cancers of the digestive tract remains controversial [13].

Our findings are consistent with some previous studies. A case-control study conducted during three years in USA showed negligible associations of colon or rectum cancers with measures of nitrate in public water supplies, including average nitrate and the number of years with elevated average nitrate levels [14]. A cohort study in Finland found no association between dietary nitrite intake and stomach cancer. Another cohort study in the Netherlands found no association between stomach cancer risk and quintiles of water nitrate intake, which was determined from public supply levels and tap water intake [4].

On the other hand, some studies demonstrated positive correlations between water content of nitrate or nitrite and gastrointestinal diseases. Some human studies revealed an association between water nitrate and N-nitroso compounds formation in the gastrointestinal tract. Though, few individual-based studies exist on the relationship of Nnitroso compounds precursors with risk of gastrointestinal cancers. Most epidemiologic studies of drinking water nitrate and stomach cancer were ecologic and found mixed results [15].

An ecological study in 2001 investigated the association of gastric cancer mortality and nitrate content of drinking water and showed significant association. This study supports the hypothesis that the high level of nitrate in drinking water may have a role in the development of gastric cancer [16].

In our study, the nitrate concentration in the wells of one of the areas under study was higher in summer than in winter. In summer time, agricultural activities and water use increase; therefore sewage and drainage will result in more nitrate production.

These two wells near the spill area are considered as the main sources of the increase in agricultural land drainage effluent nitrate concentrations in summer. In our study, nitrate, nitrite, and TOC values were under the standard levels recommended by the WHO (50, 3, and 3 mg/L).

Some research studies suggest that increasing the allowed levels of nitrate in drinking water can be without risk to human health. Furthermore, some persons with high rates of endogenous formation of carcinogenic N-nitroso compounds may be vulnerable to the development of gastrointestinal cancers. Given the extensive experimental data suggesting a role for nitrate in the formation of carcinogenic N-nitroso compounds and the widespread exposure to nitrate in the population, limited epidemiologic data exist on addressing the possible association of nitrate in drinking water with cancer risk.

Nitrate levels in water supplies have been increasing at global level; therefore, additional population-based studies with well-characterized exposures are urgently needed to further our understanding of cancer risk associated with nitrate ingestion [17] Given the importance of water quality on human health [18], future longitudinal studies should determine the effects of exposure to water content of nitrite and nitrate on development of different gastrointestinal diseases. High levels of nitrate and nitrite in water can be because of using fertilizers; relevant environment and health organizations should control these issues.

4.1. Study Limitations. The major limitation of our investigation is its cross-sectional nature; thus a causal relationship cannot be inferred from our findings, and longitudinal studies are required to test for causality and the clinical importance of our findings.

5. Conclusion

Although we did not document significant association of nitrite, nitrate, and TOC content of water with gastrointestinal diseases, it should be considered that such health hazards may develop over time, and the quality of water content should be extensively controlled to prevent different health hazards.

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Research Article

Evaluation of Chemical and Microbiological Quality in 21 Brands of Iranian Bottled Drinking Waters in 2012: A Comparison Study on Label and Real Contents

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Received 1 January 2013; Revised 23 February 2013; Accepted 17 March 2013

Academic Editor: Mohammad Mehdi Amin

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The purpose of this study was to evaluate and compare chemical and microbiological quality of the 21 Iranian bottled drinking waters reported on manufacturer's labeling and standards in 2012. Samples were analyzed for chemical properties K⁺, F⁻, SO₄²⁻, Cl⁻, Mg²⁺, Ca²⁺, and pH. Total and fecal coliform and heterotrophic plate counts of selected samples were analyzed by MPN and HPC tests, respectively, for three months. Finally, the labeled and real contents of the samples were compared. Potassium and sulfate ions about 43 and 52 percent of studied sample contents had values higher than label amounts, respectively. Ca²⁺, Cl⁻ ions, and pH were about 71, 48, and 67 percent, respectively, less than label values. Total and fecal coliforms had negative results. The mean concentrations and standard deviations for K⁺, Cl⁻, pH, Ca²⁺, Mg²⁺, SO₄²⁻, and HPC were 1.13 ± 1.06, 16.39 ± 31.97, 6.6 ± 0.7, 28.35 ± 10.34, 86.58 ± 33.21, 24.17 ± 17.30 mg/L, and 16855 ± 25603 cfu/mL, respectively. Thus, there is possibility of microorganisms' growth in favorite conditions in bottled water. It was imperative to assess the public health risks in bottled water in Iran.

1. Introduction

Recently, the consumption of bottled mineral waters has increased worldwide [1-3], because people living in developed countries have no suitable water supply at their homes [4]. Water quality can have a major impact on both individuals and communities health [5]. It is very important to human health to ensure the safety of consuming drinking water [6, 7]. Drinking water is important for survival, so that its biological and chemical contamination is a serious problem that may have severe health effects [7]. Human activities increase contamination levels through different point and nonpoint sources, which eventually cause them to be present in our drinking water resources [8]. Increasing pollution in drinking waters amplified the demand for natural mineral waters [5]. Natural mineral waters are defined as a microbiological healthy water originating in an groundwater tables or deposits and emerging from a spring tapped at one or more natural or bore exits with an individual and constant chemical composition [9, 10]. Casanovas-Massana and Blanch described that natural mineral waters are complex environments containing a large variety of autochthonous microbiota [11]. Mineral water is characterized by its purity at source, its content in minerals, trace elements, and other constituents [12]. Falcone-Dias et al. reported that mineral waters have been marketed as ideal for infant formula preparation and nursery drinking water, particularly for the immunosuppressed people [9]. In assessing the quality of drinking waters, consumers rely principally upon their senses with bottled waters being perceived as pure, safe, and of good taste; thus, their consumption is increasing despite the excessively high prices compared to tap water [3, 13]. Bottled mineral waters are relatively large proportion of bottled water (between 40 and 60% globally) [14]. Bottled drinking water has been occasionally related to diarrhea conditions known as traveller's disease. Although the microbial quality levels in processed water are often initially low, bottled mineral water is not a sterile product and can contain naturally occurring bacteria as well as those introduced during manufacturing or consumer handing [13, 15]. Fernanda also stated that natural mineral waters are not free of bacteria, and counts of 10⁴-10⁵ CFU/mL can be reached within a few days after bottling [9]. According to numerous studies, the microorganisms most frequently found in bottled natural mineral waters are aerobic heterotrophs, Pseudomonas spp, A. hydrophila, total and fecal coliform, Escherichia coli, and opportunistic pathogens (Flavobacterium and Mycobacterium) [9, 11, 13, 15-19]. Huguet et al. described that bottled mineral water includes four viruses (Polivio virus 1, Hepatitis A virus, Norovirus, and the Ms 2 phage). Several studies conducted on microbiology of water distribution systems and bottled waters showed fungal growth in water distribution systems and fungi spoilage in bottled mineral waters [20].

Mineralized water can also offer a significant amount of required nutrient such as calcium and magnesium [7]. Other components such as carcinogenic compounds, insecticides as DDT, and heavy metals [5], generally, are present in mineralized water in trace concentrations, whose effects on human health are inadequately understood or unknown [7]. Contamination of bottled water with nitrate and nitrite affects the health of infants more than adults, as they are more susceptible to serious health conditions such as Methemoglobinemia, due to the difference in their body size and chemical conditions of the body [8]. Cidu et al. testified an evaluations on the quality of drinking waters. They found that concentrations of Cl⁻, SO₄⁻²⁻, NO₃⁻, F⁻, and As⁻ were higher than water quality guidelines [3]. Chloride, sodium, and potassium amount introduced through water is actually very small, and magnesium and calcium content varies remarkably depending on the kind of water [12].

In the present study, the chemical and microbiological characteristics of 21 brands of bottled water sold in Isfahan market, one of the most important central province in Iran, were investigated and questioned their accuracy and precision with the levels reported on manufacturer's labeling. Also, the results were compared by the current Codex [21] regulation regarding bottled water in the world.

2. Materials and Methods

2.1. Sampling. The 21 analyzed brands of bottled mineral water samples in this research were the most consumable and very high sales brands between other bottled mineral waters in Isfahan, Iran. They were obtained from shops in the city of Isfahan, Iran in 2012. The bottled mineral water samples were opened in the laboratory and analyzed regarding the following anions, fluorides (F^-), chlorides (Cl^-), and sulfates (SO_4^{2-}), and cations which include potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), pH, and bacteriological contaminations for three months.

2.2. Materials Used. Only potassium reagent powder pillow was purchased from the Hach company (HACH LANGE, USA) and other materials such as reagents, acid, base, EDTA

and used salts BaCl₂, and NaCl, were purchased from the Merck company (Germany).

2.3. Laboratory Analysis. Determination of K⁺ ions was implemented according to Tetra phenyl borat method [23]. The Ca²⁺ and Mg²⁺ ions were analyzed by titration method with EDTA, and for Cl⁻ ions was performed by Mohr method. The SO₄²⁻ ions were detected by Turbidimetry method, and F⁻ ion was measured by colorimetric method [24]. Microbiological properties of sampled bottled mineral waters were analyzed according to Most Probable Number (MPN/100 mL) multiple-tube fermentation method. Analyses of heterotrophic plate count (HPC) were performed by using of R₂A agar medium as standard methods [24].

2.4. Statistical Test. All the statistical analysis was done with the SPSS statistics package program (Windows version 18.0). The results were stated as mean \pm SD. Comparison of anions and cations concentrations and pH, MPN, and HPC between natural mineral waters and Codex regulations in terms of statistical analyses were directed by student's *t*-test. In all data analysis, a value of P < 0.05, P < 0.01, and P < 0.001 was considered statistically significant.

3. Results and Discussion

In this study the amount of pH and ions: F^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , K^+ , and Cl^- was surveyed, in 21 samples of bottled mineral waters in Isfahan, Iran. Results showed that there were differences between amounts of these ions in their water contents and label insertion on the bottles (Table 1). Vandevijvere et al. reported that the fluoride levels were different between label and water contents of analyzed bottled mineral waters in Belgium [25]. This result is in opposite of our results that fluoride contents were the same as label values insertion. For magnesium, there was not any value inserted on studied bottled mineral water labels. For potassium and sulfate, respectively, about 43 and 52 percent of studied bottled mineral water contents had values higher than label amounts. Whereas for Ca²⁺, Cl⁻ ions, and pH, our data were about 71, 48, and 67 percent less than label amounts, respectively (Table 1).

Table 2 shows ranges, mean, and standard deviations of results comparing to water quality guidelines. *t*-test indicated that there were significant differences between amounts of each ion by water quality guidelines ($P_{\text{value}} < 0.001$). On the other hand, these differences were not meaningful for potassium ions (K⁺) ($P_{\text{value}} > 0.05$).

Azlan et al. presented that concentrations of manganese and fluoride in mineral waters were slightly lower than the international standard recommended limits in Malaysia [4]. However in our study, the fluoride results were higher than water quality guidelines. Cidu et al., in 2011, stated that in 20% of the bottled water samples, one or more components have been found at concentrations exceeding the Italian regulations (Cl⁻, SO₄²⁻, NO₃⁻, F⁻, and As) [3]. Also, in the present study, concentrations of these ions were exceeded the guidelines which were in opposite of this study results.

| Parameter | % equal to label amounts | % higher than label amounts | % less than label amounts | % not specified in label |
|-------------------|--------------------------|-----------------------------|------------------------------|-----------------------------|
| K ⁺ | 28.60 | 42.90 | 4.80 | 23.80 |
| Cl ⁻ | 14.30 | 9.50 | 47.60 | 28.60 |
| F^- | 52.40 | 14.30 | 0.00 | 33.33 |
| Ca ²⁺ | 4.80 | 9.50 | 71.40 | 14.30 |
| Mg ²⁺ | 0.00 | 90.50 | 0.00 | 9.50 |
| SO4 ²⁻ | 14.30 | 52.40 | 14.30 | 19.00 |
| рН | 23.80 | 0.0 | 66.70 | 9.50 |

TABLE 1: Comparison of label and real contents of bottled mineral water.

TABLE 2: Ranges, mean, and standard deviations of results compared to water quality guidelines *.

| Parameter | Ranges | Mean ± SD | Bottled mineral water quality guidelines [21] |
|------------------|--------------------|--------------------------------|---|
| K ⁺ | (-0.1)-(4.7) | $1.13 \pm 1.06 \text{ mg/L}$ | 0.7 mg/L |
| Cl^- | (140.15)-(0) | $16.39 \pm 31.97 \text{ mg/L}$ | 400 mg/L |
| F^- | (5)-(0) | _ | 1–1.5 |
| рН | (7.3)–(5.1) | 6.60 ± 0.66 mg/L | 7.75 |
| Ca ²⁺ | (49.70)-(11.22) | 28.35 ± 10.34 | 250 mg/L |
| Mg^{2+} | (189.58)-(38.40) | 86.58 ± 33.21 mg/L | 50 mg/L |
| SO_4^{2-} | (61.7)-(0.2) | $24.17 \pm 17.30 \text{ mg/L}$ | 400 mg/L |
| HPC | (79667)–(0) cfu/mL | 16855.24 ± 25603.213 cfu/mL | 500 ^{**} cfu/mL [22] |

* All units are mg/L except HPC that is as cfu/mL.

** Due to lack of bottled mineral water quality guidelines, the drinking water quality guideline was used.

Cemek et al. indicated that nitrate and nitrite levels in the mineral waters were not found in concentrations considered to be hazardous in terms of public health [5]. Also, Bertoldi et al., based on survey of the chemical composition of 571 European bottled mineral waters, reported that according to European legislation, 9% of samples had boron, nitrate, or nitrite levels above the legal limit existing in individual European countries [10]. Abouleish described that all bottled water samples demonstrated nitrate, nitrite, and other anions levels below the permissible levels accepted by U.S-EPA, U.S-FDA/CFR, and other international organizations, levels exceeding the European commission and drinking water directive (EC/DWD) permissible levels [8], and in our study the mean of all ions except potassium and magnesium had values less than codex guideline values [21]. Chiarenzelli and Pominville showed that except for one sample of mineral water, all bottled waters tested meet United States Environmental Protection Agency (US-EPA) primary standards for drinking water supplies [6].

The total and fecal coliform tests show negative results. In other words, there were not any total and fecal coliforms in these samples. However, the average of heterotrophic plate count (HPC test) in all of the monitored mineral bottled water was 16355 (cfu/mL). Because there are no specific guidelines from WHO for HPC results interpretations in bottled water, the drinking water quality guidelines in distribution systems (500 cfu/mL) were used in comparison to the results [22]. Thus, there were significant differences between obtained results and mentioned guidelines ($P_{value} < 0.05$).

Falcone-Dias et al. found difference between HPC repeated analyses on R2A and on this culture medium supplemented with the beta-lactam amoxicillin. There were insufficient clinical and epidemiological evidence to conclude that the high heterotrophic counts in drinking water pose a risk to consumer's health [9]. Kassenga reported that heterotrophic bacteria were detected in 92% of the bottled mineral waters samples analyzed and total and fecal coliform bacteria were present in 4.6% and 3.6%, respectively, in samples analyzed in Dare-s-Salaam, Tanzania [13], but in our study there were not any total and fecal coliforms. But the heterotrophic bacteria were detected in all 21 sample bottles. Zeenat et al. informed that between 28% and 68% of the samples of the bottled mineral water labels failed to meet the WHO guidelines of 100 CFU/mL and 7% of them also tested positive for fecal coliforms [15]. In the present study, standard of bottled mineral waters was considered 500 CFU/mL [22], thus the 100% of samples which were tested had positive results.

4. Conclusions

In this study, the concentrations of several ions include F^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , K^+ , and Cl^- and pH values were measured, in 21 samples of bottled mineral waters in Isfahan, Iran. Then, the sample quality contents were compared with labels on the bottles and then by water quality guidelines. Results showed that there were differences between concentration of these ions and label insertion on the bottles and there were

significant differences between concentrations of each ion by water quality guidelines. These differences were not meaningful for potassium ions (K^+). For other ions these difference were meaningful. Based on microbiological analysis, total and fecal coliforms had negative results. Though, comparison of HPC test with water quality guidelines was meaningful. There was an important total count of these heterotrophic bacteria in the samples. Thus, there is possibility of microorganisms' growth in favorite conditions in bottled water so it was necessary to evaluate the public health risks in bottled water in Iran.

Conflict of Interests

The authors have no conflict of interests to declare.

Acknowledgment

The authors wish to acknowledge the Department of Environmental Health Engineering and the Student Research Center, School of Health in Isfahan University of Medical Sciences, for financial support of the research project no. 190092.

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Research Article

Total Antioxidant Capacity and Malondialdehyde in Depressive Rotational Shift Workers

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Received 28 October 2012; Revised 20 February 2013; Accepted 7 March 2013

Academic Editor: Ajay K. Gupta

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Shift work is associated with sleep deprivation, occupational stress, and increased risk of depression. Depressed patients show increased oxidative stress. During excessive oxidative stress, Malondialdehyde (MDA) increases and total antioxidant capacity (TAC) decreases in body. This cross-sectional study was conducted to determine the serum level of TAC and MDA among depressed rotational shift workers in Shahid Tondooyan Tehran Oil Refinery. 21-item Beck Depression Inventory was used to measure depression level. The level of TAC and MDA was measured by 8 mL fasting blood sample. MDA was determined by thiobarbituric acid reaction. Serum total antioxidants were measured using the ABTS. Results of this study showed that TAC mean and standard deviation concentration was 2.451 (± 0.536) mg/dL and MDA was 3.725 (± 1.098) mic·mol/L, and mean and standard deviation of depression score and BMI were 14.07 (± 3.84) and 24.92 (± 3.65) kg/m², respectively. Depression score had a positive correlation with rotational shift work experience and work experience (r = 0.218 and r = 0.212), respectively, (P < 0.05).

1. Introduction

Shift work is defined as work scheduled outside the normal daytime working hours (7 AM to 6 PM) [1]. The trend in our society is toward an increasing pattern of shift work and it is essential for many industries such as refineries to have 24-hour work pattern [2]. More than 20 to 30 percent of workers are shift workers [3]. They are forced to work and sleep against normal chronobiological rhythms, and as a result the pattern of sleep-wake becomes misaligned [4]. Shift work can alter human Circadian system which is normally synchronized with the solar day [5]. Shift workers can never be adapted to their sleep/activity cycle, which is necessary for their work shift. They sleep at times their organism is set to activity and they work when physical effectiveness is low [6].

Disruption of normal circadian system can cause physiological and psychological problems. Shift work also negatively impacts workers' health condition [7] and cause diseases resulting in absenteeism from work. Sleep disorders are among the health problems caused by shift work [8]. The prevalence of difficulty initiating sleep is higher in rotational shift workers compared with regular day workers [9]. Based on different studies, shift workers complaining about sleep disorders and insufficient sleep range from 10% to 90% [10– 12]. Furthermore, sleep disorders and occupational stress lead to more sleepiness and reduce neurobehavioral function consequently, and, therefore, increase the risk of depression [13].

There is an association between poor sleep and symptoms of major depression in male shift workers [14]. Depression and sleep deprivation are reported to cause oxidative stress [15], resulting in the formation of reactive oxygen species (ROS) and eventually lead to neuronal and cellular damage. ROS are formed in the human body in the cytosol, mitochondria, lysosomes, peroxisomes, and plasma membranes under both physiological and pathological conditions [16]; their levels can increase by stress situations such as occupational stress [17, 18]. Stressful conditions lead to the excessive formation of ROS and cause oxidative stress [19]. Oxidative stresses occur when the production of free radicals exceeds the defensive response of the antioxidant system. Oxidative stress has a major role in the causality of some disorders that have higher prevalence in shift workers [20]. Malondialdehyde (MDA) increases in body during excessive oxidative stress [21].

Lipid peroxidation is one of the major outcomes of freeradical-mediated injury that directly damages membranes and generates a number of secondary products including aldehydes such as MDA, which is the most abundant individual aldehyde, resulting from lipid peroxidation [22]; also in oxidative stress, total antioxidant capacity (TAC) decreases [23]. Free radicals initiate a cascade, causing lipid peroxidation, DNA damage, cell death, and neurological problems. Total plasma antioxidant capacity is measured as an indicator of oxidative stress [24].

In Iran, few studies have been carried out about shift workers [25, 26]. Most of these studies are concerned with shift workers in Iranian hospitals. Studies about the shift workers in Iranian industries are rare [27]. The results of these few studies have revealed that Iranian shift workers are at risk of depression [28]; so this study was conducted to determine serum level of TAC and MDA among depressed rotational shift workers in Shahid Tongouyan Tehran Oil Refinery.

2. Methods

2.1. Research Participants. In this cross-sectional study, 456 potentially eligible candidates (all the shift workers in Tehran Shahid Tondgooyan Oil Refinery) were screened for depression symptoms by using 21-item Beck Depression Inventory questionnaire; a total of 397 (87.06%) workers returned the questionnaire. Out of 397 workers, 261 workers did not meet the inclusion criteria or met exclusion criteria. Finally, 136 shift workers aged 21–52 enrolled in the study. It should be noted that all of the shift workers in Tehran Shahid Tondgooyan Oil Refinery were men and their program was 8-hour backward shifts (from night to morning) 4 nights, 3 off, 4 afternoons, 1 off, and 4 mornings, respectively.

2.1.1. Inclusion and Exclusion Criteria. The study inclusion criteria were giving written consent to participate in the study and depression score ≥ 10 in 21-item Beck Depression Rating Scale and washout periods of two months for antidepressants medicines and two weeks for supplements were required, prior to the study entry. The exclusion criteria were history of thyroid diseases, liver diseases, kidney diseases, diabetes, cardiovascular diseases, cancer, and hypertension based physical examination, being professional sportsman, smoking, consuming alcohol, and substance abuse Information was collected using a self-administered general questionnaire.

2.2. Data Collection Tools. Data collection was performed using a self-administered general questionnaire "21-item Beck Depression Inventory" [29], which was translated into Persian. The general questionnaire elicited information on age, marital status, work experience, shift work experience, education, sports, smoking, alcoholic drinks, narcotics, and drugs. For enrolled participants, weight and height were measured with Seca standard tools (Germany) with 0.1 cm and 100 g precision while the participants had least clothes and were barefoot and body mass index (BMI) was calculated from the formula (weight (kg)/high (m)²).

Diastolic and systolic blood pressures were measured using a mercury sphygmomanometer with 5 mmHg precision from the right arm and after 10 min of resting in the sitting position. History of thyroid diseases, liver diseases, kidney diseases, diabetes, cardiovascular diseases, cancer, and hypertension was collected based on physical examination performed by the interviewing physician in the Health Center of Tehran Shahid Tondgooyan Oil Refinery.

2.2.1. Blood Sample Collection. To measure the level of TAC and MDA, 8 mL blood sample was collected from the vein anterior to the elbow at sitting position and after fasting for 10–12 hours from 7.30 AM to 8.30 AM o'clock. Needle holder 21 in a gel-containing tube without anticoagulant was used. Then, serum was separated using centrifuge for about 10 min at 1500 rpm. The extracted serum was transferred to microtubes labeled with identifier code and was kept at -70° C until the analysis time. The serum MDA level was determined using the method described by Satoh [30]. In this method, MDA was determined by thiobarbituric acid (TBA) reaction and separation on HPLC. UV detection was performed at 532 nm.

Serum total antioxidants was measured using the ABTS (2,2-Azino-bis sulfonic acid). This method is based upon reconstruct cation ABTS (the maximum absorbance at wavelengths 820, 734, and 660 nm) and the chain-breaking antioxidants are of low molecular mass. When the radical cation ABTS (green-blue) is restored to become a colorless solution, it reduces the optical absorption, proportional to the total antioxidant capacity of serum or plasma [31].

For the blinding purpose, we used samples with the identifier code. TAC was measured in the Department of Biochemistry, Tehran University of Medical Sciences, and MDA was measured in Tehran Noor Research Center.

2.3. Statistical Analyses. All analyses were performed using Statistical Package for Social Sciences (SPSS) version 16.0 for Windows (IBM Corporation, NY, USA). Descriptive statistics were shown as mean and standard deviation. The relationship between quantitative variables was tested by bivariate analysis. Linear regression was used to demonstrate the relationship of depression score with shift work experience. Difference between groups was tested by one-way regression analyses (ANOVA). The significant level was set at P < 0.05.

2.4. Ethical Consideration. The Review Board of Tarbiat Modares University approved the study. Ethical approval was obtained from the Medical Ethics Committee of Tarbiat Modares University in Tehran, Iran. All participants gave written consent to participate in the study. Participants were

| TABLE 1: Relationsh | ps between c | demographic and | l clinical vari | able and depression | n score. |
|---------------------|--------------|-----------------|-----------------|---------------------|----------|
|---------------------|--------------|-----------------|-----------------|---------------------|----------|

| Sociadamagraphic and clinical variables | Baseline (dep | ression score) |
|---|---------------|----------------------|
| Sociodemographic and chinear variables | Mean (SD) | P value ^a |
| Age (year) | 30.75 (7.19) | 0.055ª |
| Work experience (year) | 6.91 (6.76) | 0.013 ^a |
| Shift work experience (year) | 6.14 (6.24) | 0.011 ^a |
| Marital status | | |
| Single $(n = 49)$ | 13.42 (3.45) | 0.15 ^b |
| Married ($n = 87$) | 14.42 (4.01) | 0.13 |
| Education | | |
| >high school diploma | 17.67 (6.66) | |
| Diploma | 13.40 (3.65) | 0.024^{c*} |
| <high diploma<="" school="" td=""><td>14.87 (3.78)</td><td></td></high> | 14.87 (3.78) | |
| Clinical factors | | |
| BMI kg/m ² | 24.92 (3.65) | 0.780^{a} |
| Diastolic blood pressure (mmHg) | 66.84 (10.81) | 0.111^{a} |
| Systolic blood pressure (mmHg) | 110 (13.19) | 0.953ª |
| | | |

Spearman's correlation coefficient.

 ^{b}P value obtained by *t*-test.

^cP value obtained from one-way ANOVA.

* There are significant differences between diploma and high school diploma < (P = 0.029) (Tukey's test).

| TABLE 2: Relationship | between biomarker | concentration at shift work ex | perience (| year). (All | values are mean SD) |
|-----------------------|-------------------|--------------------------------|------------|-------------|---------------------|
|-----------------------|-------------------|--------------------------------|------------|-------------|---------------------|

| Parameters | ≤5 (<i>n</i> = 92) | 6-15 (n = 26) | $\geq 16 \ (n = 18)$ | P value |
|------------------------|---------------------|------------------|----------------------|---------|
| TAC, g/dL | 2.37 ± 0.57 | 2.55 ± 0.43 | 2.71 ± 39 | 0.025 |
| MDA, μ mol/L | 3.74 ± 1.11 | 3.82 ± 1.18 | 3.50 ± 0.88 | 0.60 |
| BMI, kg/m ² | 24.46 ± 3.80 | 26.06 ± 3.34 | 25.61 ± 2.88 | 0.09 |
| | | | | |

* P value obtained from one-way ANOVA.

explained that the data are considered as confidential and their identity will not be revealed and the data will not be used except for the research purpose.

3. Results

Table 1 shows the demographic characteristics and clinical examination information of participants. All the participants were males, age range from 21 to 52 years. The mean age of the participants was 30.75 year (\pm 7.19 yr) and maximum participants were in the age group of less than 30 years old (62.5%). The educational level of the maximum number of participants was high school diploma (58.8%). Regarding marital status, 64% of participants were married. 80.9% of participants were operational workers and 19.1% were firefighters. The work experience of 61% of participants was less than 6 years; 23.5% had been employed between 6 and 15 years, and 15.4% were employed for more than 15 years. Shift work experience in 67.6% was less than 6 years, 19.1% between 6 and 15 years and for 13.2% between 16 to 25 years.

Depression score ranged from 0 to 29. Mean depression score was 14.07 (\pm 3.84). 90.4% were categorized as having mild depression (depression score between 10 and 18), and 6.9% (n = 13) were categorized as having average depression (depression score between 19 and 29). The participants' BMI

ranged from 15.9 to 34.3; the mean BMI of the participants was 24.92 kg/m² (\pm 3.65 kg/m²). The mean of the measured markers in serum included mean of TAC being 2.41 (\pm 0.54) mg/dL; mean of MDA being 3.72 (\pm 1.10) μ mol/L.

Table 2 shows the association between BMI, TAC, and MDA concentrations with shift work experience. This study determined that, the amount of serum TAC increased by increasing shift work experience and differences in serum levels of TAC between the groups of shift work experience were significant (P < 0.05) (ANOVA).

Serum MDA levels and BMI values in groups with a shift experience 5 years and less, 6 to 15, and 16 years and more, there was no significant difference (all P > 0.05) (ANOVA).

Figure 1 shows correlation between depression score and shift work experience.

4. Discussion

The present study was the first study in Iran (based on the authors' knowledge) that examined the depression in shift workers and its association with oxidative stress markers (TAC and MDA as indicators of oxidative stress). The study was conducted in one of the most important industries in Iran, the refineries. In the present cross-sectional study, the association between age, BMI, shift work experience, marital



Shift work duration (year)

FIGURE 1: Regression line between depression score and shift work experience.

status on depression score, and total plasma TAC and MDA was assessed.

This study showed that the depression score was more among higher educational level group; this finding was in accordance with a study by Lin et al. which showed that the frequency of major depressive disorder (MDD) was higher among people with higher education [32]. In the present study, depression score had a positive relation with shift work experience (r = 0.218, P < 0.05). This result is in line with the result of the previous study by Scott et al. [33].

Possibly, higher education level of these people has raised their expectation from workplace and absence of expected facilities had caused repulsion and depression among them.

The results of this study did not show any correlation between BMI and TAC, MDA and depression score. While some studies showed that TAC is inversely related to weight [24] and MDA concentration was higher in the obese patients [34], also in some studies BMI and depression were reported to be associated [35] and there is a weak inverse linear trend between obesity and depressive symptoms among men [36]; but some other showed that the association between BMI and depression is nonlinear but U shaped for both genders [37].

Possibly the few numbers in high BMI group have caused this relation not to be seen in this research.

This research did not show any correlation between age and TAC or MDA; however, the study of Sharifian et al. [24] found a correlation between age and total plasma antioxidant capacity through a borderline Pearson's correlation; however, Sharifian's study, the confounding effect of BMI was not controlled and maybe this borderline correlation was related to the impact of BMI. In this study, the mean MDA concentration was $3.72 (\pm 1.10) \mu \text{mol/L}$, which is more than 5 times higher than the normal value for MDA, which is less than $0.7 \mu \text{mol/L}$ [16, 17]. This finding shows that the oxidative stress among these shift workers is much higher than general population. This finding is consistent with the findings of some studies that reported major depression to be associated with increased levels of serum MDA [38, 39].

In summary, the findings showed that mean MDA serum level was higher than reference range and there was a linear relationship between depression score and shift work experience among rotational shift workers, which show a high level of stress and depression among shift workers.

Conflict of Interests

The authors declare that they have no conflict of interests.

Acknowledgments

This study is a part of the Ph.D. thesis of F. Khajenasiri and is financially supported by Tarbiat Modares University. The authors express their deep appreciation towards help and support of Dr. Ramin Tofighi, Head of the Health Center, Dr. Mohamad Reza Yavari, Mr. Mahmoud Nikbakht, Head of the Research Center, Ahmad Kheiri, Head of the Operation Center, and Ms. Ashraf Heidari, Head of the Occupational Health Center. They are also grateful to all the participants in Tehran Shahid Tondgooyan Oil Refinery for their contribution.

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Research Article

A Qualitative Survey of Five Antibiotics in a Water Treatment Plant in Central Plateau of Iran

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Received 11 November 2012; Revised 16 December 2012; Accepted 1 February 2013

Academic Editor: Ajay K. Gupta

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Introduction. This study aimed to survey a total of five common human and veterinary antibiotics based on SPE-LC-MS-MS technology in a water treatment plant at central plateau of Iran. Also two sampling techniques, passive and grab samplings, were compared in the detection of selected antibiotics. *Materials and Methods.* In January to March 2012, grab and passive samples were taken from the influent and effluent of a water treatment plant. The samples were prepared using solid-phase extraction (SPE), and extracts were analyzed by liquid chromatography tandem mass spectrometry (LC-MS-MS). *Results.* The results showed that enrofloxacin, oxytetracycline, and tylosin were not detected in none of the samples. However, ampicillin was detected in the grab and passive samples taken from the influent (finished water) of the plant. *Conclusion.* The results imply that passive sampling is a better approach than grab sampling for the investigation of antibiotics in aquatic environments. The presence of ampicillin and ciprofloxacin in source water and finished water of the water treatment plant may lead to potential emergence of resistant bacteria that should be considered in future studies.

1. Introduction

Pharmaceuticals are used extensively in human and veterinary medicine [1]. More than 3000 different chemical substances are used as human medicines and in farming and aquaculture applications, in which antibiotic is one of the most important groups of common pharmaceuticals in our daily lives [2]. Besides the critical role of antibiotics in human health, they are potential environmental contaminants, so that there has been increasing concern within the scientific community regarding the presence of different types of drugs in the environment since the second half of the 1990s [3].

There are different pathways for releasing of antibiotics to the aquatic environment. After the administration to humans, their metabolites along with noneliminated parent compounds are excreted into the sewage [4]. Wastewater treatment plants (WWTPs) are not designed to completely remove antibiotics, and consequently they are released into natural waters. Moreover, antibiotics can pass through all natural filtrations and reach ultimately to drinking water due to their high water solubility and often poor degradability [5]. Furthermore, antibiotics are extensively used in fish farms, in which they are used as feed additives or they are directly applied into the water. The result of an overfeeding of these compounds to the fish farm is that many compounds end up in the sediments where they are slowly degraded or slowly leach out back into the surrounding waters [4]. Use of veterinary antibiotics for the treatment of bacterial infections of animals as well as prophylactic agents is another source of contamination. The animal excretion is the major route of contamination, as the most of these substances end up in manure. The parent compounds or their biologically active metabolites present in the manure may move from the field to the groundwater and eventually enter surface waters through events of rain [3, 4].

Little is known about possible human and ecological adverse effects of antibiotics in the aquatic environment. Although the concentration levels of these compounds seem not to cause toxic effects on human health and in the aquatic environment, there is a big concern on the long-term and continuous exposure of aquatic organisms to them [1, 6]. Low levels of antibiotics have been linked to the increased emergence of resistant strains of pathogenic bacteria that have potential to impact human health. In addition, a cross-resistance can be developed between antibiotics used in veterinary medicine with those of similar structures used exclusively in human medicine [7, 8]. Therefore, the occurrence of antibiotics in the environment has received considerable attention.

The analysis of antibiotics in the environment represents a difficult task due to the high complexity of the matrices analyzed and to the usually low concentrations at which target compounds are present in the aquatic environments. This condition leads to the development of very sensitive analytical methods suitable for the monitoring of these analytes in low concentration levels [4]. However, the most common approach for the analysis of antibiotics in environment includes a preconcentration step by solid-phase extraction (SPE) and a liquid chromatographic separation coupled with mass spectrometry (LC-MS) or tandem mass spectrometry (LC-MS-MS). Thus, SPE-LC-MS (MS) methods are capable of separation and qualitative and quantitative detection of antibiotics with low detection limits [1, 12].

For surveying of antibiotics in aquatic environment, traditional water-column sampling (including grab and composite samplings) is usually used. However this methodology has many shortcomings, including insufficient water sampled to satisfy the detection limit requirement of analytical methods, lack of time-weighted average (TWA) of pollutants level in aquatic media, and physical and financial difficulty for repetitive sampling. Time-integrative passive sampling, in contrast to grab or composite sampling, enables estimates of TWA contaminant concentration over extended sampling periods [13, 14]. In this way, the preconcentration of contaminants leads to an increase in the capability for detecting trace concentrations. Antibiotics similar to others pharmaceutics and polar pesticides could be sampled from water by Polar Organic Chemical Integrative Sampler (POCIS) [15]. The subsequent laboratory procedure (i.e., extraction, identification, and determination of analytes) in POCIS is the same as in the case of traditional sampling techniques [16].

Up to now, numerous studies have been done on the occurrence of antibiotics in various compartments of the aquatic environment, for example, municipal wastewater, industrial wastewater, hospital wastewater, surface water, ground water, and drinking water as well [17–21]. Also, in recent decade, detection of antibiotics in aquatic environment through passive sampling followed by SPE and LC-MS (MS) has received considerable attention [14, 15]. The aim of the present paper is to analyze a total of five common human and veterinary antibiotics, selected from four important categories, including quinolones (ciprofloxacin and enrofloxacin), macrolide (tylosin), β -lactam (ampicillin),

 TABLE 1: Physicochemical properties of the investigated antibiotic compounds.

| Compound | Formula | MW | Antibiotic class | pK _a |
|----------|--|-------|------------------|--------------------|
| AMP | $C_{16}H_{19}N_3O_4S$ | 349.4 | B-lactam | 2.7, 7.3 [9] |
| CIP | C ₁₉ H ₂₂ FN ₃ O ₃ | 331.3 | Fluoroquinolone | 3.01, 6.14 [10] |
| ENR | $C_{17}H_{18}FN_3O_3$ | 359.4 | Fluoroquinolone | 3.85, 6.19 [10] |
| OTC | $C_{22}H_{24}N_2O_9$ | 460.5 | Tetracycline | 3.22, 7.46 [10] |
| TYL | $C_{46}H_{77}NO_{17}$ | 916.1 | Macrolide | 7.5 [10], 7.1 [11] |

and tetracycline (oxytetracycline) based on SPE-LC-MS-MS technology in a water treatment plant at central plateau of Iran. In this study, we compared the Polar Organic Chemical Integrative Sampler (POCIS) as a passive sampler to standard grab sampling technique for the detection of selected antibiotics.

2. Experimental

2.1. Chemicals and Materials. Five antibiotic standards including ampicillin (analytical standard), ciprofloxacin (≥98% purity), enrofloxacin (≥98% purity), oxytetracycline (≥95% purity), and tylosin (analytical standard) were purchased from Sigma-Aldrich (Germany). Structures of the investigated compounds are shown in Figure 1. Also some physicochemical properties of the investigated antibiotic compound are described in Table 1. HPLC grade methanol and ultrapure water were purchased from Merck (Darmstadt, Germany). Oasis hydrophilic-lipophilic balance (HLB) cartridges (200 mg/6 mL) were purchased from Waters (Milford, MA, USA). 0.45 μ m cellulose acetate filter and 0.2 μ m cellulose acetate syringe filter were the products of Millipore (USA) and Whatman (Diesel, Germany). The following chemicals were all in analytical grade: sulfuric acid (purity 99%) from Fluka and disodium ethylenediamine tetraacetate (Na₂EDTA) and sodium thiosulfate (Na₂S₂O₃) from Sigma-Aldrich.

Individual stock solution for each antibiotic was prepared in the mixture (1:1, volume: volume) of MeOH and high-purity water at a concentration of 0.05 to 0.5 mg/mL and stored in a freezer (-10° C). Working standard mixture solutions (0.02 to 5 µg/mL) were made by diluting the stock solutions with the mixture of MeOH and high-purity water (3:1, v:v) every time just before use and storing at 4°C. All standard solutions (including stock and working solutions) were stored in glass bottles covered by aluminium foil at -10° C in a freezer. All glassware was washed with detergent and hot water, rinsed with distilled water and acetone, and dried in the oven at 220°C overnight.

2.2. Grab Sampling

2.2.1. Sample Collection and Preparation. From January to February 2012, grab water samples (from each site on the first and the last day of the POCISs exposure period) were taken from two locations of a water treatment plant. Source



CAS no.: 1401-69-0

FIGURE 1: Chemical structures of the antibiotics investigated.

water samples were collected at the plant intake prior to any water treatment process, and finished water samples were collected at the reservoir of treated water. A schematic design of the WTP and sampling sites is shown in Figure 2. The plant has a $12.5 \text{ m}^3 \text{s}^{-1}$ capacity and is fed by a perennial river in the central plateau of Iran. The river flows through a region with medium population density and high agriculture and aquaculture activities.

Water samples were collected in 2.51 amber glass bottles with screw cap. Before sampling, the bottles were cleaned following the procedure previously described. For finished water samples, excess quenching agent (sodium thiosulfate) was added to dechlorinate the sample. The glass bottles containing samples were shipped to laboratory under cool conditions before further treatment and analysis. In laboratory, water samples were filtered through a 0.45 μ m acetate cellulose filter and were acidified by adding 3.0 M H₂SO₄, followed by addition of 0.2 g disodium ethylenediamine tetraacetate

(Na₂EDTA). Under such conditions any antibiotic activity in the samples was kept to the minimum, and their tendency to be bound to divalent ions may be decreased. The samples were stored in dark at 4° C until they were extracted, typically within 1 week.

2.2.2. Solid-Phase Extraction. Solid-phase extraction (SPE) experiments were conducted using 200 mg/6 mL Oasis HLB cartridges on an innovative setup (Figure 3). The cartridges were preconditioned with 4 mL of MeOH and 6 mL of deionized water. A volume of 1000 mL of water sample with pH 2.8–3 (H_2SO_4) was passed through the cartridge at a flow-rate of 5–8 mL min⁻¹ using a vacuum extraction manifold at 7–9 in.Hg (Visiprepä, Supelco, Bellefonte, PA, USA; 1 in.Hg = 338.638 Pa). Afterwards the cartridges were rinsed with 10 mL of ultra-pure water and were air-dried for 5 min. The retained analytes were subsequently eluted with 10 mL of methanol



FIGURE 2: Schematic design of the WTP and sampling sites.



FIGURE 3: Schematic of SPE set up.

into a glass test tube. The extract was concentrated to dryness under a stream of *N* and reconstituted to ~250 μ L in a solvent mixture of ultra-pure water/methanol (9:1). The extract was filtered through a 4 mm i.d., 0.2 μ m pore size cellulose acetate syringe filters, transferred to an amber vial, and stored at -15°C until LC-MS/MS analysis.

2.3. Passive Sampling

2.3.1. POCISs Characterization. Polar Organic Chemical Integrative Samplers (POCISs) consist in a sequestration medium, such as HLB, enclosed within two hydrophilic micro-porous polyethersulfone membranes for the integrative sampling of polar organic chemicals such as antibiotics. A detailed description of this sampling technology and its sorbent material is described by Alvarez et al. [22]. In this study, the POCIS discs had a standard configuration, that is, 180 cm² sampling surface area per gram of sorbent [22].

2.3.2. Field Deployment of POCISs. The POCISs samples were placed in the same location and time as the grab sample was collected. At each site, a protective steel canister containing three POCISs, each with approximately 39.2 cm² of effective sampling surface area, was deployed for 30 days (from January to February 2012). Figure 4 shows the POCIS and deployment steel canister. Before deployment, the sorbent, HLB, was preconditioned with 6 mL of MeOH followed by 10 mL of HPLC-grade water and left at room temperature until dry.

The canisters were in a vertical position and at a depth of 2 m in the water column. At the end of the exposure period, the POCISs were collected, rinsed with water, kept in the containers, and transported to the laboratory under cooled conditions. Upon reception, the POCISs were stored frozen before extraction.

2.3.3. Recovery of Chemical Residues from POCIS. Procedures for the recovery of the sequestered chemical residues from the deployed POCISs are described in detail by Bueno et al. [15].



FIGURE 4: The used POCISs and deployment steel canister.

Briefly, the POCISs were disassembled, and the HLB sorbent was transferred into empty SPE cartridges (6 cm³) and packed between two polyethylene frits. The analytes from the sorbent were eluted with 15 mL of MeOH at 1 mL/min into a glass test tube. At the last step, the eluate was evaporated until almost dryness under a gentle stream of nitrogen at 35°C and reconstituted in 250 μ L in a solvent mixture of ultrapure water/methanol (9:1). The extract was filtered directly into an analysis vial using a 0.2 μ m cellulose acetate syringe filters, ampoulated, and stored at -15°C until LC-MS/MS analysis. In order to increase the total mass of sequestered residues, each ampoulated sample was a composite of three individual POCIS extracts from the same deployment canister.

2.4. LC-MS-MS Analysis. The extracts were separated on the reverse phase Zorbax Eclipse XDB-C18 column, 4.6 mm × 50 mm ID and 1.8 μ m particle size (Agilent Technologies, CA, USA) using LC system with a quaternary pump, a vacuum degasser, and an autosampler. The injection volume of sample aliquots was 5 μ L, and a binary gradient with a flow rate of 0.5 mL/min was used. Mobile phase A contained 0.1% aqueous solution of formic acid (v/v) and mobile phase B contained 0.1% formic acid (v/v), in meOH. The gradient started with 0% of mobile phase B for 0.5 min, increased to 20% from 0.5–3 min, to 70% from 3.0–7.5 min, and to 95% from 7.5–11 min, decreased to 0% from 11-12 min, and

remained at 0%. All target compounds were eluted out of the column within 15 min, and the autosampler was operated at room temperature.

The flow from the LC column was transferred to a triplequadrupole mass spectrometer equipped with an ESI source. The electrospray voltage was 4 kV, the capillary temperature 350°C, and maximum isolation time 200 ms. Nitrogen was used as the nebulising and drying gas, and a nebulizer pressure of 20 psi and a drying gas flow of 13 L/min were selected.

3. Results

The results of this study include optimal instrumental conditions for analysis of subjected antibiotics, representative MS/MS spectra for the analytes and occurrence of the antibiotics in water samples.

The optimized LC-MS/MS parameters and the information of calibration curves are summarized in Table 2. Because all antibiotics belong to groups 1 and 2 EPA Pharmaceutical compounds [23], they were separated in ESI+.

Figure 5 shows representative MS/MS spectra obtained for the antibiotics in standard solutions. The figures represent product m/z data obtained for the analytes.

Two of 5 antibiotics were detected in the analyzed samples of raw and treated water at the WTP (Table 3). Ampicillin was detected with LC-MS/MS for both grab and passive samples at influent sampling site; however ciprofloxacin was detected

| Compound | ESI | Time segment | m/z parent | m/z daughter | Collision | Fragmentation | Calibration curv | ves |
|----------|-----|--------------|------------|--------------|-------------|---------------|--------------------|-------|
| 1 | | (min) | 10N | 10n | energy (eV) | amplitude (V) | Equation, n^{a} | R^2 |
| AMP | + | 1.86-3.48 | 350 | 160 | 20 | 90 | y = 410x - 30, 3 | 0.998 |
| CIP | + | 7.33-12.58 | 332 | 314 | 20 | 110 | y = 927x + 2640, 3 | 0.993 |
| ENR | + | 6.69-13.33 | 360 | 316 | 20 | 90 | y = 211x + 1437, 3 | 0.999 |
| OTC | + | 1.49-12.87 | 461 | 426 | 20 | 90 | y = 78x + 71, 3 | 0.998 |
| TYL | + | 2.80-11.87 | 916 | 174 | 35 | 110 | y = 709x + 697, 3 | 0.998 |

TABLE 2: Optimal conditions for the analysis of selected antibiotics and related calibration curves.

^aNumber of concentrations for plotting calibration curves.



FIGURE 5: The MS/MS spectra obtained for (a) AMP, (b) CIP, (c) ENR, (d) OTC, and (e) TYL in standard solutions.

TABLE 3: Occurrence of investigated antibiotics in the subjected water treatment plant.

| Compound | Influent sa | mpling site | Effluent sampling site | | |
|-----------------|------------------|------------------|------------------------|------------------|--|
| Compound | Grab sampling | Passive sampling | Grab sampling | Passive sampling | |
| Ampicillin | Detected | Detected | ND | ND | |
| Ciprofloxacin | ND^1 | Detected | ND | Detected | |
| Enrofloxacin | ND | ND | ND | ND | |
| Oxytetracycline | ND | ND | ND | ND | |
| Tylosin | ND | ND | ND | ND | |
| 1 | | | | | |

¹Nondetected.

only for passive sample. Other analytes that are ENR, OTC, and TYL were not detected by any of sampling procedures. From all samples taken from effluent sampling site, we could detect CIP through passive sampling SPE-LC-MS/MS.

4. Discussion

In this study, the occurrence of five antibiotics was investigated qualitatively in raw and treated water at a water treatment plant in central plateau of Iran. Our primary aim was to investigate the occurrence of the antibiotics quantitatively. Thus calibration curves for each analyte were set, and their correlation coefficient were >0.99 (Table 2). However because of some limitations such as lack of valid recovery and matrix effect data, and economical and technical restrictions, we decide to report the results as present/absent.

Analyzing very low levels of analytes in aqueous environments requires optimal sampling, processing, and analyzing conditions [4]. In order to prevent glassware contamination, they were conditioned according to the literature, namely, repeatedly washing, rinsing, and baking [23]. In grab sampling, adding sodium thiosulfate to finished water samples, acidifying all samples, and storing them at low temperatures and in dark ambient all were necessary to avoid decomposition of analytes by means of chemical reactions and microbial activity [4]. In accordance with the literature in this field, a chelating agent, namely, Na₂EDTA, was applied to decrease the tendency for antibiotics to bind to metals or multivalent cations in the matrix, to improve peak shape, and to prevent interferences during the extraction of antibiotics [4, 24].

Solid-phase extraction (SPE) arrangement was nearly according to EPA Method 1694 [23]. There are some suitable cartridges for extraction of antibiotics from aqueous matrixes; however the most common SPE cartridge is hydrophilic-lipophilic balance (HLB) [25]. So we use 200 mg/6 mL Oasis HLB cartridges in an innovative extraction setup (Figure 3). Sample pH and eluant were proved to be crucial parameters for antibiotics preconcentration using SPE (14). Solution pH is expected to significantly influence speciation of the antibiotics owing to the presence of acidic and basic functional groups in their structures (Figure 1). Their acidity constants (Table 1) indicate that protonation and deprotonation of these antibiotics occur readily in the environmental pH range [26]. Acidifying samples to pH 2.5-3 was done, because the selected antibiotics belong to groups 1 and 2 EPA Pharmaceutical compounds (with acidic nature), and acidic condition leads to better recovery of them from the aqueous matrix [23]. Tong et al. reported that, at pH 2.0, recoveries of FQs and TCs were more than 70% and 60%, respectively, whereas under neutral condition, those of TCs and FQs were less than 30% [27]. Reverté et al. selected pH 2.8 for sample conditioning before SPE of TCs and Qs from river water samples [28].

According to EPA Method 1694 [23], ESI (+) mode was selected for separation of the analytes by LC. Chromatographic separation was optimized with a series of preliminary experiments, utilizing various mobile phases consisting of MeOH, formic acid, and water at various fractions. The MeOH was selected as it was commonly used as organic mobile phase in LC-MS/MS system [29, 30]. Addition of formic acid into mobile phase can affect the chromatographic separation, change the pH value of mobile phase, and affect ionization efficiency [31]. The formic acid in various concentrations in both mobile phases A and B was evaluated for the optimal chromatographic separation, and 0.1% acid formic was added to both mobile phases. Column temperatures of 25 [32], 30°C [33], and room temperatures [30] were widely applied to LC-MS/MS for selected antibiotics detection. In this study, the column was operated at room temperature. Elution with identical gradient conditions at different flow rates showed that the optimal flow rate was 0.5 mL min^{-1} .

The surveyed antibiotics belonged to fluoroquinolone (CIP and ENR), tetracycline (OTC), macrolide (TYL), and β -lactams (AMP). According to Table 3, two of all five antibiotics were detected in raw water introduced to the water treatment plant (AMO and CIP). Moreover, CIP was detected in finished water through passive sampling. The water of the plant is served by a perennial river, which flows through a region with medium population density and high aquaculture activities. The river drainage area is subjected to pollution from several point and nonpoint sources. There are one city with more than 20000 populations and several small towns and villages in upstream of the source water sampling point (WTP) in which some households and industries discharge illegally their wastewater into the main drain in the vicinity or to the river. Also there is an important fish farming area in upstream which is supplied by the river water. Therefore, the occurrence of AMP (with veterinary and human use) and CIP (human use) may possibly be explained by illegal discharges from aquaculture farms and residential areas in addition to runoff from agricultural fields located on the river banks upstream of sampling point (i.e., entrance of the water treatment plant). Ampicillin, like other β -lactam antibiotics, due to the chemically unstable β -lactam ring, readily undergoes hydrolysis [4]. Therefore, it was expectable that ampicillin was not detected in finished water.

The presence of antibiotics in aqueous environments is a matter of concern because of possible development of resistant strains of bacteria. Accordingly, there are some reports about prevalence of ampicillin- and ciprofloxacin-resistant bacteria in river waters, water treatment plants, and drinking waters [34–36]. Therefore the presence of some antibiotics in source and finished water of the subjected water treatment plant is of concern, especially in view of potential emergence of resistant bacterial strains in drinking water that is served for about 4 million people. This investigation highlights the need for surveying multiantimicrobial-resistant bacteria (at least for AMP and CIP) in the finished water of the water.

Another important message from this study is that passive sampling (or POCIS) was more efficient than grab sampling, at least qualitatively, in monitoring of the antibiotics in water environment. As can be seen from Table 3, among two sampling points and five antibiotics to be monitored, we could detect only AMP in source water through grab sampling. On the other hand, AMP and CIP in source water and CIP in finished water were detected by SPE-LC-MS-MS through passive sampling technique. This finding is in accordance with those found by Alvarez et al. [22], who showed that passive sampling could detect more organic contaminant including antibiotics than water-column sampling in aqueous environments. The reason for this is that POCIS monitors the trace contaminants over extended periods of time, for example, 30 days in our study. This feature permits preconcentration of contaminants and sequestration of residues from episodic events commonly not detected with grab sampling. In fact, by using passive sampling technique, regular monitoring of the antibiotics can serve to track both spatial and temporal trends in waters [15]. Generally, POCIS similar to other passive samplers is typically easier to handle, preserve, and transport than water samples comprised of several liters. Thus, the POCIS provides an increase in method sensitivity and simplicity in use.

5. Conclusion

An SPE-LC-MS/MS single residue method was used for the survey of 5 antibiotics in source water and finished water of a water treatment plant (WTP) in central plateau of Iran. The water samples were collected by two sampling techniques, that is, grab and passive samplings. Because of some technical and economical limitations and the lack of valid recovery and matrix effect data, the presence of the antibiotic was assessed qualitatively. The results of this study showed that ciprofloxacin and ampicillin were detected in source water, and ciprofloxacin was detected in finished water. Based on the findings, it was implied that POCIS was more efficient than grab sampling in detection of the antibiotic in water environment. The presence of AMP and CIP in water of investigated WTP may lead to potential emergence of resistant bacteria that should be considered in future studies. Finally, the implications of our findings may not be straightforward in relation to public health; nevertheless, our study does highlight the need for more extensive investigation on the occurrence of antimicrobial compounds and bacterial resistance to them in surface waters in Iran.

Conflict of Interests

There is no conflict of interests.

Acknowledgments

This paper is the result of the approved research projects in the Environment Research Center, Isfahan University of Medical Sciences (IUMS). The authors wish to acknowledge the Vice Chancellery of Research of IUMS for the financial support and Research Projects, nos. 289220 and 290084.

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Research Article

Indoor Carbon Monoxide: A Case Study in England for Detection and Interventions to Reduce Population Exposure

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Received 21 December 2012; Revised 17 February 2013; Accepted 10 March 2013

Academic Editor: Mohammad Mehdi Amin

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Background. Potential exposure to carbon monoxide (CO) in private homes is largely unquantified. *Aim.* To estimate prevalence of potential exposure to CO in residential dwellings and describe associated interventions in an inner-city community. *Methods.* A housing association in London, Hackney Homes, began fitting CO alarms in the 22,831 local authority homes it is responsible for in January 2010. A gas engineer investigated each alarm activation and recorded the information on a standard form. We undertook a cross-sectional study of all 22,831 homes, using data from these forms. Descriptive analysis was performed, including incidence, monthly variation, cause of alarm activation, and actions taken. *Results.* Between November 2011 and April 2012, 106 incidents were reported. Of these, 34.6% identified an issue with a gas appliance, and 10.6% identified misuse of cooking methods as the cause of activation. Relevant interventions were put in place, including disconnection of the gas appliance and education around cooking methods. *Discussion.* Little is known about the burden of CO poisoning in residential dwellings. This study provides important information on the path to quantifying population exposure to CO as well as establishing a possible approach to access this key information and realistic interventions to reduce potential exposure.

1. Introduction

Carbon monoxide (CO) is a potentially fatal, colourless, odourless, and tasteless gas that results from the incomplete combustion of carbon-containing fuels. In England and Wales, an estimated 40 people (range 25–45 between 2006 and 2011) die [1], and over 200 are admitted to hospital each year from accidental CO poisoning; a further 4000 present to Accident and Emergency Departments but are not admitted [2]. However, these figures are likely to be underestimated as many more people are thought to be exposed to CO and suffer from CO poisoning but remain undiagnosed or even misdiagnosed due to its nonspecific symptoms [3] which include headache, tiredness, and nausea. More severely, CO poisoning can lead to cognitive impairment, convulsions, unconsciousness, and even death. CO poisoning therefore represents a significant public health issue [4, 5].

There is an increasing recognition that the burden of morbidity and mortality relating to accidental CO poisoning may be far greater than that documented, particularly as there is little evidence to quantify those who do not even present to a healthcare establishment. However, the extent of this burden and the success of intervention methods are still unknown. A report by the All-Party Parliamentary Gas Safety Group (now the All-Party Parliamentary Carbon Monoxide Group) [6] emphasised the urgent need for research into the effects and prevalence of CO, in order to improve identification of the presence of CO and to provide a more accurate picture of the true number of people affected.

In order to estimate the burden of disease for CO, understanding potential hazards for exposure is as important as quantifying those who become ill due to CO poisoning. Hazards such as exposure from using a generator indoors are well established [7]; however, the burden of disease in the community (such as private dwellings) is less well evidenced. Karalliedde and Keshishian [8] report that the most common source of CO poisoning in the home is faulty heating or cooking appliances, and therefore CO exposure in this setting is almost entirely preventable, particularly if CO detectors are installed [9]. There are currently no reliable prevalence data to indicate the extent of the problem in the community [8]. Croxford et al. [10] looked into the association between the risk of CO exposure at low concentration and health outcomes. They found that unsafe gas appliance installations were linked to an increased risk of suffering with at least one self-reported neurological symptom, supporting the need for further research into community exposure to assess the level of burden. Another study [11] carried out continuous monitoring of levels of CO exposure in homes and found that nearly one-fifth of lower-income families could be regularly exposed to level of CO which exceeds the World Health Organisation (WHO) guidelines. The WHO guideline values (ppm values rounded) and periods of time-weighted average exposures have been determined in such a way that the carboxyhaemoglobin level of 2.5% is not exceeded, even when a normal subject engages in light or moderate exercise: 100 mg/m^3 (87 ppm) for 15 min; 60 mg/m^3 (52 ppm) for 30 min; 30 mg/m³ (26 ppm) for 1 hour; 10 mg/m³ (9 ppm) for 8 hours [12].

The purpose of this pilot study was to investigate the incidence of and reasons for CO events recorded when CO alarms are triggered and the interventions put in place.

2. Methods

2.1. Setting and Study Population. Hackney is an inner city borough of London, situated in the north east of the capital with a population of 219,200 [13], and is the second most deprived local authority in England [14]. In 2010, there were 98,950 dwellings in Hackney; of which 23% are owned by the Hackney Council [15]. From 2006, all the local authority owned housing within Hackney (n = 22, 831) was managed by Hackney Homes, an arm's length management organisation. In 2010, Hackney Homes decided that it would establish a programme to monitor CO in the homes under its care, as part of its partnership and contractual arrangements established with the local borough council of Hackney for the management of social housing in that area of London. Trained gas engineers employed by Hackney Homes used an agreed protocol to place at least one CO alarm in all homes they were responsible for starting from January 1st, 2010.

2.2. Study Design. A cross-sectional study was used for this pilot to inform possible hypotheses to be evaluated in further analytical studies [16]. The main measurement in this study concerned the hazard to health (i.e., a CO alarm being set off).

2.3. Detection of CO in the Community. The study population under investigation was all local authority homes managed by Hackney Homes which have had a CO alarm fitted (n =22,831). The CO alarms (Fire Angel Model CO-9X) contain an electrochemical cell designed to detect a concentration of CO above 50 ppm in ambient air for 60 to 90 minutes, above 100 ppm for 10 to 40 minutes, and above 330 ppm within three minutes following the initiation of exposure, as stipulated by the British standard BS EN 50291 [17, 18]. The CO alarms are powered by a nonremovable integrated lithium power pack to prevent the occupants tampering with the battery and are expected to last 7 years in normal operating conditions. The device sounds a 85 dB alarm at 1 metre and flashes LED light to alert occupants in case of CO detection. Alarms were installed in every room containing a fuel burning appliance, with a maximum of three alarms fitted per household, and they were placed between 1m and 3m from the potential source (e.g., boiler, gas cooker, and gas fire) and fixed to the wall.

Following activation of an alarm, the occupant informs National Grid and Hackney Homes. National Grid sends a staff member to the property to make it safe (e.g., turn off the gas supply). Within two days, Hackney Homes sends a qualified gas engineer to the property to investigate the alarm activation. Gas engineers employed for this role are required to have obtained registration with a professional body (Gas Safe). At each visit, the gas engineer conducted CO tests on each gas appliance present in the dwelling as well as outside the property and collected information on the occupants' reasons for concern, including whether anyone was suffering illness, any faults identified, interventions undertaken, and general observations (such as housing type). The information collected is then recorded on a Gas Safe Fumes Investigation Report, which is designed to support the standard collection of information from each alarm activation. If an appliance is found to be defective, it is always isolated regardless of the appliance. All incidents reported to Hackney Homes are investigated.

2.4. Data Collection and Study Period. All incidents investigated by Hackney Homes between November 2011 and April 2012 were included in the study. November 2011 was selected as the start of the study period as this was the date when Hackney Homes estimated that all its homes had been fitted with at least one CO alarm and therefore the study population would have remained constant during the study period. Occupant data included in *fumes investigation reports* for the study period were anonymised by Hackney Homes before being sent to the Health Protection Agency where they were entered onto a Microsoft Access 2007 Database.

2.5. Statistical Analysis. Incidents where a gas engineer was called out but did not enter the property and therefore did not carry out an assessment were excluded from further analysis. Photocopied forms where none of the information could be read were also excluded. Photocopied forms where only some of the information could not be read were included, providing the date of inspection that could be read, but the unreadable fields were coded as missing. Data entered onto the database were verified, checked, and cleaned. Data were coded to identify what the cause of the alarm was and what actions were taken or advice was issued. Descriptive analysis was undertaken to calculate incidence, monthly variation,

proportion of incidents where the householder reported illness, cause of alarm activation, and actions taken.

3. Results

Between November 2011 and April 2012, 106 incidents were reported to Hackney Homes where the CO alarm was activated. The incidence rate was 4.64 incidents per 1000 households for this six-month period. Two incidents were excluded from further analysis as the gas inspector did not gain access to the home and therefore no test was carried out. During the six-month period investigated, November reported the highest number of incidents (31), and the remaining months (December 2011–April 2012) reported between 13 and 17 incidents each month. In 6.7% of incidents, the occupant answered yes to the question "Was anyone suffering from illness?"

There were several issues highlighted during investigation of the incidents as being possible reasons for the alarm being activated (Table 1). More than one issue was identified in 11 incidents (10.6%). One of the main causes of CO alarm activation was that a gas appliance in the home was found to be unsafe due to emitting CO above guideline values when tested by gas engineers. Of the 104 incidents investigated, 36 (34.6%) found that at least one gas appliance (boiler, cooker, or fire) was defective and disconnected. Not all homes had a boiler, a gas cooker, and a gas fire, and therefore the denominator for each gas appliance differed. Of the 104 incidents investigated, 97 noted that a gas cooker was present in the property, and 102 noted that a boiler was present and four noted a gas fire was present. Taking this into account, 9.8% of all incidents had the boiler disconnected, 29.9% had the cooker disconnected, and 25% had the gas fire disconnected. It is important to note, however, that there were four incidents where both the boiler and the cooker were found to be unsafe and therefore disconnected. In 28 incidents (26.9%), the alarm was noted as being faulty (including low on battery) and/or replaced with a new CO alarm. In 12 incidents (11.5%), the CO alarm was reported to be fitted in an unsuitable place (e.g., directly above the cooker). Some of these may have been installed before the programme to fit all homes with an alarm had started. Of these 12 incidents, ten had an additional issue identified on the form, and therefore the positioning of the alarm was likely to be a secondary issue. Eight of these ten incidents also had a gas appliance disconnected by the visiting engineer and two identified misuse of cooking methods as a possible issue. Overall, one-tenth of incidents (10.6%) identified misuse of cooking as the cause of the CO alarm going off. This included using large pans on the cooking hob rings, using foil around the cooking hob ring, using charcoal on the hot plate, and bringing a barbeque indoors.

The gas inspectors also identified further issues which were cause for concern but not likely to be causing CO leakage or to be the cause of the CO alarm activation. Examples include issues with the boiler, such as a new part required or the boiler being scaled up, no flame supervision device (FSD) or stability device on the cooker, and the gas supply to the TABLE 1: Issues/faults identified during investigation of CO alarm incidents, November 2011 to April 2012 (n = 104).

| Issue identified | Ν | %* |
|---|----|------|
| (1) Cooker defective | 29 | 29.9 |
| (2) Boiler defective | 10 | 9.8 |
| (3) Fire defective | 1 | 25 |
| (4) Misuse of cooker/cooking methods | 11 | 10.6 |
| (5) CO alarm faulty/low battery/wrongly sited | 40 | 38.5 |

*Denominator for issues 1, 2, and 3 changed depending on whether each gas appliance was reported as present and tested. Number of incidents where a gas cooker was reported as present and tested: 97; number of incidents where a gas boiler was reported as present and tested: 102; number of incidents where a gas fire was reported as present and tested: 4.

TABLE 2: Main interventions put in place following investigation by gas engineer.

Disconnection of the gas appliance (cooker, boiler, or fire)

Replacing CO alarm with new alarm

Resiting of current CO alarm

Providing advice to tenant on size of pans when cooking

Providing advice to tenant on other misuse of cooker (e.g. placing foil around the gas hob)

Providing advice to tenant on other CO producing activities (e.g. bringing a barbeque inside the house or smoking a shisha pipe) Providing advice to tenant on ventilating the kitchen when cooking

Reiterating that it is mandatory for all cookers in flats to have flame supervision devices

appliances being undersized. The main interventions put in place are listed in Table 2.

4. Discussion

Little is known about the burden of CO poisoning in private dwellings; this study has documented aspects relevant to this at a specific location by using data from CO alarm incidents in local authority homes in the borough of Hackney. Between November 2011 and April 2012, 4.64 incidents per 1000 households were reported (n = 106). One of the main findings from this study is that in over one-third of incidents, an issue was identified with at least one gas appliance. This finding has important implications given that Croxford et al. [10] showed that the presence of an unsafe gas appliance installation was linked to increased risk of suffering neurological symptoms. Furthermore, although boilers are considered one of the commonest hazards for CO exposure at home, this study has highlighted that cookers are also a major source of CO exposure at home, both in terms of faulty cookers giving off excess CO and methods of cooking which produce excessive amounts of CO. Interventions undertaken by gas inspectors included disconnection of gas appliances and education concerning cooking methods. It is important to note that some boilers were isolated due to poor flue performance results but were not found to be leaking CO. Some were isolated along with gas cookers and this has no bearing on the inspection of the appliance by Hackney Homes, as defects may have occurred some time after the inspection was carried out.

A number of incidents identified an issue with the CO alarm. Twelve incidents (11.5%) reported that the alarm was not placed in a location according to the protocol. Although ten of these 12 incidents identified an additional issue which was more likely to be the reason for alarm activation (gas appliance unsafe and cooking misuse), it is important to recognise that CO alarms must be fitted in the correct place and by reputable contractors to ensure effective use. The finding that illness in the household was reported for 6.7% of incidents is likely to be due to seasonal background levels, and therefore no link can be made between potential exposure and health effects in this study.

There were a number of limitations with this study which need to be considered. First, we could not document the relationship between detection of CO concentrations and the WHO guideline values [12], which are established to protect the population not only from exposures of short duration, but also from lower exposure of longer duration that are nevertheless recognised to be toxic. The design of the devices included in this study is intended to trigger an alarm only when 50 ppm for 60-90 minutes is reached, 100 ppm for 10-40 minutes, or when dangerously high levels of 300 ppm or more where the alarm will sound within 3 minutes. Therefore, all exposures at a concentration lower than 50 ppm but over a longer time period, which may be causing chronic CO poisoning, were missed by the survey. We may also have missed alarm activations where the occupant did not report the incident to Hackney Homes or National Grid and so the incident was not investigated. If the occupant ventilates the dwelling causing CO to disperse, the alarm will reset itself. We are unable to specify how often this occurs though suspect the number to be low due to the fact that occupants are likely to be concerned about what caused the alarm activation and would want it to be investigated.

Second, the relationship between concentrations of CO in indoor air and personal exposure could not be directly estimated in our study. The Environmental Health Criteria 213 on CO suggests that individual personal exposure does not directly correlate with CO concentrations determined by using fixed site monitors alone [12]. Therefore, although our study has shown that on certain occasions CO concentration exceeded WHO guidelines resulting in an alarm being activated, it does not necessarily mean that CO carboxyhaemoglobin concentration in occupants was elevated.

A further limitation of the study concerns the representativeness of the study population and validity of any extrapolation of the results to the whole of the UK population. However, the results do provide evidence of the potential exposure to CO which exists in private dwellings and associated interventions to reduce it, particularly in local authority housing.

Despite these limitations, this study has provided important information on the path to quantifying CO exposure in this population. Little is known about the burden of CO particularly in private homes, due in part to a lack of systematic surveillance in the UK and many other countries. Often the more severe acute poisonings are known about and reported to healthcare establishments, but the less severe, more chronic poisonings are less well documented. This study has also established a possible approach to access key information on population exposure to CO and realistic interventions to reduce it. This has important implications for future studies investigating potential CO exposure in private homes aimed at quantifying population exposure to CO, as well as for CO policymakers and those developing CO awareness campaigns or targeted interventions. In particular, this information might be relevant to public health practitioners who design, develop, or implement systems for public health surveillance and tracking of CO-related hazards to health [19, 20]. Given that CO poisoning is difficult to diagnose and can often be missed by doctors due to the patients presenting with symptoms which mimic other common diseases (e.g., flu-like illness and cognitive impairment), understanding potential exposure and possible hazards is particularly important. This work concentrated on one aspect of CO exposure, providing improved understanding of potential community exposure and of environmental hazards for CO, at home. Combining this work with other relevant studies, looking at mortality, hospital admissions, accident and emergency presentations, and GP consultations, will provide a more accurate picture of the burden of disease of CO and could contribute to establishing routine surveillance of CO. The study highlights the need to develop further research in this area in order to develop understanding of the mechanisms involved in CO poisoning in private homes and the burden of disease in these settings. It is recommended that this study population should be followed up over a longer time period. Future studies on CO poisoning in the community should consider sampling a representative population and collect data on socioeconomic status of occupants, housing tenure, characteristics of the homes, and comparisons between urban and rural environments. Further work is also needed to investigate the association between exposure and health. Work in this area will contribute to developing relevant public health actions.

Acknowledgments

The authors are grateful to those staff at the Health Protection Agency who entered the forms, in particular Harriet Kilcommon and Anne Marchant. They would also like to acknowledge CO Awareness (http://www.covictim.org/) for their support with this work and for establishing the contact between HPA staff and Hackney Homes staff.

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Research Article

Application of *Glycyrrhiza glabra* Root as a Novel Adsorbent in the Removal of Toluene Vapors: Equilibrium, Kinetic, and Thermodynamic Study

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Received 21 January 2013; Accepted 9 February 2013

Academic Editor: Roya Kelishadi

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The aim of this paper is to investigate the removal of toluene from gaseous solution through *Glycyrrhiza glabra* root (GGR) as a waste material. The batch adsorption experiments were conducted at various conditions including contact time, adsorbate concentration, humidity, and temperature. The adsorption capacity was increased by raising the sorbent humidity up to 50 percent. The adsorption of toluene was also increased over contact time by 12 h when the sorbent was saturated. The pseudo-second-order kinetic model and Freundlich model fitted the adsorption data better than other kinetic and isotherm models, respectively. The Dubinin-Radushkevich (D-R) isotherm also showed that the sorption by GGR was physical in nature. The results of the thermodynamic analysis illustrated that the adsorption process is exothermic. GGR as a novel adsorbent has not previously been used for the adsorption of pollutants.

1. Introduction

Environmental pollution, as a result of industrial improvements, has created severe problems in the recent years. Volatile organic compounds (VOCs) are the major pollutants being released from various industrial plants and processes [1–4]. Some VOCs such as toluene existing in fuels, petroleum, and gasoline are widely used in many industrial solvents [5, 6]. Toluene vapors are released into the atmospheric environment over their production, transportation, application, and discharge every year [2]. Toluene can be absorbed by respiratory and gastrointestinal tracts. The human exposure to toluene results in neurotoxicity, mental depression, and various symptoms such as headache, fatigue and ataxia [7]. The US Environmental Protection Agency (USEPA) has considered toluene as a major pollutant, the concentration of which must be reduced to a very low level in the environment [8–10]. Various techniques including biofilter, biotrickling filter, bioscrubber, and adsorption have been successfully adopted to remove toluene vapors from gaseous media [1, 11–14].

Many adsorbents including zeolites [15–18], metal oxides [19], compost [11, 20], diatomaceous earth, chaff [20], ground tire rubber [11], and activated carbon [21–26] have been used for the removal of toluene vapors. Among the abovementioned adsorbents, adsorption by activated carbon is one

of the most common processes to remove VOCs, especially toluene, from gases solution, but, it is not cost effective [7]. *Glycyrrhiza glabra* is a herb that grows in various parts of the world as well as the southern areas of Iran [27]. It is a very sweet, humid, and soothing plant which has been used as a medicine to protect the liver, and to treat arthritis and the mouth ulcers for centuries in European and Eastern countries [27, 28]. The roots of *Glycyrrhiza glabra* are thick, long, cylindrical, fibrous, and multibranched [27] which after using its extract for medicine are disposed. In this study, the waste roots were, as a novel sorbent, used to remove toluene from gaseous solution. The main purpose of this study was to investigate the effect of various conditions including humidity, contact time, adsorbate concentration, and temperature on the adsorption of toluene vapor.

Literature review did not show any previous research using GGR waste as pollutant adsorbent. Only in a study, GGR was used as carbon sources in biological denitrification of drinking water [29].

2. Materials and Methods

2.1. Preparation of the Adsorbent. Glycyrrhiza glabra root (GGR) was provided by Rishmak Inc., an extract producing company located in Shiraz, Iran. The root of the herb was extracted at 3.5 bar pressure and 140°C temperature for 2 hours. Then dewatered GGR is dumped around the company as a waste material. In this paper, the GGR was ground to pieces of 0.5–1 cm, repeatedly washed with deionized water, dried in oven at 60°C for 48 h, and sterilized at 15 psi for 20 min.

2.2. Instrument. The surface area of GGR was determined with a multipoint N_2 gas adsorption method (Sorptometer Kelvin 1042, Costech International, Italy). The chemical composition of the adsorbent was also characterized by Xray fluorescence analyzer (Bruker, S4, Pioneer, Germany) and elemental combustion system (ECS 4010, Costech International, Italy). The concentration of toluene (purity of 99.5%, Merck, Germany) in the solution was quantified by a gas chromatography equipped with flame ionization detector (Agilent GC, 7890A, Netherland). The GC-FID procedure was optimized as follows.

The amount of $100 \,\mu$ L of gaseous sample was injected into the instrument by 1 mL gastight syringes (Hamilton series no. 1001; Hamilton Co., NV, USA) equipped with Teflon Minnert fittings.

Helium (with flow rate of 1.11 mL/min) and H₂ (with flow rate of 30 mL/min) were used as carrier gas and fuel gas, respectively. The characteristic of GC column was Agilent CP Sil 5: 30 m × 250 μ m × 0.25 μ m. The temperatures of the oven, injector, and detector were fixed at 100, 230, and 250°C, respectively.

The pH value and the particle size analyses of GGR were measured by digital pH meter and sieves with standard mesh, respectively. The bulk density and the water holding capacity analysis of adsorbent was conducted according to Ahn et al. [30]. 2.3. Adsorption Experiments. The experiments including adsorbent humidity (0–70%), contact time (0–24 h), and adsorbate concentration (6.928 mg/L) were carried out at room temperature (25°C) in the 250 mL vials (with PTFE airtight cap) and mixed by a rotary shaker (300 rpm for 24 h). The effect of temperature (10–50°C) on the adsorption was also determined as described above. After agitation period, 100 μ L of the polluted gas was analyzed for toluene by GC-FID. All the experiments were performed in triplicates and the mean values were considered. Blank samples were also employed to determine the amount of toluene loss. The blank recoveries ranged from 93.8 to 96% and the experimental data were adjusted for these recoveries. Calibration curve for determination of the toluene concentration was prepared according to the standard method [31].

The adsorbent capacity of GGR for toluene was calculated by

$$q_e = \frac{\left(C_0 - C_e\right)V}{m},\tag{1}$$

where q_e (mg/g) is the adsorption capacity of GGR, C_0 (mg/L) is the initial concentration of toluene, C_e (mg/L) is the equilibrium concentration of the toluene in the solution, m (g) is the mass of the adsorbent, and V (L) is the volume of the polluted gas (or volume of the vial).

3. Results and Discussion

3.1. Characterization of Media. The physical and chemical characteristics of GGR are presented in Table 1.

3.2. The Effect of Adsorbent Humidity. The effect of adsorbent humidity (0–70%) on the sorption was determined. As can be seen in Figure 1, the adsorption capacity was expanded by increasing the sorbent humidity up to 50 percent. The sorbent humidity higher than 50% may be due to the occupation of the media porosity by water content, leading to the reduction of the adsorption capacity. Acuña et al. (2000) found out that the variation of water content of peat as an adsorbent for the toluene vapors did not have significant effects on the sorption rate [32]. GGR with a humidity of 50 percent was used for the subsequent experiments.

3.3. The Effect of Contact Time. Figure 2(a) shows the effect of contact time (0-24 h) on the adsorption of toluene by GGR. The adsorption as can be seen in the figure reached its maximum capacity by the elapse of time.

The adsorption of toluene was quickly increased over the first hour of the sorption (1.3 mg/g) and steadily raised over the remaining contact time by 12 h since the adsorption sites are more accessible at the beginning of the sorption process and diminished by the passage of time. The contact time of 12 h was chosen for the rest of experiments. The adsorption capacity (q_e) of GGR for the removal of toluene vapor was 2.2 mg/g over the 12 h contact time. Table 2 compares the adsorption capacity of granular activated carbon (GAC), compost, diatomaceous earth, chaff, ground tire rubber (GTR), and GGR. The use of activated carbon may be

TABLE 1: Characteristics of the GGR (on the dry basis).

| Parameters | |
|--|-------|
| Chemical composition (%) | |
| CaO | 4.83 |
| SiO ₂ | 1.76 |
| Al_2O_3 | 0.552 |
| Fe ₂ O ₃ | 0.317 |
| SO ₃ | 0.243 |
| MgO | 0.186 |
| Na ₂ O | 0.072 |
| K ₂ O | 0.068 |
| P_2O_5 | 0.062 |
| SrO | 0.046 |
| Cl | 0.030 |
| ZnO | 0.019 |
| TiO ₂ | 0.017 |
| CuO | 0.011 |
| C | 44.6 |
| Н | 5.33 |
| N | 1.47 |
| Physical characteristics | |
| pH | 7.4 |
| BET surface area (m^2/g) | 1.532 |
| Particle diameter (cm) | 0.5-1 |
| Water holding capacity (g water/g dry GGR) | 2.9 |
| Bulk density (kg/m ³) | 37.62 |



FIGURE 1: The effect of humidity of media on the sorption of toluene (adsorbent dose = 0.6 g, temperature = 25° C, contact time = 24 h, and adsorbate conc. = 6.928 mg/L).

prohibitive due to its high cost. The capacity of GGR in the removal of toluene is higher than the other natural adsorbents (e.g., compost, diatomaceous earth, and chaff).

Due to the suitable pH, water holding capacity, chemical composition (Table 1), and adsorption capacity, GGR is recommended as anew packing material for biofiltration.

TABLE 2: Comparison between adsorption capacities of different adsorbents.

| AdsorbentsGAC [11]diatomaceous earth [20]Compost [20]Chaff GTR [20]GGRAdsorption capacity10.622.001.430.890.3982.2(mg/g) | | | | | | | |
|--|----------------------------------|-------------|----------------------------|-----------------|---------------|-------------|-----|
| Adsorption capacity 10.62 2.00 1.43 0.89 0.398 2.2 (mg/g) | Adsorbents | GAC [11] | diatomaceous earth [20] | Compost [20] | Chaff [20] | GTR [11] | GGR |
| | Adsorption capacity (mg/g) | 10.62 | 2.00 | 1.43 | 0.89 | 0.398 | 2.2 |

3.3.1. The Adsorption Kinetics. Adsorption kinetic models can be helpful to specify the effectiveness of a sorbent in the removing pollutants and to determine the sorption mechanism type. The experimental data of toluene adsorption by GGR were analyzed via two common kinetic models including pseudo-first-order and pseudo-second-order models. The pseudo-first-order kinetic model is shown by

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t,\tag{2}$$

where q_e (mg/g) and q_t (mg/g) are the quantity of toluene adsorbed onto GGR at equilibrium and at time (*t*), respectively. k_1 (1/h) is the pseudo-first-order rate constant. k_1 and q_e were calculated from the slope and intercept of the straight plotting $\ln(q_e - q_t)$ versus *t*, respectively [8].

The data obtained were also fitted by pseudo-secondorder model. This adsorption kinetic can be correlated by [33]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}.$$
 (3)

At the beginning stage of the adsorption, because t is nearly equal to zero, the initial adsorption rate, h (g/mg·h), could be represented by

$$h = k_2 q_e^2, \tag{4}$$

where q_e and q_t are the same as the pseudo-first-order model. k_2 (g/mg·h) is the pseudo-second-order rate constant. k_2 and q_e are obtained from the intercept and slope of t/q_t against t (see (3)), respectively [33].

The pseudo-second-order kinetic model for the removal of toluene vapor by GGR is presented by Figure 2(b). As shown, the higher correlation coefficient ($R^2 = 0.996$) acquired by this model with respect to the pseudo-first kinetic model ($R^2 = 0.919$) indicated that this model fitted the adsorption data better than the other kinetic models. Moreover, the calculated $q_{e,\text{cal}}$ (2.36 mg/g) through this kinetic model is rationally closer to experimental $q_{e,\text{exp}}$ (2.22 mg/g) (Table 3).

3.4. The Effect of Adsorbate Concentration. The effect of initial toluene concentration in the range of 0.86 to 13.86 mg/L is presented in Figure 3(a). As it can be observed, the GGR is saturated more rapidly as the toluene concentration in the polluted air was increased. This may be due to rising of the driving force of toluene such as van der Waal's forces taking place at higher concentration of the pollutant.

3.4.1. Adsorption Isotherms. Three adsorption isotherm models, Langmuir, Freundlich, and Dubinin-Radushkevich



FIGURE 2: (a) The effect of contact time on the removal of toluene by GGR (adsorbent dose = 0.6 g, temperature = 25° C, adsorbent humidity = 50%, and adsorbate conc. = 6.928 mg/L). (b) Pseudo-second-order kinetic model.

TABLE 3: Parameters of pseudo-second-order kinetic model obtained from this study.

| Adsorbate | a (mg/g) | Pseudo-second-order model | | | | | |
|-----------|----------------------------------|---------------------------|------------|----------------------------|-------|--|--|
| | <i>Ge</i> ,experimental (IIIg/g) | $k_2 (g/mg \cdot h)$ | h (g/mg⋅h) | $q_{e, calculated} (mg/g)$ | R^2 | | |
| Toluene | 2.22 | 0.29 | 1.67 | 2.36 | 0.996 | | |

TABLE 4: Langmuir, Freundlich, and D-R isotherm parameters for the adsorption of toluene onto GGR.

| Adaarbata | Langmuir isotherm | | Freundlich isotherm | | | D-R isotherm | | | |
|-----------|-----------------------|-----------------|---------------------|---------|------|--------------|-----------------------|------------|-------|
| Adsorbate | $Q_m (\mathrm{mg/g})$ | <i>b</i> (L/mg) | R^2 | k_{f} | п | R^2 | $q_m (\mathrm{mg/g})$ | E (kJ/mol) | R^2 |
| Toluene | 3.76 | 0.18 | 0.724 | 0.94 | 1.04 | 0.992 | 3.14 | 1.38 | 0.887 |

(D-R), were applied to analyze a relation between toluene concentration and the amounts of toluene adsorbed onto GGR.

The Langmuir isotherm forecasts the maximum monolayer adsorption capacity of the adsorbent [34]. The isotherm is shown by

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m},\tag{5}$$

where C_e (mg/L) and q_e (mg/g) are the pollutant concentration and the adsorption capacity of the sorbent at equilibrium time, respectively. *b* (L/mg) is the Langmuir constant and Q_m (mg/g) is the maximum sorbent capacity. Q_m and *b* are calculated by the intercept and slope of the plot of C_e/q_e against C_e , respectively [34].

The Freundlich isotherm model was employed for multilayer adsorption on a nonuniform adsorbent surface [35]. This isotherm model can be described by

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e,\tag{6}$$

where k_f (L/g) and *n* are the isotherm constants. k_f and *n* are obtained from the intercept and slope of plotting $\ln q_e$ versus $\ln C_e$ (Figure 3(b)), respectively [35].

The isotherm parameters are presented in Table 4. The Freundlich isotherm model described the adsorption of toluene onto GGR very well ($R^2 = 0.992$). Oh et al. (2009) showed that the adsorption of toluene vapors by wet compost, and ground tire rubber was modeled well by Freundlich isotherm [11]. The strong bond between pollutant and adsorbent occurs when the n value obtained from the Freundlich isotherm is more than 1 [8]. Thus, the *n* value of 1.04 achieved by this isotherm model suggested that toluene vapor is properly adsorbed by the adsorbent. Singh et al. (2010) reported that n value, obtained from Freundlich isotherm of toluene vapor removal with wood charcoal, was 0.73 [1]. The strength of adsorption bond between adsorbate and adsorbent (n value) obtained by Singh et al. (2010) is weaker than that of our study. Oh et al. (2009) also revealed that the *n* value obtained for the sorption of toluene via wet compost and ground tire rubber was in the range of 0.96-1.13 [11].

The Dubinin-Radushkevich isotherm (D-R) specifies that the type of adsorption process is chemical or physical in nature [36]. The D-R isotherm can be described as

$$\ln q_e = \ln q_m - \beta \varepsilon^2, \tag{7}$$



FIGURE 3: (a) The effect of toluene concentration on the adsorption by GGR (adsorbent dose = 0.6 g, temperature = 25° C, adsorbent humidity = 50%, and adsorbate Conc. = 0.86 to 13.86 mg/L). (b) Freundlich isotherm model.

TABLE 5: Thermodynamic parameters for the adsorption of toluene by GGR.

| | $\Delta G (kJ/mol)$ | | | | | | $\Delta H (kI/mol)$ | AS (I/mol·K) |
|---------|---------------------|-------|-------|-------|-------|-------|---------------------|--------------|
| | 283 K | 293 K | 298 K | 303 K | 313 K | 323 K | 323 K | 20 ()/mor R) |
| Toluene | -2.72 | -1.21 | -0.46 | 0.29 | 1.80 | 3.30 | -45.33 | -150.48 |

where q_m (mg/g) is the theoretical saturation sorption capacity, β (kJ/mol) is indicated as mean adsorption energy, and ε (Polanyi Potential) is equal to $RT \ln(1 + 1/C_e)$. R (kJ/mol·K) is the universal gas constant and T (K) is the temperature. q_m and β are determined by the intercept and the slope of plot of $\ln q_e$ versus ε^2 , respectively [36].

The type of adsorption process is specified by the E value. E (kJ/mol) is the mean adsorption energy that is given by

$$E = \frac{1}{\sqrt{2\beta}} . \tag{8}$$

The *E* value in the range of 8–16 kJ/mol indicates that the chemical ion exchange occurs. E < 8 kJ/mol indicates physical and E > 16 kJ/mol chemical sorption process [34].

Table 4 shows that the *E* value of toluene adsorption by GGR is equal to 1.38 kJ/mol. Therefore, the adsorption of toluene by GGR was identified as physical in nature.

3.5. The Effect of Temperature. The effect of temperature in the range of 10–50°C on the adsorption of toluene vapor by GGR was investigated. Equations (9)–(12) were used for the determination of thermodynamic parameters such as enthalpy (ΔH), Gibbs-free energy (ΔG), and entropy (ΔS) [8]:

$$\Delta G = -RT \ln k,\tag{9}$$

$$k = \frac{q_e}{C_e},\tag{10}$$

$$\Delta G = \Delta H - T \Delta S,\tag{11}$$



FIGURE 4: The effect of temperature of media on the sorption of toluene (adsorbent dose = 0.6 g, humidity = 50%, contact time = 12 h, and adsorbate conc. = 6.928 mg/L).

$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{RT},\tag{12}$$

where k is the equilibrium constant and C_e , q_e , and R are the same as defined before. The ΔS (J/mol·K) and ΔH (kJ/mol) of the toluene sorption were calculated from the intercept and slope of the straight plotting ln k against 1/T (see (12)), respectively [8].

The effect of temperature on the adsorption is shown in Figure 4 and the thermodynamic parameters are presented in Table 5. According to Figure 4, the amount of toluene adsorption was reduced by increasing the temperature. The negative values of ΔG in the temperature range of 10-25°C (Table 5) suggested that the adsorption process was spontaneous and feasible, but its positive values indicated that the sorption was not favorable at the temperature of 30–50°C [33]. The reduction in the ΔG value by increasing temperature also indicated that the adsorption is not proper at higher temperatures [37]. Typically, the physical and chemical adsorption occurs while ΔG is between -20 to 0 kJ/mol and -40 to -400 kJ/mol, respectively [37]. The value of the ΔG obtained in this study demonstrated that the uptake of toluene by GGR is physical adsorption as it was found by D-R isotherm earlier. The negative value of adsorption enthalpy (ΔH) also supports that the adsorption process is exothermic in nature [37]. The comparisons between the toluene adsorption capacities at the various temperatures confirm this fact (Figure 4). The entropy change of toluene onto GGR was -150.48 J/mol·K. The negative value of ΔS indicated a reduction in the liberation of adsorbed toluene on GGR [38].

4. Conclusion

In this study, *Glycyrrhiza glabra* root (GGR) waste was used as a novel adsorbent for the adsorption of toluene vapor from gaseous media. The effect of different conditions including contact time, adsorbate concentration, humidity, and temperature on the adsorption was investigated. The pseudo-second-order kinetic model and Freundlich model fitted the adsorption data better than other kinetic and isotherm models, respectively. The D-R isotherm also showed that the sorption by GGR is physical in nature. The results of the thermodynamic analysis (negative value of obtained ΔH) corroborate that this adsorption process is exothermic. This adsorbent is a waste material with a sorption capacity of 2.2 mg/g. In comparison with other natural sorbents (e.g., compost, diatomaceous earth, and chaff), GGR seems to be a cost-effective sorbent in the removal of toluene vapor.

Conflict of Interests

The authors declare that there is no conflict of interests.

Acknowledgment

This paper is partially the result of PhD thesis approved in the Isfahan University of Medical Sciences (IUMS). The authors wish to acknowledge Vice Chancellery of Research of IUMS for the financial support, Research Project, no. 390252.

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Research Article

The Relationship between Thermal Comfort and Light Intensity with Sleep Quality and Eye Tiredness in Shift Work Nurses

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Received 29 October 2012; Revised 29 December 2012; Accepted 31 December 2012

Academic Editor: Mohammad Mehdi Amin

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Environmental conditions such as lighting and thermal comfort are influencing factors on sleep quality and visual tiredness. The purpose of this study was the determination of the relationship between thermal comfort and light intensity with the sleep quality and eye fatigue in shift nurses. *Method.* This cross-sectional research was conducted on 82 shift-work personnel of 18 nursing workstations in Isfahan Al-Zahra Hospital, Iran, in 2012. Heat stress monitoring (WBGT) and photometer (Hagner Model) were used for measuring the thermal conditions and illumination intensity, respectively. To measure the sleep quality, visual tiredness, and thermal comfort, Pittsburg sleep quality index, eye fatigue questionnaire, and thermal comfort questionnaire were used, respectively. The data were analyzed with descriptive statistics, Student's *t*-test, and Pearson correlation. *Results.* Correlation between thermal comfort and sleep quality showed a positive and direct relationship (r = 0.241, P = 0.33) but the correlation between thermal comfort, which was perceived from the self-reporting of shift nurses, and WBGT index was a weak relationship (r = 0.019). *Conclusion.* Based on the obtained findings, it can be concluded that a defect in environmental conditions such as thermal conditions and light intensity and also lack of appropriate managerial plan for night shift-work nurses are destructive and negative factors for the physical and mental health of this group of practitioners.

1. Introduction

Nursing is a profession which, because of its stressful nature, is being faced with unforeseen situations, shifting, and organizational and personal factors, and these agents affected the mental and physical health of nurses. Different studies have reported that, in comparison with the mental and physical health of people of our country, the mental and physical health of this group of society is in a lower level [1]. Altered circadian rhythm of the autonomic regulation can have important implications on the psychological and medical problems related to shift work. For example, increase in job stress and deterioration in mood or cognitive performance were seen in shift workers [2, 3], which may be associated with altered autonomic function [4, 5].

Some studies have reported that interns working 12 h consecutive night shifts demonstrated a reduction in visual memory capacity over the night shift [6]. Other studies have reported that sleep-deprived residents demonstrated

impaired alertness or concentration [7, 8], were less efficient, and made more clinical errors [9]. Some studies have reported that working acute night shifts reduced the performance of monotonous tasks and increased sleepiness [10].

Findings of a research in electrical industries of Tehran in 2004 denoted that the inadequate level of illumination intensity causes headache and neurosis [11]. The results of a study showed that the level of lighting affected practitioners' performance and their eye fatigue [12]. In a research on improving nurse performance with appropriate design of light, which was done by Kamalii and Abbas in 2011, it was found that with a appropriate lighting design, the performance of nurses was improved, and their fault rate was diminished [13].

Among the other variables of workplace, thermal comfort can be mentioned. The thermal comfort feeling of an individuals depends on their thermal stability. Thermal stability also depends on different parameters such as physical activity rate, garment, and atmospheric conditions (dry bulb temperature, radiant temperature, air moisture, and air speed). Thermal comfort based on ANSI/ASHRAE-SS 1981 Standard is described as a condition in which, a human being is mentally satisfied with thermal condition [14, 15]. Mental satisfaction from thermal condition of workplace is one of the issues that should be considered in hospitals, since hospital indoor environment, because of climate conditions specific to the care of patients, can be uncomfortable for nurses. Hence, they should be noticed seriously.

Among the problems of night shift nurses, sleep quality can be named. In the past few years, nursing has been in the spotlight, because of its work injuries. In a research which was done on 2372 nurses in Baltimore, USA, it was shown that more than 1/4 of nurses work about 12 hours a day and more than half of them have more than one job; therefore, they become extremely tired and this causes work injuries [16]. There is no doubt that there is an extreme pressure and accuracy in nursing, that is why all the factors that may increase human faults should be studied. Among these factors, we can mention sleep quality. Sleep is one of the vital needs of human beings. Adequate sleep improves the performance of neurons and the immunity of body and has a dramatic influence on the learning process, growth, and evolution [17]. Another study result shows that people with sleeping problems receive 7 times more injuries compared with people who have enough sleep.

The most important factors that can influence level of comfort of people in a building can be divided in to two sets: human factors and environmental factors [18]. Environmental factors can be evaluated by heat stress monitoring, thermal comfort questionnaires, and illumination intensity measuring. Buchanan et al. showed that there is a linear relationship between each pharmacist's error rate and that pharmacist's corresponding daily prescription workload for three illumination levels (45, 102, and 146 foot candle), so that the rate of prescription-dispensing errors was associated with the level of illumination [19]. Beauchemin and Hays reported that patients in sunny rooms had an average stay of 16.6 days compared to 19.5 days for those in dull rooms, a difference of 2.6 days [20].

Nurses, in comparison with others, experience disorders like misappropriate sleep quality, pressure, and stress [1]. Based on a research which was done about effects of different shifts of female nurses, long period night shifts increase cancer risk in women, in comparison with women who do not work at night shifts [21, 22]. Also in a case-control research, they studied the work shifts and cancer risk of Danish nurses. They found out that the nurses who work in turning shifts after midnight are more likely to contract cancer in comparison with the nurses who work in a fixed shift in daylight [17]. In a reviewing research under the name of "women's sleep, their health and their illness," different aspects of inadequate sleep and sleep disorders were studied among women. The results showed that in addition to environmental parameters and work conditions, inadequate sleep and sleep quality are influenced by physical, mental, and hormonal health [23]. In another research on one effect of work-sleep cycle of physical health between shift nurses,

the results determined that the night shift nurses contract physical illnesses more than nurses who work in daylight [24]. In another research, they studied the sleep quality of night shift and fixed shift nurses. The results showed that there is a magnificent difference between the sleep qualities of the two mentioned groups. The fixed shift nurses enjoyed better sleep quality [25]. Hence, this study was done with the purpose of determining the relationship between environmental conditions of workplace such as light intensity in night shift nurses, heat stress, and thermal comfort with eye fatigue and sleep quality.

2. Method

2.1. Subjects. In this study, 88 (74 men and 14 women) of 300 nurses of night shift nurses were chosen voluntarily and simple randomly; their average (standard deviation) of age, height, BMI, and work history were 30.75 (6.42) years, 74.04 (13.15) kg, 174.65 (8.38) cm, 24.17 (3.27) kg/m², and 9.7 (3.5) years, respectively. The inclusion criteria were having at least 1-year work record, not having cardiovascular or respiratory diseases, and not receiving any sedatives. Exclusion criteria were not willing to cooperate or not filling out the questionnaires completely (two of the participants were removed).

3. Procedure

This cross-sectional study was done on night shift nurses of Isfahan Al-Zahra Hospital, in 16 nursing workstation, in 2012. In the present study, illumination intensity was measured by luxmeter (Hugner model), visual fatigue was determined by eye fatigue questionnaire that is comprising 15 questions, and answers have been designed on 0-10 Likert range. Alpha coefficient of the questionnaire was 0.755 [26], and sleep quality was also measured by Pittsburg sleep quality index (PSQI) that sensitivity and reliability of PSQI waere 89.6% and 86.5%, respectively, [27]. This questionnaire yields 7 scores for the individual's overall description of sleep quality, the period of sleeping, the period of effective sleep, effective sleep, sleep disorders, dose of receiving opiate, daily performance disorders scales, and one overall score. The score of each questionnaire has been considered from 0 to 3 in which 0, 1, 2, and 3 imply normal condition, presence of a little, mean, and intense problems, respectively [28]. The thermal conditions including dry bulb temperature, wet bulb temperature, globe temperature, and WBGT index were measured by Heat Stress Monitor (Casella Microtherm, Ireland). Data collecting carried out at between 9 PM and 1 AM Data analyzing was done by descriptive statistics, Pearson correlation analysis, and regression analysis.

4. Results

The mean (standard deviation) of WBGT indicator, for all workstations of hospital, was 20.67(0.55)°C (range 19.60–22.20°C). The mean (standard deviation) of light intensity for all hospital's workstations was 296 lux



FIGURE 1: Scatter plot between illuminance and eye fatigue in shift work nurses.

(range 70-680 lux). The mean (standard deviation) of thermal comfort score was 53.47 (17.15) (range 16.67-83.3). The mean (standard deviation) of eye fatigue score among these people was 29.06 (24.28). The results of Pearson correlation between illumination intensity and the other variables represent that eye fatigue has a reverse relation with illumination intensity (r = -0.179) (Figure 1). Pearson correlation between illumination intensity and sleep quality has a weak relation (r = 0.017). The yielded results of Pearson correlation between thermal comfort and WBGT index and the other variables represent that reverse. Pearson correlation between thermal comfort and WBGT indicator has a weak relation (r = 0.019). Pearson correlation between thermal comfort and eye fatigue shows a significant and reverse relation (P = 0.002, r = -0.38) (Figure 2). Pearson correlation between thermal comfort and sleep quality shows a positive and significant relation (P = 0.033, r = 0.24) (Figure 3). Pearson correlation between eye fatigue and sleep quality indicates a positive and significant relation (P < 0.001, r = -0.66) (Figure 4). Among the other studied relations, we can mention that the Pearson correlation between sleep quality variables, eye fatigue, and thermal comfort with age variable, which the only significant relation was the Pearson correlation between age and sleep quality. The relation in the latter was reverse and significant (P = 0.021, r = 0.26). Finally, the Pearson correlation between age and thermal comfort indicates a reverse and weak relation (r = -0.065). The correlation between age and eye fatigue has shown a weak relation (r = 0.138).

5. Discussion

Appropriate light intensity is essential and important in performance of work activities. As the results of the present study indicate too, light intensity and eye fatigue have a reverse relationship, and this indicates that with the increase of light intensity, the eye fatigue of night shift nurses diminished, and also statistical analysis of relations (Pearson



FIGURE 2: Scatter plot between thermal comfort and eye fatigue in shift work nurse.



FIGURE 3: Scatter plot between thermal comfort and sleep quality in shift work nurses.



FIGURE 4: Scatter plot between eye fatigue and sleep quality in shift work nurses.

correlation) in the present study shows that with the increase of light levels intensity, thermal comfort and sleep quality of nurses (even very little) has improved. These results are the same as the result of Hansen and Stevens 2012 study. In the mentioned study, with improving the light intensity of night nurses' workplace, their conciseness, performance, and comfort improved [17].

Sleep disorder is one of the most important issues among shift nurses, especially night shift nurses. High stress and disarranged shifts are important effective factors on sleep disorders and sleep quality [13]. The results of the current research, like the others which have been conducted before, indicate that night shift nurses (participants in this research) suffer from sleep disorders [28]. A research in 1992 is one of the researches with the same results, which describes the poor sleep quality of shift nurses very clearly. One of its reasons could be lacking an adequate sleep model, and this inadequate and disordered sleep model may have originated from personal and environmental factors such as inadequate and inappropriate light intensity in work environment (which affects eye fatigue). The results of the present study have shown such relationships, for example, a positive relation between light intensity and sleep quality [11].

Among the important and interesting results of this study is the correlation between eye fatigue and sleep quality which is a reverse and significant relation. This relation indicates that the less the level of eye fatigue decreases, the more the level of their sleep quality increases. This is because of the following reason. When people in workplace face inadequate level of light intensity, they try to make up this defect by pressuring on their eye muscles and continue to their activities and complete their tasks. This leads to eye tiredness and frequent headaches which can be a negative effective factor on sleep quality itself [12]. This defect can be fixed by improving the light intensity of the environment.

Thermal condition is one of the other environmental factors influencing physical and mental health state of people. Pearson correlation results between eye fatigue and sleep quality and nurses' thermal comfort indicate that the increase in thermal comfort contributes to the decrease in eye fatigue of nurses and improvement in their sleep quality; therefore, it can be inferred that we can decrease eye fatigue of shift nurses and improve their sleep quality by improving thermal condition of work environment.

Finally, it is presumed that the relationship between eye tiredness and sleep quality can be a mutual relationship. Level of light intensity can be an effective factor in removing eye tiredness and improving sleep quality of people, especially our shift nurses. Disorder in circadian rhythm as a consequence of inadequate level of daylight in work environment is the other reason for decrease in sleep quality of nurses which can lead to a decrease in the production of sleep hormone [29].

6. Conclusion

Sleep quality and eye fatigue in night shift, especially in night shift nurses, can readily under the different factors including

mental-psychological state, occupational and social factors, and environmental factors such as light intensity and thermal condition. Therefore, based on results of the present study, it can be said that we can diminish eye tiredness of these hard-working practitioners and improve their sleep quality by improving the workplace conditions such as light intensity and thermal condition. Thus, conducting the same and more comprehensive research is necessary and desirable to determine the relationship between other physical variables of work environment and diverse variables related to physical and mental health of this group of people more accurately.

Conflict of Interests

The authors declare that they have no conflict of interests.

Acknowledgments

All authors contributed equally to this work, and also they contributed extensively to the work presented in this paper. The present study was supported by Isfahan University of Medical Sciences. All authors have read and confirmed the paper.

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