Research Article

Photocatalytic Treatment of Shower Water Using a Pilot Scale Reactor

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Treatment of shower water deserves special consideration for reuse not only because of its low pollutant loading but also because it is produced in large quantities. In this study, a pilot scale study of photocatalytic degradation of impurities in real shower water was performed in a 31 L volume reactor using titanium dioxide as the photocatalyst. The reactor was operated in a continuous slurry recirculation mode. Several operational parameters were studied including the slurry initial pH, catalyst concentration, air flow rate, and slurry recirculation rate. Up to 57% of total organic carbon (TOC) elimination was obtained after 6 hours of treatment (for 3.0 slurry initial pH, 0.07 gL$^{-1}$ catalyst concentration, 1.8 Lmin$^{-1}$ air flow rate, and 4.4 Lmin$^{-1}$ slurry recirculation rate). This study showed that photocatalysis could be successfully transposed from bench scale to pilot scale. Furthermore, the ease of operation and the potential to use solar energy make photocatalysis an attractive prospect with respect to treatment of grey water.

1. Introduction

Fresh water is getting scarcer. The number of people living in water-stressed or water-scarce countries is estimated to increase from half a billion now to three billion in 2025 [1]. Water reuse has been dubbed as the greatest challenge of the 21st century [2], and, as such, great emphasis is being put into the development of new technologies for the treatment of wastewater for reuse.

Since the discovery, in 1977, that titanium dioxide (TiO$_2$) could decompose cyanide in water [3], the field of photocatalysis has been receiving increasing interest. Photocatalysis is an advanced oxidation process (AOP) that uses a catalyst (often TiO$_2$), UV light, and an electron acceptor (O$_2$, O$_3$, H$_2$O$_2$) to completely decompose organic pollutants found in liquids or gases. The basis of the process is the use of low energy UV-A photons (for which the energy is greater or equal to the band gap energy of the catalyst) to excite the semiconductor catalyst into charge separation and generate electron-hole pairs. The electrons and holes, on separation, assist in the production of the very reactive hydroxyl radical in the aqueous phase which can destroy many toxic organic pollutants. This technology however works best at low pollutant concentrations (mgL$^{-1}$ or mmolL$^{-1}$) and when the catalyst is finely dispersed within the medium. The overall process can be described by the following reaction equation:

$$\text{organic pollutants} + \text{O}_2 \xrightarrow{\text{semiconductor + UVA light}} \text{CO}_2 + \text{H}_2\text{O} + \text{mineral acid}. \quad (1)$$

Shower water is part of grey water and is produced by every household at a substantial amount (15–55 L day$^{-1}$) with a pollutant loading up to 100 mgL$^{-1}$ [4]. Existing technologies for the treatment of grey water include membrane filtration, coagulation, ion exchange, and membrane bioreactors [5, 6]. However these techniques are either costly or merely transfer the pollutants from one medium to another. As a result, shower water is a good candidate for photocatalytic treatment. The treated water could be reused where potable water is not required. Such applications include toilet flushing, landscape irrigation, and car washing.

Countless researches have been made on the photocatalytic treatment of single or a few organic components in water [7–9]. Real wastewaters on the other hand have a
2.1. Shower Water Characterisation. Shower water was collected daily from the researcher’s home and stocked in the laboratory prior to the experiments. The same cleaning products were used each time (shampoo, face wash, and body soap) to maintain consistency. The characteristics of the collected shower water are presented in Table 1.

<table>
<thead>
<tr>
<th>Main constituents (as per the products’ ingredients list)</th>
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<td>TOC (mgL(^{-1}))</td>
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<td>pH</td>
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The TOC level of the shower water suggests that it is a low strength grey water. The main constituents of liquid soaps and shampoos are surfactants which can add up to 80% by weight of chemicals content [23]. Some other constituents that may be present in trace amounts in the shower water include sebum, microorganisms, and dyes.

The objective of this research was to study pollutant degradation in shower water in a pilot scale photocatalytic reactor (31 L volume) operating in a recirculation mode. The effect of several parameters such as the initial slurry pH, air flow rate, slurry recirculation rate, and catalyst dosage was studied. All experiments were carried out for a period of 6 hours, which was deemed a reasonable treatment time.

2.2. Reagents and Analytical Methods. Aeroxide P25 titanium dioxide was purchased from Sigma Aldrich and was used as received. The catalyst had the following properties: 21 nm particle size, 50 ± 15 m\(^2\)g\(^{-1}\) BET specific surface area, >99.5% TiO\(_2\) content [24], and a band gap energy of 3.2 eV, corresponding to photons with wavelengths less or equal to 385 nm [25]. A 6 M hydrochloric acid was used to modify the slurry pH prior to reaction. Compressed air was used as feed gas to the reactor and for UV lamp cooling. Tap water was used to dilute the shower water (if required). Slurry pH was measured with a TPS digital pH meter, which was calibrated periodically. Samples collected were filtered with 0.45 microns syringe filters and analysed for total organic carbon (TOC) on a Shimadzu TOC-VCPN analyser (Shimadzu Corporation, Japan).

2.3. Reactor Setup. Figure 1 shows the reactor setup used in this study. The reactor volume was 31 L (30 cm diameter) and was operated in recirculation mode. Ambient air was supplied by a compressor via a 10 cm distributor centred at the bottom of the reactor. Part of the compressed air was also used as coolant for the UV lamp. The UV mercury lamp, purchased from Primarc Ltd. (PM 3426, 800 W, 20 cm length medium pressure mercury lamp), was fitted into a quartz tube and suspended in the middle of the reactor. A digital thermocouple provided the temperature within the reactor. The temperature was maintained between 26 and 28°C by varying the rate of cooling water which ran through a coiled heat exchanger located around walls at the bottom of the reactor. An Iwaki magnetic pump was used for slurry circulation. Slurry flow rate was varied using valve V2 while air flow rate was varied via valve V5.

2.4. Procedure. Shower water was diluted with tap water (if required) and mixed with the titanium dioxide powder in a 60 L tank. The pH was adjusted, and the slurry was allowed to mix for 30 minutes to allow for dark adsorption of pollutants onto the catalyst surface. Compressed air as well as cooling water was started, and the slurry was transferred to the reactor via the Iwaki magnetic pump. Once the reactor was filled, valve V1 was closed, valve V3 was opened to allow the reactor to operate in recirculation mode, and, finally, the lamp was switched on. Samples were taken in 20 mL aliquots via sample valve V6 and were filtered prior to analysis.

3. Results and Discussion

Since the shower water consisted of a myriad of organic components, a realistic way of reporting the pollutant concentration was by measuring the total organic carbon (TOC in mgL\(^{-1}\)) of the samples. The average reaction rate for TOC elimination was calculated using the following equation:

\[
-R_{\text{TOC}} = \frac{\text{TOC}_{\text{initial}} - \text{TOC}_{\text{final}}}{\tau}
\]

where \(-R_{\text{TOC}}\) is the average rate of degradation of TOC (molL\(^{-1}\)min\(^{-1}\)), \text{TOC}_{\text{initial}} and \text{TOC}_{\text{final}} are the initial and final organic carbon concentrations, and \(\tau\) is the reaction time.
3.1. Photocatalysis of Shower Water. The temporal course at optimum conditions for the photocatalysis of shower water in terms of TOC reduction is illustrated in Figure 2. Part of the TOC was adsorbed onto the catalyst surface during the dark adsorption stage. Upon irradiation, the TOC concentration increased to a maximum within the first two hours of reaction that corresponded to the initial TOC concentration prior to dark adsorption. This phenomenon had been observed previously [17, 26, 27] for the photocatalytic oxidation of anionic surfactants at low initial concentrations. The initial increase in TOC can be attributed to the formation of intermediates on the catalyst surface followed by photodesorption of the intermediates back into the liquid medium. Several types of intermediates are formed via the photooxidation of long chained hydrocarbons. Zhang et al. [27] reported the formation of aldehyde and peroxide intermediates during the photooxidation of surfactants.

A reduction in the TOC concentration was then observed after 2 hours due to the onset of oxidation of organic pollutants. This reduction was only moderate from \( t = 2 \) h to \( t = 3 \) h probably due to a large quantity of long chained organics/intermediates still remaining in the solution. However, as the photoreaction proceeded, the long chained organics/intermediates cleaved into smaller chained intermediates for which mineralisation to carbon dioxide, water, and mineral acids took place at a faster rate, as observed after \( t = 3 \) h. A maximum of 57% TOC degradation was obtained within 6 hours of treatment at optimum conditions.

3.2. Effect of Slurry Initial pH. The initial pH of the slurry is an important parameter that needs to be considered as it influences the surface charge properties of the catalyst particles [9], hence the adsorption of charged pollutants. Figure 3 shows the effect of the slurry initial pH on the average rate of TOC degradation. There was a gradual increase in the average reaction rate as the pH was decreased from 7.4 (natural pH) to 5.0. The increase in reaction rate...
became steeper as the pH was further lowered and reached a maximum at pH = 3.0. Further lowering of the pH to 2.2 led to a sharp decrease in the reaction rate.

Titanium dioxide is amphoteric by nature which means that past a certain pH, it can be either positively or negatively charged. That pH, which is called the point of zero charge (ZPC), occurs at a value of 6.5 for Aerosol P25 titanium dioxide [28]. Hence when pH < ZPC, the TiO$_2$ is positively charged while at pH > ZPC, it is negatively charged as shown as follows:

when pH < ZPC: TiOH + H$^+$ → TiOH$_2^+$, \hspace{1cm} (3)

when pH > ZPC: TiOH + OH$^−$ → TiO$^−$ + H$_2$O. \hspace{1cm} (4)

This implies that at lower pH, the positively charged TiO$_2$ surface can easily attract the negatively charged species from the solution, hence facilitating their photooxidation. The main components of the shower water used were anionic surfactants as presented in Table 1. As the pH of the slurry was decreased, the positive surface charge of the TiO$_2$ increased, attracting more and more anionic groups to its surface. This is further evident with the change in the dark adsorption with slurry pH in Figure 4, which shows that pollutant species during the dark adsorption remained constant between pH of 7.4 and 5.0 but then increased sharply to reach a maximum of 32.4% adsorption at pH 3.0. Another research involving anionic surfactants has also shown preferential photooxidation at low pH [29, 30].

Being radical scavengers, carbonate anions present in the wastewater can inhibit photooxidation [31]. However an acidic medium can remove these unwanted anions as per the following equations:

\begin{equation}
\text{HCO}_3^- + H^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2, \hspace{1cm} (5)
\end{equation}

\begin{equation}
\text{CO}_3^{2-} + 2H^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2. \hspace{1cm} (6)
\end{equation}

Nonetheless, Figure 3 shows that a further reduction of pH to 2.2 was in fact detrimental to the degradation of TOC. This was attributed to high levels of Cl$^−$ ions in the solution. Cl$^−$ ions are scavengers of hydroxyl radicals as well as holes [32] and can therefore greatly reduce the photooxidation process. As the pH was decreased from 3.0 to 2.2, the concentration of Cl$^−$ increased exponentially from $1 \times 10^{-3}$ M to $6.3 \times 10^{-3}$ M, hence explaining the rapid decrease in the TOC removal rate. The optimum pH of 3.0 was maintained throughout subsequent experiments.

3.3. Effect of Catalyst Dosage. Most wastewater photocatalytic treatment studies report an optimum catalyst concentration. Beyond that optimum, the rate of reaction either remains unchanged or decreases. Figure 5 shows the effect of catalyst loading on the average reaction rate with the range of catalyst loading investigated between 0.03 and 0.15 gL$^{-1}$. It is clear that the optimum catalyst concentration was about 0.07 gL$^{-1}$.

Reported optimum catalyst loadings for wastewater treatment are usually within a range of 0.1–1 gL$^{-1}$ [7, 8, 33]; however some studies have also reported lower optimum loadings (0.05 gL$^{-1}$) [34]. However, in all cases, the optimum value strongly depends on the reactor design, pollutant type, and concentration [35].

In the current study, a relatively low value of optimum catalyst loading could be attributed to the low concentrations of shower water as well as the large reactor diameter. Lower catalyst loadings provided sufficient sites for photodegradation and allowed a maximum possible illumination of the reaction space. Beyond those loadings, the decrease in average reaction rate was probably due to the backscattering of light by the catalyst particles, entailing a shielding effect on the remaining reaction space. Simulation studies are currently being carried out to verify these hypotheses.

The effect of catalyst concentration, $W_{\text{cat}}$ (gcatL$^{-1}$), on the average reaction rate, $-R_{\text{TOC}}$ (molL$^{-1}$min$^{-1}$), could be described as:

\begin{equation}
-R_{\text{TOC}} = A + \frac{B}{(W_{\text{cat}} - C)^2 + D}, \hspace{1cm} (7)
\end{equation}
The range of air flow rate investigated was between 1.5 and 5.0 Lmin⁻¹ as depicted in Figure 6. The average TOC degradation rate was found to increase until an optimum was reached at 1.8 Lmin⁻¹ air flow rate after which a steep decrease in the reaction rate was observed. Visual observations showed that fine bubbles were formed at the lower air flow rates. However, beyond the optimum air flow rate, larger bubbles of widespread sizes were observed. Larger bubbles meant reduced surface area for mass transfer of oxygen from the gas to liquid phase, hence the reduction in the average reaction rate. Agustina et al. [36] made a similar observation in their study of winery wastewater treatment with the same reactor. On the other hand, at low air flow rates in the vicinity of 1.5 Lmin⁻¹, air bubbles had a tendency to penetrate the slurry outlet, leading to irregular liquid pumping, hence a reduced average reaction rate.

The effect of air flow rate, $Q_{\text{Air}}$ (Lmin⁻¹), on the average reaction rate, $-R_{\text{TOC}}$ (molL⁻¹ min⁻¹), could be described as

$$-R_{\text{TOC}} = A + \frac{B}{(Q_{\text{Air}} - C)^2 + D},$$

where the values for $A$, $B$, $C$, and $D$ are $7.06 \times 10^{-5}$ molL⁻¹ min⁻¹, $5.93 \times 10^{-5}$ molL⁻¹ min⁻¹, 1.62 Lmin⁻¹, and 0.47 L² min⁻², respectively.

3.5. Effect of Slurry Recirculation Rate. The recirculation rate of the slurry was varied to study the effect of the residence time. The circulation rate was varied between 1.5 and 5.7 Lmin⁻¹, and its effect on the average reaction rate is presented in Figure 7. Maximum degradation was obtained at a recirculation rate of 4.4 Lmin⁻¹. At higher recirculation rate, the slurry inlet momentum was high enough that air bubbles had the tendency to be pushed towards the slurry outlet. Introducing air bubbles into the pipelines made pumping irregular and therefore reduced the average reaction rate.

3.4. Effect of Air Flow Rate. Upon irradiation, the catalyst particles generate positive holes and electrons. The photooxidation process requires an oxidising agent to remove electrons from the catalyst surface and prevent them from recombining with positive holes which are responsible for the creation of hydroxyl radicals. In this study, the oxidant was oxygen in the air.
reaction rate. Pareek et al. [37] found maximum degradation at a recirculation rate of 0.2 L min\(^{-1}\) in an 18 L volume reactor for the photodegradation of Bayer liquor. However in their study, catalyst suspension was assisted by fine air bubbles homogeneously distributed within the reactor. In this study, air bubbles were supplied from a 10 cm distrubutor centred at the bottom of the reactor. These bubbles were not dispersed throughout the reactor space, and, as a result, a relatively high volumetric flow rate was necessary to suspend the catalyst particles.

The effect of slurry recirculation rate, \(Q_{\text{Slurry}}\) (L min\(^{-1}\)), on the average reaction rate, \(−R_{\text{TOC}}\) (mol L\(^{-1}\) min\(^{-1}\)), could be described as

\[
−R_{\text{TOC}} = k_0 + k_1 Q_{\text{Slurry}} + k_2 Q_{\text{Slurry}}^2 + k_3 Q_{\text{Slurry}}^3. \tag{9}
\]

The values of \(k_0, k_1, k_2,\) and \(k_3\) are 3.66 \(×\) 10\(^{-6}\) mol L\(^{-1}\) min\(^{-1}\), 2.00 \(×\) 10\(^{-6}\) mol L\(^{-2}\), 8.75 \(×\) 10\(^{-7}\) mol min L\(^{-3}\), and 1.00 \(×\) 10\(^{-7}\) mol min\(^{-2}\) L\(^{-4}\), respectively.

### 3.6. Electricity Cost Analysis

Based on the current electricity cost in Perth, Australia (0.35 US$/kWh\(^{-1}\)), a cost analysis was performed as detailed in Table 2.

Therefore for a 31 L throughput, the treatment cost for shower water amounted to 49.4 US$ m\(^{-3}\). This value was close to the price range obtained by Pareek et al. [37] (60–270 US$/m\(^{-3}\)) for the photocatalytic treatment of industrial Bayer liquor but is much larger than the reported 3.75 Euros m\(^{-3}\) for the photocatalytic treatment of herbicides [38] most probably due to the size (bench scale) of the latter research. However, it is possible to operate the reactor with solar light; it is envisaged that operational cost of a large-scale photoreactor for shower water purification will be much less.

### 4. Conclusions

A pilot scale study for the photocatalytic degradation of real shower water showed that photocatalysis can be an efficient treatment process. At optimum conditions (3.0 slurry initial pH, 0.07 g L\(^{-1}\) catalyst concentration, 4.4 L min\(^{-1}\) slurry recirculation rate, and 1.8 L min\(^{-1}\) air supply), a 57% of TOC degradation was obtained after 6-hour treatment time, although higher TOC degradation is expected if the treatment time is increased. This study showed that photocatalysis could be successfully transposed from bench scale to pilot scale. Furthermore, the ease of operation of the process makes photocatalysis an attractive prospect in terms of grey water treatment.

### References


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