

Photocatalytic treatment of high concentration carbamazepine in synthetic hospital wastewater

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ABSTRACT

Effective and sustainable treatment of hospital wastewater containing high concentration of pharmaceutical compounds presents a pivotal challenge to wastewater and environmental engineers worldwide. In this study, a titanium dioxide (TiO₂) nanofiber based wastewater treatment process was assessed as a pre-treatment system to treat and enhance the biodegradability of a representative pharmaceutical compound, 5000 µg/L of carbamazepine (CBZ), in synthetic hospital wastewater. Results showed that the stand-alone TiO₂ pre-treatment system was capable of removing 78% of CBZ, 40% of COD and 23% of PO₄ concentrations from the influent wastewater within a 4 h reaction time. High performance size exclusion chromatography demonstrated that a simultaneous biodegradability enhancement of hospital wastewater was observed, whereby an apparent shift in molecular weight from higher fraction (>10–1000 kDa) to a lower fraction (<10 kDa) was induced after 0.5 h of photocatalytic treatment. Eventually, it was found that the photodegradation profile for high concentration CBZ in synthetic hospital wastewater was perfectly fitted to the Langmuir–Hinshelwood kinetics model. It is anticipated that this TiO₂ pre-treatment process can be further integrated with a biological wastewater treatment process to deliver treated hospital effluent of better quality that can minimise the associated human health and environmental risks.

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1. Introduction

Hospital wastewater represents one of the most ubiquitous water sources in the total urban water cycles, where the generated effluents are usually loaded with pharmaceutical, chemical, radioactive and other toxic chemical substances, as well as various pathogenic microorganisms [1–5]. In general, it was reported that hospitals generate a nominal range of wastewater of 400–1200 Litres per bed per day (L/bed/day), with an average at approximately 750 L/bed/day [5,6]. All of these pollutant loads and generated wastewater are usually discharged directly to the local municipal wastewater treatment plants (WWTPs), although it has been suggested to retain the wastewater on-site for further purification before discharging to local WWTPs [7]. The on-site retention and pre-treatment of hospital wastewater is to ensure that most of the hazardous pollutant loads are being treated in order to avoid their possible contaminants diffusing into the natural ecosystem.

Some previous studies had detected the presence of pharmaceutical compounds in natural ecosystems that caused contamination to groundwater, surface water and drinking water sources [8–12]. Sources of these compounds usually come from human excretion, where the administered pharmaceutical compounds are passed through the human body unaltered (i.e., as parent compound or metabolite) into both urine and faeces [8,9]. Due to the physical and chemical properties of pharmaceutical compounds, they are usually highly polar and persistent to environmental degradation processes. This can result in serious bioaccumulation problems in the environment that could affect aquatic and terrestrial ecosystems and also causing poor removal efficiency at WWTPs. Thus, there is a need for a new generation hospital wastewater treatment system that is environmentally friendly and can minimise the associated human health and environmental risks in the treated hospital effluents.

Among the new generation wastewater treatment technologies, heterogeneous semiconductor titanium dioxide (TiO₂) process appears to be an attractive pre-treatment option to enhance the degradation of organic contaminants, as well as the biodegradability of hospital wastewater for further downstream treatments. The mechanisms for the formation of electron–hole pairs on the surface of TiO₂ catalysts via a series of redox reactions are

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well-documented [13]. When the TiO₂ surfaces are photon-activated, the reactive hydroxyl radicals will react, degrade and mineralise with organic compounds without creating secondary pollution (i.e., organics are completely eliminated rather than adsorbed or phase transferred) [13]. In this instance, the TiO₂ based treatment system could be integrated as a pre- or post-biological wastewater treatment to enhance the biotransformation process for pharmaceutical compounds. Previously, we have studied the integration of TiO₂ treatment as a post-biological wastewater treatment train for simulated pharmaceutical industrial effluent [14]. Others have also investigated on the application of different TiO₂ photocatalytic treatments for the removal of pharmaceuticals and endocrine disrupting compounds found in different source waters [15–17].

The aim of this study was to assess the potential application of a TiO₂ photocatalytic process as a pre-treatment system for the treatment of high strength pharmaceutical compounds from hospital wastewater. A representative antiepileptic drug of carbamazepine (CBZ) was used as a surrogate organic indicator to measure against the treatment efficiency in synthetic hospital wastewater. CBZ is usually used as sedative, which can produce serious toxic effects on the liver and emopoietic system [17]. Previously, Radjenovic et al. [18] identified that the CBZ by-passed the secondary treatments of conventional activated sludge, hollow-fibre membrane bioreactor (MBR) and flat-sheet MBR owing to the consequence of conjugation/deconjugation processes that occur during treatment. Thus, CBZ is regarded as appropriate to be utilised as a reaction surrogate indicator in this study where an enhanced pre-treatment removal of a large proportion of CBZ found in hospital wastewater would alleviate the burden of downstream wastewater treatment processes. The TiO₂ nanofiber was used to enhance the photocatalytic activity and catalyst recovery in the system [19,20]. The photodegradation profiles and kinetics for the removal of individual CBZ compound and overall COD concentration were studied in detail. The synergistic photocatalytic action on the evolution of inorganic phosphate (PO₄³⁻) and nitrate (NO₃⁻) ions during the treatment of synthetic hospital wastewater was monitored. With this study, it is anticipated a preliminary feasible assessment and understanding on the applicability of TiO₂ based pre-treatment system can be achieved.

2. Experimental

2.1. Chemicals

Anatase particles (~325 mesh from Sigma–Aldrich) were used as received. CBZ (Sigma–Aldrich) was dissolved in the secondary municipal wastewater. Sodium hydroxide NaOH (AR grade, Aldrich) was diluted with the addition of Milli-Q water with 18.2 MΩ cm resistivity.

2.2. Preparation of TiO₂ nanofiber catalyst

The TiO₂ nanofiber catalyst was synthesized through a hydrothermal reaction between concentrated NaOH and TiO₂, and a post-synthesis ion exchange with HCl solution [21]. Specifically, 3 g of anatase particles was mixed with 80 mL of 10 M NaOH. The resultant suspensions were sonicated for 30 min and transferred into a poly-tetrafluoroethylene (PTFE) container for autoclaving. The autoclave was maintained at a hydrothermal temperature of 180 °C for 48 h. The precipitate (sodium titanate nanofibers) was recovered, washed with distilled water (to remove excess NaOH) and finally exchanged with H⁺ (using a 0.1 M HCl solution) to produce TiO₂ nanofiber. These products were repeatedly washed with distilled water until pH ~7 was reached. The hydrogen titanate product was dried at 80 °C for 12 h and then calcined at 700 °C for 3 h

to yield TiO₂ nanofiber. The resultant TiO₂ nanofiber was measured with thickness of 40–100 nm and length up to 30 μm long.

2.3. Sample preparation and wastewater collection

The municipal wastewater samples were collected from the Glenelg Wastewater Treatment Plant (WWTP), South Australia. Following this, a concentration of 5000 μg/L of CBZ was dissolved in the wastewater samples to represent the synthetic hospital wastewater. Owing to the low solubility of CBZ in water, the aqueous mixture was stirred for 5 min and followed by sonication for 5 min. This preparation step was repeated to ensure the complete dissolution of CBZ in the synthetic hospital wastewater. The final CBZ concentration in the dissolved phase was verified using the high performance liquid chromatography (HPLC) analysis. If a lower than 5000 μg/L of CBZ concentration was attained, additional CBZ was dissolved to ensure the final CBZ concentration was as close to the targeted concentration as possible. In this study, a total of wastewater samples (*N*=9) were collected. The wastewater samples were bulked and stored in the laboratory before being mixed with 5000 μg/L of CBZ concentration, to ensure the uniformity and control experimental wastewater qualities. In this instance, the use of synthetic hospital wastewater from spikes of CBZ into bulk municipal wastewater samples will allow for direct comparison in photocatalytic degradation efficiency of CBZ between the *N*=9 experiments. Although the COD concentration in the synthetic hospital wastewater samples are lowered than the real hospital effluents, the use of synthetic hospital wastewaters enables a direct quantification of the mixed-effect from wastewater qualities on the photocatalytic degradation of CBZ. This study also forms an important basis for the future studies when real hospital effluents with high COD concentration are attempted. In the current study, each experimental run was monitored and analysed in terms of the COD, NO₃⁻ and PO₄³⁻ concentrations in a time-series manner, in-line with each treatment cycle.

2.4. Setup of TiO₂ photocatalytic reactor system

In this study, a batch annular slurry photoreactor (ASP) was used as a pre-treatment system for the treatment of high concentration CBZ in synthetic hospital wastewater [22]. The ASP is a three-phase bubble column reactor, where the TiO₂ nanofiber was dispersed in the synthetic wastewater through fine bubble aeration. The conical bottom of the ASP was designed to prevent potential reaction dead zones during the photocatalytic treatment. A 45 μm air sparger was used to provide homogeneous fine bubble aeration for the suspension and mixing of TiO₂ nanofiber within the system. An UV-A black light of 8 W (NEC, Holland) was positioned annularly within the quartz thimble to prevent direct contact with the reaction wastewater, while allowing optimal UV transmission into the annulus reaction zone. Samples were collected from the four-descended level sampling ports. Electronic probes and meters for in situ data logging of pH, dissolved oxygen and temperature (TPS, Australia) were connected to the batch reactor. The experimental setup for the ASP system is shown in Fig. 1.

2.5. Analytical procedures

The CBZ concentrations were analysed using a HPLC [Varian Pro-star] with a Varian Microsorb-MW 100-5 C18 column (4.6 mm × 150 mm, 5 μm) at a flowrate of 1.0 mL min⁻¹ and UV absorbance detection at 254 nm. The mobile phase was methanol 60% plus ammonium acetate (10 mM) and acetic acid (5 mM). The injection volume was 20 μL.

High-performance size exclusion chromatography (HPSEC) and UV detection were used to investigate the changes in the apparent

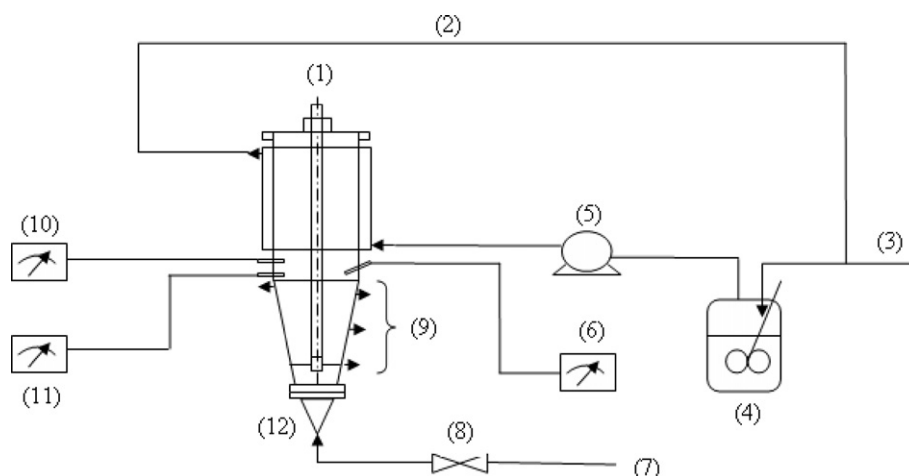


Fig. 1. Experimental setup for the annular slurry photoreactor system: (1) UV light, (2) recirculation water line, (3) fresh cool water line, (4) cooling water vessel, (5) cooling water pump, (6) temperature meter, (7) compressed air supply line, (8) compressed air regulation valve, (9) sampling ports, (10) pH meter, (11) dissolved oxygen meter, (12) photoreactor.

molecular weight (AMW) profile of synthetic hospital wastewater during photocatalytic treatment. The samples were analysed using a coupling method reported by Liu et al. [23].

Chemical oxygen demand (COD) was analysed using an open reflux method, where 2 mL of the sample was added into the low range 0–150 mg L⁻¹ COD reagent containing potassium dichromate (K₂Cr₂O₇) and subsequently heated for 2 h at 150 °C in a digestion reactor of DRB 200 (Hach Lange GmbH, Germany). The oxidisable organic compounds present will react with the K₂Cr₂O₇, and further reducing the dichromate ion to green chromic ion. Using this method, the amount of Cr³⁺ produced was measured at the wavelength of 620 nm using a spectrophotometer DR4000 (Hach Lange GmbH, Germany). The color intensity was well-correlated to the COD values.

The NO₃⁻ ion was measured using the persulfate digestion method (Hach Lange GmbH, Germany). Initially, the N contents were converted into NO₃⁻ through an alkaline persulfate digestion reagent and further heated at 105 °C for 30 min in the DRB 200 reactor. Sodium metabisulfite was added after the digestion to eliminate the interference of halogen oxide during measurement. Then the NO₃⁻ ions were reacted with chromotropic acid to yield the final yellow complex that has an absorbance maximum at 410 nm.

The vanadium molybdate spectrometry method was used to measure the PO₄³⁻ ions concentration. In this method, the orthophosphate was reacted with molybdate in an acid medium to produce a phosphomolybdate complex. A yellow vanadomolybdophosphoric acid was formed when the reaction mixture was further reacted with vanadium. The samples were then pre-treated with acid and heated at 105 °C for 30 min to hydrolyse the condensed inorganic forms of phosphorous. The intensity of the yellow color was used to correlate the PO₄³⁻ ions concentration in the hospital wastewater sample.

3. Results and discussion

3.1. Photocatalytic degradation of carbamazepine

Previous applications of TiO₂ photocatalysis for the degradation of CBZ in distilled water showed relatively good results [24–26]. It was found however that there is a lack of information on the application of TiO₂ photocatalysis process for the degradation of CBZ in real wastewaters, particularly for hospital wastewater. In this study, the photocatalytic treatment of a high concentration of pharmaceutical CBZ (~5000 µg/L) in synthetic hospital wastewater

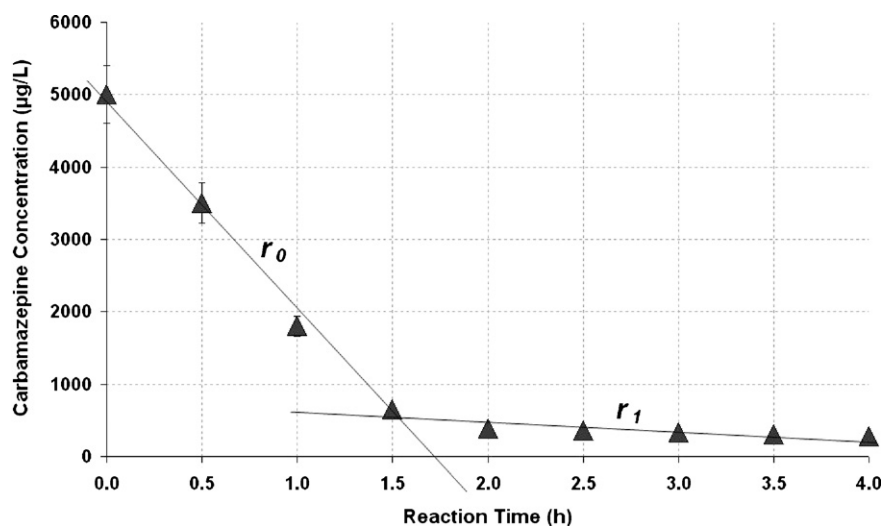


Fig. 2. Photocatalytic treatment of high concentration of CBZ in synthetic hospital wastewater. Initial CBZ concentration: 5000 µg/L.

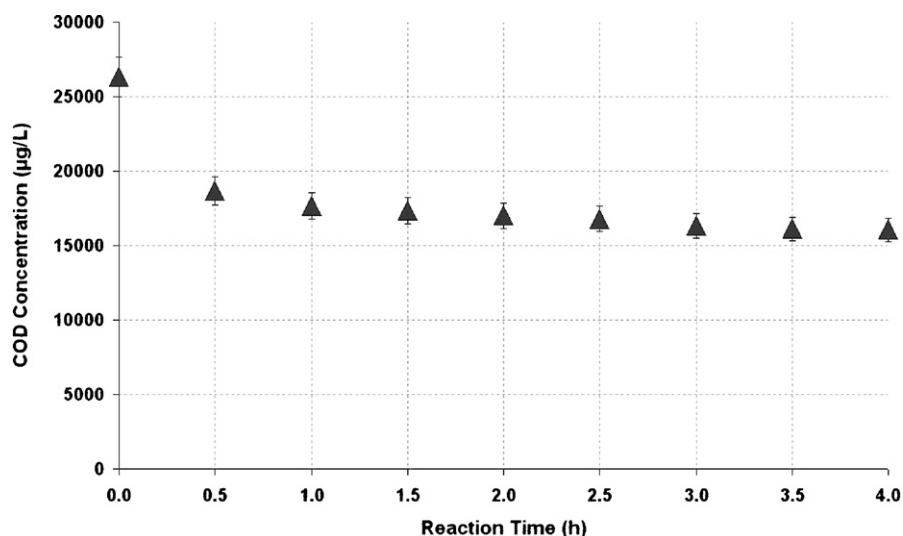


Fig. 3. COD concentration profile during the photocatalytic treatment of high concentration of CBZ in synthetic hospital wastewater. Initial CBZ concentration: 5000 µg/L.

was carried out. Table 1 shows the typical qualities values for the synthetic hospital wastewater used.

Fig. 2 shows the reduction in CBZ concentration against reaction time during the photocatalytic treatment of synthetic hospital wastewater in the TiO₂ nanofiber pre-treatment system. From Fig. 2, it was evidenced that the initial photo-degradation rate (i.e., 1.5 h) of CBZ was rapid followed by a slow attenuation rate at 1.5–4 h of reaction time. When the CBZ photo-degradation kinetics profile was fragmented into two reaction rate regimes, the initial reaction rate (r_0) was found to be 48.33 µg/L min while the latter reaction rate (r_1) was 2.47 µg/L min.

When the concurrent COD measurements were taken, it was observed that the extent of organics mineralisation in synthetic hospital wastewater was quite rapid. A 40% reduction in the overall COD concentration, from approximately 26,000 µg/L to 17,000 µg/L, was observed after 4 h of reaction time (Fig. 3). Fig. 4 shows the result from HPSEC to account for the changes in AMW fractions during the organics mineralisation in synthetic hospital wastewater. From Fig. 4, it was seen that the initial AMW peak at 100 kDa was diminished after 0.5 h of reaction time and a subsequent peak appeared at the AMW of 750 Da after 1 h of reaction time. The UV₂₆₀ absorbance intensity peaks were observed to weaken from there of, at 1 h of reaction time up to 4 h. The initial shift in AMW peaks indicated that the photocatalytic treatment of high concentration of CBZ in synthetic hospital wastewater resulted in the formation of smaller organic degradation by-products. Further analysis on the HPLC chromatograms at UV 254 nm (Supporting Fig. 1) verified that the disappearance of CBZ peak was accompanied by the formation of new organic by-products peaks between 2.5 and 3.5 min. Since these lower MW organic by-products peaks were UV-absorbing and thus, this implicated their potential aromatic properties and the need for a longer reaction time.

Table 1

The average wastewater quality for the raw synthetic hospital influent and the primary hospital treated effluent.

Wastewater parameters	Raw synthetic hospital influent	Primary hospital treated effluent
COD (mg L ⁻¹)	24.9–27.8	14.7–17.3
NO ₃ ⁻ (mg L ⁻¹)	162.0–185.6	201.8–224.2
PO ₄ ³⁻ (mg L ⁻¹)	13.2–15.3	10.4–11.9

Thus, it can be concluded that the current application of TiO₂ based pre-treatment process was effective for the removal of high concentration of CBZ compound, reduction of COD concentration and the enhancement of biodegradability in hospital wastewater. The resultant smaller organic degradation by-products were seen to be easily degradable when the TiO₂ process is integrated with a downstream biological wastewater treatment process.

3.2. Simultaneous reaction effects on NO₃⁻ and PO₄³⁻ ions

Apart from the presence of vast amounts of pharmaceutical residuals, the pre-treatment and removal of total nitrogen and phosphorus is also an important aspect of risk control and management for hospital wastewater sources. To functionalise the proposed TiO₂ nanofiber based process as a pre-treatment system for hospital wastewater, it is important to understand the simultaneous reaction effects on both nitrate (NO₃⁻) and (PO₄³⁻) ions. Low et al. [27,28] found that the photo-oxidation of nitrogen (N) will lead to the formation of ammonium (NH₄⁺), nitrate (NO₃⁻) and nitrite (NO₂⁻) ions. Similarly, they reported that the photo-oxidation of phosphorus (P) will result in the occurrence of phosphate (PO₄³⁻) ions.

Fig. 5 shows the evolution of PO₄³⁻ and NO₃⁻ ions during the photocatalytic degradation of CBZ compound in synthetic hospital wastewater. The monitoring results showed that the TiO₂ nanofiber based pre-treatment process was capable to reduce the overall phosphorus concentration, as well as the PO₄³⁻ ions concentration by 23%, from 14.2 mg L⁻¹ to 11.0 mg L⁻¹ within 4 h of reaction time. Previous study by Araña et al. [29] on the application of a mixture of TiO₂-activated carbon photocatalysis as a tertiary treatment of wastewater also observed similar reduction in PO₄³⁻ concentration. They discussed that PO₄³⁻ ions will affect the degradation of organic compounds in wastewater via the (1) inhibition of TiO₂ catalytic activity, as well as (2) the synergistic interaction between photon activated TiO₂ and the water chemistry. The strong adsorption behaviour of PO₄³⁻ on TiO₂ surface that inhibits the photocatalytic reaction has been previously examined [13]. However, the adsorption of PO₄³⁻ onto TiO₂ surface is strongly affected by the pH condition where pH < pzc (point of zero charge for TiO₂ nanofiber) will result in a potential alteration to the surface chemistry and physical property. Since the pzc of TiO₂ nanofiber was 4.6 and the operating pH was between 7.39 and 7.80, it was understood that the net PO₄³⁻ adsorption impact was

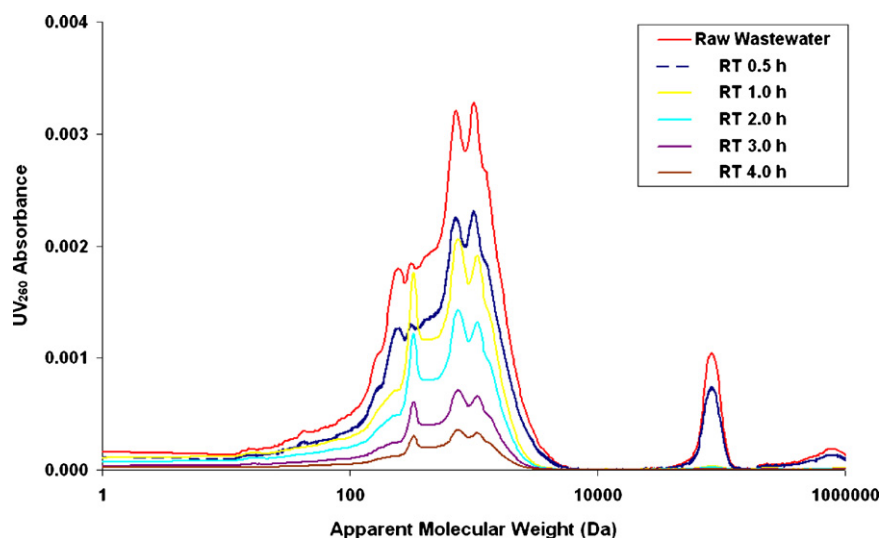
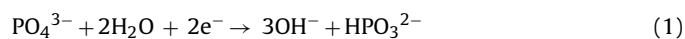


Fig. 4. High performance size exclusion chromatogram on the photocatalytic degradation of synthetic hospital wastewater at different reaction times.

minimal in this study due to the electronic repulsion between the two reaction entities [19]. Thus, the small gradual reduction in PO_4^{3-} concentration was due to the direct synergistic interaction between hydroxyl radicals OH^\bullet on the TiO_2 surface with equilibrium species of PO_4^{3-} , such as HPO_4^{2-} , H_2PO_4^- , H_3PO_4 and others. The direct interaction of PO_4^{3-} ions with OH^\bullet radicals during photocatalytic reaction are given Eqs. (1) and (2) [29]. The redox potentials for Eqs. (1) and (2) were -0.42 V and -0.52 V respectively, which proved the dominating reaction effects on PO_4^{3-} in this study.



In contrast, it was observed that the NO_3^- ions concentration increased by 24%, from 171.60 mgL^{-1} to 213.20 mgL^{-1} , after 4 h of reaction time. Chong et al. [13] reviewed that the nitrogen-containing molecules are mineralised into NH_4^+ and mostly NO_3^- . Piccinini et al. [30] found that the distribution of NH_4^+ and

NO_3^- ions varied with reaction time, initial oxidation state of nitrogen and type of initial organic substrate. It was well-correlated that the formation of NO_3^- during photocatalytic treatment was favoured by the high oxidation state of NO_3^- ions, which is +5 [30]. They found that the NO_2^- ions were not detected even at a very short irradiation time, and that after 5 h of reaction time, only traces of NH_4^+ ions (4–10%) were detected and mostly NO_3^- were formed (90–96%). Fig. 5 shows there was a build-up in NO_3^- ions concentration over a reaction time of 4 h. However, it was found that the NO_3^- ions have dissimilar fouling mechanism on the TiO_2 reaction. Burns et al. [31] reported that the NO_3^- ions will UV screen the photocatalyst from photon-activation rather than inhibiting the TiO_2 surface.

With the evolution kinetics of PO_4^{3-} and NO_3^- ions during the simultaneous photo-degradation of CBZ in synthetic hospital wastewater (in Fig. 5), it is anticipated that this feasibility study on TiO_2 based system as a pre-treatment of hospital wastewater can be extrapolated for similar application in the future. These results can be utilised effectively to design the potential downstream

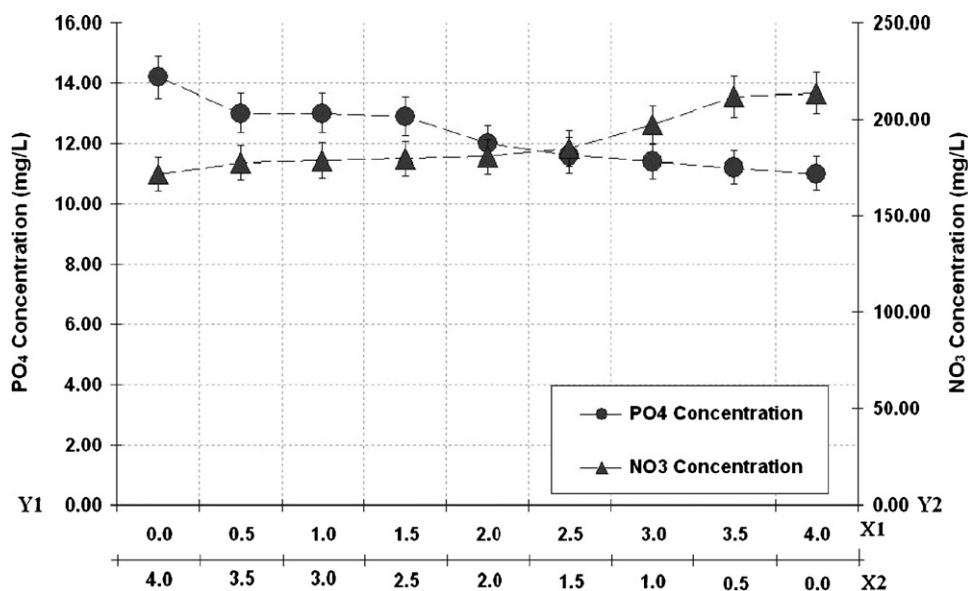


Fig. 5. Fate of PO_4^{3-} and NO_3^- ions during the photocatalytic treatment of high concentration of CBZ in synthetic hospital wastewater. Points PO_4^{3-} (axes: Y1, X1); points NO_3^- (axes: Y2, X2).

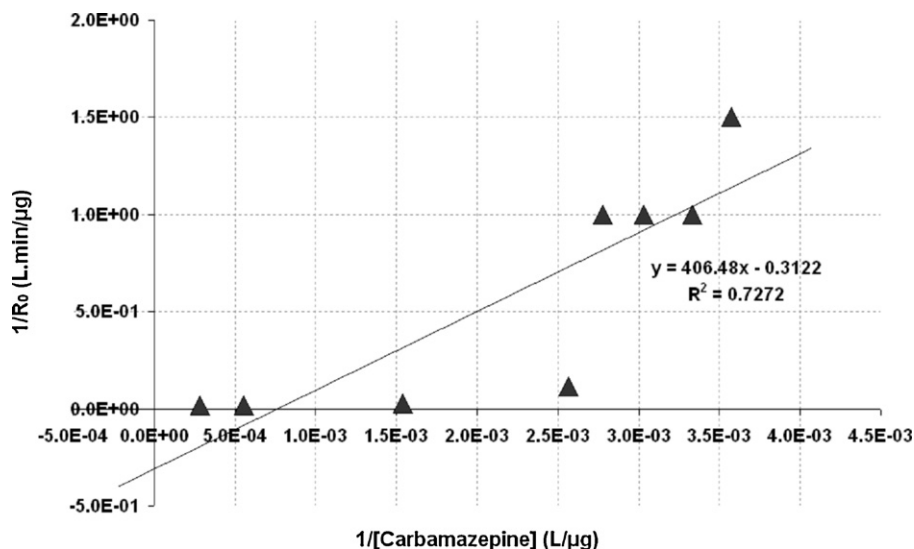


Fig. 6. Determination of dynamic Langmuir adsorption constant (K) and reaction rate constant (k_r).

treatment processes for hospital wastewater, in terms of pharmaceutical compounds, nitrification–denitrification process and phosphorus removal process. With TiO_2 based process as a pre-treatment system, it is foreseeable that the system can contribute to the overall reduction in equipment size and reaction time, as well as better risk control and management for hospital wastewater.

3.3. Photocatalytic degradation kinetics of CBZ in hospital wastewater

Kinetics studies on the photocatalytic degradation of pharmaceutical compounds in hospital wastewater are important and useful for future process design and scale-up. The accurate analysis and interpretation of experimental data with the appropriate kinetic models will enable the design and optimisation of photoreactor system with sufficient capacity and minimal non-illuminated reactor volume [13].

In this section, the Langmuir–Hinshelwood (L–H) kinetic model was used to model the photocatalytic degradation of high concentration of the CBZ compound (i.e., initial concentration: 5000 $\mu\text{g/L}$)

in synthetic hospital wastewater. The L–H model was applied to model the photocatalytic reaction rate (r) rather than a simpler zero order ($r=k$) or first order model ($r=kC$), where k is the reaction rate constant and C is the solute concentration. This is because both the zero and first order models are only applicable when the solute concentration is inadequately low, which is not the case in this study. For the L–H model, the photocatalytic reaction rate increases with reaction time until a plateau type of kinetics profile was attained (i.e., r becomes zero). The mathematical expression for L–H model is given in Eq. (3);

$$r = -\frac{dC}{dt} = k\theta_x = \frac{kKC}{1 + KC} \quad (3)$$

where the photocatalytic reaction rate (r) is proportional to the fraction of surface coverage of the TiO_2 nanofiber by organic CBZ compound (θ_x), k is the reaction rate constant, C is the concentration of organic CBZ compound in synthetic hospital wastewater and K is the dynamic Langmuir adsorption constant. In this instance, the K -value constant represents the adsorption capacity for the TiO_2 nanofiber used in this study. However, the K -value needs to be

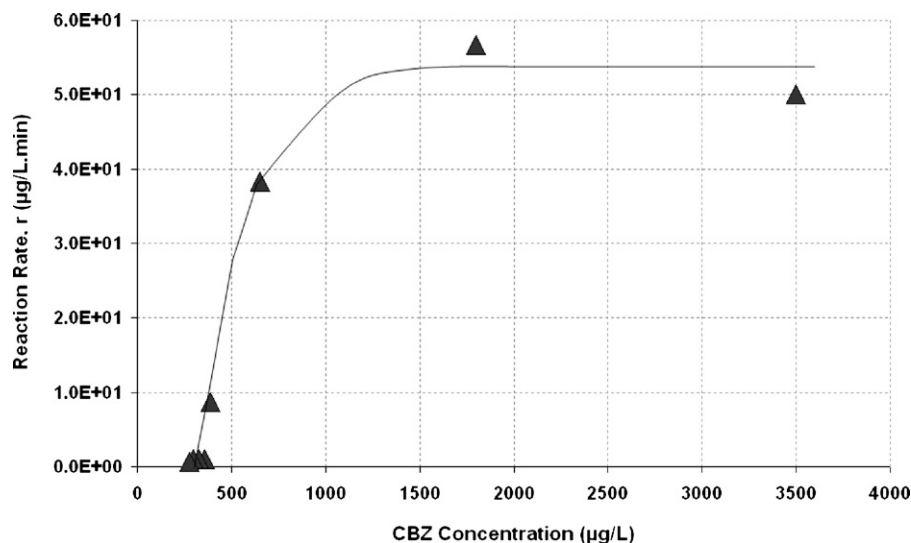


Fig. 7. Langmuir–Hinshelwood plot of reaction rate (r) versus concentration (C) for the photocatalytic degradation of 5000 $\mu\text{g/L}$.

estimated graphically using a linearised form of Eq. (4) where $1/r$ is plotted against $1/C$;

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{kKC} \quad (4)$$

Fig. 6 shows the linearised determination of the Langmuir K -value and reaction rate constant, k . From Fig. 6, it was estimated that the Langmuir K -value is $0.742 \text{ L}/\mu\text{g}$, while the reaction rate constant, k is $3.35 \times 10^{-3} \mu\text{g}/\text{L min}$. Malato et al. [32] explained that the Langmuir K -value obtained using the linearised form (using Eq. (2)) might be significantly smaller owing to the occurrence of adsorption–desorption phenomena during dark and illuminated reaction periods. However, it needs to be emphasized that the L–H model should be continually applied for this plateau kinetics profile type of heterogeneous reaction. Most studies have disregarded the L–H model and reduced Eq. (1) into a simple zero order or first order models. Such a reduction in reaction order is only valid when the $KC_0 \gg 1$ (for zero order reaction) or $KC \ll 1$ (for first order reaction) [33]. Since both conditions are inapplicable for the photocatalytic degradation of high concentrations of CBZ in synthetic hospital wastewater, the L–H model was plotted for this study as shown in Fig. 7. It can be concluded that the photodegradation profile for high concentration CBZ in synthetic hospital wastewater was perfectly represented by using the Langmuir–Hinshelwood kinetics model.

4. Conclusions

This study highlighted the feasible application of TiO_2 nanofiber based process as a pre-treatment system for the treatment of high concentrations of pharmaceutical compounds in hospital wastewater. The monitoring of degradation profiles for both CBZ and COD concentrations revealed that the proposed system was capable to treat and enhance the biodegradability of hospital wastewater. A high initial CBZ degradation rate of $48.33 \mu\text{g}/\text{L min}$ was obtained, which resulted in a concurrent 40% removal of COD concentration from the source wastewater after a 4 h reaction time. The HPSEC analysis showed that the changes in COD was accompanied by a shift in AMW for the organic fractions in synthetic hospital wastewater, where the higher fraction peaks (>10 – 100 kDa) were converted to a lower fraction ($<10 \text{ kDa}$) during photocatalytic treatment. Also, it has been demonstrated that the proposed treatment has a synergistic effect on PO_4^{3-} ions reduction, while enhancing the conversion of total nitrogen contents found in wastewater to the thermodynamically stable NO_3^- ions concentration. Finally, it was found that the photodegradation profile for high concentration CBZ in synthetic hospital wastewater was perfectly represented by using the Langmuir–Hinshelwood kinetics model. The outcomes from this study indicated that the TiO_2 based system has a high potential to be utilised as a sustainable pre-treatment system for hospital wastewater. With this TiO_2 pre-treatment system, it is foreseeable that the potential process-coupling with other advanced treatment technologies can contribute to an overall reduction in equipment size and reaction turnover time, as well as better risk control and management of hospital wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.10.067.

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