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Title: Photocatalytic Treatment of High Concentration Carbamazepine in Synthetic Hospital Wastewater

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<u>Research Highlights</u>

- This study assessed the feasible application of titanium dioxide (TiO_2) photocatalytic process as a pre-treatment system for the removal of pharmaceutical compounds from hospital wastewater.

- Results showed that the stand-alone TiO_2 pre-treatment system was capable to remove 78% of CBZ, 40% of COD concentration and 23% of PO_4 ions concentration from the influent wastewater within 4 hr reaction time.

- High performance size exclusion chromatogram demonstrated that a simultaneous biodegradability enhancement of hospital wastewater was observed, whereby an apparent shift in molecular weight from higher fraction (> 10-100 0kDa) to a lower fraction (< 10 kDa) was induced after 0.5 hr of photocatalytic treatment.

- The photodegradation profile for high concentration CBZ in synthetic hospital wastewater was perfectly fitted to the Langmuir-Hinshelwood kinetics model.

1 **Photocatalytic Treatment of High Concentration Carbamazepine in Synthetic**

2 **Hospital Wastewater**

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12

13 **Abstract**

14 Effective and sustainable treatment of hospital wastewater containing high concentration

15 of pharmaceutical compounds presents a pivotal challenge to wastewater and

16 environmental engineers worldwide. In this study, a titanium dioxide (TiO_2) nanofiber

17 based wastewater treatment process was assessed as a pre-treatment system to treat and

18 enhance the biodegradability of a representative pharmaceutical compound, 5,000 µg/L

19 of Carbamazepine (CBZ), in synthetic hospital wastewater. Results showed that the

20 stand-alone TiO_2 pre-treatment system was capable of removing 78% of CBZ, 40% of

21 COD and 23% of PO_4 concentrations from the influent wastewater within a 4 h reaction

22 time. High performance size exclusion chromatography demonstrated that a simultaneous

23 biodegradability enhancement of hospital wastewater was observed, whereby an apparent

24 shift in molecular weight from higher fraction (> 10-1000kDa) to a lower fraction (< 10

25 kDa) was induced after 0.5 h of photocatalytic treatment. Eventually, it was found that

26 the photodegradation profile for high concentration CBZ in synthetic hospital wastewater

27 was perfectly-fitted to the Langmuir-Hinshelwood kinetics model. It is anticipated that

28 this TiO_2 pre-treatment process can be further integrated with a biological wastewater

29 treatment process to deliver treated hospital effluent of better quality that can minimise

30 the associated human health and environmental risks.

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32 **Keywords:** Hospital wastewater; Carbamazepine; TiO_2; Photocatalysis; Nanofiber; Pre-Treatment

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1.0   Introduction

2   Hospital wastewater represents one of the most ubiquitous water sources in the total

3   urban water cycles, where the generated effluents are usually loaded with

4   pharmaceutical, chemical, radioactive and other toxic chemical substances, as well as

5   various pathogenic microorganisms [1 - 5]. In general, it was reported that hospitals

6   generate a nominal range of wastewater of 400-1200 Litres per bed per day

7   (L/bed/day), with an average at approximately 750 L/bed/day [5, 6]. All of these

8   pollutant loads and generated wastewater are usually discharged directly to the local

9   municipal wastewater treatment plants (WWTPs), although it has been suggested to

10   retain the wastewater on-site for further purification before discharging to local

11   WWTPs [7]. The on-site retention and pre-treatment of hospital wastewater is to

12   ensure that most of the hazardous pollutant loads are being treated in order to avoid

13   their possible contaminants diffusing into the natural ecosystem.

14

15   Some previous studies had detected the presence of pharmaceutical compounds in

16   natural ecosystems that caused contamination to groundwater, surface water and

17   drinking water sources [8-12]. Sources of these compounds usually come from human

18   excretion, where the administered pharmaceutical compounds are passed through the

19   human body unaltered (i.e. as parent compound or metabolite) into both urine and

20   faeces [8, 9]. Due to the physical and chemical properties of pharmaceutical

21   compounds, they are usually highly polar and persistent to environmental degradation

22   processes. This can result in serious bioaccumulation problems in the environment

23   that could affect aquatic and terrestrial ecosystems and also causing poor removal

24   efficiency at WWTPs. Thus, there is a need for a new generation hospital wastewater

25   treatment system that is environmentally friendly and can minimise the associated

26   human health and environmental risks in the treated hospital effluents.

27

28   Among the new generation wastewater treatment technologies, heterogeneous

29   semiconductor titanium dioxide (TiO_2) process appears to be an attractive pre-

30   treatment option to enhance the degradation of organic contaminants, as well as the

31   biodegradability of hospital wastewater for further downstream treatments. The

32   mechanisms for the formation of electron-hole pairs on the surface of TiO_2 catalysts

33   via a series of redox reactions are well-documented [13]. When the TiO_2 surfaces are

34   photon-activated, the reactive hydroxyl radicals will react, degrade and mineralise

2

1   with organic compounds without creating secondary pollution (i.e. organics are

2   completely eliminated rather than adsorbed or phase transferred) [13]. In this

3   instance, the TiO_2 based treatment system could be integrated as a pre- or post-

4   biological wastewater treatment to enhance the biotransformation process for

5   pharmaceutical compounds. Previously, we have studied the integration of TiO_2

6   treatment as a post-biological wastewater treatment train for simulated

7   pharmaceutical industrial effluent [14]. Others have also investigated on the

8   application of different TiO_2 photocatalytic treatments for the removal of

9   pharmaceuticals and endocrine disrupting compounds found in different source

10   waters [15-17].

11

12   The aim of this study was to assess the potential application of a TiO_2 photocatalytic

13   process as a pre-treatment system for the treatment of high strength pharmaceutical

14   compounds from hospital wastewater. A representative antiepileptic drug of

15   Carbamazepine (CBZ) was used as a surrogate organic indicator to measure against

16   the treatment efficiency in synthetic hospital wastewater. CBZ is usually used as

17   sedative, which can produce serious toxic effects on the liver and emopoietic system

18   [17]. Previously, Radjenovic et al. [18] identified that the CBZ by-passed the

19   secondary treatments of conventional activated sludge, hollow-fibre membrane

20   bioreactor (MBR) and flat-sheet MBR owing to the consequence of

21   conjugation/deconjugation processes that occur during treatment. Thus, CBZ is

22   regarded as appropriate to be utilised as a reaction surrogate indicator in this study

23   where an enhanced pre-treatment removal of a large proportion of CBZ found in

24   hospital wastewater would alleviate the burden of downstream wastewater treatment

25   processes. The TiO_2 nanofiber was used to enhance the photocatalytic activity and

26   catalyst recovery in the system [19, 20]. The photodegradation profiles and kinetics

27   for the removal of individual CBZ compound and overall COD concentration were

28   studied in detail. The synergistic photocatalytic action on the evolution of inorganic

29   phosphate (PO_4^{3-}) and nitrate (NO_3^-) ions during the treatment of synthetic hospital

30   wastewater was monitored. With this study, it is anticipated a preliminary feasible

31   assessment and understanding on the applicability of TiO_2 based pre-treatment system

32   can be achieved.

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1   **2.0 Experimental**

2

3   **2.1. Chemicals**

4   Anatase particles (~325 mesh from Sigma-Aldrich) were used as received. CBZ

5   (Sigma-Aldrich) was dissolved in the secondary municipal wastewater. Sodium

6   hydroxide NaOH (AR grade, Aldrich) was diluted with the addition of Milli-Q water

7   with 18.2 MΩcm resistivity.

8

9   **2.2. Preparation of TiO_2 nanofiber catalyst**

10 The TiO_2 nanofiber catalyst was synthesized through a hydrothermal reaction

11 between concentrated NaOH and TiO_2, and a post-synthesis ion exchange with HCl

12 solution [21]. Specifically, 3 g of anatase particles was mixed with 80 mL of 10 M

13 NaOH. The resultant suspensions were sonicated for 30 min and transferred into a

14 poly-tetrefluoroethylene (PTFE) container for autoclaving. The autoclave was

15 maintained at a hydrothermal temperature of 180 °C for 48 h. The precipitate (sodium

16 titanate nanofibers) was recovered, washed with distilled water (to remove excess

17 NaOH) and finally exchanged with H^+ (using a 0.1 M HCl solution) to produce TiO_2

18 nanofiber. These products were repeatedly washed with distilled water until pH ~7

19 was reached. The hydrogen titanate product was dried at 80 °C for 12 h and then

20 calcined at 700 °C for 3 h to yield TiO_2 nanofiber. The resultant TiO_2 nanofiber was

21 measured with thickness of 40 – 100 nm and length up to 30 μm long.

22

23 **2.3. Sample preparation and wastewater collection**

24 The municipal wastewater samples were collected from the Glenelg Wastewater

25 Treatment Plant (WWTP), South Australia. Following this, a concentration of 5,000

26 μg/L of CBZ was dissolved in the wastewater samples to represent the synthetic

27 hospital wastewater. Owing to the low solubility of CBZ in water, the aqueous

28 mixture was stirred for 5 min and followed by sonication for 5 min. This preparation

29 step was repeated to ensure the complete dissolution of CBZ in the synthetic hospital

30 wastewater. The final CBZ concentration in the dissolved phase was verified using

31 the high performance liquid chromatography (HPLC) analysis. If a lower than 5,000

32 μg/L of CBZ concentration was attained, additional CBZ was dissolved to ensure the

33 final CBZ concentration was as close to the targeted concentration as possible. In this

34 study, a total of wastewater samples (*N=9)* were collected. The wastewater samples

4

1 were bulked and stored in the laboratory before being mixed with 5,000 µg/L of CBZ

2 concentration, to ensure the uniformity and control experimental wastewater qualities.

3 In this instance, the use of synthetic hospital wastewater from spikes of CBZ into bulk

4 municipal wastewater samples will allow for direct comparison in photocatalytic

5 degradation efficiency of CBZ between the *N=9* experiments. Although the COD

6 concentration in the synthetic hospital wastewater samples are lowered than the real

7 hospital effluents, the use of synthetic hospital wastewaters enables a direct

8 quantification of the mixed-effect from wastewater qualities on the photocatalytic

9 degradation of CBZ. This study also forms an important basis for the future studies

10 when real hospital effluents with high COD concentration are attempted. In the

11 current study, each experimental run was monitored and analysed in terms of the

12 COD, NO_3^- and PO_4^{3-} concentrations in a time-series manner, in-line with each

13 treatment cycle.

14

15 **2.4. Setup of TiO_2 photocatalytic reactor system**

16 In this study, a batch annular slurry photoreactor (ASP) was used as a pre-treatment

17 system for the treatment of high concentration CBZ in synthetic hospital wastewater

18 [22]. The ASP is a 3-phase bubble column reactor, where the TiO_2 nanofiber was

19 dispersed in the synthetic wastewater through fine bubble aeration. The conical

20 bottom of the ASP was designed to prevent potential reaction dead zones during the

21 photocatalytic treatment. A 45-micron air sparger was used to provide homogeneous

22 fine bubble aeration for the suspension and mixing of TiO_2 nanofiber within the

23 system. An UV-A black light of 8W (NEC, Holland) was positioned annularly within

24 the quartz thimble to prevent direct contact with the reaction wastewater, while

25 allowing optimal UV transmission into the annulus reaction zone. Samples were

26 collected from the four-descended level sampling ports. Electronic probes and meters

27 for in-situ data logging of pH, dissolved oxygen and temperature (TPS, Australia)

28 were connected to the batch reactor. The experimental setup for the ASP system is

29 shown in Fig. 1.

30

31 **2.5. Analytical procedures**

32 The CBZ concentrations were analysed using a HPLC [Varian Pro-star] with a Varian

33 Microsorb-MW 100-5 C18 column (4.6 x 150 mm, 5 µm)] at a flowrate of 1.0 mL

34 min^{-1} and UV absorbance detection at 254 nm. The mobile phase was methanol 60%

5

1 plus ammonium acetate (10mM) and acetic acid (5mM). The injection volume was 20

2 μL.

3

4 High-performance size exclusion chromatography (HPSEC) and UV detection were

5 used to investigate the changes in the apparent molecular weight (AMW) profile of

6 synthetic hospital wastewater during photocatalytic treatment. The samples were

7 analysed using a coupling method reported by Liu et al. [23].

8

9 Chemical oxygen demand (COD) was analysed using an open reflux method, where 2

10 mL of the sample was added into the low range 0-150 mg L^{-1} COD reagent containing

11 potassium dichromate ($K_2Cr_2O_7$) and subsequently heated for 2 h at 150°C in a

12 digestion reactor of DRB 200 (Hach Lange GmbH, Germany). The oxidisable organic

13 compounds present will react with the $K_2Cr_2O_7$, and further reducing the dichromate

14 ion to green chromic ion. Using this method, the amount of Cr^{3+} produced was

15 measured at the wavelength of 620 nm using a spectrophotometer DR4000 (Hach

16 Lange GmbH, Germany). The color intensity was well-correlated to the COD values.

17

18 The NO_3^- ion was measured using the persulfate digestion method (Hach Lange

19 GmbH, Germany). Initially, the N contents were converted into NO_3^- through an

20 alkaline persulfate digestion reagent and further heated at 105°C for 30 min in the

21 DRB 200 reactor. Sodium metabisulfite was added after the digestion to eliminate the

22 interference of halogen oxide during measurement. Then the NO_3^- ions were reacted

23 with chromotropic acid to yield the final yellow complex that has an absorbance

24 maximum at 410 nm.

25

26 The vanadium molybdate spectrometry method was used to measure the PO_4^{3-} ions

27 concentration. In this method, the orthophosphate was reacted with molybdate in an

28 acid medium to produce a phosphomolybdate complex. A yellow

29 vanadomolybdophosphoric acid was formed when the reaction mixture was further

30 reacted with vanadium. The samples were then pre-treated with acid and heated at

31 105°C for 30 min to hydrolyse the condensed inorganic forms of phosphorous. The

32 intensity of the yellow color was used to correlate the PO_4^{3-} ions concentration in the

33 hospital wastewater sample.

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1 **3.0 Results and Discussion**

2

3 **3.1. Photocatalytic degradation of Carbamazepine**

4 Previous applications of TiO_2 photocatalysis for the degradation of CBZ in distilled

5 water showed relatively good results [24-26]. It was found however that there is a

6 lack of information on the application of TiO_2 photocatalysis process for the

7 degradation of CBZ in real wastewaters, particularly for hospital wastewater. In this

8 study, the photocatalytic treatment of a high concentration of pharmaceutical CBZ

9 (~5,000 μg/L) in synthetic hospital wastewater was carried out. Table 1 shows the

10 typical qualities values for the synthetic hospital wastewater used.

11

12 Fig. 2 shows the reduction in CBZ concentration against reaction time during the

13 photocatalytic treatment of synthetic hospital wastewater in the TiO_2 nanofiber pre-

14 treatment system. From Fig, 2, it was evidenced that the initial photo-degradation rate

15 (i.e. 1.5h) of CBZ was rapid followed by a slow attenuation rate at 1.5 to 4h of

16 reaction time. When the CBZ photo-degradation kinetics profile was fragmented into

17 two reaction rate regimes, the initial reaction rate (r_0) was found to be 48.33μg/L.min

18 while the latter reaction rate (r_1) was 2.47μg/L.min.

19

20 When the concurrent COD measurements were taken, it was observed that the extent

21 of organics mineralisation in synthetic hospital wastewater was quite rapid. A 40%

22 reduction in the overall COD concentration, from approximately 26,000 μg/L to

23 17,000 μg/L, was observed after 4h of reaction time (Fig. 3). Fig. 4 shows the result

24 from high performance size exclusion chromatography (HPSEC) to account for the

25 changes in AMW fractions during the organics mineralisation in synthetic hospital

26 wastewater. From Fig. 4, it was seen that the initial AMW peak at 100 kDa was

27 diminished after 0.5h of reaction time and a subsequent peak appeared at the AMW of

28 750 Da after 1h of reaction time. The UV_{260} absorbance intensity peaks were

29 observed to weaken from there of, at 1 h of reaction time up to 4h. The initial shift in

30 AMW peaks indicated that the photocatalytic treatment of high concentration of CBZ

31 in synthetic hospital wastewater resulted in the formation of smaller organic

32 degradation by-products. Further analysis on the HPSEC chromatograms at UV 254

33 nm (Supporting Fig. 1) verified that the disappearance of CBZ peak was accompanied

34 by the formation of new organic by-products peaks between 2.5 to 3.5 minutes. Since

7

1   these lower MW organic by-products peaks were UV-absorbing and thus, this

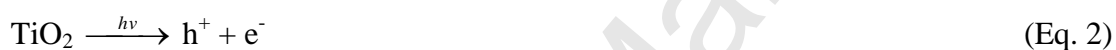2   implicated their potential aromatic properties and the need for a longer reaction time.

3

4   Thus, it can be concluded that the current application of TiO_2 based pre-treatment

5   process was effective for the removal of high concentration of CBZ compound,

6   reduction of COD concentration and the enhancement of biodegradability in hospital

7   wastewater. The resultant smaller organic degradation by-products were seen to be

8   easily degradable when the TiO_2 process is integrated with a downstream biological

9   wastewater treatment process.

10

11   **3.2. Simultaneous reaction effects on NO_3^- and PO_4^{3-} ions**

12   Apart from the presence of vast amounts of pharmaceutical residuals, the pre-

13   treatment and removal of total nitrogen and phosphorus is also an important aspect of

14   risk control and management for hospital wastewater sources. To functionalise the

15   proposed TiO_2 nanofiber based process as a pre-treatment system for hospital

16   wastewater, it is important to understand the simultaneous reaction effects on both

17   nitrate (NO_3^-) and (PO_4^{3-}) ions. Low et al. [27, 28] found that the photo-oxidation of

18   nitrogen (N) will lead to the formation of ammonium (NH_4^+), nitrate (NO_3^-) and

19   nitrite (NO_2^-) ions. Similarly, they reported that the photo-oxidation of phosphorus (P)

20   will resulted in the occurrence of phosphate (PO_4^{3-}) ions.

21

22   Fig. 5 shows the evolution of PO_4^{3-} and NO_3^- ions during the photocatalytic

23   degradation of CBZ compound in synthetic hospital wastewater. The monitoring

24   results showed that the TiO_2 nanofiber based pre-treatment process was capable to

25   reduce the overall phosphorus concentration, as well as the PO_4^{3-} ions concentration

26   by 23%, from 14.2 mg/L to 11.0 mg/L within 4 h of reaction time. Previous study by

27   Araña et al. [29] on the application of a mixture of TiO_2-activated carbon

28   photocatalysis as a tertiary treatment of wastewater also observed similar reduction in

29   PO_4^{3-} concentration. They discussed that PO_4^{3-} ions will affect the degradation of

30   organic compounds in wastewater via the (1) inhibition of TiO_2 catalytic activity, as

31   well as (2) the synergistic interaction between photon activated TiO_2 and the water

32   chemistry. The strong adsorption behaviour of PO_4^{3-} on TiO_2 surface that inhibits the

33   photocatalytic reaction has been previously examined [13]. However, the adsorption

34   of PO_4^{3-} onto TiO_2 surface is strongly affected by the pH condition where pH < pzc

8

1   (point of zero charge for TiO_2 nanofiber) will result in a potential alteration to the

2   surface chemistry and physical property. Since the pzc of TiO_2 nanofiber was 4.6 and

3   the operating pH was between 7.39-7.80, it was understood that the net PO_4^{3-}

4   adsorption impact was minimal in this study due to the electronic repulsion between

5   the two reaction entities [19]. Thus, the small gradual reduction in PO_4^{3-}

6   concentration was due to the direct synergistic interaction between hydroxyl radicals

7     $OH^{.}$ on the TiO_2 surface with equilibrium species of PO_4^{3-}, such as HPO_4^{2-}, $H_2PO_4^{-}$,

8   H_3PO_4 and others. The direct interaction of PO_4^{3-} ions with $OH^{.}$ radicals during

9   photocatalytic reaction are given Eq. 1 and 2 [29]. The redox potentials for Eq. 1 and

10   2 were -0.42 V and -0.52 V respectively, which proved the dominating reaction

11   effects on PO_4^{3-} in this study.

12

13     $PO_4^{3-} + 2H_2O + 2e^{-} \rightarrow 3OH^{-} + HPO_3^{2-}$ (Eq. 1)

14

15     $TiO_2 \xrightarrow{\ hv\ } h^{+} + e^{-}$ (Eq. 2)

16

17   In contrast, it was observed that the NO_3^{-} ions concentration increased by 24%, from

18   171.60 mg/L to 213.20 mg/L, after 4 h of reaction time. Chong et al. [13] reviewed

19   that the nitrogen-containing molecules are mineralised into NH_4^{+} and mostly NO_3^{-}.

20   Piccinini et al. [30] found that the distribution of NH_4^{+} and NO_3^{-} ions varied with

21   reaction time, initial oxidation state of nitrogen and type of initial organic substrate. It

22   was well-correlated that the formation of NO_3^{-} during photocatalytic treatment was

23   favoured by the high oxidation state of NO_3^{-} ions, which is +5 [30]. They found that

24   the NO_2^{-} ions were not detected even at a very short irradiation time, and that after 5 h

25   of reaction time, only traces of NH_4^{+} ions (4-10%) were detected and mostly NO_3^{-}

26   were formed (90-96%). Fig. 5 shows there was a build-up in NO_3^{-} ions concentration

27   over a reaction time of 4 h. However, it was found that the NO_3^{-} ions have dissimilar

28   fouling mechanism on the TiO_2 reaction. Burns et al. [31] reported that the NO_3^{-} ions

29   will UV screen the photocatalyst from photon-activation rather than inhibiting the

30   TiO_2 surface.

31

32   With the evolution kinetics of PO_4^{3-} and NO_3^{-} ions during the simultaneous photo-

33   degradation of CBZ in synthetic hospital wastewater (in Fig. 5), it is anticipated that

34   this feasibility study on TiO_2 based system as a pre-treatment of hospital wastewater

9

1 can be extrapolated for similar application in the future. These results can be utilised

2 effectively to design the potential downstream treatment processes for hospital

3 wastewater, in terms of pharmaceutical compounds, nitrification-denitrification

4 process and phosphorus removal process. With TiO_2 based process as a pre-treatment

5 system, it is foreseeable that the system can contribute to the overall reduction in

6 equipment size and reaction time, as well as better risk control and management for

7 hospital wastewater.

8

9 **3.3. Photocatalytic degradation kinetics of CBZ in hospital wastewater**

10 Kinetics studies on the photocatalytic degradation of pharmaceutical compounds in

11 hospital wastewater are important and useful for future process design and scale-up.

12 The accurate analysis and interpretation of experimental data with the appropriate

13 kinetic models will enable the design and optimisation of photoreactor system with

14 sufficient capacity and minimal non-illuminated reactor volume [13].

15

16 In this section, the Langmuir-Hinshelwood (L-H) kinetic model was used to model

17 the photocatalytic degradation of high concentration of the CBZ compound (i.e. initial

18 concentration: 5,000 µg/L) in synthetic hospital wastewater. The L-H model was

19 applied to model the photocatalytic reaction rate (r) rather than a simpler zero order (*r*

20 *= k*) or first order model (*r = kC*), where *k* is the reaction rate constant and *C* is the

21 solute concentration. This is because both the zero and first order models are only

22 applicable when the solute concentration is inadequately low, which is not the case in

23 this study. For the L-H model, the photocatalytic reaction rate increases with reaction

24 time until a plateau type of kinetics profile was attained (i.e. *r* becomes zero). The

25 mathematical expression for L-H model is given in Eq. 3;

26

27 $$r = -\frac{dC}{dt} = k\theta_X = \frac{kKC}{1+KC}$$ (Eq. 3)

28

29 where the photocatalytic reaction rate (*r*) is proportional to the fraction of surface

30 coverage of the TiO_2 nanofiber by organic CBZ compound (θ_X), *k* is the reaction rate

31 constant, C is the concentration of organic CBZ compound in synthetic hospital

32 wastewater and *K* is the dynamic Langmuir adsorption constant. In this instance, the

33 *K*-value constant represents the adsorption capacity for the TiO_2 nanofiber used in

10

1   this study. However, the *K*-value needs to be estimated graphically using a linearised

2   form of Eq. 4 where $1/r$ is plotted against $1/C$;

3

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

5

6   Fig. 6 shows the linearised determination of the Langmuir *K*-value and reaction rate

7   constant, *k*. From Fig. 6, it was estimated that the Langmuir *K*-value is 0.742 L/μg,

8   while the reaction rate constant, *k* is 3.35 x 10^{-3} μg/L.min. Malato et al. [32] explained

9   that the Langmuir *K*-value obtained using the linearised form (using Eq. 2) might be

10   significantly smaller owing to the occurrence of adsorption-desorption phenomena

11   during dark and illuminated reaction periods. However, it needs to be emphasized that

12   the L-H model should be continually applied for this plateau kinetics profile type of

13   heterogeneous reaction. Most studies have disregarded the L-H model and reduced

14   the Eq. 1 into a simple zero order or first order models. Such a reduction in reaction

15   order is only valid when the $KC_O \gg 1$ (for zero order reaction) or $KC \ll 1$ (for first

16   order reaction) [33]. Since both conditions are inapplicable for the photocatalytic

17   degradation of high concentrations of CBZ in synthetic hospital wastewater, the L-H

18   model was plotted for this study as shown in Fig. 7. It can be concluded that the

19   photodegradation profile for high concentration CBZ in synthetic hospital wastewater

20   was perfectly represented by using the Langmuir-Hinshelwood kinetics model.

21

22   **4.0 Conclusions**

23   This study highlighted the feasible application of TiO_2 nanofiber based process as a

24   pre-treatment system for the treatment of high concentrations of pharmaceutical

25   compounds in hospital wastewater. The monitoring of degradation profiles for both

26   CBZ and COD concentrations revealed that the proposed system was capable to treat

27   and enhance the biodegradability of hospital wastewater. A high initial CBZ

28   degradation rate of 48.33μg/L.min was obtained, which resulted in a concurrent 40%

29   removal of COD concentration from the source wastewater after a 4 h reaction time.

30   The HPSEC analysis showed that the changes in COD was accompanied by a shift in

31   AMW for the organic fractions in synthetic hospital wastewater, where the higher

32   fraction peaks (> 10-100 0kDa) were converted to a lower fraction (< 10 kDa) during

33   photocatalytic treatment. Also, it has been demonstrated that the proposed treatment

11

1 has a synergistic effect on PO_4^{3-} ions reduction, while enhancing the conversion of

2 total nitrogen contents found in wastewater to the thermodynamically stable NO_3^-

3 ions concentration. Finally, it was found that the photodegradation profile for high

4 concentration CBZ in synthetic hospital wastewater was perfectly represented by

5 using the Langmuir-Hinshelwood kinetics model. The outcomes from this study

6 indicated that the TiO_2 based system has a high potential to be utilised as a

7 sustainable pre-treatment system for hospital wastewater. With this TiO_2 pre-

8 treatment system, it is foreseeable that the potential process-coupling with other

9 advanced treatment technologies can contribute to an overall reduction in equipment

10 size and reaction turnover time, as well as better risk control and management of

11 hospital wastewater.

12

13 **Acknowledgement**

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1   **TABLE**

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3   **Table 1**: The average wastewater quality for the raw synthetic hospital influent and

4   the primary hospital treated effluent.

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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

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1   **<u>Figures</u>**

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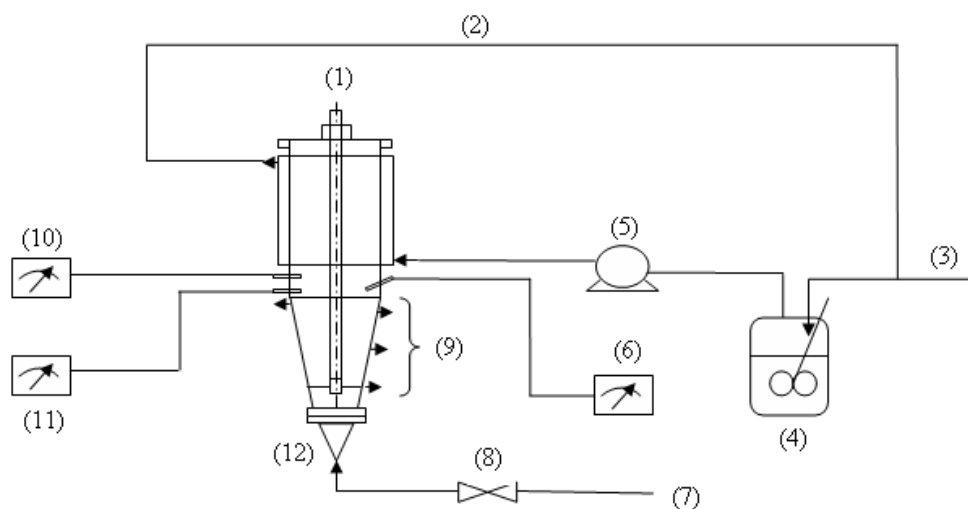
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5   **Fig. 1:** Experimental set-up for the annular slurry photoreactor system: (1) UV light, (2) Recirculation

6   water line, (3) Fresh cool water line, (4) Cooling water vessel, (5) Cooling water pump, (6)Temperature

7   meter, (7) Compressed air supply line, (8) Compressed air regulation valve, (9) Sampling ports, (10)pH

8   meter, (11) Dissolved oxygen meter, (12) Photoreactor.

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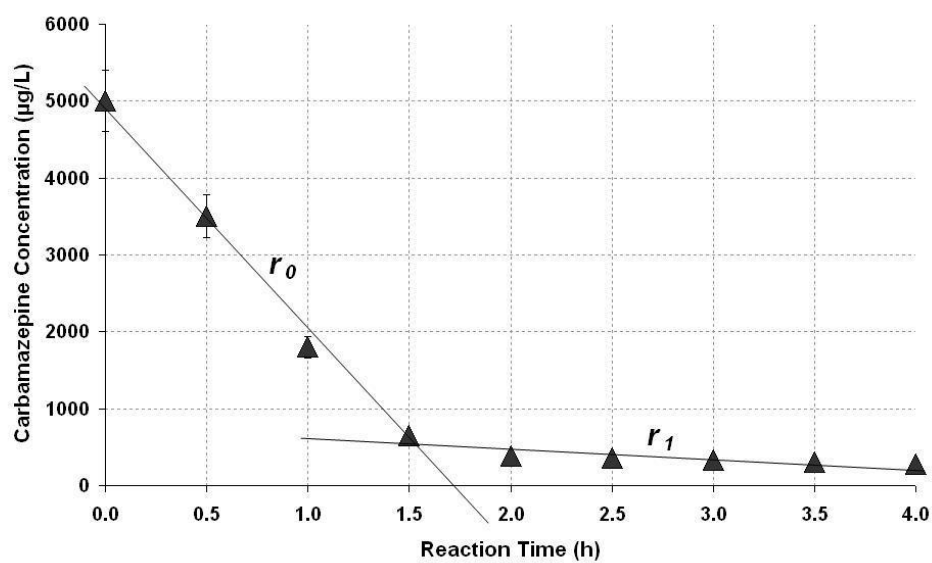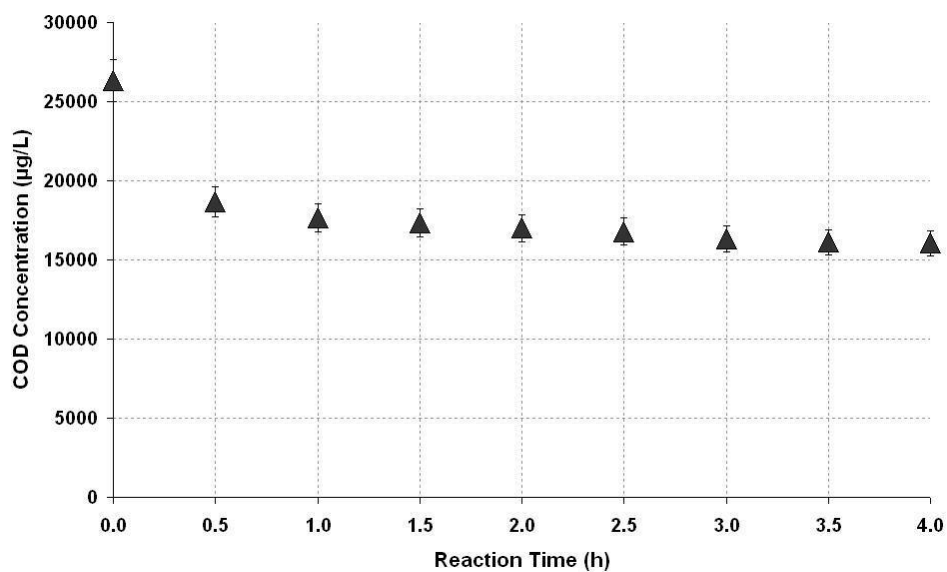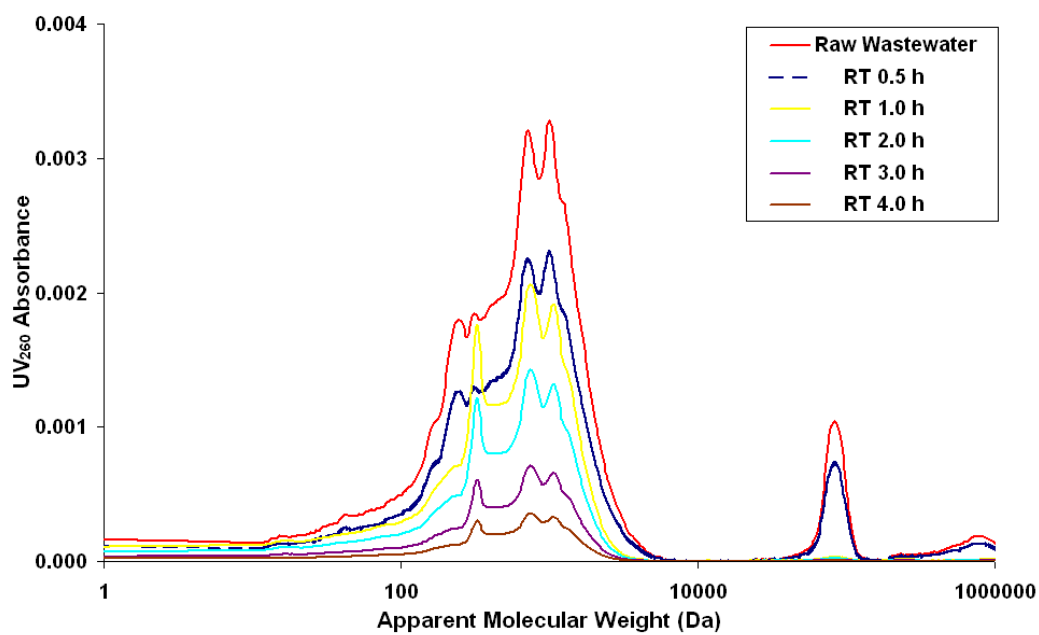
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2   **Fig. 2:** Photocatalytic treatment of high concentration of CBZ in synthetic hospital wastewater. Initial
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Fig. 3: COD concentration profile during the photocatalytic treatment of high concentration of CBZ in synthetic hospital wastewater. Initial CBZ concentration: 5,000 μg/L.

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2 **Fig.4:** High performance size exclusion chromatogram on the photocatalytic degradation of synthetic

3 hospital wastewater at different reaction times.

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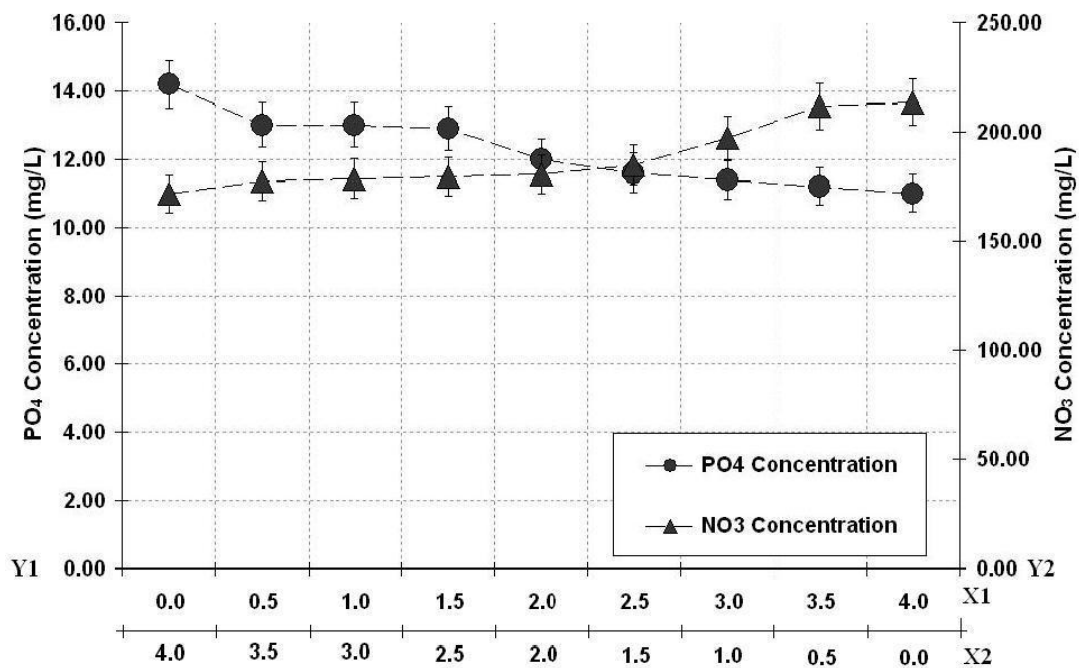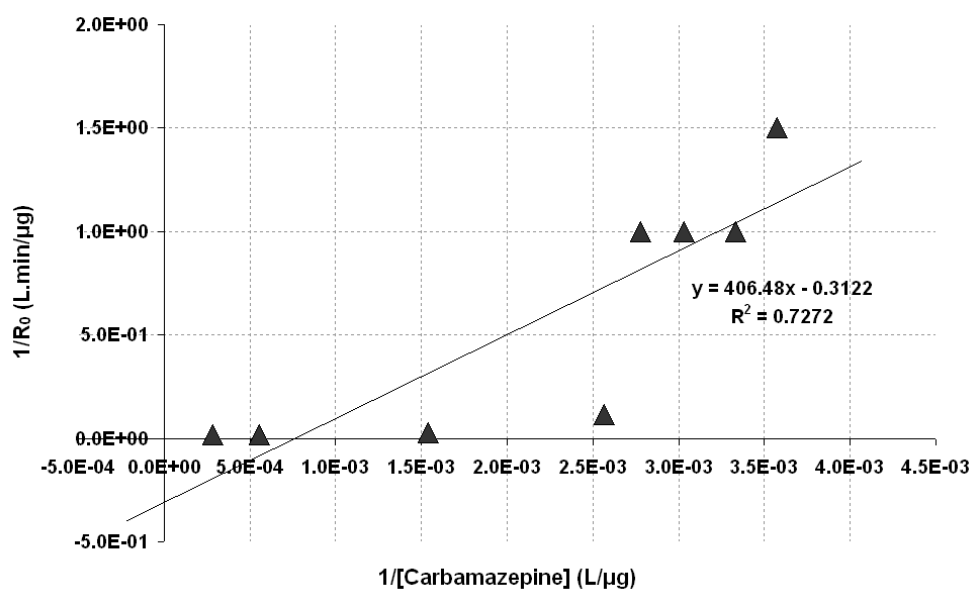21

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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).

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3 **Fig. 6:** Determination of dynamic Langmuir adsorption constant (K) and reaction rate constant (k_r).
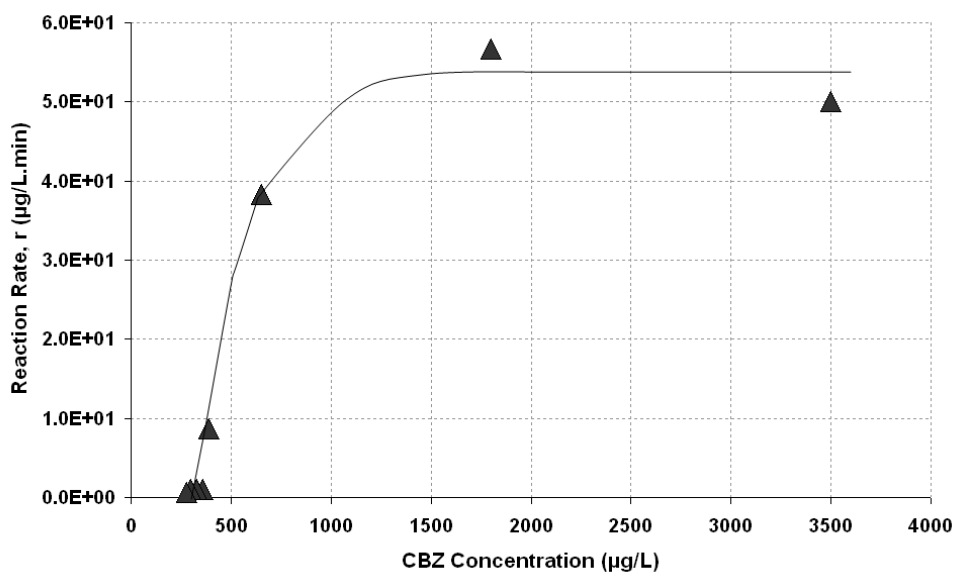
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Fig. 7: Langmuir-Hinshelwood plot of reaction rate (r) versus concentration (C) for the photocatalytic
degradation of 5,000 μg/L.

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