UV/TiO$_2$ photocatalytic oxidation of recalcitrant organic matter: effect of salinity and pH

Shobha Muthukumaran, Lili Song, Bo Zhu, Darli Myat, Jin-Yuan Chen, Stephen Gray and Mikel Duke

ABSTRACT

Photocatalytic oxidation processes have interest for water treatment since these processes can remove recalcitrant organic compounds and operate at mild conditions of temperature and pressure. However, performance under saline conditions present in many water resources is not well known. This study aims to explore the basic effects of photocatalysis on the removal of organic matter in the presence of salt. A laboratory-scale photocatalytic reactor system, employing ultraviolet (UV)/ titanium dioxide (TiO$_2$) photocatalysis was evaluated for its ability to remove the humic acid (HA) from saline water. The particle size and zeta potential of TiO$_2$ under different conditions including solution pH and sodium chloride (NaCl) concentrations were characterized. The overall degradation of organics over the NaCl concentration range of 500–2,000 mg/L was found to be 80% of the non-saline equivalent after 180 min of the treatment. The results demonstrated that the adsorption of HA onto the TiO$_2$ particles was dependent on both the pH and salinity due to electrostatic interaction and highly unstable agglomerated dispersion. This result supports UV/TiO$_2$ as a viable means to remove organic compounds, but the presence of salt in waters to be treated will influence the performance of the photocatalytic oxidation process.

Key words | humic acid, particle size, photocatalytic oxidation, salt concentration, zeta potential

Shobha Muthukumaran (corresponding author)
College of Engineering and Science,
Victoria University,
PO Box 14428,
Melbourne, VIC 8001,
Australia
E-mail: Shobha.Muthukumaran@vu.edu.au

Lili Song
Jin-Yuan Chen
College of Biological and Environmental
    Engineering,
Zhejiang University of Technology,
Hangzhou, 310032,
China

Shobha Muthukumaran
Bo Zhu
Darli Myat
Stephen Gray
Mikel Duke
Institute for Sustainability and Innovation,
Victoria University,
PO Box 14428,
Melbourne, VIC 8001,
Australia

INTRODUCTION

The presence of humic acid (HA) has received attention in water treatment research as it forms disinfection by-products (DBPs) as a result of chlorination procedures. In addition, HAs are considered as a refractory organic pollutant due to their non-biodegradability, water-soluble formation and a wide range of molecular weights and sizes (Li *et al*. 2002). Recently, advanced oxidation processes have received special attention for the treatment of polluted water due to their efficiency in mineralizing a great variety of organic pollutants, including recalcitrant compounds, through oxidation by generated hydroxyl radicals (OH•) (Al-Rasheed & Cardin 2003). In particular semiconductor photocatalytic processes such as UV/TiO$_2$ have shown potential as an environmentally friendly and sustainable treatment technology due to their non-toxic and high photocatalytic activity. The key photochemical phenomenon in the UV/TiO$_2$ process is the creation of an electron/hole pair through the absorption of light with the energy equal to or greater than the band gap of TiO$_2$ (Ebg = 3.2 eV). Energized electrons and holes can

be available for redox reactions with electron acceptor or electron donor species adsorbed on the semiconductor surface (Fiona *et al*. 2002). In aqueous solutions, highly reactive oxygen species such as OH•, H$_2$O$_2$ and O$_2$•$^-$ are formed and may lead to complete degradation of organic compounds to CO$_2$ and to the formation of low-molecular-weight carboxylic acids (Xue *et al*. 2011). Details of the reaction mechanisms have been described elsewhere in the literature (Hoffmann *et al*. 1995; Bertelli & Selli 2006). Several studies found that Degussa P25 catalyst is the most active form (hybrid mixture of rutile and anatase crystal structures) among the various types commercially available (Sakthivel *et al*. 2000; Yamazaki *et al*. 2001) and gave better degradation efficiencies, although in a few cases pure anatase-based forms of TiO$_2$ have also been reported to be the most efficient (Chen & Ray 1998; Gogate & Pandit 2004). Numerous organic contaminants including herbicides, pesticides, and halophenols have been reported to be efficiently removed by mineralizing from polluted water using this method (Hoffmann *et al*. 1995;

Bertelli & Selli 2006). Recently, TiO$_2$-based photocatalysis has been reported to effectively remove HA (Tay *et al.* 2001; Fang *et al.* 2005) and natural organic matter (Fu *et al.* 2006; Le-Clech *et al.* 2006). However, as many waters in need of treatment contain salts, exploration of the influence of salinity is important.

In work by Al-Rasheed & Cardin (2003) the effectiveness of TiO$_2$ photocatalytic oxidation of HA in artificial seawater (ASW) and natural seawater (NSW) was investigated, and it was found that HA in NSW was more easily degraded than in ASW when examined under identical conditions. Both carbonate and bicarbonate have higher concentrations in ASW and act as electron scavengers. Therefore, the higher concentrations of carbonate and bicarbonate may be responsible for lowering the organic degradation rate in ASW, although the ionic strength of the ASW employed in their work was also greater than that of NSW (Al-Rasheed & Cardin 2003). While the work of Al-Rasheed *et al.* focused on seawater, there is currently no known work exploring the effect of water salinity on photodegradation. In particular, there is no detailed study on saline wastewater that has salinity of 500–2,000 mg/L using photocatalytic oxidation processes. Such a study would be useful in providing the understanding needed for treatment of saline wastewaters.

As HA is a common organic in water systems, an indicative study of the role of salinity on photocatalytic removal of HA for water treatment would be highly informative. The aim of this study was, therefore, to examine the applicability of the UV/TiO$_2$ photocatalytic oxidation for the removal of refractory organic pollutants from saline waters modelled by HA. The model salt used was NaCl due to its abundance in most water systems. The adsorption of organic compounds onto the TiO$_2$ surface, transformations and removal efficiency during the reaction were examined by measuring changes in the particle size and zeta potential of TiO$_2$ over time with the variations in the solution pH and salinity.

METHODS

Materials

Titanium dioxide P25 from Degussa (80% anatase, 20% rutile, 99.8% purity, average particle size 30 nm and specific surface area of 50 m^2/g) was used as the photocatalyst. The TiO$_2$ catalyst was obtained as a dry powder and stored at room temperature. Before each set of experiments, the desired amount of TiO$_2$ powder was weighed and mixed

with a small quantity of deionized water to prepare TiO$_2$ slurry.

HA stock solution was prepared by mixing 6 g of HA powder (Fluka AG, Chemische Fabrik. CH-9470 Buchs, Switzerland) in 2 L deionized water, stirred over a period of 2 days with a magnetic stirrer. The stock solution was filtered through a 0.45 μm membrane filter (Advantec, Japan) to remove all suspended solids and stored in a sterilized glass bottle at 4 °C before use. The concentration of the HA stock solution was 200 mg/L. The feed solution (HA$_0$) containing 20 mg/L HA was prepared by appropriate dilution of stock solution, and resulted in an initial total organic carbon (TOC) concentration of 7 mg/L. This is the same TOC level of treated saline recycled wastewater from one of Melbourne Australia's wastewater treatment plants. Analytical grade chemicals were used without further purification in all experiments. Deionized water was used throughout the experiment.

Apparatus and experimental procedures

A schematic diagram of the photocatalytic reactor used in this work is shown in Figure 1. The photocatalytic oxidation experiments were carried out on a laboratory-scale recirculating photocatalytic system. This system comprised four parts, namely the photocatalytic flow reactor, the UV panel, the circulating pump and the feed tank. The photocatalytic reactor with a volume of 2 L was made of stainless steel with baffle plates, such that the water flowed in a zig-zag manner through five open channels. The total illuminated surface area of the reactor was 713 cm^2. A peristaltic pump (Masterflex 7592–45, Cole-Parmer, USA) was used to circulate the solution at a flow rate of 0.5 L/min.

The concentration of HA feed solution (HA$_0$) was 20 mg/L for all the experiments. Before each photocatalytic treatment, TiO$_2$ slurry and HA were mixed by a magnetic
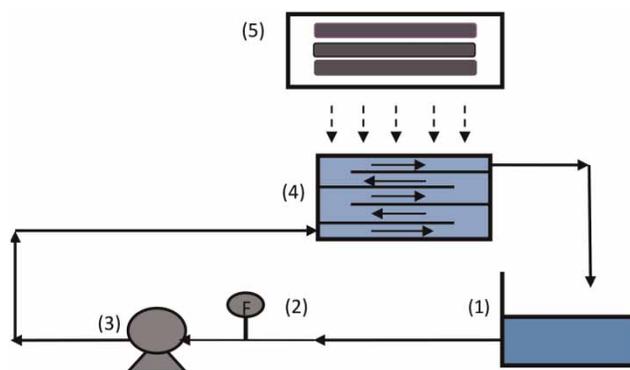

Figure 1 | Schematic diagram of the UV/TiO$_2$ photocatalytic reactor: (1) feed tank; (2) flowmeter; (3) peristaltic pump; (4) photoreactor; (5) UV lamp.

stirrer in the dark for 15 min in order to obtain equilibrium adsorption. The solution (2 L) to be treated was pumped continuously from the feed tank into the reactor at a flow rate of 0.5 L/min and was irradiated by UV. The UV panel consisted of six 18 W UV-A lamps (NEC Blacklight Lamp). UV-A intensity was measured by a UV irradiance meter with a range of 320–400 nm (UV-A, Photoelectric Instrument Factory of Beijing Normal University, China). All the experiments were carried out at room temperature, which was 21°C. Samples were withdrawn from the outlet of the photoreactor for analysis.

Analyses

TOC measurements

Over the duration of the experiment, samples were collected at designated time intervals and filtered through 0.45 μm filters. The TOC concentration of the samples was measured using a Shimadzu TOC V-CSH analyser. Control experiments with UV irradiation and without TiO₂ catalyst showed that (<22%) degradation occurred as measured by TOC.

Zeta potential and particle size analysis

The zeta potential and average particle size of the TiO₂ particles were determined using a Malvern Zetasizer (Malvern Instruments Nano series). The zeta potential of the TiO₂ particles was measured from electrophoretic mobility measurements of the particles. During the experiment, samples of suspension containing the TiO₂ particles and HA solutions were collected regularly in order to analyse the surface charge of the TiO₂ particles. Control experiments were also conducted by irradiating TiO₂ suspension in the absence of HA.

RESULTS AND DISCUSSION

Effect of NaCl concentration

Figure 2(a) shows the TOC concentrations over time at various NaCl concentrations. The first point at 15 min was measured without UV (dark period), while the remaining points were measured in the presence of UV. TOC removal
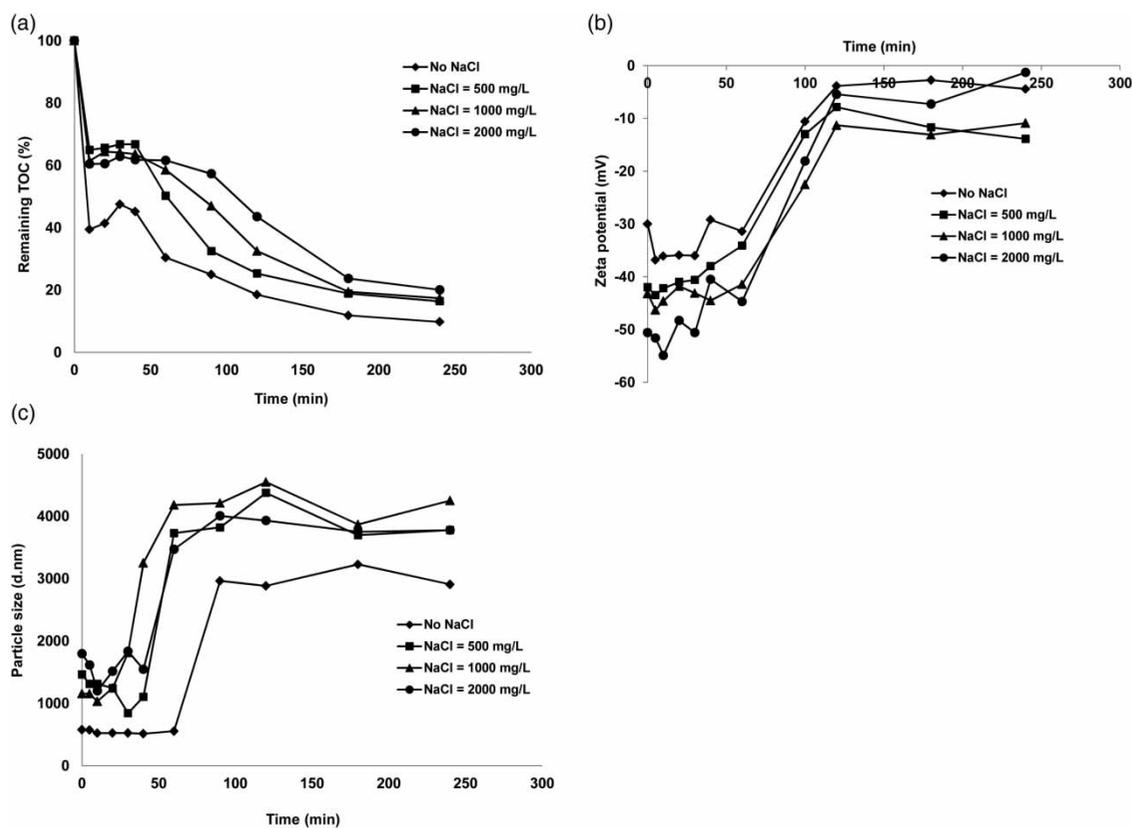

Figure 2 | (a) The remaining TOC; (b) zeta potential; and (c) particle size as a function of irradiation time at different NaCl concentrations (conditions: HA₀ = 20 mg/L; TiO₂ concentration = 0.5 g/L; UV intensity = 3.4 mW/cm²; pH: 7.5).

(Figure 2(a)) in the absence of NaCl was higher (>90%) than in the presence of NaCl, which was about 80–83% after 240 min of reaction. Further it can be noted that after 60 min of reaction, the TOC removal was slower in high concentrations of NaCl (2,000 mg/L) than in low NaCl concentration (500 mg/L) and, after 240 min of reaction, TOC removal was 80% across the range of NaCl concentrations tested in this study.

Normally, the presence of ions may affect the degradation rate via adsorption of the pollutants, reaction with hydroxyl radicals and adsorption of UV light. A study conducted using industrial effluents containing different types of salts which were in ionized form examined the effects of various anions and cations on degradation efficiency (Bertelli & Selli 2006). For example, anions such as CO_3^- and HCO_3^- act as radical scavengers and also affect the adsorption process, while Cl^- affects adsorption and also absorbs UV light, leading to strong detrimental effects on the degradation process compared to other anions such as sulfate and nitrate (Bertelli & Selli 2006). Furthermore both anions such as Cl^-, SO_4^{2-}, HCO_3^-, NO_3^- and cations such as Na^+, Ca^{2+} and Mg^{2+} present in the waters can be bound to TiO$_2$ particles or very close to their surface, so that they can have substantial effects on the interfacial behaviour of the TiO$_2$ particles (Xi & Geissen 2002).

Our results also show that the adsorption was affected by the presence of NaCl. Generally, TiO$_2$ formed larger diameter clusters in the presence of organic matter. The TiO$_2$ cluster diameter varied as a function of its zeta potential and thus as a function of pH and electrolyte concentration. This experiment was conducted at pH 7.5, which yields either close to zero or slightly negatively charged catalyst surface. In the presence of chloride ions, the TiO$_2$ particles in the slurry tend to agglomerate; therefore, the surface area available for adsorption of HA and the photon absorption were decreased.

Figures 2(b) and (c) show the zeta potential and size of the particles measured during reaction. There was a good correlation between the zeta potential and particles size over the reaction period. Increasing the ionic strength of a suspension would be expected to decrease the magnitude of the zeta potential. It can be seen for this study that the magnitude of the zeta potential was greater after the addition of three different NaCl concentrations during the initial period. This may be because more Cl ions were adsorbed onto the surface, making it more negatively charged. The adsorption of HA on the TiO$_2$ surface with three different NaCl concentrations was similar and the particle sizes remained stable. After 30 min of reaction, the

degradation of HA decreased as chloride ion concentrations increased because the photodegradation phenomenon was more significant than adsorption. According to Wang *et al.* (1999) the influence of Cl^- is dependent on the pH of the suspension. When pH is greater than the isoelectric point of TiO$_2$, chloride ion was found to have no effect on the initial rate of disappearance of 2-chlorobiphenyl, as the chloride concentration near the TiO$_2$ surface is lower than that in the bulk of the solution. When the pH is lower than the isoelectric point of TiO$_2$, the surface is positively charged and Cl^- was strongly adsorbed on the TiO$_2$ surface and reduced the photodegradation (Wang *et al.* 1999). It can be postulated that, firstly, the chloride ions reduce the rate of oxidation by scavenging oxidizing radical species and also blocking the chain reaction for hydroxyl free radicals. This lowers the concentration of HO• radicals, and in turn reduces the degradation efficiency (Yang *et al.* 2005). According to Galindo *et al.* (2001), the inorganic radical anion shows a much lower reactivity than HO• radicals and does not take part in organic degradation. Therefore, higher concentrations of chloride ions lead to lower concentrations of HO• radicals and greater inhibition is obtained. At low chloride concentration, the slowdown was also caused by the combination of Cl^- with radicals as the degradation of HA was partly by HO• radicals (Abdullah *et al.* 1990; Yang *et al.* 2005).

Secondly, the average hydrodynamic diameter of the TiO$_2$ particle increases in the presence of NaCl concentrations, compared to the absence of NaCl. Figure 2(c) shows that in the first 30 min, particle size of TiO$_2$ in the presence of NaCl was much larger (i.e. around 1,000 nm) than TiO$_2$ in the absence of NaCl, which was about 500 nm. An increase in NaCl concentration reduces electrostatic repulsive force between particles, and the attractive force becomes more dominant, resulting in an unstable highly agglomerated dispersion. Under these conditions, the average hydrodynamic size was approximately 4,000 nm after 60 min of reaction. It appears likely that the reduced TOC removal observed during the early stages of oxidation (see Figure 2(a)) was not only due to radical scavenging, but also due to an increase in TiO$_2$ particle size for the three added NaCl concentrations, resulting in decreased adsorption surface area and decreased exposure to UV radiation (shielding in agglomerated particles).

The effects of pH on the electrostatic properties of the TiO$_2$ particles

Figure 3 shows the relationship between the TOC removal, the change in the zeta potential of TiO$_2$, and the average
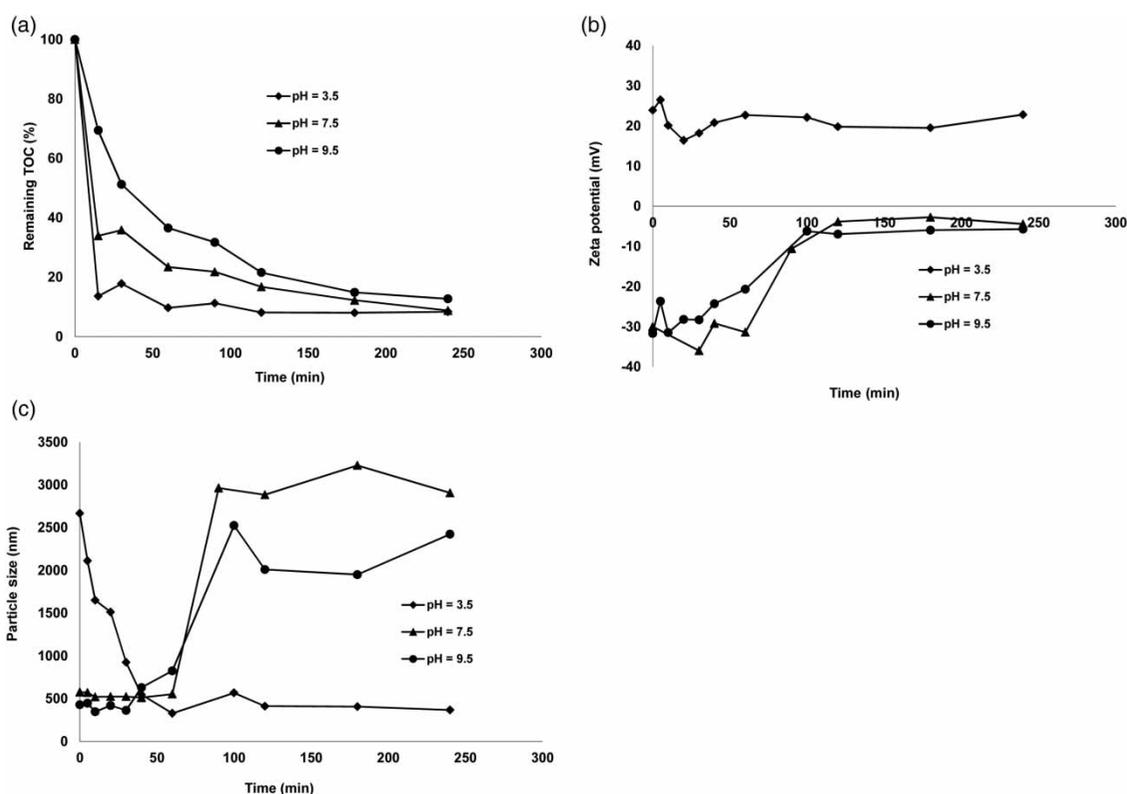
Figure 3 | The relation between (a) the remaining TOC; (b) zeta potential; and (c) particle size at different pH (condition: HA$_0$ = 20 mg/L; TiO$_2$ concentration = 1 g/L; UV intensity = 3.4 mW/cm^2).

particle size of the TiO$_2$ during the degradation of HA at different pH (3.5, 7.5 and 9.5). A simple electrostatic surface charge model can account for the effect of pH (Xue *et al.* 2011). HA has a negative charge in aqueous solutions because of the existence of many acidic functional groups (Bekbolet *et al.* 2002; Cho & Choi 2002). In this study, the measured isoelectric point for TiO$_2$ (P25 Degussa) was approximately 6.3, which is consistent with isoelectric point measurements elsewhere (Jiang *et al.* 2009). At pH < 6.3 (pH 3.5 in this work), the positively charged TiO$_2$–H$^+$ offers a suitable surface for negatively charged HA molecule adsorption, but at pH > 6.3, the surface charge of TiO$_2$ becomes close to zero or negatively charged TiO$_2$(OH)$^-$, which provides an unfavorable condition for the HA molecule to approach, because the negative–negative electrostatic repulsion increased.

According to Mandzy *et al.* (2005) the isoelectric point of TiO$_2$ P25 (Degussa, anatase form) particles was pH 5.5 and the zeta potential of the Degussa particles was +28, +10, and −42 mV for pH values of 3.5, 5.5, and 7.5, respectively. In this study, the zeta potential of the TiO$_2$ P25 (Degussa, anatase and rutile forms) particles was +38, −11 and −16 mV for pH 3.3, 7.5 and 9.5, respectively. At pH 3.5,

surface charge of the TiO$_2$ particle was highly positive and, with the addition of HA, the surface charge of the TiO$_2$ decreased to +24 mV (Figure 3(b)) and the corresponding TOC decreased, indicating the absorption of HAs onto the photocatalyst surface (Figure 3(a)). Then the following positive shift in the zeta potential can be explained by release of intermediate oxidation products from the TiO$_2$ surface; so the TOC also increased. As reported by Huang *et al.* (2008), some of these intermediate products are more hydrophilic than HA as a result of photocatalytic oxidation reaction and do not adsorb as strongly on the TiO$_2$ surface, thus dissolving back into the bulk water. Finally the zeta potential and TOC reached the plateau region after 120 min of the reaction. Similarly, at pH 7.5 and 9.5 surface charge of the TiO$_2$ particle was −30 and −32 mV with the addition of HA; the adsorption of HA on the TiO$_2$ surface was taking place, resulting in shifting zeta potential values.

It can be also seen from Figure 3(a) that during the initial period, higher adsorption of HA (>80%) is taking place at lower pH (at 3.5) compared with higher pH (at 7.5 and 9.5). This is because at pH 7.5 and 9.5, surface charge of the TiO$_2$ particle is negative but still attributed to the minimal adsorption of HA onto TiO$_2$ (Figure 3(a)).

According to Yang & Lee (2006), HA has several functional groups such as carboxyl and phenol, which also have different acid dissociation constants and these groups might be involved in the adsorption of HA onto the TiO$_2$ surface even at higher pH. However, the rate of photocatalytic reaction was faster at higher pH compared with lower pH. The apparent first-order rate constant k was calculated for the photocatalytic reaction and it was found that the k values increased rapidly with pH (from 0.0066 to 0.0086 m^{-1} for the pH 3.5 to 9.5). This indicates that at high pH, OH• was more easily generated since more OH$^-$ ions were available on the TiO$_2$ surface; thus eventually the degradation rate was enhanced. On the other hand at pH 3.5, almost all added HAs were adsorbed on the TiO$_2$ surface, reducing the photon absorption and thus lowering the photodegradation rate at the later stage of the reaction. However the results in Figure 3(a) indicated that the overall TOC removal increased when the pH decreased, and moreover complete TOC removal was achieved at lower pH.

The formation and disappearance of adsorbed intermediate products generated from photocatalytic degradation of HAs were followed and compared with the recorded particle size of TiO$_2$. In general, the change in pH can change the dispersion state by altering the zeta potential (surface charge). For instance, bringing the pH close to the isoelectric point of the nanoparticles will enhance agglomeration and results in larger hydrodynamic sizes of the particles (Jiang *et al.* 2009). As can be seen in Figures 3(b) and (c), a relationship exists between the zeta potential and average particle size. At pH 3.5, the particle size of TiO$_2$ was higher during the initial stage due to the adsorption of HAs. Then the particle size of TiO$_2$ decreased by release of intermediate oxidation products from the TiO$_2$ surface and, at the same time, the zeta potential of TiO$_2$ also increased. During the later stage of the experiment, mineralization of HAs makes the particle size and zeta potential of TiO$_2$ reach a plateau region. On the other hand at pH 7.5 and 9.5 the particle size of the TiO$_2$ was smaller during the initial stage showing lower adsorption of HAs and increases by adsorption of intermediate products; at the same time the zeta potential of TiO$_2$ is also increasing. During the later stage of the experiment, the particle size and zeta potential of TiO$_2$ reached a plateau region because of the mineralization of HA.

CONCLUSIONS

The photocatalytic oxidation of HA in TiO$_2$ suspensions has been studied under different experimental conditions in a batch photoreactor. The results demonstrated that the adsorption of HA was significantly reduced in the presence of NaCl concentrations, resulting in an unstable highly agglomerated dispersion. This is because, in the presence of NaCl, the attractive force between particles became dominant over the repulsive force. The energy barrier to prevent agglomeration decreased with increasing solution ionic strength; so the size distributions shift toward larger size ranges with increasing ionic strength. Also, Na$^+$ ions (cations) in the solution can be bound to TiO$_2$ particles or very close to the particles' surface and can have substantial effects on the interfacial behaviour of TiO$_2$ particles, resulting in reduced available surface area for HA adsorption. However, after 240 min of reaction, 80% TOC removal was reached across the range of NaCl concentrations tested in this study. The results show that the degradation rate decreased with increasing NaCl concentration. This result is important when photocatalysis was used for treating highly saline water. The adsorption of HA was significantly enhanced at low pH and photocatalytic oxidation considerably enhanced at high pH, as the pH can affect the surface characteristics of TiO$_2$, suggesting the importance of hydroxyl radicals in the photocatalytic oxidation of HA. Zeta potential measurement can be used as a surrogate tool for monitoring the adsorption and photocatalytic reactions of organic compounds on the TiO$_2$ surface, although the TiO$_2$ is still in suspension. There was a correlation between the zeta potential, TOC removal and average particle size. Future study will be extended to investigate the use of UV/TiO$_2$ photocatalytic oxidation system for the treatment of recycled water, which has salinity of 1,200 mg/L.

REFERENCES

Abdullah, M., Low, G. K. C. & Matthews, R. W. 1990 Effects of common inorganic anions on rates of photocatalytic oxidation of organic carbon over illuminated titanium dioxide. *J. Phys. Chem.* **94**, 6820–6825.

Al-Rasheed, R. & Cardin, D. J. 2003 Photocatalytic degradation of humic acid in saline waters: Part 2. Effects of various photocatalytic materials. *Appl. Catal. A.* **246**, 39–48.

Bekbolet, M., Suphandag, A. S. & Uyguner, C. S. 2002 An investigation of the photocatalytic efficiencies of TiO$_2$ powders on the decolourisation of humic acids. *J. Photochem. Photobiol. A.* **148**, 121–128.

Bertelli, M. & Selli, E. 2006 Reaction paths and efficiency of photocatalysis on TiO$_2$ and of H$_2$O$_2$ photolysis in the degradation of 2-chlorophenol. *J. Hazard. Mater.* **138**, 46–52.

Chen, D. & Ray, A. K. 1998 Photodegradation kinetics of 4-nitrophenol in TiO$_2$ suspension. *Water Res.* **32** (11), 3223–3234.

Cho, Y. & Choi, W. 2002 Visible light-induced reactions of humic acids on TiO$_2$. *J. Photochem. Photobiol. A J.* **148**, 129–135.

Fang, H., Sun, D. D., Wu, M., Phay, W. & Tay, J. H. 2005 Removal of humic acid foulant from ultrafiltration membrane surface using photocatalytic oxidation process. *Water Sci. Technol.* **51** (6–7), 373–380.

Fiona, L. P., Brian, R. E. & Heather, M. C. 2002 The effect of operational parameters on the photocatalytic degradation of humic acid. *J. Photochem. Photobiol. A* **148**, 137–143.

Fu, J. F., Ji, M., Wang, Z., Jin, L. N. & An, D. N. 2006 A new submerged membrane photocatalysis reactor (SMPR) for fulvic acid removal using a nano-structured photocatalyst. *J. Hazard. Mater.* **131**, 238–242.

Galindo, C., Jacques, P. & Kalt, A. 2001 Photochemical and photocatalytic degradation of an indigoid dye: a case study of acid blue 74 (AB74). *J. Photochem. Photobiol. A* **141** (2001), 47–56.

Gogate, P. R. & Pandit, A. B. 2004 A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Adv. Environ. Res.* **8**, 501–551.

Hoffmann, M. R., Martin, S. T., Choi, W. D. & Bahnemann, W. 1995 Environmental application of semiconductor photocatalysis. *Chem. Rev.* **95**, 69–96.

Huang, X., Leal, M. & Li, Q. 2008 Degradation of natural organic matter by TiO$_2$ photocatalytic oxidation and its effect on fouling of low-pressure membranes. *Water Res.* **42**, 1142–1150.

Jiang, J., Oberdorster, G. & Biswas, P. 2009 Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. *J. Nanopart. Res.* **11**, 77–89.

Le-Clech, P., Lee, E. K. & Chen, V. 2006 Hybrid photocatalysis/membrane treatment for surface waters containing low concentrations of natural organic matters. *Water Res.* **40**, 323–330.

Li, X. Z., Fan, C. M. & Sun, Y. P. 2002 Enhancement of photocatalytic oxidation of humic acid in TiO$_2$ suspensions by increasing cation strength. *Chemosphere* **48**, 453–460.

Mandzy, N., Grulke, E. & Druffel, T. 2005 Breakage of TiO$_2$ agglomerates in electrostatically stabilized aqueous dispersions. *Powder Technol.* **160**, 121–126.

Sakthivel, S., Neppolian, B., Arabindoo, B., Palanichamy, M. & Murugesan, V. 2000 TiO$_2$ catalysed photodegradation of leather dye, acid green 16. *J. Sci. Ind. Res.* **59**, 556.

Tay, J. H., Chen, D. & Sun, D. D. 2001 Removal of color substances using photocatalytic oxidation for membrane filtration processes. *Water Sci. Technol.* **43** (10), 319–325.

Wang, K. H., Hsieh, Y. H., Chou, M. Y. & Chang, C. Y. 1999 Photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide suspensions in aqueous solution. *Appl. Catal. B.* **21**, 1–8.

Xi, W. & Geissen, S. U. 2002 Separation of titanium dioxide from photocatalytically treated water by cross-flow microfiltration. *Water Res.* **35**, 1256–1262.

Xue, G., Liu, H., Chen, Q., Hills, C., Tyrer, M. & Innocent, F. 2011 Synergy between surface adsorption and photocatalysis during degradation of humic acid on TiO$_2$/activated carbon composites. *J. Hazard. Mater.* **186**, 765–772.

Yamazaki, S., Matsunaga, S. & Hori, K. 2001 Photocatalytic degradation of trichloroethylene in water using TiO$_2$ pellets. *Water Res.* **35**, 1022–1028.

Yang, J. K. & Lee, S. M. 2006 Removal of Cr(VI) and humic acid by using TiO$_2$ photocatalysis. *Chemosphere* **63**, 1677–1684.

Yang, S., Chen, Y., Lou, L. & Wu, X. 2005 Involvement of chloride anion in photocatalytic process. *J. Environ. Sci.* **17** (5), 761–765.