

## TiO<sub>2</sub> as an effective nanocatalyst for photocatalytic degradation of humic acid in water environment

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### ABSTRACT

Photocatalysis with TiO<sub>2</sub> is used to remove humic acid (HA) in a water environment under UVA and UVC light. The effects of operating parameters, including light intensity, HA concentration, catalyst dose, and contact time are investigated at neutral pH conditions. Results show that HA degradation increases with increasing contact time and light intensity and decreases with increasing HA concentration. Increasing catalyst dose increases the HA degradation up to an optimum value. At pH 7 with an initial HA concentration of 14 mg/L, UVA light of 0.236 mW/cm<sup>2</sup> and catalyst dose of 0.3 g/L, 100% efficiency of the HA degradation can be achieved in 3 h. Under identical experimental conditions with UVC light of 0.284 mW/cm<sup>2</sup>, the efficiency of HA degradation also reaches 100%. Based on total organic carbon (TOC) analysis, the mineralization of HA is found to be lower than the degradation of HA. A negligible amount of TOC on the catalyst surface confirms that HA removal is due to photocatalysis. Moreover, a higher degree of mineralization of HA is found under UVA light although degradation is better under UVC light. This indicates that TiO<sub>2</sub> under UVA light has relatively low selectivity to degrade different compounds, including various intermediates from HA degradation.

**Key words** | humic acid, photocatalysis, reusability, TiO<sub>2</sub>, TOC, UV light

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### INTRODUCTION

Humic acid (HA) is a major fraction of natural organic matter in surface water, originating from animal and plant material breakdown (Alberts & Takács 2004). HA causes serious problems in treatment operations. Due to the reaction of HA with chlorine during disinfection processes, numerous disinfection by-products are formed. Such chlorinated by-products are potentially carcinogenic (Singer 1999).

A number of processes have been employed to remove HA from water environments to prevent the generation of chlorinated by-products, including chemical coagulation, adsorption, Fenton treatment, membrane separation, and ion exchange. Coagulation with aluminum sulfate is a widely used method (Duan *et al.* 2002). However, it is difficult to dispose of the high aluminum concentration in residual

sludge. Adsorption with activated carbon is also a common method for HA removal (Daifullah *et al.* 2004). However, the cost of activated carbon is relatively high and HA removal is also limited by its high molecular weight. Although Fenton treatment can be a better option for HA removal due to complete destruction of HA (Katsumata *et al.* 2008), it still possesses some critical limitations. These include treatment of chemical sludge produced and biological regrowth in drinking water distribution systems. Membrane processes are actually effective for treatment of water containing HA (Tang *et al.* 2007). However, membrane fouling is still a big challenge. Ion exchange can also be an alternative for the removal of HA from a water environment (Bolto *et al.* 2002). However, it has relatively high operational and

maintenance costs. Ion exchangers are also easily contaminated which significantly reduces the exchange capacity.

Among the methods for eliminating organic contaminants in a water environment, semiconductor photocatalysis appears to be promising, mainly due to its clean, solar-driven process for complete destruction of recalcitrant organic compounds (Maleki *et al.* 2015; Sudrajat & Babel 2016c; Sudrajat *et al.* 2016). Among semiconductor materials, TiO<sub>2</sub> has been considered as a promising catalyst due to its high activity under UV light, long-term stability, low cost, and nontoxicity (Ohko *et al.* 2001). Several studies have reported the effectiveness of using TiO<sub>2</sub> for photocatalytic degradation of HA (Palmer *et al.* 2002; Al-Rasheed & Cardin 2003a, 2003b; Pansamut *et al.* 2013). Photocatalysis with TiO<sub>2</sub> can also be coupled with another process to give a better overall removal efficiency, for instance, through functionalization on nanofiber membranes (Daels *et al.* 2015). Using this TiO<sub>2</sub>-functionalized membrane, an HA removal efficiency of 83% was obtained within 2 h of UV irradiation.

The basic process of the photocatalytic degradation of HA by TiO<sub>2</sub> consists of excitation of electrons from the valence band (VB) to the conduction band of TiO<sub>2</sub>, creating holes in the VB under light irradiation with an energy equal to or higher than the band gap energy of 3.2 eV (Wiszniewski *et al.* 2002). This process leads to the formation of highly reactive species, mainly •OH radicals, on the TiO<sub>2</sub> surface, which oxidize HA molecules. It has been suggested that the adsorbed HA is degraded on the TiO<sub>2</sub> surface via the carboxylate or phenolate surface groups which leads to depolymerization and aromatic ring cleavages (Wiszniewski *et al.* 2002). This is followed by the formation of a large number of organic degradation products, mainly carboxylic acids with low molecular weights, such as oxalic, succinic, formic, acetic, and malonic acids.

Based on the literature, use of UV light is recommended to achieve high efficiency of HA degradation. Unfortunately, further information on which the UV region is the most suitable for the photocatalytic degradation of HA using TiO<sub>2</sub> is not yet available. In addition, the quantity of the HA degradation products in terms of total organic carbon (TOC) on the catalyst surface has never been determined. This matter is critical to gain insights into the mechanism of the HA removal, that is, whether it is removed by photocatalysis or adsorption or both. On the basis of all these

rationales, this research has been carried out to investigate the applicability of photocatalysis using TiO<sub>2</sub> for HA degradation in a water environment under different UV light regimes (UVA and UVC) and intensity. The optimum conditions for the HA degradation have been established. The TOC on the solid phase (catalyst surface) was also determined to understand the mechanism of removal. HA degradation kinetics was also investigated.

## EXPERIMENTAL

### Chemicals

HA stock solution was prepared by using technical grade HA sodium salt (Aldrich). TiO<sub>2</sub> P25 (99.5% trace metals basis, Aldrich) with an average particle size of 21 nm was used. Deionized water (DI) was used in all processes.

### Characterization

A Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet 6700) was employed for functional group elucidation. The crystallographic phase was evaluated using X-ray diffraction (XRD) on a diffractometer with Cu K $\alpha$  radiation and  $\lambda$  of 1.5406 Å (Pananalytical). Diffuse reflectance spectra (DRS) were obtained from a UV-Vis-NIR spectrophotometer (Cary 5000 Agilent). Textural properties were examined using N<sub>2</sub> adsorption-desorption isotherms at a liquid nitrogen temperature of 77 K by an adsorption instrument (Autosorb Quantachrome). The chemical composition was analyzed by X-ray fluorescent (XRF) spectrometer.

### Photocatalytic activity evaluation

The photocatalytic degradation of HA was carried out in a batch slurry system. A suspension (0.1 L) containing known concentrations of HA and the catalyst was transferred into a batch photoreactor (Figure S1, Supplementary material, available with the online version of this paper). Two different light sources were used for the HA degradation, UVA (315–400 nm) and UVC (100–280 nm) lamps. After the lamp was switched on for a given irradiation time, the suspension was filtered using

0.45 µm syringe filters for determining HA concentration. To study the effect of operating parameters on HA degradation, experiments were performed by varying key operating parameters, namely HA concentration, catalyst dose, contact time, and light intensity. To investigate the reusability of the catalyst, six successive runs were carried out by adding the recycled catalyst to fresh HA solutions with no change in the overall concentration of the catalyst. Separation of the catalyst from the slurry system was done by centrifugation prior to drying at 60 °C for 12 h (Adhikari et al. 2015). No additional chemical treatment, and thus no chemical reagent, is involved in the catalyst regeneration. All experiments were performed in duplicate at 25 ± 3 °C and neutral pH conditions, and the results are presented as a mean of two identical experiments.

### Analytical determinations

The HA concentration was determined based on the absorbance of HA solution at λ<sub>max</sub> of 276 nm by using a UV-vis spectrophotometer. A λ<sub>max</sub> of 276 nm was obtained after scanning the HA solution in the wavelength region of up to 800 nm. Use of λ<sub>max</sub> provides maximum sensitivity for the HA measurements. The HA concentration was determined based on the calibration plots of the absorbance versus concentration. The HA degradation efficiency was calculated from the equation:

$$\text{Degradation (\%)} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

where C<sub>0</sub> and C<sub>t</sub> are the initial HA concentration and the HA concentration after irradiation (mg/L), respectively. For simple evaluation of kinetics data, the apparent pseudo first order kinetic model was used:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{\text{app}}t \quad (2)$$

where k<sub>app</sub> is the apparent pseudo first order rate constant (1/min). Mineralization was determined by TOC measurement (TOC-LCPH/CPN, Shimadzu) for both liquid and solid phases.

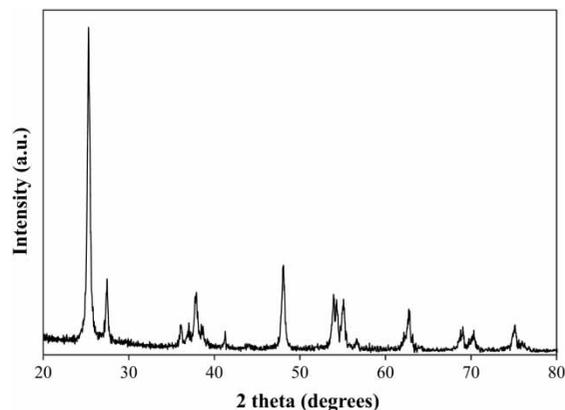


Figure 1 | XRD pattern of TiO<sub>2</sub>.

## RESULTS AND DISCUSSION

### Physicochemical properties of TiO<sub>2</sub>

Based on the XRD pattern shown in Figure 1, commercial TiO<sub>2</sub> used in this research is composed of two phases, anatase and rutile. The rutile phase shows diffraction peaks at 27°, 36°, and 55°, while those of the anatase phase are at 25° and 48° (Arbiol et al. 2002).

Figure 2 shows the FTIR spectra of TiO<sub>2</sub> before and after use. The peak centered at 3,442 cm<sup>-1</sup> corresponds to O-H stretching of Ti-OH groups and H<sub>2</sub>O molecules. The slightly narrow peaks around 1,600 and 1,400 cm<sup>-1</sup> can be assigned

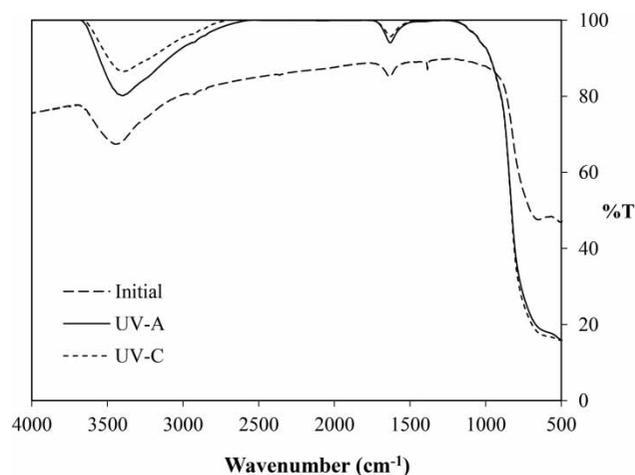


Figure 2 | FTIR spectra of TiO<sub>2</sub>.

**Table 1** | Surface properties of TiO<sub>2</sub>

Parameter	Specific surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)
TiO <sub>2</sub> (Initial)	52	0.026	2.008
TiO <sub>2</sub> (UVA)	47.30	0.023	1.974
TiO <sub>2</sub> (UVC)	49.59	0.024	1.989

to O-H bending of hydroxyl groups. The peaks around 600 cm<sup>-1</sup> correspond to the vibration of Ti-O. It is to be noted that after use, the peak of O-H stretching shifts to shorter wavenumbers and the peak of O-H bending at 1,400 cm<sup>-1</sup> disappears. These indicate that the properties of surface hydroxyl groups are altered, likely due to their interaction with the HA degradation by-products. In fact, the peak about 3,000 cm<sup>-1</sup> can also be due to the contribution of hydroxyl groups of the HA degradation by-products, which have different spectroscopic properties than those of the catalyst. Moreover, considering the decreased peak intensity of O-H bending after use, the population of surface hydroxyl groups is probably reduced. A number of surface hydroxyl groups may be consumed for the generation of hydroxyl radicals during light irradiation.

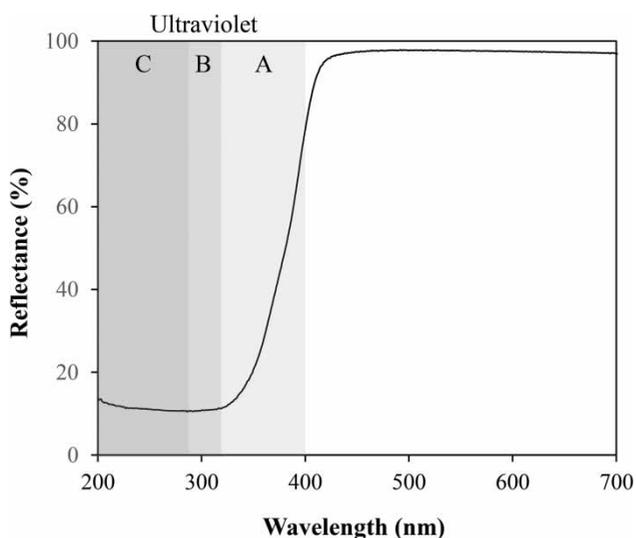
Table 1 shows the specific surface area of TiO<sub>2</sub> before use (Initial) and after use. The specific surface area slightly decreases after HA degradation. There are at least two factors which lead to decreased specific surface area. The first factor is occupation of the catalyst surface by the HA degradation by-products, which results in pore blockage. This is indicated by the decreased total pore volume and pore diameter as well as the presence of TOC on the solid phase. The second factor is agglomeration of the catalyst particles, which leads to a decrease of total surface area.

Table 2 shows the XRF results on the chemical composition of TiO<sub>2</sub> before use and after HA degradation under UVC. As the purity of the commercial TiO<sub>2</sub> used is 99.5%, some trace elements are expected, which are found to be Cl and SO<sub>3</sub>. After HA degradation, there are several substances attached on the TiO<sub>2</sub> surface, namely, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZnO, and CaO. These impurities are most likely from the HA as a technical grade of the HA sodium salt was used. Although their amount is relatively low (less than 1% in total), they may inhibit the HA degradation through passivation of the TiO<sub>2</sub> surface.

**Table 2** | Elemental composition of TiO<sub>2</sub>

Element	TiO <sub>2</sub> (Initial)	TiO <sub>2</sub> (UVC)
TiO <sub>2</sub> (%)	99.8	99.3
Cl (%)	0.128	-
SiO <sub>2</sub> (%)	-	0.462
SO <sub>3</sub> (ppm)	541	-
Fe <sub>2</sub> O <sub>3</sub> (ppm)	-	966
ZnO (ppm)	-	989
CaO (ppm)	-	366

Figure 3 shows the DR spectra of TiO<sub>2</sub>. As seen, TiO<sub>2</sub> mainly absorbs light in the UVC region and its λ<sub>max</sub> is also in the UVC region. Therefore, it is expected that more charge carriers are generated under UVC light than under UVA light. This factor can be used to explain why the HA degradation by TiO<sub>2</sub> is more effective under UVC light. Based on the DR spectra, the band gap of TiO<sub>2</sub> is estimated to be 3.15 eV, which corresponds to a wavelength of 394 nm. Considering the band gap value, •OH radical should be the main reactive species produced by the catalyst under UV light (Sudrajat & Babel 2016a). •OH radical is a very powerful, nonselective oxidant, and thus, favorable for not only degradation but also mineralization of organic compounds.

**Figure 3** | UV-DRS spectra of TiO<sub>2</sub>.

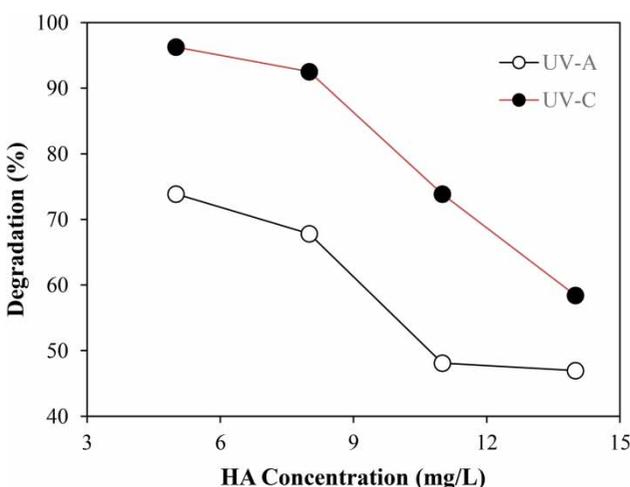
## Degradation of HA

In all the cases, HA degradation under UVC light is better than that under UVA light. This can be due to two factors. First, based on the DR spectra, TiO<sub>2</sub> mainly absorbs UVC light instead of UVA light. Therefore, more reactive species are produced when TiO<sub>2</sub> is irradiated with UVC. Second, the charge carriers (electrons and holes) generated under UVC light have stronger reduction and oxidation power compared to those produced under UVA light since UVC light has a stronger energy. As a result, reactive species are more easily produced under UVC light.

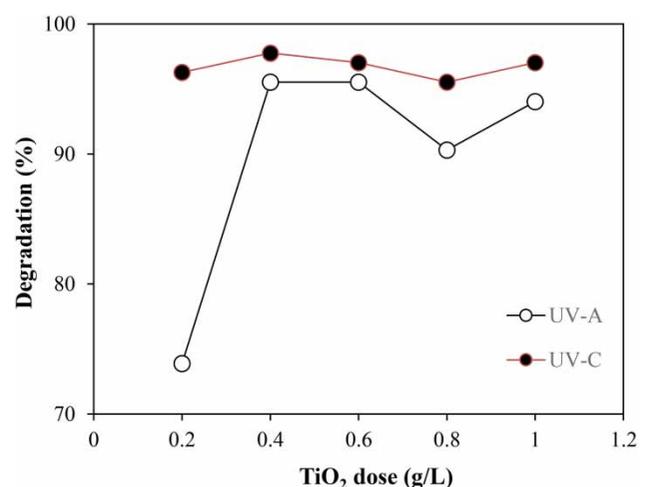
The effect of initial HA concentration on the degradation efficiency is shown in Figure 4. With increasing initial concentration from 5 to 14 mg/L, the degradation of HA decreases from 74 to 47% for UVA and 96 to 58% for UVC. These results can be explained as follows (Akpan & Hameed 2009). With increasing HA concentration, more HA molecules absorb the incoming light and the photon path length entering the solution therefore decreases. This results in less formation of reactive radicals. The HA adsorbed on the catalyst surface may also hinder the adsorption of O<sub>2</sub> and OH<sup>-</sup>. Thus, the generation of •O<sub>2</sub> and •OH radicals is suppressed. Another reason, is that, with increasing initial HA concentration, the catalyst adsorbs more HA molecules. With constant irradiation time and light intensity, the number of charge carriers

generated is also constant (Sudrajat & Babel 2016d). As a result, the relative number of charge carriers to HA molecules decreases.

As shown in Figure 5, the HA degradation under both UVA and UVC light initially increases as the catalyst concentration increases up to 0.4 g/L. With a further increase of the catalyst concentration to 0.8 g/L, the HA degradation slightly decreases. A possible explanation for the above results is as follows. With an increase of catalyst concentration, the total surface area for light absorption and HA adsorption increases. Thus, more reactive radicals are generated. Above the optimum value of catalyst concentration, the suspension turbidity increases and hence light penetration decreases. At this stage, photon intake becomes the rate-limiting factor. An increase of catalyst concentration beyond the optimum value may result in agglomeration of the catalyst particles and thus a part of the surface becomes unavailable for light absorption and HA adsorption. Interestingly, the HA degradation then increases again with increasing catalyst concentration to 1 g/L. It seems that there are competing factors which determine the HA degradation extent, such as increased catalyst surface area, increased turbidity and agglomeration of the catalyst particles. The dominant factor at a particular catalyst dose determines the trend of the HA degradation under particular conditions. It is also to be noted that, at the initial stage, the increase of the HA degradation under



**Figure 4** | Effect of HA concentration on the degradation efficiency (catalyst dose = 0.1 g/L, contact time = 60 min, UVA light intensity = 0.131 mW/cm<sup>2</sup>, UVC light intensity = 0.196 mW/cm<sup>2</sup>).

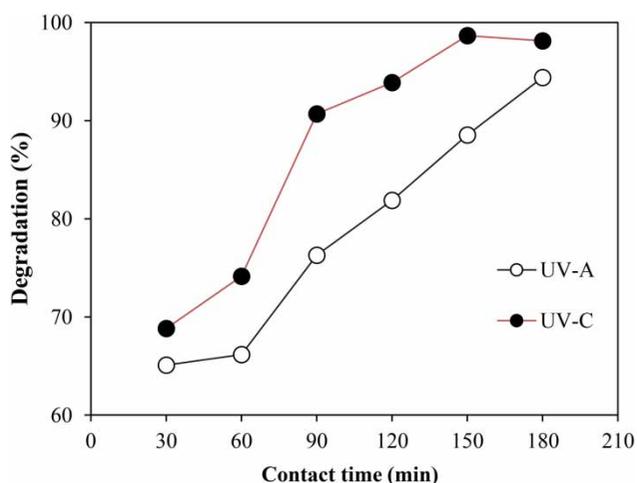


**Figure 5** | Effect of catalyst dose on the degradation efficiency (HA concentration = 5 mg/L, contact time = 60 min, UVA light intensity = 0.131 mW/cm<sup>2</sup>, UVC light intensity = 0.196 mW/cm<sup>2</sup>).

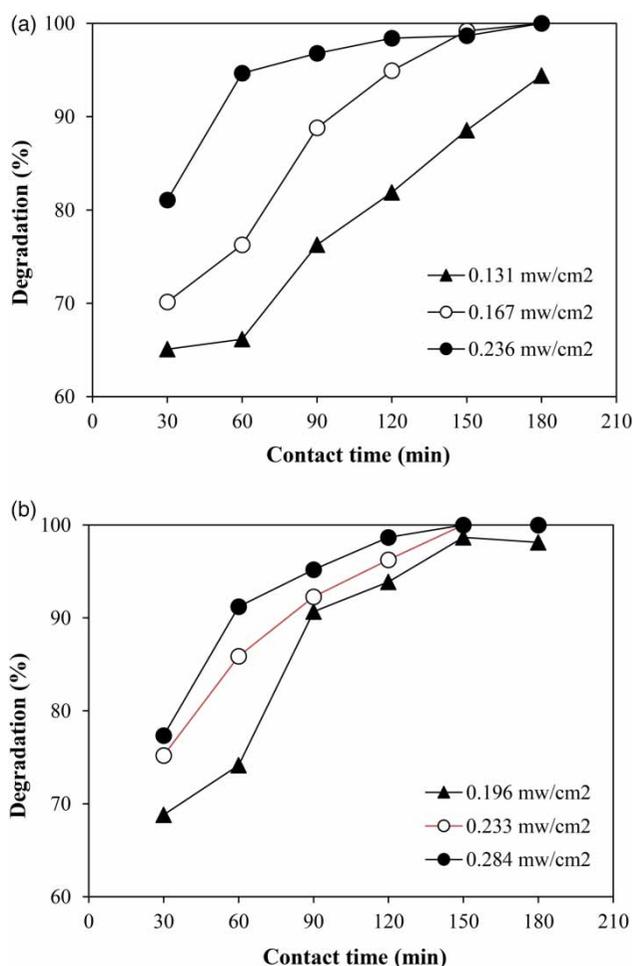
UVA light is more significant than that under UVC light. Such different results indicate the complex nature of HA degradation. It depends on many factors.

The percentage of HA degradation with respect to contact time is shown in Figure 6. As irradiation time increases, the HA degradation generally increases. This is because more light is absorbed by the catalyst for producing reactive radicals (Sudrajat & Babel 2016b). Thus, more HA molecules are degraded. However, HA degradation under UVC light slightly decreases after 150 min. This may be because the recombination of charge carriers takes place more frequently with increasing contact time (Choi *et al.* 1994). As a result, the quantum efficiency ultimately decreases. Another reason is likely due to agglomeration of the catalyst particles which then leads to a decreased total surface area exposed to the incoming light.

Figure 7 shows the effects of light intensity on the HA degradation under UVA and UVC light. As can be seen, with increasing light intensity, HA degradation increases. HA degradation approximately follows the same pattern of increase in all the cases. This is because more light is absorbed by the catalyst. Therefore, more reactive species are generated. However, with increasing contact time, the increase of HA degradation becomes insignificant, especially under UVC light. The difference in HA degradation under light with varied intensity also becomes



**Figure 6** | Effect of contact time on the degradation efficiency (HA concentration = 14 mg/L, catalyst dose = 0.3 g/L, UVA light intensity = 0.131 mW/cm<sup>2</sup>, UVC light intensity = 0.196 mW/cm<sup>2</sup>).



**Figure 7** | Effect of light intensity on the degradation efficiency under UVA (a) and UVC (b) (HA concentration = 14 mg/L, catalyst dose = 0.3 g/L).

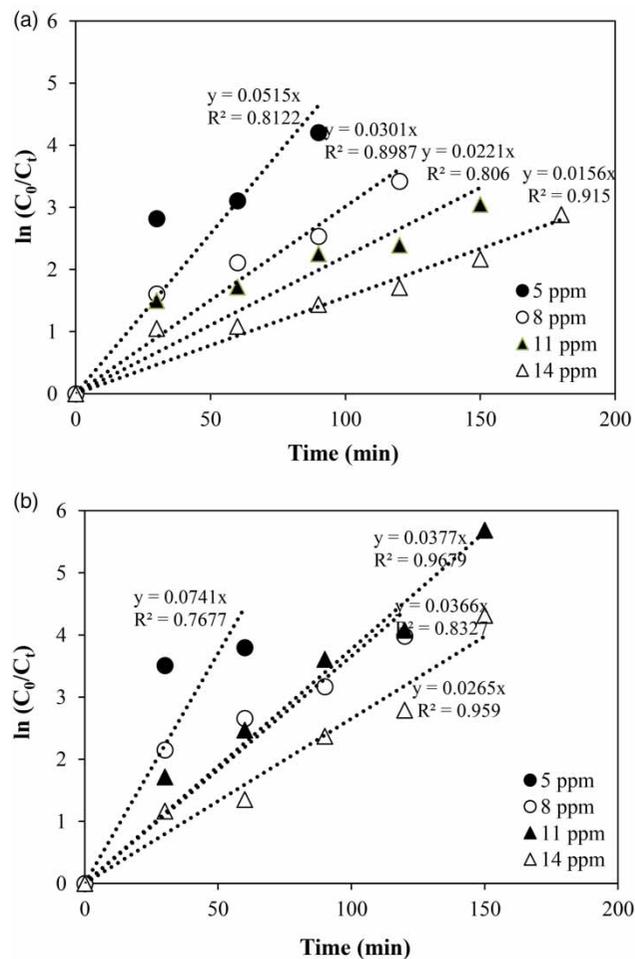
insignificant. Increased recombination of charge carriers may be the reason for those phenomena. It should be noted that direct comparison of HA degradation under UVC and that under UVA is not applicable since different light intensities are used in those two conditions. Therefore, it is advisable to carry out the HA degradation under UVA and UVC with the same light intensity. This is to confirm if the degradation efficiency only depends on light intensity instead of light wavelength.

Photocatalytic degradation of HA is a surface phenomenon. Therefore, adsorption of HA plays a critical role in the extent of HA degradation and should be determined. For this purpose, adsorption experiments were conducted in the absence of light at the optimum conditions. Results

show that around 60% of HA can be adsorbed. This exceptionally high adsorption of HA does not mean that the HA is mainly removed from the suspension through adsorption. This is because under UV light, any molecules adsorbed on the TiO<sub>2</sub> surface will be degraded by the reactive species. This conclusion is, furthermore, supported by the fact that, TOC on the solid phase (catalyst surface) is very low, less than 1% of initial TOC. Regarding the extremely high adsorption of HA on the catalyst surface, it may be due to two factors. First, TiO<sub>2</sub> used in this study possesses a relatively high specific surface area (52 m<sup>2</sup>/g) and therefore can adsorb a reasonable amount of HA. A similar result was also reported for the adsorption of HA by TiO<sub>2</sub>, in which more than 60% of HA was adsorbed by the catalyst with a concentration higher than 0.5 g/L (Dziedzic et al. 2010). The TiO<sub>2</sub> used in their study also had a relatively high specific surface area of 50 m<sup>2</sup>/g. Second, HA is a complex molecule consisting of various types of oxygen containing functional groups (Wiszniewski et al. 2003). Due to the presence of such functional groups, HA easily interacts with hydroxyl groups on the catalyst surface.

Experiments on the degradation of HA under UVA and UVC light in the absence of catalyst were also performed. Results show that the degradation of HA within 180 min under UVA light of 0.236 mW/cm<sup>2</sup> and UVC light of 0.284 mW/cm<sup>2</sup> reaches 70% and 79%, respectively. This indicates that HA is photolyzed by UV light. Indeed, UV light can directly generate highly oxidative •OH radicals without catalyst (Corin et al. 1996; Kulovaara 1996; Remoundaki et al. 2009). HA is also inherently a photosensitizer, and thus easily absorbs light to undergo a self-chemical transformation (Remoundaki et al. 2009). Therefore, the degradation of HA under light irradiation in the absence of catalyst is expected. When a small amount of catalyst (0.3 g/L of TiO<sub>2</sub>) was added to the HA solution, 100% of HA degradation is observed under both UVA and UV light within 180 min. The photocatalytic reaction is found to accelerate the degradation of HA.

Furthermore, as shown in Figure 8, the straight line represented by a plot of  $\ln(C_0/C_t)$  as a function of  $t$  indicates that the HA degradation kinetics follow approximately a pseudo first order model. Indeed, the degradation of HA by metal oxide photocatalysts typically follows pseudo first order kinetics. It was reported that the degradation of HA



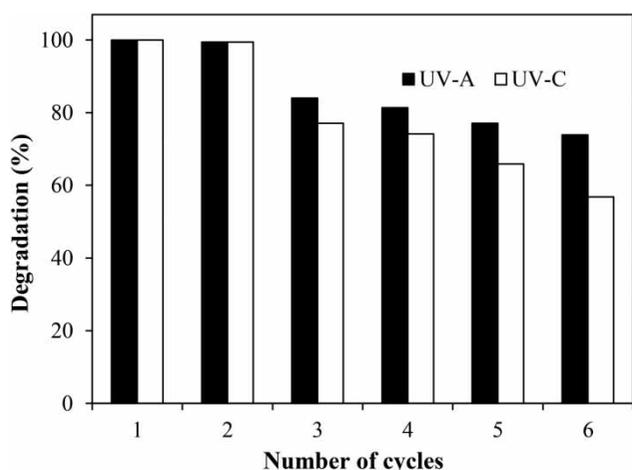
**Figure 8** | Pseudo first order kinetics of HA degradation by TiO<sub>2</sub> at various initial HA concentration under UVA (a) and UVC (b) light (catalyst dose = 0.3 g/L, UVA light intensity = 0.131 mW/cm<sup>2</sup>, UVC light intensity = 0.196 mW/cm<sup>2</sup>).

by Ag-doped ZnO under UVA light followed a pseudo first order model with excellent correlation coefficient values (Ghaneian et al. 2014). Under solar light with TiO<sub>2</sub>, the HA degradation kinetics also followed approximately a pseudo first order model, which can be described by the Langmuir–Hinshelwood model reasonably well (He 2013). As seen in Table 3, based on  $k_{app}$  obtained, at lower concentrations of HA, TiO<sub>2</sub> shows better performance.

For practical applications, catalyst reusability is a pivotal factor which must be considered. In order to evaluate the reusability of TiO<sub>2</sub> for HA degradation, recycling experiments were conducted under identical conditions. After being used three times, the HA degradation efficiencies decrease by about 20%. At the sixth cycle, the percentages

**Table 3** | Parameters of pseudo first order kinetics of HA degradation by TiO<sub>2</sub> at various initial HA concentrations

Initial HA concentration	UVA		UVC	
	$k_{app}$ (1/min)	$R^2$	$k_{app}$ (1/min)	$R^2$
5	0.052	0.812	0.074	0.768
8	0.030	0.899	0.038	0.833
11	0.022	0.806	0.037	0.968
14	0.016	0.915	0.027	0.959

**Figure 9** | Catalyst reusability under UVA and UVC light (contact time = 180 min, HA concentration = 14 mg/L, catalyst dose = 0.3 g/L, UVA light intensity = 0.236 mW/cm<sup>2</sup>, UVC light intensity = 0.284 mW/cm<sup>2</sup>).

of the HA degradation obtained are 74% for UVA and 57% for UVC (Figure 9). These decreases of HA degradation over time may be due to deposition of HA degradation by-products which hinder the absorption of light and adsorption of HA. Although the amount of HA degradation by-products attached on the catalyst surface is insignificant according to the results of the TOC solid phase (Table 4), such small organic compounds could contribute to the reduced degradation efficiency. It should be possible to improve the catalyst reusability by selecting appropriate pretreatment techniques before reuse so as to remove the attached molecules on the surface and hence increase the adsorption ability of the surface. Another reason for the reduced catalyst performance is agglomeration of the catalyst particles which results in decreased total surface area. In fact, agglomeration of the catalyst particles was observed after

**Table 4** | TOC removal under UVA and UVC light

	TOC			
	Liquid phase (mg/L)	Solid phase		
		%	(mg C/g)	Mineralization (%)
Initial	6.425	–	–	–
TiO <sub>2</sub> (UVA)	2.063	0.1037	0.0098	68%
TiO <sub>2</sub> (UVC)	3.116	0.5321	0.0787	49%

Conditions: HA concentration = 14 mg/L, catalyst dose = 0.3 g/L, contact time = 180 min, UVA light intensity = 0.236 mW/cm<sup>2</sup>, UVC light intensity = 0.284 mW/cm<sup>2</sup>.

reuse. Proper pretreatment before reuse is therefore necessary to maintain catalyst performance.

### Mineralization of HA

Degradation of organic compounds, especially those with large molecular weights such as HAs, through photocatalysis is typically not followed by complete mineralization (Ollis et al. 1991). This is because the photocatalytic degradation of HA results in the formation of a large number of organic degradation products, mostly carboxylic acids with low molecular weights such as oxalic, succinic, formic, acetic, and malonic acids (Corin et al. 1996; Wiszniewski et al. 2002). In this research, the mineralization extent of HA was evaluated by analyzing the TOC in both liquid and solid phases at optimum conditions. The results are summarized in Table 4. As can be seen, TOC removals are 68% and 49% for HA degradation under UVA and UVC light, respectively. However, these values are still lower than the degradation efficiency, which is 100% under the same experimental conditions. These results indicate a low degree of mineralization. Incomplete mineralization of HA occurred due to the generation of various HA degradation products. Similar findings are also found for the degradation of HA through photocatalysis with TiO<sub>2</sub>. For example, it was reported that the efficiency of HA degradation (76%) by TiO<sub>2</sub> under UV light was higher than that of HA mineralization (50%), particularly in the initial stage of the process (Yuan et al. 2013). These results are very close to those obtained in another research paper, in which 75% of degradation efficiency and 40% of mineralization efficiency were achieved during 1 h of UV irradiation for an HA solution in

the presence of TiO<sub>2</sub> (Bekbölet & Özkösemen 1996). Also, with different metal oxides such as ZnO, it was observed that the mineralization efficiency of HA by ZnO immobilized on a glass plate was only 59% while the degradation efficiency reached 83% within 120 min of UV irradiation (Maleki et al. 2016).

Moreover, the TOC values in the solid phase (catalyst surface) are found to be negligible. Less than 1% of TOC is observed. This result indicates that most of the HA molecules are removed from the suspension through photocatalysis instead of adsorption. Also, only a small amount of HA degradation by-products is attached on the catalyst surface. It is interesting to note that a higher degree of mineralization of HA is found under UVA light although the degradation of HA is better under UVC light. These results indicate that the TiO<sub>2</sub> under UVA light has relatively low selectivity to degrade different compounds including various intermediates from the HA degradation, which is beneficial to its mineralization. It must be noted that, different from the case of photocatalysis for the syntheses of organic compounds, in the context of photocatalysis for the degradation of organic compounds, high selectivity is detrimental to the overall performance, that is, mineralization efficiency. For achieving a high mineralization degree, the photocatalytic system should be nonselective. In other words, it should be able to degrade various types of organic compounds produced, including the small ones, and then convert them into inorganic compounds.

## CONCLUSIONS

Based on this research, it is shown that photocatalysis with TiO<sub>2</sub> is an effective method for the degradation of HA. Furthermore, the following conclusions can be made:

- UVC is shown to be a better light source for HA degradation by TiO<sub>2</sub>. This is mainly associated with the higher ability of TiO<sub>2</sub> for UVC absorption as well as the ability of TiO<sub>2</sub> to generate charge carriers with higher reduction/oxidation power under UVC light. However, in terms of the mineralization degree, UVA/TiO<sub>2</sub> is better than UVC/TiO<sub>2</sub> due to its low selectivity towards HA degradation products.
- All the parameters, including catalyst dose, light intensity, HA concentration, and contact time, have a significant effect on the HA degradation. The catalyst dose should especially be taken into account since a high dose of catalyst is detrimental to the catalyst performance and also leads to a higher cost of treatment and difficult post-separation.
- At a catalyst dose, HA concentration, and light intensity of 0.3 g/L, 14 mg/L, and 0.236 mW/cm<sup>2</sup>, respectively, complete degradation of HA can be achieved. The same result of complete HA degradation is also observed under UVA light of 0.284 mW/cm<sup>2</sup>.
- Strong adsorption of HA takes place on the catalyst surface. Around 60% of HA is adsorbed. However, this does not mean that the overall removal of HA is dominated by adsorption.
- The HA degradation kinetics under UVC and UVA light follows approximately a pseudo first order rate. The reaction rate constant decreases with increasing initial HA concentration.

## ACKNOWLEDGEMENTS

Financial support for this research by Sirindhorn International Institute of Technology of Thammasat University and the Asian Development Bank is acknowledged.

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First received 12 September 2016; accepted in revised form 4 November 2016. Available online 28 December 2016