

# Visible light-induced reactions of humic acids on TiO<sub>2</sub>

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## Abstract

We investigated the sensitized degradation of humic acids on TiO<sub>2</sub> under visible light ( $\lambda > 420$  nm) irradiation. The photolysis rates were strongly dependent on pH due to the pH-dependent adsorption of humic acids on TiO<sub>2</sub> with the maximum rate observed at pH  $\sim 3$ . Reduction in the UV–visible absorbance and fluorescence emission ( $\lambda_{\text{ex}} = 350$  nm) of humic acids was observed during the irradiation. Humic acids acted as a sensitizer for injecting electrons from their excited state to the conduction band of TiO<sub>2</sub>, which were subsequently transformed and decolorized through a series of electron transfer reactions. However, the dissolved organic carbon (DOC) of humic acid solutions remained almost unchanged under visible light while the UV-irradiation was able to remove part of the total DOC. The trihalomethane formation potential (THMFP) on the contrary increased with visible light irradiation. The macromolecular humic acids on visible light-illuminated TiO<sub>2</sub> degraded with the reduction of aromatic character but not to the complete mineralization. Humic acids that can both donate and accept electrons to and from TiO<sub>2</sub> conduction band seem to withstand many electron transfers without undergoing mineralization. Humic acids also successfully acted as a sensitizer for the reductive degradation of CCl<sub>4</sub> on platinumized TiO<sub>2</sub> under visible light irradiation, while no dechlorination was observed in the absence of either humic acids or TiO<sub>2</sub>. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Photocatalysis; Titanium dioxide; Humic acids; Visible light; Sensitization

## 1. Introduction

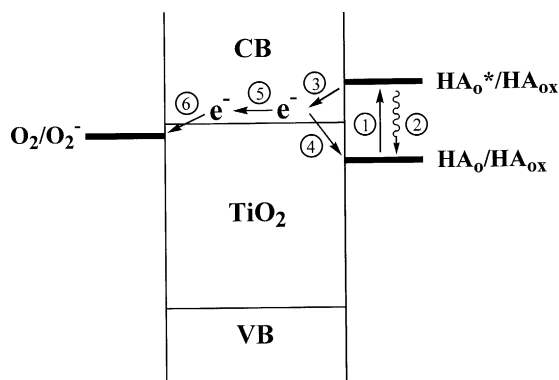
Humic acids (HAs) are macromolecular yellow-to-black colored natural organic matter derived from the degradation of plant, algal, and microbial material [1]. Although their formation mechanism and chemical structures are not well understood, they are known to be high in carbon content (50–60%) of both aliphatic and aromatic character and rich in oxygen-containing functionalities such as carboxyl, phenolic, alcoholic, and quinoid groups. HAs account for a significant fraction of natural organic carbons in surface waters and soils and play many important roles as a photosensitizer in aquatic photochemical processes, a complexing agent for heavy metal ions, and an organic coating material on mineral surfaces that affects the mobility and bioavailability of aquatic contaminants.

HAs have received much attention particularly in relation with water treatment since they are precursors of the disinfection byproducts (DBPs) (e.g., trihalomethanes (THMs)) in chlorination process. Activated carbon adsorption [2], coagulation precipitation [3,4], adsorption/ion exchange [5,6], biofiltration [7,8], ozonation [9,10], and ultrafiltration [11] have been widely studied as the humic removal process.

Recently, photocatalytic oxidation using TiO<sub>2</sub> is gaining wide attentions as an advanced water treatment technology [12–14]. TiO<sub>2</sub> photocatalyst initiates upon absorbing UV photons with generating conduction band (CB) electrons and valence band (VB) holes within the particle. In particular, the hydroxyl radicals generated through the reaction of VB holes account for the strong oxidizing power of the TiO<sub>2</sub> photocatalytic system.

Although TiO<sub>2</sub> has been widely used as a photocatalyst, the bandgap excitation of TiO<sub>2</sub> proceeds only in the presence of UV light ( $\lambda < 388$  nm). Sensitized TiO<sub>2</sub> by ruthenium-based complexes or various dyes [15–19] has been extensively investigated in order to extend the spectral response into the visible region. In particular, the dye/TiO<sub>2</sub>/visible light system where the dye serves as both a sensitizer and a substrate to be degraded could develop into a viable technology for treating dye-polluted wastewaters. A similar strategy might be applied to HA/TiO<sub>2</sub>/visible light system for drinking water treatment. HAs act as a natural photosensitizer in heterogeneous as well as homogeneous solutions [20]. Scheme 1 illustrates the principle of photosensitized degradation of HAs on TiO<sub>2</sub> under visible light. HA molecules adsorbed on TiO<sub>2</sub> are excited by absorbing visible light and subsequently inject electrons to CB of TiO<sub>2</sub>. The electron injection from excited fulvic acid into ZnO CB [21] and from excited HA into TiO<sub>2</sub> CB [22] has

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Scheme 1. Visible light-induced electron transfers from HAs on  $\text{TiO}_2$ .  $\text{HA}_0$  stands for ground-state HA molecules;  $\text{HA}^*$ , electronically excited HA;  $\text{HA}_{\text{ox}}$ , oxidized HA. The numbers represent the primary electronic pathways in photosensitization: (1) excitation of HA; (2) fluorescent decay of  $\text{HA}^*$ ; (3) electron injection from excited HA into CB; (4) back electron transfer to  $\text{HA}_{\text{ox}}$ ; (5) electron migration within the lattice onto the surface; (6) electron transfer to  $\text{O}_2$ .

been previously demonstrated. The HAs are oxidized upon electron injection and the injected electrons can transfer to substrates at the semiconductor/water interface to initiate sensitized reduction processes [22–24].

This paper describes an investigation into the visible light-induced transformation of HAs on  $\text{TiO}_2$ . The excited HAs inject electrons into  $\text{TiO}_2$  CB with subsequent changes in their absorption and fluorescence spectra. The mechanism of the HA reaction in visible light-illuminated  $\text{TiO}_2$  suspension is discussed. The HA-sensitized degradation of  $\text{CCl}_4$  on platinized  $\text{TiO}_2$  is also demonstrated.

## 2. Experimental section

### 2.1. Photolysis of HAs on $\text{TiO}_2$

Commercial HA (sodium salt) was purchased from Aldrich. HA was initially dissolved in alkaline solution (pH  $\sim$  12) at 100 mg/l and subsequently acidified to pH 3. The undissolved fraction of HA was removed by a 0.45  $\mu\text{m}$  nylon membrane filter (Gelman Sciences). The dissolved HA concentration was estimated by subtracting the weight of the filtered undissolved HA from the initially added HA amount. The filtrate was stored as an HA stock solution and its concentration was routinely checked by measuring the absorbance at 250 nm.

The  $\text{TiO}_2$  (Degussa P25) suspension was prepared at 0.5 g/l by simultaneous sonication and shaking in an ultrasonic cleaning bath (Branson 3210). An aliquot of HA stock solution was then added to the  $\text{TiO}_2$  suspension to give a desired concentration of HA (1–25 mg/l). The pH of the suspension was adjusted with 1 N HCl or 1 N NaOH solutions and equilibrated for 30 min. The suspension was air-equilibrated in most cases or purged with  $\text{N}_2$  or  $\text{O}_2$  gas for 30 min prior to irradiation.

The light source was a 300 W Xe arc lamp (Oriel). Light passed through a 10 cm IR water filter and a UV cut-off filter ( $\lambda > 420$  nm) for the visible light irradiation or a Pyrex filter ( $\lambda > 300$  nm) for UV light irradiation. The filtered light was focused onto a 90 ml Pyrex reactor with minimized headspace and a rubber septum. The suspension was magnetically stirred during the irradiation.

### 2.2. HA-sensitized degradation of $\text{CCl}_4$ on $\text{TiO}_2$

In addition to the sensitized degradation of HA itself on  $\text{TiO}_2$ , its role as a visible light sensitizer for the reductive degradation of  $\text{CCl}_4$  was tested. Both pure and Pt-loaded  $\text{TiO}_2$  were used. Platinum was directly photodeposited on  $\text{TiO}_2$  in the presence of 1 M methanol (electron donor) and 0.1 mM  $\text{H}_2\text{PtCl}_6$ . The suspension was sparged with  $\text{N}_2$  gas for 30 min before irradiation in order to remove dissolved oxygen.  $\text{CCl}_4$  was then directly injected into the suspension by a GC syringe through the rubber septum in order to give the initial concentration of ca. 1 mM. For the complete dissolution of  $\text{CCl}_4$ , the suspension was stirred magnetically for 30 min before the irradiation began. The visible light photolysis followed the same procedure as described above.

### 2.3. Sample analysis

Sample aliquots were taken from the reactor before and during the irradiation, added with 1 M NaOH to adjust their pH to 10, and stirred for 30 min to desorb HAs from  $\text{TiO}_2$  particles. Then, the suspension was filtered through a 0.45  $\mu\text{m}$  nylon membrane filter (Gelman Sciences) and the filtrate was used for further analysis. The UV–visible absorption and fluorescence spectra of the irradiated filtrate solution were recorded using a Shimadzu UV-2401PC UV–visible spectrophotometer and a Shimadzu RF-5301PC spectrofluorophotometer, respectively. Dissolved organic carbon (DOC) was measured using a Shimadzu 5000 total organic carbon analyzer. Trihalomethane formation potential (THMFP) of HA solution was measured by following the standard procedure [25]. Four THMs ( $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ ,  $\text{CHBr}_3$ ) were quantified by using a gas chromatograph (GC, HP6890) equipped with a fused silica capillary column (DB-5) and an electron capture detector (ECD). The HA-sensitized degradation of  $\text{CCl}_4$  was followed by monitoring the chloride production with an ion chromatograph (IC). The IC system was a Dionex DX-120 with a conductivity detector and a Dionex IonPac AS-14 wide bore column (4 mm  $\times$  250 mm).

The optical absorption spectra of pure  $\text{TiO}_2$ , HA-sensitized  $\text{TiO}_2$  (HA- $\text{TiO}_2$ ), and Pt-deposited  $\text{TiO}_2$  (Pt- $\text{TiO}_2$ ) powders were recorded with a UV–visible spectrophotometer equipped with a diffuse reflectance attachment (Shimadzu ISR-2200). The HA- $\text{TiO}_2$  and Pt- $\text{TiO}_2$  powder samples were prepared by filtering their aqueous suspension and drying under air.

### 3. Results and discussion

#### 3.1. Photoinduced electron transfers and spectral changes of HAs

The adsorption of HAs on TiO<sub>2</sub> is a prerequisite for an efficient electron injection and subsequent oxidation of HAs. Fig. 1 shows the adsorption isotherms of HAs on TiO<sub>2</sub> at different pHs. HA adsorption on TiO<sub>2</sub> was minimal at pH 10 and rapidly increased with decreasing pH. The strong pH-dependent adsorption of HAs on oxide surfaces has been frequently observed [24,26]. At pH 3, almost all added HAs were adsorbed on TiO<sub>2</sub> surface without showing any sign of saturation. A simple electrostatic surface charge model can account for the pH-dependent HA adsorption on TiO<sub>2</sub>, where the surface of TiO<sub>2</sub> takes positive charges at pH < 6 and negative charges at pH > 6 [27]. HAs with many acidic functional groups are deprotonated and negatively charged at alkaline solution. Therefore, the adsorption of HA at basic pH is strongly inhibited due to the negative–negative electrostatic repulsion. The HA adsorption at pH 7 showed a near saturation at [HA]<sub>i</sub> = 10 ppm, which is within the typical concentration range observed in natural waters, and further increase in [HA]<sub>i</sub> little enhanced the HA adsorption. On the other hand, most of HAs are fully protonated and sparingly soluble at acidic pH, which drives near quantitative adsorption of HAs on TiO<sub>2</sub> as shown in Fig. 1. The linear increase of [HA]<sub>ad</sub> with [HA]<sub>i</sub> implies that HA adsorption on TiO<sub>2</sub> proceeds with multilayer formation.

Fig. 2 compares the changes of UV absorbance at 250 nm (UV<sub>250</sub>) of HA solution at pH 3, 7, and 10 as a function of the visible light irradiation time. The decrease in UV<sub>250</sub> indicates the degradation of aromatic structures in HA molecules and should result from the photoinduced electron transfer from the excited HA to TiO<sub>2</sub> CB. The fact that the UV<sub>250</sub> removal efficiency decreased with pH 3 > 7 > 10 clearly shows that the adsorption of HA on TiO<sub>2</sub> is the necessary

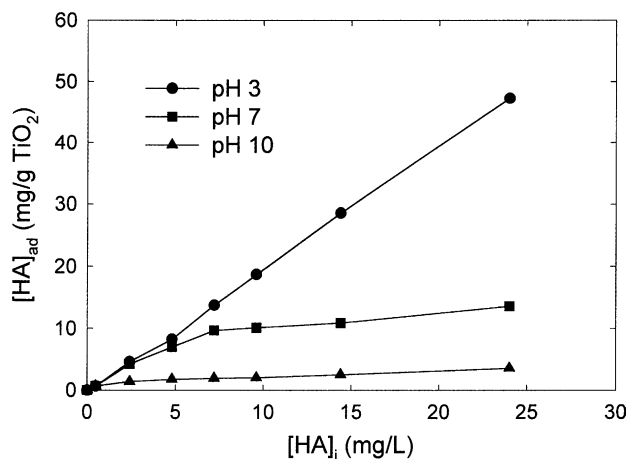


Fig. 1. Effects of pH on the adsorption isotherms of the HAs on TiO<sub>2</sub>. [HA]<sub>i</sub> represents the initial concentration.

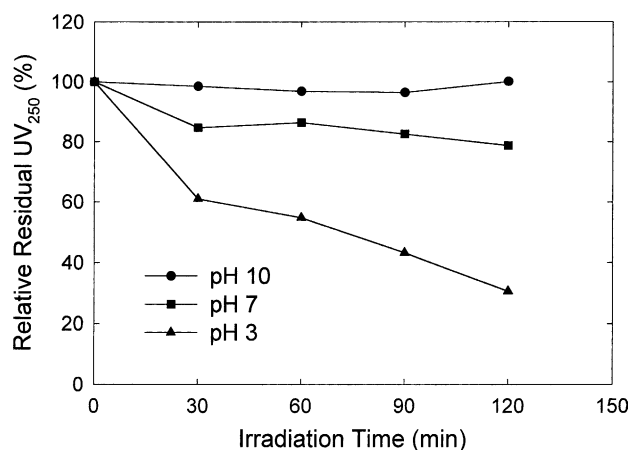
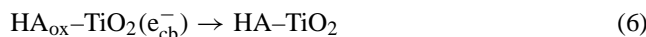
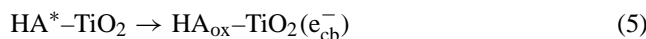
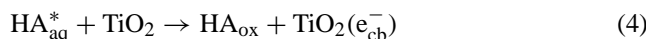


Fig. 2. Effects of pH on the UV<sub>250</sub> removal efficiency. Experimental conditions were [HA]<sub>i</sub> = 10 mg/l; [TiO<sub>2</sub>] = 0.5 g/l; λ > 420 nm.

condition for the efficient electron injection. The elementary reaction steps of HA on the TiO<sub>2</sub>/water interface can be represented by the following equations:



At pH 10 where few HAs are adsorbed on TiO<sub>2</sub>, UV<sub>250</sub> does not change at all under visible light, which implies that reaction 4 is negligible. The efficiency of the visible light-induced degradation of HAs on TiO<sub>2</sub> depends on whether the injected electrons transfer to dissolved O<sub>2</sub> (reaction 7) or recombine with HA<sub>ox</sub> (reaction 6). The back electron transfer to HA<sub>ox</sub> leads to null reaction, which significantly limits the efficiency of visible light utilization. The kinetics of the UV<sub>250</sub> decrease at pH 3 does not show the first-order behavior, which is commonly observed in other photocatalytic degradation reactions. This might be accounted for by the presence of the short circuit mechanism.

The absorption and fluorescence spectra of HA solution were recorded as a function of the visible (λ > 420 nm) or UV (λ > 300 nm) irradiation time and compared in Fig. 3. Both the absorption and fluorescence intensity of HAs gradually decreased under visible light (Fig. 3a). This confirms that the sensitized degradation of HAs in the heterogeneous system proceeded through the visible light-induced electron injection (reaction 5). The visible light absorption (or color) of HAs in TiO<sub>2</sub> suspension was almost completely

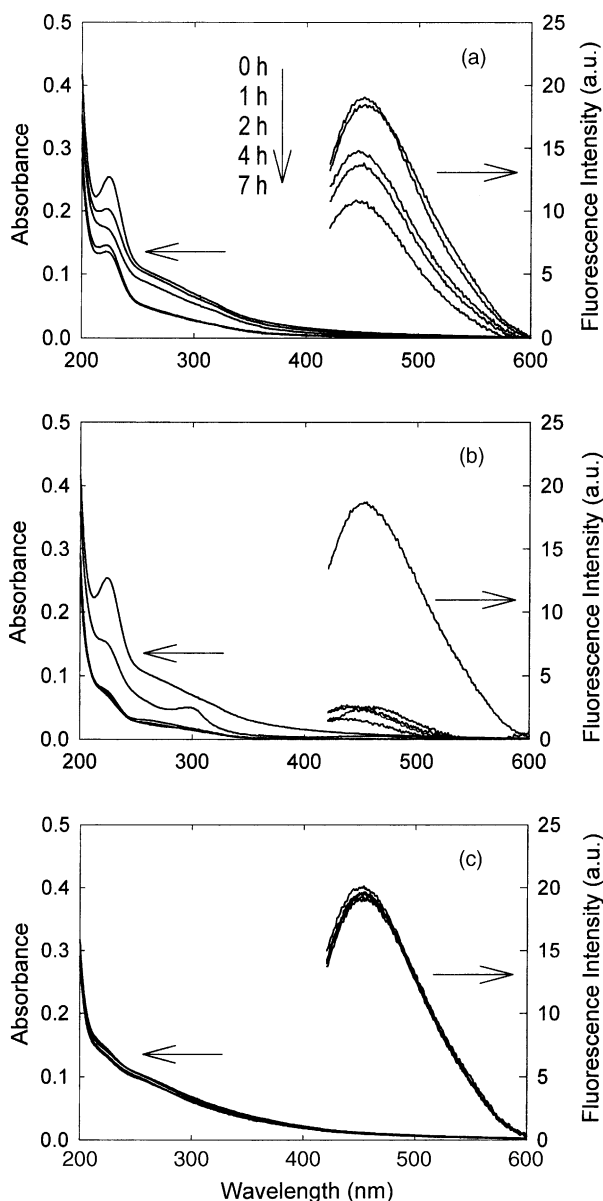


Fig. 3. UV-visible absorption and fluorescence emission (excited at  $\lambda = 350$  nm) spectra of the HAs solutions as a function of the irradiation time: (a) in the  $\text{TiO}_2$  suspension irradiated with visible light ( $\lambda > 420$  nm); (b) in the UV-illuminated  $\text{TiO}_2$  suspension; (c) visible light irradiated in the absence of  $\text{TiO}_2$ . Experimental conditions were  $[\text{HA}]_i = 10$  mg/l;  $\text{pH}_i = 3.0$ ;  $[\text{TiO}_2] = 0.5$  g/l.

depleted after 4 h irradiation and further irradiation induced little degradation. When the HA solution was irradiated with visible light in the absence of  $\text{TiO}_2$ , little change in absorption and fluorescence was observed (Fig. 3c). Although it has been demonstrated that the excited humic or fulvic acids could eject solvated electrons in the aqueous solution (reaction 8) [21,28],



its quantum yield seems to be too low to induce homogeneous oxidation of HA to a measurable extent. On the other

hand, UV illumination led to much rapid decrease of absorption and fluorescence intensity of HAs (Fig. 3b). In particular, the fluorescence intensity was drastically quenched within 1 h irradiation. Since the fluorescence is largely due to  $\pi^* \rightarrow \pi$  transitions in HA molecules, its rapid extinction under UV irradiation should be ascribed to the destruction of aromatic structures of HA. The hydroxyl radicals generated on UV-illuminated  $\text{TiO}_2$ , which are absent in the visible light-illuminated suspension, seem to be very efficient in destroying the fluorescing aromatic centers.

### 3.2. Photosensitized transformation of HAs on $\text{TiO}_2$

The effects of light irradiation on the DOC of HA solution have been investigated. Fig. 4 shows the change of DOC as a function of the irradiation time. In the UV/ $\text{TiO}_2$  system, DOC could be removed but not completely. The DOC decrease of ca. 40% was observed in 2 h but further irradiation was not effective at all in removing the remaining DOC. This indicates that part of HAs have transformed into very refractory products in the UV-illuminated  $\text{TiO}_2$  suspension. Previous studies [12,13,29] have not achieved the complete mineralization of HA in the UV/ $\text{TiO}_2$  system either. The chemical nature of the non-degradable DOC portion remains unknown. We may speculate that the reaction of OH radicals increased the portion of HAs with less hydrophobic, less adsorbing, and less aromatic characters, in general. Since the presence of dissolved natural organic matter is known to significantly change the rate and mechanism of OH radical reaction with aromatic compounds [30], the self-inhibition of HA + OH reactions by humic substances may have become important. It should be also noted that the  $\text{TiO}_2$  photocatalytic oxidation of HAs increased their biodegradability with irradiation [31].

On the other hand, visible light irradiation in the presence of  $\text{TiO}_2$  induced little change in DOC. Although the observed spectral change was the evidence of the electron

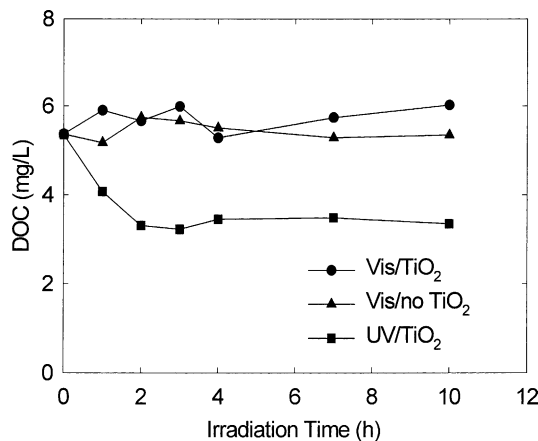
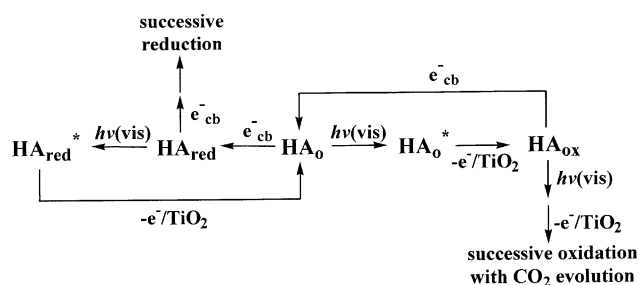
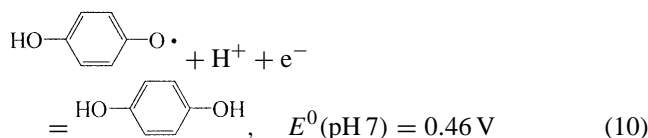
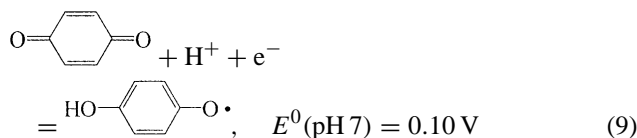


Fig. 4. DOC change of HA solutions irradiated with UV or visible light. Experimental conditions were  $[\text{HA}]_i = 10$  mg/l;  $\text{pH}_i = 3.0$ ;  $[\text{TiO}_2] = 0.5$  g/l.



Scheme 2. Sequential photoinduced electron transfers to and from TiO<sub>2</sub> CB and the accompanying transformation of HA.

transfer reactions of HAs on TiO<sub>2</sub> (Fig. 3a), they did not induce mineralization at all. Some processes that hinder the photoinduced oxidation of HAs should be present. Since HA is a macromolecule with many redox centers, a series of electron transfers may take place on TiO<sub>2</sub> surface. Scheme 2 proposes the sequential electron transfer pathways of HA on TiO<sub>2</sub>. Although the photoinduced electron-donating (oxidation) property of HA has been mainly discussed so far, the electron-accepting (reduction) property of HA should be also recognized in order to understand the overall process. Sequential electron transfers from excited HA to TiO<sub>2</sub> CB could lead to mineralization with CO<sub>2</sub> evolution while the electron transfers from CB to HA tend to inhibit the mineralization process. The electron-accepting properties of humic substances have been demonstrated in abiotic [32,33] and biotic [34] electron transfer reactions and the quinone moieties in the humic structures have been suggested to be the dominant electron acceptor. Benzoquinone (BQ) is first reduced to semiquinone (SQ) which is further reduced to hydroquinone (HQ) [35].



Since the TiO<sub>2</sub> CB edge potential is  $-0.5 \text{ V}$  at pH 7, the electron transfer from CB to BQ or SQ is thermochemically favorable. Therefore, the quinoid groups in HA molecules could be reduced by CB electrons, which significantly limits the efficiency of the photoinduced oxidation of HAs on TiO<sub>2</sub>.

In order to investigate the electron-accepting property of HAs, the visible light-induced reactions on TiO<sub>2</sub> were compared between O<sub>2</sub>- and N<sub>2</sub>-saturated suspensions. If the dissolved O<sub>2</sub> was the only electron-accepting species, the photosensitized transformation of HAs on TiO<sub>2</sub> should be negligible in the absence of O<sub>2</sub> (N<sub>2</sub>-saturated) due to the immediate recombination of injected electrons (reaction 6). However, we observed little difference between the O<sub>2</sub>- and

Table 1  
THMFP change after 2 h irradiation of HA (10 mg/l) solution

	THMFP ( $\mu\text{g CHCl}_3/\text{l}$ )	
	Before irradiation	After irradiation
UV/TiO <sub>2</sub>	117.6 $\pm$ 10.1	93.3 $\pm$ 8.8
Visible/TiO <sub>2</sub>	117.6 $\pm$ 10.1	130.0 $\pm$ 4.6
Visible/no TiO <sub>2</sub>	142.1 $\pm$ 6.1	173.2 $\pm$ 22.6

N<sub>2</sub>-saturated systems in the change of absorption and fluorescence spectra. HAs seem to be more efficient electron acceptors than the dissolved oxygen in this case.

As HAs are widely known as the principal organic precursors for THMs during chlorination process, the effects of light irradiation on the THMFP of HA solution are compared in Table 1. When HA solution was irradiated in the presence of TiO<sub>2</sub> under UV light, 20% of THMFP decreased after 2 h. On the contrary, visible light irradiation increased the THMFPs of HA solution or 10% in the presence of TiO<sub>2</sub> and by 20% in the absence of TiO<sub>2</sub>. This indicates HAs were chemically transformed in the homogeneous solution under visible light although Fig. 3c did not show such effects. The visible light effect of increasing THMFP is undesirable in view of the water treatment and should be suppressed. The photochemical transformations of HAs under visible light have many important implications also in natural water chemistry and need to be further studied in detail.

### 3.3. HA-sensitized degradation of CCl<sub>4</sub> on TiO<sub>2</sub>

We tested the ability of HA as a photosensitizer for degrading pollutants with visible light. In our previous study [19], CCl<sub>4</sub> could be reductively degraded on TiO<sub>2</sub> sensitized with ruthenium complexes under visible light irradiation, where the TiO<sub>2</sub> CB played the role of mediator that transferred electrons from the excited sensitizer to CCl<sub>4</sub>. HA could play the similar role for the ruthenium complex sensitizer. Fig. 5 compares the CCl<sub>4</sub> dechlorination in the HA-sensitized systems. No dechlorination was observed in the HA/CCl<sub>4</sub> and HA/TiO<sub>2</sub>/CCl<sub>4</sub> systems under visible light, although HA-sensitized TiO<sub>2</sub> itself could absorb the visible light as presented in Fig. 6. This shows that HA is much less efficient than the ruthenium complex as a photosensitizer. Although a few examples of HA-sensitized degradation of pollutants have been reported such as in the photosensitized degradation of microcystin in natural waters [36] and TNT transformation in the visible light-illuminated TiO<sub>2</sub> suspension [37], the HA-sensitized degradation alone was too slow to be considered as a viable remediation method. In this case of CCl<sub>4</sub> dechlorination, the photosensitization efficiency was very low due to the much slower interfacial electron transfer to CCl<sub>4</sub> (reaction 11) than the back electron transfer (reaction 6).



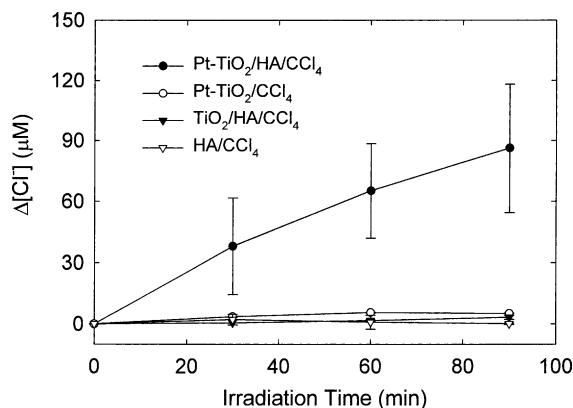


Fig. 5. Photoreductive dechlorination of  $\text{CCl}_4$  as a function of the irradiation time in the presence of HAs. The dechlorination with pure  $\text{TiO}_2$  or Pt- $\text{TiO}_2$  is compared. Experimental conditions were  $[\text{HA}]_i = 100 \text{ mg/l}$ ;  $\text{pH}_i = 3.0$ ;  $[\text{TiO}_2] = 0.5 \text{ g/l}$ ;  $\lambda > 420 \text{ nm}$ ;  $\text{N}_2$ -saturated.

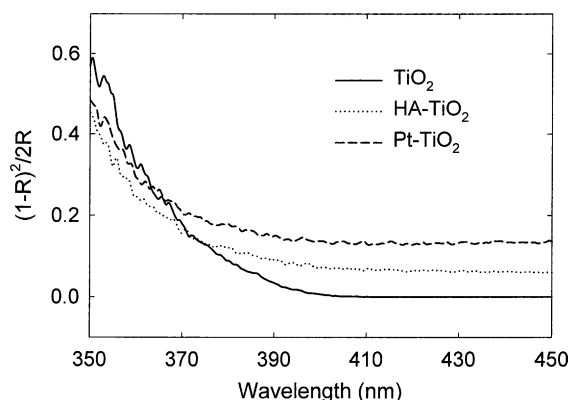


Fig. 6. UV-visible diffuse reflectance spectra of pure  $\text{TiO}_2$ , humic-sensitized  $\text{TiO}_2$ , and Pt-deposited  $\text{TiO}_2$  powders that were diluted in barium sulfate (5 wt.%). The ordinate scale is expressed in Kubelka–Munk unit ( $R$ : reflectance).

We tried to enhance the slow interfacial electron transfer rate by depositing Pt on  $\text{TiO}_2$ . Since it is well known that platinum deposits on  $\text{TiO}_2$  effectively trap CB electrons and accelerate subsequent interfacial electron transfer [38], enhanced  $\text{CCl}_4$  dechlorination (reaction 11) might be expected on Pt- $\text{TiO}_2$ . In addition, intrinsic visible light absorptivity of Pt- $\text{TiO}_2$  (see Fig. 6) might enhance  $\text{CCl}_4$  dechlorination through the increased light harvesting efficiency. Fig. 5 indeed shows a dramatically enhanced dechlorination in the Pt- $\text{TiO}_2/\text{HA}/\text{CCl}_4$  system. This confirms that Pt does play the role of electron reservoir where the subsequent electron transfer follows. However, Pt- $\text{TiO}_2$  alone induced neither  $\text{CCl}_4$  dechlorination (Fig. 5) nor DOC removal of HA solution (data not shown) under visible light.

#### 4. Conclusion

We have investigated the degradation and sensitization behaviors of HA on  $\text{TiO}_2$  under visible light irradiation. HAs

were excited by absorbing visible light and subsequently injected electrons to  $\text{TiO}_2$  CB. As a result of this photoinduced electron transfer on  $\text{TiO}_2$ , HAs were oxidized and decolorized. However, the visible light-induced reactions of HAs in the  $\text{TiO}_2$  suspension did not lead to the decrease in DOC content. Even under UV illumination, the complete mineralization of HAs could not be achieved. Having complex macromolecular structures with many redox centers, HAs seem to have both electron-donating and electron-accepting centers which shuttle electrons to and from  $\text{TiO}_2$  CB, which makes them withstand many electron transfers without undergoing mineralization. On the other hand, HA can be used as a sensitizer to degrade aquatic pollutants with visible light and  $\text{TiO}_2$ . As for  $\text{CCl}_4$  dechlorination tested in this study, HA showed significant photosensitization effect in the presence of Pt deposit on  $\text{TiO}_2$ . Platinum deposited titania could be generally used in enhancing photoefficiency of HA-sensitized reactions.

#### Acknowledgements

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#### References

- [1] F.J. Stevenson, *Humus Chemistry: Genesis, Composition, Reactions*, Wiley, New York, 1994.
- [2] S. Hesse, G. Kleiser, F.H. Frimmel, *Water Sci. Technol.* 40 (1999) 1.
- [3] H. Ødegaard, B. Eikebrokk, R. Storhaug, *Water Sci. Technol.* 40 (1999) 37.
- [4] C.R. O'melia, W.C. Becker, K.-K. Au, *Water Sci. Technol.* 40 (1999) 47.
- [5] J. Fettig, *Water Sci. Technol.* 40 (1999) 173.
- [6] S.G.J. Heijman, A.M. van Paassen, W.G.J. van der Meer, R. Hopman, *Water Sci. Technol.* 40 (1999) 183.
- [7] N.J.D. Graham, *Water Sci. Technol.* 40 (1999) 141.
- [8] P.M. Huck, *Water Sci. Technol.* 40 (1999) 149.
- [9] P. Westerhoff, G. Aiken, G. Amy, J. Debroux, *Water Res.* 33 (1999) 2265.
- [10] G. Ohlenbusch, S. Hesse, F.H. Frimmel, *Chemosphere* 37 (1998) 1557.
- [11] C.-F. Lin, Y.-J. Huang, O.J. Hao, *Water Res.* 33 (1999) 1252.
- [12] M. Bekbölet, G. Özkösem, *Water Sci. Technol.* 33 (1996) 189.
- [13] B.R. Eggins, F.L. Palmer, J.A. Byrne, *Water Res.* 31 (1997) 1223.
- [14] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [15] A. Hagfeldt, M. Grätzel, *Chem. Rev.* 93 (1995) 671.
- [16] N.J. Cherepy, G.P. Smestad, M. Grätzel, J.Z. Zhang, *J. Phys. Chem. B* 101 (1997) 9342.
- [17] A. Kay, R. Humphry-Baker, M. Grätzel, *J. Phys. Chem.* 98 (1994) 952.
- [18] B. Patrick, P.V. Kamat, *J. Phys. Chem.* 96 (1992) 1423.
- [19] Y. Cho, W. Choi, C.-H. Lee, T. Hyeon, H.-I. Lee, *Environ. Sci. Technol.* 35 (2001) 966.
- [20] R.G. Zepp, N.L. Wolfe, G.L. Baughman, R.C. Hollis, *Nature* 267 (1977) 421.
- [21] K. Vinodgopal, P.V. Kamat, *Environ. Sci. Technol.* 26 (1992) 1963.
- [22] K. Vinodgopal, *Res. Chem. Intermed.* 20 (1994) 825.

- [23] E. Selli, V. Eliet, M.R. Spini, G. Bidogli, *Environ. Sci. Technol.* 34 (2000) 3742.
- [24] E. Selli, A.D. Giorgi, G. Bidoglio, *Environ. Sci. Technol.* 30 (1996) 598.
- [25] M.A.H. Franson (Ed.), *Standard Methods for the Examination of Water and Wastewater*, United Book Press, Baltimore, 1998, part 6–36.
- [26] B. Gu, J. Schmitt, Z. Chen, L. Liang, J.F. McCarthy, *Environ. Sci. Technol.* 28 (1994) 38.
- [27] S.T. Martin, J.M. Kesselman, D.S. Park, N.S. Lewis, M.R. Hoffmann, *Environ. Sci. Technol.* 30 (1996) 2535.
- [28] R.G. Zepp, A.M. Braun, J. Hoigne, J.A. Leenheer, *Environ. Sci. Technol.* 21 (1987) 485.
- [29] S.-A. Lee, K.-H. Choo, C.-H. Lee, H.-I. Lee, T. Hyeon, W. Choi, H.-H. Kwon, *Ind. Eng. Chem. Res.* 40 (2001) 1712.
- [30] M.E. Lindsey, M.A. Tarr, *Environ. Sci. Technol.* 34 (2000) 444.
- [31] M. Bekbölet, F. Ceçen, G. Özkösem, *Water Sci. Technol.* 34 (1996) 65.
- [32] F. Durnivant, R. Schwarzenbach, D. Macalady, *Environ. Sci. Technol.* 26 (1992) 2133.
- [33] G. Curtis, M. Reinhard, *Environ. Sci. Technol.* 28 (1994) 2393.
- [34] D.T. Scott, D.M. McKnight, E.L. Blunt-Harris, S.E. Kolesar, D.R. Lovley, *Environ. Sci. Technol.* 32 (1998) 2984.
- [35] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, *Environmental Organic Chemistry*, Wiley, New York, 1993 (Chapter 12).
- [36] M. Welker, C. Steinberg, *Environ. Sci. Technol.* 34 (2000) 3415.
- [37] D.C. Schmelling, K.A. Gray, P.V. Kamat, *Water Res.* 31 (1997) 1439.
- [38] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, *Water Res.* 33 (1999) 661.