Water Science & Technology

Photodegradation of Pb-3,4-dihydroxybenzoic acid complex under UV light illumination

Xuefeng Hu and Wei Qin

ABSTRACT

The degradation of 3,4-dihydroxybenzoic acid (3,4-DHBA) in the presence and absence of Pb^{2+} under UV illumination was studied. Addition of Pb^{2+} caused the formation of precipitate during photoreaction when the solution pH was higher than 6. The presence of Pb^{2+} remarkably inhibited the degradation of 3,4-DHBA and its photodegradation intermediates, while complexation of 3,4-DHBA and its photodegradation intermediates with Pb^{2+} decreased the free Pb^{2+} in aqueous solutions. Molecular oxygen played an important role in photodegradation of 3,4-DHBA in the presence of Pb^{2+}. UV–Vis spectroscopy was used to investigate the interaction between Pb^{2+} and 3,4-DHBA at different pH conditions, and FT-IR was used to characterize the precipitate formed during photoreaction. The mineralization of 3,4-DHBA was investigate by total organic carbon analysis.

Key words | 3,4-dihydroxybenzoic acid, Pb^{2+} complex, photodegradation, precipitate

Xuefeng Hu (corresponding author)
Wei Qin
Key Laboratory of Coastal Zone Environmental
  Processes, CAS;
Shandong Provincial Key Laboratory of Coastal
  Zone Environmental Processes,
Yantai Institute of Coastal Zone Research,
Chinese Academy of Sciences,
Yantai, 264003,
China
E-mail: xfhu@yic.ac.cn

INTRODUCTION

Pb^{2+} and its metallic compounds are toxic substances widely used in various industries especially in the production of automotive and industrial lead–acid batteries. These metallic species can be found in wastewaters from such industrial effluents. If automobile components and electronic equipment containing lead are disposed of improperly, it may also cause water pollution because lead is easily dissolved by acid rain (Jang & Townsend 2003). However, the total lead concentration is not the only factor that governs its environmental impact. Dissolved organic matter (DOM) has a profound impact on the chemistry of natural waters (Toro *et al.* 2001; Bejarano *et al.* 2005). The toxicity of metal ions to aquatic organisms is alleviated by precipitation and complexation with DOM (Schwartz *et al.* 2004; Jiraroj *et al.* 2006; Ytreberg *et al.* 2011). Some functional groups on DOM have a high affinity for trace metals, and DOM may therefore strongly affect the mobility of trace metals in aquatic systems (Baken *et al.* 2011). Among the large variety of environmental pollutants, aromatic compounds occupy an important place due to their toxicities and unusual stability. Catechol and its derivatives are important intermediates in the photo-degradation of benzene and its derivatives because OH radicals attack the aromatic ring before the latter is cleaved (Yawalkar *et al.* 2001; Chen *et al.* 2002). The two hydroxyl groups of catechol and its

derivatives lead to strong adsorption on metal ions. Metal binding by humic substances mostly occurs at carboxylic and phenolic sites (Baken *et al.* 2011). How the metal ions are complexed and how they can transfer are very important questions, particularly with regard to bioavailability and cycling.

Transformations of DOM play important roles in a number of reactions in surface waters and wastewater treatment under photoillumination. In these reactions, DOM acting as light absorbing substances can cause photochemical transformation either directly or indirectly by generating highly reactive intermediates (e.g. organic radicals) and reactive oxygen species (e.g. singlet oxygen, hydrogen peroxide, hydroxyl radicals, and superoxide) (Golimowski & Golimowska 1996; Zhang *et al.* 1998; Puma *et al.* 2008). Some studies have reported on the phototransformation of the photoreactive metals (e.g. iron, mercury) and organic compound complexes (Voelker *et al.* 1997; Lalonde *et al.* 2001; Dai *et al.* 2011). However, the investigation of phototransformation of non-photoreactive metals and organic compound complexes has seldom been reported in the literature (Jiraroj *et al.* 2006). The photochemical transformation will change the metal complexation with organic compounds and the metal toxicity. However, the photochemical transformation of

DOM and metals is complicated and has been poorly understood so far.

In this paper, Pb^{2+} and 3,4-dihydroxybenzoic acid (3,4-DHBA) were used as model pollutants to investigate their photochemical transformation under UV light illumination. This research is useful for assessing and predicting the transport, transformation, and bioavailability of the Pb^{2+} and DOM coexisting system in natural and wastewaters.

METHODS

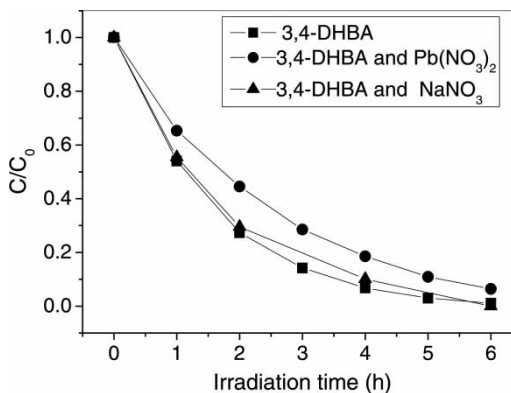3,4-Dihydroxybenzoic acid, $Pb(NO_3)_2$, and $NaNO_3$ were of analytical reagent grade and used without further purification; 0.2 mol/L HAc–NaAc buffer solutions were used as the supporting electrolyte for free Pb^{2+} determination. The initial pH of each solution was adjusted by diluted NaOH and HNO_3 aqueous solutions. Deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout. UV light was provided by PLS-SXE300UV xenon light source. A UVREF filter was used to keep the solution illuminated by light at 250–380 nm UV light. All photoreactions were carried out in a 50 mL quartz reactor. UV–Vis spectra were measured on a Beckman DU-800 UV spectrophotometer. The photodegradation of 3,4-DHBA was analyzed by Agilent 1,200 high performance liquid chromatography (HPLC) on a C18 5 μm column (250×4.6 mm) at 30 °C. Signals were detected at 256 nm by using an eluent composed of 2‰ H_3PO_4 aqueous solution/acetonitrile solution (95/5) at a flow rate of 1.0 mL/min. The samples were centrifuged, and then filtered through a Millipore filter (pore size 0.2 μm) to remove the insoluble substances. Changes in total organic carbon (TOC) were determined using a total organic carbon analyzer (Shimadzu TOC 5000). Solutions containing suspended precipitate were determined directly. Lead concentration was measured using the differential pulse anodic stripping voltammetry (DPASV) method on a CHI 660C Electrochemical Workstation. A glassy carbon (GC) disk working electrode was used as the working electrode. A platinum foil was applied as the counter electrode, and a saturated calomel electrode (SCE) served as the reference electrode. FT-IR spectra in KBr pellets were recorded on a Jasco-4100 spectrometer. Pb^{2+} and 3,4-DHBA complex solid sample was obtained by freeze-drying its aqueous solution. The precipitate sample was separated by centrifuging, washed three times with deionized water, and then dried under vacuum for 24 h.

RESULTS AND DISCUSSION

Interaction of Pb^{2+} and 3,4-DHBA under UV Illumination

Although 3,4-DHBA was not oxidized in the dark during the control experiment period (12 h), it was significantly degraded under UV light illumination, as shown in Figure 1. In the presence of $Pb(NO_3)_2$, 3,4-dihydroxybenzoic acid can also undergo photodegradation but with a decreased degradation rate. It is well known that NO_3^- can absorb UV light and induce photoreaction of organic compounds (Vione et al. 2002; Yu et al. 2008). Complexation of Pb^{2+} with catechol derivatives results in an enhancement of semiquinone radical stabilization at pH > 4 (Giannakopoulos et al. 2005). Both Pb^{2+} and NO_3^- are possible to change the photodegradation rate of 3,4-DHBA under experimental conditions. To make clear which (Pb^{2+} or NO_3^-) caused the photodegradation rate change, $NaNO_3$ was added to the reaction solution of 3,4-DHBA. No significant difference was observed in the presence or absence of 2×10^{-4} mol/L $NaNO_3$, indicating that NO_3^- in this low concentration did not change 3,4-DHBA degradation rate, but the complexation with Pb^{2+} decreased it.

The reaction components of 3,4-DHBA and 3,4-DHBA/$NaNO_3$ were soluble during the full reaction period. However, yellow turbidity developed slowly as the reaction proceeded and precipitate was formed after standing for a long time in the 3,4-DHBA/Pb^{2+} system, although it was soluble before photoreaction. The precipitate should be related to Pb^{2+} because it was formed only in the presence of $Pb(NO_3)_2$. To confirm this, differential pulse amperometry was used to measure the concentration of Pb^{2+}. DPASV measures voltammetrically labile lead, which consists of
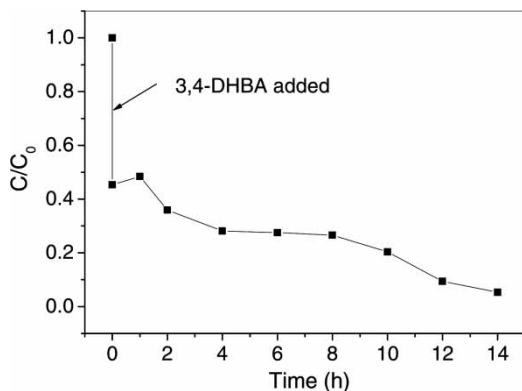

Figure 1 │ Effects of $Pb(NO_3)_2$ and $NaNO_3$ on the photodegradation of 3,4-DHBA at pH 6. The initial concentrations of $Pb(NO_3)_2$, $NaNO_3$ and 3,4-dihydroxybenzoic acid are 2×10^{-4} mol/L.
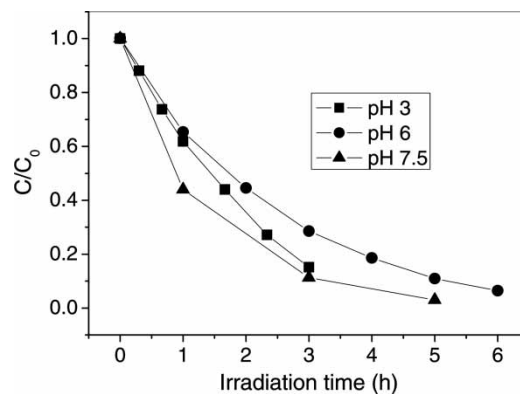
the free lead ions plus the lead complexes that dissociate within the timescale of the experiment (Oomen *et al.* 2003). The complexation of 3,4-DHBA with Pb^{2+} leads to the concentration of Pb^{2+}, which can be detected by DPASV method, decreasing ca. 50% after 3,4-DHBA was added, as shown in Figure 2. Photodegradation of 3,4-DHBA intends to release Pb^{2+} from its complex, however, the voltammetrically labile lead decreased as the photoreaction proceeded. This was attributed to the fact that the new formed lead complex during photodegradation cannot be detected by the DPASV method. The bioavailability of metal in synthetic media appears to be controlled by the free metal ion concentration, as predicted by the free ion activity model (Hudson 2005; Ytreberg *et al.* 2011). The DPASV data indicated the bioavailable Pb^{2+} decreased due to the complexation of 3,4-DHBA and the photoreaction. This is a possible route for the alleviation of lead toxicity in aquatic organisms in natural waters.

Influence of initial solution pH

To investigate the effect of initial solution pH on the Pb^{2+}/3,4-DHBA photoreaction, illuminations of solutions at various pHs were carried out, as depicted in Figure 3. Degradation rate at pH 3 is higher than that at pH 6. Addition of Pb^{2+} caused no significant change at pH 3 as shown in Figure 4, which indicated that Pb^{2+} had no or a rather weak interaction with 3,4-DHBA at this pH value, so that the organic substance underwent degradation quickly. The UV–Vis absorption spectrum of 3,4-DHBA at pH 6 shifted toward longer wavelengths when Pb^{2+} was added because the electron transferred from 3,4-DHBA to Pb^{2+}. The further increase of pH value facilitates the electron transfer and the

Figure 3 │ Effect of the initial solution pH on Pb^{2+}/3,4-DHBA photoreaction. The initial concentrations of $Pb(NO_3)_2$ and 3,4-dihydroxybenzoic acid were 2×10^{-4} mol/L.
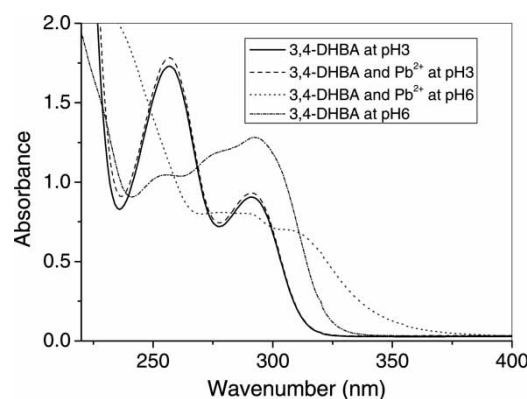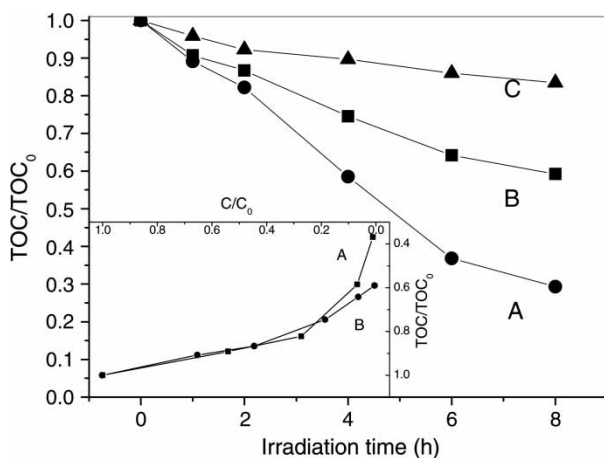

Figure 4 │ UV–Vis spectra of 3,4-DHBA and its complex with Pb^{2+} at different pHs. The concentrations of $Pb(NO_3)_2$ and 3,4-dihydroxybenzoic acid are 2×10^{-4} mol/L.

Figure 2 │ Pb^{2+} changes during 3,4-DHBA complexation and photoreaction measured by DSPASV. The initial concentrations of $Pb(NO_3)_2$ and 3,4-dihydroxybenzoic acid are 2×10^{-4} mol/L.

self-oxidation of 3,4-DHBA in the presence of oxygen (Giannakopoulos *et al.* 2005; Sun *et al.* 2009), thus increasing the degradation rate at pH 7.5. The reaction solution remained clear during photoreaction at pH 3. However, we observed evident yellow turbidity during photoreaction and precipitation after the solution stood for 12 h at pH 6 and pH 7.5. The amount of precipitate at pH 7.5 was much more than that at pH 6, indicating that the high pH value is favorable for the formation of precipitate. The initial pH 3 and pH 6 samples were kept at pH 3 and pH 5–6 during photoreaction, respectively. In the low pH case, the degradation intermediates (carboxylic acids, as shown below) were in non-ionized form, Pb^{2+} was difficult to complex with them. However, in the high pH case, Pb^{2+} was complexed by the ionized degradation intermediates directly or displacing H^+ from the protonated degradation intermediates.

Total organic carbon changes

The decrease of solution TOC reflects the mineralization of 3,4-hydroxybenzoic acid. Temporal TOC changes of 3,4-dihydroxybenzoic acid under UV light illumination in different reaction conditions are depicted in Figure 5. In the 3,4-dihydroxybenzoic acid case, 70% TOC was removed quickly within 8 h (curve A). However, TOC elimination decreased to 40% when Pb^{2+} existed together with 3,4-dihydroxybenzoic acid (curve B) during the same reaction time. The C/C_0 (3,4-DHBA) $\sim$ TOC/TOC$_0$ (solution) curves in the absence and presence of Pb^{2+} are shown in the inset. TOC removal is similar in the presence and absence of Pb^{2+} when the same amount of 3,4-DHBA degraded at the initial photoreaction stage. However, the TOC removal quickly increased in the absence of Pb^{2+} case when above 70% of the 3,4-DHBA was degraded. This indicates that Pb^{2+} interacts not only with 3,4-dihydroxybenzoic acid but also with its photodegradation intermediates. The newly formed insoluble substance was difficult to degrade under UV illumination, which was suspended in the solution even after 20 h photoreaction. It can be proposed that the precipitate should be the complex of Pb^{2+} and organic compounds, which are difficult to photodegrade, thus decreasing the mineralization rate of the reaction solution. Only ca. 17% TOC decrease was observed in the Pb^{2+} and 3,4-dihydroxybenzoic acid combined system in an N_2 atmosphere. It is apparent that O_2 is essential for the mineralization reaction of 3,4-dihydroxybenzoic acid in the presence of Pb^{2+}.

Influence of oxygen

Oxygen as an electron acceptor during organic photodegradation plays an important role in the formation of reactive oxygen species (e.g. singlet oxygen, hydroxyl radicals, and superoxide), which can induce the organic transformation. The direct formation of singlet oxygen and superoxide from oxygen will be inhibited in an N_2 atmosphere. It has been reported that highly reactive organic oxidant, hydroxyl radical, can be generated directly by the redox cycling of quinone (Alegría *et al.* 1997; Gómez-Toribio *et al.* 2009). Pb^{2+}/3,4-DHBA complex shows stable semiquinone radical as illustrated by ESR signals (Giannakopoulos *et al.* 2005). Semiquinone radical is the intermediate of quinone redox cycling (Scott *et al.* 1998). Hydroxyl radical is possibly formed from Pb^{2+} and 3,4-DHBA complex in the present work. The photodegradation of 3,4-DHBA solution in an N_2 atmosphere was observed but with a slower rate than that in air atmosphere as shown in Figure 6. These results show that hydroxyl radicals derived from 3,4-DHBA redox played key roles in the photodegradation of 3,4-DHBA and its degradation intermediates. Oxygen and its related reactive species also enhanced the photodegradation of 3,4-DHBA. C/C_0 (3,4-DHBA) $\sim$ TOC/TOC$_0$ (solution) curves shown in the inset indicate that the photodegradation of 3,4-DHBA degradation intermediates can also be inhibited in the absence of oxygen. Oxygen and its related
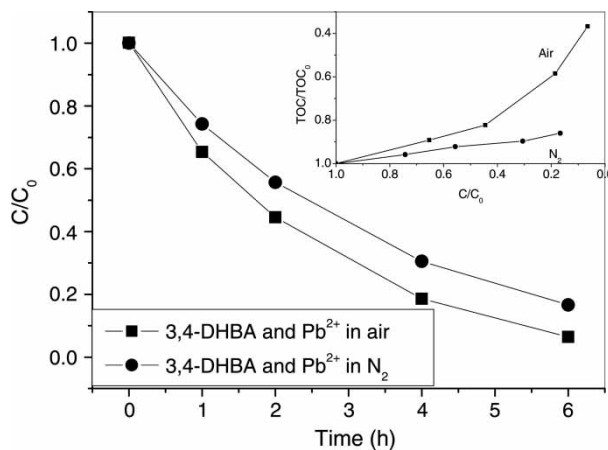

Figure 5 | TOC changes of (A) 3,4-dihydroxybenzoic acid solution in air atmosphere, (B) 3,4-dihydroxybenzoic acid solution in the presence of Pb^{2+} in air atmosphere and (C) 3,4-dihydroxybenzoic acid solution in the presence of Pb^{2+} in N_2 atmosphere under UV light illumination. Inset: C/C_0 (3,4-DHBA) $\sim$ TOC/TOC$_0$ (solution) in the (A) absence and (B) presence of Pb^{2+} during photoreaction. Both the initial concentrations of Pb^{2+} and 3,4-dihydroxybenzoic acid are 2×10^{-4} mol/L in all experiments.

Figure 6 | Effect of oxygen on Pb^{2+}/3,4-DHBA photoreaction. Inset: C/C_0 (3,4-DHBA) $\sim$ TOC/TOC$_0$ (solution) in air and N_2 atmosphere in presence of Pb^{2+} as the photoreaction proceeds. Both the initial concentrations of Pb^{2+} and 3,4-dihydroxybenzoic acid are 2×10^{-4} mol/L.

reactive species are crucial to the mineralization rates of 3,4-DHBA.

FT-IR of 3,4-DHBA complex and insoluble substance

Phenol derivatives usually mineralize to CO_2 with carboxylic acid and dicarboxylic acid as intermediates during UV light oxidation. Theoretically, in the presence of free lead at concentrations of higher than 0.14 mmol/L, lead will probably precipitate as its hydroxide ($K_{sp} = 1.43 \times 10^{-20}$) (Weast 1998) at pH 6. The solution of 2×10^{-4} mol/L Pb^{2+} and 3,4-DHBA at pH 6 remains soluble in water in the present study, implying that the complexation with 3,4-DHBA improves the solubility of lead. However, complexation with dicarboxylic acid may form an insoluble Pb^{2+} complex (e.g. lead oxalate, $K_{sp} = 8.51 \times 10^{-10}$) (Lide 2003) in water. The precipitate formed during photoreaction might be insoluble Pb^{2+}-organic complex or lead hydroxide. Figure 7 shows FT-IR spectra of Pb^{2+} and 3,4-DHBA complex (A) before and (B) after 8 h UV illumination. The most intense bands of (A) at 1,623, 1,574 and 1,380 cm^{-1} are assigned to carboxylate vibrations, 1,450–1,550 cm^{-1} and 600–900 cm^{-1} are assigned to the C–C ring vibration and the C–H vibration of substituted benzene ring respectively, and 1,270 cm^{-1} is assigned to the C–O vibration of phenolic group (Giannakopoulos *et al.* 2005; Guan *et al.* 2006). For the insoluble substance, however, benzene ring and phenolic group absorption bands disappeared and absorption bands of carboxylate vibrations changed to 1,647, 1,523, and 1,394 cm^{-1}. The intense absorption bands at 970–1,200 cm^{-1} suggest the formation of aliphatic compounds containing hydroxyl group. The spectra provide evidence that the benzene ring is opened, and aliphatic carboxyl acid and hydroxyl aliphatic compounds are formed during UV illumination. The complex
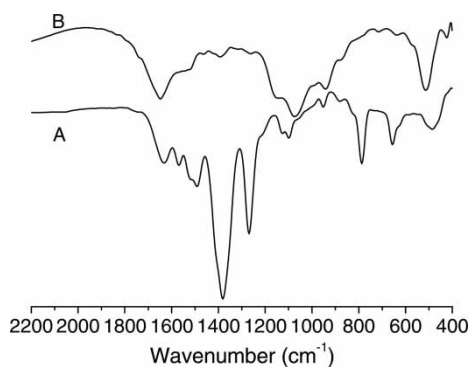
formed from aliphatic compounds with lead is not soluble in water. From the C/C_0 (3,4-DHBA) ~ TOC/TOC_0 (solution) curves in Figure 5 and the existence of the insoluble substance even after 20-hour photoreaction, it can be concluded that the formed insoluble complex of aliphatic compounds with lead is difficult to photodegrade under the experimental conditions.

CONCLUSIONS

In our investigation, Photodegradation and mineralization of 3,4-DHBA can be inhibited in the presence of Pb^{2+}. The results from UV–Vis absorption spectra showed that 3,4-DHBA complexed with Pb^{2+} while the electron transferred from 3,4-DHBA to Pb^{2+} at pH 6. Hydroxyl radicals play a key role in the degradation and mineralization of 3,4-DHBA, while the existence of oxygen enhances the degradation and mineralization rates. Formation of insoluble substance in aqueous solution was observed when the initial solution pH was higher than 6. FT-IR and DSPASV were used to study the composition of insoluble substance and the free Pb^{2+} concentration respectively. Based on the free Pb^{2+} concentration decrease in the solution and the FT-IR signals of the insoluble substance, it was proposed that the insoluble substance was the complex of photodegradation intermediates of 3,4-DHBA and lead. This research is useful for assessing and predicting the transport, transformation, and bioavailability in the heavy metal and DOM coexistent wastewater system.

Figure 7 | FT-IR spectra of (A) Pb^{2+} and 3,4-DHBA complex and (B) insoluble substance formed during UV illumination of Pb^{2+} and 3,4-DHBA complex.

REFERENCES

Alegría, A. E., Ferrer, A. & Sepúlveda, E. 1997 Photochemistry of water-soluble quinones. Production of a water-derived spin adduct. *Photochem. Photobiol.* **66**, 436–442.

Baken, S., Degryse, F., Verheyen, L., Merckx, R. & Smolders, E. 2011 Metal complexation properties of freshwater dissolved

organic matter are explained by its aromaticity and by anthropogenic ligands. *Environ. Sci. Technol.* **45**, 2584–2590.

Bejarano, A. C., Chandler, G. T. & Decho, A. W. 2005 Influence of natural dissolved organic matter (DOM) on acute and chronic toxicity of the pesticides chlorothalonil, chlorpyrifos and fipronil on the meiobenthic estuarine copepod *Amphiascus tenuiremis*. *J. Exp. Mar. Biol. Ecol.* **321**, 43–57.

Chen, J., Eberlein, L. & Langford, C. H. 2002 Pathways of phenol and benzene photooxidation using TiO_2 supported on a zeolite. *J. Photochem. Photobiol. A: Chem.* **148**, 183–189.

Dai, R. N., Yu, C., Gou, J., Lan, Y. Q. & Mao, J. D. 2011 Photoredox pathways of Cr(III)-tartrate complexes and their impacting factors. *J. Hazard. Mater.* **186**, 2110–2116.

Di Toro, D. M., Allen, H., Bergman, H. L., Meyer, J. S., Paquin, P. R. & Santore, R. C. 2001 Biotic ligand model of the acute toxicity of metals. 1. Technical Basis. *Environ. Toxical. Chem.* **20**, 2383–2396.

Giannakopoulos, E., Christoforidis, K. C., Tsipis, A., Jerzykiewicz, M. & Deligiannakis, Y. 2005 Influence of Pb(II) on the radical properties of humic substances and model compounds. *J. Phys. Chem. A* **109**, 2223–2232.

Golimowski, J. & Golimowska, K. 1996 UV-photooxidation as pretreatment step in inorganic analysis of environmental samples. *Anal. Chim. Acta* **325**, 111–133.

Gómez-Toribio, V., García-Martín, A. B., Martínez, M. J., Martínez, Á. T. & Guillén, F. 2009 Enhancing the production of hydroxyl radicals by pleurotus eryngii via quinone redox cycling for pollutant removal. *Appl. Environ. Microbiol.* **75**, 3954–3962.

Guan, X. H., Shang, C. & Chen, G. H. 2006 ATR-FTIR investigation of the role of phenolic groups in the interaction of some NOM model compounds with aluminum hydroxide. *Chemosphere* **65**, 2074–2081.

Hudson, R. J. M. 2005 Trace metal uptake, natural organic matter, and the free-ion model. *J. Phycol.* **41**, 1–4.

Jang, Y. C. & Townsend, T. G. 2003 Leaching of lead from computer printed wire boards and cathode ray tubes by municipal solid waste landfill leachate. *Environ. Sci. Technol.* **37**, 4778–4784.

Jiraroj, D., Unob, F. & Hagege, A. 2006 Degradation of Pb-EDTA complex by a H_2O_2/UV process. *Water Res.* **40**, 107–112.

Lalonde, J. D., Amyot, M., Kraepiel, A. M. L. & Morel, F. M. M. 2001 Photooxidation of Hg(0) in artificial and natural waters. *Environ. Sci. Technol.* **35**, 1367–1372.

Lide, D. R. 2003 *Handbook of Chemistry and Physics*, 84th edition. CRC Press LLC, FL.

Oomen, A. G., Tolls, J., Sips, A. J. A. M. & Van den Hoop, M. A. G. T. 2003 Lead Speciation in artificial human digestive fluid. *Arch. Environ. Contam. Toxicol.* **44**, 107–115.

Puma, G. L., Bono, A., Krishnaiah, D. & Collin, J. G. 2008 Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor deposition: a review paper. *J. Hazard. Mater.* **157**, 209–219.

Schwartz, M. L., Curtis, P. J. & Playle, R. C. 2004 Influence of natural organic matter source on acute copper, lead, and cadmium toxicity to rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* **23**, 2889–2899.

Scott, D. T., McKnight, D. M., Blunt-Harris, E. L., Kolesar, S. E. & Lovley, D. R. 1998 Quinone moieties act as electron acceptors in the reduction of humic substances by humics-reducing microorganisms. *Environ. Sci. Technol.* **32**, 2984–2989.

Sun, W., Jiang, Q., Xi, M. Y. & Jiao, K. 2009 Determination of 3,4-dihydroxybenzoic acid by electrocatalytic oxidation at an ionic liquid modified electrode. *Microchim. Acta* **166**, 343–348.

Vione, D., Maurino, V., Minero, C. & Pelizzetti, E. 2002 New processes in the environmental chemistry of nitrite: nitration of phenol upon nitrite photoinduced oxidation. *Environ. Sci. Technol.* **36**, 669–676.

Voelker, B. M., Morel, F. M. M. & Sulzberger, B. 1997 Iron redox cycling in surface waters: effects of humic substances and light. *Environ. Sci. Technol.* **31**, 1004–1011.

Weast, R. C. 1998 *Handbook of Chemistry and Physics*, 1st student edition. CRC Press Inc., FL.

Yawalkar, A. A., Bhatkhande, D. S., Pangarkar, V. G. & Beenackers, A. A. 2001 Solar-assisted photochemical and photocatalytic degradation of phenol. *J. Chem. Technol. Biotechnol.* **76**, 363–370.

Ytreberg, E., Karlsson, J., Hoppe, S., Eklund, B. & Ndungu, K. 2011 Effect of organic complexation on copper accumulation and toxicity to the estuarine red macroalga ceramium tenuicorne: a test of the free ion activity model. *Environ. Sci. Technol.* **45**, 3145–3153.

Yu, Y., Ezell, M. J., Zelenyuk, A., Imre, D., Alexander, L., Ortega, J., Thomas, J. L., Gogna, K., Tobias, D. J., D'Anna, B., Harmon, C. W., Johnson, S. N. & Finlayson-Pitts, B. J. 2008 Nitrate ion photochemistry at interfaces; a new mechanism for oxidation of a-pinene. *Phys. Chem. Chem. Phys.* **10**, 3063–3071.

Zhang, F. L., Zhao, J. C., Shen, T., Hidaka, H., Pelizzetti, E. & Serpone, N. 1998 TiO_2-assisted photodegradation of dye pollutants II. Adsorption and degradation kinetics of eosin in TiO_2 dispersions under visible light irradiation. *Appl. Catal. B: Environ.* **15**, 147–156.