



Photo-induced transformations of Hg(II) species in the presence of *Nitzschia hantzschiana*, ferric ion, and humic acid

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Abstract

Effects of algae *Nitzschia hantzschiana*, Fe(III) ions, humic acid, and pH on the photochemical reduction of Hg(II) using the irradiation of metal halide lamps ($\lambda \geq 365$ nm, 250 W) were investigated. The photoreduction rate of Hg(II) was found to increase with increasing concentrations of algae, Fe(III) ions, and humic acid. Alteration of pH value affected the photoreduction of Hg(II) in aqueous solution with or without algae. The photoreduction rate of Hg(II) decreased with increasing initial Hg(II) concentration in aqueous solution in the presence of algae. The photochemical kinetics of initial Hg(II) and algae concentrations on the photoreduction of Hg(II) were studied at pH 7.0. The study on the total Hg mass balance in terms of photochemical process revealed that more than 42% of Hg(II) from the algal suspension was reduced to volatile metallic Hg under the conditions investigated.

Key words: photoreduction; *Nitzschia hantzschiana*; Hg(II); Fe(III); humic acid

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Introduction

Mercury is a toxic element and has no known essential biological function (Allen, 1994). However, unlike many organic pollutants, Hg or its compounds can be changed from one form to another within chemical reactions. These reactions can result in the formation of more toxic Hg species such as methyl mercury formed in the biological or abiotic methylation processes of inorganic mercury in natural environment (Rudd, 1995; Zuo and Pang, 1985; Celso et al., 2006; Siciliano et al., 2002). Mercury research also suggests that the more recent Hg occurrences in many regions result from atmospheric deposition of Hg from anthropogenic and natural sources through long-distance atmospheric transport (Poissant et al., 2000; Schroeder and Munthe, 1998). Once deposited in natural waters, Hg undergoes an aquatic redox cycling between oxidized mercury (Hg(II)), and elemental mercury (Hg(0)). Among the Hg(II) pool are toxic, bioaccumulative CH_3Hg^+ and $(\text{CH}_3)_2\text{Hg}$, and inorganic Hg(II) species, while Hg(0) dominates dissolved gaseous mercury (DGM) in freshwater (Schroeder and Munthe, 1998; Vandal et al., 1991), which is subject to evasion back to the atmosphere (Fitzgerald et al., 1991). Elemental Hg is the main volatile form of Hg in natural waters (Mason and Fitzgerald, 1990; Mason et al., 1993). The formation of volatile dissolved mercury favors the removal of Hg from lakes and ocean through gas evasion. On a local scale, this may be significant

in the regulation of Hg accumulation in aquatic wildlife by decreasing the Hg burden in the water column at a given site and by limiting the amount of Hg available for methylation and bioaccumulation. On a global scale, Hg(0) evasion from the ocean surface constitutes a significant part of the global Hg cycle, accounting for about 40% of the current total flux of Hg(0) to the atmosphere (Mason and Sheu, 2002). It is therefore important to understand the processes leading to the formation of dissolved Hg(0).

The diel changes of DGM have been observed in natural freshwater, e.g., the Everglades, FL, USA (Zhang and Lindberg, 2000; Lindberg et al., 2000; Krabbenhoft et al., 1998) and Lake Superior, MI, USA (Vette, 1998; Zhang and Lindberg, 2002). These findings implicate an intrinsic role of sunlight in controlling aquatic DGM dynamics. Recent researches of sunlight incubations of northern lake water in Teflon bottles further suggested that sunlight-induced photochemical reduction of Hg(II) in freshwater can induce the natural production of DGM (Amyot et al., 1994, 1997a, 1997b). Because the competition between the sunlight-driven pathway and the methylation pathway would reduce Hg toxic hazards in local aquatic ecosystems through removal of Hg(II) as a result of its reduction to Hg(0) and its subsequent evasion. Although the last decades witnessed the increasing efforts on the observations of sunlight-induced aquatic production of DGM in both northern and southern aquatic systems (Vette, 1998; Lindberg et al., 1999), the fundamental understanding of such phenomena still remains interesting but yet

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challenging. The volatilization rate of Hg is controlled by the rate of the formation of Hg(0) which is relative to the biotic and abiotic processes of Hg(II). The abiotic reduction of Hg(II) to Hg(0) in water can be initiated by humic substances (Alberts et al., 1974). For instance, Turner et al. (1989) suggested that the abiotic reduction could account for as much as 10%–70% of the volatile Hg released from some contaminated streams. It is assumed that intermediates such as semiquinones present in humic substances, are involved in this case. As such, it is also indicated that the rate of such abiotic reduction can be photochemically enhanced under laboratory conditions (Allard and Arsenie, 1991). Among the abiotic photochemical pathways involved, Schroeder et al. (1991) have suggested that H₂O₂, mainly originating from UV-induced transformations of dissolved organic matter in surface waters (Cooper et al., 1994), could act as a reducing or oxidizing agent for the Hg-based evolution, depending on the pH. Some biotic processes leading to the reduction of Hg(II) have also been identified in the literature. The primary Hg-detoxifying mechanism in the case of Hg-resistant bacteria was explained as the reduction of mercuric ion to volatile Hg(0) (Steffan et al., 1988). Photosynthesis may produce the reductants of Hg(II) (Ben-Bassat and Mayer, 1975, 1978), and the increased rates for producing metallic Hg(0) have been observed during the course of algal blooms (Siciliano et al., 2002; Poulain et al., 2004; Deng et al., 2008).

Although photochemical and/or photobiological processes are considered as one of the most important factors to affect the rate of volatile Hg producing in lake water, little research work has been reported on the reduction of Hg(II) in the system containing algal complexes. This article would focus on the photoreduction of Hg(II) in the presence of algal complexes under the irradiation of metal halide lamps. The mechanisms involved in this study may also explain the observed photochemical production of DGM in the sunlit natural freshwaters (Zhang and Lindberg, 1999), since algae are commonly present in natural aquatic systems. This research will be helpful for understanding the photochemical transformation of Hg(II) and the formation of DGM in natural water in the presence of algal complexes.

1 Experimental

1.1 Chemicals and reagents

HNO₃, KBr, KBrO₄, HCl, NH₂OH·HCl, (NH₄)₂SO₄, SnCl₂, NaOH, NaCl, ascorbic acid, and ferric citrate were analytical grade and obtained from Beijing Chemical Reagents Company (Beijing, China), humic acid was analytical grade and purchased from Aldrich Chem. Co., (Milwaukee, USA). Unless stated otherwise, double-distilled water and N₂ (98.5%) were used in all experiments. HgCl₂ was analytical grade and obtained from Beijing Chemical Reagents Company (Beijing, China), and denoted as Hg(II) by dissolving in the aqueous solution with nitric acid and potassium dichromate.

1.2 Preparation of algal suspension

Nitzschia hantzschiana, a common and typical algal species in natural lake, was obtained from the Wuhan Hydrobiology Institute of Chinese Academy of Sciences (Wuhan, China). The algae were grown in a culture medium using 24 hr light cycle in a culturing room at 25°C equipped with constant temperature air-conditioner (the room light intensity was 2000 Lux). For *N. hantzschiana*, the culture medium consisted of (mg/L): NaNO₃ 120, MgSO₄·7H₂O 70, K₂HPO₄·3H₂O 40, KH₂PO₄ 80, CaCl₂·2H₂O 20, NaCl 10, Na₂SiO₃·9H₂O 100, MnSO₄·4H₂O 2, H₃BO₃ 2.86, MnCl₂·4H₂O 1.81, ZnSO₄·7H₂O 0.22, CuSO₄·5H₂O 0.079, Na₂MoO₄·2H₂O 0.039, and ferric citrate 5, and 0.5 mL/L soil extract (the soil extract was heated at 100°C for 2 hr with soil to water ratio 1/5 (*m/m*), and then cooled in brown bottle). The medium was adjusted to pH 7.0–7.2 by using 0.1 mol/L Na₂CO₃. The algae were cultured in axenic medium. After growing for 12–14 days, the algae were prepared for the experiments.

Prior to the photoreduction of Hg(II) in algal suspension, to remove colloidal ferric hydroxide particles that might have adsorbed on the algal cells, a modified version of the procedure (Zepp and Schlotzhauer, 1983) was used in the experiments. Briefly, cells were washed by gentle agitation for 30 min with 0.01 mol/L aqueous ascorbic acid (pH 3.0). Then the algae were washed with double-distilled water for three times by filter centrifugal to obtain algae suspension. The cell counting was carried out under inverted microscope at 400× and the density of algae (cells/L) was calculated (Liu et al., 2005). Different concentrations of algae were prepared through diluting the washed algae with double-distilled water. These experiments were performed at a room temperature (26 ± 2)°C.

1.3 Irradiation procedure

Irradiation experiments were carried out in a cylindrical reactor (20.0 cm length, 10.0 cm diameter, 1.0 cm wall thickness) made of quartz glass (Fig. 1a), with a 250-W metal halide lamp ($\lambda \geq 365$ nm, Changzhou Shangzi Lamp Co., Ltd., China) placed in cooling trap for maintaining constant temperature by water circulation. Cylindrical reactor was unsealed and kept in the dark before and after irradiation. HCl and/or NaOH were used to adjust the pH of algal suspension. Different concentrations of Hg(II) and humic acid, Fe(III) or algae were mixed thoroughly and transferred into the cylindrical reactor. After the radiations of metal halide lamp drill through water circulation, the light intensity was 159,000 Lux detected using Digit Lux meter (TES 1332, Taiwan, China). During the irradiation, samples with Hg(II) and Fe(III), humic acid or algae were taken from the cylindrical reactor at different time intervals. For the solution with algae, 5 mL sample was digested with 2 mL HCl-HNO₃ (*V/V* = 1). Then the samples and a Teflon-coated stir bar were placed in a capped and secured glass flask and heated to 90°C in a water bath for 1 hr or more (Luo, 2005). Upon cooling, the samples were analyzed by a cold vapor

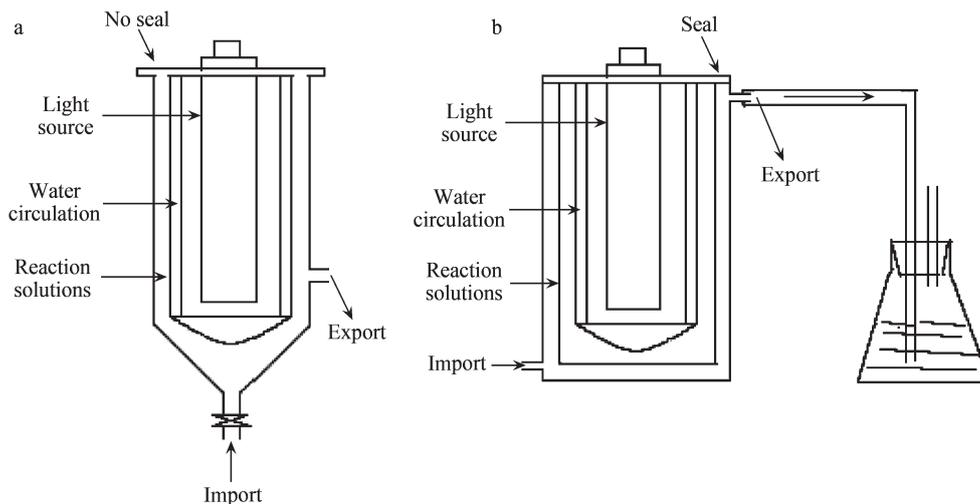


Fig. 1 Cylindrical reactors a and b.

atomic absorption spectrometer (AAS, F732-V) (Shanghai Huaguang Machinery and Instrument Company, China). The algae-free samples were analyzed directly by AAS.

For the overall Hg mass balance, the release of volatile Hg from the photochemical processes was determined in another sealed cylindrical reactor (20.0 cm length, 9.0 cm inside diameter, 11.0 cm outside diameter, 1.0 cm wall thickness) (Fig. 1b) with a 250-W metal halide lamp ($\lambda \geq 365$ nm) placed in cooling trap to maintain constant temperature by water circulation. The reaction solution was pumped with N_2 at a fixed flow rate throughout the experiment. The produced Hg vapor was taken by N_2 into an imbibing flask filled with 200.0 mL KBr-KBrO₄ solutions (10 g/L KBr and 2.784 g/L KBrO₄) and 2.0 mL H₂SO₄ (98%). The imbibing samples were analyzed by AAS.

1.4 Chemical analyses

For the determination of Hg(II) concentration by AAS, the calibration equation for Hg(II) was $A_{\text{peak area}} = 95.14 C_{\text{Hg(II)}} - 6.24$ ($r = 0.992$), when $C_{\text{Hg(II)}}$ was the concentration of Hg(II) in the range of 0.0–200.0 $\mu\text{g/L}$. All vitreous apparatus were dipped in HNO₃/water (V/V, 1:3) overnight to remove impurities. Reaction solution 3.0 mL was transferred into a 20.0-mL reduction bottle. A mixture of 2.0 mL HNO₃ (5%) and 2.0 mL SnCl₂ (10%) was added into the reduction bottle before analyzing.

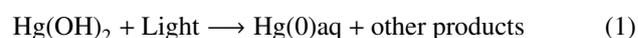
During the course of the overall Hg mass balance experiments in the presence of algae, 5 mL sample was taken from the imbibing flask at 1 hr time intervals and NH₂OH·HCl-NaCl solution was stepwise added until the yellow color of the sample disappeared. Then the samples were allowed to stand for 5 min (Qun, 2000). Finally the mercury concentration in samples was determined by AAS. All the experiments were conducted in triplicates. The results presented were the mean values with a less than 5% total analytical error.

2 Results and discussion

2.1 Effects of algae on Hg(II) photoreduction

Figure 2 shows the typical time series for the

photochemical reduction of Hg(II) in the absence/presence of *N. hantzschiana*. The corresponding control experiments were performed in the dark. In the presence of *N. hantzschiana*, 9.9% of Hg(II) was removed from the suspension after 7 hr, which may due to the slow absorption and/or reduction by the biological and thermal chemical processes (Deng and Liu, 1986). Under the metal halide lamp irradiation, 13.0% of Hg(II) disappeared after 7 hr irradiation even in the absence of algae, suggesting the slow thermal reduction, absorption and the direct photoreduction of Hg(II). The direct photoreduction of Hg(II) could be responsible for the increased disappearance of Hg(II) (Deng and Wu, 2003), as shown by the following reaction.



In the presence of *N. hantzschiana*, 33.3% of Hg(II) disappeared from the suspension after 7 hr irradiation under the metal halide lamps, indicating that the photolysis of *N. hantzschiana* could promote the reduction of Hg(II). *N. hantzschiana* might undergo photolysis to generate smaller organic molecules and aquated electrons that are capable of reducing Hg(II) (Marc et al., 1994). The enzymatic reaction at the algae cell surface could be another possible mechanism involved in the reduction of Hg(II) (Mason et al., 1993).

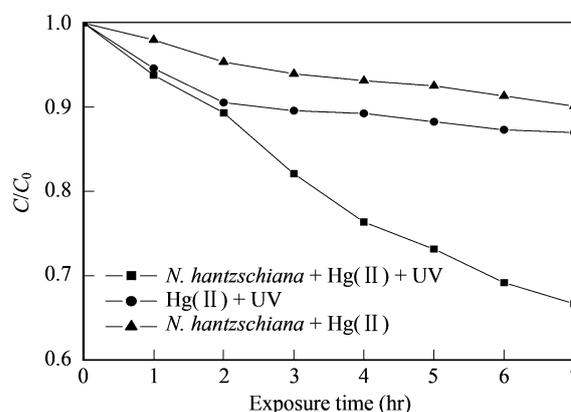


Fig. 2 Hg(II) concentration change in the control experiments. Initial Hg(II) concentration: 100 $\mu\text{g/L}$; *N. hantzschiana*: 7.0×10^9 cells/L.

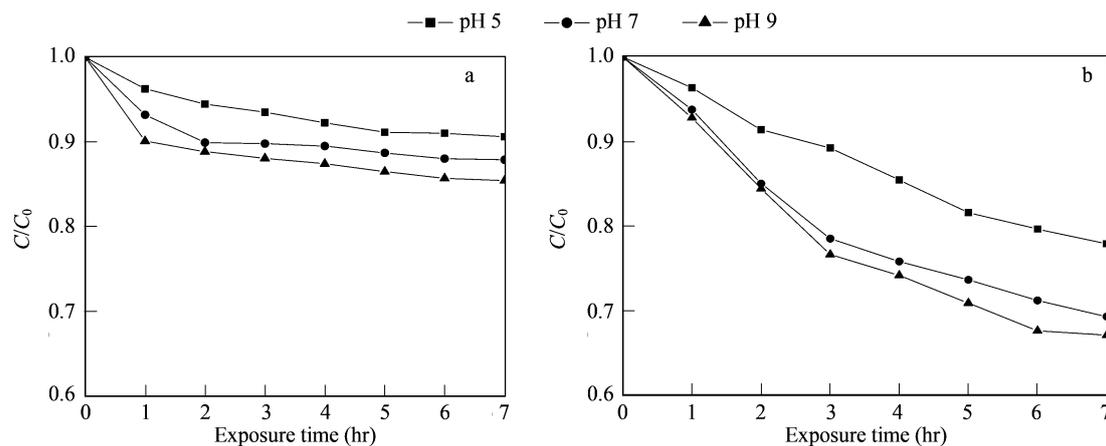


Fig. 3 Effects of pH on photoreduction of Hg(II) without (a) or with (b) algae. Light source: 250 W metal halide lamps; C_0 of Hg(II): 100 $\mu\text{g/L}$; *N. hantzschiana*: 4.5×10^9 cells/L.

2.2 Effects of pH on Hg(II) photoreduction

The photoreduction experiment was performed in Hg(II) aqueous solutions in the pH range 5–9. As shown in Fig. 3a, in the absence of algae the photoreduction efficiency of Hg(II) increased slightly with increasing pH. At pH 5, up to 9.4% and at pH 9, up to 15.8% of Hg(II) were removed from the suspension after 7 hr irradiation. The pH effect demonstrated that $\text{Hg}(\text{OH})_2$ could be the reactive species of Hg(II) involved in the direct photochemical reduction of Hg(II) in aqueous solution, which was in consistent with that reported previously (Alberts et al., 1974; Allard and Arsenie, 1991; Matthiessen, 1998).

On the other hand, in the presence of *N. hantzschiana* under metal halide lamps the photoreduction of Hg(II) increased with increasing pH (Fig. 3b). At pH 5, 7, and 9, 22.1%, 30.8%, and 32.9% of Hg(II) was removed from the algal suspension after 7 hr irradiation. In the aqueous suspension of *N. hantzschiana*, the photochemical and biological processes are more complex. There were many factors which can accelerate the conversion of Hg(II) to Hg(0). One of them is that the higher concentration of $\text{Hg}(\text{OH})_2$ at higher pH leads to a higher photoreduction of Hg(II). pH 7.0 was selected in the following experiments, because both natural water and the algal suspension have a similar pH value.

2.3 Effects of initial Hg(II) concentrations on Hg(II) photoreduction

The influence of initial Hg(II) concentration on the photoreduction of Hg(II) with the algae was examined by irradiating the suspensions of *N. hantzschiana* at pH 7.0 with initial Hg(II) concentrations (C_0) 50, 100, 150 and 200 $\mu\text{g/L}$. As shown in Fig. 4, the metal halide lamp (250 W) could evidently induce photoreduction of Hg(II) in aqueous solution with algae. After 7 hr irradiation, 34.3%, 31.2%, 27.1%, and 25.9% of Hg(II) was removed from the suspension at C_0 50, 100, 150, and 200 $\mu\text{g/L}$, respectively. The photoreduction rate of low Hg(II) concentration decreased faster than that of high Hg(II) concentration in aqueous solution with algae. Under these conditions, the reduction rate decreased with C_0 of Hg(II) increasing.

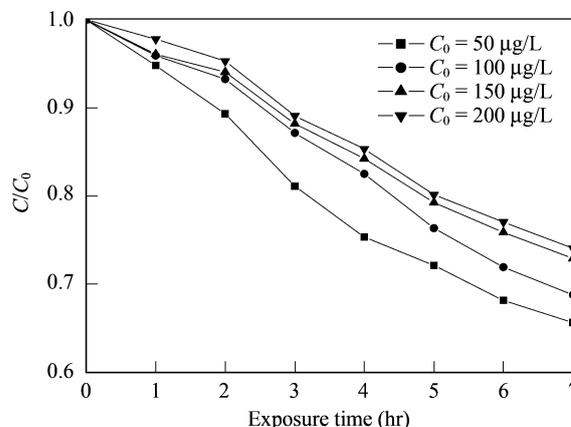


Fig. 4 Effects of initial Hg(II) concentrations on Hg(II) photoreduction with algae. pH: 7.0; *N. hantzschiana*: 7.0×10^9 cells/L.

Table 1 Kinetics analysis of initial concentrations of Hg(II) affecting the photoreduction of Hg(II)

Hg(II) conc. ($\mu\text{g/L}$)	Initial rate v_0 ($\mu\text{g/min}$)	Kinetics equation
50	3.12	$-\text{d}C_{\text{Hg(II)}}/\text{d}t = 0.16C_{\text{Hg(II)}}^{0.76}$ $r = 0.9968, n = 4$
100	5.61	
150	7.01	
200	9.18	

N. hantzschiana concentration: 7.0×10^9 cells/L, pH 7.0.

Over the experiment, the Hg(II) concentration vs. time curve looks very much like an exponential decay curve. Therefore, the equation $\ln C/C_0 = -kt$ was used to calculate the initial rates (v_0) under different conditions according to the equation $v_0 = kC_0$. The initial concentrations of different influence factor and corresponding v_0 were fitted according to the equation $v_0 = aC_0^b$. According to linear equation, the initial rates v_0 obtained was fitted against corresponding $C_{\text{Hg(II)}}^{0.76}$. The apparent kinetics equations were then obtained, and shown in Table 1. It could be seen that the initial rate of Hg(II) photoreduction increased with increasing the initial concentrations of Hg(II).

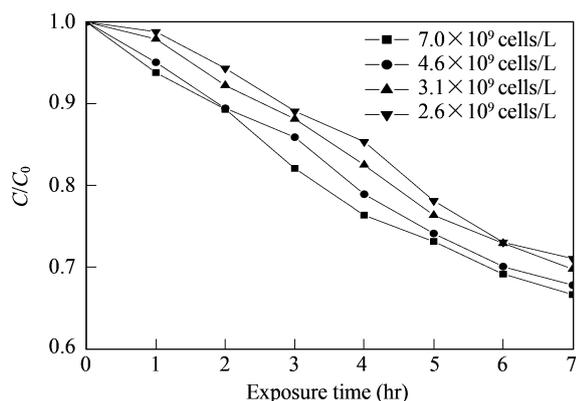


Fig. 5 Effects of *N. hantzschiana* concentrations on photoreduction of Hg(II). Initial Hg(II) concentration: 100 $\mu\text{g/L}$, pH: 7.0.

2.4 Effects of algae concentration on Hg(II) photoreduction

As shown in Fig. 5, the faster photoreduction of Hg(II) occurred with a higher *N. hantzschiana* concentration. After 7 hr irradiation, 33.3%, 32.2%, 30.2%, and 28.9% of Hg(II) was removed from the suspension at the initial algal concentration 7.0×10^9 , 4.6×10^9 , 3.1×10^9 , and 2.6×10^9 cells/L, respectively. A higher *N. hantzschiana* concentration probably results in a faster photoproduction of aquated electrons and some dissolved organic matter (Amyot et al., 1994). The dissolved organic matter, such as humic and fulvic acid, could serve as photosensitizers and thus accelerate the photoreduction of Hg(II) (Franke and Franke, 1999).

The initial concentrations of *N. hantzschiana* and corresponding v_0 were fitted according to the equation $v_0 = aC_0^b$. It could be seen that the initial rate of Hg(II) photoreduction increased with increasing the concentrations of the initial algal concentration. The initial rates v_0 obtained was fitted against corresponding $C_{\text{algae}}^{1.12}$ according to linear equation. The apparent kinetics equations were obtained and shown in Table 2. Comparing the reaction orders in the kinetics equation, algae had the larger power (1.12) than Hg(II) (0.76), which implied that the initial concentration of algae was the dominant factor contributing to reaction rate under the studied experimental conditions.

2.5 Effects of humic acid on Hg(II) photoreduction

The effects of humic acid on photoreduction of Hg(II) are shown in Fig. 6. In the presence of 8.0 mg/L humic acid, 9.7% Hg(II) was removed from a suspension of *N. hantzschiana* stood in the dark for 7 hr. While, after 7 hr

Table 2 Kinetics analysis of initial concentrations of *N. hantzschiana* affecting the photoreduction of Hg(II)

<i>N. hantzschiana</i> conc. (cells/L)	Initial rate v_0 ($\mu\text{g/min}$)	Kinetics equation
2.6×10^9	0.139	$-dC_{\text{Hg(II)}}/dt = 0.048 C_{\text{algae}}^{1.12}$ $r = 0.9998, n = 4$
3.1×10^9	0.171	
4.6×10^9	0.268	
7.0×10^9	0.419	

Initial Hg(II) concentration: 100 $\mu\text{g/L}$, pH: 7.0.

irradiation, 35.2%, and 40.9% Hg(II) disappeared in the presence of 8.0 and 12.0 mg/L humic acid, respectively, and only 32.2% Hg(II) was removed in the absence of humic acid. These results indicated that the photoreduction rate of Hg(II) in algal suspension was enhanced by adding humic acid. Several research groups have also report that humic substances could promote the reduction of Hg(II) in aqueous solution (Alberts et al., 1974; Allard and Arsenie, 1991; Skogerboe and Wilson, 1981; Matthiessen, 1998).

2.6 Effects of Fe(III) on Hg(II) photoreduction

Fe(III) can accelerate the photoreduction of Hg(II) in algal suspensions under metal halide lamps irradiation as shown in Fig. 7. In the dark, only 7.5% Hg(II) disappeared in the suspension of *N. hantzschiana* containing 0.02 mmol/L Fe(III). After 7 hr irradiation, 32.2% of Hg(II)

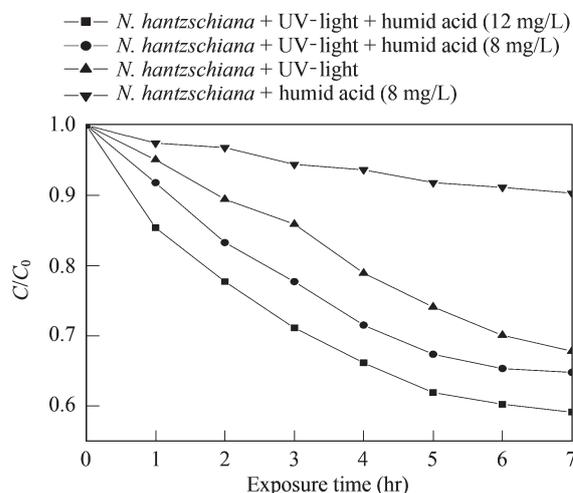


Fig. 6 Effects of humic acid on photoreduction of Hg(II) with algae. pH: 7.0, initial Hg(II) concentration: 100 $\mu\text{g/L}$, *N. hantzschiana* concentration: 4.6×10^9 cells/L.

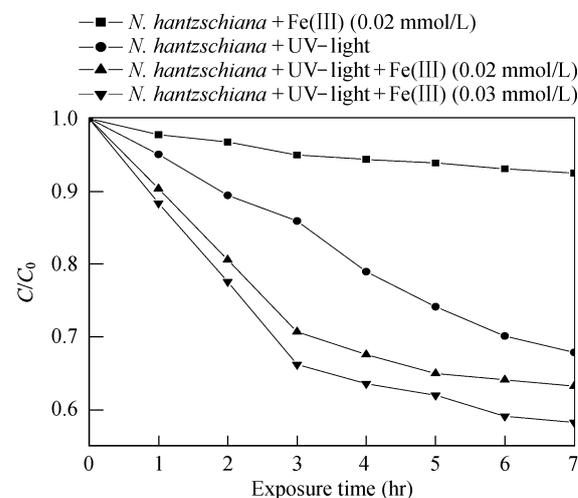


Fig. 7 Effects of Fe(III) on photoreduction of Hg(II) with algae. pH: 7.0, initial Hg(II) concentration: 100 $\mu\text{g/L}$, *N. hantzschiana* concentration: 4.6×10^9 cells/L.

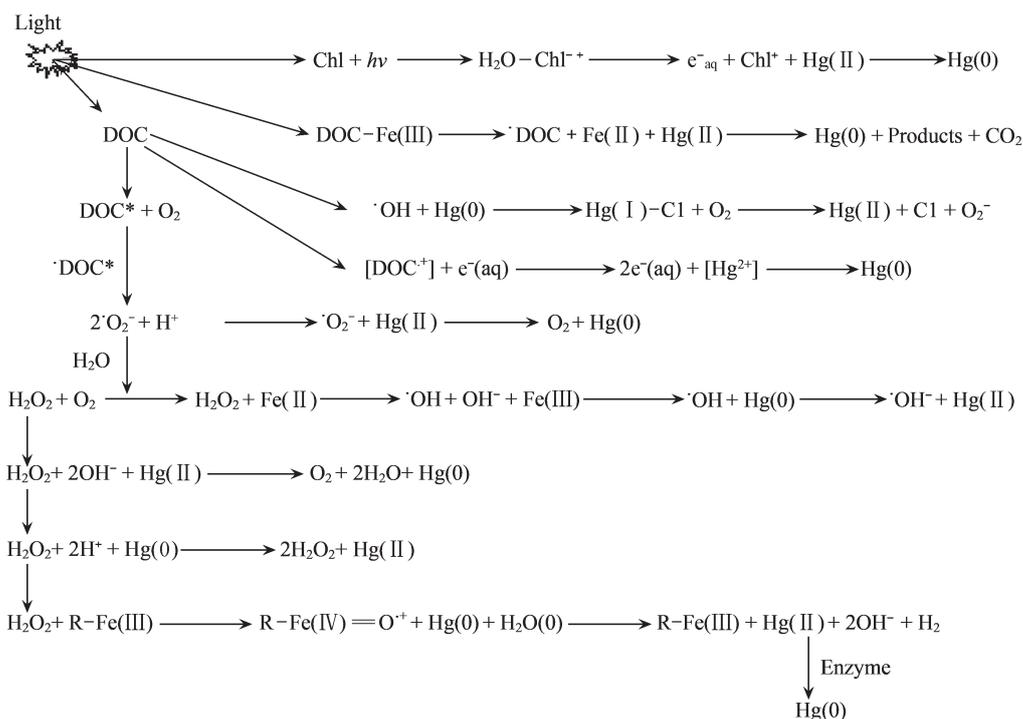
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was removed from suspension of *N. hantzschiana* without Fe(III), while 36.8% and 41.8% of Hg(II) disappeared in the presence of 0.02 and 0.03 mmol/L Fe(III), respectively. The involved abiotic mechanisms for the acceleration of photoreduction of Hg(II) by Fe(III) are light-induced photochemical production of highly reducing organic free radicals through photolysis of Fe(III)-organo coordination compounds (Fe(III)-org) and subsequent reaction of Hg(II) with the organic and inorganic free radicals formed. After analyzing above experiments result and references (Matthiessen, 1998; Zhang and Lindberg, 2001; Aguer and Richard, 1996; Vaughan and Blough, 1998; Ma et al., 2006; Lan et al., 2008; Li et al., 2007), the mechanism of photochemical reduction of Hg(II) in the presence of algae was considered to have many important photochemical processes for enhancement of Hg(II) reduction by algae, including the enzymatic reduction at the algae cell surface, reduction by aquated electrons and dissolved organic matter produced via the photolysis of algae under the irradiation, as shown in following Scheme 1.

Fe(III) is highly photochemically reactive in aqueous media and its role in mediating photochemical redox cycling of heavy metals in natural aqueous systems is well known (Faust, 1994; Stumm and Morgan, 1996; Brezonik, 1994). Photochemical reduction of heavy metal ions by highly reducing organic free radicals has been implicated to be one of the most important mechanisms for the redox cycling of these metals (Hug et al., 1997; Zuo and Hoigne, 1992; Wang et al., 2008). The reducing organic free radicals produced through photolysis of Fe(III)-organo coordination compounds. The same mechanisms may also act in natural water because both algae and Fe(III) are commonly present in nature aquatic environment.

2.7 Hg mass balance on the photoreduction of Hg(II) in algal suspensions

To confirm whether the disappeared Hg(II) in the suspensions was predominantly reduced to volatile metallic Hg during the reactions, 50 µg/L mercuric chloride in the suspensions of *N. hantzschiana* at four different algal concentrations (7.1×10^9 , 4.5×10^9 , 3.3×10^9 , and 2.7×10^9 cells/L) at pH 7.0 in a new cylindrical reactor (Fig. 1b) was exposed to the irradiation of a 250-W metal halide lamp for 11 hr. The volatile metallic Hg(0) was blown out from the reaction suspensions using pure N₂ and absorbed into an imbibing flask filled with 2 mL H₂SO₄ and 200 mL KBr-KBrO₄ solutions and subsequently determined by AAS. The photoreduction of Hg(II) increased with increasing algae concentration in consistent with the results presented in Fig. 5. To further confirm the decrease of Hg concentration in the irradiated samples, we measured the percentages of total Hg in the initial algae suspension (HgT₀), in the algae suspension after 11 hr (LHgT₁₁), in the solution left in the imbibing flask after 11 hr (ΔHgT₁₁) and the total Hg taken from a imbibing flask every hour (ΔHgT). The results for the overall mass balance studied are given in Table 3. On average, more than 90.24% of initial Hg(II) in the suspension was well balanced. The photoreduction process revealed that more than 41.85% of Hg(II) from the algal suspension were reduced to volatile metallic Hg. O'Driscoll et al. (2006) used a similar technique to study the gross photo-reduction mercury mass balance in temperate freshwater lakes and rivers with a consumption that Hg(0) was bubbled out as it was formed, and found that of the total mercury available in each sample a mean of 37.8% was reduced during the experiments.



Scheme 1 Pathway of photochemical reduction of Hg(II) in the presence of algae.

Table 3 Mass balance of Hg

Hg term	Sample 1	Sample 2	Sample 3	Sample 4
HgT ₀ (%)	100	100	100	100
LHgT ₁₁ (%)	37.96	30.52	25.35	20.80
ΔHgT ₁₁ (%)	41.85	45.94	48.45	52.71
ΔHgT (%)	10.84	14.47	16.75	16.73
ΔHgT + ΔHgT ₁₁ + LHgT ₁₁ (%)	90.65	90.73	90.55	90.24

pH: 7.0, initial Hg(II) concentration: 50 μg/L, initial algae concentrations were 7.1×10^9 , 4.5×10^9 , 3.3×10^9 , 2.7×10^9 cells/L for samples 1–4, respectively.

3 Conclusions

It was demonstrated that algae, *N. hantzschiana*, could significantly accelerate the photochemical reduction of Hg(II) under the irradiation of metal halide lamps ($\lambda \geq 365$ nm, 250 W). The photoreduction of Hg(II) increased with increasing concentration of algae, Fe(III) and humic acid. Increasing pH value also led to a higher photoreduction rate of Hg(II) in algal suspensions. Comparing the reaction orders in the kinetics equation, algae had a larger power than Hg(II), which implied that the initial concentration of algae was the dominant factor contributing to reaction rate under the experimental conditions. The DGM concentration increased with increasing exposure time and then appeared to approach a steady state in the irradiated suspensions. Under these conditions, with initial concentration of Hg(II) increasing, the reduction rate decreased. The overall Hg mass balance study on the photochemical process revealed that more than 41.85% of Hg(II) from the algal suspension was reduced to volatile metallic Hg. Three mechanisms may have been involved in the algae enhanced reduction of Hg(II), including the enzymatic reduction at the algae cell surface, reduction by aquated electrons and dissolved organic matter produced via the photolysis of algae under the irradiation. This research will be helpful for understanding the photochemical transformation of Hg(II) and the formation of DGM in natural water in the presence of algae complexes.

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