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Photoinduced reduction of high concentration Hg(II) to Hg_2Cl_2 from acid wastewater with the presence of fulvic acid under anaerobic conditions

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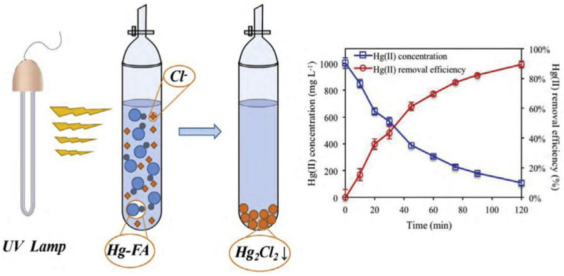
HIGHLIGHTS

- Hg(II) containing wastewater was treated with UV with the presence of FA and Cl^-.
- Hg_2Cl_2 precipitant was generated as the end product instead of Hg(0).
- 90% of Hg(II) removal efficiency were obtained for simulated wastewater treatment.
- Reductive species produced by the breakdown of FA-Hg(II) after UV light promoted Hg(II) reduction.
- Direct reduction by reductive functional groups on FA also contributed to the Hg(II) removal.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to recover mercury from high concentration Hg(II) acid wastewater, UV irradiation was used to reduce Hg(II) to Hg_2Cl_2 with the presence of fulvic acid and chloride ion. When simulated wastewater with Hg(II) concentration of 1000 mg L^{-1} was treated, > 90% of Hg(II) removal efficiency was achieved under the condition of extra Cl^- dosage of 5 g L^{-1}, FA dosage of 2 g L^{-1}, pH of 3.0 and 120 min of UV irradiation. Kinetics study showed that the photoreduction process could be well described by pseudo-first order kinetic mode, and the Hg(II) reduction rate was tested to be 0.0422 min^{-1}. Characterization results indicated that FA-Hg(II) complexes were firstly formed and then broken down into smaller molecules after the UV treatment, in which process highly reductive species (i.e. COO, –COOH) were produced. These reductive species mediated the reduction of Hg(II). With the presence of Cl^-, Hg_2Cl_2 was practically the only detected Hg-based product in the photoreduction process. This technique was also employed to treat COD_{Cr} analysis wastewater (initial Hg(II) concentration > 1000 mg L^{-1}). With 90 min of reaction, most of the Hg(II) was removed from the system leaving less than 30% that could be further treated by chemical participation or adsorption method.

1. Introduction

Mercury (Hg) pollution has been a serious threat due to its increasing discharge, high toxicity, bioaccumulation nature and

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other adverse effects on human health and the environment (Bao et al., 2017; Jiang et al., 2006). The presence of mercury in human body can endanger human health even at a trace level, causing sever diseases like deafness, vision lost, insanity, paralysis coma and Alzheimer's (Tchounwou et al., 2003). For all three chemical species of mercury, Hg(II) with a strong migration and low degradability in waters is known as the main factor that lead to mercury pollution. Hg(II) is commonly found in wastewaters from industries engaged in oil refining, pulp paper, chlor-alkali rubber processing and fertilizer production (Dil et al., 2017).

Several methods are commonly employed for the removal of Hg(II) in wastewater, such as chemical precipitation (Matlock et al., 2001; Zhu et al., 2009), ion exchange (Monteagudo and Ortiz, 2015; Oehmen et al., 2014), adsorption (Husein, 2013; Namasivayam and Senthilkumar, 1997), membrane filtration (Urgun-Demirtas et al., 2012), electrochemical treatment technologies (Nanseu-Njiki et al., 2009), liquid extraction (Huebra et al., 2003) and biological treatment (Okino et al., 2000). However, most of those techniques showed some drawbacks, especially when acidic wastewaters with high concentrated Hg(II) is considered as the target wastewater. With chemical precipitation, the solution has to be set to neutral or basic pH range to achieve satisfactory removal efficiency. Methods like ion exchange, adsorption and biological treatment are only applicable for the treatment of wastewater with low Hg(II) concentration.

Photoreduction of Hg(II) to Hg(0) is an important part of the global Hg cycle that can prevent Hg from accumulating in natural aquatic system and reduce the available Hg for methylation (Jeremiason et al., 2015; Mason and Sheu, 2002). It was widely reported that the presence of dissolved organic matter (DOM), such as oxalic acid and humic acid, could significantly promote the Hg(II) photoreduction process due to its role as photosensitizer (Deng et al., 2010). This Hg(II) reduction pathway in natural system can also be adopted to remove Hg(II) from wastewater. Berkovic et al. (2012) reported satisfactory Hg(II) removal performance using photoreduction technique with the presence of formic acid. As described in their work, the high Hg(II) removal efficiency was caused by the mediation of $CO_2^{-}\bullet$ radicals generated from quenching of the triplet states of 1,4-naphthoquinone by formic acid. The usage of formic acid can be replaced by natural organic matters, such as previously mentioned humic acid and fulvic acid (FA), in which quinone and semiquinone function groups are abundantly presented (Hernández-Montoya et al., 2012; Huang et al., 2012).

During the Hg(II) photoreduction process, Hg(II) was firstly reduced to Hg(I) and been further reduced to Hg(0) upon prolonged irradiation time. It is important to control the photoreaction to the first stage and avoid the production of Hg(0), which is subject to evasion back to the atmosphere and possibly cause secondary pollution, especially when wastewater with high concentration Hg(II) is treated. To address this problem, chloride ion (Cl^-) can be introduced to the system in order to decrease the Hg(I)/Hg(0) potential and stabilize Hg(I) in solution (Lalonde et al., 2001). This method could not only address the problem of Hg pollution, the retrieved Hg_2Cl_2 could also be reused by certain industries (e.g. batteries factory).

In this work, high concentration Hg(II) was reduced into Hg_2Cl_2 from acid simulated wastewater using UV irradiation with the presence of FA and Cl^-. The effects of experimental parameters, including reaction time, initial pH, fulvic acid dosage and chloride ion concentration on Hg(II) removal efficiency were investigated. On the basis of the reduction properties of Hg(II) in the simulated wastewater, the removal of Hg(II) in COD_{Cr} analysis wastewater was also studied. The involved reaction mechanism was proposed based on characterization analysis.

2. Material and methods

2.1. Materials

HCl and $HgCl_2$ used in this research were purchased from Kelong Chemical Reagent Company (Chengdu, China). $HgCl_2$ standard solution was from National Center for analysis and testing of nonferrous and electronic materials (BW079810, China). NaCl was from Guangfu Chemical Company (Tianjin, China). All chemicals used in this research were of analytical grade. Fulvic acid was from D&B Chemical Technology Co. Ltd (Shanghai, China), and the element analysis result of the employed fulvic acid was presented in Table S1 in the supporting information (SI).

2.2. Photolysis procedure

The photolysis experiments were carried out in the photochemical reacting device (see Fig. S1 in SI) with a 300 W high-pressure metal mercury lamp ($\lambda = 365$ nm, Bilon Instrument Manufacturing Co. Ltd., Shanghai, China) placed in the cooling trap to maintain constant temperature by water circulation. The cylindrical quartz reactor (200.0 mm length, 35.0 mm diameter, 2.0 mm wall thickness) was sealed and placed around the cooling trap. HCl and NaOH were used to adjust the solutions pH. All solutions were mixed thoroughly and transferred into the cylindrical quartz reactor. Nitrogen gas was passed through the sealed reactor for few minutes prior to the experiment to maintain anaerobic condition. The cylindrical quartz reactor was kept in a dark condition before and after UV irradiation. After the setting photolysis time, the samples were collected from the cylindrical quartz reactor. The irradiated solutions were then filtered by vacuum filter (0.45 μm, Millipore).

2.3. Batch experiment

The synthetic acid wastewater was prepared by adding 1.08 g HgO into 500 mL 0.1 mol/L HCl and dilued to 1000 mL with deionized water in a 1000 mL volumetric flask. The synthetic acid wastewater was freshly prepared before each experiment. The COD_{Cr} wastewater was obtained from a COD online monitoring equipment in a local municipal wastewater treatment plant (Chengdu, China). The COD_{Cr} wastewater was shipped to the laboratory overnight and stored in a refrigerator. Prior to each photoreduction experiment, each 1000 mL COD_{Cr} wastewater was pretreated with 3 g NaCl to precipitate Ag(I) and 3 g activated carbon to reduce Cr(VI). The obtained solutions were filtered before further analysis. The employed initial Hg(II) concentration of the COD_{Cr} wastewater was determined after the pretreatment.

Removal efficiency of Hg by photoreduction and the involved mechanisms were investigated with a series of batch experiments. Cylindrical quartz reactors each containing 50 mL of a synthetic acid wastewater with initial Hg(II) concentration of 1000 mg L^{-1}. Subsequently, NaCl was added into each cylindrical quartz reactor (Cl^- concentration from 0 to 5 g L^{-1}, total Cl^- concentration for synthetic wastewater from 1.75 to 7.75 g L^{-1}), and FA was then added into each bottle (the mass ratio of FA to Hg(II) from 0:1–4:1). The cylindrical quartz reactors were placed on photochemical reacting box and agitated at 125 rpm under controlled temperature (20 °C) and light conditions (300 W/400 mL). The irradiated solutions were finally filtered by vacuum filter (0.45 μm) and the mercury concentrations were measured. The outlet gas were collected by two stage absorbent (20 mL of 5 mmol L^{-1} $KMnO_4$ and 1 mol L^{-1} H_2SO_4, respectively) to monitor the Hg(0) produced during the photoreduction process (Fig. S1).

Each photoreduction experiment was conducted in triplicates