

Photocatalytic removal and recovery of mercury from water using TiO₂-modified sewage sludge carbon

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Abstract

An activated carbon was developed from municipal sewage sludge (SS) using ZnCl₂ as chemical activation reagent. Combined with TiO₂, the carbon was tested for photocatalytic removal and recovery of ionic mercury [Hg(II)] in the form of metallic mercury [Hg(0)] from water. Hg(II) was first photoreduced to Hg(0) which was followed by adsorption on the SS carbon and TiO₂ surfaces, then was recovered on a silver trap by means of heating. Combination of the SS carbon with TiO₂ and under ultraviolet irradiation could double the adsorption capacity of mercury on the SS carbon, and the removal rate was increased to 151 g/kg compared to 87 g/kg for SS carbon only. The optimum amount of TiO₂ for the photocatalytic reaction was 5–20% of the weight of SS carbon for photoreducing 10–80 mg/L of Hg(II) solutions. The optimum illumination time was 20 min and longer illumination could not enhance the photochemical reaction. Hg(II) removal from the solution increased with the increase of pH value, and reached a plateau value at the pH range of 5–12, and furthermore, the removal increased linearly with the increase of Hg(II) concentration. Introduction of methanol into the adsorption system could greatly enhance mercury adsorption capacity of the SS carbon, and the optimum methanol addition amount was found to be 5%, which doubled the adsorption capacity. The adsorption isotherm of mercury onto the SS carbon was found to follow Freundlich isotherm model perfectly. The recovery percentage of Hg(0) from water was around 40–65%. Accordingly, it is believed that the method developed in this study is effective and practical in industrial wastewater treatment for Hg(II) disposal.

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1. Introduction

Numerous studies have been conducted on the carbonization of waste materials from sewage sludge (SS) disposal plant. The carbonaceous products were reported to have a surface area of around 100–400 m²/g, and were investigated for the adsorption of various pollutants such as toluene, hydrogen sulfide, nitrogen dioxide, sulfur dioxide, phenol, dye, etc. [1–4]. However, little information is available concerning their adsorption properties on the removal of mercury from aqueous solution.

Mercury is generally released into the environment through human activities such as coal burning, trash incineration, and industrial emission. It is usually used in metallurgical, pharmaceutical, chemical and petrochemical industries and in paints, electronics, batteries, dental

materials, pesticides, fungicides, herbicides, insecticides bactericides, etc. [5–8]. Mercury is cumulatively toxic and cannot be degraded biologically or chemically. A special characteristic of mercury is its strong attraction to biological tissues and slow elimination from the biological system. The health hazards due to the toxic effect of mercury at Minamata, Japan and Iraq are very well known [9]. Polluted water treatment should remove mercury or its salts without creating more toxic products.

At high concentration, mercury can successfully be removed from solution by precipitation, membrane filtration, and ion exchange, etc. However, these methods are much less efficient for concentrations lower than about 100 ppm [10], for which they can be prohibitively expensive and can even fail to achieve legal limits. For example, when mercury is precipitated as sulfide, high mercury residuals are still often observed. This is because ionic mercury in the solution is partly reduced to metallic mercury, which is soluble in water at about 25 µg/L [11]. For low concentration of mercury,

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it is preferable to perform adsorption techniques. Activated carbon has been proved to be the most effective adsorbent for mercury removal, but it is too expensive for large-scale treatment. Thus it is urgent to develop cheap adsorbents and methods for mercury polluted water decontamination.

Recently, TiO_2 has been used as a photocatalyst to eliminate mercury from aqueous solution [12,13]. In the photoreductive processing, Hg(II) is removed from the solution by photoreduction to metallic mercury which is followed by adsorption on the TiO_2 surface. Mercury reduction can occur by several mechanisms, including direct reduction, where the electrons are transferred to sorbed mercury, and indirect reduction, whereby an organomercury complex is oxidized resulting in metallic mercury deposition on TiO_2 . However, the adsorption capability of TiO_2 is rather low, since it usually has a low surface area of around $50 \text{ m}^2/\text{g}$ [9,13].

In this study, an activated carbon with high surface area was developed from organic municipal sewage sludge (SS). The activated carbon was used combining with TiO_2 to perform photocatalytic removal of ionic mercury [Hg(II)] from aqueous solution. Hg(II) was first photocatalytically reduced to metallic mercury [Hg(0)] which was followed by adsorption on the surfaces of SS carbon and TiO_2 , and then was recovered on a silver trap by heating. The optimum illumination time, photocatalyst amount, and the effects of pH, Hg(II) concentration, carbon dose on the removal of mercury were extensively investigated.

2. Experimental details

A 16-light Rayonet Photochemical Reactor (Southern New England Ultraviolet Company, USA), producing 253.7 nm light, was used as irradiation source, and Degussa Titanium Dioxide P-25 (anatase), with a surface area of $51 \text{ m}^2/\text{g}$, was used as photocatalyst. An activated carbon developed from organic sewage sludge (SS) was used as adsorbent. To manufacture the activated carbon, SS sample was activated by 5 M ZnCl_2 and pyrolyzed in a quartz tube (42 mm i.d.) in N_2 atmosphere at 650°C for 60 min. The activated carbon was washed with 1 M HNO_3 solution, followed by washing with distilled water for several times until the pH value of the leachate was above 6, and sieved to <2 mm after vacuum dried. The surface area of the activated carbon was $555 \text{ m}^2/\text{g}$.

In the Hg(II) adsorption experiments, an adsorbate stock solution of 1000 mg/L was prepared from $\text{Hg(NO}_3)_2$ (Aldrich). This solution was diluted to 10–120 mg/L for use. In this section, optimum illumination time, suitable TiO_2 addition amount, pH range, effects of carbon doses and mercury concentrations on the adsorption were examined. The SS activated carbon doses varied from 0.1 to 10 g/L and TiO_2 varied from 0.001 to 8 g/L, and mercury concentrations varied from 10 to 120 mg/L. Photocatalytic runs were carried out in capped cylindrical 200 ml quartz bottles. In all cases, Hg(II) solution was added to the bottle where

a known amount of SS carbon and catalyst were previously added. The suspension was adjusted to a desired pH, sonicated for 2 min, then vibrated in the dark for 30 min to assure the catalyst particles adsorbed on the surface of the SS carbon. The suspension was then illuminated for a desired time. The amount of mercury removal was calculated from the differences between the Hg(II) concentrations in the solution before and after adsorption. Mercury concentration in the solutions was determined using a cold vapor atomic fluorescence spectrometry (CVAFS) mercury detector (Tekran 2500) connected with a Hewlett-Packard printer (HP 3396A integrator). Method detection limit (MDL) for this instrument is 0.2 ng/L.

For mercury recovery experiments, 200 ml of 60–200 mg/L solutions was performed, and 10 g SS carbon combined with 2 g TiO_2 was used. The adsorption procedure was the same as described above. After adsorption process, the SS carbon together with TiO_2 was separated by filtration and transferred to a triangle flask immediately. The flask was then sealed up with a glass cap. The cap was fitted with inlet and outlet glass tubes (0.25 in. i.d.). The inlet tube was connected to an argon gas cylinder by plastic tube while the outlet tube was connected to a soda column, and a silver trap was connected after the soda column. The soda column was used to capture water steam and other possible gaseous by-products. The tip of the inlet tube was set at approximately 1 cm from the bottom of the flask while the tip of outlet tube was at the top of the flask. The flask was then heated on a hotplate to around 350°C for 20 min with the flow of the inlet gas of argon. The metallic mercury contained in the outlet gas steam was captured by the silver trap. Preliminary studies showed that all of metallic mercury was captured by the first trap and that the use of a second trap was not necessary. Mercury recovery was calculated by weighing the differences of the silver trap before and after the experiments.

3. Results and discussion

3.1. Effect of light illumination

The adsorption capacity of Hg(II) onto TiO_2 is limited. As shown in Fig. 1, mercury adsorption amount by TiO_2 (no light) was 23% of that of SS adsorbent. UV light treatment has great effect on Hg(II) removal. For example, when TiO_2 was used alone, the adsorption amount of light treatment increased 76% compared to no light. When SS carbon was used combined with TiO_2 , Hg(II) removal amount at light treatment was 151 g/kg compared to 87 g/kg at no light, giving an increase rate of 73%. It is well known that as TiO_2 was illuminated by UV light, electrons and holes are produced, the electrons could reduce Hg(II) to metallic mercury. Therefore, under the condition of light illumination, mercury adsorbed on SS carbon and TiO_2 was metallic form but not Hg(II) [12–14]. The adsorption procedure could be

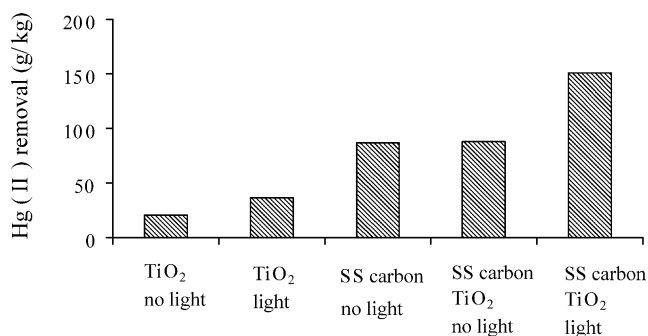
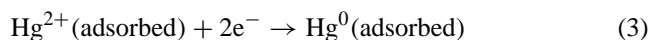
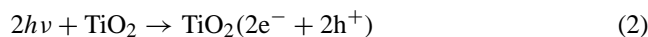
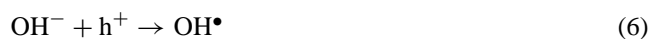


Fig. 1. Effect of UV light irradiation on Hg(II) removal by SS carbon and TiO₂. Conditions—Hg(II) concentration: 80 mg/L; initial solution pH: 6.0; photochemical reaction time: 20 min; SS carbon dose: 100 mg in 200 ml solution; TiO₂ dose: 100 mg in 200 ml solution.

assumed as follows: TiO₂ was first sorbed onto the surface of SS carbon, and Hg(II) was sorbed onto the surface of TiO₂ and SS carbon. Ultraviolet illumination excited electrons from TiO₂ and reduced Hg(II) to Hg(0). The metallic mercury was supposed to be mainly adsorbed on SS carbon because it has a surface area of 555 m²/g, much higher than that of TiO₂, which is only 51 m²/g. The stoichiometry of the photocatalyzed reduction of Hg(II) to Hg(0) could be summarized as follows:



On the other hand, the activation and HNO₃ washing during the SS carbon preparation could generate some oxygen-containing groups (such as –C–OH, –C=O, –COOH) on the surface of the carbon [15]. These groups could also contribute to the photocatalysis, which may be indicated as follows:



The high affinity of metallic mercury with SS carbon than cation mercury could be explained by the Pearson rule, because SS carbon and mercury are soft base and soft acid, respectively. According to Pearson theory, during acid–base reaction, hard acid prefer to co-ordinate with hard base and soft acid to soft base, and neutral atoms are softer acids than metal cations [16].

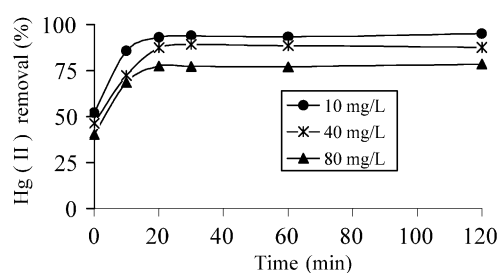


Fig. 2. Effect of illumination time on Hg(II) removal by SS carbon in the presence of TiO₂. Conditions—initial solution pH: 6.0; SS carbon dose: 100 mg in 200 ml solution; TiO₂ dose: 20 mg in 200 ml solution.

3.2. Optimum illumination time and TiO₂ addition percentage

A 20 min of ultraviolet illumination is sufficient for the photocatalysis, and longer illumination could not enhance the photochemical reaction (Fig. 2). This result is consistent with the result obtained by Serpone et al., who have shown that in 1 M HCl aqueous solution, mercury cation was removed from solution in the first 20 min of irradiation, but further irradiation regenerated Hg(II) [17]. This was ascribed to possible photoadsorption/photodesorption process or to photoadsorption/photoreduction followed by re-oxidation of the Hg(0) by the valence band holes of TiO₂.

Fig. 3 depicts the optimum amount of TiO₂ for the reduction of Hg(II). The removal the Hg(II) increased rapidly at a lower amount of TiO₂, and then increased very slightly with increasing the amount of TiO₂, indicating that the major adsorption comes from the SS carbon, and the major role of TiO₂ is to provide electrons in the adsorption system. For example, at the Hg(II) concentration of 80 mg/L, increasing the TiO₂ amount from 20 to 80% could only increase 6.2% of Hg(II) removal, which is attributed to the adsorption from TiO₂. The optimum amount of TiO₂ needed was different according to Hg(II) concentrations, i.e., the optimum amount of TiO₂ is 5% at 10 mg/L of Hg(II), and 10 and 20% at the concentrations of 40 and 80 mg/L, respectively.

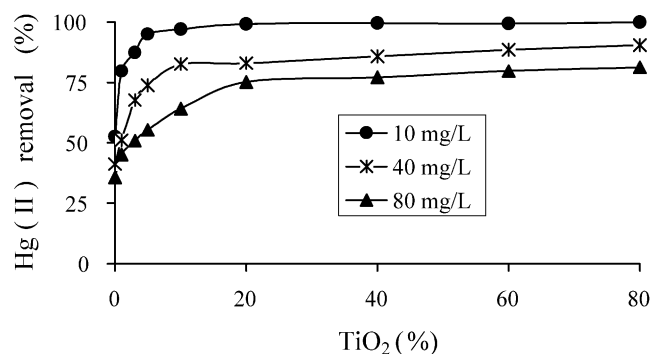


Fig. 3. Effect of TiO₂ addition percentage on the removal of Hg(II) by SS carbon. TiO₂ percentage was based on the weight of the carbon. Conditions—initial solution pH: 6.0; photochemical reaction time: 20 min; SS carbon dose: 100 mg in 200 ml solution.

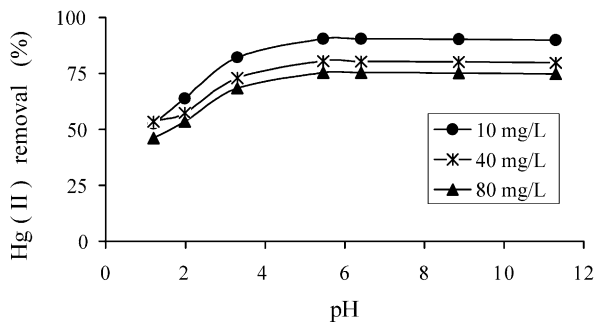


Fig. 4. Effect of pH on Hg(II) removal by SS carbon in the presence of TiO₂. Conditions—photochemical reaction time: 20 min; SS carbon dose: 100 mg in 200 ml solution; TiO₂ dose: 20 mg in 200 ml solution.

3.3. Effects of pH, SS carbon dosage and methanol addition

It has been reported that in the range of pH value of 1–4.1, decreasing pH value decreases the amount of Hg(II) photoreduced [13]. Similar results were also obtained in this study. Fig. 4 illustrates the effect of pH on the photochemical reaction and mercury adsorption. It is noticed that Hg(II) removal percentage increased with the increase of pH value, and then reached a plateau value at the pH range of 5–12.

Fig. 5 depicts the effect of SS carbon dosage on the removal of mercury in the presence of TiO₂. Mercury removal percentage increased with the increase of the carbon dose. Two grams of SS carbon is sufficient to remove 100 mg of Hg(II) from 1 L aqueous solution.

Methanol addition to the adsorption system could greatly enhance the mercury adsorption capacity of the SS carbon. Under the condition of this study, the optimum methanol addition amount was found to be 5%, which doubled the adsorption capacity, and more methanol addition could not increase the adsorption effect (Fig. 6). Methanol, which acts as a hole-scavenger, inhibits electron–hole recombination, thereby enhancing the photoreduction of Hg(II) ion. In this study, 5% of methanol is sufficient to scavenge the holes emitted from TiO₂. Furthermore, methanol has been shown to have a current doubling effect on the TiO₂ surface, i.e.,

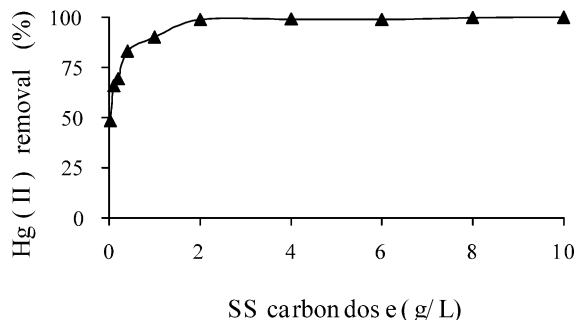


Fig. 5. Effect of SS carbon dose on Hg(II) removal in the presence of TiO₂. Conditions—Hg(II) concentration: 100 mg/L; initial solution pH: 6.0; photochemical reaction time: 20 min; TiO₂ dose: 20 mg in 200 ml solution.

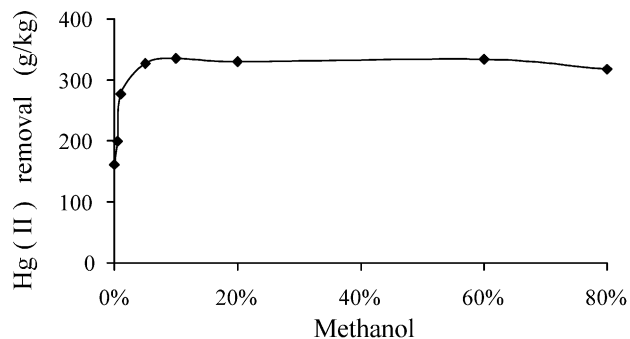


Fig. 6. Effect of methanol addition amount on the removal of Hg(II) by SS carbon in the presence of TiO₂. The percentage represents methanol percent of the total adsorbate. Conditions—Hg(II) concentration: 120 mg/L; initial solution pH: 6.0; photochemical reaction time: 20 min; SS carbon dose: 100 mg in 200 ml solution; TiO₂ dose: 20 mg in 200 ml solution.

with methanol present, absorption of one photon leads to the injection of two electrons into the TiO₂ conduction band, thus doubling the current [18].

Mercury adsorption by the SS carbon increased linearly with the increase of Hg(II) concentration. The removal amount was 217 mg/kg at 200 mg/l compared to 21 mg/kg at 10 mg/L. In the presence of methanol, the removal amount was enhanced to 326 mg/kg at 200 mg/L compared to 52.6 mg/kg at 10 mg/L (Fig. 7).

3.4. Adsorption isotherm

Adsorption isotherm of mercury was examined with Hg(II) concentration ranged from 10 to 200 mg/L. The isotherm data were fitted to Freundlich equation and the result was illustrated in Fig. 8. Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface. The equation was presented elsewhere [15]. In Fig. 8, q_e is mercury adsorption amount in the unit of mg/kg, C_e is the equilibrium concentration of the adsorbate in the unit of mg/L. The linear plot in Fig. 8 indicates that

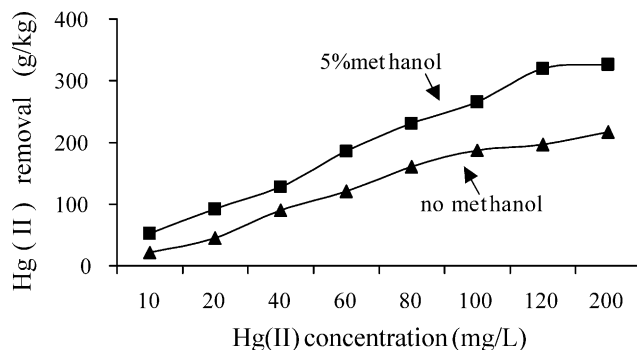


Fig. 7. Hg(II) removal by SS carbon in the presence of methanol and TiO₂ as a function of different Hg(II) concentrations. Conditions—initial solution pH: 6.0; photochemical reaction time: 20 min; SS carbon dose: 100 mg in 200 ml solution; TiO₂ dose: 20 mg in 200 ml solution.

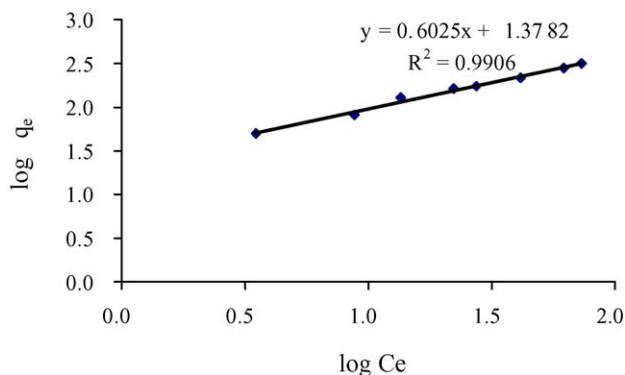


Fig. 8. Freundlich isotherm for Hg(0) adsorption onto SS carbon in the presence of TiO₂.

mercury adsorption on the SS carbon and TiO₂ follows Freundlich isotherm model. The Freundlich constants K_F and n were calculated using the slope and intercept of the line and were found to be 23.9 and 1.67, respectively.

3.5. Recovery of metallic mercury

Metallic mercury adsorbed on the SS carbon was recovered by transferring it to a silver trap. In this section, 10 g SS carbon and 2 g TiO₂ was used to assure complete removal of mercury from the solution. Additionally, Hg(II) concentration of 60–200 mg/kg was performed because according to our preliminary experiment, if the concentration was less than 50 mg/kg, where the total mercury in the adsorption system was less than 10 mg, it was difficult to recover the mercury. In that case, large volume of solution was necessary. Fig. 9 presents the recovery percentage of mercury at different concentrations. The recovery was found to be around 40–65%, with the standard deviations of around 6–17%. A higher recovery percentage was found at higher concentration range while a higher deviation value was obtained at the lower concentration range. After adsorption experiment, total mercury concentration in the solution was determined and was found to be less than 5 µg/L. Therefore, it is supposed that almost all the mercury was adsorbed on the SS carbon and TiO₂, however, as shown in Fig. 9, the

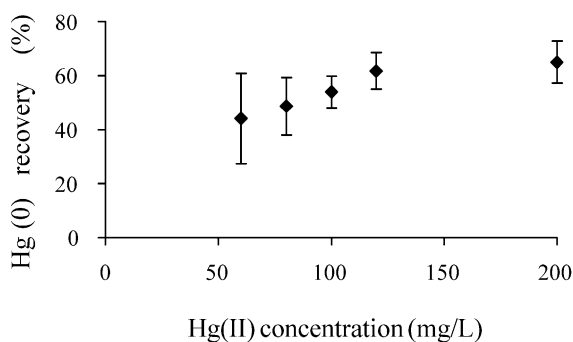


Fig. 9. Recovery of metallic mercury at different Hg(II) concentrations.

recovery percentages were low. Accordingly, it is assumed that some of the mercury was lost during the transferring procedure, hence more detailed work should be conducted so as to enhance the recovery percentage of the metallic mercury.

4. Conclusions

The photocatalytic removal and recovery of Hg(II) in the form of Hg(0) from water by SS carbon and TiO₂ was well demonstrated in this study. The introduction of TiO₂ into the system with UV irradiation increased 73% of mercury removal rate from the solution. Two grams of SS carbon combined with 0.4 g TiO₂ under 20 min of UV irradiation was sufficient to remove 100 mg of Hg(II) from 1 L aqueous solution. Methanol addition into the adsorption system could greatly enhance the mercury adsorption capacity of the SS carbon. Under the condition of this study, the optimum methanol addition amount was found to be 5%, which doubled the adsorption capacity. The metallic mercury on the SS carbon and TiO₂ could be recovered on a silver trap, and a recovery range of 40–65% was obtained. We believed that the method developed in this study is practical for industrial use in mercury-contaminated wastewater treatment.

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