Removal of Cu(II) from Wastewater Using Acidified Sewage Sludge Ash*

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ABSTRACT: Sewage sludge ash (SSA), the waste generated in sewage sludge incineration, was obtained from Wuhan Sewage Treatment Plant and used as a low-cost sorbent for removing Cu(II) from wastewaters. The sorbent was first modified with 5% sulfuric acid to increase its sorption capacity. The specific surface area, porosity, cation-exchange capacity (CEC) and pHZEC of the sorbent were measured. Batch experiments were made to study the effect of contact time, solution pH value and temperature on sorption. Both Langmuir and Freundlich models well described the Cu(II) sorption process, with correlation coefficient ($R^2$) values of 0.993 4 and 0.989 9 respectively. And the sorption process follows the Lagergren first order kinetic model. The equilibrium sorption capacity of acidified SSA to Cu(II) is estimated to be 7.78 mg/g under optimal conditions.
KEY WORDS: sewage sludge ash, Cu(II), removal, acidification, sorption.

INTRODUCTION

With industrial advances, current interests in the study of water pollution problems have stimulated interest for the removal of heavy metal ions from wastewater by various methods and sorbents. Safe and effective disposal of wastewater containing heavy metals is always a challenging task for industrialists and environmentalists due to the fact that the cost-effective treatment alternatives are not available. As Cu(II) is a highly toxic element to people’s health, the removal of Cu(II) from wastewater has been the subject of many studies (Alkan and Dogan, 2001; Jung et al., 2001; Lee and Davis, 2001; Vengris et al., 2001; Korngold et al., 1996).

In recent years, with the rapid industrialization and urbanization, the treatment and disposal of sewage sludge have received rising concerns by the public. In order to achieve acceptable volume-reduction and stabilization of sewage sludge, more and more sewage sludge incineration facilities were built and operated (Pan et al., 2003). Simultaneously, with the heating value of sewage sludge increasing, incineration becomes a potential way to sewage sludge disposal.

Although incineration can help to stabilize and reduce the volume of sewage sludge, the residue produced from incineration facilities, i.e. the sewage sludge ash (SSA), still needs to be disposed. In order to minimize the need of final disposal, many studies have been dedicated to develop reuse technologies of SSA. Among those feasible reuse technologies, most utilize SSA as a recycled material since it is rich in silicon oxide and aluminum oxide (Pan et al., 2003; Pan and Tseng, 2001). In addition to the silicon and aluminum-rich characteristics, the SSA also exhibits significant specific surface area and cation-exchange capacity (CEC) (Pan and Tseng, 2001). Many recycled materials, which have similar compositions as SSA has, such as fly ash, electric furnace slag, have been found to have the capability of adsorbing or removing heavy metals ions (Pan et al., 2003; Rao et al., 2002; Dimitrova and Mehandjiev, 1998).

The researches mentioned above imply that SSA can potentially be used to remove heavy metal ions
from wastewater. The feasibility of Cu(II) removal by SSA has been discussed (Pan et al., 2003). However, the removal efficiency of Cu(II) is unsatisfactory and the maximum capacity of Cu(II) adsorbed by SSA was primarily between 3.2 and 4.1 mg/g (Pan et al., 2003). The further investigation is necessary to utilize the CEC fully when using SSA to remove heavy metal ions from wastewater.

The purpose of this study is to enhance the sorption capacity of SSA and make it as a low-cost sorbent material to wastewater treatment. The initial SSA was acidified firstly, and the adsorptive characteristics of acidified SSA including specific surface area, porosity, CEC, and pH of zero point of charge (pH_{ZPC}) were then analyzed. Then the effects on Cu(II) removal, sorption isotherms, sorption kinetic of acidified SSA for Cu(II) removal were discussed.

**MATERIALS AND METHODS**

**Sewage Sludge Ash**

The sewage sludge ash used herein was obtained from the Wastewater Treatment Plant of Wuhan City, China. Firstly, the sample was dried at 105 °C, and then was incinerated at 850 °C for 3 h. The sewage sludge ash was ground by ball mill and used after being sieved through a 200 mesh sieve. The chemical compositions of the SSA are displayed in Table 1; the major components of the SSA are silica, alumina, calcium and iron oxides.

**Acidification of SSA**

In this work, various modifications were tried to increase the uptake capacity of SSA. Among various modification methods, we find that acidification is a low-cost and effective method. Firstly, after acidification, the porous channels of SSA were dredged because the extraneous matters in pore passage of SSA, such as SiO_{2}, Fe_{2}O_{3} and some organic, were clean-up. Secondly, the hydrogen ion in H_{2}SO_{4} with small radius can replace the cations with large radius such as Ca^{2+}, Mg^{2+} and Na^{+}, and this can widen the useful space of porous in SSA.

The dried SSA was mixed with 5 % (V/V) sulfuric acid solution and heated in a muffle furnace for 16 h at 100 °C, after that, the heated material was washed repeatedly with distilled water and soaked in 1 % sodium bicarbonate solution overnight to remove the residual acid. The material was dried at 105 °C for 24 h and used for the further study.

**Characterization of Acidified SSA**

The specific surface area of acidified SSA was tested by the nitrogen sorption method and the BET sorption model was used in the calculation. The CEC was calculated according to the method of Chapman (1965). The pH_{ZPC} of acidified SSA was tested by the titration method described by Stumm and Morgan (1981). The adsorptive characteristics of SSA are shown in Table 2.

**Removal Studies**

Batch sorption experiments were conducted using 1.0 g of sorbent (dosage=20 g/L) with 50 mL of solutions containing Cu(II) of desired concentration at different temperatures in 100 mL polyethylene bottles which were immersed in a temperature controlled water bath. In all of the sorption experiments, the ionic strength was 0.1 M; the solutions were agitated by mechanical shaking at a speed of 100 strokes/min. Samples were taken and filtered by 0.45 μm membrane at predetermined times, the pH values of equilibrium solutions were measured using microcomputer pH meter (HI8424). The concentrations of Cu(II) in the filtrate were measured using an atomic sorption spectrophotometer (Perkin-Elmer 5100). The parameters affecting the sorption process, viz. contact time, pH and temperature were studied. The pH of the aqueous solution was adjus-

### Table 1 Chemical compositions of sewage sludge ash

<table>
<thead>
<tr>
<th>component</th>
<th>value/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO_{2}</td>
<td>57.44</td>
</tr>
<tr>
<td>Al_{2}O_{3}</td>
<td>14.12</td>
</tr>
<tr>
<td>MgO</td>
<td>1.64</td>
</tr>
<tr>
<td>CaO</td>
<td>6.86</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>component</th>
<th>value/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_{2}O</td>
<td>1.97</td>
</tr>
<tr>
<td>Na_{2}O</td>
<td>0.94</td>
</tr>
<tr>
<td>TiO_{2}</td>
<td>0.88</td>
</tr>
<tr>
<td>P_{2}O_{5}</td>
<td>2.81</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>component</th>
<th>value/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>0.08</td>
</tr>
<tr>
<td>Fe_{2}O_{3}</td>
<td>6.26</td>
</tr>
<tr>
<td>H_{2}O</td>
<td>0.20</td>
</tr>
<tr>
<td>Cu</td>
<td>0.026</td>
</tr>
</tbody>
</table>

**Table 2 Adsorptive characteristics of acidified SSA**

<table>
<thead>
<tr>
<th>index</th>
<th>specific surface area/(m^{2} * g^{-1})</th>
<th>porosity/ %</th>
<th>CEC/ (meq/100g)</th>
<th>pH_{ZPC}</th>
</tr>
</thead>
<tbody>
<tr>
<td>value</td>
<td>10.2±0.1</td>
<td>69–70</td>
<td>23.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>
tested using 0.01 N HCl and 0.01 N NaOH solution.

The removal efficiency of Cu(II) was calculated by the formula Cu(II) uptake (%) = (C0 - Ce) / C0; the sorption capacity q (mg of metal L⁻¹) was calculated by the formula q = (C0 - Ce)V/m, where C0, Ce, V and m are the initial and equilibrium concentrations (mg of metal L⁻¹), the volume of solution (L) and the sorbent mass (g), respectively.

RESULTS AND DISCUSSION

Factors Affecting Cu(II) Removal

Effect of contact time

To evaluate the time of sorption equilibrium, 1 g of acidified SSA was added to 50 mL solution with 50 mg/L of Cu(II) and agitated for 24 h at room temperature.

The removal efficiency of Cu(II) increases with the adding of shaking time in the experiment (Fig. 1). In the first 60 min, the removal efficiency of Cu(II) is up to 70 %, and in the following time, the removal efficiency is less than 30 %. The initial Cu(II) concentration is largely different between the solution and the surface of acidified SSA, so Cu(II) can be absorbed to the surface of SSA quickly. With the decrement of concentration difference, the rate of sorption decreases continuously and reaches the sorption equilibrium finally. When the shaking time is over 600 min, the removal efficiency of Cu(II) fluctuates and takes on the decreasing tendency in a certain numerical extent, and this shows that the total sorption procedure is up to balance. So we can take 10 h as sorption equilibrium time.

Effect of pH

pH is an important parameter which controls the sorption of the Cu(II) at the acidified SSA interface (Naseem and Tahir, 2001). Blank experiment (without sorbent material) was hold to investigate the effect of pH value on Cu(II) removal. It is shown in Fig. 2, the removal efficiency is optimum when pH value is between 4.5 and 5.0, because the pHZPC of acidified SSA is 4.1, when the pH value of solution is less than pHZPC value, the surface of acidified SSA would hold positive charge, and this is unfavorable to the removal of Cu(II). When the pH value of solution is greater than pHZPC value, the surface of acidified SSA would hold negative charge, and this is favorable to the removal of Cu(II). Although the removal efficiency is rising with the enhance of the pH value, it will produce Cu(OH)₂ precipitation as the pH value is greater than 5, and then the precipitation is the main way of Cu(II) removal instead of sorption.

![Figure 2. Effect of initial pH on the sorption of Cu(II) by acidified SSA.](image1)

**Figure 1. Effect of contact time on the sorption of Cu(II) by acidified SSA.**

**Effect of temperature**

Sorption is a thermodynamics procedure, and the effect of temperature could not be ignored. To observe the Cu(II) sorption with different temperatures, 20, 30 and 40 °C are considered (Fig. 3). When the temperature rises from 20 to 30 °C, the removal efficiency of Cu(II) increases. The reason is that the sorption of Cu(II) accompanying with the desorption of water molecule, the increment of entropy value produced by the water molecule desorption is larger than the decrement of entropy value produced by the sorption, so it makes the net enthalpy of system as positive, simultaneously the existing of chemistry sorption is an important factor. So it results in that the removal efficiency of Cu(II) increases with the temperature increment of reaction system. When the reaction temperature is up to 40 °C, the removal efficiency of Cu(II) is higher than that at 20 °C, but is generally lower than that at 30 °C.
Figure 3. Effect of temperature on sorption of Cu(II) by acidified SSA at various concentrations.

The reason is that during the course of sorption, the thickness of boundary layer is thinning with the rising of temperature and then the escaping tendency of the adsorbed Cu(II) increases, simultaneously the existing of physical sorption is also an important factor. In this study, 30 °C is the optimum temperature to remove Cu(II) by acidified SSA.

Sorption Isotherms

The well-known Langmuir and Freundlich equations are the typical isothermal sorption models. The linear equation of Langmuir model and the logarithm equation of Freundlich equation are as follows respectively

\[ \frac{C_e}{Q_e} = \frac{C_0}{Q_m} + \frac{1}{Q_m b} \]  

Langmuir equation

\[ \log Q_e = \log K_F + \frac{1}{n} \log C_0 \]  

Freundlich equation

where \( Q_e \) is the amount of metal ions adsorbed per unit weight of sorbent at equilibrium time (mg/g); \( C_e \) is the concentration of metal at the equilibrium time (mg/L); \( Q_m \) is the mass of sorption solute completely required to saturate a unit mass of sorbent (mg/g); \( b \) is a constant related to the energy or net enthalpy of sorption (L/mg); \( K_F \) and \( n \) are the equilibrium constants indicative of sorption capacity and sorption intensity, respectively.

In order to investigate the rule of the Cu(II) removal and ascertain the sorption capability of acidified SSA, the tests were conducted as batch experiments at a temperature of 30 °C. The sorption data of Cu(II) have been correlated with Langmuir and Freundlich equations (Figs. 4 and 5). From the figures, it can be concluded that the experimental data fit these two models well, the square of correlation coefficients are 0.993 4 and 0.989 9 respectively, and this further certifies chemical sorption and physical sorption exist simultaneously in the removal system. From Fig. 4, we can calculate the equilibrium sorption capacity of acidified SSA to Cu(II) is 7.78 mg/g, and this value is very close to the actual measured value. From Fig. 5, we can get the value of \( n \) is 7.56, which is between 2 and 10 to achieve complete sorption (Mckay et al., 1980).

Sorption Kinetics Studies

The Lagergren rate equation was the first rate equation for the sorption of liquid/solid system based on solid capacity (Ho and Mckay, 1999), and the equation is one of the most widely used sorption rate equation for the sorption of a solute from a liquid solution. The linear equation of Lagergren kinetic model can be represented

\[ \log (Q_e - Q_t) = \log Q_e - \frac{k}{2.303} t \]

where \( Q_e \) and \( Q_t \) (both in mg/g) are the amounts of metal adsorbed per unit weight of sorbent at equilibrium time and time \( t \) respectively; \( k \) is the rate constant of pseudo first-order sorption (min\(^{-1}\)). The plot of \( \log (Q_e - Q_t) \) vs. \( t \) gives straight line for 30 °C
in Fig. 6 indicating the appropriateness of the Lagergren model. The pseudo first-order equation was successfully used to describe the sorption kinetics of Cu(II) by acidified SSA with the square of correlation coefficient 0.994 3, and the rate constant $k$ is $11.75 \times 10^{-3}$ min$^{-1}$.

CONCLUSIONS

Sewage sludge ash, the by-product of the sewage sludge incineration, which was traditionally considered as waste, can be used as low-cost absorber material. An efficient sorbent for Cu(II) removal has been explored by making simple chemical modification of SSA by sulfuric acid. This study shows that the acidified SSA has higher removal efficiency of Cu(II) than the original SSA, and the equilibrium sorption capacity of acidified SSA to Cu(II) is $7.78 \text{ mg/g}$. The sorption of Cu(II) on acidified SSA was markedly influenced by contact time, solution pH and temperature. It was found that both the Langmuir and Freundlich models can successfully describe the isothermal sorption course, and this indicates physical sorption and chemical sorption are all the main removal ways of Cu(II). The sorption of Cu(II) on acidified SSA obeyed the first order kinetic model, from which the rate constant was calculated as $11.75 \times 10^{-3}$ min$^{-1}$.

In addition to Cu(II), acidified SSA can potentially be used to remove other heavy metal ions, it can be used as an effective sorbent for sewage treatment. However, the application of acidified SSA to industrial effluents with high concentration would provide an answer to its economic feasibility.

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REFERENCES CITED


Stumm, W., Morgan, J. J., 1981. Aquatic Chemistry. 2nd Ed., Wiley, New York, USA