Removal effect of Cr (VI) by adsorbent made from sewage sludge
L. Y. Deng, G. R. Xu, Z. C. Yan, Q. H. Liu and G. B. Li

ABSTRACT
Adsorbent made from sewage sludge is used to remove the Cr (VI) in wastewater. In this paper, the adsorption capacity, adsorption mechanism and regeneration of the adsorbent are studied. A systematic research is carried out to investigate the influence of adsorption capacities in various conditions, such as contact time, pH and initial dosage of adsorbent. The results show that: the equilibrium time is 6 h; the optimal pH is 2.5. The adsorption capacity increases as the initial concentration increase and as the dosage of activated carbon decrease. The data of adsorption capacity are more fit in Langmuir isotherms. The adsorption follows a pseudo-second-order kinetic model perfectly. From this research, the adsorption rate controlling step is film diffusion when the Cr (VI) concentration is low; otherwise, the adsorption rate controlling step is the diffusion among particles. The results of regeneration of saturated adsorbent show that the saturated adsorbent can be perfectly regenerated using alkali treatment. The regeneration ratio of the saturated adsorbent can reach more than 90% with proper concentration of alkali.

Key words | adsorbent, adsorption, Cr (VI), regeneration, sewage sludge

INTRODUCTION
The wastewater of leather, electroplating and other industries contain much Chromium. Chromium exists in aquatic environment is mainly in two states: trivalent Cr (III) and hexavalent Cr (VI). Hexavalent chromium primarily exists in the form of chromate (CrO4^{2-}) and dichromate (Cr2O7^{2-}) ions; the latter form is the most toxic one (Sharma et al. 1995). Unlike the organic pollutants which are often biodegraded, metal ions do not degrade into harmless end products (Sitting 1981). Contact with chromium can cause several health problems, ranging from simple skin irritation to lung carcinoma (Huang & Wu 1977; Khezami & Capart 2005). French regulations for drinking water fixed the maximum contaminant level of chromium at 0.05 mg l^{-1} (APHA et al. 1998).

The sludge volume and the organic content of sewage sludge are increasing in recent years. The sludge production is expected to increase from 64,000 tons of dry solids in 1997 to 170,000 tons in 2006, Hong Kong (Yasuhiko & Kazuhiro 1999; Wong et al. 2001). In terms of high production volumes, both current and forecasted, the convenient management of sludge produced at sewage plants is a fundamental requirement. Disposal of waste sludge is a major economical factor in operation of wastewater treatment plants, 30--50% of the annual operating costs are related to sludge dewatering alone (Mikkelsen & Keiding 2002).

Several conventional ways to dispose this kind of waste includes landfill, application to farmland and forestry, incineration and sea dumping (Otero et al. 2003). However, all of the above mentioned methods are banned or limited for either secondary pollution or high costs. Therefore, it is pressing to seek a cost-effective and innovative solution to the problem caused by the sludge disposal.

Taking high organic content of sewage sludge (about 60--80%) and the presence of volatile components into account, sludge is potentially suitable for the production of
cost-effective, efficient activated carbons (Calvo et al. 2001; Tay et al. 2001; Netpradit et al. 2003). If sludge is dried, pyrolyzed under controlled conditions and/or with some chemical treatment, maybe it is one of the most promising approaches for the reuse of waste sludge (Xu et al. 2005).

This paper describes the removal effect of Cr (VI) in water by adsorbent from sewage sludge which involves mixing time, pH and dosage of adsorbent, analysis of adsorption isotherms and adsorption kinetics. In addition, this paper also discusses the regeneration of the adsorbent.

**METHODS**

The sludge used in the experiment was dry sludge. Dewatered sludge with moisture content of about 80% was collected from the Harbin Wenchang Sewage Treatment Plant. The sludge is the mixture of primary sludge and secondary sludge from activated sludge process. The dewatered sludge was dried by natural air drying. In the experiment, the sludge was broken up. The chemical compositions of the dry sewage sludge are shown in Table 1.

The adsorbent was made from the dry sludge by thermal treatment and the conditions were as follows: the dry sludge was mixed with the sulfuric acid (3 mol L\(^{-1}\)) by the ratio of 1:0.8, then heated 30 minutes in muffle furnace at 650°C with the heating rate of 30°C per minute.

The surface features of the dry sludge and adsorbent which are shown in Figure 1 were scanned by JSM-6330F Scanning Electron Microscopy. The surface feature of the dry sludge was smooth and low in strength, while the surface feature of the adsorbent was ragged and high in strength with many pores.

The characteristic of the distributed pores in the surface of dry sludge and adsorbent are shown in Figure 1. The pores with diameter smaller than 0.7 nm are called ultramicropore, with diameter between 0.7 nm to 2 nm are called micropore. Pores with diameter between 2 nm and 50 nm or larger than 50 nm are called mesopore or macropore. The classification is based on the characteristic effect of the adsorption isotherm according to APHA. The capability of micropore and mesopore can be described by Iodine number and methylene blue number (see Table 2).

In the process of making adsorbent from sludge, part of the quality was lost: the TG (thermo gravimetric) and DTG (thermo gravimetric rate) curves of adsorbent drawn by ZRY-2P thermo gravimetric analysis instrument are shown in Figure 2. The conditions of thermo gravimetric analysis

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**Table 1** The chemical compositions of the dry sewage sludge (%)

<table>
<thead>
<tr>
<th>Element</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>P(_2)O(_5)</th>
<th>K(_2)O</th>
<th>Zn</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16.28</td>
<td>6.35</td>
<td>5.15</td>
<td>4.10</td>
<td>1.67</td>
<td>1.65</td>
<td>1.12</td>
<td>0.19</td>
<td>4.30</td>
<td>0.17</td>
<td>16.3</td>
<td>0.045</td>
<td>4.14</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.034</td>
<td>1.25</td>
<td>0.56</td>
<td>1.15</td>
<td>6.66</td>
<td>0.22</td>
<td>C</td>
<td>S</td>
<td>N</td>
<td>Other element</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>61.20</td>
<td>0.06</td>
<td>1.55</td>
<td>&lt;0.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2** Iodine number and methylene blue number

<table>
<thead>
<tr>
<th>Sorting</th>
<th>Dry sludge</th>
<th>Adsorbent</th>
<th>Activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine number (mg g(^{-1}))</td>
<td>50.7</td>
<td>188.2</td>
<td>1,207.8</td>
</tr>
<tr>
<td>Methylene blue number (mg g(^{-1}))</td>
<td>11.8</td>
<td>67.1</td>
<td>249.7</td>
</tr>
</tbody>
</table>
were nitrogen protecting (the aerate rate was 30 ml per minute) and the heating rate was 15°C per minute the temperature range was from 20°C to 1,000°C. There were two visible gravimetric summits at 79.5°C and 574°C. The gravimetric ratio was 3.1% at 79.5°C because of the volatilization of the water and some volatile organics. The gravimetric ratio was 43.7% at 574°C because of the scission of the macromolecule organics. A lot of macromolecule organics were decomposed into smaller gaseous molecules. In this process, the carbon skeleton was formed, the adsorbent generated much pores, and the capability of absorption enhanced. From the TG and DTG curves, the volatile constituent was about 46.8% in the dry sludge.

All the analyses were carried out according to APHA et al. (1998). All the reagents were analysis grade. The dosage was measured in mass of Cr.

At first, the powder of K₂Cr₂O₇ was dried for 2 hours at 110°C to wipe off water in the K₂Cr₂O₇. The solution of Cr (VI) was confected by K₂Cr₂O₇ and deionized water. 50 ml solution of Cr (VI) and definite magnitude adsorbent were put into four 100 ml ground-glass stoppered flask, the concentrations were 20 mg L⁻¹, 50 mg L⁻¹, 100 mg L⁻¹ and 100 mg L⁻¹. The pH of the solution was 2.5 except in effect of pH experiment, which was adjusted by sulfuric acid, and then the flasks were vibrated. Temperatures of the solutions were 25°C, the adsorbent dosage was 4 g L⁻¹ except in effect of adsorbent dosage experiment. At last, the mixed solution was centrifuged at the condition of 4,000 rpm for 10 minutes, and the Cr (VI) contents of the supernatant were determined. In the regeneration experiments, the adsorbent was regenerated by sodium hydrate solution with three recirculation cycles. All of the experiments were repeated twice, and the results were in average. The calculation of the removal rate was as follows: the dosage of Cr (VI) and the volume of the supernatant are known, so the total content of Cr (VI) can be calculated, the ratio of them is the removal rate.

**RESULT AND DISCUSSION**

**Optimum conditions for Cr (VI) removal**

**Effect of contact time on Cr (VI) removal**

It could be seen in Figure 3 that the removal rate of Cr (VI) was increasing with rising of contact time. When the contact times of the solutions containing adsorbent or activated carbon were above 6 hours or 60 minutes, the removal rates did not increase. It could be seen that the
adsorbent efficiency of activated carbon was much more rapid than adsorbent. The optimum contact time was 6 hours of adsorption, the removal rates were 99.22, 92.55 and 65.32% of the adsorbent, and the removal rate was 95.30% of the activated carbon. So the optimum contact time was set at 6 hours.

**Effect of pH on removal rate**

It could be seen from Figure 4 that the removal rate of Cr (VI) was increasing with the decline of contact time. In the acidic solution, the main form of Cr (VI) is HCrO$_4^-$ (Benefield et al. 1982), and the HCrO$_4^-$ is the most easily absorbed in all kinds of Cr (VI) forms (Garg et al. 2004). The H$^+$ can neutralize the anion on the surface of the adsorbent. It is profitable for the spread of HCrO$_4^-$ (Rao et al. 2002). Other Cr (VI) in the acidic solution which can be reduced to Cr (III) by the adsorbent also can reduce the content of Cr (VI). The chemical equations are as follows:

\[
3C + 2Cr_2O_7^{2-} + 16H^+ = 3CO_2 + 4Cr^{3+} + 8H_2O \quad (1)
\]

\[
C + 2Cr_2O_7^{2-} + 12H^+ = CO + 2Cr^{3+} + 6H_2O \quad (2)
\]

When the pH was lower than 2, the removal rate did not increase significantly. The removal rates were 97.78, 97.73 and 75.00% of the adsorbent and the removal ratio was 99.97% of the activated carbon. So the optimum pH was set at 2.

**Effect of adsorbent dosage on removal rate**

It could be seen from Figure 5 that the removal rate of Cr (VI) was increasing with the rising of adsorbent dosage. When the adsorbent dosage was below 4 g L$^{-1}$, the removal
rate increased visibly; while the adsorbent dosage was above 4 g L$^{-1}$, the removal rate did not rise. More adsorbent could supply more adsorption sites, so the removal rate increased. Cr (VI) in the solution disappeared when the adsorbent dosage was above 4 g L$^{-1}$, so the removal rate did not rise. The optimum adsorbent dosage was 4 g L$^{-1}$, the removal rates were 99.96, 86.48 and 83.56% of the adsorbent and the removal ratio was 99.61% of the activated carbon. The adsorption capacity of adsorbent was only 3.04 mg g$^{-1}$ lower in condition that the concentration was 100 mg L$^{-1}$. So the optimum adsorbent dosage was set at 4 g L$^{-1}$.

**Adsorption kinetics**

The purpose of adsorption kinetics research is to obtain the effect of the temperature, pressure, concentration, reaction time on reaction rate, and analyze the reaction mechanism by mathematic calculation.

The results of the isothermal adsorption are shown in Figure 6. In the first 4 hours, the adsorption quantity increased and reached the max quantity after 6 hours, so the adsorption equilibrium time was 6 hours.

**Pseudo first-order reaction kinetics**

The log ($q_e - q_t$) to $t$ curve showed the pseudo first-order reaction kinetics, the rate constant was 0.00848 min$^{-1}$, 0.0105 min$^{-1}$, 0.01122 min$^{-1}$ respectively. The change of rate constant should proportionately increase in the actuating force (concentration gradient) of the first-order reaction. But when the internal diffusion became the main controlling factor of the adsorbent rate, the relations no longer fitted. From Figure 7, the fit was optimum in the first 30 minutes, and then there were more deviations, the result of which could also be find in the Ho and McKay’s experiments. The results showed that only rapid reaction could finish in the first 30 minutes, the pseudo first-order reaction kinetics model was suited (Ho & McKay 1998).

In this reaction, the fit of the first-order reaction kinetics model was not optimum, the related coefficient $R^2$ were between 0.9523 and 0.9988. Although the reaction fitted the first-order reaction kinetics model, it was not suitable to all the reaction processes (see Table 3).

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Comparison of the pseudo-first-order and pseudo second-order adsorption rate constants for different initial concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (mg L$^{-1}$)</td>
<td>$q_e$ (mg g$^{-1}$)</td>
</tr>
<tr>
<td>20</td>
<td>0.9410</td>
</tr>
<tr>
<td>50</td>
<td>2.7413</td>
</tr>
<tr>
<td>100</td>
<td>9.9156</td>
</tr>
<tr>
<td>$K_2$ (g mg$^{-1}$ min$^{-1}$)</td>
<td>$h$ (mg g$^{-1}$ min$^{-1}$)</td>
</tr>
<tr>
<td>0.03661</td>
<td>1.0206</td>
</tr>
<tr>
<td>0.00835</td>
<td>1.2205</td>
</tr>
<tr>
<td>0.00218</td>
<td>0.6807</td>
</tr>
</tbody>
</table>
Pseudo second-order reaction kinetics

The $tq_t^{-1}$ to $t$ curve showed the pseudo second-order reaction kinetics figure, the rate constant was $0.03661 \text{ g mg}^{-1} \text{ min}^{-1}$, $0.00835 \text{ g mg}^{-1} \text{ min}^{-1}$ and $0.00218 \text{ g mg}^{-1} \text{ min}^{-1}$ respectively; the related coefficient $R^2$ was 0.99995, 0.99937 and 0.99768, the reaction fitted the second-order reaction kinetics model well. From Figure 8, the fit was optimum in all reactions, which showed that Cr (VI) compound to the radical of the adsorbent in the reaction and was fixed onto the adsorbent surface. Pseudo second-order reaction kinetics model could explain the reaction better than pseudo first-order reaction kinetics model.

Research of adsorption kinetics mechanism

The $q_t$ to $t^{0.5}$ curve in Figure 9 showed that the reaction should be separated to two parts. The first part showed the boundary layer effect and the second part showed the spread internal diffusion effect of the particle spread and the pores spread, the gradient of the line showed the internal diffusion rate constant, the intercept of the line showed the boundary layer effect, which increased with the influence of the surface absorption in the rate controlling step on the adsorbent surface.

Adsorption isotherms

Isothermal adsorption equilibrium processes can be mathematically described to obtain an adsorption isotherm equation, called an adsorption isotherm model. There are several models to describe the adsorption isotherm equation, and the most common models are Langmuir isothermal adsorption empirical equation and the Freundlich isothermal adsorption empirical equation. The results of the isothermal adsorption are shown in Figure 10. In the condition of 6 hours, adsorbent dosage 4 g L$^{-1}$, 25°C, initial concentration of the Cr (VI) increased from 10 mg L$^{-1}$ to 100 mg L$^{-1}$.

The adsorption quantity of Cr (VI) on adsorbent surface increased with the rising of initial concentration of Cr (VI). The adsorption isotherm fitted the Langmuir isothermal adsorption empirical equation. The Langmuir isothermal adsorption empirical equation was processed to linearity, the linear equation of the Langmuir isothermal adsorption model.
is shown as follows:

\[
\frac{C}{q} = \frac{C}{q_{\text{max}}} + \frac{1}{K_a q_{\text{max}}} 
\]

In the equation, \( q \) (mg \( g^{-1} \)) is the adsorption quantity by unit mass adsorbent when the isothermal adsorption is poised. \( C \) (mg L\(^{-1} \)) is the final concentration when the isothermal adsorption is poised, called equilibrium concentration. \( q_{\text{max}} \) (mg g\(^{-1} \)) is the maximum theoretical adsorption quantity when the elements of the Cr (VI) formed the one-layer adsorption on the adsorbent surface. \( K_a \) (L mg\(^{-1} \)) is the Langmuir adsorption equilibrium constant. Fitting the isothermal adsorption data with the linear equation of the Langmuir isothermal adsorption, the results are shown in Figure 11, \( q_{\text{max}} = 18.30496 \) mg g\(^{-1} \), \( K_a = 0.9582529381 \) L mg\(^{-1} \), and the related coefficient \( R^2 = 0.9924 \). The data could fit the linear equation well.

The adsorption quantity \( q \) (mg \( g^{-1} \)) and the equilibrium concentration \( C \) (mg L\(^{-1} \)) of the isothermal adsorption were processed by logarithm, which could fit the Freundlich isothermal adsorption empirical equation. The Freundlich isothermal adsorption empirical equation was processed to logarithm linearity, the logarithm linear equation of the Freundlich isothermal adsorption is shown as follows:

\[
\ln q = \frac{1}{n} \ln C + \ln K_f
\]

In the equation, \( q \) (mg \( g^{-1} \)) is the adsorption quantity by unit mass adsorbent when the isothermal adsorption is poised. \( C \) (mg L\(^{-1} \)) is the final concentration when the isothermal adsorption is poised, called equilibrium concentration. \( K_f \) (mg \( g^{-1} \) (L mg\(^{-1} \))\(^n\) is the Freundlich adsorption equilibrium constant, which is the adsorptive capacity of the adsorbent, \( n \) is the constant of the adsorption density. Fitting the isothermal adsorption data with the logarithm linear equation of the Freundlich isothermal adsorption, the results are shown in Figure 12. \( K_f = 1.223518 \) (mg g\(^{-1} \) (L mg\(^{-1} \))\(^n\), \( n = 0.44376 \), and the related coefficient \( R^2 = 0.96652 \). The data could fit the Langmuir model better than the Freundlich model, so it should be a monomolecular layer adsorption rather than a multilayer adsorption.

**Adsorbent regeneration**

**Effect of time on the regeneration of Cr (VI)**

It could be seen from Figure 13 that the regeneration of Cr (VI) was increasing with the rising of contact time, the adsorbent dosage (saturated) was 4 g L\(^{-1} \). The concentration of the regenerate solution was 0.1 mol L\(^{-1} \) NaOH, and the temperature was 25°C. When the contact time was
above 9 hours, the regeneration ratio did not increase any more. The optimum contact time was 9 hours.

**Effect of NaOH concentration on the regeneration of Cr (VI)**

It could be seen from Figure 14 that the regeneration of Cr (VI) was increasing with the rising of NaOH concentration, the adsorbent dosage (saturated) was 4 g L\(^{-1}\), the initial concentration of the Cr (VI) solution was 100 mg L\(^{-1}\), the contact time was 9 hours, and the temperature was 25°C. When the concentration was above 1 mol L\(^{-1}\), the regeneration ratio did not increase. On the adsorbent surface, OH\(^-\) could react with HCrO\(_4\) generating CrO\(_4^{2-}\), because the adsorptive capacity of the CrO\(_4^{2-}\) was not strong enough and Cr (VI) was regenerated. In order to save the NaOH and reduce the cost of the adsorbent regeneration, the optimum concentration of NaOH was 1 mol L\(^{-1}\).

\[
\text{HCrO}_4^- + \text{OH}^- = \text{CrO}_4^{2-} + \text{H}_2\text{O}
\quad (5)
\]

**Repeat recycles of adsorbent**

The adsorbent (saturated) was recycled by HCl solution, because H\(^+\) could neutralize the OH\(^-\) coming from the regenerate solution. Three repeat recycles are shown in Table 4. In the first repeat recycle, 99% of the adsorbent could be regenerated, and in the second and the third recycles were 87% and 63%. The adsorbent was not only wide-ranging but also very efficient. It was an excellent adsorbent to dispose the wastewater which contains Cr (VI).

**CONCLUSIONS**

According to the findings in this paper, the optimum condition for Cr (VI) removal was that: the mixing time was 6 h, the pH was 2 and the dosage of adsorbent was 4 g L\(^{-1}\). Under optimum conditions, the removal rate of Cr (VI) was close to 100%. The adsorption capacity of adsorbent was 7.49 mg g\(^{-1}\) lower and the removal rate was 29.98% lower than activated carbon. The optimum condition for adsorbent regeneration was that: the dissolved time was 9 h and the dissolved reagent concentration was 1 mol L\(^{-1}\). Adsorbent made from sludge for removing the Cr (VI) in wastewater solved the difficulties in disposing sludge, while the waste water containing Cr (VI) could also be treated with lower cost processing at the same time.

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**REFERENCES**


