Preparation of xanthated bentonite and its removal behavior for Pb(II) ions

Y. F. He, F. R. Li, R. M. Wang, F. Y. Li, Y. Wang and Z. H. Zhang

ABSTRACT

Xanthate was successfully grafted onto bentonite by a relatively simple solution reaction. The obtained xanthated bentonite (XBent) was characterized by FT-IR spectrophotometer, thermogravimetric analysis (TG), particle size analysis, x-ray diffraction (XRD) and scanning electron microscopy (SEM). XBent acting as a type of environmentally friendly adsorbent was applied to remove lead ions from aqueous solutions. The optimum conditions were as follows: [Pb^{2+}] = 500 mg L^{-1}, [XBent] = 2 g L^{-1}, pH = 5.0; oscillating 60 min under 200 rpm at 25°C. The removal rate of lead was up to 99.9%. It was found that the lead(II) ions—XBent adsorption isotherm model fitted well to the Freundlich isotherm. The adsorption mechanism was also investigated by SEM and XRD, which concluded that lead ions were complexed or chelated with XBent. XBent appears to have potential to be used later in water treatment as a type of inorganic polymer reagent.

Key words | adsorbent of lead ion, adsorption mechanism, bentonite, modified bentonite, water-treatment

INTRODUCTION

Heavy metals and their compounds are widely used in industrial applications such as metallurgy and chemistry, and in battery, paper and paint manufacturing. These compounds are non-degradable and therefore continue to accumulate in water bodies. The presence of heavy metals in the aquatic environment is a major concern due to their extreme toxicity to aquatic life, human beings, and the environment (Bhattacharyya & Gupta 2007). Lead(II) ions is one of the most toxic heavy metal elements which accumulates in the body and causes long-term damage to the nervous and hematopoietic systems (Stathi et al. 2007). It can also damage reproductive cells and reduce sexual function. Therefore, strict control of lead emissions is necessary to reduce lead pollution, which can be effective in reducing the assimilation of lead in humans via drinking water and food intake (Khaloudun et al. 2006).

Although various treatment techniques have been employed to treat wastewater containing heavy metal ions, such as chemical precipitation (Chen et al. 2007; Li et al. 2008), ion exchange, filtration and adsorption (Ma & Zhu 2006; Yang et al. 2007; Zhu & Ma 2008; Zohra et al. 2008), most of these techniques suffer from drawbacks. These drawbacks include lack of effectiveness, expense, the generation of secondary pollution and some are ineffectiveness for low metal concentrations. Hence, there is a crucial need to develop a method that is not only cost effective and economical, but can also be easily implemented. Among these methods, adsorption is a simple and widely used process. The cheaper, easily obtainable absorbent materials can be used for the adsorption of heavy metals.

Because of its high specific surface area, bentonite (Bailey et al. 1999), a type of clay with a negative surface charge, can be offset by exchangeable cations (e.g. H^+, Na^+ or Ca^{2+}) (Liu et al. 2006). Bentonite has been used in wastewater containing heavy metal ions treatment (Arfaoui et al. 2008; Eren 2008). However, as it has highly hydrophilic layers, it can not effectively remove hydrophobic pollutants. It is also difficult to separate bentonite...
from wastewater because of high dispersion. The modification of bentonite may be an effective method to increase its application in environmental protection. In this study, in order to obtain a highly efficient method for adsorbing heavy metal ions, bentonite was modified by xanthate and was applied in the removal of lead(II) ions from aqueous solutions. The structure and adsorption mechanism of xanthated bentonite (XBent) were also investigated.

MATERIALS AND METHODS

Materials

Natural bentonite (NB) as Ca-bentonite was obtained from the Xinjiang Uygur Autonomous Region of China. After the removal of impurities, pure Ca-bentonite (CaB) was obtained. Sodium bentonite (NaB) was obtained by further treatment with sodium carbonate for improving its dispersibility. Anhydrous sodium carbonate (AR), CS₂ (AR), acetone (AR), magnesium sulfate (AR), Pb(NO₃)₂ (AR), and NaOH (AR) were commercially available and used to the experiments.

Preparation of xanthated bentonite (XBent)

The typical procedure for preparation of xanthated-bentonite (XBent) was as follows: 20.0 g of NaB was dispersed in 120 mL of water, which afforded NaB suspensions. The suspensions were quickly mixed with 32 g of NaOH under vigorous stirring at 35°C. 7.23 mL of CS₂ solution was slowly added over 1 hr. Then 50 mL of 10% MgSO₄ solution was added with stirring. After reacting for 30 min, XBent was filtered and washed with 10% MgSO₄ solution until the filtrate was colorless. The light green pre-product was obtained after several washings with acetone. After drying under vacuum at 45°C for 10 h, the obtained XBent was ground and separated with a 100 Mesh.

Procedures of the adsorption test

An imitation lead aqueous solution (concentration: 1,000 mg L⁻¹) was prepared using Pb(NO₃)₂ (Sabriye Doyurum & Ali Celik 2006). Adsorption experiments were carried out in a 250 mL batch reactor containing various amounts of adsorbent and 100 mL of the metal solution at different concentrations and pH. The batch reactors were then shaken at 200 rpm for 5–60 min. After standing for about 5–10 min, the content of residual lead(II) ions was measured using a WXY-402C flame atomic absorption spectrophotometer (Shenyang Analytical Instrument Co., China).

Instruments for characterization

FT-IR spectrophotometer

The samples of NB, CaB, NaB and XBent as KBr pellets were subjected to FT-IR spectral analysis on a FTS-3000 spectrometer (DigiLAB Merlin, USA) at a range of 4,000 to 400 cm⁻¹ transmission.

Thermogravimetric analysis (TG)

All the samples (10.0 mg) used had been dried in vacuum at 70°C for 12 h. The thermal degradation test was conducted on TG/DTA (Pyris Diamond, PerkinElmer) at a heating rate of 10°C/min under nitrogen. The change in the weight differential difference with temperature was recorded.

Scanning electron microscopy (SEM)

The surface morphology of NaB, XBent and Pb-XBent were observed and the images captured by a JSM-5600LV Scanning Electron Microscope (JEOL, Japan). After drying for more than 10 h under vacuum at 60°C, the particles were then coated with gold powder and attached to the microscope support with silver glue. SEM photographs were taken under a voltage of 20 kV and magnified 2,000 times.

X-ray diffraction (XRD)

NaB, XBent and Pb-XBent were dried in an oven at 60°C for more than 10 h. The x-ray diffraction of the powdered samples was analyzed using a D/max-2400 X-ray Diffractionmeter (Japan) under the following conditions: graphite monochromatized Cu Kα radiation; voltage 40 kV; electric current 100 mV; scanning ratio: 2θ = 5°/min.
Determination of the particle size

The Zetasizer analyzer (Nano series, Malvern Instruments Ltd., UK) was used to measure the particle size of NB, CaB, NaB and XBent. Suspensions of these substances were prepared by adding 0.03 g of each substance to 100 mL of distilled water, and the suspensions were ultrasonically vibrated for 30 min after 10 min of gentle stirring. The samples were analyzed and the data were recorded.

RESULTS AND DISCUSSION

Characterization of XBent

FT-IR spectra

The IR spectra of NB, CaB, NaB and XBent were shown in Figure 1. The broad peaks near 1,000 cm\(^{-1}\) were ascribed to Si-O-Si stretching vibrations. The \(-\text{O-H}\) stretching vibration frequencies near 3,500 cm\(^{-1}\) and the \(-\text{O-H}\) stretching vibrational frequencies at 1,650 cm\(^{-1}\) were evidence of zeolitic water in for NB, CaB and NaB (Ning 2000). For XBent, peaks were seen at 1,250–1,020 cm\(^{-1}\) (broad), and 1,675 cm\(^{-1}\) due to the absorption of C-S (Yin et al. 2004), and at 1,090–1,020 cm\(^{-1}\) due to the characteristic peak of Si-O-C. This indicated that xanthate was attached to bentonite.

TG measurement

The TG curve of XBent and its materials (NB, CaB, NaB) were shown in Figure 2. For NB, CaB and NaB, the adsorbed water was lost in the range from room temperature to 100\(^\circ\)C. The main interlayer water was lost at 130–210\(^\circ\)C. The structural water was lost in 550–700\(^\circ\)C. For XBent, there was more weight loss in the range of R.T.–100\(^\circ\)C and in the range of 320–550\(^\circ\)C than in NB, CaB and NaB. This indicated that there were a large number of internal organic groups in XBent. The reduced weightlessness in the range of 550–700\(^\circ\)C also indicated that the xanthate group significantly reduced bentonite’s hydrophilicity to the structural water.

X-ray diffraction analysis of XBent

X-ray diffraction (XRD) was used to measure structural changes of XBent to its raw material (NaB). The results were shown in Figure 3. In the charts of NaB, the characteristics of the bentonite diffraction peaks in the small angle range (5°–7°) were narrow and sharp (Li et al. 2005). Its interlayer distances (d001 values) were 1.23 nm, and
the corresponding 2θ was 7.18°, which was consistent with the typical Na-based bentonite (Miao 1984; Tu et al. 2007). For XBent, the xanthated NaB, its miscellaneous peaks with 2θ > 35° were similar to those of NaB. However, the characteristic peaks in the small angle range (5°–7°) changed, 2θ became 6.06°. The shape of the peak was slightly blunt and weak, and the d001 value was 1.46 nm. At 2θ = 17.88°, a new peak appeared with a d001 value of 0.496 nm. It was suggested that hydroxyl groups of bentonite were partly substituted by xanthate groups.

**Particle size**

Information on the dispersion ability of NB, CaB, NaB and XBent were obtained from the measurements of particle size (Table 1). These measurements showed that the size of XBent was uniform and near to 6 μm, which was larger than its materials. It was suggested that the particles of bentonite were easy to gather for a greater structural unit after being modified by xanthate and post-treatment by MgSO4.

![XRD chart of XBent and NaB](image)

**Figure 3** The XRD chart of XBent and NaB.

The particle size of NB and CaB were larger than 1 μm with large dispersivity. The particle size of NaB was the smallest (<1 μm). This is one of the reasons why the solid–liquid separation of NaB was very difficult in adsorption experiments.

**Surface images of XBent and its materials**

The surface morphology of XBent and its materials was observed by SEM (Figure 4). NaB was a layered amorphous aggregate with a lamellar ambiguous edge. The surface of XBent was significantly changed compared with that of NaB. The tight lamella structure of bentonite was loosened after being xanthated, but the bentonite particles aggregated easily. It indicated that XBent had an extensive surface area and may be used as a sorbent material.

**The adsorption behavior of XBent for removing lead(II) ions from aqueous solutions**

The adsorption behavior of XBent and its materials (NB, CaB and NaB) in the treatment of lead(II) ions solutions were investigated (Table 2). It was found that the lead(II) ions removal rate was up to 99.9%. After disposal, the residual concentration of lead(II) ions in the solution was less than 1.0 mg L⁻¹. Although NB and CaB showed adsorption activity for lead(II) ions, the adsorbing materials were difficult to filter as the particles were too small, thus they would easily form a colloid in aqueous solutions and to be difficult to settle. NaB was more difficult to settle than the others. These findings indicated that the adsorption capacity of XBent for lead(II) ions was very high and that the particle size was large. The sedimentation and filtration of XBent were also very easy.

pH value, adsorbent dosage, contact time and temperature were investigated for the determination of the optimum adsorption conditions. And every experiment had been done three times, respectively.

**Effect of adsorbent dosage**

The effect of adsorbent dosage on the adsorption capacity of XBent was measured at room temperature (Figure 5). When the initial concentration of lead(II) ions was maintained

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB</td>
<td>1.04 ± 0.53</td>
</tr>
<tr>
<td>CaB</td>
<td>1.33 ± 0.29</td>
</tr>
<tr>
<td>NaB</td>
<td>0.85 ± 0.37</td>
</tr>
<tr>
<td>XBent</td>
<td>5.87 ± 0.67</td>
</tr>
</tbody>
</table>

**Table 1** The particle size of XBent and its materials (25°C, water dispersants)
([Pb^{2+}]_{\text{initial}} = 800 \text{ mg L}^{-1}) in the raw lead(II) ions solutions, the lead(II) ions removal rates by XBent increased when the adsorption dosage increased. If the adsorbent dosage increased from 0.4 g L^{-1} to 2.0 g L^{-1}, the removal rate of lead(II) ions rose from 38.2% to 95.5%. When the adsorbent dosage increased to 4.0 g L^{-1}, residual lead(II) ions could not be detected. Taking into account the actual cost of the process application and the residual concentration of lead(II) ions in the solution, the optimum dosage was 2 g L^{-1}.

Effect of initial lead(II) ions concentration

The effect of initial metal concentration on the adsorption of lead(II) ions was shown in Figure 6. When the initial concentration of lead(II) ions was increased from 20 mg L^{-1} to 500 mg L^{-1}, the removal rate increased from 98.0% to 99.9%. If the initial concentration of lead(II) ions exceeded 500 mg L^{-1}, the removal rate decreased slightly.

Effect of contact time

The effect of contact time on the adsorption of lead(II) ions by XBent was shown in Figure 7. When the contact time increased from 10 min to 60 min, the removal rate increased from 79.8% to 99.9%. This showed that most of the adsorption was completed within 60 min, and the residual lead(II) ions concentration was 0.83 g L^{-1}, which is less than 1.0 mg L^{-1}.

Effect of temperature

The effect of temperature on lead(II) ions adsorption was shown in Figure 8. The removal rate of lead(II) ions increased slightly to 98.6–99.5% when the temperature increased from 15 to 45°C. At 25°C, the removal rate reached 99.2%. This indicated that the XBent adsorbing materials were suitable in environmental temperatures.

Effect of pH value

The effect of pH on lead(II) ions removal by XBent was investigated in the pH range 3–9 (Figure 9). The removal

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>NB</th>
<th>CaB</th>
<th>NaB</th>
<th>XBent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal rate (%)</td>
<td>57.2</td>
<td>39.3</td>
<td>57.3</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Cond.: [Pb^{2+}]_{\text{initial}} = 500 \text{ mg L}^{-1}; [XBent] = 2 g L^{-1}; 25°C; pH = 5.0.
rates were above 99%, which suggested that lead(II) ions adsorption was not obviously influenced by pH value.

**Freundlich adsorption isotherm of lead(II) ions onto XBent**

Isotherm experiments were carried out at room temperature (25°C) for different initial lead(II) ions concentrations. The adsorption data were analyzed to see whether the isotherm obeyed the Langmuir (Langmuir 1918), Freundlich (Freundlich 1906; Sabriye Doyurum & Ali Celik 2006) and Dubinin–Radushkevich (D–R) (Dubinin & Radushkevich 1947) isotherm models. It was evident from the above isothermal conditions that the adsorption of lead(II) ions onto XBent was fitted well to the Freundlich isotherm, as the experimental index of Pb²⁺-XBent adsorption was 0.56. The adsorption isotherms were shown in Figure 10. This indicated that adsorption of lead(II) ions onto XBent was easily performed.

The optimized adsorption conditions were: [XBent] = 2 g L⁻¹, 500 mg L⁻¹ lead(II) ions solution, an initial pH value 5.0, oscillating 60 min under 200 rpm at 25°C. The removal rate of lead(II) ions was up to 99.9%. Compared with reported results of modified bentonite clay in literatures, for example, adsorption capacity of 8-hydroxy quinoline-immobilized bentonite (Ozcan et al. 2009), hexadecyltrimethylammonium bentonite clay and benzyltriethylammonium bentonite clay (Oyanedel-Craver et al. 2007) was 142.9, 69.1 and 36.2 mg/g, respectively, the adsorption capacity of XBent (249.8 mg/g) was higher.
Adsorption mechanism of lead (II) ions onto XBent

The suggested adsorption process of XBent was shown in Scheme 1. XBent adsorbent contained radical anion functional xanthated groups. The electrons on sulfur atoms showed comparative fluidity with more electron donating effects, which enabled single-bond sulfur atoms to be in the larger context of a negative electric field. The heavy metal cations (Diao et al. 2006) had strong catching ability to generate small soluble chelates or salts (Bose et al. 2002; Abollino et al. 2003). The original radical xanthate anion of bentonite could not only form bentonite-based xanthalato lead complexes with lead(II) ions in aqueous solution (1a, 1c), but also form insoluble chelates with lead(II) ions (1b).

In order to confirm the adsorption mechanism of lead(II) ions onto XBent, XRD spectra and SEM images of Pb-XBent, where the lead(II) ions had been adsorbed onto XBent, were measured.


**Figure 10** The isothermal adsorption of XBent adsorbent on lead(II) ions. Cond.: [XBent] = 2 g L⁻¹; Temp: 25°C; pH 5.0; 60 min.
In the XRD spectra of Pb-XBent (Figure 11), the characteristic peaks in the small angle range (5°–7°) showed some obvious changes. 2θ was changed to 5.880°. The shape of the peak was slightly blunt and weak, and the d001 value was 1.50 nm. At 2θ = 34.08°, a new peak appeared with a d001 value of 0.263 nm. It was suggested that the lead(II) ions were adsorbed onto the surface of xanthated bentonite. The peaks after 35° were also changed. It was suggested that chelates were formed.

The surface image of Pb-XBent was also measured when lead(II) ions had been adsorbed onto XBent (Figure 12). After adsorbing lead(II) ions, the basic shape of Pb-XBent was similar to XBent. However, lamellar dissection and curling phenomenon was even more apparent because lead(II) ions had entered the surface layer.

CONCLUSIONS

A new highly efficient adsorbent for the removal of heavy metal ions, xanthated bentonite (XBent) was prepared. Its structure and surface morphology were characterized by FT-IR, TG, particle size analysis, XRD and SEM. XBent was applied to the removal of lead(II) ions from the aqueous solutions. The removal rate of lead(II) ions was up to 99.9%. The optimized adsorption conditions were: [XBent] = 2 g L⁻¹, 500 mg L⁻¹ lead(II) ions solution, an initial pH value 5.0, oscillating 60 min under 200 rpm at 25°C. It was found that the lead(II) ions–XBent adsorption isotherm model fitted well to the Freundlich isotherm. The adsorption mechanism was also suggested and it thought that lead(II) ions were complexed or chelated with XBent. Xanthated-bentonite (XBent) is an efficient adsorbent of lead(II) ions, where the adsorption of metal ions is rapid. The materials are cheap and from large resources. So, XBent appears to have potential to be used later in water treatment as a type of inorganic polymer reagent in further.

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