The Factors on Removal of Zinc Cation from Aqueous Solution by Bentonite

Shuli Ding¹, Juanjuan Shen¹, Bohui Xu¹, Qinfu Liu², Yuzhuang Sun¹

¹Key Laboratory of Resources Reconnaissance of Hebei Province, Hebei University of Engineering, Handan, China; ²School of Resources and Safety Engineering, China University of Mining & Technology, Beijing, China.
E-mail: dingshulil@126.com

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ABSTRACT

The removing zinc cation from aqueous solution by Ca-bentonite and Na-exchanged bentonite was studied. The factors such as the initial concentration of Zn²⁺, the liquid-to-solid ratio, pH, adsorption time, stirring speed, coexisting ions, temperature and bentonite particle size were investigated. The results show that the adsorption process of bentonite accorded with the Freundlich isotherm model, the removal of Zn²⁺ by Ca-bentonite and Na-exchanged bentonite reached equilibrium in 2 h, and adsorption of Na-bentonite was superior to Ca-bentonite. The adsorption rate of zinc increased with increasing pH, temperature, stirring speed, time span and with decreasing bentonite particle, the initial concentration of Zn²⁺ and the liquid-to-solid ratio. In mixed solution which contains Pb²⁺ and Cr⁶⁺, Pb²⁺ has no influence on the removal of Zn²⁺ by both the bentonites while Cr⁶⁺ can decrease it.

Keywords: Bentonite, Zn²⁺, Adsorption

1. Introduction

Heavy metals are typical and persistent environmental pollutants. Because of its toxicity and nonbiodegradable nature, metals are of special significance. The presence of heavy metals in wastewater and surface water is becoming a severe environmental and public health problem. Recently, natural materials, which are good sorbents and inexpensive have received much attention in heavy metal wastewater treatment [1-3]. Bentonite is the most abundant phyllosilicate mineral and its main mineral component is montmorillonite. Bentonite which was used in wastewater treatment has the advantage of simple device, low cost, no repollution etc.

The adsorption capacity of montmorillonite for heavy metal ions has been concerned since 1960s [4-8]. In literature various types of bentonite adsorbents have been cited. H. Omar et al. [9] investigated the adsorption potential of raw and formaldehyde modified-bentonite for the removal of ⁶⁰Co radionuclide from radioactive waste solutions. S. T. Akar et al. [10] combined white rot fungi and montmorillonite, this proposed was successfully used to sequester of copper ions from real wastewater in continuous mode. E. Alvarez-Ayuso et al. [11], concluded that both the Ca-montmorillonite and na-montmorillonite can remove heavy metals from the industrial effluent efficiently. W. Matthes et al [12], studied sorption of Al and Zr-hydroxy intercalated and pillared bentonite and found that the adsorption of heavy metal by montmorillonite was majorly due to the coordination of surface hydroxyl groups as well as the interchange with cation among crystal layers.

The major objective of this work is to study the adsorption of Zn²⁺ in aqueous solution as well as its influencing factors. Handan Ca-bentonite and Na-exchanged bentonite were used in the experiments with the view to discovering their metal ion recovery potential from effluents. The adsorption effect of Cr⁶⁺ and Pb²⁺ compete with Zn²⁺ in aqueous solution was analyzed.

2. Materials and Methods

2.1. Equipment

The X-ray diffraction (D/max-2200 diffractometer at a scanning speed 4° (2θ)/min, using CuKα radiation at 40kV, 100mA) was used to identify the Mineral composition. 721 model spectro-photometer was used to measure the content of Zn²⁺, Cr⁶⁺ and Pb²⁺ in solutions. Also, the AW120 electron balance, HJ-5 constant temperature magnetic force beater, pHS-3C acidimeter, anion and cation exchange column, GL-20G-II model high-speed refrigerated centrifuge and some other instruments were...
used in experiments.

2.2. Materials

The Ca-bentonite M-1 was obtained from Handan district (Hebei Province, China). It was purified in the laboratory to remove carbonates, iron, hydroxide and organic matter. The bentonite was then crushed, ground, sieved through 200 mesh and dried at 105°C in an oven. Its mineralogical composition, chemical components and physicochemical properties are listed in Table 1 to 3 respectively.

All the other reagents used were of analytical grade and were obtained from Merck (Darmstadt, Germany). Metal salts of ZnCl₂·2H₂O, Pb(NO₃)₂, potassium dichromate(K₂Cr₂O₇) were used to prepare metal ion solutions. The solutions (1000 g/L) were prepared by dissolving appropriate amounts of metal salts in doubly distilled water. The working solutions were prepared by diluting the stock solutions to appropriate volumes. pH adjustments of these solutions were made by 0.01, 0.1 and 1 M HNO₃ and NaOH solutions.

2.3. Preparation of Na-Bentonite

The Na-exchanged bentonite M-2 was prepared as follows: the raw bentonite M-1 was mixed up with Na₂CO₃ according to 100:3, the slurry was made with deionized water in liquid-to-solid ratio of 10:1 afterwards. This suspension was stirred using the magnetic stirrer for 1 h, then standing, removal of the underlying sandy, centrifuging, drying, grinding. The sample was subsequently referred to as Na-exchanged bentonite adsorbent.

2.4. Method

Adsorption on the samples was determined in batch sorption experiments in the single species system. Adsorption experiments were carried out by shaking a certain particle size of the bentonite with 100 mL of metal ions solution at a certain concentration in covered polyethylene containers. The pH of the solution was kept constant by the addition of HNO₃ or NaOH solutions as needed. Subsequently, the suspension was stirred on the magnetic stirrer at controlled temperature and stirring rate. Standing for 2 h after equilibrium and then centrifuged for 10 min at 9000 r/min. The supernatants collected were analyzed for the metal ion. All of these uncertain influence conditions were predetermined before respective adsorption experiments based on previous literature [13,14]. The amounts of the metal ion adsorbed by the adsorbents were calculated by dithizone spectrophotometry [15].

The sorption rate (P%) and amount of metal ion adsorbed by the bentonite adsorbents (Q) were calculated as:

\[
P% = 100 \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

\[
Q = \frac{(C_0 - C_e)V}{m}
\]

where C₀ and Cₑ are the concentration of metal ion in the initial and equilibrium concentration of metal ion in solution (mg/L), V is the volume of metal ion solution used (mL) and m is the weight of the adsorbent used (g).

3. Results and Discussion

3.1. Effect of Contact Time

A fixed particles size of the adsorbents reagent (through 200 mesh) was added to 100 mL of zinc ions solution which adjusted pH to 5 at concentration 0.005 mol/L, with liquid-to-solid ratio of 100 mL/g at 20°C. At different time an interval of 0-120 min, the adsorption rate of Zn²⁺ on the bentonite adsorbents has shown in Figure 1.

As seen from the figure, there is a rapid uptake within the first 15 min. Increasing contact time allows greater amounts of Zn²⁺ to be removed from the aqueous solution. 120 min later, the adsorption reached equilibrium.

Ünlü N. et al. [16] took kinetic considerations into account and found that the presence of functional groups
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is greatly determined by porous structure of polymeric matrices. As was shown by H. Woehlecke et al. [17], in our study the observed rapid uptake can be attributed to the porous structure of the bentonite adsorbents.

3.2. Effect of Temperature

In order to evaluate the effect of temperature on adsorption characteristics of the bentonites, the experiment was studied at a constant initial concentration of $5 \times 10^{-3}$ mol/L, bentonite particles size through 200 mesh, liquid-to-solid ratio of 100 mL/g and pH 5 at stirring speed of 1200 r/min, adsorption time 120 min. The results of the studies on the influence of temperature on cation adsorption are presented in Figure 2 in terms of amount of metal removed versus temperature. It can be seen that the percentage zinc uptake on both M-1 and M-2 increases with increasing temperature. The reason for this is that as the temperature increases, the ionic velocity accelerates. The ion exchange reaction was hastened.

In earlier publication, the effect of temperature on adsorption is important not only because it affects the rate and extent of adsorption but also due to the fact that temperature dependence of adsorption provides information about possible adsorbate-adsorbent interaction [18-20].

Figure 2. Effect of solution temperature on the adsorption of Zn$^{2+}$ ions onto bentonite and Na-bentonite.

3.3. Effect of Initial Concentration

The effect of initial concentration was investigated under the following conditions: the bentonite particles size (through 200 mesh), liquid-to-solid ratio (100 mL/g), pH (through 200 mesh), liquid-to-solid ratio (100 mL/g), pH (5), temperature (20°C), stirring speed (1200 r/min), adsorption time (120 min). Figure 3 has shown the adsorption of zinc ions onto M-1 and M-2 samples. The amount of metal ion adsorbed increased gradually with different initial concentration varying from 0 to 0.02 mol/L. However, the adsorption rate decreased with increasing initial metal ion concentration.

The adsorption mechanism of Zn$^{2+}$ by bentonite in zinc chloride solution is:

$$2\text{Zn}^2+ + \text{M-Mont} \rightarrow \text{Zn-Mont} + 2\text{M} \quad (3)$$

where M is the cation in montmorillonite interlayer, M-Mont and Zn-Mont are M-montmorillonite and zinc-montmorillonite.

With other conditions unchanged, the increase of Zn$^{2+}$ concentration controls the direction of adsorption reactions for positive reaction. The amount of zinc ion adsorbed increased. On the other hand, the higher concentration of Zn$^{2+}$ is, the more Zn$^{2+}$ remained after equilibrium. For this reason, the percentage of zinc ion adsorbed decreased with increasing initial concentration.

3.4. Effect of Liquid-to-Solid Ratio

In condition of initial concentration is $5 \times 10^{-3}$ mol/L, bentonite particles size through 200 mesh, pH 5, temperature of 20°C, stirring speed of 1 200 r/min, contact time 120 min. The amount of zinc adsorbed reduced with increasing liquid-to-solid ratio as shown in Figure 4. It indicates that the adsorption capacity of M-1 and M-2 improved with the increase of bentonite dosage.

In terms of Equation (3), the increase of bentonite dosage (that is liquid-to-solid ratio reduced) is propitious
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3.5. Effect of PH

To determine the pH necessary for adsorption, liquid-to-solid ratio is 100 mL/g of solution containing 0.005 mol/L metal ion and particles size through 200 mesh were stirred at 1200 r/min at varying time intervals (0-120 min) at 20°C. Figure 5 indicates that the adsorption capacity of M-1 and M-2 was dependent on pH.

In general, the adsorption of ion on clay mineral includes exchange adsorption and specific adsorption. The exchange adsorption is of pH-independent constant, which has relation to permanent charge of clay mineral [21]. Therefore, it can be seen that the pH-dependent percentage of zinc ion adsorbed belongs to reinforcement of specific adsorption.

3.6. Effect of Stirring Speed

The impact studies of stirring speed on zinc ion uptake capacities under the following conditions: initial concentration is $5 \times 10^{-3}$ mol/L, bentonite particles size through 200 mesh, pH is 5, temperature of 20°C and adsorption time is 120 min. As shown in Figure 6, we can get the effect of stirring speed.

Experimental data is processed to obtain regression equation of stirring speed and adsorption rate respectively:

$$W_{M-1} = 1.78\nu + 31.25, \quad R_{M-1} = 0.9957 \quad (4)$$

$$W_{M-2} = 2.2331\nu + 39.003, \quad R_{M-2} = 0.9994 \quad (5)$$

where $W_{M-1}$ and $W_{M-2}$ are adsorption rate of M-1 and M-2, $\nu$ is stirring speed.

From above equations and Figure 6, we can draw the conclusion that adsorption rate of bentonite are increased by stirring speed and they are linear correlation. The reason is that with other conditions unchanged, accelerate stirring speed makes the velocity of Zn$^{2+}$ increased and then facilitates adsorption. Furthermore, a higher stirring speed would be propitious to bentonite dispersion, increase BET of bentonite and enhance bentonite adsorption.

3.7. Effect of Particle Size

Figure 7 shows the removal efficiencies for different particle sizes under the conditions of the initial concentration $5 \times 10^{-3}$ mol/L, liquid-to-solid ratio 100 mL/g, 20°C, pH 5, stirring speed of 1200 r/min, adsorption time 120 min. As can be seen from the graph, the smaller particle size is, the higher adsorption rate is. This may be in connection with crystal morphology and surface properties of montmorillonite. The crystal of montmorillonite overlapped in lamellar-type. Binding force between the crystal face is weaker, this led to peeling along the layer easily. When particle size becomes smaller, radius-thickness ratio would largen and the BET double increase. The electroactive of grain cross-section simultaneously enhances, resulting in the removal rate of Zn$^{2+}$ by bentonite improved obviously [19].

3.8. Effect of the coexisting ions

In order to investigate the respective effect of the Pb$^{2+}$ and Cr$^{6+}$ presence in the aqueous solution on the sorption
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Figure 7. Effect of particle size on the adsorption of Zn$^{2+}$ ions onto bentonite and Na-bentonite.

Figure 8. Effect of competing ionic concentration on the adsorption of Zn$^{2+}$ ions onto bentonite and Na-bentonite.

of Zn$^{2+}$ onto the bentonite adsorbents, we prepared various amounts of Pb$^{2+}$ and Cr$^{6+}$ solutions with maintaining all other conditions as above. The results, shown in Figure 8, clearly indicate that the simultaneous presence of Cr$^{6+}$ and Zn$^{2+}$ in aqueous solutions reduced the equilibrium adsorption capacity of bentonite adsorbents, while there was hardly effect in the simultaneous aqueous solution of Pb$^{2+}$ and Zn$^{2+}$.

This may be attributed to the ionic radius, hydrated radii and valence of the ions [22]. The higher the electro valence is, the smaller is the ion radius with easier interchanges reaction. Cr$^{6+}$ is of the greatest electro valence, the least hydrated radii and the strongest competitiveness among Cr$^{6+}$, Pb$^{2+}$ and Zn$^{2+}$.

Accordingly, Cr$^{6+}$ displaces zinc cation, resulting in a decline of percentage of zinc ion. Pb$^{2+}$ is of larger hydrated radii than Zn$^{2+}$. Similarly, Pb$^{2+}$ could not displace zinc cation, resulting in no effect on adsorption of Zn$^{2+}$.

3.9 Adsorption isotherm

The adsorption behavior of M-1 and M-2 samples was studied and the results obtained depicted in Figure 9. As shown in Figure 10, the plot of (lg $Q$) versus (lg $C_e$) for adsorption of Zn$^{2+}$ onto bentonites can be seen.

In this study, linear coefficients of determination test were used. Linearised forms of the two curves were:

$\log Q_{\text{M-1}} = 1.8671 \log C_e - 1.849$, $R_{\text{M-1}} = 0.9278$ (6)

$\log Q_{\text{M-2}} = 0.7829 \log C_e - 0.8811$, $R_{\text{M-2}} = 0.99$ (7)

As is seen from above, both (6) and (7) are found to fit the linearised form of Freundlich equation [23]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where $q_e$ is the amount of solute adsorbed per unit weight of adsorbent (mg/g), $C_e$ the equilibrium concentration of solute in the bulk solution (mg/l), $K_F$ the constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and $1/n$ the constant indicative of the intensity of the adsorption. We can conclude that adsorption isotherms of bentonites for zinc ion could be expressed mathematically in terms of Freundlich models. Rearranged these equations, we obtain:

$$Q_{\text{M-1}} = 0.0142C_e^{0.5335}$$

$$Q_{\text{M-2}} = 0.1315C_e^{1.2773}$$

4. Conclusions

Local bentonite and its Na-modified form were tested as
吸附材料用于锌离子的去除。结果表明，钠交换的蒙脱土比钙-蒙脱土更有效。

吸附实验在不同条件下进行。锌离子的吸附量随着pH值、温度、搅拌速度的增加而增加，在粒子大小、初始浓度、接触时间及溶液体积固体比例的情况下发生变化。

在复杂系统中，同时存在Cr(VI)和Zn(II)的溶液中，锌离子的吸附量在等温线、吸附动力学和等温吸附中保持一致。与已发表的数据一致，钠交换的蒙脱土吸附能力比钙-蒙脱土更有效。

吸附的Zn(II)离子在蒙脱土和钠交换的蒙脱土上，而没有在钙-蒙脱土上。

5. 识别

这项研究得到中国自然科学基金和河北科学院的支持。

REFERENCES


