Scientific
Research

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

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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 Zn^{2+}, 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 Zn^{2+} 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 Zn^{2+} and the liquid-to-solid ratio. In mixed solution which contains Pb^{2+} and Cr^{6+}, Pb^{2+} has no influence on the removal of Zn^{2+} by both the bentonites while Cr^{6+} can decease it.

Keywords: Bentonite, Zn^{2+}, 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 ^{60}Co 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 Zn^{2+} 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 Cr^{6+} and Pb^{2+} compete with Zn^{2+} 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 CuK α radition at 40kV, 100mA) was used to identify the Mineral composition. 721 model spectro-photometer was used to measure the content of Zn^{2+}, Cr^{6+} and Pb^{2+} 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 $ZnCl_2 \cdot 2H_2O$, $Pb(NO_3)_2$, potassium dichromate($K_2Cr_2O_7$) 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 HNO_3 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 Na_2CO_3 according to 100:3, the slurry was made with deionized

Table 1. Mineral composition of Ca-bentonite

Mineral	Percentage
calcium montmorillonite	61.7
kaolinite	0 ~ 6
illite	2 ~ 8
feldspar	2 ~ 11
quartz	2 ~ 9
gypsum	2 ~ 20
cristobalite	1 ~ 8

Table 2. Chemical component of Ca-bentonite

Components	Percentage
SiO_2	61.10
Al_2O_3	18.19
Fe_2O_3	5.48
CaO	1.59
MgO	1.90
Na_2O	1.30
K_2O	1.28
TiO_2	0.54
LOI (loss on ignition)	8.62

Table 3. Physicochemical properties of Ca-bentonite

Properties	Value
Cation exchange capacity (mmol/g)	0.61
Specific surface area (m²/g)	20
Colloid index (mL/g)	4.13
Epansion multiple (mL/g)	9

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 HNO_3 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:

$$P\% = 100(C_o - C_e)C_o \qquad (1)$$

$$Q = \frac{(C_o - C_e)V}{m} \qquad (2)$$

where C_o and C_e 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 Zn^{2+} 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 Zn^{2+} 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

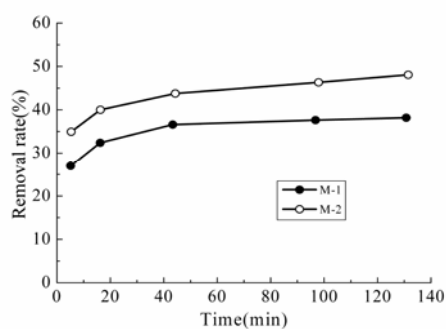**Figure 1. Effect of contact time on the adsorption of Zn^{2+} ions onto bentonite and Na-bentonite.**

is greatly determined by porous structure of polymeric matrics. 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 5×10^{-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].
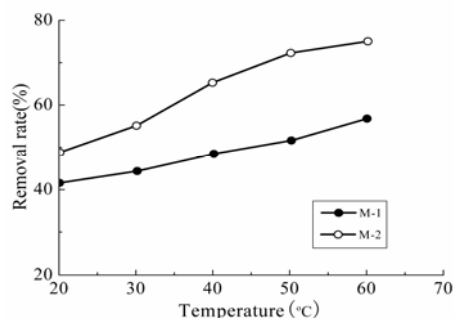
Figure 2. Effect of solution temperature on the adsorption of Zn^{2+} ions onto bentonite and Na-bentonite.
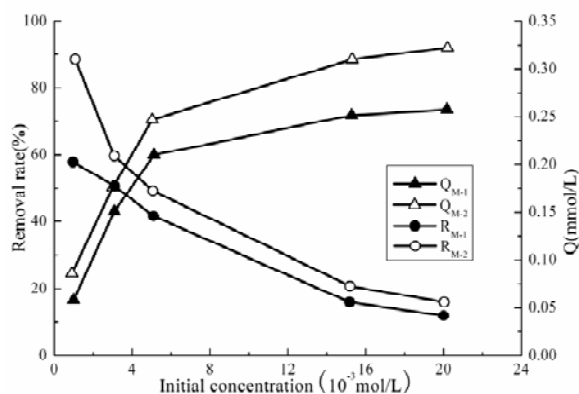
Figure 3. Relationship between initial metal ion concentration and Zn^{2+} adsorption.

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:

$$Zn^{2+} + M\text{-}Mont = Zn\text{-}Mont + 2M \qquad (3)$$

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 5×10^{-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
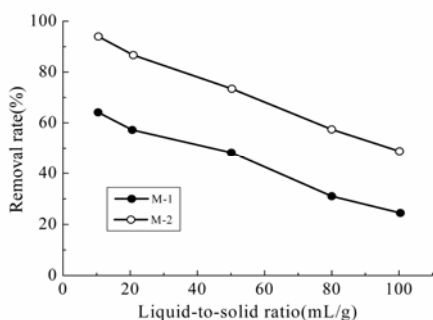
Figure 4. Effect of liquid-to-solid ratio on the adsorption of Zn^{2+} ions onto bentonite and Na-bentonite.
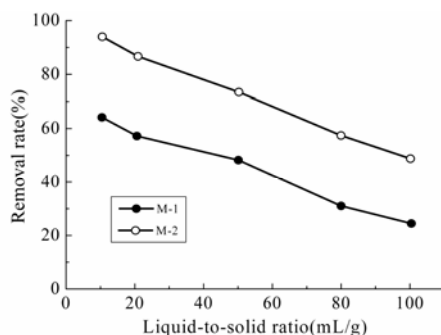
Figure 5. Effect of pH on the adsorption of Zn^{2+} ions onto bentonite and Na-bentonite.

to positive reaction with other conditions unchanged. As a result, the concentration of Zn^{2+} remained after equilibrium declined, register as a raise in percentage of metal ion adsorbed.

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 5×10^{-3} mol/L, bentonite particles size through 200 mesh, pH is 5, temperature of 20˚C and adsorption
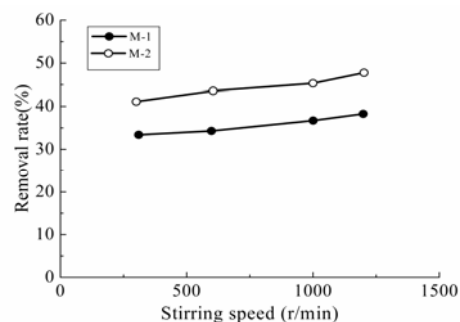
Figure 6. Effect of stirring speed on the adsorption of Zn^{2+} ions onto bentonite and Na-bentonite.

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:

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

$$W_{M-2} = 2.2331\nu + 39.003, \quad R_{M-2} = 0.999\,4 \quad (5)$$

where W_{M-1} and W_{M-2} are adsorption rate of M-1 and M-2, ν 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 5×10^{-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
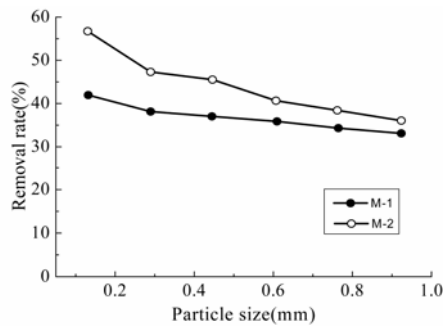
     NR

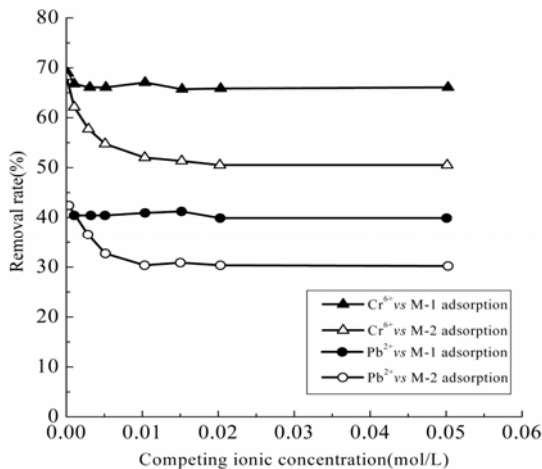**Figure 7. Effect of particle size on the adsorption of Zn^{2+} ions onto bentonite and Na-bentonite.**

Figure 9. Adsorption isotherm 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.
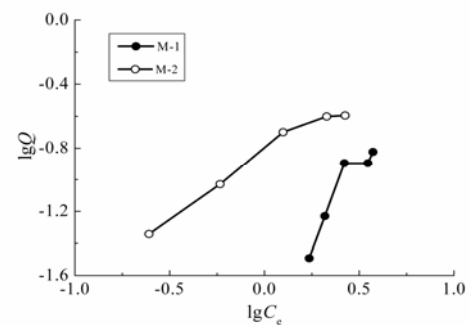
Figure 10. Relationship between lgQ and lgC_e.

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

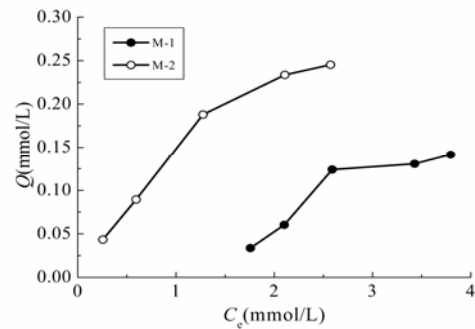The adsorption behavior of M-1 and M-2 samples was

studied and the results obtained depicted in **Figure 9**. As shown in **Figure 10**, the plot of (lgQ) versus (lgC_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:

$$lgQ_{M-1} = 1.8671lgC_{e,M-1} - 1.849, \quad R_{M-1} = 0.9278 \quad (6)$$

$$lgQ_{M-2} = 0.7829lgC_{e,M-2} - 0.8811, \quad R_{M-2} = 0.99 \quad (7)$$

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

$$lgq_e = lgK_F + 1/nlgC_e \quad (8)$$

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:

$$Q_{M-1} = 0.014\,2C_{e,M-1}^{0.5356} \quad (9)$$

$$Q_{M-2} = 0.131\,5C_{e,M-2}^{1.2773} \quad (10)$$

4. Conclusions

Local bentonite and its Na-modified form were tested as

adsorbent material for the removal of zinc ions from waste solutions. The results indicate that removal of Zn^{2+} by Na-exchanged bentonite is more effective than by Ca-bentonite. Compared to the published data in the same field, it is found to be in agreement with most of them.

The adsorption experiments were conducted under different conditions. The extent of zinc adsorption increased with increase in pH, temperature, stirring speed, contact time and decrease in particle size, initial concentration, liquid-to-solid ratio.

In a complex system, the simultaneous presence of Cr^{6+} and Zn^{2+} in aqueous solutions reduced the equilibrium adsorption capacity of bentonite adsorbents, while there was no effect in the simultaneous aqueous solution of Pb^{2+} and Zn^{2+}.

The adsorption of Zn^{2+} ions onto bentonite and Na-exchanged bentonite can be expressed with Freundlich type sorption isotherms.

5. Acknowledgements

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