Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2014, 5(6): 52-55

ISSN: 0976-8505
CODEN (USA) CSHIA5

Preparation of organic chelating agents modified bentonite for Cd^{2+} removal from aqueous solutions

Yin-Xia Sun*, Xin-Ran Li, Chun-Yu Li, Ya-Yuan Zhao and Zong-Li Ren

School of Chemical and Biological Engineering Lanzhou Jiaotong University, Lanzhou, P. R. China

ABSTRACT

Natural Na-bentonites were modified with an organic chelating agent, citric acid (CA), to prepare a new adsorbent (CA-bentonite) for Cd^{2+} contaminant removal. The optimal conditions for preparation the CA-bentonite were investigated. Moreover, the CA-bentonite showed significant adsorption for Cd^{2+} from aqueouss solution. The Langmuir and Freundlich isotherm equations were applied to the data and values of parameters of these isotherm equations were evaluated.

Keywords: CA-bentonite; preparation; adsorption isotherm

INTRODUCTION

The wastewater containing heavy metal which is generated in many economic activities, such as heavy metal producing industries, leathering, dyeing, electroplating industries, paint, resin, pharmaceutical and agrochemicals [1], extremely harms the environment. Although chemical precipitation is a main way to treat the wastewater, it is limited due to the higher cost and secondary pollution coming from sludge.

Bentonite, whose main component is montmorillonite, is a potential and important adsorption material because of its large surface area, large number of interlayer exchangeable inorganic cations and abundance in nature [2]. Commonly, the adsorption of organic pollutants by bentonite is poor because the mineral surfaces are hydrophilic. The adsorption of specific organic contaminants and heavy metal by organic chelating agents modified Na-bentonite was found to be obviously improved [3–6]. The stronger adsorption is generally attributed to stronger H-bonding between more polar water molecule and polar organic compounds, also the chelation of the heavy metal and the organic chelating agents [7].

Herein, a new bentonite adsorbent material was prepared by modifying bentonite with organic chelating agents (citric acid, CA). The sorption of the heavy metals (Cd^{2+}) onto the modified bentonites from aqueous solutions was investigated. Because of its hybrid properties, the modified bentonite has potential application in treating wastewater containing heaving metals.

MATERIALS AND METHODS

Materials. Bentonite used was primarily Na-montmorillonite from Henan. Its cation-exchange capacity (CEC) is 102.66 mmol /100 g. CA and other reagents used were of analytical grade.

Analytical Methods. The Cd^{2+} concentration was measured by a flame atomic absorption spectrometer.

Preparation of CA-bentonite. A total of 6.0 g of previously dried bentonite was mixed with 200 mL of CA (1.18 g) mixed solutions. The mixtures were subjected to mechanical stirring for 2 h in a 60-70 °C water bath. The treated bentonites were separated from water by vacuum filtration and washed twice by distilled water. The bentonites were dried at 80-90 °C, activated for 1 h at 105 °C, and mechanically ground to less than 200 mesh. Thus a series of CA-bentonites were prepared.

Procedures for Water Treatment. A combination of 0.600 g of CA-bentonite and 40 mL of solution with an appropriate concentration of the heavy metals Cd^{2+} was combined in 125 mL Erlenmeyer flasks with glass caps. The flasks were shaken for 2 h at 25 °C on a gyratory shaker at 120 rpm. After being centrifuged, the heavy metals were determined by flame atomic absorption spectrophotometry. The removal percentages for CA-bentonite to treat the contaminant in water were calculated. The amount of Cd^{2+} adsorbed per unit weight of an adsorbent, Q_e, was calculated using the following formula:

$$Q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

Where, C_o is the initial concentration of contaminant (mg/L), C_e is the equilibrium concentration of contaminant in solution (mg/L), m is the mass of the bentonite (mg) and V is the volume of solution (L).

RESULTS AND DISCUSSION

Optimal conditions for preparation the CA-bentonite.

Effect of modifier (CA) concentrations: The experimental conditions for preparation CA-bentonite: pH of 8.0, water bath temperature of 60 °C, heating time of 1.5 h, only change the ratio of modifier, CA to Na-bentonite: 80% CEC, 100% CEC and 120% CEC. The experimental results are shown in Fig. 1. As shown in Fig. 1, the maximum percentage removal of Cd^{2+} is 96.2%, when the ratio of modifier, CA to Na-bentonite is 100%CEC. Because the organic modifiers are exchanged into the interlamellar space of the bentonite and the interlayer spacings were increased, some micropores of the bentonite were occupied by CA. Thus, the specific surface areas of the organobentonites were reduced with increasing concentrations of modifiers incorporated into the bentonite. Therefore, as the concentrations of modifiers increased, the removal rates of pollutant from water by organobentonite were enhanced.

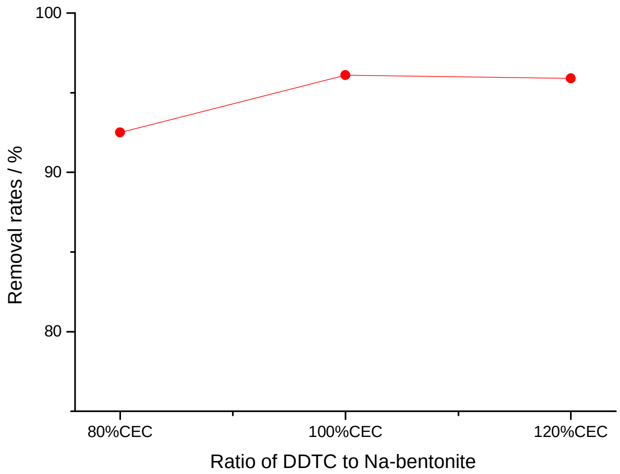

Figure 1. Effect of ratio of CA to Na-bentonite on the adsorption property of CA-bentonite

Effect of modification temperature: Only change the preparation temperature: 50°C, 60°C and 70°C, and the other experimental conditions remain unchanged. The experimental results are shown in Fig. 2. The maximum the removal rates of Cd^{2+} is 93.6%, when the modification temperature is 60 °C (Fig. 2). Concerning the effect of temperature on the adsorption process, the pollutant uptake is favored at higher temperatures, since a higher temperature activates the pollutant ions for enhancing adsorption at the coordinating sites of the minerals. Also, it is mentioned that modifier move faster with increasing temperature lead to the reduction of the modification effect.

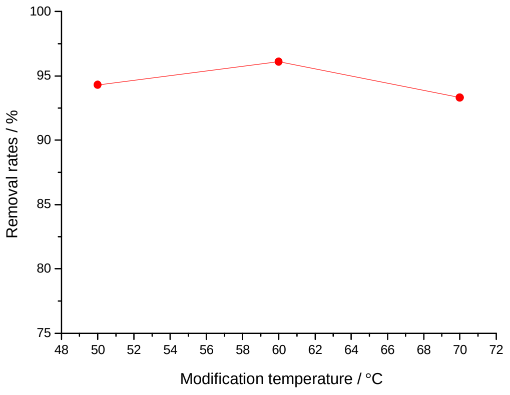

Figure 2. Effect of modification temperature on the adsorption property of CA-bentonite

Effect of modification time: Only change the preparation temperature: 1 h, 1.5 h and 2 h. The experimental results are shown in Fig. 3. The optimal adsorption effect are found at the modification time about 1.5 h (Fig. 3). The results showed that the modifiers exchanged into the bentonite interlamination meet the cation-exchange capacity of the bentonite, and the exchange equilibrium was attained about 1.5 h. After this equilibrium period, maybe the modifier move from the bentonite interlamination lead to the reduction of the modification effect.

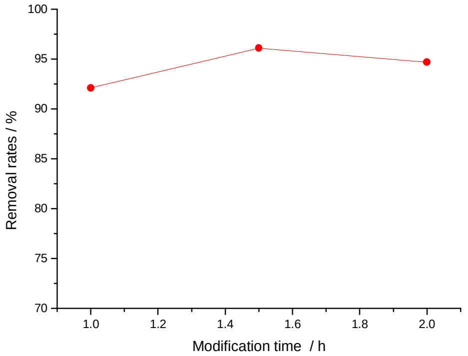

Figure 3. Effect of modification temperature on the adsorption property of CA-bentonite

Adsorption Isotherm Models.

Solid-liquid equilibrium can be easily described by adsorption isotherms. The Langmuir equation is the mathematical function most commonly used to describe this process. The Langmuir isotherm can be expressed as

$$Q_e = \frac{Q_{max} K C_e}{1+K C_e} \qquad (2)$$

where Q_e = amount of Cd^{2+} per unit weight of adsorbent (mg/g), C_e = concentration of contaminant remaining in solution at equilibrium (mg/L), Q_{max} = amount of Cd^{2+} adsorbed per unit weight (mg/g) and K = a constant related to the energy or net enthalpy.

Unlike the Langmuir model, Freundlich model can account for the differences in sorption enthalpy between different types of sites [8]. The amount of adsorbed solute (Q_e) is related to the concentration of solute in the solution (C_e) as equation (3).

$$Q_e = K_f\, C_e^{\frac{1}{n}} \qquad (3)$$

Both K_f and n are empirical constants, being indicative of the extent of sorption and the degree of nonlinearity between solution and concentration, respectively.

The results concerning Cd^{2+} contaminant adsorption for CA-bentonite are presented in Fig. 4 and Fig. 5. And together with experimental data, the corresponding theoretical adjustment of experimental determinations by the Langmuir and Freundlich equations were also plotted, respectively.▲

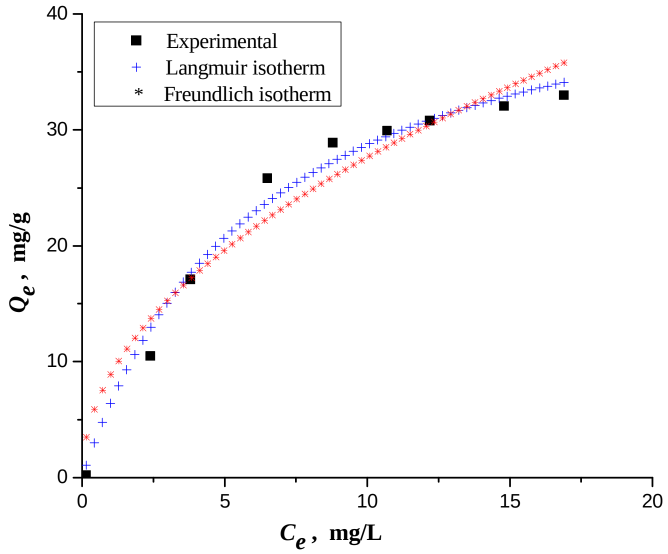

Figure 4. Adsorption isotherm of Cd2+ on CA-bentonite. + : Langmuir isotherm; * : Freundlich isotherm

Table 1 Parameters for the calculation using langmuir and freundlich models

Langmuir			Freundlich		
Q_{max} (mg/g)	K (L/mg)	R^2	1/n	K_f (mg^{1-n}L/g)	R^2
48.86	0.159	0.985	0.493	8.887	0.949

The relative values calculated from the two models are listed in Table 1. For the Langmuir model, the sorption capacity of CA-bentonite for Cd^{2+} is calculated to be 48.86 mg/g under the experimental conditions. The values of Q_{max} and K calculated from the slopes and intercepts of the Langmuir plots and correlation coefficients R^2, are reported in Table 1. As it can be seen most of the adsorption isotherms fitted the Langmuir equation with correlation coefficients R^2>0.98. Many experimental isotherms conforming to a Langmuir isotherm involve monolayer coverage. The large value of K_f (Freundlich model) indicates that CA-bentonite has a high sorption affinity towards Cd^{2+}. The deviation of n from unity indicates that a nonlinear sorption takes place on the heterogeneous surfaces. The nonlinear behavior implies that the sorption energy barrier increases exponentially as the fraction of filled sites on the sorbent increases [9]. The Langmuir isotherm model provides better description of the experimental data than the Freundlich model.

CONCLUSION

A new adsorbent, CA-bentonite, were prepared for Cd^{2+} contaminant removal. The optimum conditions for preparation the CA-bentonite as follows: the optimum ratio of CA to bentonite is 100%CEC; the optimum modification temperature is 60 °C; the optimum modification time is 1.5 h. Moreover, the CA-bentonite showed significant adsorption for the Cd^{2+} contaminant from aqueous solution. This could be explained by adsorption interaction between the adsorbed contaminants molecules and organic chelating agents on CA-bentonite, which should enhance the adsorptive capacity of the bentonite. There was a good fit between the experimental data for CA-bentonite the Langmuir and Freundlich models. At the end of the adsorption studies, it can be said that CA-bentonite may be used as an adsorbent for adsorption of some heaving metals from waste water solutions.

Acknowledgements
This work was supported by the science and technology supporting program of Gansu province (1204GKCA052), which is gratefully acknowledged.

REFERENCES

[1] R. Kidak, N.H. Ince, *Ultrason. Sonochem.*, **2006**, 13, 195.
[2] R.E. Grim, Applied clay mineralogy, (first ed., McGraw-Hill Book Company, New York, **1962**) 16-44.
[3] B.L. Sawliney, S.S. Singh, *Clays Clay Miner.*, **1997**, 45, 333.
[4] A. Pusino, W. Liu, C. Gessa, *Clays Clay Miner.*, **1993**, 41, 335.
[5] P. Alba, B. Ilaria, C. Gessa, *Clays Clay Miner.*, **2000**, 48, 19.
[6] P. Alba, B. Ilaria, C. Gessa, *Clays Clay Miner.*, **2003**, 51, 143.
[7] I. Ukraincyk, K. Smith, *Environ. Sci. Technol.*, **1996**, 30, 3167.

[8] P.W. Atkins, Physical Chemistry, (4th ed. Oxford: Oxford Univ Press, **1990**) 995
[9] T. Shahwan, H.N. Erten, *J. Radioanal Nucl. Chem.*, **2002**, 253, 115.