Asian Journal of Chemistry Vol. 22, No. 8 (2010), 6503-6508

Adsorptive Removal of Cadmium from Aqueous Solution onto Na-Bentonite

ZHI-RONG LIU* and SHAO-QI ZHOU
College of Environmental Science and Technology, South China University of Technology, Guangzhou 510006, Guangdong Province, P.R. China
Tel: (86)(20)38902939; E-mail: liuzhirongoyx@hotmail.com

The removal of cadmium from aqueous solution on the Na-bentonite has been studied under static conditions. Experiments were carried out as a function of solution pH, dosage of Na-bentonite, contact time. The adsorption equilibrium for cadmium onto Na-bentonite is reached in 120 min. The adsorption of cadmium is pH dependent in the pH range 2-8. The kinetic process of adsorption can be described by the pseudo-second-order kinetic equation satisfactorily.

Key Words: Na-Bentonite, Cadmium, Adsorption, Kinetics.

INTRODUCTION

Toxic heavy metals have been discharged into the environment as industrial wastewaters, causing serious water and soil pollution. The most important technologies for the heavy metal ions removal from wastewater include precipitation, ion exchange, adsorption, coagulation, evaporation and reverse osmosis. Adsorption on solid matrices has been shown to be an economically feasible alternative method[1-6]. Cheap and available inorganic material, Na-bentonite, has been found to be so useful for removal of heavy metallic ions from aqueous solutions that it has attracted geologists and environmental engineers[7,8].

A wide usefulness of Na-bentonite is a result of its high specific surface area, high chemical and mechanical stability, structural properties, resistance to high temperatures and radiations. The interest about adsorption of heavy metal ions onto Na-bentonite has mainly focused on adsorption of Cu(II), Ni(II), Co(II), Zn(II), Hg(II) and Cr(IV) ions *etc*. However, cadmium is commonly found in the industrial wastewater and reported to be a potent carcinogen and teratogen. Few studies on the adsorption of Cd(II) on Na-bentonite has been found in the literature. The isothermal adsorption behaviour and kinetic information of cadmium on Na-bentonite have been investigated in order to provide essential parameters and fundamental theory for the understanding of adsorption removal of cadmium by Na-bentonite from an aqueous environment.

EXPERIMENTAL

The Na-bentonite from Gaomiaozi of Inner Mongolia of China, was dried in an oven at 105 ºC for a period of 24 h and then screened through a 200-mesh sieve before being used. Surface area of the particles was analyzed by volumetric BET method using Belsorp-min II (BEL Japan, Inc.) and was found to be 1.5832 m^2/g. The total pore volume and the mean pore diameter were up to 0.0091555 cm^3/g and 2.3132 nm, respectively. Its cation exchange capacity (CEC) was 74.05 mmol/100 g. The chemical composition of Na-bentonite is given in Table-1.

TABLE-1
CHEMICAL COMPOSITION OF Na-BENTONITE

Constituent	(%)
SiO_2	69.17
Al_2O_3	14.43
Fe_2O_3	3.12
FeO	0.02
Na_2O	1.95
K_2O	0.83
CaO	1.29
MgO	3.31
MnO	0.04
TiO_2	0.13
Loss of ignition	5.40

Stock solutions of cadmium ions (50 mg/L) were prepared from $CdSO_4·8H_2O$ with reagent grade (Hunan Xiangzhong Geological Experiment Research Institute). Atomic absorption spectrometer (Model GGX-9, Beijing Geological Instrument Factory of People's Republic of China Ministry of Geology and Mineral Resources) was used to analyze the concentration of cadmium ions. X-ray diffraction (XRD) data was obtained by a Philips PW 1710 diffractometer with powdered sample using CuK_α radiation. Fourier transform infrared spectroscopy (Nicolet 380) was done to identify the chemical functional groups present on Na-bentonite. IR spectrograms of Na-bentonite embedded in KBr pellets were recorded for wavenumbers in the range of 4000-400 cm^{-1}. XRD Pattern and IR spectrogram indicate that the presence of montmorillonite together quartz and alumina in Na-bentonite. The solution pH was adjusted by adding a small amount of 0.1000 mol/L HCl or NaOH.

Methods: Adsorption experiments were carried out at 25 ºC by shaking 0.1000 g of Na-bentonite samples with iodine flask filled with an aliquot of cadmium ions solutions of different concentrations, dosage and pH values. The concentrations of the cadmium ions left in the filtrates after adsorption was analyzed using atomic absorption spectrometer. The amount adsorbed per mass unit of Na-bentonite at time 't' (q_t), the amount adsorbed per mass unit of Na-bentonite at equilibrium (q_e) and adsorption percentage (D) were calculated by the following equations:

$$q_t = \frac{V(C_o - C_t)}{W} \tag{1}$$

$$q_e = \frac{V(C_o - C_e)}{W} \quad (2)$$

$$D = \frac{(C_o - C_t)}{C_o} \times 100\,\% \quad (3)$$

where C_o = initial concentration of cadmium ions in aqueous solutions, mg/L; C_t = concentration of cadmium ions left in aqueous solutions at time 't', mg/L; q_t = amount adsorbed per mass unit of Na-bentonite at time 't', mg/g; C_e = equilibrium concentration of cadmium ions in aqueous solutions, mg/L; q_e = amount adsorbed per mass unit of Na-bentonite at equilibrium, mg/g; V = volume of the aqueous solution, L; W = amount of the dry Na-bentonite, g; D = adsorption percentage, %.

RESULTS AND DISCUSSION

Effect of pH on adsorption of cadmium: The adsorption percentage of cadmium as a function of pH was presented in Fig. 1. The raw Na-bentonite has two kinds of acidic groups (XNa and SOH) and exists as a negatively charged particle in the aqueous solutions. The adsorption percentage of Cd(II) on Na-bentonite increased with the increase of pH from 2-8. Because of the protonation and deprotonation of acidic groups of Na-bentonite, the adsorption behaviour for cadmium is controlled by the pH value. Less hydrogen ion can compete with heavy metal ions with the increase of pH in solution. Na-bentonite showed three distinct regions in the pH curve. Karabulut *et al.*[9] also noted a similar phenomenon with low-rank Turkish coal. The adsorption of Cd(II) increases rapidly in the pH range of 2-4. However, there is no obvious difference in adsorption percentage at pH 4-8. Below pH 4 more than 99 % of Cd(II) is present in the aqueous media. The solubility product

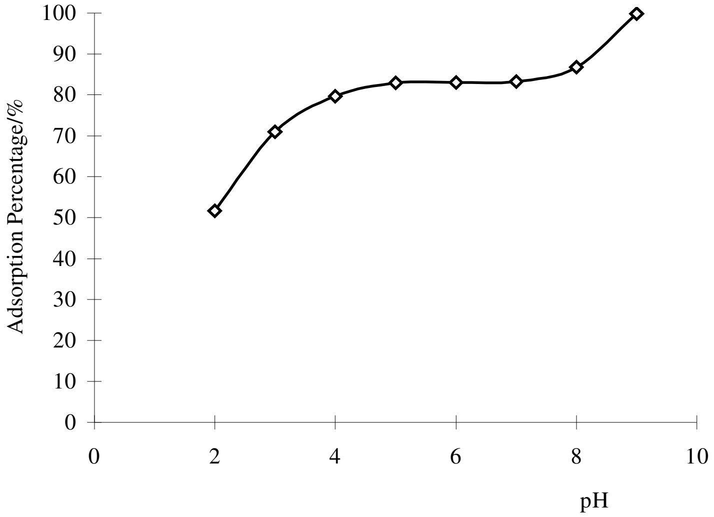

Fig. 1. Effect of pH on the adsorption of cadmium on Na-bentonite

of cadmium hydroxide is 2.2×10^{-14}. Several low-soluble cadmium hydroxy species and cadmium hydroxide precipitation are formed above pH 8. The d(100) values of Na-bentonite before and after cadmium adsorption are 1.44769 and 1.52793 nm (not shown). Gallery expansion occurs possibly due to adsorption of cadmium on silanol groups within interlayer of Na-bentonite. The IR spectrograms of Na-bentonite before and after cadmium adsorption are same owing to no new chemical bond formation between cadmium and Na-bentonite.

Effect of dosage of Na-bentonite on adsorption of cadmium: As shown in Fig. 2, the adsorption percentage of removed Cd(II) increased as dosage of Na-bentonite increased from 1-6 g/L. It may be explained that the cadmium ions was competing for limiting adsorption sites at lower Na-bentonite dosage. However, as per unit mass of Na-bentonite was increased, the more available vacant adsorption sites eased resulting in greater adsorption percentage of cadmium. These observations are in agreement with others reported in literature for the adsorption of metals ions by different materials[2].

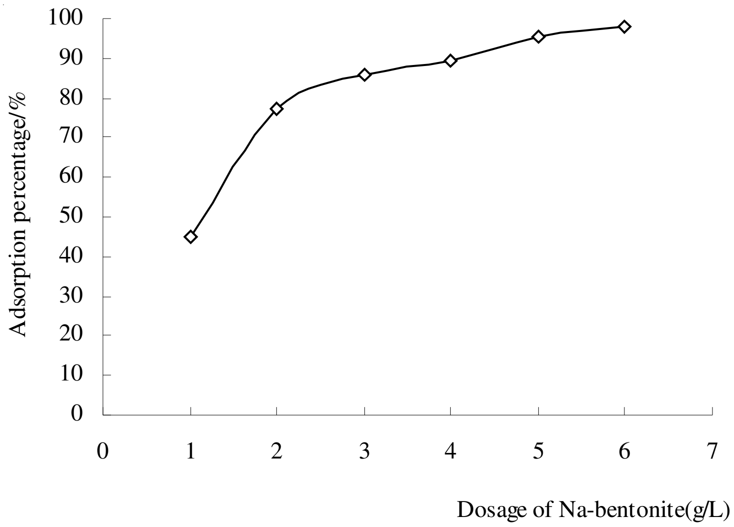

Fig. 2. Effect of dosage of Na-bentonite on adsorption of cadmium

Isothermal adsorption characteristics of cadmium on Na-bentonite: The data from isothermal adsorption experiments of cadmium ions on Na-bentonite were fitted by the following Langmuir model

$$q_e = \frac{dq_m C_e}{1 + dC_e} \tag{4}$$

where C_e = equilibrium concentration of Cd^{2+} in aqueous solution, mg/L; q_e = amount adsorbed on Na-bentonite at equilibrium, mg/g; q_m = maximum adsorption capacity on Na-bentonite; d = adsorption equilibrium constant of Langmuir model indicative of the adsorption affinity.

The adsorption isotherm of Cd(II) on Na-bentonite was shown in Fig. 3. It was observed that amount of Cd^{2+} adsorbed on Na-bentonite at equilibrium increases with the increase of equilibrium concentration of Cd^{2+} in aqueous solutions. The results of Langmuir isotherm analyses by using experimental data in Fig. 3 represent the adsorption process very well; the correlation coefficients were higher than 0.99.

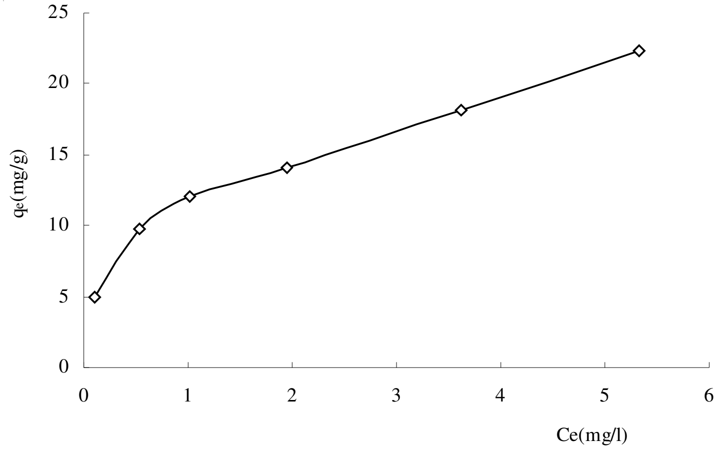

Fig. 3. Isothermal adsorption for cadmium by Na-bentonite

Kinetics of cadmium adsorption: As seen from Fig. 4 the adsorbed amounts of Cd(II) on Na-bentonite increase with the increase of contact time. The adsorption rate of Cd^{2+} on Na-bentonite reaches equilibrium in initial 120 min.

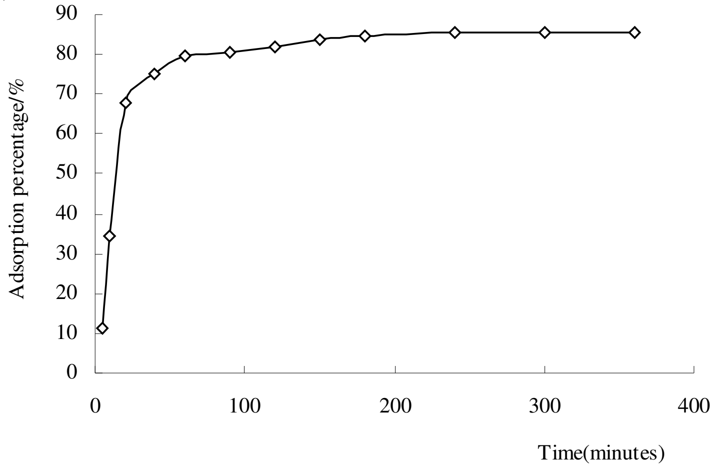

Fig. 4. Adsorption kinetics for cadmium on Na-bentonite

In order to find out the applicability of rate law kinetic data were fitted to pseudo-first-order equation and pseudo-second-order equation. The pseudo-first-order equation expresses as:

$$\ln (q_e - q_t) = \ln q_e - K_1 t \tag{5}$$

where q_t = adsorbed amount of metal ions on Na-bentonite in time t (mg/g); t = contact time (min); K_1 = first-order rate constant. A plot of ln (q_e - q_t) against time (t) should yield a straight line with K_1 obtained from the slope.

The data may be fitted to the pseudo-second-order equation expressed as[10]:

$$\frac{t}{q_t} = \left(\frac{1}{K_2}\right)\left(\frac{1}{q_e^2}\right) + \frac{t}{q_e} \tag{6}$$

A plot of t/q_t against t should yield a straight line with K_2, the second-order rate constant and is obtained from the intercept.

Table-2 shows that the pseudo-second-order equation gives a higher regression value compared to the pseudo-first-order equation, showing adherence to the pseudo-second-order rate law.

TABLE-2
CONSTANTS OF KINETIC EQUATION FOR CADMIUM ON Na-BENTONITE

Metal ions	Pseudo-first-order equation			Pseudo-second-order equation		
	q_e (mg/g)	K_1	R^2	q_e (mg/g)	K_2	R^2
Cd^{2+}	21.55	5.56	0.9322	21.79	0.0070	0.9999

Conclusion

The pH value of solution is an important factor for the adsorption of heavy metal ions on Na-bentonite. The adsorption of cadmium on Na-bentonite increases with the increase of pH from 2-8. The change of d(100) values of XRD and IR spectrograms of Na-bentonite before and after cadmium adsorption show that ion exchange take place within Na-bentonite. The adsorption of cadmium ions can be described by pseudo-second-order equation well and the adsorption isotherm be fitted to the Langmuir model by means of regression analyses very well. As a result, the Na-bentonite may be used for removal of cadmium ions from aqueous solutions. The data obtained could be used to guide the process design for the treatment of cadmium containing wastewaters.

REFERENCES

1. O. Abollino, M. Aceto and M. Malandrino, *Water Res.*, **37**, 1619 (2003).
2. P.A. Brown, S.A. Gill and S.J. Allen, *Water Res.*, **34**, 3907 (2000).
3. A. Kapoor, *J. Environ. Eng.*, **124**, 1020 (1998).
4. Q.Y. Ma, S.J. Traina and T.J. Logan, *Environ. Sci. Tech.*, **28**, 1219 (1994).
5. D. Mohan and K.P. Singh, *Water Res.*, **36**, 2304 (2002).
6. Z.X. Xuan, Y.R. Tang, X.M. Li and Y.H. Liu, *Bio. Eng. J.*, **31**, 160 (2006).
7. B.S. Krishna, D.S.R. Murty and B.S.J. Prakash, *J. Colloid Interf. Sci.*, **229**, 230 (2000).
8. G.N. Mathavan, *Water Res.*, **26**, 91 (1992).
9. S. Karabulut, A. Karabakan, A. Denizli and Y. Yurum, *Sep. Purif. Tech.*, **18**, 177 (2000).
10. Y.S. Ho and G. McKay, *Water Res.*, **34**, 735 (2000).

(*Received*: 4 January 2010; *Accepted*: 17 May 2010) AJC-8719