ELSEVIER

Chemical Engineering Journal 138 (2008) 187–193

Chemical Engineering Journal

www.elsevier.com/locate/cej

Adsorption behavior of Cr(VI) on organic-modified rectorite

Yun Huang, Xiaoyan Ma*, Guozheng Liang, Yongxia Yan, Shuhui Wang

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, China

Received 24 March 2007; received in revised form 8 May 2007; accepted 24 June 2007

Abstract

The natural rectorite (REC) was modified with the surfactant of dodecyl benzyl dimethyl ammonium chloride, hexadecyl trimethyl ammonium bromide and octadecyl trimethyl ammonium bromide, respectively. Three kinds of organic-modified rectorite (OREC), termed OREC1, OREC2 and OREC3, respectively, were prepared. Three kinds of OREC were used as adsorbents for Cr(VI) removal in aqueous solution. Through FTIR and X-ray diffraction (XRD) analyses, it was confirmed that they indeed carried out cation exchange reaction between REC and surfactant. Through the research of Cr(VI) adsorption, the removal percentage (%) of Cr(VI) increased with increasing adsorbents dose. The adsorption efficiency of OREC adsorbent was greatly affected by the initial solution pH value. According to thermodynamics study, it can be concluded that the adsorption of Cr(VI) with three adsorbents was carried out spontaneously. The research of adsorption isotherm demonstrated that, adsorption reactions of three prepared OREC adsorbents belonged to Langmuir model. The kinetic data of Cr(VI) with OREC adsorbents were well fitted to the Lagergren rate equation, which indicated that the three adsorption processes belonged to first-order adsorption reaction. Values of coefficients of intra-particle diffusion and mass transfer have been determined for three different OREC adsorbents. Intra-particle diffusion analysis demonstrated that Cr(VI) ions diffused quickly at the beginning of the adsorption process, and then intra-particle diffusion slowed down and stabilized. Mass transfer analysis showed the process of transfer of Cr(VI) removal onto the adsorbents surface was rapid enough.

Keywords: Surfactant; Rectorite; Chromium; Adsorption kinetic; Adsorption isotherm

1. Introduction

Chromium ion, especially Cr(VI), present in the effluents of electroplating, tanning, mining and fertilizer industries and causing problems of skin dermatitis, liver damage, carcinogenicity, etc. [1–5], is a kind of toxic inorganic pollutants. Treatment processes for Cr(VI) contaminating waste water included chemical precipitation, membrane filtration, ion exchange, carbon adsorption [6–9], coprecipitation [8] and adsorption in layered double hydroxides [10,11]. But all these means were all expensive, cost effective alternative technologies or adsorbents for treatment of Cr(VI) contaminated waste water were needed. Clay was chosen to decrease the pollutant of Cr(VI) released into the environment, owing to their high specific surface area, low cost and ubiquitous presence in most soils [12–18]. But these clays mainly were montmorillonite (MMT) and Kaolinite, it was necessary to study adsorption of Cr(VI) with another kind of clay mineral of rectorite (REC).

Structure and characteristics of REC are much similar to that of MMT [19]. REC is a sort of regularly interstratified clay mineral with alternate pairs of dioctahedral mica-like layer (non-expansible) and dioctahedral smectite-like layer (expansible) existing in 1:1 ratio. The cations of Na^+, K^+ and Ca^{2+} lie in the interlayer region between 2:1 mica-like layers and 2:1 smectite-like layers, while the exchangeable hydrated cations reside in the latter. The REC structure can also cleave easily between smectite-like interlayers, forming monolithic REC layers (2 nm thick). However, nearly no attention has been paid to the research of REC on adsorption study until the high quality of REC mineral was discovered in 1983.

Until now, there have been few reports on adsorption study of REC. So in this paper, we studied the adsorption of Cr(VI) from aqueous solution with REC modified by dodecyl benzyl dimethyl ammonium chloride, hexadecyl trimethyl ammonium bromide and octadecyl trimethyl ammonium bromide, respectively, reviewed the effect of adsorbents dose, initial solution pH, adsorption time and temperature on the adsorption, and

---

* Corresponding author. Tel.: +86 29 88474157; fax: +86 29 88474080.
E-mail address: m_xiao_yana@nwpu.edu.cn (X. Ma).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.06.017

discussed adsorption kinetics and adsorption isotherm of three adsorbents for Cr(VI).

2. Experimental

2.1. Materials

Sodium rectorite (Na-REC) was refined from clay minerals in Wuhan, China. The CEC was found to be 45 meq/100 g, and the *d*-spacing 2.22 nm. Dodecyl benzyl dimethyl ammonium chloride, hexadecyl trimethyl ammonium bromide and octadecyl trimethyl ammonium bromide were supplied by Xi'an Chemistry Glass Station, China. All chemicals used in this work, were of analytical reagent grade and were used without further purification.

2.2. The synthesis of organic clay

Na-REC was screened with a sieve of 300-mesh in order to remove impurities. Certain amount of screened clay was suspended in deionized water in glass vessel using a glass-rod. Surfactant was dissolved in certain amount of water, and then added into the suspended clay–water solution, stirring vigorously for several minutes at room temperature. The mixture was transferred into three-necked flask, heated to 85 °C, and stirred for additional 8 h. Then the treated products were washed and filtered repeatedly in order to ensure a complete removal of chloride or bromide ions, and the filtrate was titrated with $AgNO_3$ until no AgCl or AgBr precipitate was found. The product was then dried under vacuum at 90 °C for several hours, and the product, termed OREC1, OREC2 and OREC3, were obtained. In the modification experiment, weight of 30 g REC needs water of 1700 mL, while the molar of surfactant was about 75% of cation exchangeable capability (CEC).

2.3. Characterization

FTIR studies were performed using a WQF-310 machine over the wave number range 4000–400 cm^{-1}. The IR spectra of REC or OREC was obtained using KBr wafer which was prepared by mixing a given weight of the REC or OREC with KBr crystals. The resulting mixture was then ground into powder and heated for 1 h at 373 K. Finally, the mixture was pressed into a KBr wafer under vacuum conditions and used as such for IR studies. X-ray diffraction (XRD) measurements of REC and OREC were conducted with a Rigaku D/max-3C using nickel-filtered Cu K_α ($\lambda = 0.154$ nm) radiation (40 kV, 40 mA) and a scan range of 1–10°.

2.4. Adsorption procedure

Various weights of the OREC adsorbents ranging from 0.2 to 1.0 g/L were used to study the effect of adsorbent dose on the adsorption of Cr(VI) with the concentration of 100 mg/L. The stock solution of Cr(VI) (500 mg/L) was prepared in distilled water using analytical grade reagent of $K_2Cr_2O_7$.

Fifty-milliliter solutions of 100 mg/L of Cr(VI) were adjusted to various pH ranging from 3 to 12. These were added to 1 g/L of OREC sample in 120 mL polyethylene plastic containers. They were agitated for enough time at room temperature (26 ± 1 °C) and centrifuged at 1500 rpm for 10 min. The amount of Cr(VI) adsorbed by the adsorbents was calculated by difference about initial and final solution concentrations.

The effect of temperature on adsorption equilibrium was studied by varying temperature from 20 to 80 °C.

Kinetic studies were carried out for 50 mL working solution at constant pH 6 with initial concentration (100 mg/L) and the adsorbent dose of 1 g/L. After shaking, the samples were centrifuged for 10 min at 1500 rpm.

Working solutions of 50–130 mg/L were subsequently prepared from the stock solution. The various working solutions were adjusted pH 6 with 0.1 M HCl. A 50 mL of the various working solutions were introduced into 1.0 g/L of the OREC sample in 120 mL polyethylene plastic containers. They were agitated for 60 min at room temperature (26 ± 1 °C). The suspensions were then centrifuged for 10 min at 1500 rpm. The supernatants collected were analyzed for Cr(VI). The amount of the Cr(VI) adsorbed by the adsorbents was calculated by difference about initial and final solution concentrations.

3. Results and discussion

3.1. FTIR and XRD analysis of OREC

In the present work, three different surfactants were used for ion exchanging of Na^+ to modify the REC. The structure of REC and OREC can be characterized by FTIR spectra, and are shown in Fig. 1. For OREC, there appeared two peaks at 2927 and 2853 cm^{-1}, which represent the stretching vibration of $–CH_3$ and $–CH_2$, respectively. The characteristic peaks confirmed that the organic cations of quaternary ammonium salt of surfactant were exchanged with the interlayer Na^+ of REC.

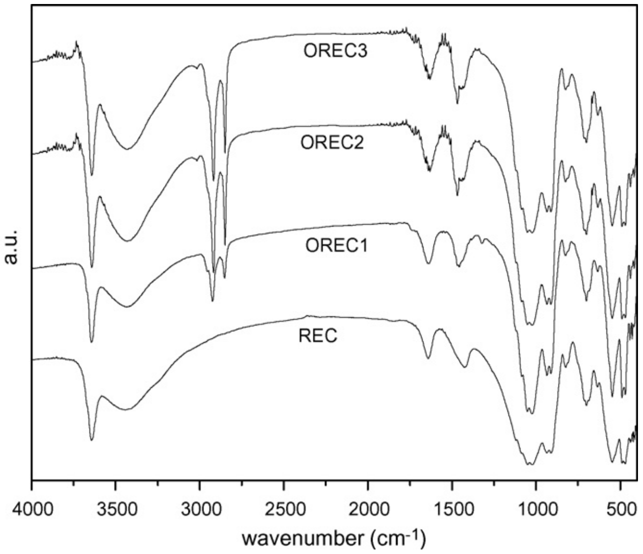

Fig. 1. FTIR spectra of REC, OREC1, OREC2 and OREC3.

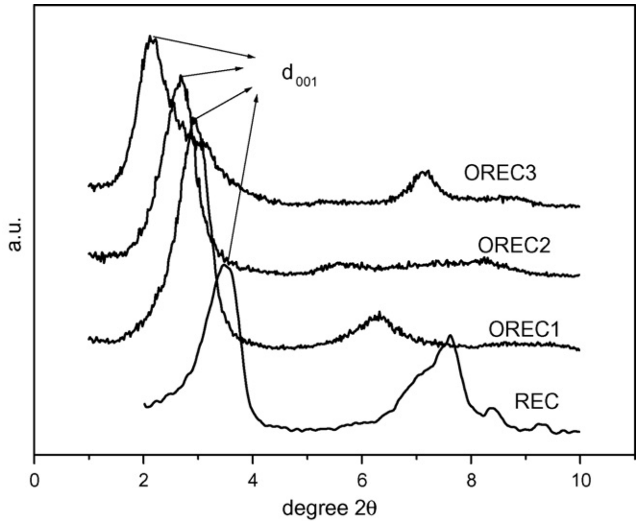

Fig. 2. Analysis of XRD of REC, OREC1, OREC2 and OREC3.

The analysis of X-ray diffraction for natural clay and organic clays was shown in Fig. 2. We can obtain the *d*-spacing of the clays from their characteristic peaks based on Bragg equation. The *d*-spacing of OREC1, OREC2 and OREC3 was 2.99, 3.24 and 4.08 nm, respectively. All of these data were larger than that of raw REC (2.22 nm), which indicated that cationic exchange reaction occurred between the clay and the surfactant, and the galleries in the REC were filled with the molecules of organic cations, and *d*-spacing increased with increasing chain length.

3.2. Effect of adsorbents dose

Adsorbent dose is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The influence of OREC dose on the adsorption of Cr(VI) was depicted in Fig. 3. As the adsorbent dose was increased from 0.2 to 1.0 g/L, the Cr(VI) removal percentage increased from 30.3 to 55.2% for OREC1, from 45.7 to 81.6% for OREC2 and from 54.6 to 96.8% for OREC3. The increased percentage adsorption of Cr(VI) with increasing OREC dose could be due to increased absolute adsorption surface. For OREC, when the *d*-spacing increased, more adsorption surface was produced, and OREC3 with the largest *d*-spacing produced the most adsorption surface.

3.3. Effect of pH

The pH of the aqueous solution is an important controlling parameter that strongly affects the adsorption of metals on surface of the clay. The influence of pH on the adsorption of Cr(VI) was investigated at pH values 3–12, and the results were shown in Fig. 4. A significant decrease in the adsorption of Cr(VI) was observed at pH values of 6–8. Therefore, the pH 6 was selected for all further studies for the practice use.

3.4. Effect of agitation time

The distribution of adsorbate between adsorbent and solution is influenced by agitation time. The effect of shaking time on adsorption at room temperature was studied. The results were presented in Fig. 5. In general, a two-stage kinetic behavior was observed: rapid initial adsorption in a contact time about 30 min for OREC1, OREC2 and OREC3, followed by a second stage with a much lower adsorption rate. According to these results, the 40 min of agitation time was considered to be sufficient for the adsorption of Cr(VI) onto OREC.

3.5. Effect of temperature and thermodynamic parameters

In order to investigate the effect of temperature on the adsorption of Cr(VI), the distribution coefficient, *A*, was calculated at temperature values of 20–80 °C by using Eq. (1):

$$A = \frac{C_s}{C_e} \tag{1}$$

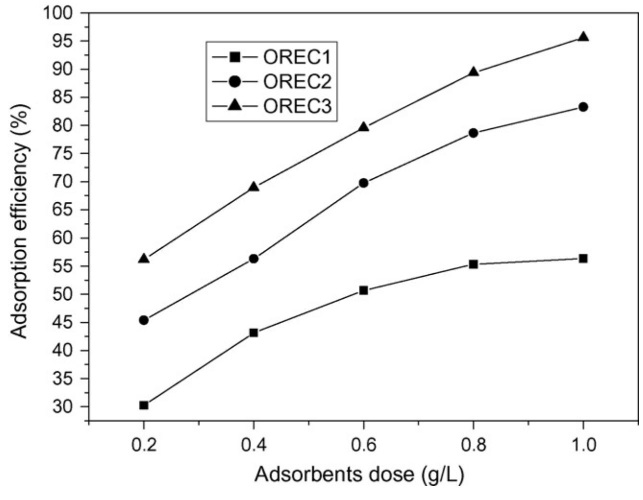

Fig. 3. Effect of OREC adsorbents dose on adsorption of Cr(VI) (Cr(VI) concentration: 100 mg/L; shaking time: 40 min; pH 6.0; *V*: 50 mL; at room temperature, 26 ± 1 °C).

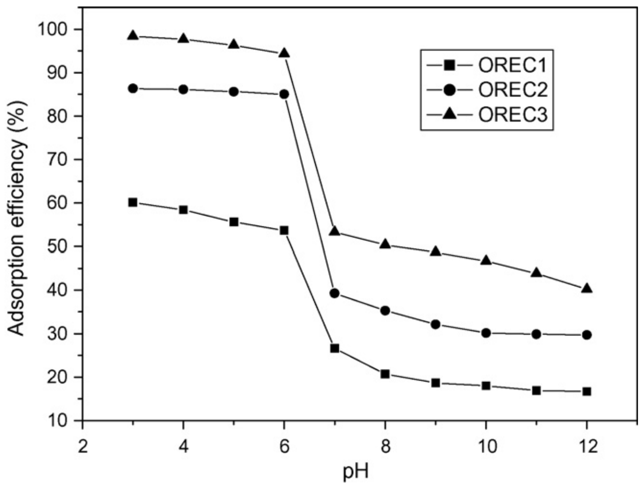

Fig. 4. The effect of pH on adsorption of Cr(VI) with OREC adsorbents (Cr(VI) concentration: 100 mg/L; adsorbent dose: 1 g/L; shaking time: 40 min; *V*: 50 mL; at room temperature, 26 ± 1 °C).

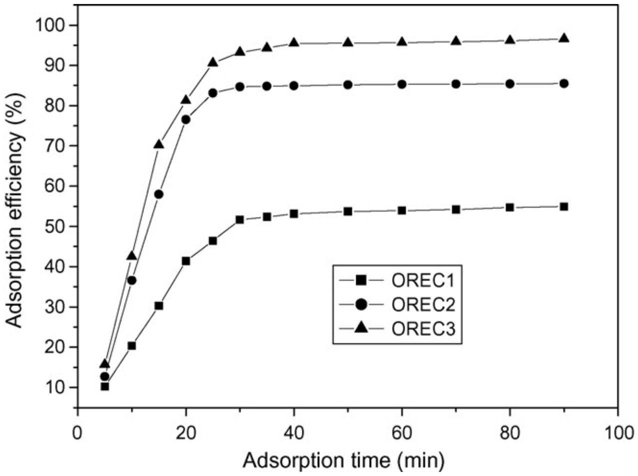

Fig. 5. Effect of shaking time on adsorption of Cr(VI) with OREC adsorbents (Cr(VI) concentration: 100 mg/L; adsorbent dose: 1 g/L; pH 6.0; V: 50 mL; at room temperature, 26 ± 1 °C).

According to thermodynamics temperature coefficient formula [20,21]:

$$\ln A = \frac{-\Delta H}{RT} + \frac{2.303\ \Delta S}{R} \tag{2}$$

where C_s (mg/L) is the equilibrium concentration of Cr(VI) adsorbed on OREC, and C_e (mg/L) is the equilibrium concentration of Cr(VI) in aqueous solution. ΔH is the enthalpy change, ΔS the entropy change, R the gas law constant (8.314 J/(mol K)) and T is the absolute temperature (K).

We obtained linear relation coefficient r and adsorption thermodynamics equations of $\ln A$ versus T^{-1} (shown in Fig. 6) from slope and intercept of obtained equations. The linear results were listed in Table 1.

From Table 1, we can see enthalpy change of three adsorbents for Cr(VI) is negative, which means all adsorption reactions are exothermic in nature. According to thermodynamics formula $\Delta G = \Delta H - T\Delta S$, Gibbs free enthalpy change, ΔG, at room temperature (T = 26 °C) is calculated. Negative Gibbs free enthalpy change demonstrated the adsorption of Cr(VI) with three adsorbents carried out spontaneously. The negative ΔS values revealed that the orderliness of the adsorbed system was higher than the solution phased before adsorption. In addition, it was obvious that OREC2 and OREC3 had less ΔG values than OREC1, which demonstrated that OREC2 and OREC3 more easily adsorbed Cr(VI). This was explained as that the large d-spacing of OREC2 and OREC3 produced much adsorption area which undoubtedly increased the adsorption capacity of adsorbents.

Table 1
Thermodynamics model of three kinds of adsorbent and thermodynamic parameters

Adsorbent	Linear relation coefficient, r	ΔH (kJ/mol)	ΔS (J/(mol K))	ΔG (kJ/mol)
OREC1	0.998	−14.22	−31.30	−5.04
OREC2	0.995	−10.73	−19.09	−5.15
OREC3	0.993	−19.20	−29.35	−10.60

3.6. Adsorption isotherm

Langmuir isotherm model was applied to establish the relationship between the amount of Cr(VI) adsorbed by OREC and their equilibrium concentration in aqueous solutions. The experimental data conformed to the linear form of Langmuir model expressed as the following equation [22]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

where C_e is equilibrium concentration of Cr(VI) (mg/L) and q_e is the amount of Cr(VI) adsorbed by per unit of OREC (mg/g). q_m and K_L are Langmuir constant related to adsorption capacity (mg/g) and the energy of adsorption (L/g), respectively. q_m and K_L constants were evaluated from slope and intercept of the linear plots of C_e/q_e versus C_e, respectively.

Langmuir plots for the Cr(VI) adsorption at room temperature (26 ± 1 °C) was given in Fig. 7. It illustrated that adsorption

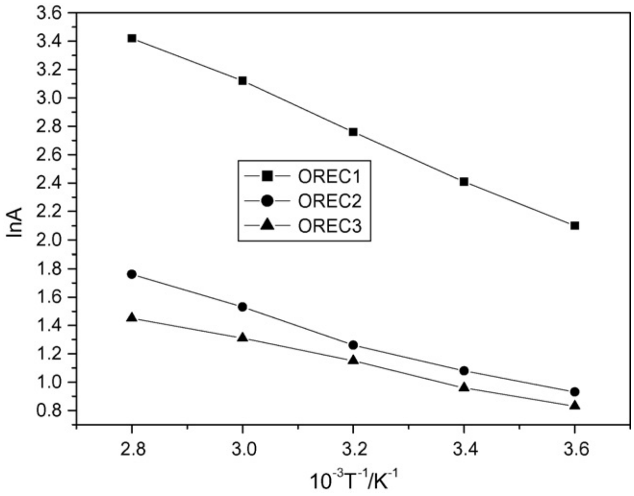

Fig. 6. Thermodynamics plots of adsorption.

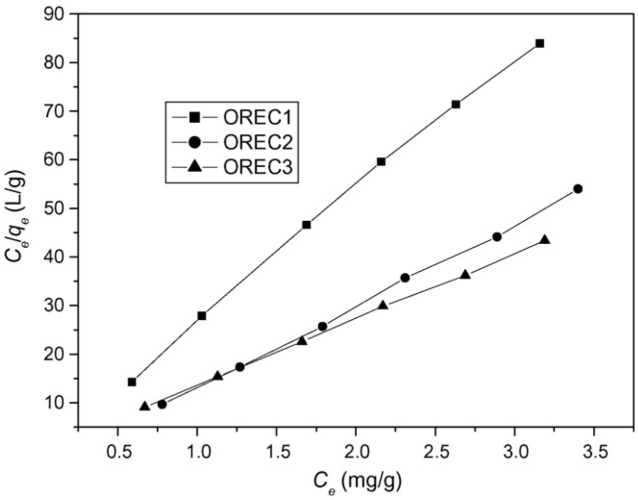

Fig. 7. Adsorption isotherm plots of OREC1, OREC2 and OREC3.

Table 2
Langmuir's constants for the removal of Cr(VI) by adsorption on OREC

Adsorbent	Max adsorption capacity, q_m (mg/g)	Langmuir constant, K_L (L/mg)	Linear relation coefficient, r
OREC1	0.97	0.87	0.998
OREC2	2.39	0.69	0.996
OREC3	3.57	0.51	0.996

of Cr(VI) onto OREC adsorbents well obeyed the Langmuir isothermal model. The corresponding isotherm constants q_m and K_L together with the correlation coefficients r were listed in Table 2. Values of q_m derived from the Langmuir theory is an indicator of the adsorption capacity of a given adsorbent. We also founded that for OREC1, OREC2 and OREC3, the values of q_m orderly increased, which further confirmed the ordinal improved adsorption capacity. The constant K_L was less than unity at room temperatures in Table 2 indicated a favorable adsorption process.

3.7. Adsorption kinetics

The kinetic data were fitted to the Lagergren rate equation [23]

$$\ln(q_e - q_t) = \ln q_e - k_{ad}t \tag{4}$$

where q_e and q_t are the amounts of Cr(VI) adsorbed (mg/g) at equilibrium and time 't', respectively. k_{ad} is the first-order rate constant. The plots of $\ln(q_e - q_t)$ versus t give straight lines (Fig. 8) and agree with the linearity of the Lagergren equation. The values of k_{ad} for different concentrations and temperatures were obtained from the slopes of the plots.

At 26 °C, and pH 6, the k_{ad} values of OREC1, OREC2 and OREC3 at initial concentration of 100 mg/L were found to be 1.05×10^{-2}, 1.58×10^{-2} and 1.95×10^{-2} min^{-1}, respectively. The straight-line plots of '$\ln(q_e - q_t)$ versus t' (Fig. 8) indicate that the proposed model fits well the data of the system studied.

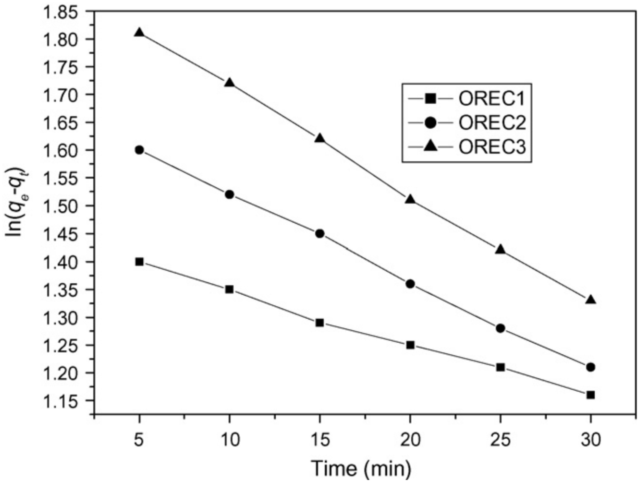

Fig. 8. $\ln(q_e - q_t)$ vs. t plots for the adsorption of Cr(VI) onto OREC at different initial concentrations.

3.8. Intra-particle diffusion analysis

Intra-particle diffusion was characterized using the relationship between specific sorption (q_t) and the square root of time ($t^{1/2}$). The relation is expressed as follows [24]:

$$q_t = k_d t^{1/2} + C \tag{5}$$

where q_t is the quantity of metal ion adsorbed at time t (mg/g), k_d the initial rate of intra-particle diffusion (mg/(g min$^{1/2}$)) and C is the y-intercept. There are four main stages in the process of adsorption by porous adsorbent: (i) solute transfer from the bulk solution to the boundary film that surrounds the adsorbent's surface, (ii) solute transport from the boundary film to the adsorbent's surface, (iii) solute transfer from the adsorbent's surface to active intra-particle sites, and (iv) interactions between the solute molecules and the available adsorption sites on the internal surfaces of the adsorbent. One or more of these four steps control the adsorption rate. Fig. 9 showed a double straight-line nature: initial and final stages. The initial stage indicated boundary layer diffusion and straight-line portions in final stage indicated that the process of removal was dominated by intra-particle diffusion in this part of process. Values of the rate constant of intra-particle diffusion, k_d, at room temperature of 26 ± 1 °C for OREC1, OREC2 and OREC3, were calculated by using slopes of Fig. 9 and have been given in Table 3. Table 3 shows that Cr(VI) ions diffused quickly among the particles at the beginning of the adsorption process, and then intra-particle diffusion slowed down and stabilized.

3.9. Mass transfer analysis

For any process of removal by adsorption it is important to know the extent of transfer of pollutant species from bulk to the surface of the solid adsorbent particles and at the interface of solid adsorbent particles or at the interface of liquid and solid particles. For the present studies this probability was examined

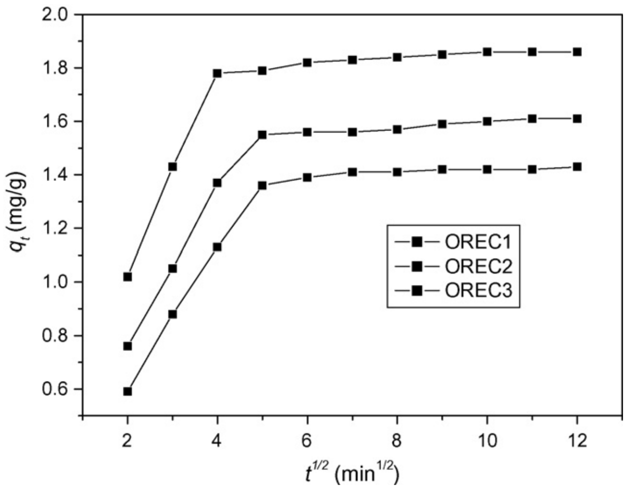

Fig. 9. Plots of the intra-particle diffusion kinetics of OREC for Cr(VI) at room temperature (26 ± 1 °C).

Table 3
The values of the intra-particle diffusion coefficients (k_d) in two stages

Adsorbent	Intra-particle diffusion coefficient, k_{d1} (mg/(g min$^{1/2}$))	Linear relation coefficient, r_1	Intra-particle diffusion coefficient, k_{d2} (mg/(g min$^{1/2}$))	Linear relation coefficient, r_2
OREC1	0.272	0.998	0.00371	0.994
OREC2	0.316	0.995	0.00898	0.993
OREC3	0.383	0.996	0.00965	0.996

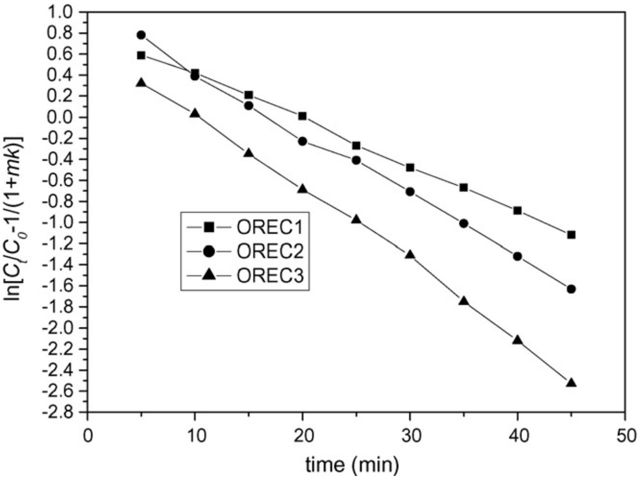

Fig. 10. Mass transfer plots for the removal of Cr(VI) by adsorption on OREC.

by using following mass transfer model [25]:

$$\ln\left[\frac{(C_t/C_0)-1}{1+mk}\right] = \ln\left[\frac{mk}{1+mk}\right] - \left[\frac{1+mk}{mk}\right]\beta_1 S_s t \qquad (6)$$

where 'k' is a constant and is the product of Langmuir's parameters. The values of 'm' and 'S_s' have been determined as follows:

$$m = \frac{W}{V} \qquad (7)$$

$$S_s = \frac{6m}{d_P \rho_P (1 - C_P)} \qquad (8)$$

where C_P is porosity of the adsorbent, and values of β_1, the coefficient of mass transfer, calculated by the slopes and intercepts of the plots of 'ln[((C_t/C_0) − 1)/(1 + mk)] versus t' (Fig. 10), were 70.6, 83.7 and 95.9 cm/min for OREC1, OREC2 and OREC3, respectively.

All the values of mass transfer coefficient are indicative of a sufficiently rapid transfer of adsorbate species from bulk to the surface interface. When the value of β_1 in the order of 10^{-4} cm/min or greater, the rate of transfer of mass from bulk to the solid surface is rapid enough and the adsorbent of OREC can be recommended for the removal of Cr(VI) from aqueous solutions.

4. Conclusions

The OREC adsorbents were successfully prepared with cation exchange reaction between raw REC and the surfactant. The experimental results indicated that OREC can be successfully used for the adsorption of Cr(VI) from aqueous solutions. Experimental parameters such as adsorbent dose, solution pH, shaking time and temperature must be optimally selected to obtain the highest possible removal of Cr(VI) from aqueous solutions. The negative Gibbs free enthalpy change, ΔG, values showed that the adsorption of Cr(VI) with OREC adsorbents was feasible and spontaneous. The equilibrium data well followed the linear Langmuir model. Intra-particle diffusion analysis demonstrated that Cr(VI) ions diffused quickly among the particles at the beginning of the adsorption process, and then the diffusion slowed down and stabilized. Mass transfer analysis showed the process of transfer of Cr(VI) removal onto the adsorbents surface to be rapid enough and confirmed that its suitability for the present systems.

Acknowledgements

The authors gratefully acknowledge the financial support from the Nature Science Fund of Shaanxi (2005B23) and the National Nature Science Fund (20674062).

References

[1] J.R. Mudakavi, G. Venkateshuar, M. Ravindram, Removal of chromium from electroplating effluents by the sulphide process, Indian J. Chem. Technol. 2 (1995) 53–58.
[2] M.E. Conti, F. Botre, Honeybees and their products as potential bioindicators of heavy metals contamination, Environ. Monit. Assess. 69 (2001) 267–282.
[3] J.T. Nyangababo, L. Henry, E. Omutange, Heavy metal contamination in plants, sediments, and air precipitation of katonga, simiyu, and nyando wetlands of Lake Victoria basin, East Africa, Bull. Environ. Contam. Toxicol. 75 (2005) 189–196.
[4] S. Hora, G. Simu, R. Rad, A. Popa, M. Milos, Utilizarea unor suporturi polimere care contin coloranti imobilizati pentru separarea ionilor de Cu(II) si Zn(II) din solutii apoase, Rev. Chim. 55 (2004) 948–951.
[5] Y. Bulut, Z. Baysal, Removal of Pb(II) from wastewater using wheat bran, J. Environ. Manage. 78 (2006) 107–113.
[6] S.J.T. Pollard, G.D. Fowler, C.J. Sollars, R. Perry, Low-cost adsorbents for waste and wastewater treatment: a review, Sci. Total Environ. 116 (1992) 31–52.
[7] M.M. Johns, W.E. Marshall, C.S. Toles, Agricultural by-products as granular activated carbons for adsorbing dissolved metals and organics, J. Chem. Technol. Biotechnol. 71 (1998) 131–140.
[8] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.
[9] R. Verina, V. Bhardwaj, Technology for the removal of chromate from industrial waste water, J. Ind. Pollut. Control 10 (2) (1994) 71–82.
[10] K. Chibwe, W. Jones, Intercalation of organic and in organic anions into layered double hydroxides, J. Chem. Soc. (1989) 926–929.
[11] R.L. Goswamee, P. Sengupta, K.G. Bhattacharyya, D.K. Dutta, Adsorption of Cr(VI) in layered double hydroxides, Appl. Clay Sci. 13 (1998) 21–34.
[12] B.S. Krishna, D.S.R. Murty, B.S. Prakash Jai, Surfactant-modified clay as adsorbent for chromate, Appl. Clay Sci. 20 (2001) 65–71.

[13] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na-montmorillonite effect of pH and organic substances, Water Res. 37 (2003) 1619–1627.

[14] Y.C. Sharma, Cr(VI) removal from industrial effluents by adsorption on an indigenous low cost material, Colloid Surf. A: Phys. Eng. Asp. 215 (2003) 155–162.

[15] K.R. Reddy, S. Chinthamreddy, Effects of initial form of chromium on electrokinetic remediation in clays, Adv. Environ. Res. 7 (2003) 353–365.

[16] Y. Bayrak, Y. Yesiloglu, U. Gecgel, Adsorption behavior of Cr(VI) on activated hazelnut shell ash and activated bentonite, Microporous Mesoporous Mater. 91 (2006) 107–110.

[17] M.B. Fritzen, A.J. Souza, T.A.G. Silva, L. Souza, R.A. Nome, H.D. Fiedler, F. Nome, Distribution of hexavalent Cr species across the clay mineral surface-water interface, J. Colloid Interface Sci. 296 (2006) 465–471.

[18] J.H. Potgieter, S.S. Potgieter Vermaak, P.D. Kalibantonaga, Heavy metals removal from solution by palygoskite clay, Min. Eng. 19 (2006) 463–470.

[19] J.P. Olivier, M.L. Occelli, Surface area and microporosity of pillared rectorite catalysts from a hybrid density functional theory method, Microporous Mesoporous Mater. 57 (2003) 291–296.

[20] S.S. Gupta, Bhattacharyya, Interaction of metal ions with clays. I. A case study with Pb(II), Appl. Clay Sci. 30 (2005) 199–208.

[21] G. Bereket, A.Z. Aroğuz, M.Z. őzel, Removal of Pb(II), Cd(II), Cu(II), and Z(II) from aqueous solutions by adsorption on bentonite, J. Colloid Interface Sci. 187 (1997) 338–343.

[22] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[23] Y.C. Sharma, Uma, V. Srivastava, J. Srivastava, M. Mahato, Reclamation of Cr(VI) rich water and wastewater by wollastonite, Chem. Eng. J. 127 (2007) 151–156.

[24] Y.S. Ho, D.A.J. Wase, C.F. Forster, Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat, Environ. Technol. 17 (1996) 71–77.

[25] G. Mckay, The adsorption of basic dye onto silica from aqueous solution–solid diffusion model, Chem. Eng. Sci. 39 (1984) 129–138.