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Chemical Engineering Journal 141 (2008) 1–8

Chemical Engineering Journal

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Adsorption of phenol with modified rectorite from aqueous solution

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Received 22 May 2007; received in revised form 26 September 2007; accepted 4 October 2007

Abstract

The natural rectorite (REC) was modified with surfactant of dodecyl benzyl dimethyl ammonium chloride, hexadecyl trimethyl ammonium bromide and octadecyl trimethyl ammonium bromide, respectively, to form three kinds of organic-modified rectorite (OREC), termed OREC1, OREC2 and OREC3. Three kinds of ORECs were used as adsorbents for phenol in aqueous solution. Through FTIR and XRD analysis, it confirmed the cation exchange reaction between REC and surfactant. The amount of surfactant exchanged in OREC1, OREC2 and OREC3 were determined as 0.27, 0.51 and 0.62 mmol/g, respectively, through incineration method. Through the research of phenol adsorption, it was found that the removal percentage (%) of phenol increased with the increase in adsorbents dose, whereas the adsorption amount q_e (mg/g) decreased. The adsorption efficiency of OREC adsorbents was greatly affected by the initial phenol solution pH value. The thermodynamics study of adsorption process showed that the adsorption of phenol with three adsorbents was carried out spontaneously, and that the process was exothermic in nature. The adsorption kinetic data of phenol with OREC adsorbents were well fitted to the Lagergren rate equation. The Freundlich isotherm model was employed and well represented in the experimental data.

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

1. Introduction

Phenol is considered as a priority pollutant since it is harmful to organisms even at low concentrations and has been classified as hazardous pollutant because of its potential harm to human health. Stringent US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1 mg/L. Phenol is a widespread and highly toxic component of water and soil pollutants. Phenol concentrations of over 2 mg/L are toxic to fish and concentrations between 10 and 100 mg/L result in death of aquatic life within 96 h. Apart from their toxicity and carcinogenity, phenol can cause bad taste and odor, even at a low concentration. So it is necessary that wastewater containing phenol needs careful treatment before discharging into the receiving bodies of water.

Recently, modified clay has brought people considerable interest in applying it to adsorb organic substances from aqueous solution because of its low cost and better adsorption capability [1–15]. There are many modified clays, such as inorganic–organic pillared MMT [4], dye–clay complexes [16], tetramethyl ammonium- and tetramethyl phonium-exchanged MMT [2], chromia- and titania-pillared MMT [3] and organic polyions modified clay [17], but these clays are mainly montmorillonite (MMT) and Kaolinite [18,19]. The effect of operating parameters such as agitation speed, solid–liquid ratio, temperature, and initial concentration, together with equilibrium isotherms were studied, and the mechanism of adsorption between modified clay and organic substances was also investigated.

But there were few reports about clay of rectorite (REC) modified by surfactant with long alkyl chain used to absorb organic materials, so in this paper three kinds of surfactants with long alkyl chain were used to modify REC.

Structure and characteristics of REC are much similar to those of MMT [20]. It is a sort of regularly interstratified clay mineral with alternate pairs of dioctahedral mica-like layer (nonexpansible) and dioctahdral smectite-like layer (expansible) existing in 1:1 ratio. The cation 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,

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doi:10.1016/j.cej.2007.10.009

nearly no attention was paid to the research of REC on adsorption study until the high quality of REC mineral was discovered in 1983.

Up to now, there were few reports on adsorption study of REC, especially about organic modified REC which was used to adsorb organic substance. So in this paper, we studied the adsorption of phenol from aqueous solution with REC modified with 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 discussed adsorption kinetics and isotherm of three adsorbents for the adsorption of phenol.

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 (1227), hexadecyl trimethyl ammonium bromide (1631) and octadecyl trimethyl ammonium bromide (1831) were supplied by Xi'an Chemistry Glass Station, China.

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 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) of REC.

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 Kα ($\lambda = 0.154$ nm) radiation (40 kV, 40 mA) and a scan range of 1–10°. To ensure an accurate assessment of the level of surfactant in each OREC, dried OPREC samples (1 g) were placed in a furnace at 500 °C for 30 min, and the amount of residue was determined. The results were corrected for fire loss. The weight of surfactant in OREC was calculated from

$$N_s = \left[1 - \frac{1 - W_{loss}}{1 - 7.28\%}\right] \times 10^3 / M_s \qquad (1)$$

where N_s (mmol/g) is the molar number of surfactant per gram of OREC, and W_{loss} (g) is fire loss weight. 7.28% in the equation accounts for the fire loss percentage of original REC during incineration at 500 °C. The molecular mass (M_s) of surfactant of 1227, 1631 and 1831 is 304, 284 and 312 g/mol, respectively.

2.4. Adsorption process

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 phenol at 300 mg/L. The stock solution of phenol (500 mg/L) was prepared in distilled–deionized water using analytical grade reagent of phenol.

Fifty-milliliter solutions of 300 mg/L of phenol were adjusted to various pH ranging from 3 to 9 with either 0.1 M HCl or 0.1 M NaOH. These were added to 1 g 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 phenol adsorbed by the adsorbents was calculated by difference.

The effect of temperature on adsorption equilibrium was studied by varying temperature from 4 to 60 °C.

Kinetic studies were carried out for 50 ml working solution at constant pH 6 with initial concentration (300 mg/L) and the adsorbent dose of 1 g/L at various temperatures (4–60 °C). After shaking, the samples were centrifuged for 10 min at 1500 rpm.

Working solutions of 20–500 mg/L were subsequently prepared from the stock solution. The various working solutions were adjusted to pH 6. A 50 ml of the various working solutions were introduced into 1.0 g of the OREC sample in 120 ml polyethylene plastic containers. They were agitated for enough time at room temperature (26 ± 1 °C). The suspensions were then centrifuged for 10 min at 1500 rpm. The supernatants collected were analyzed for phenol. The final equilibrium concentrations were determined spectrophotometrically using a Spectronic UNICO UV-2100 spectrophotometer (China). The amount of the phenol adsorbed by the adsorbents was calculated by difference.

$$\text{Removal}\% = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (2)$$

$$q_e = \frac{C_0 - C_e}{m_s} \qquad (3)$$

C_0 (mg/L) is the initial concentration of phenol solution, C_e (mg/L) the equilibrium concentration of phenol in aqueous solution and m_s (g/L), the adsorbent dose added into phenol solution. q_e (mg/g) is the calculated phenol adsorption amount on adsorbents.

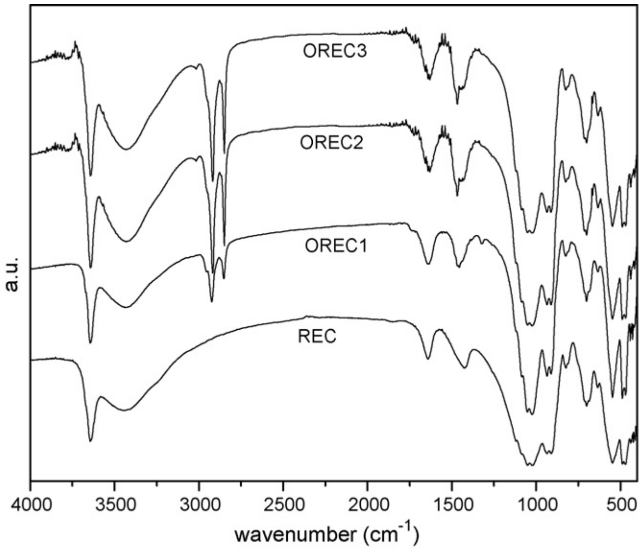


Fig. 1. FTIR spectra of REC, OREC1, OREC2 and OREC3.

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, as shown in Fig. 1. For the modified REC, there appeared two peaks at 2927 and 2853 cm^{-1}, which represented the stretching vibration of $-CH_3$ and $-CH_2$, respectively. The characteristic peaks confirmed the cationic exchange reaction between organic cations of quaternary ammonium salt of surfactant and Na^+ of REC.

The analysis of X-ray diffraction (XRD) for natural clay and organic clay 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 were 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 surfactant, and the galleries in the REC were filled with the molecules of organic cations, and *d*-spacing increased with the chain length increasing.

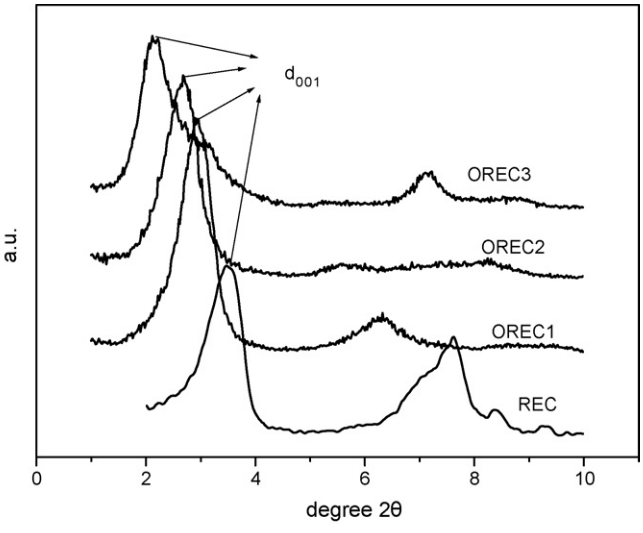


Fig. 2. Analysis of XRD of REC, OREC1, OREC2 and OREC3.

The amount of surfactant exchanged into REC was determined through incineration method. The weight loss during incineration for OREC1, OREC2 and OREC3 was 0.1298, 0.2075 and 0.2539 g, respectively. According to Eq. (1), the number of surfactant per gram OREC (N_s) was calculated as 0.27, 0.51 and 0.62 mmol/g, respectively.

3.2. Effect of adsorbents dose

The effect of adsorbent dose on the removal (%) and adsorption amount q_e (mg/g) of phenol were illustrated in Fig. 3. As the adsorbent dose (m_s) was increased from 0.2 to 1.0 g/L, for OREC1, the equilibrium adsorption amount, q_e, decreased from 150.6 to 50.9 mg/g, whereas, the phenol removal efficiency, increased from 20.4 to 66.1%; for OREC2, q_e, decreased from 218.0 to 79.4 mg/g, and the removal increased from 41.4 to 85.8%; for OREC3, q_e, decreased from 241.6 to 60.3 mg/g and the removal increased from 50.7 to 92.9%. The increased percentage removal of phenol with increasing OREC dose could be due to increased absolute adsorption surface, however the decreased equilibrium adsorption capacity, q_e, of OREC for phenol could be attributed to two reasons. First, with increasing adsorbent dose there was decreasing total surface area of the adsorbent and an increase in diffusion path length, which was the result of aggregation of OREC particles. The aggregation becomes increasingly significant as the weight of the adsorbent is increased. Secondly, the increase in adsorbent dose at constant phenol concentration and volume will lead to unsaturation of adsorption sites through the sorption process. It is therefore clear that the equilibrium adsorption capacity of each adsorbent is function of its weight.

3.3. Effect of pH

The effect of initial solution pH on the adsorption of phenol by OREC was shown in Fig. 4. Fig. 4 showed the adsorption efficiency of OREC2 or OREC3 was much better than that of OREC1 at any pH value of solution. For all adsorbents, the best adsorption efficiency was achieved at the pH 6, while pH was less or higher than 6 the adsorption efficiency decreased. This phenomenon can be explained as that the long alkyl chain forms organic phase on the clay surface, and longer chain, bigger organic phase. The adsorption of phenol on OREC mainly depends on affinity between phenol molecule and the organic phase. In the lower or higher pH of solution, phenol forms two kinds of ionic, which is unfavorable for the affinity between phenol molecule and the organic phase. It was concluded that OREC1, OREC2 and OREC3 used as adsorbents can achieve promising results at pH 6.

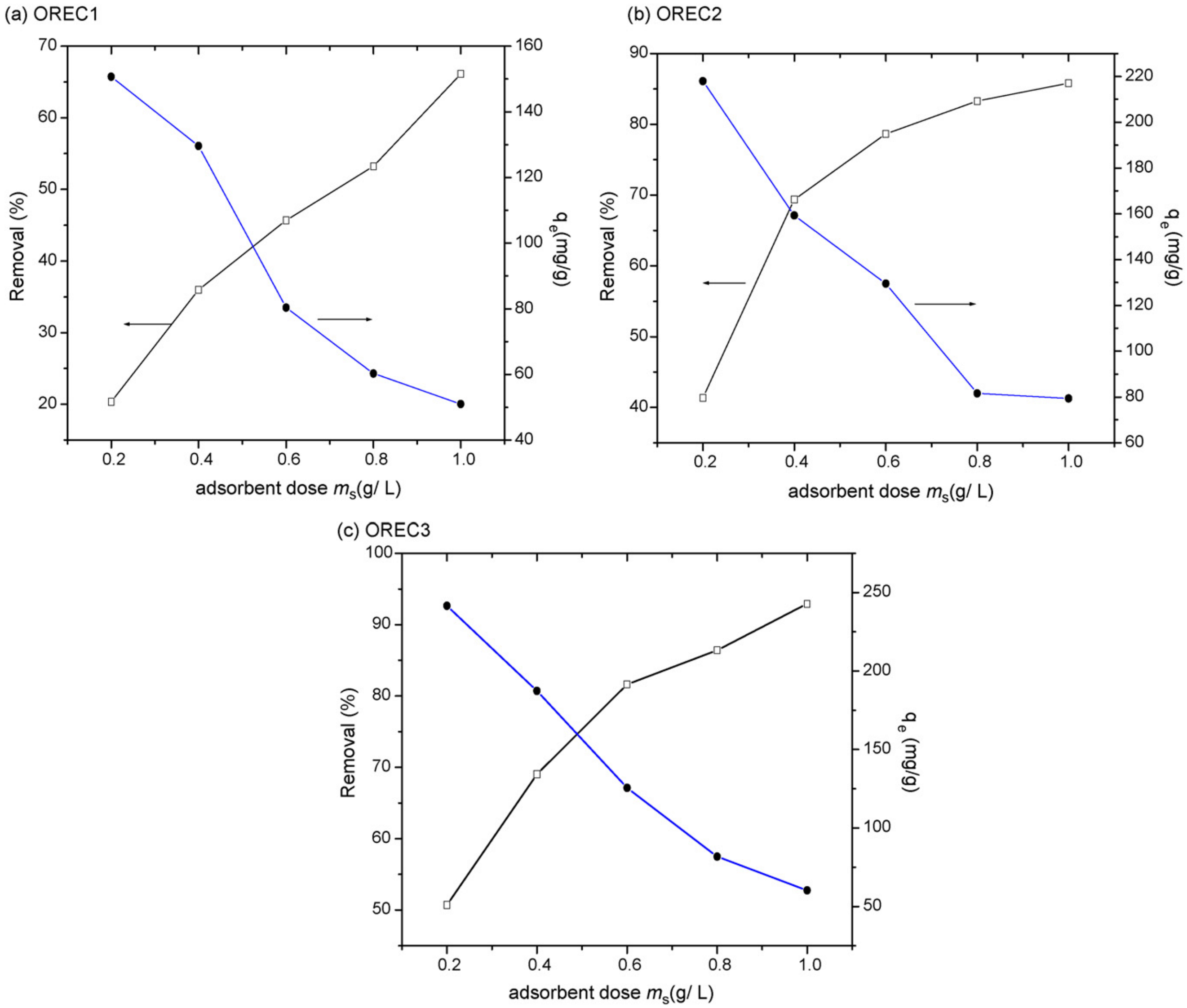


Fig. 3. The effect of adsorbent dose on the removal (%) and adsorption amount q_e (mg/g).

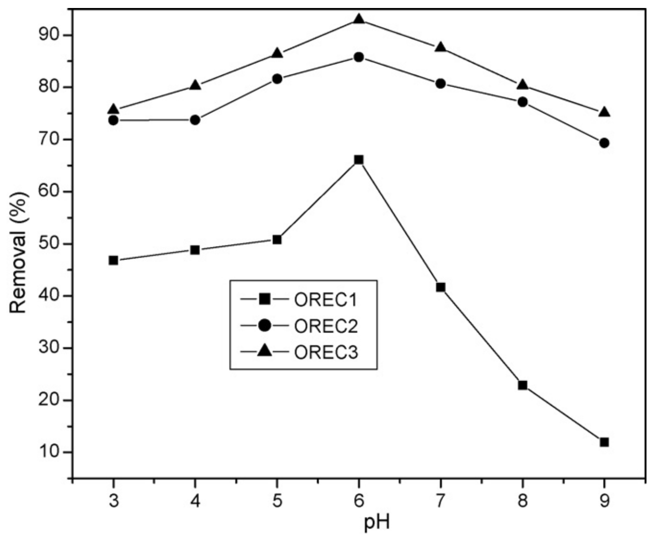


Fig. 4. The effect of initial solution pH on the removal (%).

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 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 of 80, 20 and 40 min, respectively, for OREC1, OREC2 and OREC3, followed by a second stage with a much lower adsorption rate. According to these results, the 100, 40 and 60 min agitation time was considered to be sufficient for the adsorption of phenol onto OREC1, OREC2 and OREC3, respectively.

From above researches, we also found that under any adsorbent adding dose, any initial solution pH and any adsorption time, OREC3 had the best adsorption capacity for phenol, whereas OREC1 had the least capacity, and OREC2 was between both of them. So it was concluded that for OREC adsorbents, larger *d*-spacing and more adsorption capacity, which was attributed to that larger *d*-spacing made them more eas-

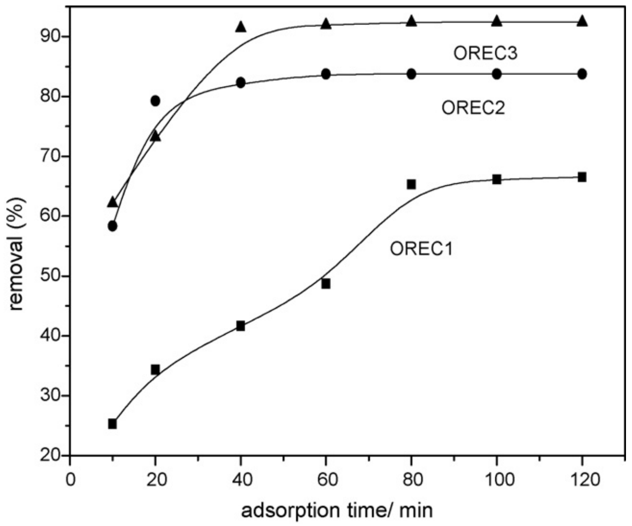


Fig. 5. The effect of adsorption time on removal (%).

ily separated in phenol solution and produced more adsorption area.

3.5. Thermodynamics analysis

According to thermodynamics temperature coefficient formula

$$\ln A = \frac{-\Delta H}{RT} + \frac{2.303\,\Delta S}{R} \tag{4}$$

where A is the allocation coefficient, $A = C_s/C_e$, and C_s (mg/L) is the equilibrium concentration of phenol adsorbed on OREC, while C_e (mg/L) is the equilibrium concentration of phenol in aqueous solution. ΔH is the enthalpy change, ΔS the entropy change, R the gas law constant (8.314 J/mol K) and T, 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 and entropy change of three adsorbents for phenol is negative, which means all adsorption reactions are exothermic and entropy values decrease. According to thermodynamics formula $\Delta G = \Delta H - \mathrm{T}\Delta \mathrm{S}$, Gibbs free energy change, ΔG, at room temperature ($T = 26\,°\mathrm{C}$) also is figured out. Negative Gibbs free energy change demonstrated the adsorption of phenol with three adsorbents carried out spontaneously. In addition, it was obvious that OREC2 and OREC3 had less ΔG values than OREC1, which demonstrated that when OREC2 and OREC3 more easily

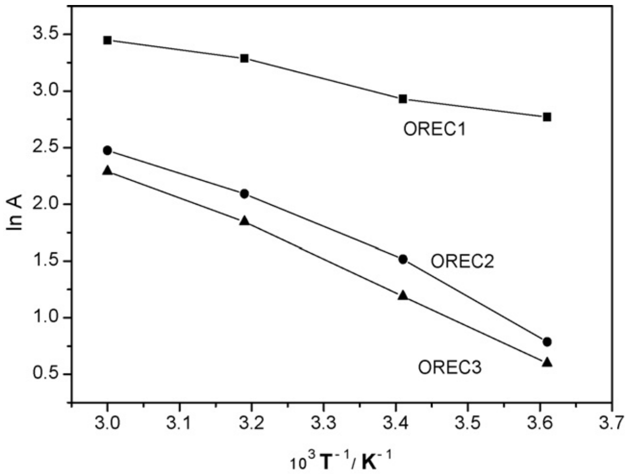


Fig. 6. Thermodynamics plots of adsorption.

adsorb phenol. This was explained as that the larger *d*-spacing of OREC2 and OREC3 produce more adsorption area which undoubtedly increase the adsorption capacity of adsorbents.

3.6. Adsorption kinetics analysis

The kinetic data were fitted to the Lagergren rate equation

$$\ln(q_e - q_t) = \ln q_e - k_{ad} \times t \tag{5}$$

where q_e and q_t are the amounts of phenol 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. 7) 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.

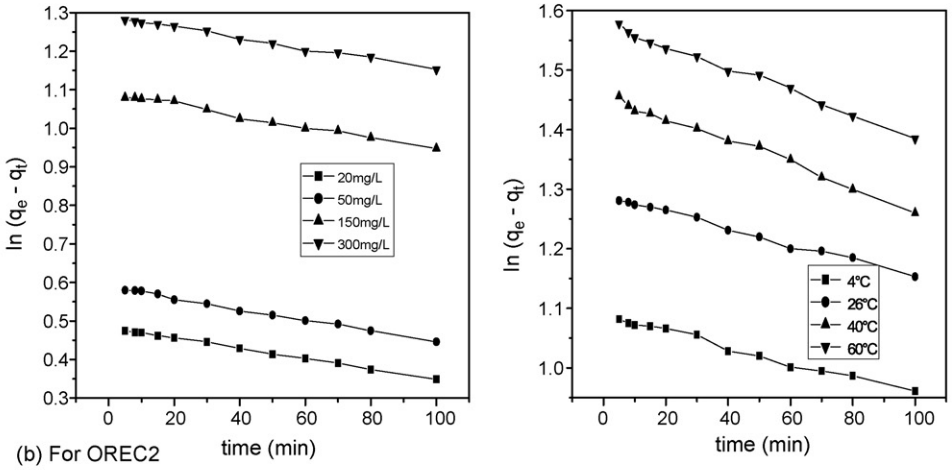
At 26 °C, and pH 6, the k_{ad} values of OREC1 at initial concentration of 20, 50, 150 and 300 mg/L were found to be 1.15×10^{-3}, 1.16×10^{-3}, $1.16 \times 10^{-3}$and $1.17 \times 10^{-3}\,\mathrm{min}^{-1}$, respectively. For OREC2, k_{ad} values were 6.22×10^{-3}, 6.17×10^{-3}, 6.21×10^{-3} and $6.37 \times 10^{-3}\,\mathrm{min}^{-1}$, respectively; for OREC3, 4.18×10^{-3}, 4.19×10^{-3}, 4.25×10^{-3} and $4.32 \times 10^{-3}\,\mathrm{min}^{-1}$. The results at different initial concentrations clearly indicated that for three adsorbents, the parameter was totally independent of initial concentration.

For OREC1, the values of k_{ad} at 4, 26, 40 and 60 °C were found to be 1.06×10^{-3}, 1.17×10^{-3}, 1.08×10^{-3} and $1.19 \times 10^{-3}\,\mathrm{min}^{-1}$, respectively for an initial concentration of 300 mg/L. For OREC2, the values of k_{ad} is 6.41×10^{-3}, 6.37×10^{-3}, 6.28×10^{-3} and $6.39 \times 10^{-3}\,\mathrm{min}^{-1}$, respectively; for OREC3, the value is 4.21×10^{-3}, 4.32×10^{-3}, 4.28×10^{-3} and $4.33 \times 10^{-3}\,\mathrm{min}^{-1}$. So it was clearly indicated that the

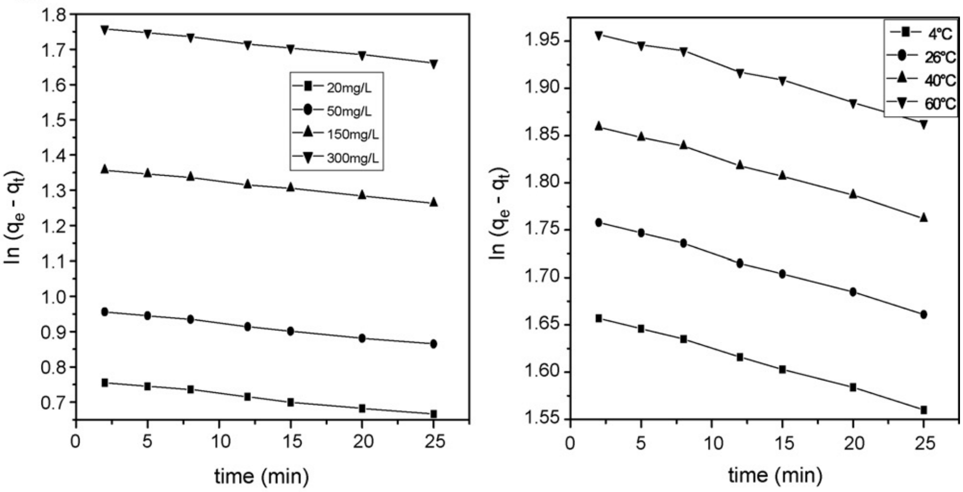
Table 1
Thermodynamics model of three kinds of adsorbents and thermodynamic parameters

Adsorbent	Linear relation coefficient r	Adsorption thermodynamics equation	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
OREC1	0.994	$\ln A = -1.17 \times 10^3/T + 6.99$	−9.73	−25.23	−2.33
OREC2	0.996	$\ln A = -2.75 \times 10^3/T + 10.81$	−22.86	−39.02	−11.23
OREC3	0.999	$\ln A = -2.79 \times 10^3/T + 10.72$	−23.20	−38.70	−11.66

(a) For OREC1



(b) For OREC2



(C) For OREC3

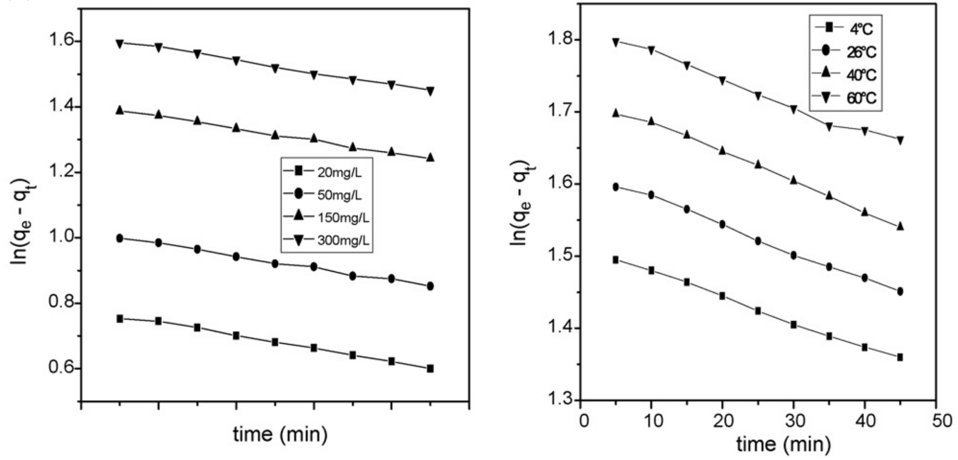


Fig. 7. $\ln(q_e - q_t)$ vs. time plots for the adsorption of phenol onto OREC at different initial concentrations and temperatures.

adsorption process of adsorbent of OREC1, OREC2 and OREC3 was exothermic. The decrease in adsorption process with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate species and also between the adjacent molecules of the adsorbed phase.

3.7. Adsorption isotherm

The Freundilich isotherm based on adsorption on a heterogeneous surface is as follows:

$$q_e = K_F C_e^{1/n} \tag{6}$$

Table 2
Adsorption coefficient K_F and adsorption constant n of Freundlich isotherm

Adsorbent	Linear relation coefficient r	Adsorption coefficient K_F	Adsorption constant n
OREC1	0.9982	4.41	1.04
OREC2	0.9976	5.44	1.25
OREC3	0.9978	5.48	2.19

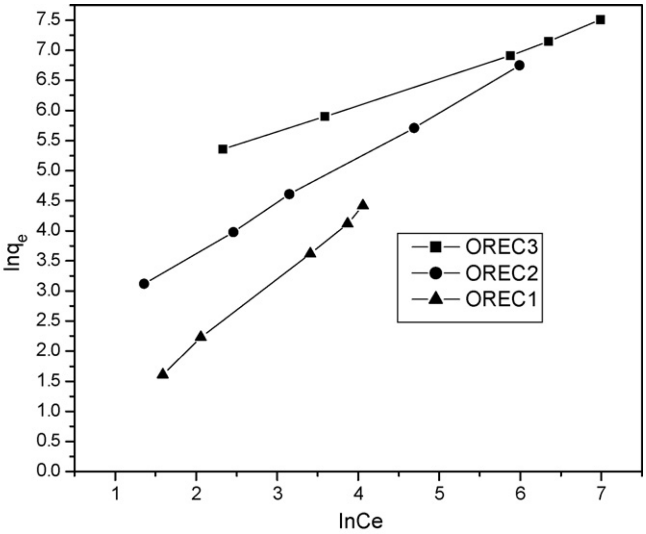


Fig. 8. Adsorption isotherm of OREC1, OREC2 and OREC3.

where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration (mg/L). K_F and n are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively. The linearized form of Freundlich adsorption isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

Freundlich plots for the phenol adsorption at room temperature (26 ± 1 °C) were given in Fig. 8. It illustrated that adsorption of phenol onto OREC adsorbents obeyed the Freundlich isothermal model as well. The corresponding Freundlich isotherm constants K_F and n together with the correlation coefficients r were also listed in Table 2. Values of K_F derived from the Freundlich theory are an indicator of the adsorption capacity of a given adsorbent. The exponent n was greater than unity at room temperatures in Table 2 indicated a favorable adsorption processes. We also found that for OREC1, OREC2 and OREC3, the values of K_F and n orderly increased, which further confirmed the ordinal improved adsorption capacity.

4. Conclusions

The OREC adsorbents were successfully prepared with cation exchange reaction between raw REC and the surfactant. For OREC1, OREC2 and OREC3, the satisfying adsorption efficiency was achieved with adsorption time of 100, 40 and 60 min, respectively, initial phenol solution pH 6 and at room temperature. Through the thermodynamics study of adsorption process, the adsorption of phenol with three adsorbents carried out spontaneously. The adsorption kinetic data of phenol with OREC adsorbents indicated that the three adsorption processes belonged to one order adsorption reaction. The research of adsorption isotherm demonstrated that, for three prepared OREC adsorbents, adsorption reactions belonged to Freundlich model.

Acknowledgement

The authors gratefully acknowledge the financial support from the Nature Science Fund of Shaanxi (2005B23), the National Nature Science Fund (20674062) and New Century Excellent Talents in University (NCET-06-0880).

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