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Chemical Engineering Journal 143 (2008) 117–123

Chemical Engineering Journal

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Equilibrium, kinetic and thermodynamic studies on the sorption of 4-hydroxyphenol on Cr-bentonite

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Received 1 October 2007; received in revised form 14 December 2007; accepted 20 December 2007

Abstract

With synthetic wastewater, the sorption characteristics of 4-hydroxyphenol on Cr-bentonite were investigated using a lab-scale batch experiment technique. The effects of relevant parameters, such as pH value of solution, contact time and temperature of solution were examined. Equilibrium modeling data were fitted to linear Langmuir and Freundlich models. Dubinin-Redushkevich (D-R) isotherm was applied to describe the nature of 4-hydroxyphenol uptake and it was found that it occurred physically. The pseudo first-order, second-order kinetic models and intraparticle diffusion model were used to describe the kinetic data. The pseudo second-order kinetic model provided excellent kinetic data fitting ($R^2 > 0.999$) and intraparticle diffusion affects 4-hydroxyphenol uptake. Thermodynamic functions, the change of free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of sorption were also calculated. These parameters show that the sorption process of 4-hydroxyphenol on Cr-bentonite is spontaneous and exothermic at 15–45 °C. The results indicate that there is significant potential for Cr-bentonite as an adsorbent material for phenolic compounds removal from aqueous solutions.

Keywords: 4-Hydroxyphenol; Cr-bentonite; Isotherm; Kinetics; Thermodynamics

1. Introduction

Phenolic compounds including substituted phenols are widespread as environmental pollutants due to their common presence in the effluents of many industrial processes, including petrochemical plants, oil refineries, pharmaceutical plants, phenol producing industries, and other chemical processes. Their high toxicity, even at low concentrations, has motivated the search and improvement of many treatment techniques. Among various physicochemical processes including adsorption [1–4], oxidative coupling polymerization [5], enzyme-catalyzed polymerization [6], photocatalytic degradation [7] and electrochemical treatment [8] adsorption is widely used for the removal of phenolic compounds from wastewater [9,10]. Adsorption onto activated carbons in the form of grains or powder is a well-known process for organic contaminant removal [11]. However, the cost is high and recovering activated carbon particles from wastewater may be difficult. 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 [12]. Commonly, the adsorption of organic pollutants by bentonite is poor because the mineral surfaces are hydrophilic. The adsorption of specific organic contaminants by high valence metal cation-saturated montmorillonite, however, was found to be obviously improved [13–16]. The stronger adsorption is generally attributed to stronger H-bonding between more polar water molecule associated with high valence metal cations than low valence cations and polar organic compounds [17].

The wastewater containing chromium which is generated in many economic activities, such as chromium producing industries, leathering, dyeing and electroplating industries, 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.

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doi:10.1016/j.cej.2007.12.022

In the previous study, Cr-bentonite prepared using the wastewater containing chromium was found to be an effective and potential adsorbent for phenolic compounds [18,19]. In this paper, isotherms, kinetics and thermodynamics about the sorption of 4-hydroxyphenol, a typical phenolic compound, on Cr-bentonite was studied.

2. Materials and methods

Ca-bentonite used in this investigation was obtained from Xuanhua City, Hebei Province, China, and compose of 87.4% of montmorillonite, 3.6% of quartz, 7.3% of α-cubic quartz, and 1.0% of other components. It was treated and converted to Na-bentonite by 5% Na_2CO_3 solution before being used to prepare Cr-bentonite. Analytical grade 4-hydroxyphenol and deionised water were used in the preparation of the stock 4-hydroxyphenol solutions. The stock solutions were diluted to prepare for working solutions. The initial pH value was adjusted by addition of 5% NaOH or 5% HCl to designed value.

Cr-bentonite was prepared using the following method [18,19]: a complete mixing of 500 mL of 1g/L $Cr(NO_3)_3$ solution and 5 g of Na-bentonite sample was performed in a 1000 mL plug-contained conical flask, and then the bottle was shaken in HZS-H water bath and constant temperature oscillator for 12 h at a speed of 150 round per min and a room temperature of 25 ± 0.2 °C. Excessive $Cr(NO_3)_3$ was removed by deionised water washings until the supernatant was free of chromium ion, as tested by 1 mol/L NaOH solution. The Cr-bentonite prepared was dried at 70 °C, and sieved using 200-mesh (75 μm) sieve.

The batch experiments were initiated by a complete mixing of 20 mL synthetic 4-hydroxyphenol solution of 10 mg/L initial 4-hydroxyphenol concentration with designed pH value and 0.1 g of Cr-bentonite samples except the experiment of the effect of the adsorbent dosage in a serial of 100 mL plug-contained conical flasks, and then the bottles were shaken in HZS-H water bath and constant temperature oscillator at a speed of 150 round per min and a room temperature of 25 ± 0.2 °C except the experiment of the effect of temperature. Water samples in conical flasks were filtrated rapidly with 0.45 μm membranes at 120 min except the dynamic experiments at frequent intervals, and the filtrates were used immediately to analyze the concentration of 4-hydroxyphenol at wavelength of 288 nm using UV-2450 Ultraviolet Spectrophotometer (Japan). The sorption efficiency (%) and amounts of adsorbed 4-hydroxyphenol (q_e) by Cr-bentonite were calculated using Eqs. (1) and (2), respectively:

$$\text{Sorption efficiency}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where V is the solution volume (L), C_0 is initial concentration of adsorbate (mg/L), C_e is the concentration of adsorbate in equilibrium solution (mg/L), and m is the adsorbent weight (g).

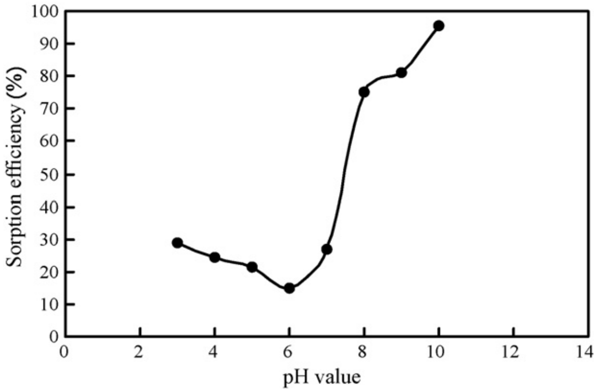


Fig. 1. Effect of pH value on 4-hydroxyphenol sorption on Cr-bentonite.

3. Results and discussion

3.1. Effect of pH value

The pH of solution is the most important variable affecting 4-hydroxyphenol sorption on Cr-bentonite. Fig. 1 shows the effect of pH value on 4-hydroxyphenol sorption on Cr-bentonite. As shown in Fig. 1, the effect of pH value on 4-hydroxyphenol sorption on Cr-bentonite was found to be complicated. Sorption efficiencies of 4-hydroxyphenol decrease with the increase of pH value when pH values are between 3.02 and 5.98, and then increase with the increase of pH value when pH values are between 5.98 and 9.97. The possible reason is attributed to the different form of 4-hydroxyphenol and different structure of bentonite at different pH value. Bentonite is activated by acid in acidic medium and sorption efficiency is increased. The lower the pH value is, the higher the sorption efficiency is. When pH is higher than 5.98, chromium ion in interlayer coordinates with more water molecules, and the water molecules adsorb 4-hydroxyphenol by hydrogen bond, as shown in Fig. 2.

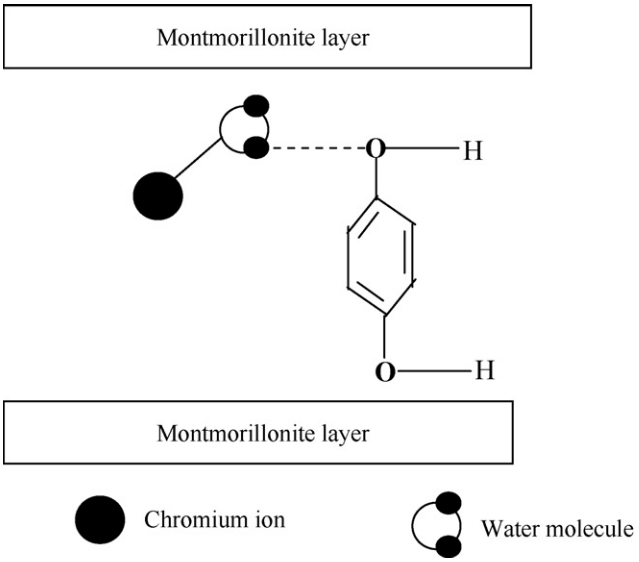
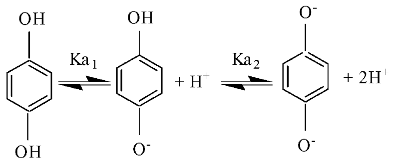


Fig. 2. H-bonding between 4-molecule and water molecule coordinated with Cr-bentonite interlayer surface.

The results are accordant with those reported about agricultural chemicals [13–16]. With the increase of pH value, 4-hydroxyphenol is dissociated as follows:



(3)

where Ka_1 is first-order dissociation constant and Ka_2 is second-order dissociation constant. Sorption is attributed to hydrogen bond and electrostatic attractions and sorption efficiency increases. The pH value of 8 was selected as optimum pH value for all further experiments.

3.2. *Effect of adsorbent dosage*

The adsorbent dosage is important factor for the sorption capacity of 4-hydroxyphenol. Fig. 3 shows influence of adsorbent dosage on 4-hydroxyphenol adsorption on Cr-bentonite. The results show that sorption efficiency of 4-hydroxyphenol increases with the increase of adsorbent dosage but sorption capacity decreases with the increase of adsorbent dosage. Therefore, 0.1 g of adsorbent was selected as optimum adsorbent dosage for all further experiments.

3.3. *Effect of contact time*

Fig. 4 shows influence of contact time on 4-hydroxyphenol sorption on Cr-bentonite. It can be seen that sorption efficiency of 4-hydroxyphenol increases with the increase of shaking time up to 120 min. Maximum sorption efficiency was attained as 80.5% at 25 °C. It is much higher than 26.2% of Na-bentonite and 36.4% of Ca-bentonite [18,19]. Therefore, 120 min was selected as optimum shaking time for all further experiments.

3.4. *Effect of temperature*

Fig. 5 shows the influence of temperature on the sorption of 4-hydroxyphenol by Cr-bentonite. As shown in Fig. 5, the sorption efficiency slightly decreased with the increase of temperature. When the temperature was increased from 15 °C to 45 °C, sorption efficiency decreased from 80.5% to 65.2%. These results indicated the exothermic nature of 4-hydroxyphenol sorption on Cr-bentonite. This attributed to the tendency of 4-hydroxyphenol to desorb from the solid surfaces with increasing temperature. These results are accordant with those of agricultural chemicals adsorbed by high valence metal cation-saturated montmorillonite [13–16].

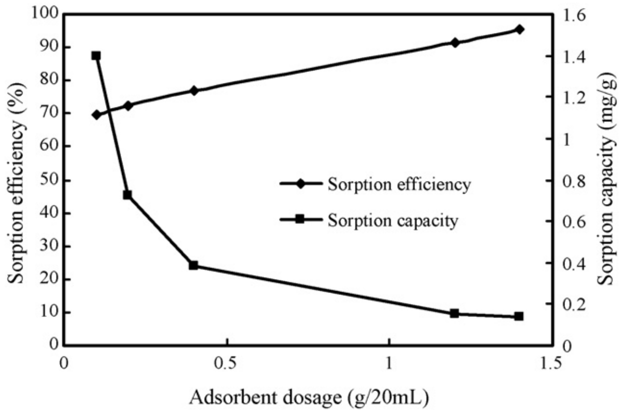


Fig. 3. Effect of the adsorbent dosage on 4-hydroxyphenol sorption on Cr-bentonite.

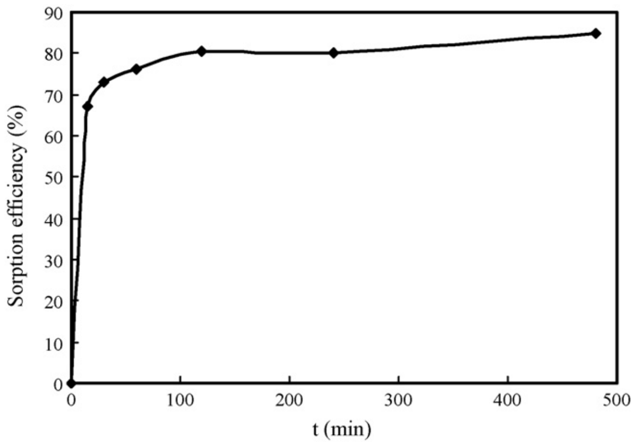


Fig. 4. Effect of contact time on 4-hydroxyphenol sorption on Cr-bentonite.

3.5. *Sorption isotherm models*

Three important isotherms are selected to reveal the specific relation between the equilibrium concentration of 4-hydroxyphenol and its sorption degree on Cr-bentonite at a constant temperature of 25 °C in this study, which are, namely the Langmuir, Freundlich and the D-R isotherm models.

The Langmuir model assumes that adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes. The linear form of Langmuir model is expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_0}C_e + \frac{1}{q_0 k} \tag{4}$$

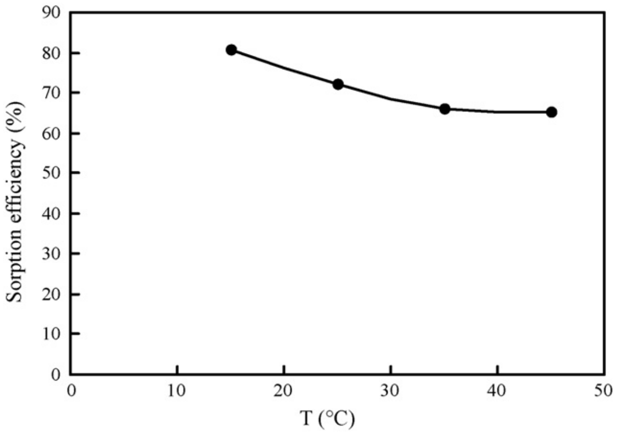


Fig. 5. Effect of temperature on 4-hydroxyphenol sorption on Cr-bentonite.

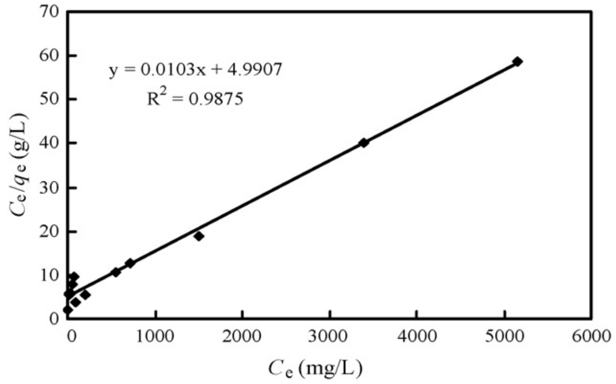


Fig. 6. Linear plot of Langmuir isotherm of 4-hydroxyphenol sorption on Cr-bentonite.

where q_e is the equilibrium amount of adsorbate adsorbed (mg) by per unit mass of adsorbent (g), C_e is the concentration of adsorbate in equilibrium solution (mg/L), and the values of q_0 (mg/g) and k (L/mg) are maximum sorption capacity of adsorbent and the sorption energy coefficient, respectively.

As shown in Fig. 6, the correlation coefficient value of the linear plot is satisfactory ($R^2 = 0.9875$). The maximum sorption capacity of Cr-bentonite (q_0) and the sorption energy coefficient (k) calculated from the slope and the intercept of the linear plot were 97.09 mg/g and 0.0021 L/mg at 25 °C, respectively.

The essential features of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L:

$$R_L = \frac{1}{1 + kC_0} \tag{5}$$

where C_0 (mg/L) is initial concentration of adsorbate and k is the Langmuir constant (L/mg). There are four probabilities for the R_L value: for favorable sorption, $0 < R_L < 1$; for unfavorable sorption, $R_L > 1$; for linear sorption, $R_L = 1$; for irreversible sorption, $R_L = 0$ [20–22].

Fig. 7 shows the variation of separation factor (R_L) with initial 4-hydroxyphenol concentration. The results that the R_L values were in the range of 0–1 indicate that the sorption of 4-hydroxyphenol on Cr-bentonite is favorable.

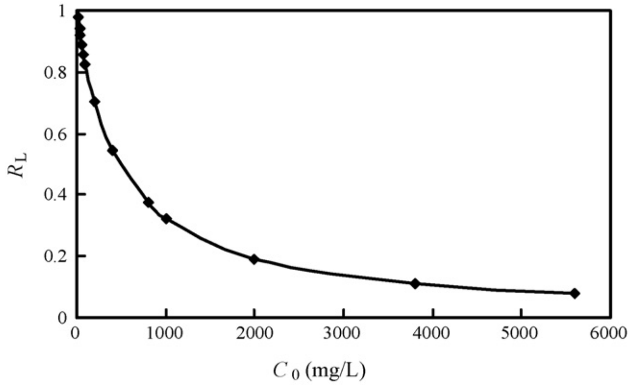


Fig. 7. Variation of separation factor (R_L) as a function of initial 4-hydroxyphenol concentration.

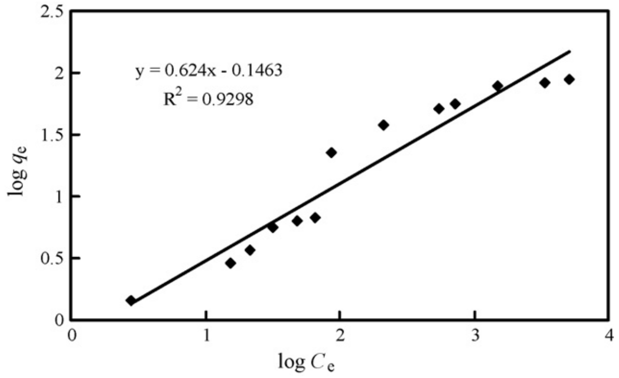


Fig. 8. Linear plot of Freundlich isotherm of 4-hydroxyphenol sorption on Cr-bentonite.

The Freundlich model [23] can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The linear form of Freundlich model is expressed as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{6}$$

where K_f is Freundlich constant (mg/g), the measure of the sorption capacity of the adsorbent, and $1/n$ is the heterogeneity factor, a constant relating to sorption intensity or surface heterogeneity.

Fig. 8 shows the linear plot of Freundlich isotherm of 4-hydroxyphenol sorption on Cr-bentonite. Compared with the correlation coefficient value of the linear plot of Langmuir isotherm, that of Freundlich model was found less satisfactory ($R^2 = 0.9298$). Freundlich constant (K_f) and the heterogeneity factor ($1/n$) calculated from the slope and the intercept of the linear plot were 0.7140 mg/g and 0.624, respectively. The value of $1/n$ smaller than 1 points out the favorable sorption conditions [20,24].

The equilibrium data were also applied to the D-R model [20,23,25,26] to determine the type of sorption (physical or chemical). The linear form of D-R isotherm is presented as the following equation:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{7}$$

where q_e is the amount of 4-hydroxyphenol adsorbed onto per unit dosage of Cr-bentonite (mol/g), q_m is the theoretical monolayer sorption capacity (mol/g), β is the constant of the sorption energy (mol^2/J^2), which is related to the average energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution [20,25], the ε is Polanyi potential, which described as

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \tag{8}$$

where T is the solution temperature (K) and R is the gas constant and is equal to 8.314 J/mol K.

The value of mean sorption energy, E (kJ/mol), can be calculated from D-R parameter β as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{9}$$

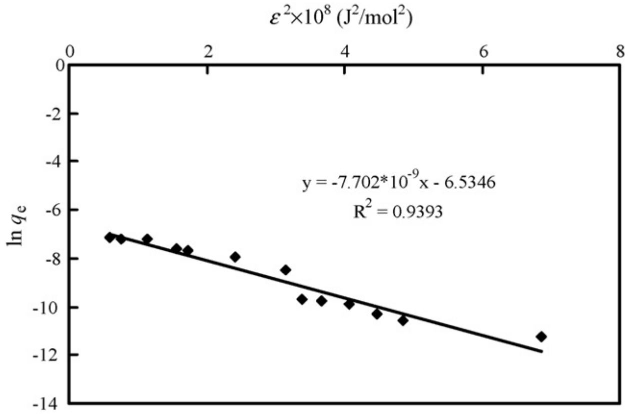


Fig. 9. D-R isotherm plot of 4-hydroxyphenol sorption on Cr-bentonite.

The value of mean sorption energy gives information about chemical and physical sorption. The E value ranges from 1 kJ/mol to 8 kJ/mol for physical sorption and from 8 kJ/mol to 16 kJ/mol for chemical sorption [20,23,25]. The E value (7.9 kJ/mol) was found in the range of 1–8 kJ/mol (Fig. 9), indicating that the type of sorption of 4-hydroxyphenol on Cr-bentonite is physical.

3.6. Sorption kinetics

Lagergren's pseudo first-order, pseudo second-order and diffusion models were used for analysis of sorption kinetics.

The Lagergren's equation for first-order kinetics can be written as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{10}$$

where q_t is the amount of adsorbate adsorbed (mg/g) at time t, k_1 is the rate constant (min^{-1}). Pseudo first-order kinetic plotted at 25 °C is given in Fig. 10.

Pseudo second-order model is represented as [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{11}$$

where k_2 is the rate constant (g/mg min). Pseudo second-order kinetic plotted at 25 °C is given in Fig. 11.

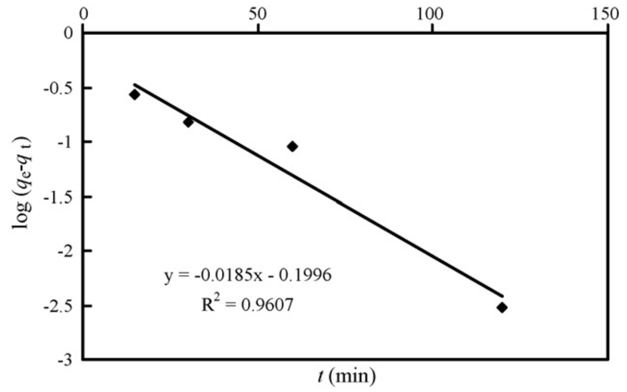


Fig. 10. Pseudo first-order kinetic plot for 4-hydroxyphenol sorption on Cr-bentonite.

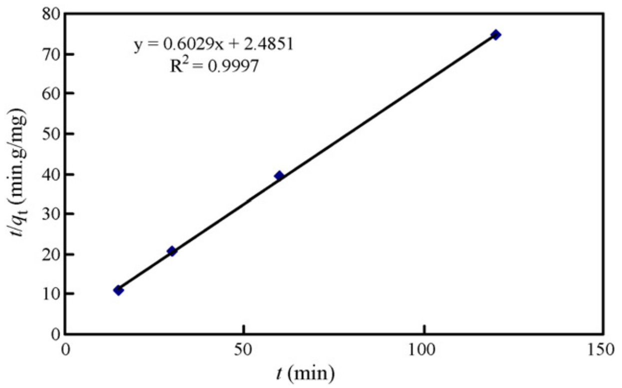


Fig. 11. Pseudo second-order kinetic plot for 4-hydroxyphenol sorption on Cr-bentonite.

The intraparticle diffusion equation can be written as follows:

$$q_t = k_d t^{1/2} + C \tag{12}$$

where k_d is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and C is the intercept. Fig. 12 presents plot of q_t versus $t^{1/2}$ at 25 °C.

When the correlation coefficients are compared (pseudo first-order kinetic $R^2 = 0.9607$, pseudo second-order kinetic $R^2 = 0.9997$ and intraparticle diffusion kinetic $R^2 = 0.9456$), the higher correlation coefficient confirms that 4-hydroxyphenol uptake by Cr-bentonite follows pseudo second-order model.

As can be seen from Fig. 12, 4-hydroxyphenol sorption by Cr-bentonite involves two stages, that is, surface sorption and intraparticle diffusion. The first linear portion is attributed to the boundary layer diffusion effect and the final linear portion may be due to the intraparticle diffusion effect [24,28].

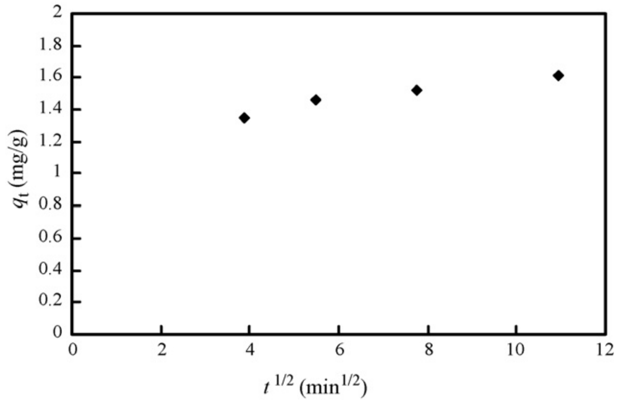


Fig. 12. Intraparticle diffusion kinetic plot for 4-hydroxyphenol sorption on Cr-bentonite.

Table 1
Change of thermodynamic parameters with temperature

Temperature (°C)	K_C	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/K mol)
15	4.13	−3.39	−20.39	−59.80
25	2.57	−2.34		
35	1.94	−1.70		
45	1.87	−1.66		

Table 2
The sorption heat of different force (kJ/mol) [30]

Van der Waals force	Hydrophobic action	Hydrogen bond	Dentate exchange	Dipole attraction	Chemical bond
4 ∼ 10	About 3	2 ∼ 40	About 40	2 ∼ 29	>60

3.7. *Sorption thermodynamics*

Thermodynamic parameters such as changes in the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be calculated using following equations:

$$K_C = \frac{C_{Ae}}{C_{Se}} \tag{13}$$

$$\Delta G^0 = -RT \ln K_C \tag{14}$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{15}$$

where K_C is the equilibrium constant, C_{Ae} is the amount of adsorbate on the adsorbent per litre of the solution at equilibrium (mg/L), C_{Se} is the equilibrium concentration of adsorbate in the solution (mg/L).

The amount of 4-hydroxyphenol adsorbed at equilibrium at different temperature for 15, 25, 35 and 45 °C was used to calculate and obtain thermodynamic parameters. Based on Eqs. (13)–(15), ΔH° and ΔS° were calculated from the slope and intercept of linear plot of $\ln K_C$ versus $1/T$ (as shown in Fig. 13). The values of K_C, ΔG°, $\Delta H^\circ$and ΔS° parameters were summarized in Table 1.

The change in the standard free energy ΔG° with negative values for −3.39, −2.34, −1.70 and −1.66 kJ/mol at all the experimental temperature indicates that 4-hydroxyphenol sorption by Cr-bentonite is spontaneous. Furthermore, 4-hydroxyphenol sorption has physical characteristics since the free energy change is between 0 kJ/mol and −20 kJ/mol [29].

Change in the standard enthalpy ΔH° has a value of −20.39 kJ/mol. The negative ΔH° exhibits that the 4-hydroxyphenol sorption by Cr-bentonite is exothermic. According to the sorption heat of different force (Table 2) determined by von Oepen et al. [30], sorption mechanisms of 4-hydroxyphenol by Cr-bentonite are attributed to hydrogen bond and dipole attraction between 4-hydroxyphenol and water molecule. The negative value of the standard entropy change ΔS° (−59.80 J/K mol) indicates that the randomness decreases with the sorption of 4-hydroxyphenol on Cr-bentonite.

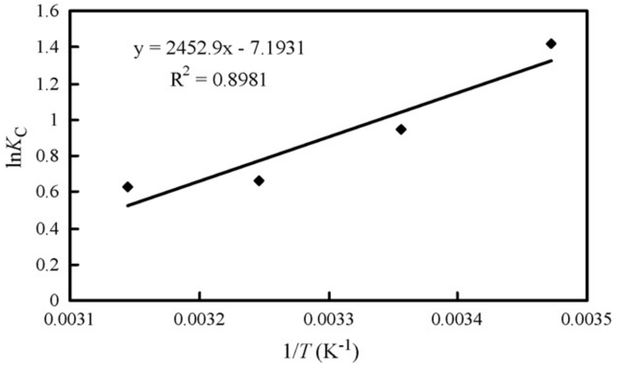


Fig. 13. Variation of equilibrium constant (K_C) as a function of temperature.

4. Conclusions

(1) 4-Hydroxyphenol sorption on Cr-bentonite was studied in batch mode and found to be strongly dependent on pH value and contact time, and low temperature favors 4-hydroxyphenol uptake on Cr-bentonite.
(2) 4-Hydroxyphenol sorption data on Cr-bentonite fitted to Langmuir model ($R^2 = 0.9875$), Freundlich model ($R^2 = 0.9298$) and D-R model ($R^2 = 0.9393$). R_L value from Langmuir isotherm and $1/n$ from Freundlich isotherm indicate that the sorption of 4-hydroxyphenol on Cr-bentonite is favorable. E value (7.9 kJ/mol) from D-R model indicates that the type of sorption of 4-hydroxyphenol on Cr-bentonite is physical.
(3) The pseudo second-order kinetic model agrees very well with the dynamic data for 4-hydroxyphenol sorption on Cr-bentonite.
(4) The negative values of ΔG° at the experimental temperature for 15, 25, 35 and 45 °C indicate that sorption of 4-hydroxyphenol on Cr-bentonite is spontaneous. The negative values of ΔH° and ΔS° exhibit that sorption of 4-hydroxyphenol on Cr-bentonite is exothermic and the randomness decreases with the sorption of 4-hydroxyphenol on Cr-bentonite.

Acknowledgement

This work was supported by Open Fund Projects of National Laboratory of Mineral Materials, P.R. China (nos. A05006 and 07A001) and Open Fund Project of State Key Library of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (no. 2001010).

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