



## Sorption isotherm and kinetic modeling of aniline on Cr-bentonite

Hong Zheng<sup>a,b,\*</sup>, Donghong Liu<sup>a,b</sup>, Yan Zheng<sup>a,b</sup>, Shuping Liang<sup>b</sup>, Zhe Liu<sup>a,b</sup>

<sup>a</sup> National Laboratory of Mineral Materials, China University of Geosciences, Beijing 100083, PR China

<sup>b</sup> School of Materials Science and Technology, China University of Geosciences, Beijing 100083, PR China

### ARTICLE INFO

#### Article history:

Received 11 November 2008

Received in revised form 17 December 2008

Accepted 17 December 2008

Available online 27 December 2008

#### Keywords:

Aniline  
Sorption  
Cr-bentonite  
Isotherm  
Kinetics

### ABSTRACT

In this paper, the sorption characteristics of aniline on Cr-bentonite prepared using synthetic wastewater containing chromium was investigated in a batch system at 30 °C. The effects of relevant parameters, such as pH value of solution, adsorbent dosage and initial aniline concentration were examined. The experimental data were analyzed by the Langmuir and Freundlich, and Temkin models of sorption. The sorption isotherm data were fitted well to Langmuir isotherm and the monolayer sorption capacity was found to be 21.60 mg/g at 30 °C. Dubinin–Redushkevich (D–R) isotherm was applied to describe the nature of aniline uptake and it was found that it occurred chemically. The kinetic data obtained at different concentrations were analyzed using a pseudo first-order, pseudo second-order kinetic equation and intraparticle diffusion model. The experimental data fitted very well the pseudo second-order kinetic model. Intraparticle diffusion affects aniline uptake. The results indicate that there is significant potential for Cr-bentonite as an adsorbent material for aniline removal from aqueous solutions.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Aniline is frequently used by the chemical industry in several processes such as the synthesis of dyes and several pesticides. It is also a common by-product from paper and textile industries. Aniline and its derivatives are known to be toxic water pollutants and their presence in wastewater even in very low concentrations has been shown to be harmful to aquatic life [1]. Moreover, aniline can be easily adsorbed in sediments, fact that can extend its persistence in the aquatic environment [2]. There are many processes, including biodegradation [3], oxidation by ozone [4], ligand exchanger [5], adsorption [6] and some other processes that can be used for the removal of aniline from wastewater. These processes can decompose or remove aniline in wastewater to some extent, but it is very difficult to decompose aniline completely. Adsorption onto activated carbons in the form of grains or powder is a well-known process for organic contaminant removal [7]. However, the cost is high and recovering activated carbon particles from wastewater may be difficult. Bentonite, whose main component is montmorillonite, is potentially important adsorption material because of its large surface area, large number of inter-layer exchangeable inorganic cations and abundance in nature [8]. The adsorption of specific organic contaminants by high valence metal cation-saturated montmorillonite was found to be obviously improved because of stronger H-bonding between more polar

water molecule associated with high valence metal cations than low valence cations and polar organic compounds [9–13].

In this work, we attempt to use Cr-bentonite prepared using synthetic wastewater containing chromium as an adsorbent to remove aniline from aqueous solution. Cr-bentonite was found to be an effective and potential adsorbent for phenolic compounds and aniline [14–17]. The objective of this work was to investigate the sorption isotherm and kinetic modeling of aniline on Cr-bentonite and reveal the sorption characteristics of aniline on Cr-bentonite. The sorption characteristics are important to predict the adsorption process.

### 2. Materials and methods

Ca-bentonite used in this investigation was obtained from Xuanhua City, Hebei Province, China, and is composed of 87.4% montmorillonite, 3.6% quartz, 7.3%  $\alpha$ -cubic quartz, and 1.0% other components. It was treated and converted to Na-bentonite by 5% NaCO<sub>3</sub> solution before being used to prepare Cr-bentonite.

Cr-bentonite was prepared using following method [14–17]: a complete mixing of 500 mL of 1 g/L Cr(NO<sub>3</sub>)<sub>3</sub> 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 rpm and a temperature of 25 ± 0.2 °C. Excessive Cr(NO<sub>3</sub>)<sub>3</sub> was removed by deionized 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  $\mu$ m) sieve.

\* Corresponding author. Tel.: +86 10 82322759; fax: +86 10 82322974.  
E-mail address: [zhengh@cugb.edu.cn](mailto:zhengh@cugb.edu.cn) (H. Zheng).

For the determination of the contents of the sodium and calcium in different types of bentonites, 100 mg of bentonites was dissolved with concentrated sulphuric acid and hydrofluoric acid, and then their sodium and calcium contents (calculated as Na<sub>2</sub>O and CaO, respectively) were determined using Flame spectrometry and EDTA titration, respectively. Another 100 mg of bentonites was dissolved using Na<sub>2</sub>O<sub>2</sub> and NaOH and chromium contents (calculated as Cr<sub>2</sub>O<sub>3</sub>) were analyzed using sys-diphenyl carbazide spectrophotometry at wavelength of 540 nm using UV-2450 Ultraviolet Spectrophotometer (Japan). Three types of bentonites were characterized by using X-ray diffraction (XRD, D/Max-RC). XRD patterns were obtained at the scan speed of 1°/min with CuK $\alpha$  radiation at 40 kV and 80 mA. Water adsorbed was determined by using gravimetric method.

Analytical grade aniline and deionized water were used in the preparation of the stock aniline solutions. The stock solutions were diluted to prepare for working solutions by using deionized water. The initial pH value was adjusted by addition of NaOH or HCl to designed value.

The batch experiments were carried out in a serial of 100 mL plug-contained conical flasks where 0.02–0.25 g of Cr-bentonite samples and 20 mL synthetic aniline solution of 20–200 mg/L initial aniline concentration were added. The pH value of the solutions in contact with adsorbents was designed to be in the range 4.4–5.0 (original pH values of the synthetic aniline solutions), except the experiment of the effect of pH value. The bottles were shaken in HZS-H water bath and constant temperature oscillator at a speed of 150 rpm and a temperature of 30  $\pm$  0.2 °C (room temperature in summer). Water samples in conical flasks were filtrated rapidly with 0.45  $\mu$ m membranes at 30 min, except the dynamic experiments at frequent intervals, and the filtrates were used immediately to analyze the concentration of aniline at wavelength of 230 nm using UV-2450 Ultraviolet Spectrophotometer. The sorption efficiency (%) and amounts of adsorbed aniline ( $q_e$ ) by Cr-bentonite were calculated using Eqs. (1) and (2), respectively:

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

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

where  $C_0$  and  $C_e$  (mg/L) are the liquid-phase concentrations of aniline initially and at equilibrium, respectively.  $V$  is the volume of the solution (L),  $m$  is the mass of dry adsorbent used (g) and  $q_e$  (mg/g) is the amount of adsorbed aniline at equilibrium.

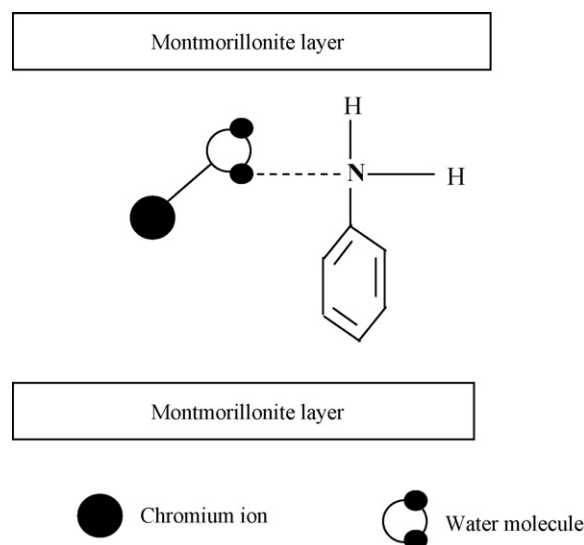
### 3. Results and discussion

#### 3.1. Characterization of Cr-bentonite

The results of XRD show that d001 value of Cr-montmorillonite is evidently enlarged, compared with the original Ca- and Na- montmorillonite. The d001 values of Na-, Ca- and Cr- montmorillonite are 1.3065, 1.5019, and 1.6598, respectively. Larger interlayer distance can help aniline molecule enter the interlayer of montmorillonite. The results of the chemical analysis (Table 1) indicate that the contents of Cr<sub>2</sub>O<sub>3</sub> in Na-, Ca-, and Cr-bentonite are 0, 0, and 2.47%,

**Table 1**  
Contents of Na<sub>2</sub>O, CaO, Cr<sub>2</sub>O<sub>3</sub>, and water adsorbed in different types of bentonites.

Constituent	Value (wt.%)		
	Na-bentonite	Ca-bentonite	Cr-bentonite
Na <sub>2</sub> O	3.38	0.26	0.23
CaO	0.47	1.25	0.27
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	2.47
H <sub>2</sub> O	6.32	6.82	10.09



**Fig. 1.** H-bonding between aniline molecule and water molecule coordinated with Cr-bentonite interlayer surface.

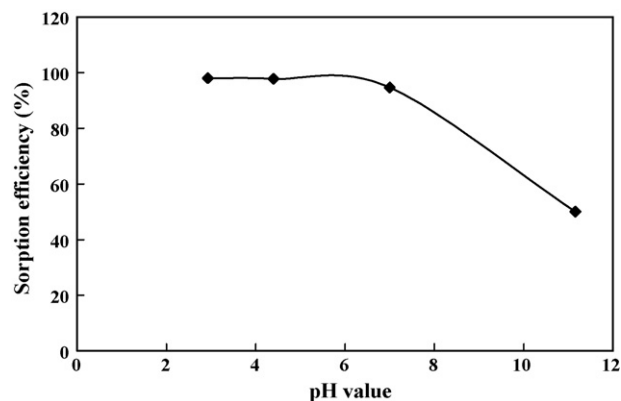
respectively. The fact that the contents of Na<sub>2</sub>O and CaO in Cr-bentonite are evidently lessened, showing that Cr<sup>3+</sup> has succeeded in exchanging with Na<sup>+</sup> and Ca<sup>2+</sup>. The higher water adsorbed content in the Cr-bentonite shows that more polar water molecules are associated with Cr<sup>3+</sup> than Na<sup>+</sup> and Ca<sup>2+</sup>. Chromium ion in interlayer coordinates with water molecules and the water molecules adsorb aniline by hydrogen bond, as shown in Fig. 1.

#### 3.2. Effect of solution pH value on aniline sorption

The pH of solution is one of the most important variables, affecting aniline sorption on Cr-bentonite. Fig. 2 shows the effect of pH value on aniline sorption on Cr-bentonite. As shown in Fig. 2, sorption efficiencies of aniline are high and stable under acidic and neutral pH conditions and decrease with the increase of pH value under alkaline pH conditions. Lower sorption of aniline at alkaline pH is probably due to the presence of excess OH<sup>-</sup> ions competing with aniline for hydrogen bond formed with water molecules coordinated with chromium ion in interlayer.

#### 3.3. Effect of adsorbent dosage on aniline sorption

The adsorbent dosage is an important factor for the sorption capacity of aniline. Fig. 3 shows influence of adsorbent dosage on



**Fig. 2.** Effect of pH value on aniline sorption on Cr-bentonite ( $C_0 = 20$  mg/L, temperature 30 °C, adsorbent dosage 0.2 g/20 mL, shaking time 30 min).

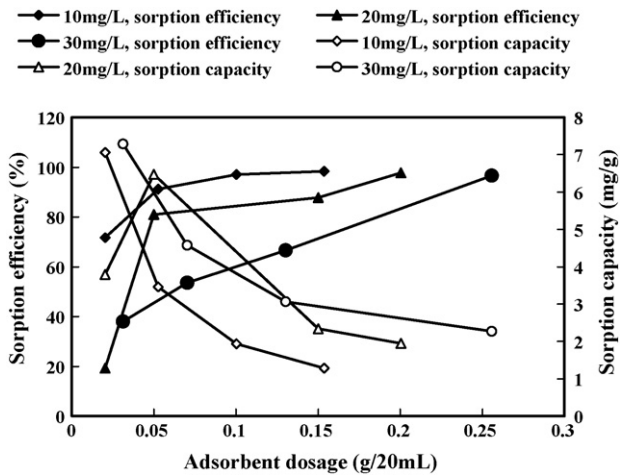


Fig. 3. Effect of the adsorbent dosage on aniline sorption on Cr-bentonite at different initial aniline concentrations (temperature 30 °C, pH 4.4–5.0, shaking time 30 min).

aniline sorption by Cr-bentonite. The results show that sorption efficiency of aniline increases with the increase of adsorbent dosage but sorption capacity decreases with the increase of adsorbent dosage. Similar results were reported for 4-hydroxyphenol sorption on Cr-bentonite from aqueous solution [16]. A 0.20 g of adsorbent was selected as adsorbent dosage for all further experiments in this paper because of higher sorption efficiency and acceptable sorption capacity.

#### 3.4. Effect of initial aniline concentration on aniline sorption

The effect of the initial aniline concentration on the intake rate on Cr-bentonite at adsorbent dosage of 0.20 g is shown in Fig. 4. It can be seen that the sorption at different concentrations is rapid in the initial stages and gradually decreases with the progress of sorption until the equilibrium is reached. The amount of aniline adsorbed at equilibrium ( $q_e$ ) increased from 1.96 to 17.89 mg/g as the initial concentration was increased from 20 to 200 mg/L. The initial concentration provides an important driving to overcome all mass transfer resistances of the aniline between the aqueous and solid phases. Hence, a higher initial concentration of aniline will enhance the sorption process. The aniline removal efficiency decreased from 97.80 to 89.46% as the aniline concentration was increased from 20 to 200 mg/L. The equilibrium conditions were reached about 15 min for low concentration (less than 120 mg/L),

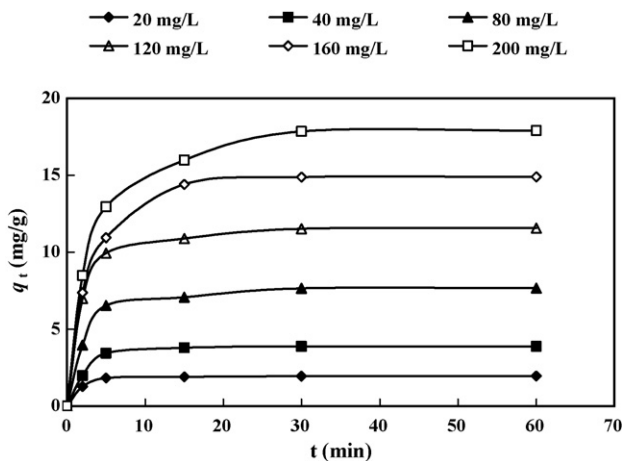


Fig. 4. Effect of initial concentration on aniline sorption on Cr-bentonite (temperature 30 °C, adsorbent dosage 0.2 g/20 mL, pH 4.4–5.0).

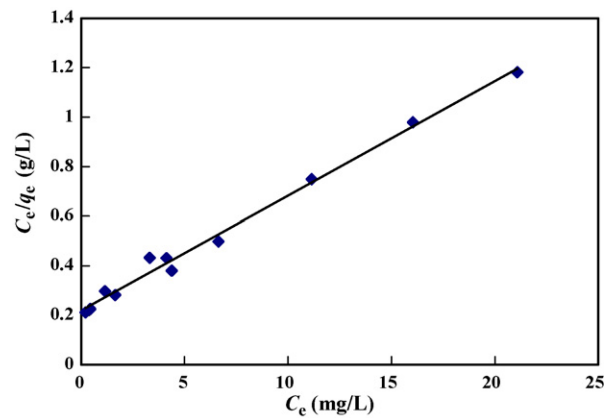


Fig. 5. Linear plot of Langmuir isotherm of aniline sorption on Cr-bentonite at 30 °C.

while the rate of sorption was slower for concentration ranging from 160 to 200 mg/L (approximately 30 min). When initial concentration of aniline is 20 mg/L, maximum sorption efficiency on Cr-bentonite was attained as 97.80% at 30 °C. It is much higher than 13.84% of Na-bentonite and 23.69% of Ca-bentonite [17]. The possible reason is attributed to more polar water molecules associated with  $\text{Cr}^{3+}$  than  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , further indicating H-bonding mechanism.

#### 3.5. Sorption isotherms

The purpose of the sorption isotherms is to reveal the specific relation between the equilibrium concentration of adsorbate in the bulk and the adsorbed amount at the surface. The isotherm results of aniline on Cr-bentonite at a constant temperature of 30 °C were analyzed using four important isotherms including the Langmuir, Freundlich, Temkin, and Dubinin–Redushkevich (D–R) isotherm models.

The Langmuir adsorption model [18] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules. The Langmuir adsorption isotherm has been successfully used in many monolayer adsorption processes. The expression of the Langmuir model is given by Eq. (3)

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (3)$$

where  $q_e$  (mg/g) and  $C_e$  (mg/L) are the amount of adsorbed adsorbate per unit mass of adsorbent and unadsorbed adsorbate concentration in solution at equilibrium, respectively. The value of  $Q_0$  (mg/g) is the maximum amount of adsorbate per unit mass of adsorbent to form a complete monolayer on the surface bound at high  $C_e$  and  $b$  is a constant related to the affinity of the binding sites (L/mg). The Langmuir equation can be described by the linearized form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0} C_e + \frac{1}{Q_0 b} \quad (4)$$

The linear plot of specific sorption ( $C_e/q_e$ ) against the equilibrium concentration ( $C_e$ ) (Fig. 5) shows that the sorption of aniline on Cr-bentonite obeys the Langmuir model. The Langmuir constants  $Q_0$  and  $b$  were determined from the slope and intercept of the plot and are presented in Table 2.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor  $R_L$  that is given by the following equation:

$$R_L = \frac{1}{1 + b C_0} \quad (5)$$

**Table 2**  
Langmuir, Freundlich, Temkin, and the D–R isotherm model constants and correlation coefficients for sorption of aniline on Cr-bentonite.

Isotherm	Parameters
Langmuir	
$Q_0$ (mg/g)	21.60
$b$ (L/mg)	0.21
$R^2$	0.9917
Freundlich	
$K_f$ (mg/g (L/mg) <sup>1/n</sup> )	3.45
$n$	1.59
$R^2$	0.9595
Temkin	
$A$ (L/g)	3.59
$B$	3.91
$R^2$	0.9522
D–R	
$\beta$ ( $\times 10^8$ mol <sup>2</sup> /J <sup>2</sup> )	0.47
$q_m$ (mol/g)	0.0019
$E$ (kJ/mol)	10.31
$R^2$	0.9792

where  $C_0$  (mg/L) is initial concentration of adsorbate and  $b$  (L/mg) is Langmuir constant. 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,  $R_L = 0$  [16,19–21].

Fig. 6 shows the variation of separation factor ( $R_L$ ) with initial aniline concentration. The  $R_L$  values were in the range of 0–1 at 30 °C, indicating that the sorption of aniline on Cr-bentonite is favorable. Also, the  $R_L$  value approaches zero with the increase of  $C_0$  means that the sorption of aniline on Cr-bentonite is less favorable at high initial aniline concentration.

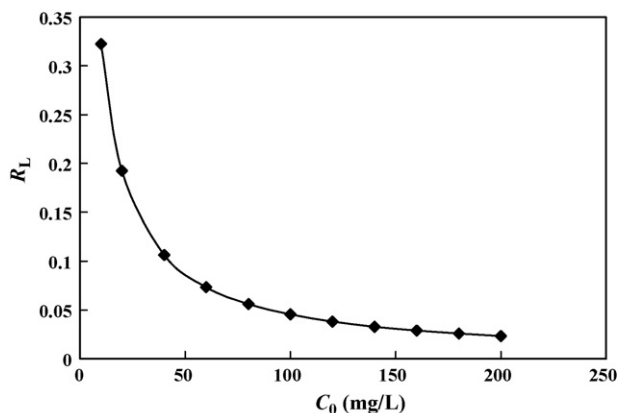
The Freundlich isotherm [22] can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlich equation is expressed as:

$$q_e = K_f C_e^{1/n} \quad (6)$$

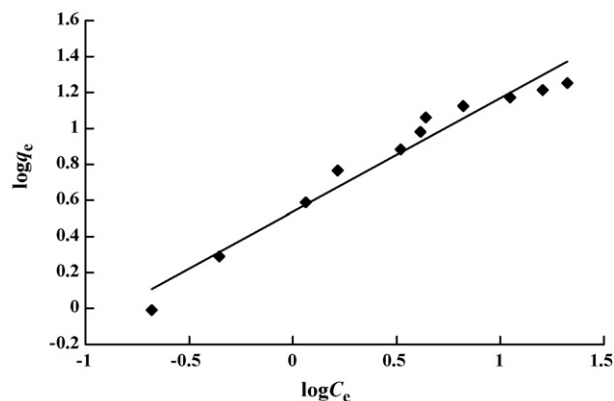
where  $K_f$  and  $n$  are Freundlich constants with  $K_f$  (mg/g (L/mg)<sup>1/n</sup>) being the sorption capacity of the adsorbent, and  $n$  giving an indication the favorability of the sorption process. Values of  $n > 1$  represent favorable adsorption condition [23–25]. To determine the constants  $K_f$  and  $n$ , the Freundlich equation can be described by the linearized form:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

Fig. 7 shows the linear plot of Freundlich isotherm of aniline sorption on Cr-bentonite at 30 °C. Values of  $K_f$  and  $n$  are calculated from the intercept and slope of the plot and are presented in Table 2.



**Fig. 6.** Variation of separation factor ( $R_L$ ) as a function of initial aniline concentration.



**Fig. 7.** Linear plot of Freundlich isotherm of aniline sorption on Cr-bentonite at 30 °C.

Temkin and Pyzhev considered the effects of some indirect adsorbate/adsorbate interaction on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage [26]. The Temkin isotherm has been generally applied in the following form:

$$q_e = \left(\frac{RT}{b}\right) \ln(AC_e) \quad (8)$$

and can be linearized as:

$$q_e = B \ln A + B \ln C_e \quad (9)$$

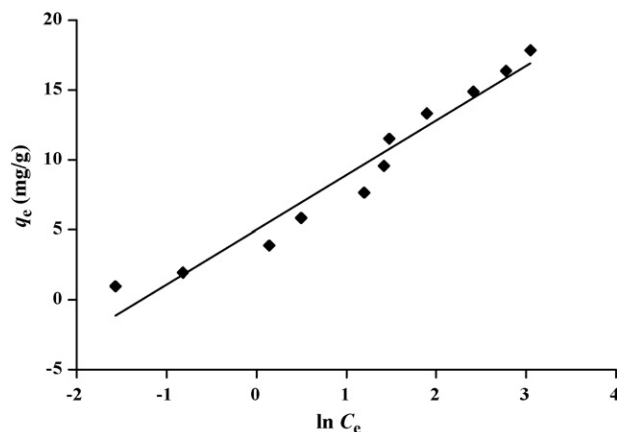
where  $B = RT/b$ ,  $b$  is the Temkin constant related to heat of sorption (J/mol),  $A$  is the Temkin isotherm constant (L/g),  $R$  is the gas constant (8.314 J/mol K), and  $T$  is the absolute temperature (K).

Fig. 8 shows the linear plot of Temkin isotherm of aniline sorption on Cr-bentonite at 30 °C. The constants  $A$  and  $B$  are calculated from the intercept and slope of the plot and are listed in Table 2.

The equilibrium data were also applied to the D–R model [16,19,27,28] to determine the type of sorption (physical or chemical). The linear form of D–R isotherm is presented as the following equation:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (10)$$

where  $q_e$  is the amount of aniline adsorbed onto per unit dosage of Cr-bentonite (mol/g),  $q_m$  is the theoretical monolayer sorption capacity (mol/g),  $\beta$  is the constant of the sorption energy (mol<sup>2</sup>/J<sup>2</sup>), which is related to the average energy of sorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite



**Fig. 8.** Temkin isotherm for aniline sorption on Cr-bentonite at 30 °C.

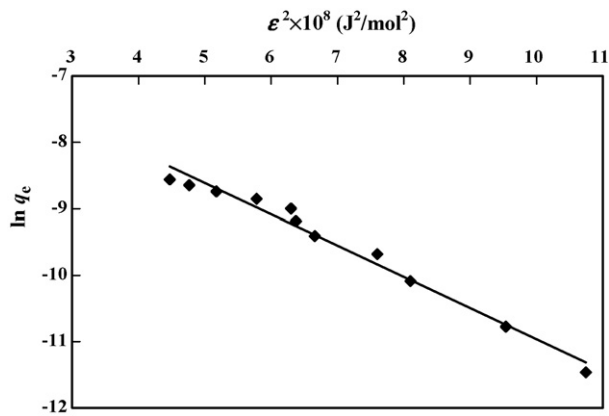


Fig. 9. D–R isotherm plot of aniline sorption on Cr-bentonite at 30 °C.

distance in the solution [19,27], and  $\varepsilon$  is Polanyi potential, which is described as

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (11)$$

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  $\beta$  as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (12)$$

The value of mean sorption energy gives information about chemical and physical sorption. The  $E$  value ranges from 1 to 8 kJ/mol for physical sorption and from 8 to 16 kJ/mol for chemical sorption [16,19,27].

Values of  $q_m$  and  $\beta$  are calculated from the intercept and slope of the plot by plotting  $\ln q_e$  versus  $\varepsilon^2$  (Fig. 9) and are listed in Table 2.

As seen in Table 2, the Langmuir isotherm fits quite well with the experimental data (correlation coefficient  $R^2 > 0.99$ ). This indicates that the Langmuir model was very suitable for describing the sorption equilibrium of aniline on Cr-bentonite. Similar results were reported for 4-hydroxyphenol sorption on Cr-bentonite from aqueous solution [16]. The maximum sorption capacity of aniline on Cr-bentonite ( $Q_0$ ) was 21.60 mg/g at 30 °C. The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogeneous distribution of active sites on Cr-bentonite surface, since the Langmuir equation assumes that the surface is homogeneous. Compared with the correlation coefficient value of the linear plot of Langmuir isotherm, those of Freundlich model, Temkin model, and D–R model were found less satisfactory ( $R^2 < 0.98$ ). The value of Freundlich constant  $n$  larger than 1 points out the favorable sorption conditions. The  $E$  value (10.31 kJ/mol) was found in the range of 8–16 kJ/mol, indicating that the type of sorption of aniline on Cr-bentonite is essentially chemical. The result is different from that reported about 4-hydroxyphenol physical sorption on Cr-bentonite [16]. The possible reason is attributed to the polarity of N atom in aniline molecule is stronger than that of O atom in 4-hydroxyphenol molecule.

### 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 [29]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (13)$$

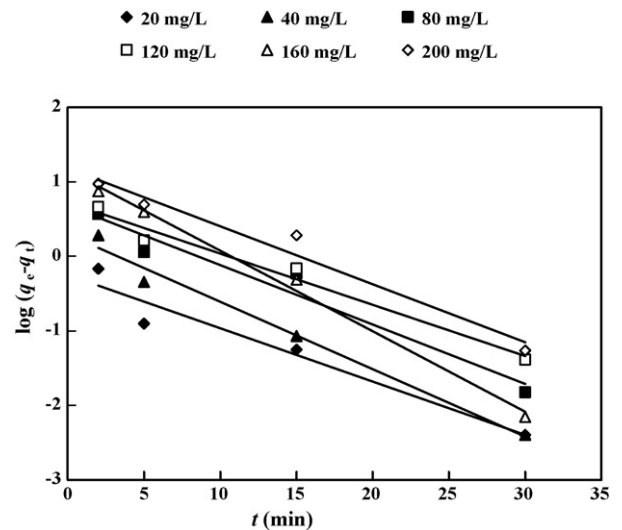


Fig. 10. Pseudo first-order sorption kinetics of aniline on Cr-bentonite.

where  $q_t$  is the amount of adsorbate adsorbed (mg/g) at time  $t$ ,  $k_1$  is the rate constant ( $\text{min}^{-1}$ ). Pseudo first-order kinetic plotted at 30 °C is given in Fig. 10. The Lagergren's first-order rate constant ( $k_1$ ) and  $q_e$  are calculated from the intercept and slope of the plot and are listed in Table 3 along with the corresponding correlation coefficients. It was observed that the pseudo first-order model did not fit well. It was found that the calculated  $q_e$  values do not agree with the experimental  $q_e$  values at lower concentrations. This suggests that the sorption of aniline on Cr-bentonite does not follow first-order kinetics at lower concentrations.

Pseudo second-order model is represented as [30]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (14)$$

where the equilibrium sorption capacity ( $q_e$ ) and the second-order constant  $k_2$  (g/mg min) can be determined experimentally from the slope and intercept of plot  $t/q_t$  versus  $t$  (Fig. 11). The  $k_2$  and  $q_e$  calculated from the model are also listed in Table 3 along with the corresponding correlation coefficients. It can be seen from Table 3 that there is an agreement between experimental and calculated  $q_e$  values for the pseudo second-order model. Hence, the pseudo second-order model better represents the sorption kinetics. Similar phenomenon has been observed in the sorption of 4-hydroxyphenol on Cr-bentonite [16].

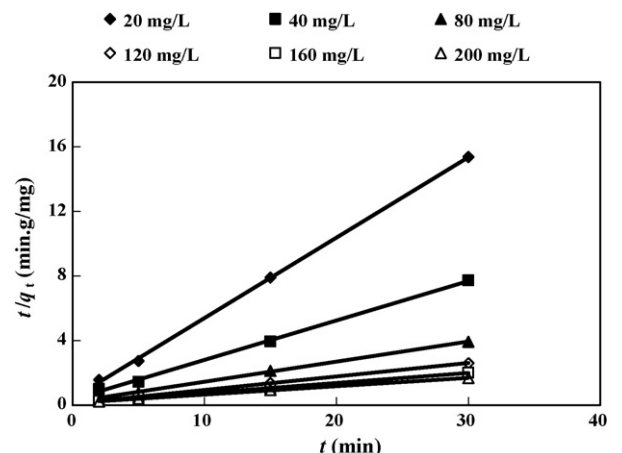
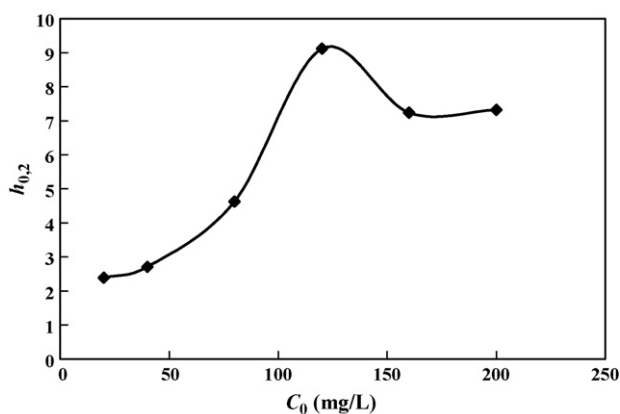


Fig. 11. Pseudo second-order sorption kinetics of aniline on Cr-bentonite.



**Table 3**  
Comparison of the pseudo first-order, pseudo second-order and intraparticle diffusion sorption rate constants and calculated and experimental  $q_e$  values obtained at different initial aniline concentrations.

Initial concentration (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first-order kinetic model			Pseudo second-order kinetic model			Intraparticle diffusion model		
		$k_1$ (min <sup>-1</sup> )	$q_{e,cal}$ (mg/g)	$R^2$	$k_2$ (g/mg min)	$q_{e,cal}$ (mg/g)	$R^2$	$k_d$ (mg/g min <sup>1/2</sup> )	$q_{e,cal}$ (mg/g)	$R^2$
20	1.96	0.17	0.56	0.9446	0.59	2.01	0.9995	0.14	2.04	0.6181
40	3.89	0.21	1.97	0.9842	0.16	4.10	0.9982	0.40	4.16	0.6638
80	7.67	0.18	4.78	0.9535	0.07	8.07	0.9988	0.77	8.03	0.7366
120	11.56	0.16	5.31	0.9754	0.06	11.99	0.9997	0.98	12.01	0.7735
160	14.89	0.25	14.33	0.9943	0.03	16.08	0.9994	1.79	15.89	0.8580
200	17.89	0.18	15.29	0.9676	0.02	19.89	0.9994	2.16	18.60	0.9027



**Fig. 12.** The variation of the initial rate of sorption with the initial aniline concentration.

The initial sorption rates  $h_{0,2}$  (mg/g min) can be calculated from the pseudo second-order model by the following equation:

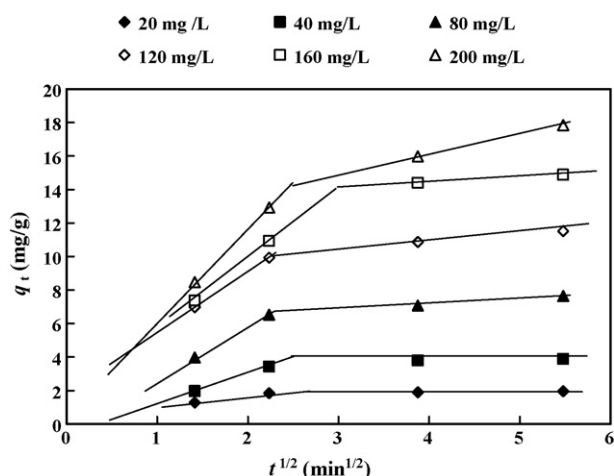
$$h_{0,2} = k_2 q_e^2 \quad (15)$$

and the results are plotted in Fig. 12. It was found that the initial rate of sorption increases with increase of the initial aniline concentration at lower initial concentrations ( $C_0 < 120$  mg/L) and decreases to a stable value at higher initial concentrations.

The intraparticle diffusion equation can be written as follows [31]:

$$q_t = k_d t^{1/2} + C \quad (16)$$

where  $k_d$  is the intraparticle diffusion rate constant (mg/g min<sup>1/2</sup>) and  $C$  is the intercept. Fig. 13 presents plot of  $q_t$  versus  $t^{1/2}$  at



**Fig. 13.** Intraparticle diffusion kinetics for aniline sorption on Cr-bentonite.

30 °C. If the regression of  $q_t$  versus  $t^{1/2}$  is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. The intraparticle diffusion rate constant ( $k_d$ ) and  $q_e$  are calculated from the intercept and slope of the plot and are also listed in Table 3 along with the corresponding correlation coefficients. It was observed that the correlation coefficients were not satisfactory.

As can be seen from Fig. 13, aniline 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 [16,32,33].

### 3.7. Design of batch sorption from isotherm data

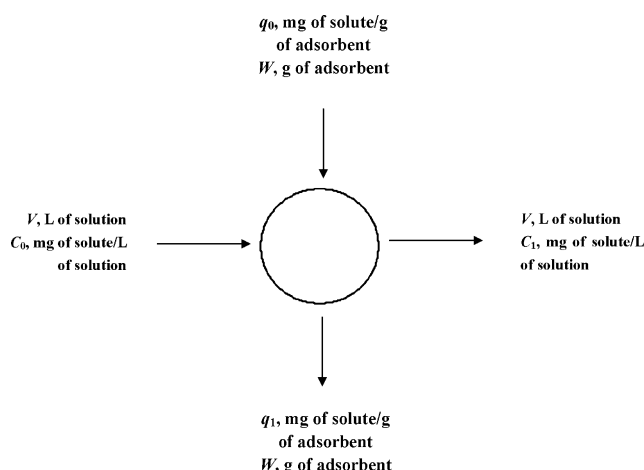
A schematic diagram of a batch sorption process is shown in Fig. 14 where the effluent contains  $V$  (L) of aquatic solution and an initial aniline concentration  $C_0$ , which is to be reduced to  $C_1$  in the sorption process. In the treatment stage  $W$  (g) Cr-bentonite (aniline-free) is added to solution and the amount of adsorbed aniline on the solid changes from  $q_0=0$  (initially) to  $q_1$ . The mass balance for the aniline in the single stage is given by

$$V(C_0 - C_1) = W(q_1 - q_0) \quad (17)$$

Under equilibrium conditions,  $C_1 \rightarrow C_e$  and  $q_1 \rightarrow q_e$

$$VC_0 + Wq_0 = VC_e + Wq_e \quad (18)$$

For the sorption of aniline on Cr-bentonite, the Langmuir isotherm gives the best fit to experimental data. Consequently, equation can be best substituted for  $q_1$  in the rearranged form of



**Fig. 14.** A single-stage batch adsorber.

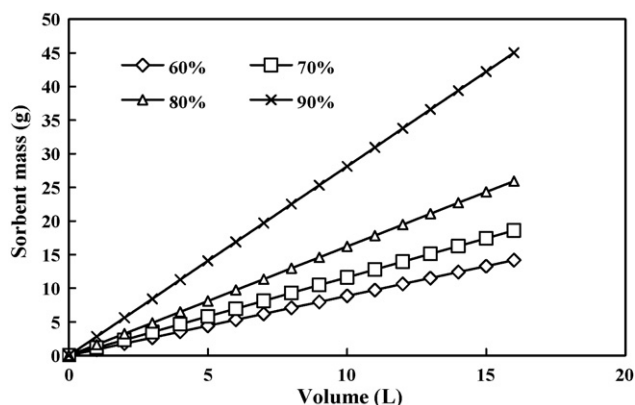


Fig. 15. Sorption mass ( $W$ ) against volume of effluent ( $V$ ) treated for different percentages of aniline removal ( $C_0 = 20$  mg/L).

Eq. (18) giving adsorbent/solution ratios for this particular system,

$$\frac{W}{V} = \frac{(C_0 - C_e)}{q_e} = \frac{C_0 - C_e}{Q_0 b C_e (1 + b C_e)} \quad (19)$$

Fig. 15 shows a series of plots (60, 70, 80, and 90% aniline removal at different solution volumes) derived from Eq. (19) for the sorption of aniline on Cr-bentonite at initial concentration of 20 mg/L. The amount of Cr-bentonite required for the 90% removal of aniline solution of concentration 20 mg/L was 2.81, 5.63, 8.44, and 11.25 g for aniline solution volumes of 1, 2, 3, and 4 L, respectively.

#### 4. Conclusions

(1) Aniline sorption on Cr-bentonite was studied in batch mode and found to be strongly dependent on pH value of solution, adsorbent dosage, and initial aniline concentration.

(2) Aniline sorption isotherm data were fitted well to Langmuir isotherm and the monolayer sorption capacity was found to be 21.60 mg/g at 30 °C.  $0 < R_L < 1$  from Langmuir isotherm and  $n > 1$  from Freundlich isotherm indicate that the sorption of aniline on Cr-bentonite is favorable.  $E$  value (10.31 kJ/mol) from D–R model indicates that the type of sorption of aniline on Cr-bentonite is chemical.

(3) The pseudo second-order kinetic model agrees very well the dynamic data for aniline sorption on Cr-bentonite. Intraparticle diffusion affects aniline uptake.

#### 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 Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (No. 2001010).

#### References

[1] M. Chanda, K.F. O'Driscoll, G.L. Rempel, Ligand sorption of aromatic amines on resin-bound ferrous ion, *React. Polym.* 2 (1984) 279–290.  
 [2] J. Sarasa, S. Cortés, P. Ormad, R. Gracia, J.L. Ovelheiro, Study of the aromatic by-products formed from ozonation of anilines in aqueous solution, *Water Res.* 36 (2002) 3035–3044.

[3] F. Orshansky, N. Narkis, Characteristics of organics removal by PACT simultaneous adsorption and biodegradation, *Water Res.* 31 (1997) 391–398.  
 [4] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Ozonation of aniline promoted by activated carbon, *Chemosphere* 67 (2007) 809–815.  
 [5] A.A. Gürten, S. Uçan, M.A. Özler, A. Ayar, Removal of aniline from aqueous solution by PVC-CDAE ligand-exchanger, *J. Hazard. Mater.* 120 (2005) 81–87.  
 [6] J. Yao, X. Li, W. Qin, Computational design and synthesis of molecular imprinted polymers with high selectivity for removal of aniline from contaminated water, *Anal. Chim. Acta* 610 (2008) 282–288.  
 [7] N. Kyuya, A. Namba, S.R. Mukaia, H. Tamona, P. Ariyadejwanichb, W. Tanthapanichakoon, Adsorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes, *Water Res.* 38 (2004) 1791–1798.  
 [8] R.E. Grim, *Applied clay mineralogy*, 1st ed., McGraw-Hill, New York, 1962, pp. 16–44.  
 [9] B.L. Sawliney, S.S. Singh, Sorption of atrazine by Al- and Ca-saturated smectite, *Clays Clay Miner.* 45 (1997) 333–338.  
 [10] A. Pusino, W. Liu, C. Gessa, Dimefiperate adsorption and hydrolysis on  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Ca^{2+}$ ,  $Na^{+}$ -montmorillonite, *Clays Clay Miner.* 41 (1993) 335–340.  
 [11] P. Alba, B. Ilaria, C. Gessa, Adsorption and degradation of triasulfuron on homoionic montmorillonite, *Clays Clay Miner.* 48 (2000) 19–25.  
 [12] P. Alba, B. Ilaria, C. Gessa, Adsorption of two quinolinecarboxylic and herbicides on homoionic montmorillonite, *Clays Clay Miner.* 51 (2003) 143–149.  
 [13] I. Ukrainczyk, K. Smith, Solid state  $^{15}N$  NMR study of pyridine adsorption on clay minerals, *Environ. Sci. Technol.* 30 (1996) 3167–3176.  
 [14] H. Zheng, Y. Wang, B. Hu, Z. Luan, Q. Zhang, Utilization of  $Cr^{3+}$ -modified bentonite to treat specific organic wastewater, *Acta Scientiarum Nat. Univ. Sunyatseni* 44 (2005) 55–60.  
 [15] Y. Wang, H. Zheng, H. Li, Z. Wu, S. Liang, The adsorption of 1,4-dihydroxybenzene on  $Cr^{3+}$  modified bentonite and its regeneration, *Nonmetallic Mines* 28 (2005) 42–47.  
 [16] H. Zheng, Y. Wang, Y. Zheng, H. Zhang, S. Liang, M. Long, Equilibrium, kinetic and thermodynamic studies on the sorption of 4-hydroxyphenol on Cr-bentonite, *Chem. Eng. J.* 143 (2008) 117–123.  
 [17] H. Zheng, Y. Peng, Z. Luan, Sorption of aniline on  $Cr^{3+}$ -bentonite, *Environ. Chem.* 22 (2003) 369–372.  
 [18] J. Eastoe, J.S. Dalton, Dynamic surface tension and adsorption mechanisms of surfactants at the air water interface, *Adv. J. Colloid Interface Sci.* 85 (2000) 103–144.  
 [19] K. Saltalı, A. Sari, M. Aydın, Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality, *J. Hazard. Mater.* 141 (2007) 258–263.  
 [20] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid- diffusion kinetics in fixed-bed adsorption under constant-pattern condition, *Ind. Eng. Chem. Fundam.* 5 (1966) 212–223.  
 [21] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, *Process. Biochem.* 37 (2002) 1421–1430.  
 [22] H. Freundlich, Über die adsorption in lösungen (adsorption in solution), *Z. Phys. Chem* 57 (1906) 384–470.  
 [23] R.E. Treybal, *Mass transfer operations*, 2nd ed., McGraw Hill, New York, 1968.  
 [24] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115–124.  
 [25] B.H. Hameed, D.K. Mahmoud, A.L. Ahmad, Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocos nucifera*) bunch waste, *J. Hazard. Mater.* 158 (2008) 65–72.  
 [26] M.J. Temkin, V. Pyzhev, 1940. Recent modifications to Langmuir isotherms, *Acta Physiochim.*, URSS 12, 217–222.  
 [27] M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, Sorption and structure of active carbons. I. Adsorption of organic vapors, *Zh. Fiz. Khim.* 21 (1947) 1351–1362.  
 [28] K. Saltalı, A. Sari, Sorption capacity and thermodynamic properties of natural Turkish (Resadiye) bentonite for the removal of ammonium ions from aqueous solution, *Adsorp. Sci. Technol.* 24 (2006) 749–760.  
 [29] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska Vetenskapsakad. Handl.* 24 (1898) 1–39.  
 [30] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.  
 [31] W.J. Weber Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. Proceed. Am. Soc. Civil Eng.* 89 (1963) 31–59.  
 [32] D. Karadag, Y. Koc, M. Turan, B. Armagan, Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite, *J. Hazard. Mater. B* 136 (2006) 604–609.  
 [33] K.V. Kumar, V. Ramamurthi, S. Sivanesan, Modeling the mechanism involved during the sorption of methylene blue onto fly ash, *J. Colloid Interface Sci.* 284 (2005) 14–21.