

Adsorption of naphthalene onto the carbon adsorbent from waste ion exchange resin: Equilibrium and kinetic characteristics

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants that can result in serious health problems and genetic defects in humans. In this research, a spherical microporous carbon adsorbent (CR-1) had been obtained by carbonization and activation of the waste polysulfonated cation exchange resin. Naphthalene was adopted as a model compound to examine the adsorption effectiveness for removing PAHs from the aqueous solution by CR-1. Nonlinear isotherms models, i.e., Freundlich, Langmuir, Brunauer–Emmett–Teller and Polanyi–Dubinin–Manes models were tested to fit experimental data. The adsorption equilibrium data of naphthalene on CR-1 was fitted well by the Polanyi–Dubinin–Manes model. Through both isotherm modeling and constructing “characteristic curve”, Polanyi theory was useful to describe the adsorption process of naphthalene by CR-1, providing evidence that a micropore filling phenomenon is involved. In addition, among the tested kinetic models in this study (e.g., pseudo-first-order and pseudo-second-order equations), the pseudo-first-order equation successfully predicted the kinetic adsorption process.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are important family of environmental pollutants which are capable of reacting with DNA to promote mutagenic and carcinogenic response. Due to the refractoriness and poor biodegradability of PAHs, while their solubility is quite low and usually decreases with increasing molecular weight, they can exist and accumulate in the environment for long times. Therefore, immediate attention to the effective treatment of PAHs is needed.

Presently, various methods have been investigated to treat PAHs such as catalytic oxidation, biological degradation and adsorption [1–7], but there are only a few technologies that are economically feasible for the removal of trace organic contaminants from aqueous solution. Owing to the high concentrating

ability of typical adsorbents, adsorption is proved to be one of the most attractive and effective techniques to remove organic contaminants from aqueous streams in water/wastewater treatment. A number of workers have used different materials as the adsorbent for the removal of various pollutants. The activated carbons are extensively used as adsorbent for removing various pollutants from water. Charcoal is a basic material for obtaining activated carbons. However, owing to the high production costs of activated carbons and insufficient supply, recently there has been noticed a growing interest in the production of carbon adsorbents from agricultural by-products, such as nutshells, coconut shells and peach stones [8–10].

Ion-exchange resins are used mainly for demineralization of boiler water, sewage treatment and metal separation from aqueous solutions, etc. Generally they become waste in 3–5 years of their exploitation and are practically undegradable in the environment. In China, the amount of the waste ion exchange resins is increasing owing to the rapid economic development. Therefore, the effective method to treat and utilize the waste resin is required. Polymeric resins have been found to be suitable precursors for the production of activated carbons because of high

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carbon yield and low ash content [11–13]. From the practical point of view, the use of waste ion-exchange resins for manufacturing carbon adsorbents may be of a very big economic and ecological advantage. Therefore, the waste ion exchange resins were utilized as precursors to prepare the microporous carbon adsorbent (CR-1) in the present paper. The final product would be tried for removal of PAHs from aqueous solution.

Naphthalene is a natural constituent of coal tar and commonly used as a wood preservative, moth repellent and raw material to produce methylantranilate, phthalate esters, chloronaphthalene and synthetic resins, etc. Being compared with other PAHs species, naphthalene, the simplest PAH, has less toxicity and is easily found in the environment. Therefore, the adoption of naphthalene as the target compound in this study can provide useful information not only for the treatment of naphthalene but also for dealing with complicated PAHs. The aim of this study is to investigate the feasibility of using CR-1 to remove naphthalene from aqueous. The adsorption characteristics of naphthalene on CR-1 are evaluated by the isotherms models (e.g., Langmuir, Freundlich, Brunauer–Emmett–Teller and Polanyi–Dubinin–Manes isotherms) and kinetic models (e.g., pseudo-first-order and pseudo-second-order rate equations).

2. Materials and methods

2.1. Materials

Waste ion-exchange resins 001 × 7 (sulfonated poly(styrene-divinylbenzene) cation exchange resin) had been used for demineralization of boiler water for about 2 years. Naphthalene, purchased from Sigma–Aldrich Chemical Co., was used as the representative compound of PAHs in this study. Naphthalene was dissolved in methanol (HPLC grade), and subsequently diluted by de-ionized distilled water to the final concentration for adsorption experiments. The properties of naphthalene are listed in Table 1.

2.2. Preparation of carbon adsorbent (CR-1)

Waste ion-exchange resins 001 × 7 were used as the starting material to produce carbon adsorbents by carbonization and subsequent activation. Prior to use, Waste ion-exchange resins 001 × 7 were packed into a column and first treated with 10 bed volumes of 1.0 N HCl and then washed by de-ionized water until the wash solution had achieved a neutral pH value. Carbonization was carried out in a temperature-controlled flow

quartz reactor (20–450 °C at 6 °C/min in a deoxygenated nitrogen atmosphere). The resins were kept at 450 °C for 90 min.

Obtained chars were activated in a flow quartz reactor using carbon dioxide as an activator. The carbonization samples were continuously heated to 850 °C at 6 °C/min in a deoxygenated nitrogen atmosphere. At 850 °C, the nitrogen flow was stopped and carbon dioxide was introduced. Activation was carried out for 180 min and then the reaction system was cooled in the nitrogen atmosphere to room temperature. The activated carbons (0.5–0.8 mm in diameter) were washed sequentially with 0.5N HCl solutions, and distilled water to remove some of the ash and decomposed fragments and then dried at 110 °C for 24 h.

Nitrogen adsorption–desorption isotherms were measured using an ASAP 2010 (Micromeritics Instrument Co., USA) at 77 K. The specific surface area was determined using the N₂ isotherms data by means of the BET equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.95. The micropore pore volume and mesopore pore volume were calculated from the N₂ isotherms data by Dubinin–Astakov (DA) and BJH methods, respectively. Pore size distributions were calculated by applying the density functional theory (DFT) to N₂ isotherm data using the Micromeritics Software.

2.3. Static adsorption experiments

Equilibrium adsorption studies of naphthalene were performed at 288, 298 and 308 K, respectively. Thus, dry adsorbent CR-1 of certain amount ranging from 0.0200 to 0.100 g, followed by 150 mL distilled water containing 30 mg/L naphthalene, 0.005 M CaCl₂ and 0.02% NaN₃ (by weight) was introduced directly into each of a series of 250 mL conical flasks. All flasks were immediately sealed and shaken in an incubator for 7 days (preliminary tests indicated that adsorption equilibrium was reached before 6 days). The residual concentration of the aqueous phase, C_e (mg/L), was then determined by a high-performance liquid chromatography (HPLC) with diode array detector (Waters Associates, USA) at a wavelength of 219 nm, employing a water/methanol (10:90, v/v) solution as the mobile phase. The amounts adsorbed by CR-1, q_e (mg/g), was then calculated via Eq. (1):

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

where V is the volume of solution (L) and W is the weight of dry adsorbent (g).

Table 1
Selected properties of naphthalene

MW ^a (g/mol)	C _s ^b (mg/L)			Density (g/cm ³)	V _s ^c (cm ³ /mol)	σ ^d (nm)
	288 K	298 K	308 K			
128.2	21.7	31.7	45.6	0.997	128.6	0.62

^a MW: molecular weight.

^b C_s: water solubility calculated from Ref. [14].

^c V_s: molar volume.

^d σ: molecular size taken from Ref. [15].

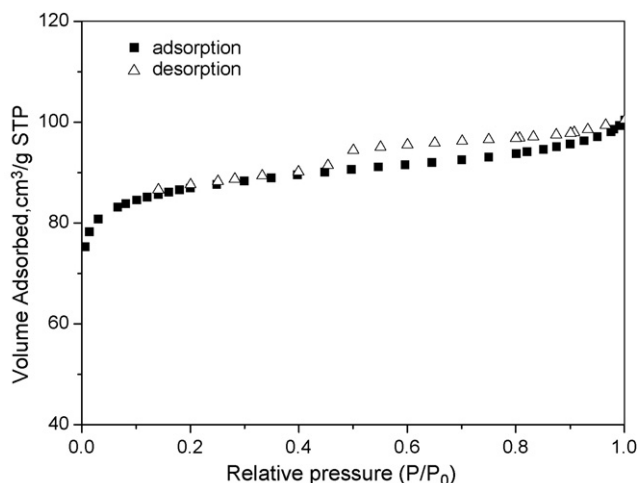


Fig. 1. N₂ adsorption–desorption isotherms of carbon adsorbent CR-1 at 77 K.

2.4. Kinetic adsorption experiments

Such kinetic experiments were conducted employing the batch method. Thus, 0.1 g dry adsorbent and 200 mL of 10.24 mg/L of naphthalene were introduced into a 250 mL flask which was then placed in a water bath at 308 K and shaken. At given time intervals, about 0.1 mL of the naphthalene solution was withdrawn from the flask via a syringe and its concentration determined by HPLC methods.

3. Results and discussion

3.1. Characterization of carbon adsorbent CR-1

The N₂ adsorption–desorption isotherms at 77 K of CR-1 are demonstrated in Fig. 1. It is observed that the adsorption isotherm is close to type I of the IUPAC classification typical of microporous materials, and that the isotherms show a hysteresis loop, characteristics of mesopore. Thus, the initial part of the adsorption isotherm at lower relative pressure (P/P_0), where the nitrogen uptake increases quickly with the increment of relative pressure, represents micropore filling. The slope of the plateau at higher relative pressures is due to multilayer adsorption on the mesopore and macropore surface. The textural parameters of CR-1, calculated from its N₂ adsorption isotherm, are collected in Table 2.

Fig. 2 is the micropore size distributions of CR-1 obtained according to the DFT procedure. It can be observed that CR-1 has mainly a unimodal distribution with the majority of pores between 0.7 and 1.2 nm. Generally speaking, the micropores of this size or even twice or three times the size of this molecule, where the adsorption potentials overlapping occurs, will be appropriate for the adsorption process. The molecular size of

Table 2
Textural characteristics obtained from N₂ isotherm data for CR-1

S_{BET} (m ² g ⁻¹)	S_{micro} (m ² /g)	V_t (mL/g)	V_{micro} (mL/g)	V_{meso} (mL/g)
292.15	32.47	0.152	0.132	0.034

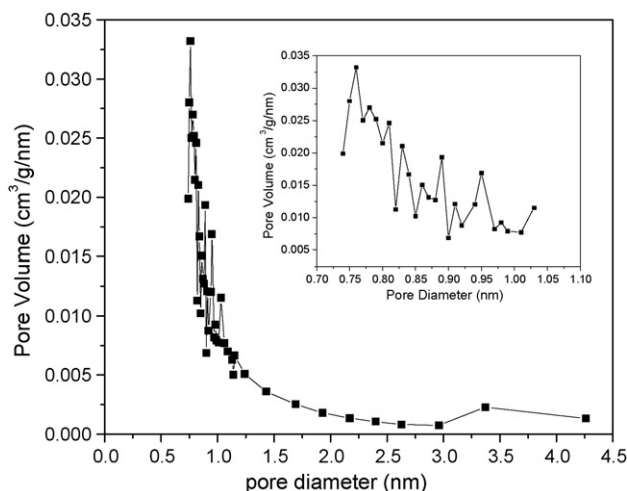


Fig. 2. DFT pore size distribution for CR-1.

naphthalene has a value of 0.62 nm; therefore, CR-1 would be appropriate materials for naphthalene adsorption.

3.2. Isotherms modeling

The equilibrium adsorption isotherms of naphthalene from aqueous solution onto CR-1 at different temperatures are depicted in Fig. 3. Favourable adsorption isotherms were exhibited for naphthalene with the extent of adsorption increasing as the equilibrium concentration of the adsorbate increased in the aqueous solution. In addition, all the adsorption isotherms are close to type I of IUPAC classification. Therefore, the adsorption is mainly produced in the region of micropores which size is similar to that of naphthalene.

The equilibrium adsorption data of naphthalene on CR-1 at different temperatures were fitted using the nonlinear isotherm models (Table 3), i.e., Freundlich (FM), Langmuir (LM), Brunauer–Emmett–Teller (BET) and Polanyi–Dubinin–Manes (PDM) models. The corresponding correlation coefficients (R^2), mean weighted square error (MWSE), equal to $1/v [\sum (q_{\text{measured}} - q_{\text{model}})^2 / q_{\text{measured}}^2]$, together with other model fitting parameters obtained are given in Table 4; where v is the degree of freedom [$v = N - 2$ for FM, LM and BET; $v = N - 3$ for PDM], N the number of experimental data points, q_{measured} the measured equilibrium adsorbed concentration and q_{model} is the estimated equilibrium adsorbed concentration by the respective models. It is quite obvious from the data listed that the Polanyi–Dubinin–Manes model provided a good fit for all the isotherms (Fig. 3), supported by the largest R^2 and the lowest MWSE value (Table 4). Significant deviation of model estimation from the experimental data was observed for FM, LM and BET at the whole range of concentrations. Overall, the model fitting results indicate that the adsorption process of naphthalene on the CR-1 would be neither monolayer formation on a homogeneous surface (i.e., LM) nor simple multilayer formation (i.e., BET), also cannot be described by assuming a continuous energy distribution of sorption sites (i.e., FM), the pore filling may be a plausible mechanistic explanation of our

Table 3
Nonlinear isotherm models

Name	Abbreviation	Equation	Capacity term
Freundlich model	FM	$q_e = K_f C_e^{1/n}$	K_f [(mg/g)/(mg/L) ^{1/n}], Freundlich affinity coefficient; n , Freundlich exponential coefficient
Langmuir model	LM	$q_e = Q_0 K_L C_e / (1 + K_L C_e)$	K_L [mg/L], affinity coefficient
Brunauer–Emmett–Teller model	BET	$q_e = Q_0 B C_e / [(C_s - C_e) \{1 + (B-1)(C_e/C_s)\}]$	B , BET constant
Polanyi–Dubinin–Manes model	PDM	$\log q_e = \log Q_0 + a(\varepsilon/V_s)^b$	ε [kJ/mol], effective adsorption potential; V_s [mL/mol], molar volume of solute; a [(mL) ^{b+1} /(kgJ ^b)] and b , fitting parameters; R [8.314×10^{-3} kJ/(mol K)], universal gas constant; T [K], absolute temperature

$$\varepsilon = RT \ln(C_s/C_e)$$

Q_e [mg/g], equilibrium adsorbed concentration; C_e [mg/L], equilibrium solution phase concentration; Q_0 [mg/g], adsorbed capacity; C_s [mg/L], aqueous water solubility.

data, supported by the fact that the observed adsorption results agree well with PDM model.

3.3. Characteristic curve of Polanyi theory

The Polanyi theory was originally used to describe gas adsorption on activated carbon, and further developed by Dubinin into Theory of Volume Filling of Micropores [16]. Manes extended the Polanyi modeling framework to describe the adsorption from aqueous solution on activated carbon [17]. The overall theory is hereafter referred to as a Polanyi–Dubinin–Manes modeling approach [18]. In brief, the theory postulates that adsorption is a process of (micro)pore filling mechanism and that the volume occupied by the adsorbed compound is a temperature-independent function of the adsorption potential (ε). For adsorption of partially miscible solutes from aqueous solution, the adsorption potential (ε) can be

defined as $\varepsilon = RT \ln(C_s/C_e)$; where C_s and C_e are the solubility and the equilibrium concentration of the solute at the absolute temperature T (K), respectively, and R is the universal gas constant.

A direct consequence of these assumptions is that, for a given sorbent, a plot of adsorbed volume (q_v) against equilibrium adsorption potential (ε) at different temperatures should yield a unique curve that is temperature-invariant and determined by the structure of the sorbent. This curve was known as “characteristic curve”. Therefore, characteristic curves can be employed to examine whether the Polanyi theory mechanistically captures the adsorption process of naphthalene by CR-1. Plots of adsorbed volume/mass of CR-1 against the adsorption potential density for naphthalene at 288, 298 and 308 K are shown in Fig. 4. As the Polanyi theory would predict, they fell on a single curve. Thus, the application of Polanyi theory to describe naphthalene adsorption on CR-1 is mechanistic useful, and pore-filling is the dominating sorption mechanism for naphthalene.

Table 4
Results of model fits to adsorption isotherms of naphthalene

Temperature (K)	K_f	n	R^2	MWSE	
Freundlich model					
288	90.573	9.434	0.909	0.0125	
298	84.1340	10.0	0.922	0.00897	
308	79.0679	8.929	0.933	0.00697	
Temperature (K)	K_L	Q_0	R^2	MWSE	
Langmuir model					
288	88.319	100.200	0.92	0.0105	
298	75.0	95.238	0.937	0.00811	
308	33.028	92.593	0.978	0.00374	
Temperature (K)	B	Q_0	R^2	MWSE	
Brunauer–Emmett–Teller model					
288	-1.03E+46	68.014	0.449	0.0759	
298	-1.04E+46	69.912	0.518	0.0710	
308	-4.71E+45	72.107	0.473	0.0794	
Temperature (K)	Q_0	a	b	R^2	MWSE
Polanyi–Dubinin–Manes model					
288	106.905	-38.664	2.466	0.952	0.00608
298	101.391	-20.728	2.242	0.959	0.00607
308	97.949	-57.596	2.733	0.988	0.00156

3.4. Adsorption kinetics

The kinetics describes the solute uptake rate which determines the residence time required for completing adsorbate adsorption at the solid–solution interface. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate adsorption treatment plants. The typical kinetic models normally consider both the external and internal mass transfers. Furthermore, the mass transfers of adsorption often involve many controlling mechanisms. Therefore, for the simplicity and practical use of engineering applications, the global kinetic expressions such as the Lagergren pseudo-first-order and pseudo-second-order equations, were used to describe the adsorption kinetics experimental data in the study.

The pseudo-first-order rate expression of Lagergren may be written as [19]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

or

$$q_t = q_e - \exp(\ln(q_e) - k_1 t) \quad (3)$$

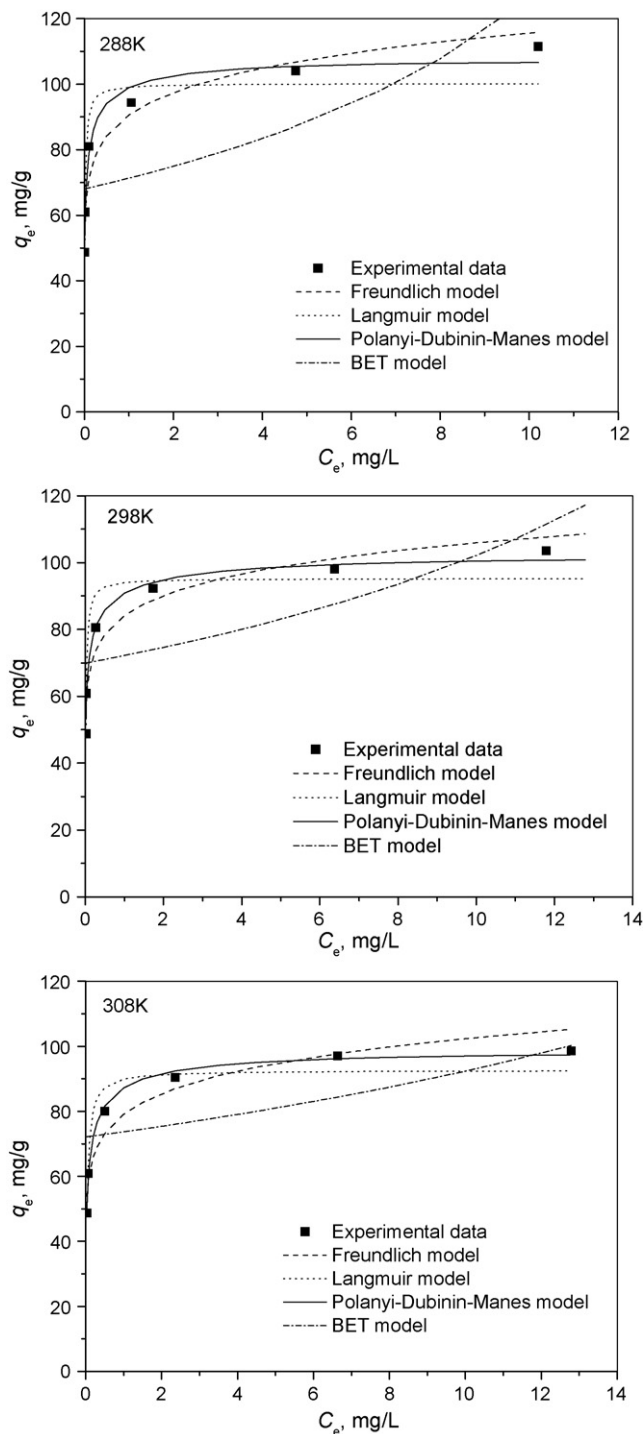


Fig. 3. Adsorption isotherms of naphthalene onto carbon adsorbent CR-1 at 288, 298 and 308 K.

where q_e and q_t are the amounts of naphthalene adsorbed onto CR-1 at equilibrium and at time t , respectively (mg/g), and k_1 is the rate constant arising from the first-order model (min^{-1}).

The pseudo-second-order kinetic model may be expressed by the following relationships [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

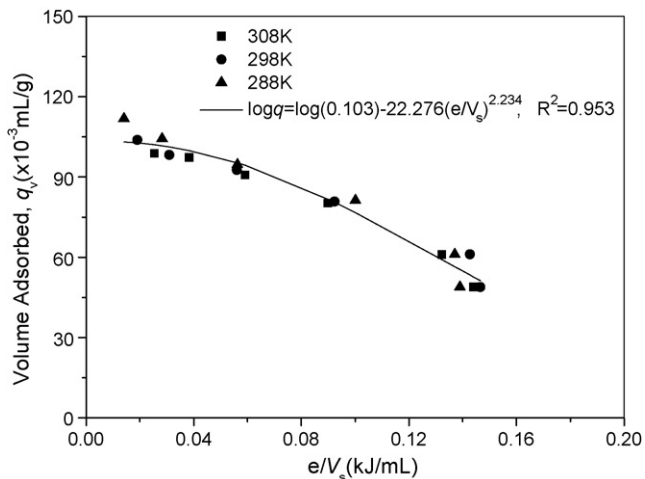


Fig. 4. Characteristic curves of Polanyi adsorption theory for naphthalene adsorption on CR-1.

Table 5
Parameters and correlation coefficients (R^2) of two kinetic models

Pseudo-first-order equation		Pseudo-second-order equation			
k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
0.0129	20.539	0.994	0.00056	24.832	0.991

or

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{5}$$

where k_2 is the rate constant arising from the second-order adsorption model (g/mg min).

The rate constants and equilibrium adsorption capacities of two kinetic equations were calculated by means of the nonlinear curve fitting analysis. A comparison of results with the correlation coefficients (R^2) is listed in Table 5. As shown by the data listed, the correlation coefficients for the pseudo-first and second-order kinetic model were both larger than 0.99. However,

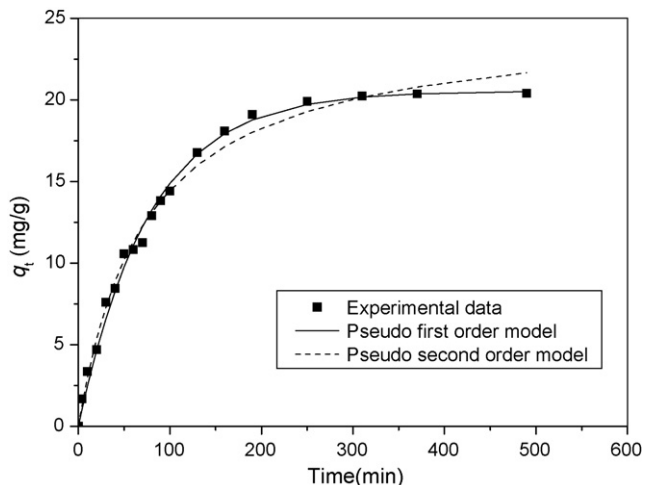


Fig. 5. Pseudo-first and pseudo-second-order kinetics for adsorption of naphthalene onto CR-1.

it was observed that the calculated q_t data based on the pseudo-first-order kinetic model were closer to the experimental data, while significant deviation of the pseudo-second-order kinetic model estimation from the experimental data was observed at later periods of the adsorption process (shown in Fig. 5). Therefore, the pseudo-first-order kinetic model may be suitable to describe the kinetics adsorption process of naphthalene onto CR-1.

4. Conclusions

A microporous carbon adsorbent CR-1 was obtained by carbonizing and subsequent activating waste ion exchange resin. The micropore volume is approximately 87% of the total pore volume. The adsorption behavior of naphthalene on the CR-1 from aqueous solution has been investigated. All adsorption isotherms were fitted well by Polanyi–Dubinin–Manes model, and plots of adsorbed volumes against equilibrium adsorption potential at 288, 298 and 308 K yielded basically a single curve, providing evidence that a pore-filling within CR-1 is the dominating sorption mechanism for naphthalene. In addition, the batch kinetic studies show that the simple kinetic model of pseudo-first-order kinetic equation had been successfully applied to predict the adsorption of naphthalene on CR-1.

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