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ScienceDirect
Journal of Hazardous Materials 144 (2007) 200–207
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Analysis of adsorption characteristics of 2,4-dichlorophenol from aqueous solutions by activated carbon fiber

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Received 7 June 2006; received in revised form 1 October 2006; accepted 3 October 2006
Available online 11 October 2006

Abstract

In this study experiments were conducted to investigate the adsorption of 2,4-dichlorophenol (2,4-DCP) by activated carbon fiber (ACF) activated by static air. With the results of batch experiments at various temperatures, the adsorption isotherms, kinetics and thermodynamics of this adsorption process were evaluated. Four adsorption isotherm models, Langmuir, Freundlich, Redlich-Peterson and Toth equations, were used to fit the experimental data and the results reveal that the adsorption isotherm models fitted the data in the order of: Langmuir > Redlich-Peterson > Toth > Freundlich isotherms. A pseudo second-order adsorption model was better to describe the adsorption data than the pseudo first-order model and the Bangham model at the temperatures tested. The activation energy was calculated to be 40.90 kJ/mol, while the thermodynamic parameters ΔH and ΔS were estimated to be −5.82 kJ/mol and 0.07 kJ/(mol K), respectively.

Keywords: 2,4-DCP; ACF; Adsorption; Isotherm; Kinetics; Thermodynamics

1. Introduction

Chlorophenols are mainly produced in chemical industries, such as petroleum refineries, plastics, pharmaceuticals, pesticide, and wood preservation. As one type of the most hazardous materials [1,2], they are carcinogenic, mutagenic and resistant to biodegradation, and thus have to be decomposed before discharging into receiving waters, in order to avoid the biomagnified toxicity to aquatic flora and fauna through various food chains. Many efforts have been made for the physicochemical and/or biological treatments of chlorophenol-rich wastewaters. For instance, they could be removed effectively through adsorption process by using a variety of adsorbents. Among various adsorbents, activated carbon is most commonly used in wastewater treatment, attributed to its vast surface area and great affinity for organics [3]. Activated carbon fiber (ACF) is a new form of activated carbon and has been developed in recent years following powdered activated carbon (PAC) and granular activated carbon (GAC). Because it is used in the form of fabric, the handling of ACF is more facilitated than that of PAC [4]. On the other hand, compared with conventional GAC, it has the advantages of greater adsorption–desorption rate, much vaster surface area, faster equilibrium rate and higher fluid permeability [5–9].

A large number of studies have been carried out to investigate the adsorption of chlorophenols by activated carbon [10–14]. Carrott et al. [11] studied the adsorption equilibrium of phenol, 4-nitrophenol, 4-chlorophenol and 2-chlorophenol onto commercial activated carbon before and after the oxidation of activated carbon at various pHs. Khan et al. [14] investigated the adsorption isotherms of phenol, *p*-chlorophenol, and *p*-nitrophenol from aqueous solutions using activated carbon at different temperatures. They also compared the influences of different adsorbents, sorbate concentration and solution pH on the adsorption efficiency. However, at the present time little information is available concerning the adsorption of chlorophenols onto ACF, a new excellent adsorbent.

Therefore, the objective of this study was to investigate the adsorption of 2,4-dichlorophenol (2,4-DCP), a typical chlorophenol, onto ACF from aqueous solutions, and to evaluate the adsorption efficiency of ACF as a new type of adsorbent. In this work, four isotherm models, Langmuir, Freundlich, Redlich-Peterson and Toth equations, were compared for describing the adsorption isotherms. In addition, the

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doi:10.1016/j.jhazmat.2006.10.003

adsorption kinetics was explored using three kinetic models. With the experimental data of adsorption isotherms and kinetics, the thermodynamics of the adsorption process was also analyzed.

2. Experimental

2.1. Adsorbent

The ACF used in this study was prepared at a yield of 33.0% using a spinning polyvinyl alcohol (PVA) as precursor. The preparation process was described in our previous paper [15]. The ACF used in this work was activated by static air at 900 °C for 1 h. The textual properties of ACF are given in Table 1. In addition to the micropores, there were many mesopores with a diameter around 3.90 nm in the ACF, which was beneficial to facilitating the transportation of 2,4-DCP in the adsorption process. The ACF was washed in boiling water for three times to remove impurities and then dried at 120 °C for 2 h prior to adsorption.

2.2. Chemicals

Continuous filament yarns of raw wet spinning PVA fiber was purchased from Hunan Xiangwei Co., China. The chemicals used in this study, i.e., diammonium phosphate and 2,4-dichlorophenol (2,4-DCP), were purchased from Shanghai Chemical Reagent Co., China. All the reagents were of analytical reagent grade and were used without further purification.

Table 1
Textural properties of the ACFs used in this work

Item	Value
Surface area (m^2/g)	702
Pore volume (cm^3/g)	0.280
Average micropore diameter (nm)	0.70
Average mesopore diatmeter (nm)	3.90
Adsorption capacity for iodine (mg/g)	1678
Adsorption capacity for methylene blue (mg/g)	184

2.3. Adsorption experiments

Adsorption experiments were conducted in flasks by allowing an accurately weighted amount of ACF to reach equilibrium with 100-mL 2,4-DCP solution at temperatures of 293, 303, 313 and 323 K. These flasks were then agitated in a temperature-controlled shaker at 150 rpm. At equilibrium, the supernatant were sampled for analysis. The experiments of adsorption kinetics were carried out at 283, 293, 303, 313 and 323 K. Samples were analyzed at given time intervals. Each run of the experiments was replicated at least three times.

2.4. Analysis

The concentration of 2,4-DCP was determined using a UV–Vis spectrophotometer (UV751GD, Shanghai Analytical Instrument Co., China) at an absorbance wavelength of 280 nm. The surface area and pore structure of the ACF were determined by the N_2-BET method. The measurements were performed at 77.4 K with a volumetric adsorption analyzer (OMNISORP 100 CX, Coulter, USA) in relative pressures of 10^{-6} to 1. All samples were degassed for 3 h at 573 K prior to the vacuum volumetric analysis.

3. Results and discussion

3.1. Adsorption isotherms

In order to understand the adsorption mechanisms of 2,4-DCP onto ACF, four adsorption isotherm models, Langmuir, Freundlich, Redlich-Peterson and Toth, were used to fit the adsorption experimental results. The Langmuir model is usually used with an ideal assumption of an entirely homogeneous adsorption surface, whereas the Freundlich model is appropriate for a heterogeneous surface. The Redlich-Peterson and Toth isotherm models, the combinations of the Langmuir and Freundlich, are applicable to describing microporous adsorption. These isotherm equations are given in Table 2.

The Langmuir and Freundlich isotherms, which have two parameters, could be respectively linearized as follows:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{k_L Q_{max}} + \frac{C_{eq}}{Q_{max}} \quad (1)$$

Table 2
Isotherm models adopted in this work and their parameters

Isotherm	Model	Parameters
Langmuir	$q_e = \frac{Q_{max} k_L C_e}{1 + k_L C_e}$	C_e: equilibrium liquid phase concentration (mg/L); Q_e: equilibrium adsorption capacity; k_L: constant of Langmuir (L/mg); Q_{max}: the maximum adsorption capacity (mg/g)
Freundlich	$q_e = k_F C_e^{1/n}$	k_F: constant of Freundlich ($mg^{1-1/n}\ g^{1/n} L^{1/n}$); n: constant of Freundlich
Redlich-Peterson	$q_e = \frac{k_{RP} C_e}{1 + p_e C_e^g}$	k_{RP}: constant of Redlich-Peterson (L/g); p_e: constant of Redlich-Peterson $(L/mg)^g$; g: constant of Redlich-Peterson
Toth	$q_e = \frac{A C_e}{(B + C_e^D)^{1/D}}$	A: constant of Toth (L/g); B: constant of Toth $(mg/L)^D$; D: constant of Toth