Chemical Engineering Journal 157 (2010) 348–356

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers

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ARTICLE INFO

Article history:
Received 14 July 2009
Received in revised form 3 November 2009
Accepted 10 November 2009

Keywords:
Adsorption
Activated carbon fibers
Substituted phenols
Isotherm
Kinetics
Mechanism

ABSTRACT

Activated carbon fibers (ACFs) were used for the adsorption of phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (DNP) from aqueous solutions, and the adsorption capacities followed the order of TCP > DNP ≈ DCP > 4-NP > 4-CP > 2-CP > phenol. Adsorption isotherms at different temperatures were determined and modeled with Langmuir, Freundlich and Redlich–Peterson equations. Thermodynamic parameters were calculated and correlated with the adsorption behaviors. The effects of solution pH on the adsorption were also studied. The adsorption mechanism was discussed based on the experimental results, and the π–π interactions, solvent effects, hydrophobic interactions and molecular dimensions were considered to be important in the adsorption. Kinetic studies showed rapid adsorption kinetics of the phenols, due to the open pore structure of the ACFs. The kinetics was fitted with the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Steric effects on adsorption kinetics were observed for TCP, 4-NP and DNP, but serious impact on the ultimate uptake was only found for DNP. The relationship between the steric effects and the molecular dimension was also proposed.

1. Introduction

Phenol and its derivatives are used in a number of applications such as chemical, pharmaceutical, petroleum, paper, wood, rubber, dye and pesticide industries [1]. Phenols are classified as priority pollutants due to their toxicity to organisms even at low concentrations. Their adverse environmental and public health impacts have been proved by increasing evidences, such as death of aquatic life, inhibition of the normal activities of microbial community and carcinogenicity to animals [2]. In view of the high toxicity, wide prevalence and poor biodegradability of phenols, it is necessary to remove them from wastewaters before discharge into water bodies.

Various processes have been employed for the removal of phenols from aqueous media including advanced oxidation [3], membrane filtration [4], biological degradation [5], electrochemical oxidation [6], photocatalytic degradation [7] and adsorption [8,9]. Among these methods, adsorption is still the most versatile and widely used, since it can effectively remove many types of pollutants and the design and operation are convenient. Activated carbon remains extensively used in practice due to their mechanic stability, high adsorption capacity and fast adsorption rate [10]. In recent years, a new form of carbon adsorbent: activated carbon fibers (ACFs) have been intensively developed and applied [11]. ACFs are commonly microporous with large surface area and narrow pore size distribution. The microporous nature endows ACFs with advantages in adsorption, as the adsorption energy is enhanced within low-size pores [12]. Furthermore, ACFs have large external surface and their micropores are directly exposed on the surface, giving rise to a fast adsorption rate [13].

The adsorption of organics onto activated carbon has been studied in a large number of literatures, and the results demonstrated that the adsorption behaviors depend mainly on the characteristics of the activated carbon, the molecular properties of the organics and the operational conditions. The characteristics of the activated carbon such as surface area, pore size distribution and surface functional groups play an important role in the adsorption, as they determine the interactions between the organics and the activated carbon at the interface [14,15]. The effects of the molecular properties such as molecular size, solubility, pK_a and electron distribution have been revealed, which might influence the affinity between the organics and the carbon surface [16–18]. Furthermore, the operational conditions such as solution pH and temperature are also involved in the adsorption, which might have implications on the adsorbent/adsorbate interactions [19,20].

The adsorption performance of ACFs for some phenols including 2,4-dichlorophenol [21,22], pentachlorophenol [23], 4-nitrophenol [24] and chlorophenols [25] have been reported in previous stud-

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doi:10.1016/j.cej.2009.11.013

ies. However, a comparative study is still needed to improve our knowledge about the adsorption properties of ACFs and the impact of the substituent groups. It is generally assumed that the substituent groups are not directly involved in the interactions with the carbon surface [8], but they would change the molecular properties which in turn affect the adsorption process. In this study phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (DNP) were adsorbed from aqueous solutions onto ACFs, and the adsorption characteristics including isotherm, kinetics, thermodynamics, mechanism and effects of molecular properties and pH were studied.

2. Experimental

2.1. Materials

The ACFs were pitch-based in the form of unwoven fabrics from Sainuoda Co., China, with an average diameter of 4 μm (according to SEM image). They were washed with distilled water and dried at 105 °C for 24 h, stored in a desiccator before use. The phenols were of analytical grade, purchased from Shanghai Chemical Reagent Co., China. Some properties of the phenols are summarized in Table 1.

2.2. ACFs characterizations

The surface physical properties of the ACFs were characterized with a Micromeritics ASAP 2020, using N_2 as the adsorbate at 77 K. The surface area (S) was calculated with the BET equation, the micropore volume (V) was evaluated by converting the adsorption amount at $P/P_0 = 0.99$ to a volume of liquid adsorbate. Based on the assumption of slit-shape pores [27], the average pore size (r) was estimated by the following equation:

$$r = \frac{2V}{S} \tag{1}$$

The Horvath–Kawazoe method was applied to analyze the pore size distribution, which was expected to be suitable for porous carbons with predominant micropores of width below 1 nm [28,29].

The analysis of surface oxygen functional groups was based on the acid–base titration method [30]. For each time 0.5 g ACFs were put in 20 ml 0.01 mol/L NaOH or HCl solution to determine the acidic and basic groups, respectively.

The point of zero charge (pH_{PZC}) was determined by a mass titration method proposed by Noh and Schwarz [31]. Various amounts of ACFs (0.05–0.5 g) were put in 10 ml 0.1 mol/L NaCl solutions (prepared with boiled water). The bottles were sealed and shaken in a thermostat shaker overnight, the equilibrium pH values of the mixtures were measured and the limiting pH was taken as the pH_{PZC}.

Table 1
Some physical properties of the phenols in study.

Phenols	Molecular weight (g/mol)	Molecular size[a] (Å)	Solubility[b] (g/L)	pK_a[b]
Phenol	94.1	5.76 × 4.17	93	9.89
2-CP	128.6	5.76 × 4.82	28	8.52
4-CP	128.6	6.47 × 4.17	27	9.37
DCP	163.0	6.47 × 4.82	15	7.90
TCP	197.4	6.47 × 5.47	0.9	5.99
4-NP	139.1	6.84 × 4.17	1.7	7.15
DNP	184.0	6.84 × 5.76	0.6	4.09

[a] Ref. [26].
[b] Ref. [8], at 25 °C.

2.3. Adsorption procedure

Adsorption experiments were conducted by batch mode in stoppered conical flasks. Stock solutions were prepared by dissolving the phenols in deionized water. For each time 0.100 g ACFs and 100 mL phenol solution were mixed in a flask, which was then shaken in a thermostat shaker at 150 rpm.

In adsorption isotherm studies, solutions with different initial concentrations were added, the pH was not adjusted, and the equilibrium time was set as 24 h, which was enough according to the preliminary experiments. Samples were separated by filtration and the phenol concentrations were analyzed by UV spectroscopy (UV-2550, Shimadzu) at λ_{max} 270, 274, 280, 284, 290, 318 and 353 nm for phenol, 2-CP, 4-CP, DCP, TCP, 4-NP and DNP, respectively [32,33]. Each experiment was duplicated under identical conditions. Blanks containing no ACFs were done and the loss (generally quite low) was considered. The uptake of the adsorbate at equilibrium, q_e (mmol/g), was calculated by the following equation:

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

where C_0 and C_e are the initial and equilibrium concentrations of the phenols (mmol/L) in solution, respectively; V is the volume of the solution (L) and m is the weight of the adsorbent (g).

In pH studies, the solution pH was adjusted by the addition of HCl or NaOH after the mixing of phenols with ACFs, which showed little change during the adsorption process. Experiments were conducted at 25 °C, samples were separated after 24 h. The initial concentration for phenol, 2-CP, and 4-CP was 1.5 mmol/L, for DCP was 1.85 mmol/L, for TCP, 4-NP and DNP was 2.0 mmol/L.

The kinetic studies were performed following a similar procedure at 25 °C, solution pH was not adjusted, the initial concentration was set as 1.5 mmol/L for each phenol, and the samples were separated at predetermined time intervals. The uptake of the adsorbate at time t, q_t (mmol/g), was calculated by the following equation:

$$q_t = V \cdot \frac{C_0 - C_t}{m} \tag{3}$$

where C_t is the concentration of the adsorbate (mmol/L) in solution at time t.

3. Results and discussion

3.1. Surface characteristics of ACFs

The nitrogen adsorption isotherm of the ACFs and the pore size distribution based on the Horvath–Kawazoe method are presented in Fig. 1. The isotherm is H-type characterized of a sharp rise at low-pressure range and a plateau at high pressure range [34], indi-

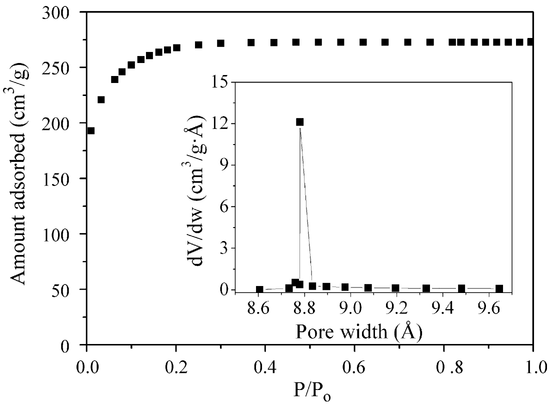

Fig. 1. Nitrogen adsorption isotherm (77 K) and pore size distribution of the ACFs.