ELSEVIER

Adsorption of *p*-nitrophenol from aqueous solutions onto activated carbon fiber

Dengyong Tang, Zheng Zheng*, Kui Lin, Jingfei Luan, Jibiao Zhang

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment,
Nanjing University, Nanjing 210093, PR China

Abstract

The adsorption of *p*-nitrophenol (PNP) onto activated carbon fiber (ACF) was investigated in simulated wastewater in a batch system to evaluate the effects of solution pH, presence of sodium chloride, adsorbent doses and temperature. It was found that PNP adsorption amount depended on pH, sodium chloride content, adsorbent doses and temperature. Langmuir and Freundlich models were applied to describe the adsorption isotherms. Freundlich model agreed with experimental data well, indicating the possibility of more than just one monomolecular layer of coverage. SEM photographs of ACF before and after adsorption revealed that it was in part with multimolecular layers of coverage on ACF surfaces. The change of free energy, enthalpy, and entropy of adsorption were also evaluated for the adsorption process. The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic data. The experimental data fitted very well the pseudo-second-order kinetic model. Attempts were made to desorb PNP from ACF using dilute NaOH solution and water, and desorption efficiency was obtained to the extent of 92.7% with 0.025 M NaOH and water at 368 K.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Adsorption; *p*-Nitrophenol (PNP); Activated carbon fiber (ACF); Desorption

1. Introduction

There has been growing concern for public health and environmental safety over the last few decades. Introduction of toxic pollutants can have a severe impact on many organisms that live in aquatic ecosystems. *p*-Nitrophenol (PNP) is an important fine chemical intermediate, serving as a precursor of pharmaceuticals and pesticides [1]. Diesel fuel and gasoline exhaust also contain PNP that enters water body through rainwater [1,2]. PNP has been selected as one of the persistent, bioaccumulative and toxic (PBT) chemicals by the US Environmental Protection Agency [3].

Due to its harmful effects, wastewaters containing PNP have to be treated before being discharged to receiving water bodies. Many treatment technologies such as advanced oxidation processes (AOPs) [4–6], extraction [7,8], and adsorption have been developed to remove PNP from domestic and industrial wastew-

aters. Adsorption is widely used because of its simple design, easy operations and relatively simple regeneration.

Although varieties of adsorbents [9–11] have been tried to remove nitrophenol from wastewaters, activated carbon (AC) [12–17] remains the most widely used adsorbent. Activated carbon fibers (ACFs) are novel adsorbents of high efficiency. The raw materials of ACFs are polyacrylonitrile fibers, viscose, phenolic resin fibers or pitch fibers, etc. They are first pyrolyzed and then activated at a temperature of 700–1000 °C in an atmosphere of steam or carbon dioxide [18]. ACFs have many favorable characteristics such as high adsorption capacities and high mass transfer rates for both adsorption and desorption, and are easier to be handled in a batch adsorber than granular and powdered AC [19]. Thus, they have received increasing attention in recent years as adsorbents for water treatment [20–23]. Furthermore, activated carbon cloths, one kind of ACFs were used as adsorbent to adsorb phenolic compounds including PNP by some researchers [24,25]. However, there is little report on thermodynamic and kinetic studies of PNP adsorption onto ACF.

The aim of this work is to study the use of ACF as an adsorbent for the removal of PNP from aqueous solutions by static batch

---

* Corresponding author. Tel.: +86 25 83593109; fax: +86 25 83707304.
E-mail address: zzheng@nju.edu.cn (Z. Zheng).

experiments. Factors affecting adsorption, such as pH, presence of NaCl, adsorbent dosage and temperature were investigated. Isotherm, thermodynamic and kinetic studies were carried out. In addition, desorption of adsorbed PNP from ACF was also studied.

2. Experimental

2.1. Adsorbent

The viscose-based ACF used in the experiments was A12 provided by the Institute of Liaoning Province Academy of Safety Science, Shenyang, China. The ACF was boiled, washed three times in distilled water and dried at 383 K for 24 h before being used as adsorbent. The specific surface area of A12 was measured with a Micrometics ASAP-2020 surface area measurement instrument (Micromeritics Instrument, Norcros, USA) following the BET method. The pH at the point of zero charge (pH$_{PZC}$) of A12 was determined by batch equilibrium method described by Babic et al [26]. The elemental analysis of A12 was obtained from a CHN-O-Rapid Elemental Analytical Instrument (Elementer, Germany). Main characteristics of A12 are summarized in Table 1.

2.2. Chemicals

All of the reagents used were A.R. grade and without further purification. Hydrochloric acid, sodium hydroxide and sodium chloride were purchased from Nanjing Chemical Reagent Plant (Nanjing, China). PNP was obtained from The Third Chemical Reagent Plant of Shanghai (Shanghai, China), and PNP solution (1000 mg/L) was prepared by dissolving required amount of PNP in distilled water in the adsorption test.

2.3. Adsorption studies

In batch adsorption experiments, certain amounts of ACF were added into several 250 mL Erlenmeyer flasks, each containing 100 mL solution (1000 mg/L PNP). And then the flasks were shaken at 150 rpm in a Constant Temperature Shaker (Shanghai Scientific Instrument Co. Ltd., China) at a pre-settled temperature for 24 h. Samples were separated by a fast filtration, and concentrations of PNP at equilibrium (C_e) were determined.

Table 1
Main characteristics of A12

Parameters	Value
Bulk density (g/cm^3)	0.04
BET surface area (m^2/g)	1413
Total pore volume (cm^3/g)	0.69
Micropore volume (cm^3/g)	0.51
Average pore width (nm)	1.95
pH$_{PZC}$	4.4
Elemental analysis (wt.%)	
C	83.32
H	1.90
O	14.78

The effect of pH on PNP adsorption onto ACF was studied by adjusting the pH of PNP solutions with dilute HCl or NaOH solution at 293 K. A PHS-2C pH meter (Shanghai Kangyi Instrument Co., China) was used to measure the pH values of the solutions. The effect of NaCl on the adsorption was also studied. Different doses of adsorbent (0.03–0.50 g) were introduced to respective 100 mL 1000 mg/L PNP solution at 293, 308 and 323 K, respectively, in order to determine adsorption isotherms and evaluate the effect of adsorbent dosage and temperature on PNP adsorption. In kinetic studies, batch experiments were conducted at different periods by adding 1.00 and 2.00 g ACF into each 500 mL solution, respectively, at pH 4.3 and 293 K.

The adsorbent phase concentrations of PNP (q_e) were calculated according to the following equation:

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

Adsorption efficiency (AE) was calculated from following equation:

$$AE\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of PNP (mg/L), respectively, V the volume of the solution (L), and W is the mass of adsorbent (g).

2.4. Scanning electron micrography of ACF before and after adsorption of PNP

A JSM-5610 scanning electron microscope (JEOL, Japan) was used to visualize the surface morphology and structure of A12 before and after adsorption of PNP.

2.5. Batch desorption

The recovery of the adsorbed material and regeneration of adsorbent are quite important in field applications of adsorption processes. It was found that the adsorption capability for adsorption of PNP onto ACF was small at high pH values. Hence, NaOH was chosen as the regeneration reagent. Ten samples of 0.40 g ACF pre-adsorbed with 100 mL solution containing 1000 mg/L PNP were added to 50 mL NaOH solutions of various concentrations (0–0.3 M) and shaken at 150 rpm in a Constant Temperature Shaker at 293 K for 2 h to determine the optimal concentration of NaOH. Studies evaluating the effect of temperature on desorption were carried out at 293, 333 and 368 K, respectively. In order to increase the desorption efficiency, the equal amount of hot water was used to rinse the ACF after dilute NaOH solution.

Desorption efficiency (DE) was calculated from the following equation:

$$DE\,(\%) = \frac{C_d V_d}{W_a q_e} \times 100, \qquad (3)$$

where C_d is the desorbed adsorbate concentration of desorption solution (mg/L), V_d the volume of the desorption solution (L),