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Journal of Hazardous Materials B128 (2006) 123–129

Journal of Hazardous Materials

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Synergistic adsorption of phenol from aqueous solution onto polymeric adsorbents

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Received 10 November 2004; received in revised form 26 January 2005; accepted 2 March 2005

Abstract

Adsorption of phenol from aqueous solution onto a nonpolar adsorbent, aminated adsorbent and weak base adsorbent (Amberlite XAD4, NDA103 and Amberlite IRA96C, respectively) at temperatures from 293 to 313 K was studied for the weak interactions between the phenol molecules and the polymeric adsorbents. Isotherms of Langmuir and Freundlich equation with characteristic parameters for different adsorbents were well fitted to the batch equilibrium adsorption data. The adsorption capacity on NDA103 driven by hydrogen bonding and van der Waals interaction together is higher than that on IRA96C driven by hydrogen bonding interaction only and on XAD4 driven by van der Waals interaction only. For evaluating synergistic adsorption for phenol–water systems onto polymeric adsorbents, the adsorption capacity is normalized to the amounts of specific surface area and amino groups of adsorbents. The synergistic effect with other weak interactions would contribute more to the adsorption as acting simultaneously than that of acting individually.

Keywords: Polymeric adsorbent; Phenol; Adsorption behavior; Synergistic effect

1. Introduction

Contamination of surface water and groundwater with aromatic compounds is one of the most serious environmental problems human being faces today. Owing to its acute toxicity and good solubility, phenol has already been listed as one of the top priority contaminants and also the most important substructure of potentially carcinogenic pollutants discharged from fine chemical plants. Therefore, the efficient removal of phenol from waste streams has increasingly become a significant environmental concern [1,2]. Now many water treatment technologies are available to remove phenol from receiving water body including biological degradation, chemical oxidation and adsorption on activated carbon. In the past two decades, polymeric adsorbents have been viewed as a practical alternative to activated carbon for efficient removal of aromatic pollutants from wastewater [3–6], and adsorption mechanism of target compounds on polymeric adsorbents is of great interest today.

For phenol adsorption on a specific polymeric adsorbent, the solute–adsorbent interaction will play an important role in the adsorption capacity from aqueous solution. For a commercially available polymeric adsorbent, such as XAD4, it is generally known that van der Waals interaction is the main force to drive phenol molecules from bulk solution to adsorbent phase [6]. Also, hydrogen bonding interaction was taken as another driving force in some cases including phenol adsorption on a weakly anion exchanger [7–10]. In order to enhance adsorption capacity, scientists have now made much effort on chemical modification of polymeric adsorbents to improve their adsorption properties and some mechanisms have been reported to elucidate the adsorption enhancement on the functionalized adsorbents [11–14]. But study on the synergistic effect, which arises from more than two types of driving forces occur simultaneously on a specific polymeric adsorbent, is still scarce [15,16].

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doi:10.1016/j.jhazmat.2005.03.036

Table 1
Physical properties of phenol at 298 K [4]

Adsorbate	Phenol
Surface area (nm^2/molecule)	0.305
Cross-sectional distance (nm)	0.43
Saturated concentration in water, C_s (mol/m^3)	925
pK_a	9.89

In this paper, a newly developed adsorbent NDA103 with amino group on the polymeric matrix was employed to mimic the multiple weak interactions on phenol adsorption from aqueous solution. Through batch phenol adsorption runs on XAD4, NDA103 and a weakly anion exchanger IRA96C, the present work was aimed at achieving a better understanding on the interactions of phenol and adsorbent and elucidating the synergistic mechanism of weak interactions.

2. Experimental studies

Phenol (analytical grade) was purchased from the Shanghai Chemical Reagent Station (Shanghai, PR China) and used in the study without further purification. Phenol was dissolved in deionized water in the batch adsorption runs without pH adjustment. Some physiochemical properties of phenol are presented in Table 1.

Amberlite XAD4 (a nonpolar adsorbent) and IRA96C (a weak base adsorbent) were purchased from Rohm & Haas (Philadelphia, PA, USA), while NDA103 (an aminated adsorbent developed by our research group) was produced in Langfang Electrical Resin Co. Ltd. (Hebei Province, PR China).

Batch adsorption tests were performed using the conventional bottle-point technique in 100 mL glass flasks at different temperatures (293, 303 and 313 K). Prior to use, all the adsorbents were extracted with ethanol for 8 h in a Soxhlet apparatus and vacuum desiccated at 325 K for 24 h. Fixed adsorbent dosages of 0.050 g were directly introduced into a 100 mL glass flask. Owing to its nonpolarity, XAD4 was necessarily wetted with 0.5 mL of methanol and then rinsed three times with deionized water before use. Subsequently, 50 mL of an aqueous solution of phenol with an initial concentration ranging from 0.15 to 2 mmol/L was added into each flask.

The flasks were then transferred into a G 25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.) at a given temperature and shaken under 150 rpm for 24 h. Note that adsorption reaches equilibrium in 24 h according to the preliminary kinetic study. The amount adsorbed of phenol can be calculated by the following equation:

$$Q_e = V_L \frac{(C_0 - C_e)}{W} \quad (1)$$

where C_0 and C_e denote the initial concentration (mmol/L) and the residual concentration at equilibrium (mmol/L), respectively, Q_e refers to the amount adsorbed of phenol on the adsorbents (mmol/g), V_L is the volume of the aqueous solution (mL) and W is the mass of dry adsorbents (g).

The solution concentrations were determined using high performance liquid chromatography (HPLC), which was connected to Waters 600 controller, Waters 600 pump and Waters 2487 Dual Absorbance UV detector at 274 nm (Waters, USA). Mobile phase was 0.1% $KH_2PO_4{\cdot}H_2O$:methanol = 70:30 (v/v) and flow rate was 1 mL/min.

3. Results and discussion

3.1. Characterization of the polymeric adsorbents

The aminated polymeric adsorbents NDA103 was obtained by aminating a macroreticular polymeric adsorbent NDA100 with dimethylamine [10]. The specific surface area and the pore distribution of all the employed polymeric adsorbents were determined in dry state with a Micromeritics ASAP 2010 M surface area measurement instrument (Micromeritics Instrument, Norcros, USA). Infrared spectra were obtained from a Nexus 870 SX IR spectrometer (USA) with KBr pelletted samples. The basic exchange capacity was measured by titration with 0.1 mol/L HCl and NaOH solutions.

The characteristics of the polymeric adsorbents are listed in Table 2. IR spectra (not shown) indicates that the absorbance peaks at 2771 and 2816 cm^{-1} are for C–H stretching vibration of the methyl group connecting to tertiary amino group on NDA103 and IRA96C, the vibration peak for C–N bond being at 1261 cm^{-1}.

Table 2
Characteristic properties of XAD4, NDA103 and IRA96C

Property	XAD4	NDA103	IRA96C
Structure	Polystyrene	Aminated polystyrene	Weak base polystyrene
Polarity	Nonpolar	Moderately polar	Strong polar
BET surface area (m^2/g)	914	611	36
Average pore diameter (nm)	5.8	3.4	20.7
Desorption average pore diameter (nm)	8.4	17.6	30.5
Particle size (mm)	0.4–0.6	0.4–0.6	0.4–0.6
Tertiary amino group (mmol/g)	0	1.57	5.1
Colour	White	Deep brown	Yellow