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Binary adsorption breakthrough curves in fixed bed: Experiment and prediction

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ABSTRACT

Phenolic compounds are extensively used as raw materials in a wide variety of manufacturing processes and thus result in wastewaters containing phenolic compounds. In order to design a fixed-bed carbon adsorption process for wastewater containing phenol and *p*-nitrophenol, batch and column adsorption tests at 250 °C were performed to measure the adsorption isotherms and breakthrough curves of phenol and *p*-nitrophenol, respectively. The Freundlich adsorption isotherm model for single-component systems was found to correlate the adsorption equilibrium data better than the Langmuir model. Algorithms for applying the ideal adsorbed solution theory along with the Langmuir and Freundlich adsorption isotherm models were derived to predict the *p*-nitrophenol–phenol binary adsorption data. Compared with the experimental data, the Freundlich model along with the ideal adsorbed solution theory can best predict the binary adsorption data with the least errors. Thus, the wave propagation theory along with the ideal adsorbed solution theory using the Freundlich isotherm model was applied to predict the breakthrough curves of binary adsorption satisfactorily. This study demonstrates a novel methodology to predict the binary adsorption breakthrough curves using the adsorption isotherm model, the ideal adsorbed solution theory, and the wave propagation theory.

1. Introduction

Phenolic compounds such as phenol and *p*-nitrophenol are extensively used as raw materials in a wide variety of manufacturing processes. For example, phenol is used to produce phenolic resin, polycarbonate, epoxide resin, nonionic detergent, aspirin, herbicide, cosmetics, and many pharmaceuticals [1]. Para-nitrophenol is used to manufacture drugs (*e.g.*, acetaminophen), fungicides, methyl and ethyl parathion insecticides, and dyes to darken leather [2]. Since phenolic compounds are commonly present in industrial manufacturing processes, wastewaters containing phenolic compounds need to be properly treated before they can be discharged to aquatic environment. Various secondary and tertiary treatment methods have been developed to remove phenolics compounds in wastewaters. Typically, secondary wastewater treatment processes use microorganisms to convert organic compounds to harmless carbon dioxide and water. The operating costs of such biological treatment processes are relatively low, but the reaction rates are relatively slow so that the required reactor sizes are relatively large. In contrast, tertiary wastewater treatment processes use chemical oxidation or adsorption can reduce the treatment unit size but the operating costs are relatively higher. Since most wastewater treatment facilities currently use secondary biological processes to treat organic compounds, studies on improvement of the biological processes still remain as important topics of research. In the recent years, tertiary wastewater treatment processes attract great attention for the purpose of developing suitable and cost-effective technologies to treat industrial wastewaters.

Ucun et al. investigated phenol biodegradation in a batch jet loop bioreactor using activated sludge and found phenol removal rate could be up to 100% [3]. El-Naas et al. evaluated the continuous biodegradation of phenol using *Pseudomonas putida*, immobilized in polyvinyl alcohol (PVA) gel matrices in a specially designed spouted bed bioreactor [4]. Mungmart et al. used impregnated metal catalysts to decompose aqueous phenol in a three-phase fluidized-bed reactor and found that the use of Co catalyst with the presence of ozone led to the best phenol removal [5]. El-Naas et al. used date-pit activated carbon to remove phenol from petroleum refinery wastewater [6]. Damjanović investigate the phenol removal from aqueous solutions by zeolites as solid adsorbents [7]. Shimizu et al. used zero-valent iron powder in the presence of dissolved oxygen to remove phenol and found that phenol was removed by the Fenton reaction and adsorption/precipitation mechanism [8]. An et al. used salicylic acid-grafted adsorbent to adsorb phenolic compounds from aqueous solution and concluded that the Langmuir model fit the isotherm data better than the Freundlich model [9].

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Nomenclature

A	specific surface area per unit mass of adsorbent (m^2/g)
A_c	cross-sectional area of the bed (m^2)
C	solute concentration in the single-component system (mmol/L)
C_i	concentration of solute i in the mobile phase (mmol/L)
C_i^0	solute concentration in the mobile phase in single-component adsorption system (mmol/L)
C_{Fi}	feed concentration of solute i in the mobile phase (mmol/L)
C_{Ii}	intermediate-zone concentration of solute i in the mobile phase (mmol/L)
C_{Pi}	presaturation-zone concentration of solute i in the mobile phase (mmol/L)
K	adsorption constant in the Langmuir model defined in Eq. (7) (L/mmol)
k	adsorption constant in the Freundlich model defined in Eq. (8) (mmol/g/(mmol/L)^n)
n	Freundlich isotherm parameter defined in Eq. (8)
Q	adsorption capacity in the Langmuir model defined in Eq. (7) (mmol/g)
q	solute adsorption in the single-component system (mmol/g)
q_i	concentration of solute i in the stationary phase (mmol/g)
q_{Fi}	feed concentration of solute i in the stationary phase (mmol/g)
q_{Ii}	intermediate-zone concentration of solute i in the stationary phase (mmol/g)
q_{Pi}	presaturation-zone concentration of solute i in the stationary phase (mmol/g)
q_i^0	solute concentration in the stationary phase in single-component adsorption system (mmol/g)
R	gas constant (J/mol K)
T	temperature (K)
t	operating time (s)
ti	breakthrough times (s)
uo	linear velocity of the carrier fluid (m/s)
Vi	breakthrough volume (L)
Vb	volume of packed bed (L)
x_i	adsorbed fraction of component i in the stationary phase
z	distance from the inlet of the mobile phase (m)
ε	void fraction of the bed (Lsolution/Lbed)
ρ	carbon bed density (g/Lbed)
Π_i^0	spreading pressure of solute i (N/m)
ψ	modified spreading pressure defined in Eq. (9) (mmol/g)

Salehi et al. studied aerobic biodegradation of *p*-nitrophenol (PNP) by acclimated waste activated sludge in a bubble column [10]. Zhao et al. used Fe-doped TiO_2 catalysts under UV light irradiation to decompose PNP in aqueous solution and found that PNP could be completely degraded after 60 min in the presence of 4.9 mM H_2O_2 [11]. Sabio et al. [12] studied the adsorption of PNP on activated carbon fixed bed and confirmed the constant pattern wave hypothesis proposed by Chern and Chien [13]. Sreenivasulu et al. [14] studied the degradation of *p*-nitrophenol by immobilized cells of Bacillus spp. Isolated from soil and found the immobilized cell retained the ability of *p*-nitrophenol even after two years of immobilization. Zhao et al. [15] used ultrasound irradiation to enhance *p*-nitrophenol oxidation by Fenton's Reagent and found obvious synergetic effect in the combined ultrasound-Fenton's reagent process by a factor of 2.06. Khatamian and Alaji used ZnO/HZSM-5 nanocomposite particles to remove *p*-nitrophenol from aqueous solution and found the HZSM-5 had a high adsorbent capacity for *p*-nitrophenol while ZnO could retard the recombination of photogenerated electron–hole [16]. Zhang et al. [17] used nitric-acid-activated fly ash as a heterogeneous Fenton-like catalyst for *p*-nitrophenol removal from water and found higher removal rate was observed at lower pH when the leached iron concentration increased. Cotoruelo et al. [18] evaluated the adsorbent ability of 9 lignin-based activated carbons for the removal of *p*-nitrophenol from aqueous solutions.

Among the many tertiary treatment processes, fixed-bed adsorption technology has been widely employed to remove organic pollutants from wastewaters. Although powder activated carbon and low-cost adsorbents [19–23] may be directly disposed of, in many countries wastewater treatment sludge and spent adsorbents are viewed as hazardous solid wastes and thus direct disposal of them is prohibited by laws. In industries, granular activated carbon is usually packed in columns to adsorb pollutants in the fluids passing through the columns. The packed columns continue to operate until the packed activated carbon is breakthroughed with the pollutants and lose its adsorption capacity. In order to appropriately design fixed-bed adsorption processes, the adsorption isotherms of pollutants onto activated carbon must be known first. The adsorption isotherms of many different organic pollutants onto various adsorbents could be found in the literature. However, those adsorption isotherms are for single component only, *i.e.*, there are no competitive adsorbates in the systems. Industrial wastewater streams usually contain more than one pollutant that can be adsorbed by activated carbon columns; each pollutant has its own breakthrough curve. For known adsorption isotherms, the non-linear wave propagation theory was used to predict the breakthrough curves of single-component systems [13,24–26] and a binary component system [27]. Because multicomponent adsorption isotherms are difficult to measure, prediction of multicomponent adsorption isotherms using single component adsorption isotherm data are highly desirable. In this study, the ideal adsorbed solution theory (IAST) that was widely used in organics and/or heavy metal adsorption [28–34,6] is applied to predict the phenol/*p*-nitrophenol binary adsorption isotherm from single component isotherm data. Furthermore, the breakthrough curves of the binary adsorption system with constant feed compositions will be predicted by the nonlinear wave propagation theory using the IAST and compared with the experimental data.

2. Theory

2.1. Wave propagation theory

Assuming local adsorption equilibrium and neglecting axial dispersion, the column dynamics of binary fixed-bed adsorption systems can be described by the following governing equations:

$$\rho\frac{\partial q_i}{\partial t}+\varepsilon\frac{\partial C_i}{\partial t}+u_0\varepsilon\frac{\partial C_i}{\partial z}=0 \quad i=1,2 \tag{1}$$

$$q_i=f_i(C_1,C_2) \quad i=1,2 \tag{2}$$