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Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters

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Abstract

The adsorption equilibrium isotherms of five phenolic compounds from aqueous solutions onto granular activated carbon (GAC) were studied and modeled. Phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP) were chosen for the adsorption tests. To predict the adsorption isotherms and to determine the characteristic parameters for process design, seven isotherm models: Langmuir (five linear forms), Freundlich, Elovich, Temkin, Fowler–Guggenheim, Kiselev, and Hill–de Boer models were applied to experimental data. The results reveal that the adsorption isotherm models fitted the data in the order: Fowler–Guggenheim > Hill–de Boer > Temkin > Freundlich > Kiselev > Langmuir isotherms. Adsorption isotherms modeling shows that the interaction of phenolic compounds with activated carbon surface is localized monolayer adsorption, that is adsorbed molecules are adsorbed at definite, localized sites. Each site can accommodate only one molecule. The interaction among adsorbed molecules is repulsive and there is no association between them, adsorption is carried out on energetically different sites and is an exothermic process. Uptake of phenols increases in the order Ph < 2-CP < 4-CP < DCP < TCP, which correlates well with respective increase in molecular weight, cross-sectional area, and hydrophobicity and decrease in solubility and pK_a. Additionally, for the four tested chlorophenols, it seems that the magnitude of adsorption is directly proportional to their degree of chlorination.

Keywords: Modeling; Adsorption; Isotherms; Phenol; Chlorophenols; GAC

1. Introduction

Phenolic compounds including substituted phenols which are generated by petroleum and petrochemical, coal conversion, phenol producing industries, and other chemical processes, are common contaminants in wastewater. Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications. Phenols as a class of organics are similar in structure to the more common herbicides and insecticides in that they are resistant to biodegradation. Their presence in water supplies is noticed as bad taste and odor. In the presence of chlorine in drinking water, phenols form chlorophenols, which have a medicinal taste, which is quite pronounced and objectionable.

Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential to harm human health. Because of their toxicity, the US Environmental Protection Agency (EPA) and the European Union have designated phenols as priority pollutants [1,2].

Increasing concern for public health and environmental quality has led to the establishment of rigid limits on the acceptable environmental levels of specific pollutants. Thus, the removal or destruction of phenols from process or waste streams becomes a major environmental problem.

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Nomenclature

b	Langmuir constant related to the free energy of adsorption ($L\,mg^{-1}$)
C_e	the equilibrium concentration of the solute in the bulk solution ($mg\,L^{-1}$)
C_0	the initial concentration of the solute in the bulk solution ($mg\,L^{-1}$)
GAC	granular activated carbon
k_n	the equilibrium constant of the formation of complex between adsorbed molecules
k_1	Kiselev equilibrium constant ($L\,mg^{-1}$)
K_E	Elovich equilibrium constant ($L\,mg^{-1}$)
K_F	Freundlich constant indicative of the relative adsorption capacity of the adsorbent ($mg^{1-(1/n)}\,L^{1/n}\,g^{-1}$)
K_{FG}	Fowler–Guggenheim equilibrium constant ($L\,mg^{-1}$)
K_0	Temkin equilibrium constant ($L\,mg^{-1}$)
K_1	Hill–de Boer equilibrium constant ($L\,mg^{-1}$)
K_2	the energetic constant of the interaction between adsorbed molecules ($kJ\,mol^{-1}$)
$\log K_{ow}$	octanol/water partition coefficient
n	Freundlich constant indicative of the intensity of the adsorption
N	the number of experimental points
q_e	the amount of solute adsorbed per unit weight of adsorbent at equilibrium ($mg\,g^{-1}$)
q_m	the maximum adsorption capacity ($mg\,g^{-1}$)
ΔQ	variation of adsorption energy ($kJ\,mol^{-1}$)
r	coefficient of correlation
R	universal gas constant ($kJ\,mol^{-1}\,K^{-1}$)
T	temperature (K)
W	the interaction energy between adsorbed molecules ($kJ\,mol^{-1}$)

Greek letter

θ	surface coverage (q_e/q_m)

Adsorption is well-established technique for the removal of low concentrations of organic pollutants from large volumes of potable water, process effluents, wastewater, and aqueous solutions. Adsorption onto activated carbon is often considered as the most economical and efficient process for the removal of organic compounds in dilute aqueous solutions. Activated carbon adsorption has been cited by the USEPA as one of the best available environmental control technologies [2]. Activated carbons are profusely used as adsorbents for decontamination processes because of their extended surface area, high adsorption capacity, microporous structure, and special surface reactivity. The adsorption of phenol and substituted phenols from aqueous solution on activated carbons has been intensively investigated for decades [3–12].

Adsorption equilibria information is the most important piece of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredient for the understanding of how much those components can be accommodated by a solid adsorbent. The present paper aims to study and model the isotherms of adsorption of phenol and chlorophenols from aqueous solutions onto granular activated carbon (GAC). The representation of the adsorption isotherms onto activated carbon can be based on models with two, three, even with more parameters [13–17]. The goal of this first part is to apprehend the interactions phenols–GAC through the validity of isotherm models. In the case of the models with two-parameter, the Langmuir and Freundlich equations are largely used. Additionally, other models such as the Temkin, Fowler–Guggenheim, Kiselev, and Hill–de Boer equations exist and allow the determination of the energy of adsorption, interaction energy between adsorbed molecules, and complex formation between adsorbate.

2. Materials and methods

2.1. Adsorbent

The GAC used in this study was purchased from Prolabo. Prior to use, the carbon was pretreated by boiling in ultra-high quality (UHQ) water for 1 h and washed repeatedly with UHQ water until the electric conductivity and the UV absorbance were equal to zero, and the pH remains constant. Finally, the washed activated carbon was dried in an oven at 110 °C to constant weight and stored in a desiccator until use. The BET (Brunauer–Emmett–Teller) surface area of the carbon ($929\,m^2\,g^{-1}$) was obtained from N_2 adsorption isotherms at 77 K. The GAC has an average granulometry of 3 mm, a bulk density of $0.45\,g\,cm^{-3}$, a micropore volume of $0.38\,cm^3\,g^{-1}$, an average pore diameter of 16 Å, an ash content of 5.6%, and a pH of zero point charge (pH_{PZC}) of 4.1. The majority of functional groups on GAC surface were found to be acidic (see the second part).

2.2. Adsorbates

Five organic molecules were selected for the study of adsorption onto granular activated carbon: phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). The adsorbates, purchased from Sigma with purity greater than 99.5%, and UHQ water (Milli-Q 18.2 MΩ) were used to prepare the aqueous solutions for the adsorption tests. The principal characteristics of the studied adsorbates are regrouped in Table 1. The phenolic compounds are weak acids, whose acidity increases with the number of chlorine atoms. The octanol/water partition coefficient ($\log K_{ow}$) of chlorophenols, which can be used as a measure of solvent hydrophobicity, increases with the degree of chlorination.

2.3. Equilibrium isotherms

For the determination of adsorption isotherms, accurately weighted amount of GAC ($0.05–1\,g\,L^{-1}$) were continuously