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Adsorption of benzoic acid onto high specific area activated carbon cloth

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Abstract

The adsorption of benzoic acid from aqueous solution onto high area carbon cloth at different pH values has been studied. Over a period of 125 min the adsorption process was found to follow a first-order kinetics and the rate constants were determined for the adsorption of benzoic acid at pH 2.0, 3.7, 5.3, 9.1, and 11.0. The extents of adsorption and the percentage coverage of carbon cloth surfaces were calculated at 125 min of adsorption. Adsorption isotherms at pH values of 2.0, 3.7, and 11.0 were derived at 25 °C. Isotherm data were treated according to Langmuir and Freundlich equations and the parameters of these equations were evaluated by regression analysis. The fit of experimental isotherm data to both equations was good. It was found that both the adsorption rate and the extent of adsorption at 125 min were the highest at pH 3.7 and decreased at higher or lower pH values. The types of interactions governing in the adsorption processes are discussed considering the surface charge and the dissociation of benzoic acid at different pH values.

Keywords: Adsorption; Benzoic acid; Carbon cloth; Surface charge

1. Introduction

Adsorption of organic molecules from aqueous solution on activated carbon is a widely used method in raw and wastewater treatments and in food, beverage, pharmaceutical, and chemical industries [1]. The adsorption capacity of activated carbon is related to its surface area, pore structure, and surface chemistry. The surface chemistry of activated carbon is characterized by heteroatoms that compose the surface such as oxygen, nitrogen, hydrogen, sulfur, and phosphorous [2]. Those heteroatoms are in the form of functional groups such as ketones, carboxyls, phenols, ethers, lactones, or nitro groups and they have a significant effect on the chemical character, acidity, and degree of hydrophobicity of the carbon surface [3,4]. The characteristics of the adsorbate also influence the adsorption process. These characteristics are molecular size, solubility, pK, and the nature of adsorbate molecules. Ionic strength and pH of the medium affect the adsorption process by controlling electrostatic interactions between the adsorbent and the adsorbate. The carbon surface charge and the dissociation or protonation of the adsorbate are determined mainly by the pH of the solution. The carbon surface charge will be positive when the pH is lower than the pH at the point of zero charge of the surface (pH_{pzc}) and will be negative when pH is higher than pH_{pzc} [5].

Benzoic acid constitutes a simple model for complex matrices that may be present in the aqueous phase. Therefore there are many reports in the literature on the adsorption of benzoic acid from the aqueous phase on various materials such as activated carbon, synthetic calcite, soil, metal hydroxides, mineral surfaces, silica, calcite, dolomite, and some metal oxides [6–14]. In recent literature the use of high specific area carbon cloth appears to be an attractive alternative for selection of the adsorbent. For example, studies on adsorption and electrosorption at high area carbon cloth have been reported for various adsorbates such as inorganic S-containing anions [15], ethylxanthate and thiocyanate [16,17], phenol, phenoxide and chlorophenols [18], some aromatic heterocyclic compounds [19], pyridine [20], and some pesticides [21,22] in relation to wastewater purification.

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The aim of the present study is to determine the kinetics and equilibrium states of adsorption of benzoic acid onto high specific surface area activated carbon cloth. A systematic study is conducted in order to observe the influence of pH on the adsorption process.

2. Materials and methods

2.1. Materials

The carbon cloth used in the present work was obtained from Spectra Corp. (MA) coded as Spectracarb 2225, having a specific area of 2500 $m^2\,g^{-1}$ (measured using the Kr, BET method by the manufacturer). Benzoic acid, hydrochloric acid, and sodium hydroxide were obtained from Merck (Germany). Deionized water was used in the adsorption experiments.

2.2. Treatment of the carbon cloth

The carbon cloth material was found [15] to provide spontaneously a small but significant quantity of ions into the conductivity water used, probably due to its complex structure originating from its somewhat unknown proprietary preparation procedure. A deionization cleaning procedure was therefore applied, as described previously to avoid desorption of ions during the adsorption measurements [15].

In this procedure, a carbon cloth sample was placed in a flow-through washing cup and eluted with 5 L of warm (60 °C) conductivity water in a kind of successive batch operation for 2 days with N_2 bubbling in order to avoid possible adsorption of CO_2 that might have been dissolved in water. The outflow water from each batch was tested conductometrically for completeness of the washing procedure. The washed carbon cloth modules were then dried under vacuum at 120 °C and kept in a desiccator for further use. The carbon cloth was cut to desired dimensions (about 0.5×1.5 cm) and weighed accurately.

2.3. Adsorption cell

A specially designed cell was used to carry out the adsorption studies and simultaneously to perform in situ concentration measurements by means of UV absorption spectrophotometry. The cell (Fig. 1) was V shaped with one arm containing the carbon cloth attached to a short Pt wire sealed to a glass rod and the other arm containing a thin glass tube through which N_2 gas was passed for the purposes of mixing and eliminating any dissolved CO_2. The two arms were connected to a glass joint leading to a vacuum pump at the upper part of the V-shaped cell in order to provide the opportunity for initial outgassing of the carbon adsorbent, and the cell and solution. A quartz spectrophotometer cuvette was sealed to the bottom of the adsorption cell.

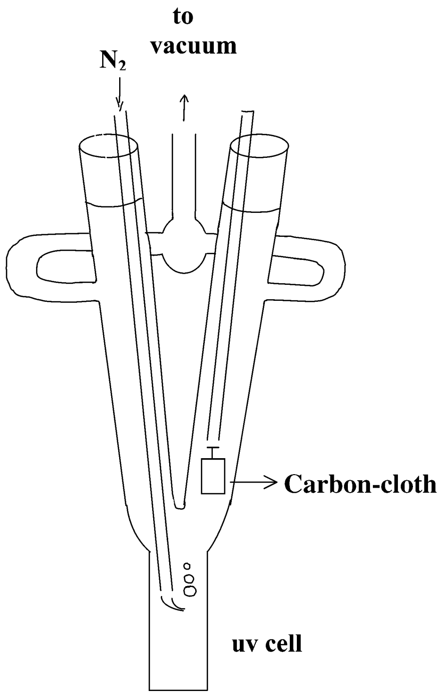

Fig. 1. Diagram of the adsorption cell.

2.4. Optical absorbance measurements

Adsorbate solutions were prepared by dissolving a fixed amount of benzoic acid in water and adjusting the pH to 2.0, 3.7, 5.3, 9.1, and 11.0 by additions of 0.1 M HCl or 0.1 M NaOH and diluting to a final volume to keep the benzoic acid concentration the same in all solutions. pH values of solutions were measured with a pH meter (Jenway 3040 ion analyzer). Calibration curves were prepared at each pH value to convert the absorbance data of kinetic and equilibrium experiments to concentration data. A Shimadzu 160A UV/Vis spectrophotometer was used for optical absorbance measurements. The absorbance measurements were conducted in situ during the study of the kinetics of adsorption process as follows. In all experiments, the size and the mass of the carbon cloth were kept as constant as possible (about 18.0 ± 0.1 mg). Its mass was accurately measured and recorded each time for calculation of fractional coverage, θ, or the amount of adsorption per unit area, M, of the carbon cloth. Carbon cloth pieces were prewetted by leaving in water for 24 h before use. The idea of using prewetted carbon cloth originates from our previous findings that prewetting enhances the adsorption process [15,16].

Carbon cloth was dipped into the adsorption cell initially containing only water and vacuum was applied to remove all air in the pores of the carbon cloth. Then wetted and degassed carbon cloth was removed from the cell for a short time and water in the cell was replaced with a known volume of sample solution (20 mL). The sliding door of the sample compartment of the spectrophotometer was left half open and the quartz cuvette fixed at the bottom of the adsorption cell (which now contained the sample solution) was