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Adsorption of aromatic organic acids onto high area activated carbon cloth in relation to wastewater purification

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Abstract

Adsorption of aromatic organic acids: benzoic acid (BA), salicylic acid (SA), *p*-aminobenzoic acid (*p*ABA) and nicotinic acid (NA), onto high area activated carbon cloth from solutions in 0.4 M H_2SO_4, in water at natural pH, in 0.1 M NaOH and also from solutions having pH 7.0 were studied by in situ UV-spectroscopic technique. The first-order rate law was found to be applicable for the kinetic data of adsorption. The rates and extents of adsorption of the organic acids were the highest from water or 0.4 M H_2SO_4 solutions and the lowest from 0.1 M NaOH solution. The order of rates and extents of adsorption of the four organic acids in each of the four solutions (0.4 M H_2SO_4, water, solution of pH 7.0 and 0.1 M NaOH) was determined as SA > BA > NA ∼ *p*ABA. These observed orders were explained in terms of electrostatic, dispersion and hydrogen bonding interactions between the surface and the adsorbate species, taking the charge of the carbon surface and the adsorbate in each solution into account. Adsorption of BA in molecular form or in benzoate form was analyzed by treating the solution as a mixture of two components and applying Lambert–Beer law to two-component system. The adsorption isotherm data of the systems studied were derived at 30 °C and fitted to Langmuir and Freundlich equations.

Keywords: Activated carbon cloth; Adsorption; Aromatic organic acids; UV spectroscopy; Ionization; Wastewater purification

1. Introduction

Benzoic acid and its derivatives are commonly used as a preservative or reaction intermediate, as well as antiseptic agents in various industrial branches such as food, pharmaceutics, textile and cosmetic. Therefore they are often found in domestic and industrial wastewaters [1–3]. Salicylic acid is used today in wart-removing medicines, to externally treat fungus infections, as an acne topic treatment and to increase the cell turnover as a component of skin creams. Other applications of salicylic acid are related to the plant protection against insects and pathogens. Salicylic acid may enter the environment through a variety of sources including homes, hospitals, animal feeding operations and pharmaceutical manufactures [4]. Salicylic acid is also used as an intermediate in the manufacture of dyes [5].

Because of their harmful effects, wastewaters containing aromatic acids must be treated before discharging to receiver water bodies. Popular treatment processes are destruction of these compounds by biological degradation or chemical oxidation and removal of them by adsorption [1]. For the treatment by adsorption, some of the main adsorbents in commercial and laboratory use include activated carbon, alumina, silica, bentonite, peat, chitosan and ion-exchange resins [6].

Activated carbon is one of the oldest and the most widely used adsorbents for the adsorption of organic compounds. It has been utilized in powder or granular form. These forms have been the primary adsorbent material for many adsorption studies on organics [7–11]. In recent years, activated carbon cloth or fiber has received considerable attention as a potential adsorbent for water treatment applications. These materials in the form of felt or cloth have the advantages of having high specific surface area (as high as 2500 $m^2\ g^{-1}$), mechanical integrity, easy handling and minimal diffusion limitation to adsorption [12].

Activated carbon cloth has been used for successful adsorptive removal of various inorganic anions. Adsorption of related sulfur containing anions onto carbon cloth was reported by Ayranci and Conway [13]. Sulfide and thiocyanate anions were

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found to be adsorbed to greater extents than others. A reduction of 68% in SCN^- concentration was achieved on open circuit with 0.5 g activated carbon cloth from 20 mL 5×10^{-4} M solution. This degree of removal was increased to 95% upon polarization of carbon cloth. Adsorbability of such impurity ions was related to their hydration properties in water. Afkhami [14] reported adsorptive and electrosoprtive removal of some other oxyanions by activated carbon cloth. It was concluded that carbon cloth was an effective sorbent for Cr(VI), Mo(VI), W(VI) and V(V) ions and acidification of the solution significantly increased adsorption of investigated ions except V(IV). Therefore it was suggested that the method provides an interesting mean for separation of V(IV) and V(V) species in solution. Afkhami and Conway [15] achieved lowering of initial 1×10^{-4} M concentration of $NO_3{}^-$ and $NO_2{}^-$ by 22 and 10%, respectively, using the method of adsorption onto carbon cloth. Adsorption and electrosorption of another noxious sulfur containing anion, ethyl xanthate, onto carbon cloth was studied by Ayranci and Conway [16] and the results were compared with those of SCN^-. The possibility of using carbon cloth for effective and selective separation of anions was demonstrated. Increase in adsorbability upon pre-wetting of carbon cloth was first noted in this work. Successful use of activated carbon cloth for adsorptive removal of various groups of organic compounds has also been demonstrated. A series of phenolic and anilinic compounds were studied for their removal from aqueous solutions by adsorption onto activated carbon cloth [17–21]. Kinetic and equilibrium aspects of adsorption were given in these works. A similar adsorption work onto activated carbon cloth was also carried out by Conway et al. [22] for a series of aromatic heterocyclic compounds. Thiophene was found to exhibit the highest adsorption rate among seven compounds studied. This was attributed to the presence of electron donative S heteroatom in the structure of thiophene. The influences of dipole moment, the orientation at the carbon cloth surface and the size of the compound as well as the type of heteroatom in the ring and the adsorbates' hydration parameters, on the extent of adsorption of these compounds at the carbon cloth were investigated. Niu and Conway [23] have taken pyridine alone and investigated an extensive study on its adsorption and electrosorption on carbon cloth. The present work takes another important group of compounds, aromatic organic acids, to investigate their adsorption behavior on activated carbon cloth.

The adsorption behavior of activated carbon from adsorbate solutions is affected by both the surface and the solution properties [10]. The presence of surface functional groups such as carboxyl, lactone, phenol, carbonyl, ether, pyrone and chromene, gives activated carbon an acid–base character [24]. Surface charge density is also an important factor in determining the adsorption characteristics of activated carbon. It is determined by the solution pH and by the parameter pH_{PZC} which is the pH of a solution when the net surface charge is zero. The net charge on carbon surface is positive at a solution pH lower than pH_{PZC} and is negative at a solution pH higher than pH_{PZC} [25]. Not only the net surface charge but also the amount of ionic species arising from ionizable adsorbates is determined by the pH of the solution. The pK_a or pK_b values of the ionizable molecule are also important together with the solution pH for determining the extent of ionization.

The purpose of the present work was to investigate the adsorption behaviors of benzoic acid (BA), salicylic acid (SA), *p*-aminobenzoic acid (*p*ABA) and nicotinic acid (NA) from aqueous solutions having a range of pH onto high area activated carbon cloth by means of in situ UV spectroscopy. The examination of the effect of ionization of these aromatic acids on their adsorption was also aimed.

2. Materials and methods

2.1. Materials

The activated carbon cloth (ACC) used in the present work was obtained from Spectra Corp. (MA, USA) coded as Spectracarb 2225. Benzoic acid and nicotinic acid (pyridine-3-carboxylic acid) were obtained from Merck, salicylic acid (*o*-hydroxy benzoic acid) from BDH and *p*-amino benzoic acid from Riedel-de Häen. NaOH, H_2SO_4, HCl, $NaHCO_3$, Na_2CO_3, HNO_3 and $NaNO_3$ were reagent grade. Deionized water was used in adsorption experiments.

2.2. Treatment and properties of the carbon cloth

The activated carbon fibers are known to provide spontaneously a small but significant quantity of ions into the conductivity water probably due to their complex structures originating from their somewhat unknown proprietary preparation procedure [13,26]. Therefore a deionization cleaning procedure was applied to avoid desorption of these ions during adsorption studies, as described previously [13,20,22]. 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 a series of batch operations for 2 days with N_2 bubbling in order to avoid possible adsorption of CO_2 that might have been dissolved in water. The out-flow 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 vacuum desiccator for further use.

The specific surface areas of the treated and untreated carbon cloth pieces were measured as 1870 and 2200 $m^2\,g^{-1}$, respectively, by N_2 adsorption isotherm method. (These measurements were done by central laboratory of Middle East Technical University, Ankara, Turkey, according to multipoint BET method.) There is an obvious decrease in specific surface area upon the washing treatment. A similar decrease was observed in surface area of granular activated carbon upon aqueous treatment by László et al. [27]. Pore size distribution measurements were also carried out in the same laboratory for the treated ACC. The pore volume distribution curve obtained according to density functional theory (DFT) is given in Fig. 1. Calculations have shown that the total pore volume is 0.827 $cm^3\,g^{-1}$. The portions of micro- and meso-pores in this total volume were found to be 0.709 and 0.082 $cm^3\,g^{-1}$, respectively. SEM pictures of treated (washed) carbon cloth were previously given [16]. The average