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Removal of anionic surfactants from aqueous solutions by adsorption onto high area activated carbon cloth studied by in situ UV spectroscopy

Erol Ayranci *, Osman Duman

Department of Chemistry, Akdeniz University, 07058 Antalya, Turkey

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Abstract

The removal of anionic surfactants, benzene sulfonate (BS), *p*-toluene sulfonate (TS), 4-octylbenzene sulfonate (OBS) and 4-dodecylbenzene sulfonate (DBS) from water and 0.01 M H_2SO_4 solutions by adsorption onto high area activated carbon cloth (ACC) were studied by in situ UV-spectroscopic technique. The various properties of the ACC were given and the in situ UV-spectroscopic technique was described. Both kinetic and isotherm data were obtained for the adsorption of surfactants. Kinetic data were treated according to intraparticle diffusion, pseudo-first-order, pseudo-second-order and Elovich models. They were found to fit the pseudo-second-order model best. Isotherm data were treated according to well-known Langmuir and Freundlich models. The regression analysis of the data showed that Freundlich model represents the isotherm data of the surfactants better. The rate and extent of adsorption of surfactants were found to increase in the order $BS < TS < OBS \sim DBS$. The main type of interaction between the ACC surface and surfactants was found to be of hydrophobic origin in H_2O solutions. The adsorption was found to be enhanced by the presence of 0.01 M H_2SO_4 in the surfactant solution due to electrostatic attractions between the negatively charged surfactant molecules and the ACC surface which acquired a net positive charge in acidic medium. An inert electrolyte such as NaCl was found to decrease the adsorption capacity of the ACC for the anionic surfactants.

Keywords: Adsorption; Removal; Surfactants; Activated carbon cloth; In situ UV spectroscopy; Benzene sulfonates

1. Introduction

Surfactants are classified into four groups based on charge possessed by the molecular chain; anionic, cationic, zwitterionic and non-ionic. Ionic surfactants constitute two-thirds of all surfactants and anionics constitute more than 90% of all ionics [1]. Anionic surfactants, having high degree of foaming capability, are extensively used in the production of toothpaste, soap, shampoo and many industrial detergents [2]. Surfactants are also being used in textile, food, dye, polymer, cosmetic, pesticide, mining and paper industries. Textile industry alone consumes about 10% of total surfactant products and discharges wastewaters containing considerable amounts of surfactants [3]. Surfactants in wastewaters can partly be biodegraded especially under aerobic conditions. However under anaerobic conditions they are not biodegradable and show adverse affects on aquatic life. Furthermore, they can act synergistically with some other toxic chemicals which may be present in wastewaters increasing their negative effects on the environment [1]. Therefore, the amount of surfactants present in wastewaters of many industries, especially detergent and textile, must be reduced at least to acceptable levels before discharging to the environment. The removal or destruction of surfactants from wastewaters can be achieved by methods such as chemical or electrochemical oxidation, membrane technology, chemical precipitation, photocatalytic degradation and adsorption or electrosorption onto various adsorbents. Adsorption is by far the most widely applied method among others [3].

Mishra et al. [4] reported the adsorption behavior of sodium dodecylbenzene sulfonate on raw and demineralized coal samples. The effects of surfactant concentration, temperature, pH and presence of electrolyte on adsorption were examined. There are some works in literature about the adsorption of surfactants on metal oxides [3,5–7]. However activated carbon materials are the most widely used adsorbents for the removal of surfactants from aqueous solutions by adsorption. Gonzalez-Garcia et al. [8]

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* Corresponding author. Tel.: +90 242 310 23 15; fax: +90 242 227 89 11.
E-mail address: eayranci@akdeniz.edu.tr (E. Ayranci).

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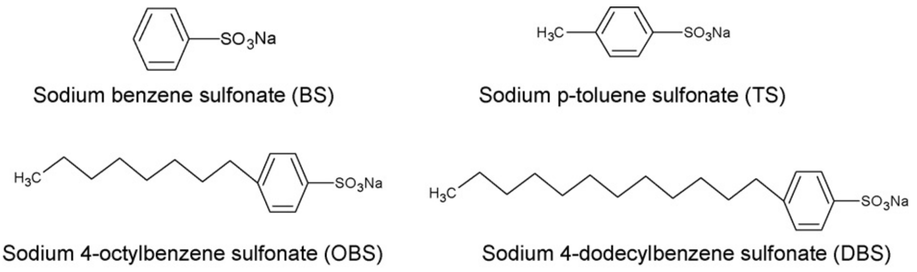

Sodium benzene sulfonate (BS)

Sodium p-toluene sulfonate (TS)

Sodium 4-octylbenzene sulfonate (OBS)

Sodium 4-dodecylbenzene sulfonate (DBS)

Fig. 1. Molecular structures of the surfactants.

studied the adsorption of sodium dodecyl sulfate onto a set of activated carbon from aqueous solutions and derived adsorption isotherms. Basar et al. [9] reported removal of surfactants by powdered activated carbon and microfiltration. Zor [10] investigated the adsorption of anionic surfactants at different pH values by means of activated carbon. Gupta et al. [1] examined the performance of waste activated carbon as a low-cost adsorbent for the removal of anionic surfactants from aquatic environment. Paria and Khilar [11] reviewed experimental studies of surfactant adsorption at the hydrophilic solid–water interface and suggested a four-regime mechanism for the adsorption of surfactants.

The purpose of the present study is to investigate the adsorption characteristics of some anionic surfactants onto high specific surface area activated carbon cloth by in situ UV-spectroscopic technique in relation to wastewater purification. This is a continuation of the series of works being carried out in our laboratories for the removal of various groups of hazardous compounds such as aromatic organic acids [12,13], phenolics [14], anilinics [15,16], heterocyclics [17], pesticides [18] and dyes [19]. Two important characteristics of these works are the use of high specific surface area activated carbon cloth as the adsorbent and the application of the so-called in situ UV-spectroscopic technique to monitor the adsorption process from the beginning till the equilibrium while the adsorption process is in progress.

2. Materials and methods

2.1. Materials

The activated carbon cloth (ACC) was obtained from spectra Corp. (MA, USA) coded as Spectracarb 2225. Although the full details of its mode of preparation are regarded as proprietary, it originates by pyrolysis of phenolic polymer fibers followed by heat treatment in O_2-free N_2 between 800 and 900 °C for some hours. In this respect, it differs from other fibrous materials derived by pyrolysis of rayon [20].

Anionic surfactants chosen to study in this work are benzene sulfonate (BS), *p*-toluene sulfonate (TS), 4-octylbenzene sulfonate (OBS) and 4-dodecylbenzene sulfonate (DBS). They were obtained from Aldrich in the form of sodium salts. The molecular structures of them are given in Fig. 1. All chemicals used in this study were reagent grade and the water was deionized.

2.2. Treatment and properties of the ACC

The ACC was found to provide spontaneously a small but significant quantity of ions into the conductivity water in our earlier work [21]. These ions are expected to be introduced into the fibers of the ACC during the activation process. Therefore a deionization cleaning procedure was applied to avoid desorption of these ions during adsorption studies. A carbon cloth sample having an approximate apparent area of $250\,cm^2$ was placed in a flow-through washing cup and washed, batchwise, with a total of 5 L of warm (60 °C) conductivity water for 2 days with N_2 bubbling to exclude CO_2 and O_2. Outcoming water from each batch was tested conductometrically for completeness of washing. The washed ACC modules were then dried under vacuum at 120 °C and kept in desiccator for use in adsorption studies.

Various properties of an adsorbent must be known in order to evaluate and interpret the kinetic and equilibrium data of adsorption. Some of these properties were determined for the ACC used in this work with methods described in detail in our earlier works such as specific surface area, micropore volume, mesopore volume [12], average fiber diameter [14], elemental analysis [12], point of zero charge (pH_{PZC}) [14,15], acidic and basic group contents [12]. Numerical values for these properties are given in Table 1. Pore size distribution curve of the ACC used in this work was given in our earlier works [12,15].

2.3. The monitoring of adsorption by in situ UV spectroscopy

In situ UV-spectroscopic technique as described in detail in our earlier works [14,15,21] was applied in monitoring the adsorption process. As a non-destructive analytical technique, it allows the adsorption process to be monitored continuously from the beginning till the equilibrium. It utilizes a specially designed adsorption cell which is V-shaped containing an ACC piece attached to a short Pt wire sealed to a glass tubing in one arm, a N_2 bubbling tube in the other arm and a quartz UV-cuvette sealed at the bottom.

A Carry 100 model UV–vis spectrophotometer interfaced to a computer was used for optical absorbance measurements. The absorbance determinations were conducted in situ during the study of the adsorption process by the following procedure. A piece of the ACC accurately weighed and pre-wetted more than a day was placed in the adsorption cell as described above. The idea of using the pre-wetted ACC originates from our previ-