

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

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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 H₂SO₄ 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 ~ DBS. The main type of interaction between the ACC surface and surfactants was found to be of hydrophobic origin in H₂O solutions. The adsorption was found to be enhanced by the presence of 0.01 M H₂SO₄ 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.

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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 effects 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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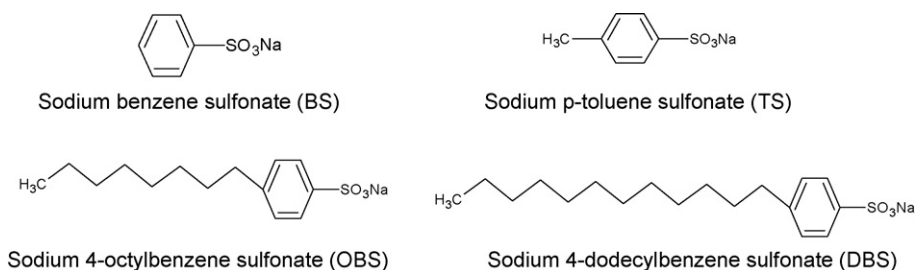


Fig. 1. Molecular structures of the surfactants.

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], anilines [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 O₂-free N₂ 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 cm² 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 N₂ bubbling to exclude CO₂ and O₂. 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 N₂ 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-

Table 1
Properties of activated carbon cloth (washed)

Specific surface area	1870 m ² g ⁻¹
Ratio of apparent surface area to the total BET surface area	4.1 × 10 ⁻⁶
Total pore volume	0.827 cm ³ g ⁻¹
Micropore volume	0.709 cm ³ g ⁻¹
Mesopore volume	0.082 cm ³ g ⁻¹
Average fiber diameter	17 μm
Carbon content	95.14%
Hydrogen content	0.37%
Oxygen content	4.49%
Nitrogen and sulfur content	0%
pH _{PZC}	7.4
Total acidic group content	0.25 mmol g ⁻¹
Carboxylic group content	0.093 mmol g ⁻¹
Lactonic group content	0.020 mmol g ⁻¹
Phenolic group content	0.14 mmol g ⁻¹
Total basic group content	0.28 mmol g ⁻¹

ous findings that pre-wetting enhances the adsorption [21,22]. The surfactant solution was then introduced into the cell and evacuation was applied to the whole cell in order to remove air from pores of the ACC and to achieve access of solution to the whole carbon surface. The sliding door of the sample compartment of the spectrophotometer was left half-open and the quartz cuvette fixed at the bottom of adsorption cell containing the adsorbent ACC and the adsorbate surfactant solution. N₂ was bubbled through the solution continuously for mixing the solution and eliminating CO₂ or O₂. Then an opaque curtain was spread above the sample compartment of the spectrophotometer, over the cell, to prevent interference from the external light.

The scanning-kinetics program for monitoring the absorbance of the specific surfactant was then run on the computer. This program enabled the absorbance spectrum to be recorded over a pre-selected, limited wavelength range in programmed time intervals (1 min). In this way, it was possible to record as many as 1000 data points for an adsorption period of 1000 min. This is one of the most important advantages of in situ UV spectroscopic technique as applied in scanning-kinetics mode. In most classical adsorption studies, batch analysis method is employed. In this method, samples are withdrawn from the adsorption system at certain time intervals and analyzed separately. Usually 10–20 data points are obtained for most kinetic studies. Each sample withdrawal, of course, destructs the main adsorption system.

A typical scanning kinetic output obtained during the adsorption of OBS from water onto the ACC was reproduced in Fig. 2 in which only scans in 5 min intervals are shown. The downward movement of the absorbance maximum at 224 nm as the adsorption goes on is clearly seen in this figure and marked by an arrow. Any change in spectrum during the process could be seen in such a scanning-kinetic output. After completion of the adsorption run, a separate absorbance versus time curve could be printed at any wavelength in the scanned range. This wavelength is usually the one at maximum absorbance (λ_{max}) unless there is change in spectrum such as shift in λ_{max} .

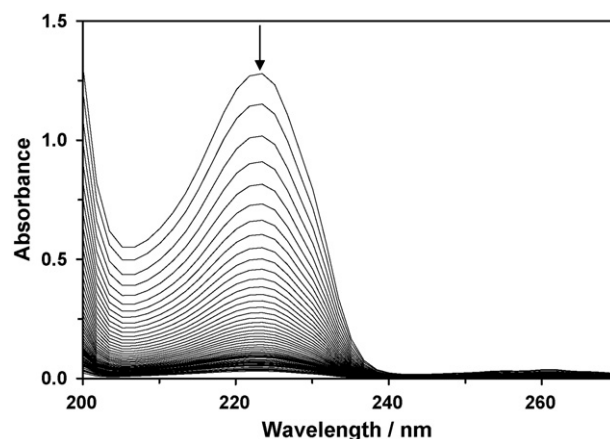


Fig. 2. A typical scanning kinetic output for the adsorption of OBS in 5 min intervals over 300 min. Initial concentration: 1×10^{-4} M, solvent: H₂O. Arrow shows the direction of movement of absorbance maximum with adsorption.

Absorbance data were converted into concentration data using calibration relations pre-determined at the wavelength of maximum absorbance for each surfactant.

2.4. Determination of adsorption isotherms

The adsorption isotherms of surfactants were determined on the basis of batch analysis. The ACC pieces of varying masses were allowed to equilibrate with solutions of surfactants in water, in 0.005 M NaCl, in 0.01 M NaCl or in 0.01 M H₂SO₄ with known initial concentrations at 30 °C for 48 h. Preliminary tests showed that the concentration of adsorbates remained unchanged after 20–24 h contact with the ACC. So, the allowed contact time of 48 h ensures the equilibration. Hundred millilitres Erlenmeyer flasks containing the ACC and adsorbate solution were kept in Nüve ST 402 shaking water bath at a constant shaking speed of 150 rpm for equilibration. The concentrations at the end of equilibration period were measured spectrophotometrically. The amount of surfactant adsorbed per unit mass of the ACC at equilibrium, q_e , was calculated by Eq. (1):

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where V is the volume of the solution of surfactant (L), C_0 and C_e are the initial and equilibrium concentrations, respectively (mM) and m is the mass of the ACC (g). Then Eq. (1) gives q_e in mmol surfactant adsorbed per gram ACC.

3. Result and discussion

3.1. Chemical nature, optical absorbance characteristics and calibration data of the surfactants

Two of the four surfactants studied; OBS and DBS, contain long hydrocarbon chain in their structures (Fig. 1). The critical micelle concentration (CMC) of DBS is 1.4×10^{-3} M [23]. That of others is expected to be higher. The initial concentrations of surfactants were kept well below their CMC

Table 2
Absorbance and calibration data of surfactants

Adsorbate	Solvent	λ_{\max} (nm)	ϵ (cm ⁻¹ M ⁻¹)	r
BS	H ₂ O	212	7,800	0.9991
	0.01 M H ₂ SO ₄	212	7,800	0.9994
TS	H ₂ O	222	10,300	0.9994
	0.01 M H ₂ SO ₄	222	10,100	1.000
OBS	H ₂ O	224	12,700	0.9995
	0.01 M H ₂ SO ₄	224	12,700	0.9993
DBS	H ₂ O	224	10,500	0.9995
	0.01 M H ₂ SO ₄	224	10,600	0.9997

in adsorption studies. The reason for this is that the system becomes heterogeneous above CMC in which in situ analysis of adsorbate solutions by UV spectroscopy cannot be free from errors that might be even more serious at higher concentrations.

All of the surfactants are more than 99% in monovalent anionic sulfonate form in water. The adsorption of them was studied both in water and in 0.01 M H₂SO₄ solutions. The reason for selection of 0.01 M H₂SO₄ solution for adsorption medium is to lower the pH of solution well below 7.4, pHPZC of the ACC (Table 1), thus to make the ACC surface positively charged while keeping the surfactants still 99% in anionic sulfonate form with the expectation that the electrostatic attractions between the surface and the surfactant would enhance the adsorption.

Optical absorbance characteristics and calibration data of the surfactants both in H₂O and in 0.01 M H₂SO₄ are given in Table 2. These data include the wavelength of maximum absorbance (λ_{\max}), the molar absorptivity (ϵ) and the regression coefficient (r).

3.2. Adsorption behaviors and kinetics of surfactants

The adsorption behaviors of surfactants from water solutions onto the ACC over about 1000 min are shown in Fig. 3. The

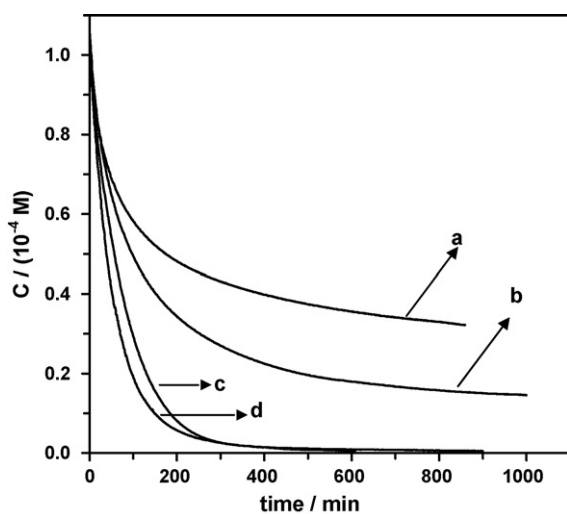


Fig. 3. Adsorption behaviors of (a) BS, (b) TS, (c) DBS and (d) OBS from water solutions. Initial concentration: 1×10^{-4} M, the amount of ACC: 18.3 mg, the volume of adsorbate solution: 20 mL.

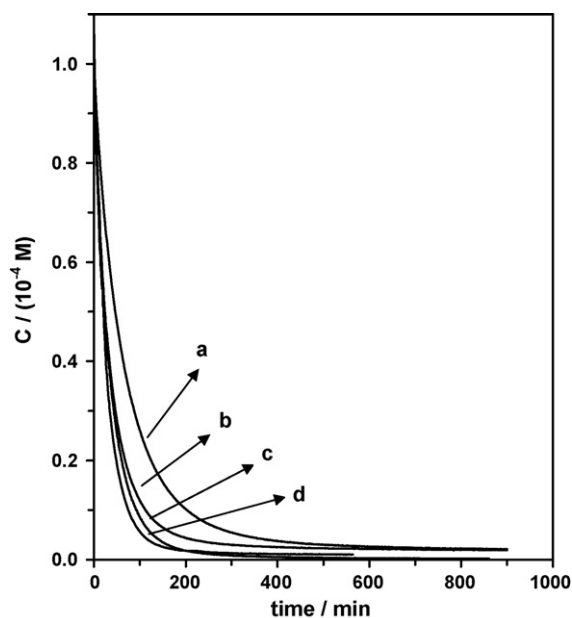


Fig. 4. Adsorption behaviors of (a) BS, (b) TS, (c) OBS and (d) DBS from 0.01 M H₂SO₄ solutions. Initial concentration: 1×10^{-4} M, the amount of ACC: 18.3 mg, the volume of adsorbate solution: 20 mL.

lowest rate and extent of adsorption is observed with BS and then comes TS. OBS and DBS show the highest rate and extent of adsorption. Furthermore, it is seen that the latter two surfactants have very similar adsorption behaviors. The higher rates and extents of adsorption of OBS and DBS can be attributed to the presence of hydrophobic long chain hydrocarbons in the structures of these molecules (Fig. 1). This shows that predominant interaction between the surface and the surfactants is hydrophobic in water solutions. The pH of these adsorbate solutions in water is around 6, close to the pHPZC of the ACC surface. Therefore, although we cannot exclude the electrostatic interactions, they are of secondary importance compared to hydrophobic interactions in adsorption from H₂O solutions. Absence of hydrocarbon chains in the structures of BS and TS weakens the hydrophobic interactions and explains the lower rates and extents of adsorption of these two surfactants compared to OBS and DBS. When the rate and extent of adsorption of BS and TS are compared with each other it can clearly be seen from Fig. 3 that just a single hydrophobic -CH₃ group present in the structure of TS causes a considerable enhancement in its adsorption compared to BS in which there is no hydrophobic substituent in phenyl group.

In order to see the effect of electrostatic interactions, adsorption experiments were repeated from 0.01 M H₂SO₄ solutions. The results are given in Fig. 4. While the surfactants maintain their single negative charge in 0.01 M H₂SO₄ solutions, the net charge on the surface of the ACC becomes positive since the pH of solution is now much less than pHPZC in this case [24]. It is clear from Fig. 4 that the rates and extents of adsorption of all surfactants increased considerably due to the electrostatic interactions between the positively charged ACC surface and the negatively charged surfactants in addition to the hydrophobic interactions discussed above.

Table 3

The parameters of kinetic models for the adsorption of surfactants onto the ACC obtained by linear regression analysis of experimental data

Adsorbate	Solvent	Pseudo-first-order		Pseudo-second-order			Elovich equation		
		k_1 (min ⁻¹)	r	k_2 (g (mmol min) ⁻¹)	h ($\times 10^3$ mmol (g min) ⁻¹)	r	α (g (mmol min ²) ⁻¹)	β ($\times 10^3$ mmol (g min) ⁻¹)	r
BS	H ₂ O	0.00501	0.9542	0.16400	1.0975	0.9996	24.261	13.8	0.9950
BS	0.01 M H ₂ SO ₄	0.0073	0.9857	0.275825	3.5878	0.9996	52.150	17.5	0.9344
TS	H ₂ O	0.0056	0.9736	0.13164	1.5152	0.9999	17.8995	18.1	0.9855
TS	0.01 M H ₂ SO ₄	0.0062	0.9499	0.79000	11.145	0.9999	1885.65	12.5	0.8635
OBS	H ₂ O	0.0121	0.9876	0.248517	3.5038	0.9976	30.1000	20.3	0.9474
OBS	0.01 M H ₂ SO ₄	0.0063	0.9240	0.824073	10.345	0.9998	1030.24	12.6	0.8514
DBS	H ₂ O	0.0078	0.9702	0.239239	3.3842	0.9992	31.1840	19.5	0.9276
DBS	0.01 M H ₂ SO ₄	0.0117	0.9534	0.908341	11.138	0.9997	445.672	14.2	0.8709

It is to be noted that size factors may also become important in determining the extent of adsorption. In order to examine the effects of size factors one must have an idea about the pore sizes of the adsorbent and molecular sizes of the adsorbates. Assuming the adsorbates studied in this work to have a cylindrical shape, the approximate diameters and heights of them could be calculated using a program called ChemSketch. This treatment showed that the diameters of all the adsorbates were determined by the width of the benzene ring and found to be about 4.8 Å. The heights were 7.04, 8.04, 15.09 and 20.21 Å for BS, TS, OBS and DBS, respectively. On the other hand the percentage of total pores of the ACC having pore size greater than 4.8 Å was 98 as deduced from the pore size distribution curve given in our earlier works [12,15]. The same percentages for pore sizes greater than 7, 8, 15 and 20 Å were 80, 75, 16 and 3, respectively. Here, the orientation of presumably cylindrical molecules is important during their diffusion into the pores. If they take vertical orientation, it seems that almost 98% of the pores are accessible to all the adsorbate molecules. Since the longer molecules OBS and DBS are found to have higher extents of adsorption, the vertical orientation assumption is true. Thus the extents of adsorption are mainly determined by the various interactions discussed above rather than by the size factors.

Enormous amount of data obtained for the adsorption of surfactants (around 1000 concentration versus time data points for each surfactant obtained in 1 min intervals) allowed us to make a detailed kinetic analysis. This was only possible with the in situ UV spectroscopic technique described briefly above and in detail in our previous works [13,14,17]. Four kinetic models were tested to fit the experimental data points; intraparticle diffusion, pseudo-first-order, pseudo-second-order and Elovich models. Mathematical expressions of these models are given in Eqs. (2)–(5), respectively [25–28]:

$$q_t = k_1 t^{0.5} \quad (2)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$q_t = \beta \ln(\alpha \beta) + \beta \ln t \quad (5)$$

where q_t and q_e are the amounts of surfactant adsorbed at time t and at equilibrium, respectively. k_i is the intraparticle diffusion constant. k_1 and k_2 are pseudo-first- and pseudo-second-order rate constants, respectively. The product $k_2 q_e^2$ in Eq. (4) is usually symbolized by h and termed as initial sorption rate. α and β are Elovich coefficients representing initial sorption rate and desorption constants, respectively.

The plot of q_t versus $t^{0.5}$ for intraparticle diffusion model gave a very poor linear fit. Therefore the results of this treatment were not given and it was concluded that the intraparticle diffusion model is not the rate controlling step. In order to test the other models, linear regression analysis was applied to $\ln(q_e - q_t)$ versus t data for pseudo-first-order, t/q_t versus t data for pseudo-second-order and q_t versus $\ln t$ data for Elovich models. The parameters of the respective models according to this analysis are given in Table 3 together with regression coefficients. The poorest fit is obtained for Elovich model and the best fit is for pseudo-second-order model according to regression coefficients.

The supporting evidence for the best fit by pseudo-second-order model comes from comparison of q_e values obtained from regression analysis and experimental q_e values reached at the end of long adsorption run shown in Figs. 3 and 4. This comparison can be seen in Table 4 with the parameters of percent deviation between experimental q_e values and the predicted q_e values according to each model. It is clearly seen that percent deviations are much smaller for pseudo-second-order model than pseudo-first-order model. So, it can be concluded that the kinetic of adsorption of surfactants onto the ACC from water or 0.01 M H₂SO₄ solutions obeys the pseudo-second-order model.

3.3. Adsorption isotherms

Isotherm data for the adsorption of surfactants from water and 0.01 M H₂SO₄ solutions at 30 °C were derived according to the method described in Section 2.4. The isotherm data were also derived for the adsorption from aqueous solutions of these surfactants in the presence of 0.005 M and 0.01 M NaCl in order to make the system more real and to see the effect of ionic strength on adsorption. All the isotherm data were treated according to the two well-known isotherm models: Langmuir and Freundlich. The linearized forms of Langmuir and Freundlich isotherm

Table 4
Comparison of experimental and predicted q_e values from pseudo-first-order and pseudo-second-order models for the adsorption of surfactants onto the ACC

Adsorbate	Solvent	$(q_e)_{\text{experimental}}$	$(q_e)_{\text{first-order}}$	Deviation (%)	$(q_e)_{\text{second-order}}$	Deviation (%)
BS	H ₂ O	0.07634	0.00501	+93.4	0.08181	+7.17
BS	0.01 M H ₂ SO ₄	0.10923	0.0073	−93.3	0.11405	+4.41
TS	H ₂ O	0.0999	0.0056	−94.4	0.10729	+7.40
TS	0.01 M H ₂ SO ₄	0.1171	0.0062	−94.7	0.11878	+1.43
OBS	H ₂ O	0.1108	0.0121	−89.1	0.11874	+7.17
OBS	0.01 M H ₂ SO ₄	0.1103	0.0063	−94.3	0.11204	+1.58
DBS	H ₂ O	0.1131	0.0078	−93.1	0.11894	+5.16
DBS	0.01 M H ₂ SO ₄	0.1082	0.0117	−89.2	0.11074	+2.35

equations are given in Eqs. (6) and (7), respectively [29,30]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \quad (6)$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (7)$$

where q_e and C_e are the amount of surfactant adsorbed per gram of the ACC and concentration of surfactant in adsorbate solution at equilibrium, respectively. q_{\max} is the maximum adsorption at monolayer coverage, b the adsorption equilibrium constant related to the energy of adsorption, K_F the Freundlich constant representing the adsorption capacity and n a constant related to surface heterogeneity.

Experimental isotherm data at 30 °C were fitted to Langmuir and Freundlich equations by linear regression analysis: C_e/q_e versus C_e for Langmuir and $\ln q_e$ versus $\ln C_e$ for Freundlich models. The best fitted parameters together with regression coefficients are given in Table 5. It is seen that the regression coefficients, being all greater than 0.98 are not decisive about which model represent the experimental data better. A better criterion for the assessment of experimental isotherm data is a parameter known as normalized percent deviation [31] or in some literature as percent relative deviation modulus, P , [32,33] defined by the following equation:

$$P = \frac{100}{N} \sum_{i=1}^N \frac{|q_{e(\text{pred})} - q_{e(\text{exp})}|}{q_{e(\text{exp})}} \quad (8)$$

Table 5
The parameters of Langmuir and Freundlich equations obtained by linear regression analysis of adsorption isotherm data at 30 °C

Adsorbate	Solvent	Langmuir parameters				Freundlich parameters			
		q_{\max} (mmol g ^{−1})	b (L mmol ^{−1})	r	P	K_F (mmol g ^{−1}) (L mmol ^{−1}) ^{1/n}	$1/n$	r	P
BS	H ₂ O	0.3009	22.24	0.9878	2.784	0.7158	0.5116	0.9901	2.568
BS	0.01 M H ₂ SO ₄	0.5584	97.45	0.9971	4.209	0.8129	0.1995	0.9898	1.725
TS	H ₂ O	0.3244	46.41	0.9848	4.597	0.7916	0.4177	0.9869	2.993
TS	0.01 M H ₂ SO ₄	0.6013	313.2	0.9993	7.045	0.8349	0.1377	0.9910	1.825
OBS	H ₂ O	1.223	101.4	0.9920	8.975	2.299	0.2824	0.9935	2.263
OBS	0.005 M NaCl	1.063	195.9	0.9971	11.42	1.853	0.2267	0.9909	3.275
OBS	0.01 M NaCl	1.017	189.1	0.9975	10.59	1.723	0.2207	0.9901	3.177
OBS	0.01 M H ₂ SO ₄	1.477	184.5	0.9935	10.45	2.709	0.2434	0.9791	4.887
DBS	H ₂ O	1.136	137.6	0.9931	8.818	2.408	0.2931	0.9926	3.135
DBS	0.005 M NaCl	1.003	188.2	0.9953	12.68	1.8653	0.2452	0.9889	3.671
DBS	0.01 M NaCl	0.9137	206.5	0.9976	10.10	1.655	0.2329	0.9868	4.263
DBS	0.01 M H ₂ SO ₄	1.388	139.8	0.9802	16.94	2.657	0.2691	0.9848	4.131

where $q_{e(\text{exp})}$ is the experimental q_e at any C_e , $q_{e(\text{pred})}$ the corresponding predicted q_e according to the equation under study with the best fitted parameters and N is the number of observations. It is clear from Eq. (8) that the lower the P -value, the better is the fit. It is generally accepted that when the P -value is less than 5, the fit is considered to be excellent [32].

The P -values for Freundlich model (Table 5) are seen to be much lower than those for Langmuir model and are also all well below the value of 5. Therefore it can be concluded that Freundlich model represents the experimental isotherm data of surfactants at 30 °C better than Langmuir model. The best fitted isotherm curves of BS, TS, OBS and DBS in H₂O and in 0.01 M H₂SO₄ according to Langmuir and Freundlich models together with experimental data points are reproduced in Figs. 5–8, respectively. The better fit of Freundlich equation than Langmuir equation to the experimental isotherm data can clearly be seen from these figures.

In Figs. 7 and 8, the Langmuir and Freundlich isotherms for adsorption of the two anionic surfactants from 0.005 M NaCl and 0.01 M NaCl solutions are also presented. It is clear that there is a slight decrease in the extent of adsorption at equilibrium along the equilibrium concentration range studied in the presence of 0.005 M NaCl. Furthermore, it is also noticeable that there is some further slight decrease in the extent of adsorption when the concentration of NaCl is increased to 0.01 M. This can be attributed to a slight weakening of the ionic field of the surfactants in the presence of an inert electrolyte such as NaCl.

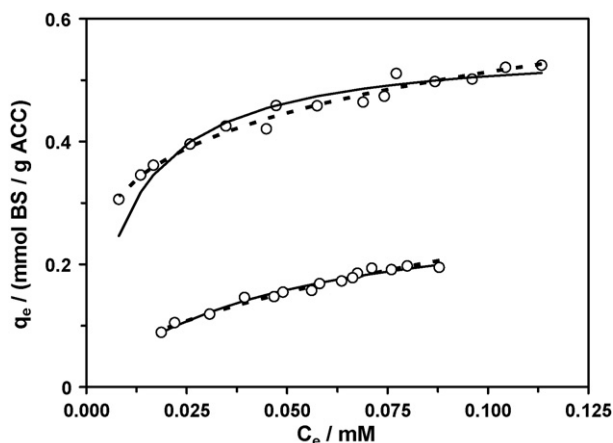


Fig. 5. The isotherm for the adsorption of BS from H_2O (upper curves and data) and from $0.01 M H_2SO_4$ solutions (lower curves and data). (—) Langmuir isotherms, (---) Freundlich isotherms, (○) experimental data points.

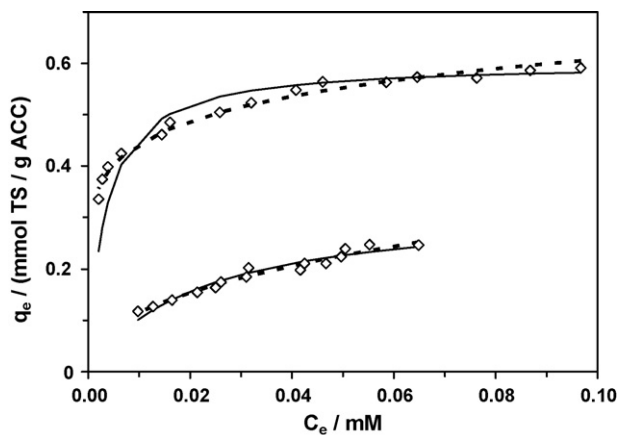


Fig. 6. The isotherm for the adsorption of TS from H_2O (upper curves and data) and from $0.01 M H_2SO_4$ solutions (lower curves and data). (—) Langmuir isotherms, (---) Freundlich isotherms, (◇) experimental data points.

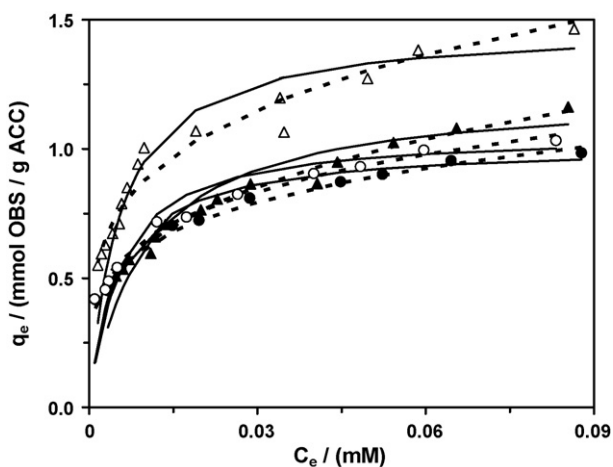


Fig. 7. The isotherm for the adsorption of OBS from H_2O (▲), from $0.01 M H_2SO_4$ (△), from $0.005 M NaCl$ (○) and from $0.01 M NaCl$ (●). (—) Langmuir isotherms, (---) Freundlich isotherms.

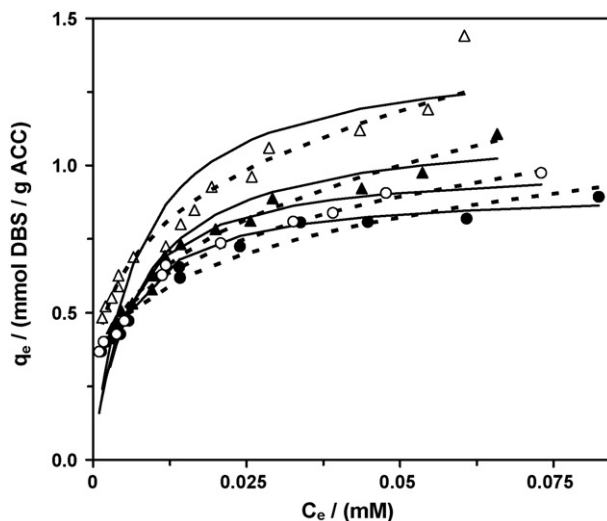


Fig. 8. The isotherm for the adsorption of DBS from H_2O (▲), from $0.01 M H_2SO_4$ (△), from $0.005 M NaCl$ (○) and from $0.01 M NaCl$ (●). (—) Langmuir isotherms, (---) Freundlich isotherms.

The parameters q_{max} and K_F in Table 5 are measures of the adsorption capacity of the ACC for the surfactants studied. It is seen that the adsorption capacity increases in the order $BS < TS < DBS \sim OBS$ for the surfactants studied both in water and in $0.01 M H_2SO_4$. This result is in agreement with that found on the basis of kinetic data in Section 3.2. It is again clear from Table 5 that both q_{max} and K_F (as adsorption capacity parameters) values for the adsorption of anionic surfactants decrease with increasing concentration of an inert electrolyte such as NaCl.

A final comment can be made about the desorption of adsorbates from the ACC in order to give some idea about regeneration of the ACC. It was found that when the ACC saturated with DBS, OBS, TS or BS is contacted with pure water at $70^\circ C$ for 5 h by continuous stirring in a shaking water bath at 150 rpm, 0.6%, 1.8%, 47% and 58% of the respective adsorbates were desorbed. It is seen that for the adsorbates having no hydrocarbon chain such as BS and TS, the degree of desorption and thus of regeneration is relatively high. On the other hand adsorbates with long hydrocarbon chains such as DBS and OBS show very small extent of desorption from the ACC under the studied conditions. This can be attributed to strong hydrophobic interactions between these molecules and the ACC surface which cannot be weakened by stirring at $70^\circ C$. It should be recognized that these results are from preliminary desorption experiments. Further detailed work may be required for the regeneration of the ACC.

4. Conclusions

It is found that the ACC can efficiently adsorb the surfactants BS, TS, OBS and DBS from water solutions predominantly by hydrophobic interactions. The adsorption is enhanced by acidifying the surfactant solution with H_2SO_4 due to the electrostatic interactions between the ACC surface and

surfactants in addition to the hydrophobic interactions. Kinetic of adsorption of surfactants onto the ACC was found to follow pseudo-second-order model. Isotherm data at 30 °C were fitted to Freundlich model better than to Langmuir model. The rate and extent of adsorption of the surfactants onto the ACC was found increase in the order BS < TS < DBS ~ OBS. An inert electrolyte such as NaCl was found to decrease the adsorption capacity of the ACC for the surfactants.

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References

- [1] S. Gupta, A. Pal, P.K. Ghosh, M. Bandyopadhyay, Performance of waste activated carbon as a low-cost adsorbent for the removal of anionic surfactant from aquatic environment, *J. Environ. Sci. Health Part A-Toxic/Hazard. Substances Environ. Eng.* 38 (2003) 381–397.
- [2] T. Zhang, T. Oyama, S. Horikoshi, J. Zhao, N. Serpone, H. Hidaka, Photocatalytic decomposition of the sodium dodecylbenzene sulfonate surfactant in aqueous titania suspensions exposed to highly concentrated solar radiation and effects of additives, *Appl. Catal. B: Environ.* 42 (2003) 13–24.
- [3] A. Adak, M. Bandyopadhyay, A. Pal, Removal of anionic surfactant from wastewater by alumina: a case study, *Colloids Surf. A: Physicochem. Eng. Aspects* 254 (2005) 165–171.
- [4] S.K. Mishra, S.B. Kanungo, Rajeev, Adsorption of sodium dodecyl benzenesulfonate onto coal, *J. Colloid Interf. Sci.* 267 (2003) 42–48.
- [5] R.P. Bhagat, Kinetics of sodium dodecyl benzene sulfonate adsorption on hematite and its interaction with polyacrylamide, *Colloid Polym. Sci.* 279 (2001) 33–38.
- [6] K. Dao, A. Bee, C. Treiner, Adsorption isotherm of sodium octylbenzenesulfonate on iron oxide particles in aqueous solutions, *J. Colloid Interf. Sci.* 204 (1998) 61–65.
- [7] E.M. Lee, L.K. Koopal, Adsorption of cationic and anionic surfactants on metal oxide surfaces: surface charge adjustment and competition effects, *J. Colloid Interf. Sci.* 177 (1996) 478–489.
- [8] C.M. Gonzalez-Garcia, M.L. Gonzalez-Martin, R. Denoyel, A.M. Gallardo-Moreno, L. Labajos-Broncano, J.M. Bruque, Ionic surfactant adsorption onto activated carbons, *J. Colloid Interf. Sci.* 278 (2004) 257–264.
- [9] C.A. Basar, A. Karagunduz, A. Cakici, B. Keskinler, Removal of surfactants by powdered activated carbon and microfiltration, *Water Res.* 38 (2004) 2117–2124.
- [10] S. Zor, Investigation of the adsorption of anionic surfactants at different pH values by means of active carbon and the kinetics of adsorption, *J. Serb. Chem. Soc.* 69 (2004) 25–32.
- [11] S. Paria, K.C. Khilar, A review on experimental studies of surfactant adsorption at the hydrophilic solid–water interface, *Adv. Colloid Interf. Sci.* 110 (2004) 75–95.
- [12] E. Ayranci, O. Duman, Adsorption of aromatic organic acids onto high area activated carbon cloth in relation to wastewater purification, *J. Hazard. Mater.* 136 (2006) 542–552.
- [13] E. Ayranci, E. Bayram, Adsorption of phthalic acid and its esters onto high-area activated carbon-cloth studied by in situ UV-spectroscopy, *J. Hazard. Mater.* 122 (2005) 147–153.
- [14] E. Ayranci, O. Duman, Adsorption behaviors of some phenolic compounds onto high specific area activated carbon cloth, *J. Hazard. Mater.* 124 (2005) 125–132.
- [15] O. Duman, E. Ayranci, Structural and ionization effects on the adsorption behaviors of some anilinic compounds from aqueous solution onto high-area carbon cloth, *J. Hazard. Mater.* 120 (2005) 173–181.
- [16] O. Duman, E. Ayranci, Adsorption characteristics of benzaldehyde, sulphanilic acid and *p*-phenolsulfonate from water, acid or base solutions onto activated carbon cloth, *Sep. Sci. Technol.* 41 (2006) 3673–3692.
- [17] B.E. Conway, G. Ayranci, E. Ayranci, Molecular structure effects in the adsorption behaviour of some aromatic heterocyclic compounds at high-area carbon-cloth in relation to waste-water purification, *Zeitschrift für Physikalische Chemie* 217 (2003) 315–331.
- [18] E. Ayranci, N. Hoda, Studies on removal of metribuzin, bromacil, 2,4-D and atrazine from water by adsorption on high area carbon cloth, *J. Hazard. Mater.* 112 (2004) 163–168.
- [19] N. Hoda, E. Bayram, E. Ayranci, Kinetic and equilibrium studies on the removal of acid dyes from aqueous solutions by adsorption onto activated carbon cloth, *J. Hazard. Mater.* 137 (2006) 344–351.
- [20] E. Ayranci, B.E. Conway, Removal of phenol, phenoxide and chlorophenols from waste-waters by adsorption and electrosorption at high-area carbon felt electrodes, *J. Electroanal. Chem.* 513 (2001) 100–110.
- [21] E. Ayranci, B.E. Conway, Adsorption and electrosorption at high-area carbon felt electrodes for waste-water purification: systems evaluation with inorganic, S-containing anion, *J. Appl. Electrochem.* 31 (2001) 257–266.
- [22] E. Ayranci, B.E. Conway, Adsorption and electrosorption of ethyl xanthate and thiocyanate anions at high-area carbon-cloth electrodes studied by in situ UV spectroscopy: development of procedures for wastewater purification, *Anal. Chem.* 73 (2001) 1181–1189.
- [23] P. Pandit, S. Basu, Removal of ionic dyes from water by solvent extraction using reverse micelles, *Environ. Sci. Technol.* 38 (2004) 2435–2442.
- [24] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, *Carbon* 42 (2004) 83–94.
- [25] S. Lagergren, About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens. Handlingar* 24 (1898) 1–39.
- [26] G. McKay, Y.S. Ho, J.C.Y. Ng, Biosorption of copper from waste waters: a review, *Sep. Purif. Meth.* 28 (1999) 87–125.
- [27] S.H. Chien, W.R. Clayton, Application of Elovich equation to the kinetics of phosphate release and sorption in soils, *Soil Sci. Soc. Am. J.* 44 (1980) 265–268.
- [28] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 89 (1963) 31–59.
- [29] J.M. Smith, *Chemical Engineering Kinetics*, McGraw-Hill Company, New York, 1981.
- [30] H. Freundlich, W. Heller, The adsorption of *cis*- and *trans*-azobenzene, *J. Am. Chem. Soc.* 61 (1939) 2228.
- [31] R.-S. Juang, R.-L. Tseng, F.-C.S.-H. Wu, Liquid-phase adsorption of phenol and its derivatives on activated carbon fibers, *Sep. Sci. Technol.* 31 (1996) 1915–1931.
- [32] C.J. Lomauro, A.S. Bakshi, T.P. Labuza, Evaluation of food moisture sorption isotherm equations. Part I. Fruit, vegetable and meat products, *Lebensm.-Wiss. Technol.* 18 (1985) 111–117.
- [33] E. Ayranci, O. Duman, Moisture sorption isotherms of cowpea (*Vigna unguiculata* L. Walp) and its protein isolate at 10, 20 and 30 °C, *J. Food Eng.* 70 (2005) 83–91.