



Research article

Adsorptive removal of cationic surfactants from aqueous solutions onto high-area activated carbon cloth monitored by in situ UV spectroscopy

Osman Duman^a, Erol Ayranci^{b,*}^a Faculty of Education, Akdeniz University, 07058 Antalya, Turkey^b Chemistry Department, Faculty of Arts and Sciences, Akdeniz University, 07058 Antalya, Turkey

ARTICLE INFO

Article history:

Received 22 April 2009

Received in revised form

11 September 2009

Accepted 14 September 2009

Available online 19 September 2009

Keywords:

Adsorption

Cationic surfactant

Activated carbon cloth

In situ UV spectroscopy

Quaternary ammonium chlorides

ABSTRACT

Activated carbon cloth (ACC) was used as adsorbent for the removal of cationic surfactants such as benzyltrimethylammonium chloride (BTMACl), benzyltriethylammonium chloride (BTEACl), benzyltributylammonium chloride (BTBACl), benzyltrimethyldecylammonium chloride (BDMDACl), benzyltrimethyltetradecyl ammonium chloride (BDMTDACl), benzyltrimethylhexadecylammonium chloride (BDMHDAcL), N-dodecylpyridinium chloride (N-DPCl) and N-cetylpyridinium chloride (CPCl) from aqueous solutions. The adsorption efficiency of the ACC was evaluated for cationic surfactants. Adsorption process was followed by in situ UV spectroscopic technique. The kinetic data, so obtained, were treated according to the pseudo first-order, the pseudo second-order, the Elovich and the intraparticle diffusion models in order to understand the adsorption mechanism of cationic surfactants onto the ACC. The best fit was found with the pseudo second-order model. The experimental isotherm data were obtained at 30 °C and analyzed by the Freundlich and the Langmuir models. The parameters of isotherm equations were determined. The Freundlich model was found to represent the experimental data better than the Langmuir model. The observed adsorption behaviors are discussed in terms of the pH of the solution, the nature of cationic surfactants (e.g. functional groups, size, and hydrophobicity) and the nature of the ACC (e.g. surface charge, pore size). A fair linear correlation was found between some adsorption parameters and apparent molar volumes at infinite dilution for benzyltrialkylammonium chlorides.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Surfactants constitute the most important group of detergent components and are present in all types of detergents [1]. They are of toxic nature and their presence in water creates health hazards like dermatitis, unpleasant taste and smell. They cause foams in waters. Some surfactants are biodegradable, but many of them are not [2]. For this reason the amount of surfactants in wastewaters should be reduced at least to acceptable levels.

There are four types of surfactants: anionic, cationic, zwitterionic and non-ionic. Cationic surfactants are widely used as textile softeners, dispersants, emulsifiers, dye-fixing agents, wetting agents, disinfecting agents and corrosion inhibitors in various industries [3].

One of the commonly used methods for removal of pollutants from wastewaters is adsorption and probably the most widely used adsorbent in adsorption is activated carbon [4]. There are three types of activated carbon in commercial use: powder activated carbon, granular activated carbon and activated carbon fiber or cloth.

Activated carbon fiber or cloth has several unique characteristics compared with conventionally used granular or powder activated carbons. These materials are composed of thin fibers of the order of ten microns in diameters leading to greater adsorption rates, and hence contributing to the minimization of the reactor size. The cloth or fiber form of activated carbon also makes the handling of adsorbents much easier [5]. For these reasons, the activated carbon cloth (ACC) has received considerable attention, in recent years, as a potential adsorbent for water treatment applications. ACC has been used for successful adsorptive removal of some organic compounds [6–14], various inorganic anions [15] and some metal ions [16–18].

The adsorption of some cationic surfactants was studied previously using various adsorbents such as silica [19,20], quartz [21], zeolite and clinoptilolite [22], rutile [23], cellulose [24], carbon black [25], coal [26] and activated carbon [27–29]. However, we have not met any study for the adsorption of cationic surfactants using the ACC adsorbent in literature.

The aim of the present study is to investigate the adsorption behaviors of some cationic surfactants from aqueous solutions onto the ACC by in situ UV spectroscopic method. Eight cationic surfactants were selected in such a way that the structural factors affecting their adsorption behavior could be examined. The names,

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

Table 1
Chemical structures of cationic surfactants.

Cationic surfactant	Abbreviation	Chemical structure
Benzyltrimethylammonium chloride	BTMACI	
Benzyltriethylammonium chloride	BTEACI	
Benzyltributylammonium chloride	BTBACI	
Benzyltrimethyldecylammonium chloride	BDMDACI	
Benzyltrimethyltetradecylammonium chloride	BDMTDACI	
Benzyltrimethylhexadecylammonium chloride	BDMHDACI	
N-dodecylpyridinium chloride	N-DPCI	
N-cetylpyridinium chloride	CPCI	

abbreviations and structures of the selected cationic surfactants are given in Table 1.

2. Materials and methods

2.1. Materials

The ACC used in the present work 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 from 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 carbon materials derived by pyrolysis of rayon [16].

BTMACI, BTEACI, BTBACI and CPCI were obtained from Aldrich, BDMDACI, BDMTDACI and BDMHDACI from Fluka and N-DPCI from Merck. All chemicals used in this study were reagent grade. Deionized water was used in adsorption experiments.

2.2. Treatment and properties of the ACC

A washing procedure was applied for the ACC as described previously [6,7,12]. Several properties of the ACC such as specific surface area, volumes of micropores and mesopores, elemental composition, pH_{PZC} which is the pH of solution at which net charge on the surface of the ACC is zero, and acidic and basic group contents

were determined in our previous works [7,12,14]. These properties are listed in Table 2. The SEM pictures and electrochemical characterization of the ACC were also reported earlier [30].

2.3. The design of the adsorption cell and optical absorbance measurements

A specially designed cell was used to carry out the adsorption and simultaneously to perform in situ concentration measure-

Table 2
Properties of the ACC.

Specific surface area	1870 m ² g ⁻¹
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

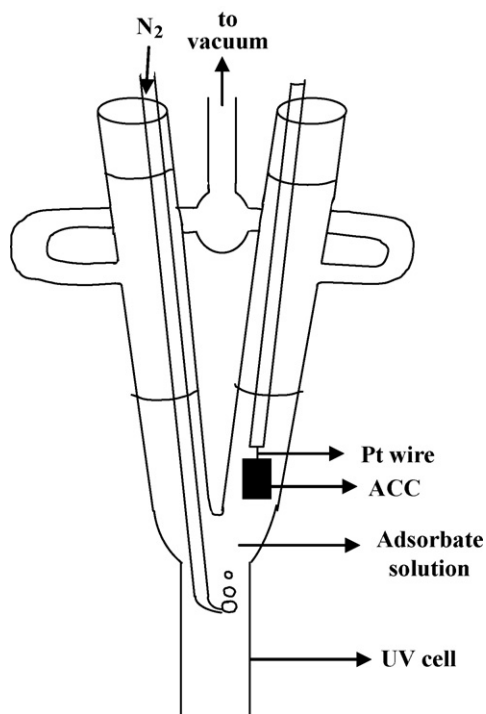


Fig. 1. Diagram of the adsorption cell.

ments by means of UV absorption spectrophotometry. This cell, also used in our previous works [7,12], was V-shaped (Fig. 1) 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 dual 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.

With the use of the adsorption cell described above it was possible to follow the changes in concentration of the adsorbate solution during the course of adsorption by in situ UV spectroscopy. The procedure for this process is summarized as a flow diagram in Fig. 2 and explained in detail below.

Solutions of adsorbates were prepared in water. The initial concentrations of surfactants and the amount of the ACC were kept as constant as possible for kinetic studies of adsorption of individual adsorbates in order to make an easy comparison among their adsorption behaviors (concentration: 1×10^{-4} M, mass of the ACC: 18.3 ± 0.1 mg). The ACC pieces were pre-wetted by leaving in water for 24 h before use. During this long contact period with water, the pores of the ACC may expand and become more accessible for the adsorbates, in the actual adsorption process. The idea of using pre-wetted ACC originated from our previous findings that pre-wetting enhances the adsorption process [30]. Pre-wetted ACC was inserted into the adsorption cell containing a known volume of sample solution (20 mL) which had been degassed by vacuum application for a short time. The sliding door of the sample compartment of the spectrophotometer was left half-open and quartz cuvette fixed at the bottom of the adsorption cell (which now contained the sample solution) was inserted into the front sample compartment. A Teflon tube connected to the tip of a thin N_2 -bubbling glass tube was lowered from one arm of the adsorption cell down the spectrophotometer cuvette to a level just above the light path to provide effective mixing. Then, quickly, an opaque curtain was spread above

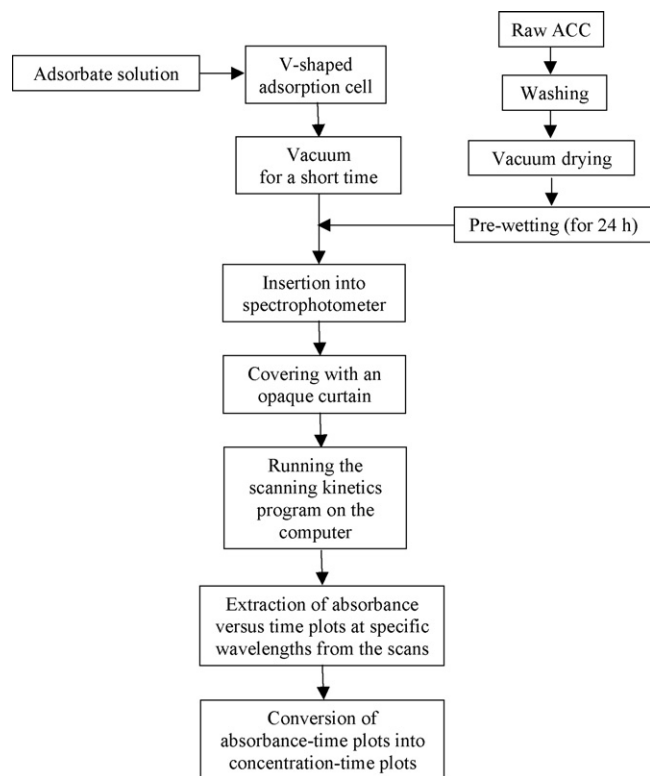


Fig. 2. Flow diagram for measurement process of the in situ UV spectroscopic method.

the sample compartment of the spectrophotometer, over the cell, to prevent interference from external light. A Cary 100 UV-vis spectrophotometer was used for the optical absorbance measurements.

The scanning-kinetics program for monitoring the absorbance of any 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 at each wavelength in the selected region without destructing the adsorption system. This possibility constitutes the superior advantage of in situ UV spectroscopic technique as applied in scanning-kinetics mode over most classical adsorption study techniques. In those techniques, batch methods are usually employed in which, samples are withdrawn from the adsorption system at certain time intervals and analyzed separately. Usually 10–20 data points are obtained in such kinetic studies. Each sample withdrawal, of course, destructs the main adsorption system.

A typical scanning-kinetic output obtained during the adsorption of BTMACl from water onto the ACC was reproduced in Fig. 3 in which only scans in 5 min intervals are shown. The downward movement of the absorbance maximum at 208 nm, as the adsorption goes on is clearly seen in this figure and marked by an arrow. If any change occurs in spectrum during the adsorption process, this could be seen in such a scanning-kinetic output. Such changes are usually observed in electrosorption studies [6,31]. No change was noted in the present systems. 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 one of the absorption maxima (λ_{max}). Then, the absorbance data were converted into concentration data using calibration relations pre-determined at the wavelength of maximum absorbance for each adsorbate. The calibration data for the cationic surfactants studied are given in Table 3.

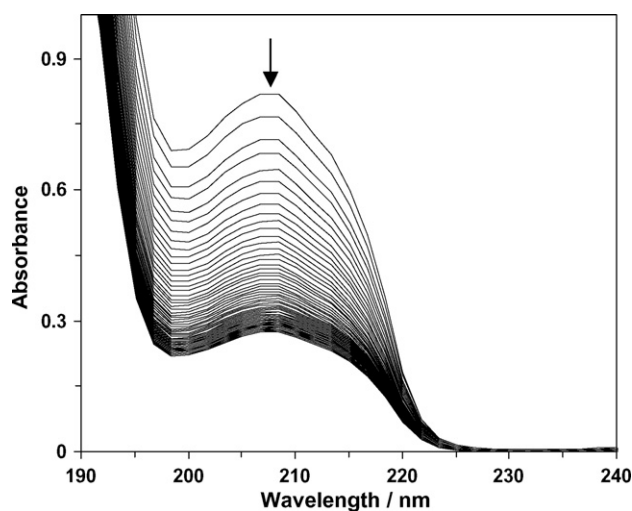


Fig. 3. Scans during the adsorption of BTMACI onto the ACC in 5 min intervals over 300 min. Arrow shows direction of change (diminution) of optical absorbance maximum with adsorption.

2.4. Determination of adsorption isotherms

The adsorption isotherms of adsorbates were determined on the basis of batch analysis. The ACC pieces of varying masses were allowed to equilibrate with solutions of adsorbates in water 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. The equilibration was allowed in 100 mL Erlenmeyer flasks kept in Nüve ST 402 shaking waterbath at a constant shaking speed of 150 rpm. The concentrations after the equilibration period were measured spectrophotometrically. The amount of adsorbate adsorbed per unit mass of the ACC, 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 adsorbate, C_0 and C_e are the initial and equilibrium concentrations, respectively, and m is the mass of the ACC.

3. Results and discussion

3.1. Adsorption behaviors of cationic surfactants

The concentration versus time plots for the adsorption of cationic surfactants onto the ACC over about 1000 min are shown in Fig. 4. The concentrations (1×10^{-4} M) were kept below the critical

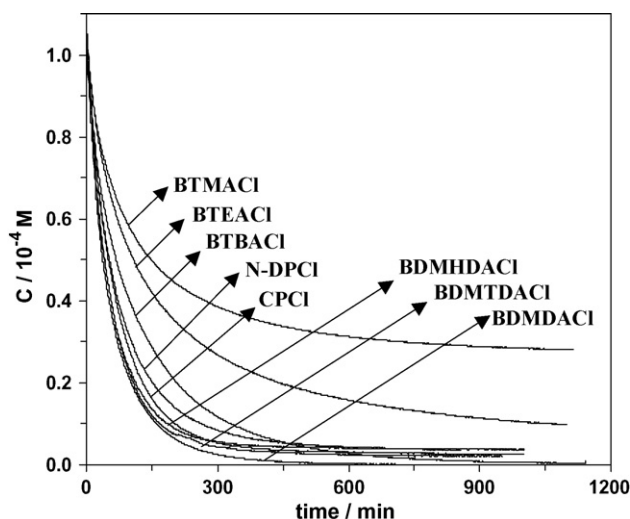


Fig. 4. Concentration versus time plots for the adsorption of cationic surfactants onto the ACC. Initial concentration is 1×10^{-4} M and mass of the ACC is 18.3 ± 0.1 mg in all cases.

micelle concentrations of adsorbates to avoid handling heterogeneous systems.

The removal percentages of BTMACI, BTEACI, BTBACI, BDMDACL, BDMTDACL, BDMHDACL, N-DPCI and CPCI after 1000 min of adsorption are 72, 90, 100, 100, 98, 98, 99 and 99, respectively. It is seen that except BTMACI and BTEACI, all the surfactants reach to almost complete removal (>98%). Similar extent of adsorption of BTMACI and BTEACI as well as the small differences in extents of adsorption of other (almost completely removed) surfactants can be explained on the basis of the pH of the solution, the nature of cationic surfactants (e.g. functional groups, size, hydrophobicity) and the nature of the ACC (e.g. surface charge, pore size).

pH_{PZC} is an important property of an adsorbent in determining the electrostatic interactions between adsorbate and adsorbent during adsorption. 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} [32]. The initial pH values of cationic surfactant solutions were measured in the range of 5.48 and 5.70. The pH values of them at equilibrium were in the range of 5.80 and 5.91, except N-DPCI and CPCI, which were 5.15 and 5.20, respectively. The pH_{PZC} of the ACC used in the present work (7.4, Table 2) is close but slightly higher than the above measured pH values. Thus, the surface of the ACC is expected to be slightly positive in all cases and to remain so during the whole adsorption period. For this reason slight repulsion can be expected between a surface having a small positive charge and the cationic surfactants as far as the electrostatic interactions are concerned. However quite high extents of adsorption observed for all the surfactants (Fig. 4) suggest that the main adsorption forces should be hydrogen bonding, hydrophobic

Table 3
Spectral and calibration data for in situ UV spectroscopic analysis of cationic surfactants.

Cationic surfactant	Wavelength of maximum absorption λ_{max} (nm)	Molar absorptivity ϵ ($M^{-1} cm^{-1}$)	Correlation coefficient r
BTMACI	208	8000	0.9985
BTEACI	208	8000	0.9985
BTBACI	208	8250	0.9988
BDMDACL	208	8200	0.9999
BDMTDACL	208	8100	0.9986
BDMHDACL	208	8100	0.9962
N-DPCI	214	4950	0.9996
	259	4400	0.9999
CPCI	214	4800	0.9994
	259	4300	0.9997

Table 4

The parameters and regression coefficients of the three kinetic models applied for experimental adsorption kinetic data of the cationic surfactants.

Cationic surfactant	Pseudo first-order		Pseudo second-order			Elovich equation		
	$k_1 \times 10^3$ (min ⁻¹)	r (g (mmol min) ⁻¹)	k_2 (mmol (g min) ⁻¹)	$h \times 10^3$ (mmol (g min) ⁻¹)	r	$\alpha \times 10^3$ (g (min) ⁻¹)	β	r
BTMACI	4.90	0.9745	0.152	1.15	0.9999	4.36	68.2	0.9806
BTEACI	4.53	0.9710	0.095	1.24	0.9999	4.45	50.5	0.9890
BTBACI	5.84	0.9868	0.133	1.87	0.9997	71.7	5.07	0.9692
BDMDACI	7.80	0.9820	0.334	4.65	0.9997	25.4	58.7	0.9237
BDMTDACI	7.30	0.9793	0.323	4.34	0.9989	7.65	60.7	0.9050
BDMHDACI	6.20	0.9709	0.281	3.67	0.9995	17.1	58.2	0.9185
N-DPCI	6.80	0.9912	0.229	3.42	0.9998	31.2	65.2	0.9532
CPCI	5.90	0.9489	0.368	4.61	0.9992	15.1	52.3	0.8978

and van der Waals interactions. Hydrogen bonding can be formed between the surfactant molecules and the carboxylic, lactonic and phenolic groups on the surface of the ACC (Table 2).

The cationic surfactants under study can be grouped into three. The first group can be named as benzyltrialkylammonium chlorides and is composed of BTMACI, BTEACI and BTBACI. The second group is benzyldimethylalkyl ammonium chlorides and is composed of BDMDACI, BDMTDACI and BDMHDACI. The third group is alkylpyridinium chlorides and includes N-DPCI and CPCI.

In the first group of surfactants, a benzyl group and three alkyl groups are bonded to an N center. The increase in chain length of the three alkyl groups from BTMACI to BTBACI is reflected in the increase of the extent of adsorption in the same order (Fig. 4). The increasing hydrophobicity of the adsorbate is expected to be the predominating factor in determining the order of extent of adsorption in this group of surfactants. Another important property in determining the extent of adsorption is the size of adsorbate species relative to that of pores of the ACC. The widths and lengths of surfactant molecules were determined using a program called ChemSketch. The dimensions (widths \times lengths) of BTMACI, BTEACI and BTBACI are 4.8 Å \times 8.4 Å, 5.0 Å \times 9.0 Å and 5.8 Å \times 11.7 Å, respectively. On the other hand, the percentages of total pores of the ACC having pore size greater than 4.8, 5.0 and 5.8 Å were 98, 98 and 85, respectively, as deduced from the pore size distribution curve given in our earlier works [14,33]. The same percentages for pore sizes greater than 8.4, 9.0 and 11.7 Å were 72, 63 and 42, respectively. The orientation of molecules may be important during their diffusion into the pores of the ACC. It seems that regardless of benzyltrialkylammonium chlorides take vertical or horizontal orientation, the most accessible surfactant to the pores of the ACC is expected to be BTMACI. However, BTMACI shows the smallest extent of adsorption in Fig. 4. This result indicates that hydrophobic interaction of benzyltrialkylammonium chlorides with the ACC surface is more important in determining the extent of adsorption than steric effects.

The removal percentages of surfactants in the second and third group are so high and close to each other that it is difficult to correlate their adsorption behaviors with their structures. The overall hydrophobicity of surfactants in the second and third group is expected to be higher than those in the first group. Once again,

hydrophobic interactions appeared to determine the extent of adsorption in an important manner.

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 [34–37];

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

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

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

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t \quad (5)$$

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 constant, 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 4 together with regression coefficients. The best fit is for pseudo second-order model according to regression coefficients. So, it can be concluded that the kinetics of adsorption of cationic surfactants onto the ACC obeys the pseudo second-order model.

3.2. Adsorption isotherms

Adsorption isotherm data obtained at 30 °C in water are given in Fig. 5 for BTMACI, BTEACI and BTBACI, in Fig. 6 for BDMDACI, BDMTDACI and BDMHDACI and in Fig. 7 for N-DPCI and CPCI.

Table 5Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) and normalized percent deviation (P) values for cationic surfactants at 30 °C.

Cationic surfactant	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
BTMACI	0.0895	76.6	0.9805	5.19	0.256	0.404	0.9874	2.91
BTEACI	0.383	70.0	0.9869	6.79	0.925	0.377	0.9943	2.67
BTBACI	0.715	160	0.9930	11.8	1.41	0.266	0.9944	2.43
BDMDACI	0.987	181	0.9962	11.4	0.987	0.283	0.9970	2.42
BDMTDACI	0.950	142	0.9970	8.23	0.950	0.293	0.9934	3.36
BDMHDACI	0.941	96.6	0.9967	5.93	0.941	0.292	0.9938	2.39
N-DPCI	1.29	141	0.9950	8.35	2.06	0.221	0.9774	4.59
CPCI	1.19	89.6	0.9933	9.59	1.99	0.260	0.9877	3.16

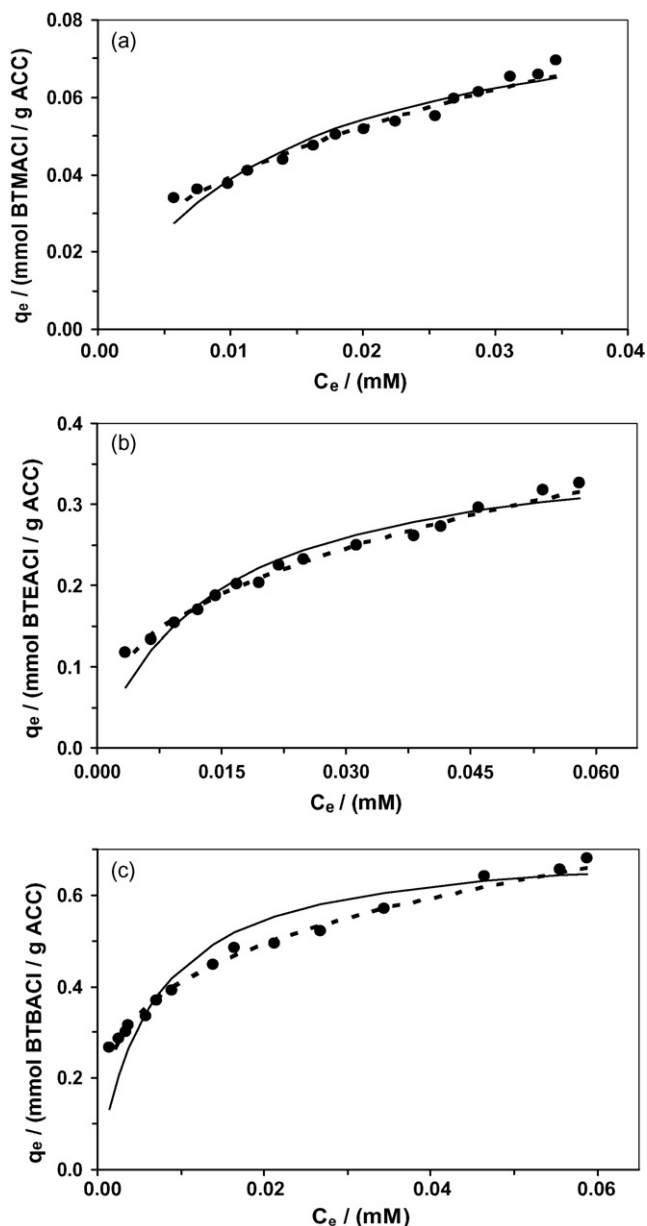


Fig. 5. The fit of experimental adsorption data (●) to Langmuir (—) and Freundlich (···) models for (a) BTMACl, (b) BTEACl and (c) BTBACl.

These isotherm data were treated according to the two well-known isotherm models: Langmuir and Freundlich. The linearized forms of Langmuir and Freundlich isotherm models are given in Eqs. (6) and (7), respectively [38,39].

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

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

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

The regression analysis of C_e/q_e versus C_e data for Langmuir and $\ln q_e$ versus $\ln C_e$ data for Freundlich models provided the

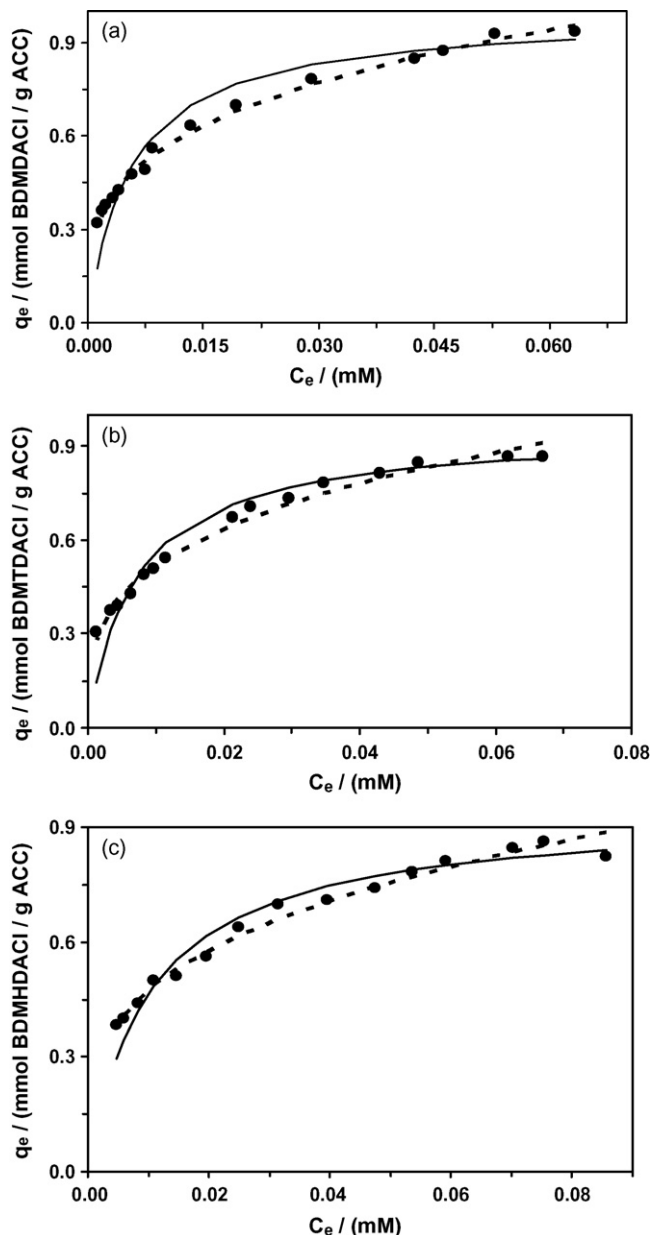


Fig. 6. The fit of experimental adsorption data (●) to Langmuir (—) and Freundlich (···) models for (a) BDMDACl, (b) BDMTDACl and (c) BDMHDACl.

parameters of these models. They are given in Table 5 together with regression coefficients. It is seen that the regression coefficients, being all greater than 0.98 are not decisive about which model represent the experimental data better. For the assessment of experimental isotherm data, the so-called normalized percent deviation [40] or in some literature percent relative deviation modulus, P [41,42] is a better criterion. It is defined by the following equation:

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

where $q_{e(\text{exp})}$ is the experimental q_e at any C_e , $q_{e(\text{pred})}$ is 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 [41].

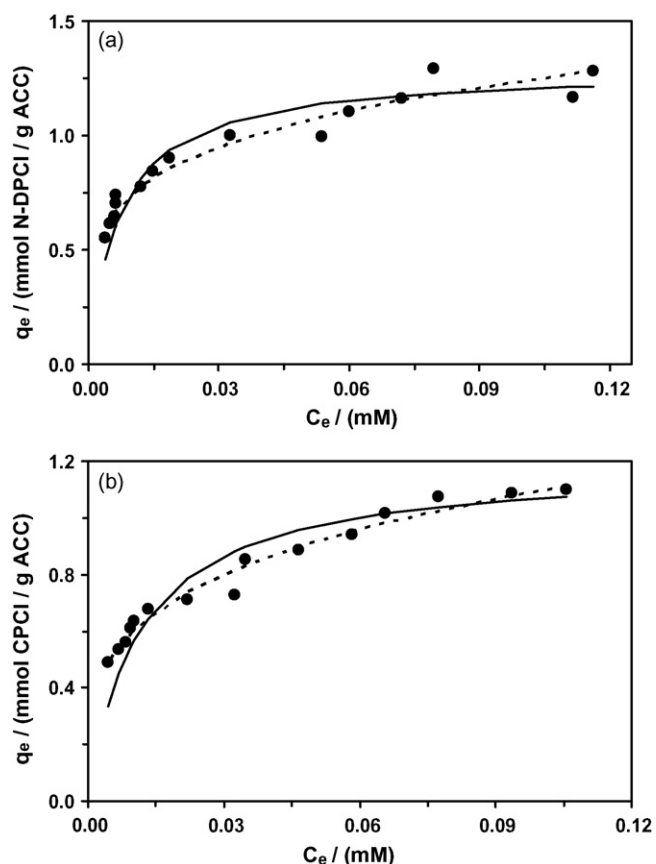


Fig. 7. The fit of experimental adsorption data (●) to Langmuir (—) and Freundlich (---) models for (a) N-DPCL and (b) CPCl.

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 cationic surfactants at 30 °C better than Langmuir model. The best fitted isotherm curves according to Langmuir and Freundlich models together with experimental data points are reproduced in Fig. 5 for BTMACl, BTEACl and BTBACl, in Fig. 6 for BDMDACl, BDMTDACl and BDMHDACl and in Fig. 7 for N-DPCL and CPCl. The better fit of Freundlich equation than Langmuir equation to the experimental isotherm data can clearly be seen from these figures.

The parameter K_F is the measure of the adsorption capacity of the ACC for the cationic surfactants. It is seen from the K_F values given in Table 5 that the adsorption capacity increases in the order

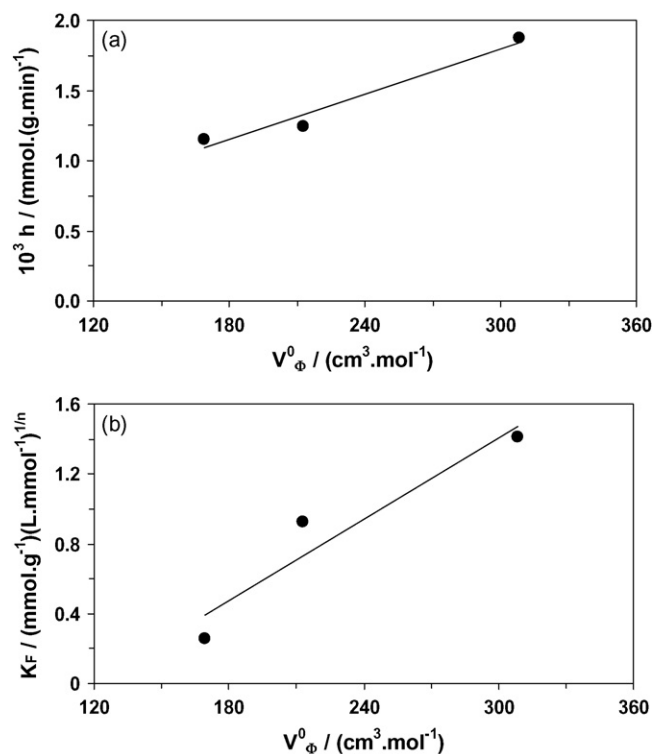


Fig. 8. (a) Variation of h and (b) variation of K_F with apparent molar volume at infinite dilution for benzyltrialkylammonium chlorides.

BTMACl < BTEACl < BDMHDACl \approx BDMTDACl < BDMDACl < BTBACl < N-DPCL \approx CPCl for the cationic surfactants. This result is in fair agreement with the order of removal percentage for cationic surfactants given in Section 3.1. Moreover, the values of $1/n$ are found to be less than 1 (Table 5), suggesting a favorable adsorption behavior for the cationic surfactants onto the ACC [43].

The parameters of the isotherm equations given in Table 5 are difficult to compare with the literature values because the isotherm data are collected under different conditions: temperature, type of adsorbent and the form of adsorbate species. The most important parameter to compare is probably the Langmuir q_{max} value since it is a measure of adsorption capacity of the adsorbent. Some of the literature q_{max} values and the conditions under which they were obtained are listed in Table 6. The comparison of these literature values with our values reported in Table 5 shows that the ACC used in our work has adsorption capacities either higher than or comparable to those adsorbent materials used in other works.

Table 6

Literature values of q_{max} for the adsorption of some cationic surfactants onto various adsorbents.

Adsorbent	Cationic surfactant	T (°C)	q_{max} (mmol g ⁻¹)	Reference
Powder activated carbon	Cetyltrimethylammonium bromide	30	1.00	[28]
Montmorillonite	Decyltrimethylammonium bromide	25	0.743	[44]
Montmorillonite	Dodecyltrimethylammonium bromide	25	0.813	[44]
Montmorillonite	Tetradecyltrimethylammonium bromide	25	0.827	[44]
Montmorillonite	Hexadecyltrimethylammonium bromide	25	0.892	[44]
Kaolinite (well crystallized)	Dodecyltrimethylammonium bromide	–	0.050	[45]
Kaolinite (well crystallized)	Hexadecyltrimethylammonium bromide	–	0.058	[45]
Kaolinite (poorly crystallized)	Dodecyltrimethylammonium bromide	–	0.070	[45]
Kaolinite (poorly crystallized)	Hexadecyltrimethylammonium bromide	–	0.085	[45]
Kaolinite	Dodecyltrimethylammonium bromide	25	0.045	[46]
Kaolinite	Hexadecyltrimethylammonium bromide	25	0.035	[46]
Natural clinoptilolite	Cetylpyridinium bromide	24	0.692	[22]
Natural clinoptilolite	Cetylpyridinium bromide	30	0.731	[22]
Natural clinoptilolite	Cetylpyridinium bromide	34	0.769	[22]
Natural clinoptilolite	Cetylpyridinium bromide	40	0.802	[22]

3.3. Correlation of adsorption behaviors of surfactants with their apparent molar volumes in aqueous solutions

Apparent molar volumes of some of the surfactants in aqueous solutions have recently been reported from this laboratory [47]. It is expected that there might be a correlation between adsorption behaviors of adsorbates and their apparent molar volumes at infinite dilution. Such a correlation was explored with the available data by plotting the so called “initial sorption rate”, h , and the K_F parameter, which is a measure of adsorption capacity, as a function of apparent molar volume at infinite dilution, V_{ϕ}^0 , in Fig. 8. A fair linear correlation is seen in both graphs for BTMACl, BTEACl and BTBACl.

This seems, at first glance, to contradict with our finding that hydrophobic interactions, rather than size factor, play the main role in determining adsorption behaviors of the surfactants under study. However, it should be recognized that apparent molar volume at infinite dilution does not reflect solely the size of the adsorbate but it also reflects adsorbate–water interactions including hydrophobic interactions. So, the observed correlation is reasonable. Similar correlations between adsorption parameters and volumetric properties were also observed in our previous work [13].

4. Conclusions

Adsorption of eight cationic surfactants onto the ACC from aqueous solutions was found to follow pseudo second-order kinetics. Six of the eight cationic surfactants were almost completely removed from aqueous solution under the same experimental conditions. Smaller extents of adsorption of the two adsorbates, BTMACl and BTEACl, were attributed to their smaller hydrophobicity than the other six adsorbates. On the overall, the adsorption of the cationic surfactants under study was found to be determined mainly by hydrophobic interactions. The influences of electrostatic interactions and size factors were less important under the present working conditions. Freundlich isotherm model represented the adsorption data of the cationic surfactants better than Langmuir model. A fair linear correlation was found between the adsorption parameters h or K_F and the apparent molar volume at infinite dilution of benzyltrialkylammonium chlorides.

Acknowledgement

The authors would like to thank to the Scientific Research Projects Unit of Akdeniz University for the support of this work through the project 2003.03.0121.012.

References

- [1] G. Jakobi, A. Löhr, Detergents and Textile Washing, Weinheim, VCH, 1987, p. 63.
- [2] 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. Subst. Environ. Eng.* 38 (2003) 381–397.
- [3] M. Howe-Grant, Kirk–Othmer Encyclopedia of Chemical Technology, vol. 23, John-Wiley & Sons, New York, 1992, p. 523.
- [4] C.C. Huang, Y.C. Lin, F.C. Lu, Dynamic adsorption of organic solvent vapors onto a packed bed of activated carbon cloth, *Sep. Sci. Technol.* 34 (1999) 555–570.
- [5] A. Sakoda, M. Suzuki, R. Hirai, K. Kawazoe, Trihalomethane adsorption on activated carbon fibers, *Water Res.* 25 (1991) 219–225.
- [6] 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.
- [7] 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.
- [8] 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.
- [9] 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.
- [10] H. Pignon, C. Faur-Brasquet, P. Le Cloirec, Treatment of complex aqueous solutions by the coupling of ultrafiltration and adsorption onto activated carbon cloth, *Environ. Technol.* 21 (2000) 1261–1270.
- [11] C. Brasquet, B. Bourges, P. Le Cloirec, Quantitative structure-property relationship (QSPR) for the adsorption of organic compounds onto activated carbon cloth: comparison between multiple linear regression and neural network, *Environ. Sci. Technol.* 33 (1999) 4226–4231.
- [12] E. Ayranci, O. Duman, Adsorption behaviors of some phenolic compounds onto high specific area activated carbon cloth, *J. Hazard. Mater.* 124 (2005) 125–132.
- [13] B.E. Conway, G. Ayranci, E. Ayranci, Molecular structure effects in the adsorption behavior of some aromatic heterocyclic compounds at high-area carbon-cloth in relation to waste-water purification, *Z. Phys. Chem.* 217 (2003) 315–331.
- [14] 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.
- [15] A. Afkhami, Adsorption and electrosorption of nitrate and nitrite on high-area carbon cloth: an approach to purification of water and waste-water samples, *Carbon* 41 (2003) 1320–1322.
- [16] C. Faur-Brasquet, K. Kadirvelu, P. Le Cloirec, Removal of metal ions from aqueous solution by adsorption onto activated carbon cloths: adsorption competition with organic matter, *Carbon* 40 (2002) 2387–2392.
- [17] K. Kadirvelu, C. Faur-Brasquet, P. Le Cloirec, Removal of Cu(II), Pb(II) and Ni(II) by adsorption onto activated carbon cloths, *Langmuir* 16 (2000) 8404.
- [18] A. Afkhami, B.E. Conway, Investigation of removal of Cr(VI), Mo(VI), W(VI), V(IV) and V(V) oxy-ions from industrial waste-waters by adsorption and electrosorption at high-area carbon cloth, *J. Colloid Interf. Sci.* 251 (2002) 248–255.
- [19] R. Aubourg, A. Bee, S. Cassaignon, V. Monticone, C. Treiner, Adsorption isotherms of cetylpyridinium chloride with iron III salts at air/water and silica/water interfaces, *J. Colloid Interf. Sci.* 230 (2000) 298–305.
- [20] I.V. Mikhailova, I.I. Gerashchenko, Adsorption of cationic surfactants on highly dispersed silica, *Colloid J.* 63 (2001) 437–440.
- [21] D.W. Fuerstenau, R. Jia, The adsorption of alkylpyridinium chlorides and their effect on the interfacial behavior of quartz, *Colloid Surf. A* 250 (2004) 223–231.
- [22] M. Ghiaci, R. Kia, R.J. Kalbasi, Investigation of thermodynamic parameters of cetyl pyridinium bromide sorption onto ZSM-5 and natural clinoptilolite, *J. Chem. Thermodyn.* 36 (2004) 95–100.
- [23] 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.
- [24] J. Lukaszczyk, E. Lekawska, K. Lunikwitz, G. Petzold, Sorbent for removal surfactants from aqueous solutions: surface modification of natural solids to enhance sorption ability, *J. Appl. Polym. Sci.* 92 (2004) 1510–1515.
- [25] M. Bele, A. Kodre, I. Arcon, J. Grdadolnik, S. Pejovnik, J.O. Besenhard, Adsorption of cetyltrimethylammonium bromide on carbon black from aqueous solution, *Carbon* 36 (1998) 1207–1212.
- [26] S.K. Mishra, D. Panda, Studies on the adsorption of Brij-35 and CTAB at the coal–water interface, *J. Colloid Interf. Sci.* 283 (2005) 294–299.
- [27] H. Tamai, M. Kunihiro, H. Yasuda, Adsorption of tetraalkylammonium ions on microporous and mesoporous activated carbons prepared from vinylidene chloride copolymer, *J. Colloid Interf. Sci.* 275 (2004) 44–47.
- [28] C.A. Basar, A. Karagunduz, A. Cakici, B. Keskinler, Removal of surfactants by powdered activated carbon and microfiltration, *Water Res.* 38 (2004) 2117–2124.
- [29] J.-X. Xiao, Y. Zhang, C. Wang, J. Zhang, C.-M. Wang, Y.-X. Bao, Z.-G. Zhao, Adsorption of cationic surfactant mixtures on activated carbon, *Carbon* 43 (2005) 1032–1038.
- [30] 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.
- [31] E. Bayram, N. Hoda, E. Ayranci, Adsorption/electrosorption of catechol and resorcinol onto high area activated carbon cloth, *J. Hazard. Mater.* 168 (2009) 1459–1466.
- [32] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, *Carbon* 42 (2004) 83–94.
- [33] O. Duman, E. Ayranci, Adsorption characteristics of benzaldehyde, sulphanic acid and p-phenolsulfonate from water, acid or base solutions onto activated carbon cloth, *Sep. Sci. Technol.* 41 (2006) 3673–3692.
- [34] S. Lagergren, About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens Handlingar* 24 (1898) 1–39.
- [35] G. McKay, Y.S. Ho, J.C.Y. Ng, Biosorption of copper from waste waters: a review, *Sep. Purif. Methods* 28 (1999) 87–125.
- [36] T.H. Shek, A. Ma, V.K.C. Lee, G. McKay, Kinetics of zinc ions removal from effluents using ion exchange resin, *Chem. Eng. J.* 146 (2009) 63–70.
- [37] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 89 (1963) 31–59.
- [38] J.M. Smith, *Chemical Engineering Kinetics*, McGraw-Hill Company, New York, 1981.
- [39] H. Freundlich, W. Heller, The adsorption of cis- and trans-azobenzene, *J. Am. Chem. Soc.* 61 (1939) 2228.
- [40] 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.

- [41] 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.
- [42] 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.
- [43] A.S. Ozcan, B. Erdem, A. Ozcan, Adsorption of acid blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite, *J. Colloid Interf. Sci.* 280 (2004) 44–54.
- [44] F. Li, M.J. Rosen, Adsorption of gemini and conventional cationic surfactants onto montmorillonite and the removal of some pollutants by the clay, *J. Colloid Interf. Sci.* 224 (2000) 265–271.
- [45] Z. Li, L. Gallus, Adsorption of dodecyl trimethylammonium and hexadecyl trimethylammonium onto kaolinite—competitive adsorption and chain length effect, *Appl. Clay Sci.* 35 (2007) 250–257.
- [46] J. Wang, B. Han, M. Dai, H. Yan, Z. Li, R.K. Thomas, The role of chain length and structure in surfactant adsorption at Na-kaolinite, *Adsorp. Sci. Technol.* 16 (1998) 565–575.
- [47] O. Duman, E. Ayranci, Apparent molar volumes and isentropic compressibilities of benzyltrialkylammonium chlorides in water at (293.15, 303.15, 313.15, 323.15 and 333.15) K, *J. Chem. Thermodyn.* 41 (2009) 911–915.