Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

In-Situ UV-Visible Spectroscopic Study on the Adsorption of some Dyes onto Activated Carbon Cloth

Erol Ayranci[a]; Osman Duman[b]
[a] Department of Chemistry, Faculty of Arts and Sciences, Akdeniz University, Antalya, Turkey [b] Faculty of Education, Akdeniz University, Antalya, Turkey

To cite this Article Ayranci, Erol and Duman, Osman(2009) 'In-Situ UV-Visible Spectroscopic Study on the Adsorption of some Dyes onto Activated Carbon Cloth', Separation Science and Technology, 44: 15, 3735 — 3752
To link to this Article: DOI: 10.1080/01496390903182891
URL: http://dx.doi.org/10.1080/01496390903182891

Separation Science and Technology, 44: 3735–3752, 2009

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903182891

In-Situ UV-Visible Spectroscopic Study on the Adsorption of some Dyes onto Activated Carbon Cloth

Erol Ayranci[1] and Osman Duman[2]
[1]Department of Chemistry, Faculty of Arts and Sciences,
Akdeniz University, Antalya, Turkey
[2]Faculty of Education, Akdeniz University, Antalya, Turkey

Abstract: Adsorptive removal of the dyes C.I. Basic Blue 9, C.I. Basic Red 2, and C.I. Acid Blue 74 from aqueous solution onto the activated carbon cloth (ACC) has been investigated. The removal of each dye has been followed by in-situ UV-visible spectroscopic method using the so-called scanning kinetics technique. Kinetic data obtained in this way were tested according to pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion models. Pseudo-second order model was found to be the best in representing the experimental kinetic data. Adsorption isotherms at 30°C were derived for each dye. Isotherm data were found to fit best to Freundlich isotherm model among the three isotherm models tested; Langmuir, Freundlich, and Redlich-Peterson. High specific surface area of the ACC allowed almost complete removal of each dye under the experimental conditions applied. Adsorption capacity of the ACC for the three dyes was correlated with the dimensions of dye molecules and pore sizes of the ACC.

Keywords: Activated carbon cloth, adsorption, dye, in-situ UV spectroscopy

INTRODUCTION

The dyes usage is increasing day by day. Textile companies, dye manufacturing industries, paper and pulp mills, tanneries, electroplating factories,

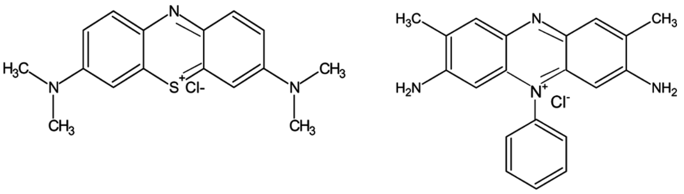
Received 2 December 2008; accepted 12 May 2009.

Address correspondence to Erol Ayranci, Department of Chemistry, Akdeniz University, Antalya 07058, Turkey. Tel.: (90) (242) 310 23 15; Fax: (90) (242) 227 89 11. E-mail: eayranci@akdeniz.edu.tr

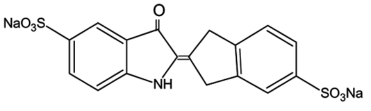
and food companies discharge colored wastewater (1). Colored waters are objectionable on aesthetic grounds for drinking and other agricultural purposes. Color affects the nature of the water, inhibits sunlight penetration into the stream, and reduces the photo-synthetic action. Some of the dyes are carcinogenic and mutagenic (2). Therefore, the dyes should be removed from wastewater before discharging the effluent to the environment to avoid health hazards and destruction of the ecosystem.

Most dyes are stable to biological degradation. Various treatment methods such as coagulation, chemical oxidation, and membrane separation can be used for the removal of dyes from industrial effluents. These methods do not operate at low concentration of colored compounds in the effluent. Adsorption has received considerable attention for color removal from wastewater (3). Various adsorbents such as activated carbon, silica gel, natural clay, peat, wood chips, rice husk ash, living or dead microbial biomass have been used for the removal of dyes from waste water (4). Among these adsorbents, activated carbon in granular or powder form has been widely used in the treatment of industrial wastes to remove dyes. Kannan and Sundaram (5) have studied the kinetics and mechanism of methylene blue (C.I. Basic Blue 9) adsorption on commercial activated carbon and prepared activated carbons from bamboo dust, coconut shell, groundnut shell, rice husk, and straw. Suteu and Bilba (6) have studied the equilibrium and kinetics of a reactive dye Brilliant Red HE-3B adsorption by powdered activated charcoal. They found that the adsorption followed the pseudo-second order kinetic model. Senthilkumaar et al. (7) have studied the adsorption of methylene blue onto jute fiber activated carbon from aqueous solution. Kumar and Sivanesan (8) have reported the adsorption of safranine (C.I. Basic Red 2) onto activated carbon at 305 and 313 K. They found that Freundlich, Langmuir, and Redlich-Peterson models represented the sorption of safranin onto activated carbon quite well. Adsorption of a basic dye, methylene blue, from aqueous solutions onto as-received activated carbons and acid-treated carbons has been investigated by Wang et al. (9). They found that the adsorption of methylene blue on all carbons followed the pseudo-second order kinetics.

In recent years, activated carbon cloth (ACC) or fiber has received considerable attention as a potential adsorbent for water treatment applications. The ACC has been used for successful adsorptive removal of various inorganic anions (10,11), some phenolic, anilinic, and heterocyclic compounds (12–15). Recently, we have reported a work on adsorption of some acid dyes onto the ACC (16). The present work is a continuation of a series of works on adsorption of different class of compounds onto the ACC being carried out in our laboratories. Here we take a group of dyes, namely C.I. Basic Blue 9, C.I. Basic Red 2, and C.I. Acid Blue 74, and report the kinetics and isotherms for their adsorption onto the ACC.



C.I. Basic Blue 9 **C.I. Basic Red 2**



C.I. Acid Blue 74

Figure 1. Molecular structures of studied dyes.

The selected dyes are of acidic or basic nature. The reason for selecting dyes of varying structures was to investigate the removal performance of the ACC for dyes of different structures (Fig. 1).

MATERIALS AND METHODS

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 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 carbon materials derived by pyrolysis of rayon (12).

C.I. Basic Blue 9 (Merck, Germany) with 80% dye content, C.I. Basic Red 2 (Sigma, Germany) with 85% dye content, and C.I. Acid Blue 74 (Merck, Germany) with 96% dye content were used as adsorbates. The molecular structures of these adsorbates are given in Fig. 1. All chemicals used in this study were reagent grade. Deionized water was used in adsorption experiments.

Treatment and Properties of the ACC

A washing procedure was applied for the ACC as described previously (12,14,15). Several properties of the ACC such as specific surface area, volumes of micropores and mesopores, elemental composition, pH_{PZC}

Table 1. Properties of the ACC

Specific surface area	$1870\,m^2 \cdot g^{-1}$
Total pore volume	$0.827\,cm^3 \cdot g^{-1}$
Micropore volume	$0.709\,cm^3 \cdot g^{-1}$
Mesopore volume	$0.082\,cm^3 \cdot g^{-1}$
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	$0.25\,mmol \cdot g^{-1}$
Carboxylic group content	$0.093\,mmol \cdot g^{-1}$
Lactonic group content	$0.020\,mmol \cdot g^{-1}$
Phenolic group content	$0.14\,mmol \cdot g^{-1}$
Total basic group content	$0.28\,mmol \cdot g^{-1}$

which is the pH of solution at which the net charge on the surface of the ACC is zero, and acidic and basic group contents were determined in our previous works (14,15,17). These properties are listed in Table 1. The SEM pictures and electrochemical characterization of the ACC were also reported earlier (18).

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 measurements by means of UV-visible absorption spectrophotometry. This cell, described in detail including a diagram in our previous works (10,14,15), was V-shaped with one arm containing the carbon cloth attached to a short Pt wire sealed to a glass rod and the other arm containing a thin glass tube through which N_2 gas was passed for the 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-visible spectroscopy. Solutions of adsorbates were prepared in water. The initial concentrations of dyes and the amount of the ACC were kept as constant as possible for kinetic studies of adsorption in order to make an easy comparison among adsorption behaviors of different dyes (concentration: 4×10^{-5} 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 (10,18).

The ACC piece was dipped into the adsorption cell initially containing only water and vacuum was applied to remove all air in the pores of the ACC. Then wetted and degassed ACC was removed from the cell for a short time and water in the cell was replaced with a known volume of the sample solution (20 mL). The sliding door of the sample compartment of the spectrophotometer was left half-open and the quartz cuvette fixed at the bottom of the adsorption cell (which now contained the sample solution) was inserted into the front sample compartment. A teflon tube connected to the tip of a thin N_2-bubling 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. Finally, the carbon cloth, which had been removed temporarily after wetting and degassing, was re-inserted from the other arm of the adsorption cell into the solution. Then, quickly, an opaque curtain was spread above 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 the specific dye 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 750 data points for an adsorption period of 750 min at each wavelength in the selected region. This is one of the most important advantages of in-situ UV-visible spectroscopic technique as applied in the scanning-kinetics mode. In most classical adsorption studies, the batch analysis method is 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 C.I. Acid Blue 74 from water onto the ACC was reproduced in Fig. 2 in which only scans in 10 min intervals are shown. The downward movement of the absorbance maxima at three wavelengths as the adsorption goes on is clearly seen in this figure and marked by arrows. 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

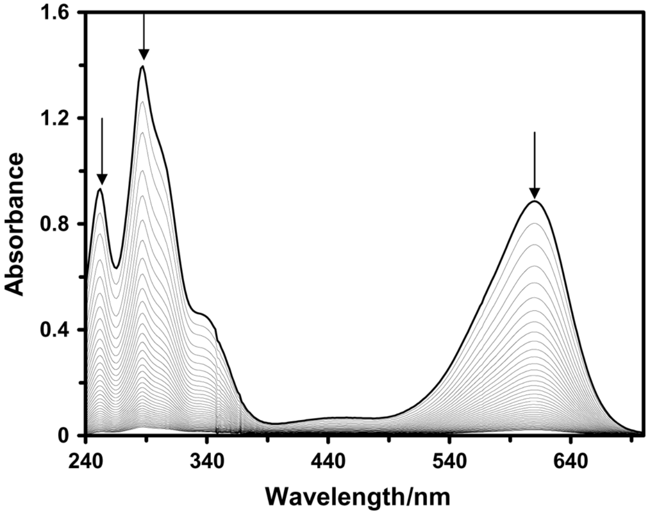


Figure 2. Scans during the adsorption of C.I. Acid Blue 74 onto activated carbon cloth in 10 min intervals. Arrows show directions of change (diminution) of optical absorbance at three wavelengths of absorption maxima, with time.

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}) unless there is change in spectrum such as shift in λ_{max}.

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 dyes studied are given in Table 2.

Table 2. Calibration data for in-situ UV spectroscopic analysis of dyes. M_w: molecular weight, λ_{max}: wavelength of maximum absorption, ε: molar absorptivity and r: correlation coefficient

Dye	M_w ($g \cdot mol^{-1}$)	λ_{max} (nm)	ε($M^{-1}\,cm^{-1}$)	r
C.I. Basic Blue 9	319.86	664	78000	0.9935
		292	43000	0.9993
		246	19250	0.9996
C.I. Acid Blue 74	466.36	610	22700	0.9995
		287	36000	0.9996
		252	24100	0.9998
C.I. Basic Red 2	350.85	519	45400	0.9981
		276	46700	0.9979
		249	31400	0.9996

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 a 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)

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

where V is the volume of the solution of adsorbate in L, C_0 and C_e are the initial and equilibrium concentrations, respectively, in $\mathrm{mol \cdot L^{-1}}$, and m is the mass of the ACC in g.

RESULTS AND DISCUSSION

Adsorption Kinetics

The concentration versus time curves for the adsorption of dyes under study onto the ACC over 750 min are shown in Fig. 3. Although there are some differences in adsorption behaviors of different dyes during the course of adsorption, all of them become almost completely removed from aqueous solution after about 500 min. It is to be noted that the initial concentration of each dye and the mass of the ACC used for the adsorption of each dye were the same.

In order to make more quantitative kinetic evaluation and to investigate the adsorption mechanism of dyes onto the ACC, some well-known kinetic models, such as pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion, were tested. The mathematical expressions for the pseudo-first order rate equation of Lagergren (19), the pseudo-second order rate equation (20,21) and Elovich equation (20,22) are given in Eqs. (2), (3), and (4), respectively.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

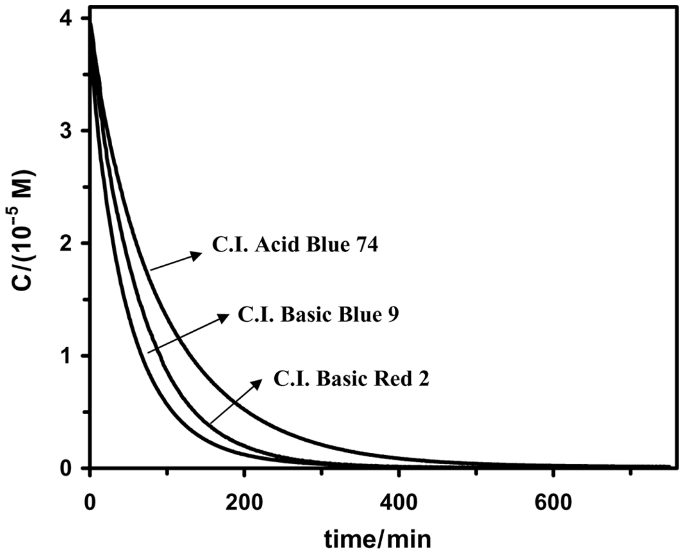


Figure 3. Concentration versus time plot for the adsorption of C.I. Basic Blue 9, C.I. Basic Red 2 and C.I. Acid Blue 74 onto the activated carbon cloth. Initial concentration is 4×10^{-5} M and mass of ACC is 18.3 ± 0.1 mg in all cases.

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \tag{4}$$

In these equations q_e is the amount of dye adsorbed per unit mass of the ACC at equilibrium in $\text{mmol} \cdot \text{g}^{-1}$, q_t is that at time t in $\text{mmol} \cdot \text{g}^{-1}$, k_1 is the first order rate constant in min^{-1}, k_2 is the second order rate constant in $\text{g} \cdot (\text{mmol} \cdot \text{min})^{-1}$, α (initial sorption rate) in $\text{g} \cdot (\text{mmol} \cdot \text{min}^2)^{-1}$, and β (desorption constant) in $\text{mmol} \cdot (\text{g} \cdot \text{min})^{-1}$ are Elovich coefficients. All kinetic equations (Eqs. (2), (3), and (4)) are in linear form and their parameters can be determined from linear regression analysis of the experimental kinetic data; $\ln(q_e–q_t)$ versus t in Eq. (2), t/q_t versus t in Eq. (3) and q_t versus $\ln t$ in Eq. (4). It is convenient to define the product $K_2 \cdot q_e^2$ in Eq. (3) as the initial sorption rate and denote by h. All these parameters and regression coefficients for treatment according to each kinetic equation are given in Table 3.

Regression coefficient values of the pseudo-second order model for adsorption of dyes onto the ACC ($r > 0.99$) is higher than those of the pseudo-first order and Elovich models. This suggests that the adsorption of dyes under study follows the pseudo-second order kinetic model. The deviation in q_e values predicted from the models compared to the experimentally determined values is another criterion in determining the correct model. Table 4 lists the experimental q_e values, the q_e values calculated

Table 3. The parameters and regression coefficients of the three kinetic models applied for experimental adsorption kinetic data of the dyes studied

	Pseudo first-order		Pseudo second-order			Elovich equation		
Dye	$k_1\,(\mathrm{min}^{-1})$	r	k_2 $(g \cdot (mmol \cdot min)^{-1})$	$h \times 10^3$ $(mmol \cdot (g \cdot min)^{-1})$	r	α $(g \cdot (mmol \cdot min^2)^{-1})$	$\beta \times 10^3$ $(mmol \cdot (g \cdot min)^{-1})$	r
C.I. Basic Blue 9	0.0119	0.9848	1.143	2.298	0.9996	272.5	6.54	0.9183
C.I. Basic Red 2	0.0102	0.9565	1.416	1.474	0.9990	85.06	7.61	0.9295
C.I. Acid Blue 74	0.0108	0.9892	2.826	0.800	0.9987	29.02	8.85	0.9667

Table 4. Experimental and calculated q_e values in $mmol \cdot g^{-1}$ from pseudo first-order and pseudo second-order kinetics models for the adsorption of dyes on the ACC

Dye	$(q_e)_{experimental}$	$(q_e)_{first\text{-}order}$	Deviation (%)	$(q_e)_{second\text{-}order}$	Deviation (%)
C.I. Basic Blue 9	0.0432	0.0187	−56.7	0.0448	+3.70
C.I. Basic Red 2	0.0432	0.0170	−60.6	0.0457	+5.79
C.I. Acid Blue 74	0.0432	0.0495	+14.6	0.0476	+10.2

from the pseudo-first and the pseudo-second order models upon regression analysis of experimental kinetic data together with percent deviations. The deviations are much smaller for the pseudo-second order model than for the pseudo-first order model. This supports the finding that the pseudo-second order model is being followed during the adsorption of dyes onto the ACC.

Pseudo-second order rate constants of dyes decreased in the order C.I. Acid Blue 74 > C.I. Basic Red 2 > C.I. Basic Blue 9. On the other hand the initial sorption rate values (h) of dyes increased in the order C.I. Acid Blue 74 < C.I. Basic Red 2 < C.I. Basic Blue 9 (Table 3). This final order according to h values is in agreement with the visually observed adsorption behavior in Fig. 3. It is apparent that C.I. Acid Blue 74 has the lowest adsorption rate.

Adsorption proceeds in several steps involving transport of the solute molecules from the aqueous phase to the surface of the adsorbent and diffusion of the solute molecules into the interior of the pores which is usually a slow process. The intra-particle diffusion rate constant, k_i, in $mmol \cdot g^{-1} \cdot min^{-0.5}$ is given by the following equation (23):

$$q_t = k_i t^{0.5} \tag{5}$$

When intra-particle diffusion plays a significant role in controlling the kinetics of the adsorption process, the plots of q_t versus $t^{0.5}$ yield straight lines passing through the origin and the slope gives the rate constant, k_i. The plots of q_t versus $t^{0.5}$ for the present results did not yield a straight line passing through the origin. This suggested that the intraparticle diffusion model is not the rate-limiting control step for the adsorption of dyes.

Adsorption Isotherms

The adsorption isotherm data of C.I. Basic Blue 9, C.I. Basic Red 2, and C.I. Acid Blue 74 obtained at 30°C in water are given

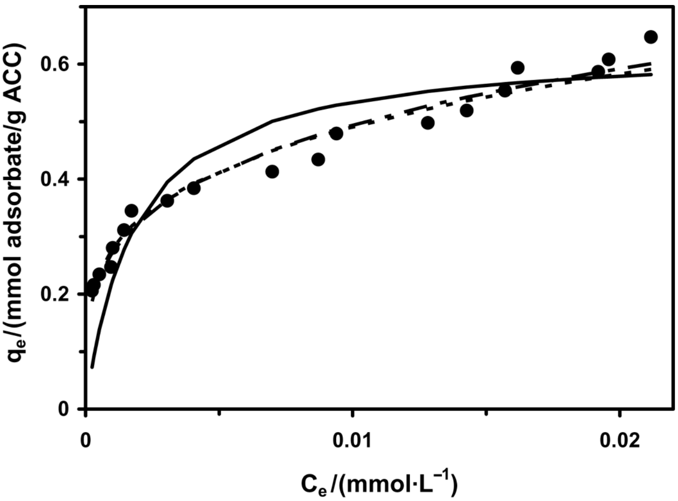


Figure 4. The fit of experimental adsorption data (●) to Langmuir (––––), Freundlich (— — — —) and Redlich-Peterson (—— —— ——) models for C.I. Basic Blue 9.

in Figs. 4, 5 and 6, respectively. The isotherm data were treated according to three well known isotherm equations; Langmuir, Freundlich, and Redlich-Peterson. The linearized forms of Langmuir

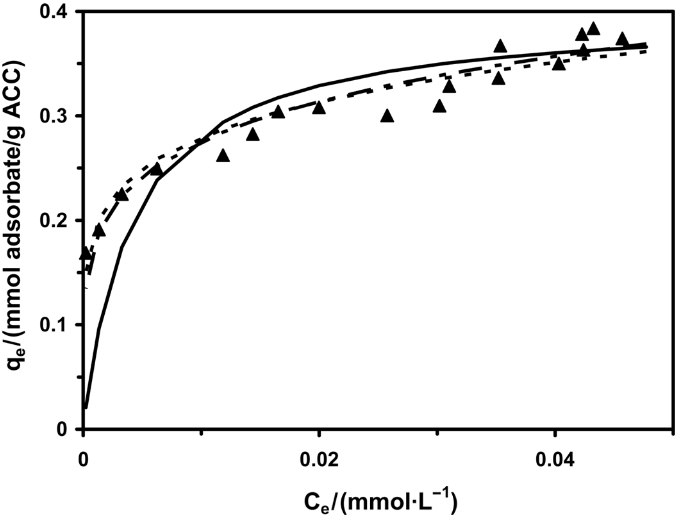


Figure 5. The fit of experimental adsorption data (▲) to Langmuir (––––), Freundlich (— — — —) and Redlich-Peterson (—— —— ——) models for C.I. Basic Red 2.

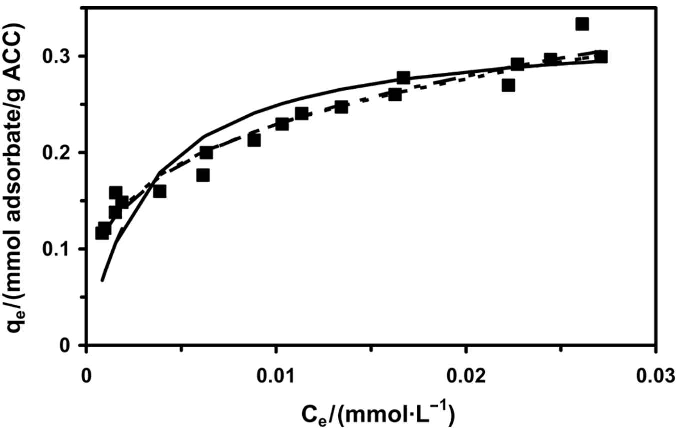


Figure 6. The fit of experimental adsorption data (■) to Langmuir (– – – –), Freundlich (— — — —) and Redlich-Peterson (—— —— ——) models for C.I. Acid Blue 74.

and Freundlich isotherm equations can be given in Eqs. (6) and (7), respectively (24);

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{6}$$

$$\ln q_e = \ln K_F + (1/n)\ln C_e \tag{7}$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in $mol \cdot g^{-1}$, C_e is the final concentration at equilibrium in $mol \cdot L^{-1}$, q_{max} is the maximum adsorption at monolayer coverage in $mmol \cdot g^{-1}$, b is the adsorption equilibrium constant related to the energy of adsorption in $L \cdot mmol^{-1}$, K_F is the Freundlich constant representing the adsorption capacity in $(mmol \cdot g^{-1}).(L \cdot mmol^{-1})^{1/n}$, and n is a constant related to surface heterogeneity. Freundlich constant, 1/n, is also a measure of the deviation of the adsorption from linearity. If n is equal to unity the adsorption isotherm is linear. This means that the adsorption sites are homogeneous in energy and no interaction takes place between the adsorbed species. If the value of 1/n is smaller than 1, the adsorption is favorable. When the value of 1/n is larger than 1, the adsorption interactions become weak and unfavorable adsorption takes place (25). The Langmuir and Freundlich isotherm equations (Eqs. (6) and (7)) have two parameters, but the Redlich-Peterson isotherm equation (26) has three parameters and its nonlinear equation is expressed as follows:

$$q_e = \frac{qAC_e}{1 + AC_e^B} \tag{8}$$

where q and A are the Redlich-Peterson isotherm constants in $\text{mmol}\cdot\text{g}^{-1}$ and $\text{L}\cdot\text{mmol}^{-1}$, respectively, and B is an exponent which lies between 0 and 1.

The Freundlich isotherm equation was developed for heterogeneous surfaces. In this case, there is a continuously varying energy of adsorption as the most actively energetic sites are occupied first and the surface is continually occupied until the lowest energy sites are filled at the end of the adsorption process. The Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness and that all sites are equal, resulting in equal energies and enthalpies of adsorption. The Redlich-Peterson equation is a combination of the Langmuir and the Freundlich equations. In the limit, as the exponent B tends to zero, the equation approaches to Freundlich equation and as the exponent B tends to 1, the equation approaches to Langmuir equation (27).

The parameters of Eqs. (6) and (7) were obtained by linear regression analysis, while those of Eq. (8) were obtained by nonlinear regression analysis using the GRAPHPAD PRISM program, as this equation cannot be put into linear form and they were collectively given in Table 5. The values of 1/n are found to be less than 1, which suggests favorable adsorption behavior of dyes onto the ACC (25). The regression coefficients for all three tested models are higher than 0.960 and thus it is difficult to judge which isotherm model is best for representing the experimental isotherm data. A better criterion for the assessment of the experimental isotherm data is a parameter known as normalized percent deviation (28) or in some literature as percent relative deviation modulus, P, (29,30) given by the following equation;

$$P = \frac{100}{N}\sum_{i=1}^{N}\frac{|q_{e(pred)} - q_{e(exp)}|}{q_{e(exp)}} \tag{9}$$

where $q_{e\,(exp)}$ is the experimental q_e in $\text{mmol}\cdot\text{g}^{-1}$ at any C_e, $q_{e\,(pred)}$ is the corresponding q_e predicted from the equation under study with the best-fitted parameters and N is the number of observations. It is clear 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 (29). The P values for the Freundlich model are generally found to be lower than those for other models (Table 5). Thus, it can be concluded that the Freundlich isotherm model represents the experimental isotherm data for the dyes under study better than the other two models. Freundlich constant, K_F, representing the adsorption capacity (Table 5) increased in the order C.I. Basic Red 2 < C.I. Acid Blue 74 < C.I. Basic Blue 9. The same order was observed for the adsorption capacity parameter of Redlich-Peterson model, q.

Table 5. Parameters of Langmuir, Freundlich and Redlich-Peterson isotherm equations, regression coefficients (r) and normalized percent deviation (P) values for dyes studied at 30°C

	Langmuir parameters				Freundlich parameters				Redlich-Peterson parameters				
Dye	q_{max} $(mmol \cdot g^{-1})$	B $(L \cdot mol^{-1})$	R	P	K_F $(mmol \cdot g^{-1})$ $(L \cdot mmol^{-1})^{1/n}$	1/n	r	P	q $(mmol \cdot g^{-1})$	A $(L \cdot mmol^{-1})$	B	r	P
C.I. Basic Blue 9	0.632	543	0.9871	17.6	1.53	0.247	0.9886	4.43	1.63	130000	0.741	0.9856	4.85
C.I. Basic Red 2	0.398	238	0.9874	13.9	0.597	0.165	0.9649	5.18	0.650	55000	0.814	0.9601	4.90
C.I. Acid Blue 74	0.330	307	0.9875	13.8	0.804	0.272	0.9825	3.86	0.852	130000	0.715	0.9812	4.30

Correlation of Adsorption Results with the Adsorbent Properties

pH_{PZC} is an important property of an adsorbent in determining the electrostatic interactions between the adsorbent and adsorbate during adsorption (31). The pH_{PZC} of the ACC used in the present work is 7.4 (Table 1). The pH values of the adsorbate solutions at the beginning and at the end of adsorption during the isotherm studies are given in Table 6. It is seen that the pH values of the adsorbate solutions do not change appreciably during the course of adsorption and they are quite close to the pH_{PZC} value of the ACC. This shows that no strong electrostatic interaction is expected between the adsorbates and the ACC surface. Thus the main adsorptive force, operative in removing the dyes almost completely from the aqueous solution, is probably $\pi-\pi$ dispersion forces.

The order of adsorption capacity of the ACC for the three dyes as determined by the K_F values can be correlated with the size of molecules and the size of pores in the ACC. The lengths and widths of the dyes under study were determined using a program called ChemSketch and are given in Table 7. It is more probable for the molecules to be adsorbed on the ACC by entering the pores through their narrower dimensions; i.e. widths. In this way, more molecules can be accommodated in the pores. The analysis of pore size distribution data of the ACC, reported previously (32), has shown that the percentages of total pores having pore sizes greater than 5.1, 6.4, and 7.2 Å (the widths of the three dyes) are 98, 83, and 80, respectively. So, the highest adsorption capacity is expected for C.I. Basic Blue 9 with a width of 5.1 Å, and then for C.I. Acid Blue 74 with a width of 6.4 Å and finally for C.I. Basic Red 2 with a width of 7.2 Å. This order is the same as the order of K_F values determined experimentally (Table 5).

Table 6. The pH values of adsorbate solutions at the beginning (pH_i) and at the end of adsorption (pH_f) during isotherm studies

Dye	pH_i	pH_f (a)
C.I. Basic Blue 9	6.08	6.11–6.50
C.I. Basic Red 2	6.41	6.92–7.11
C.I. Acid Blue 74	6.40	6.91–7.43

(a) pH_f values varied with the amount of the ACC used in isotherm studies. Thus a range is given for this value.

Table 7. The lengths and widths of the dyes determined from ChemSketch program

Dye	Length (Å)	Width (Å)
C.I. Basic Blue 9	13.7	5.1
C.I. Basic Blue 9	13.7	5.1
C.I. Acid Blue 74	15.5	6.4

CONCLUSIONS

The ACC used as an adsorbent in this work was found to be very effective in removing the dyes, C.I. Basic Blue 9, C.I. Basic Red 2, and C.I. Acid Blue 74, from aqueous solutions by adsorption. Almost complete removal was achieved under certain conditions. In-situ UV-visible spectroscopic method as applied in scanning kinetics mode was very powerful in following the concentrations of dyes during the course of adsorption. The pseudo-second order model for the kinetics and the Freundlich isotherm model for the equilibrium of the adsorption were found to fit the experimental data reasonably well. A fair correlation was found between the adsorption capacity of the ACC for dyes and the sizes of the dye species and pores of the ACC. It is recognized that the presented adsorption work is for model systems including the dye and the solvent water. However, it is predicted that the actual system can be approached by including more than one type of dye in the aqueous system and such systems can successfully be studied with the powerful in-situ UV-visible spectroscopic method used in this work.

ACKNOWLEDGEMENTS

The authors would like to thank to the Scientific Research Projects Unit of Akdeniz University for the support of this work through the project 2003.01.0300.009.

REFERENCES

1. McKay, G.; Porter, J.F.; Prasad, G.R. (1999) The removal of dye colors from aqueous solutions by adsorption on low-cost materials. *Water, Air and Soil Pollution*, *114*: 423–438.
2. Namasivayam, C.; Yamuna, R.T.; Arasi, D.J.S.E. (2002) Removal of procion orange from wastewater by adsorption on waste red mud. *Separation Science and Technology*, *37*: 2421–2431.

3. Raghuvanshi, S.P.; Singh, R.; Kaushik, C.P. (2004) Kinetics study of methylene blue dye bioadsorption on bagasse. *Applied Ecology and Environmental Research*, *2*: 35–43.
4. Safarikova, M.; Ptackova, L.; Kibrikova, I.; Safarik, I. (2005) Biosorption of water-soluble dyes on magnetically modified Saccharomyces cerevisiae subs. uvarum cells. *Chemosphere*, *59*: 831–835.
5. Kannan, N.; Sundaram, M.M. (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-a comparative study. *Dyes and Pigments*, *51*: 25–40.
6. Suteu, D.; Bilba, D. (2005) Equilibrium and kinetic study of reactive dye brilliant red HE-3B adsorption by activated charcoal. *Acta Chimica Slovenica*, *52*: 73–79.
7. Senthilkumaar, S.; Varadarajan, P.R.; Porkodi, K.; Subbhuraam, C.V. (2005) Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies. *Journal of Colloid and Interface Science*, *284*: 78–82.
8. Kumar, K.V.; Sivanesan, S. (2005) Comparison of linear and non-linear method in estimating the sorption isotherm parameters for safranin onto activated carbon. *Journal of Hazardous Materials*, *123*: 288–292.
9. Wang, S.; Zhu, Z.H.; Coomes, A.; Haghseresht, F.; Lu, G.Q. (2005) The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *Journal of Colloid and Interface Science*, *248*: 440–446.
10. Ayranci, E.; Conway, B.E. (2001) Adsorption and electrosorption at high-area carbon felt electrodes for waste-water purification systems evaluation with inorganic, S-containing anion. *Journal of Applied Electrochemistry*, *31*: 257–266.
11. Afkhami, A. (2003) Adsorption and electrosorption of nitrate and nitrite on high-area carbon cloth: an approach to purification of water and waste-water samples. *Carbon*, *41*: 1309–1328.
12. Ayranci, E.; Conway, B.E. (2001) Removal of phenol, phenoxide and chlorophenols from waste-waters by adsorption and electrosorption at high-area carbon felt electrodes. *Journal of Electroanalytical Chemistry*, *513*: 100–110.
13. Conway, B.E.; Ayranci, G.; Ayranci, E. (2003) Molecular structure effects in the adsorption behavior of some aromatic heterocyclic compounds at high-area carbon-cloth in relation to waste-water purification. *Zeitschrift für Physikalische Chemie*, *217*: 315–331.
14. Duman, O.; Ayranci, E. (2005) Structural and ionization effects on the adsorption behaviors of some anilinic compounds from aqueous solution onto high-area carbon cloth. *Journal of Hazardous Materials*, *120*: 173–181.
15. Ayranci, E.; Duman, O. (2005) Adsorption behaviors of some phenolic compounds onto high specific area activated carbon cloth. *Journal of Hazardous Materials*, *124*: 125–132.
16. Hoda, N.; Bayram, E.; Ayranci, E. (2006) Kinetic and equilibrium studies on the removal of acid dyes from aqueous solutions by adsorption by adsorption onto activated carbon cloth. *Journal of Hazardous Materials*, *137*: 344–351.

17. Ayranci, E.; Duman, O. (2006) Adsorption of aromatic organic acids onto high area activated carbon cloth in relation to wastewater purification. *Journal of Hazardous Materials*, *136*: 542–552.
18. Ayranci, E.; Conway, B.E. (2001) 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. *Analytical Chemistry*, *73*: 1181–1189.
19. Lagergren, S. (1898) About the theory of so-called adsorption of soluble substances. Kungliga Svenska Vetenskapsakademiens. *Handlingar*, *24*: 1–39.
20. McKay, G.; Ho, Y.S.; Ng, J.C.Y. (1999) Biosorption of copper from waste waters: a review. *Separation and Purification Methods*, *28*: 87–125.
21. Azizian, S. (2006) A novel and simple method for finding the hetereogeneity of adsorbents on the basis of adsorption kinetic data. *Journal of Colloid and Interface Science*, *302*: 76–81.
22. Chien, S.H.; Clayton, W.R. (1980) Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Science Society of America Journal*, *44*: 265–268.
23. Weber, W.J.; Morris, J.C. (1963) Kinetics of adsorption on carbon solution. *Journal of the Sanitary Engineering Division: Proceedings of the American Society of Civil Engineers*, *89*: 31–59.
24. Smith, J.M. (1981) *Chemical Engineering Kinetics*; New York: McGraw-Hill Company.
25. Özcan, A.S.; Erdem, B.; Özcan, A. (2004) Adsorption of acid blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. *Journal of Colloid and Interface Science*, *280*: 44–54.
26. Baker, H.; Khalili, F. (2004) Analysis of the removal of lead (II) from aqueous solutions by adsorption onto insolubilized humic acid: temperature and pH dependence. *Analytica Chimica Acta*, *516*: 179–186.
27. Ng, J.C.Y.; Cheung, W.H.; McKay, G. (2002) Equilibrium studies of the sorption of Cu(II) ions onto chitosan. *Journal of Colloid and Interface Science*, *255*: 64–74.
28. Juang, R.S.; Tseng, R.L.; Wu, F.C.; Lee, S.H. (1996) Liquid-phase adsorption of phenol and its derivatives on activated carbon fibers. *Separation Science and Technology*, *31*: 1915–1931.
29. Lomauro, C.J.; Bakshi, A.S.; Labuza, T.P. (1985) Evaluation of food moisture sorption isotherm equations, Part I: fruit, vegetable and meat products. *Lebensmittel Wissenschaft und Technologie*, *18*: 111–117.
30. Ayranci, E.; Duman, O. (2005) Moisture sorption isotherms of cowpea (Vigna unguiculata L. Walp) and its protein isolate at 10, 20, and 30°C. *Journal of Food Engineering*, *70*: 83–91.
31. Moreno-Castilla, C. (2004) Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon*, *42*: 83–94.
32. Duman, O.; Ayranci, E. (2006) Adsorption characteristics of benzaldehyde, sulphanilic acid and p-phenolsulfonate from water, acid or base solutions onto activated carbon cloth. *Separation Science and Technology*, *41*: 3673–3692.