

## Sorption of acid red 57 from aqueous solution onto sepiolite

Mahir Alkan\*, Özkan Demirbaş, Sermet Çelikçapa, Mehmet Doğan

*Department of Chemistry, Faculty of Science and Literature, University of Balıkesir, Balıkesir 10100, Turkey*

Received 10 May 2004; received in revised form 27 July 2004; accepted 13 August 2004

### Abstract

Sepiolite, a highly porous mineral, is becoming widely used as an alternative material in areas where sorptive, catalytic and rheological applications are required. High ion exchange capacity and high surface area and more importantly its relatively cheap price make it an attractive adsorbent. In this study, the adsorption of acid red 57 by natural mesoporous sepiolite has been examined in order to measure the ability of this mineral to remove coloured textile dyes from wastewater. For this purpose, a series of batch adsorption tests of acid red 57 from aqueous sepiolite solutions have been systematically investigated as a function of parameters such as pH, ionic strength and temperature. Adsorption equilibrium was reached within 1 h. The removal of acid red 57 decreases with pH from 3 to 9 and temperature from 25 to 55 °C, whereas it increases with ionic strength from 0 to 0.5 mol L<sup>-1</sup>. Adsorption isotherms of acid red on sepiolite were determined and correlated with common isotherm equations such as Langmuir and Freundlich models. It was found that the Langmuir model appears to fit the isotherm data better than the Freundlich model. The physical properties of this adsorbent were consistent with the parameters obtained from the isotherm equations. Approximately, 21.49% weight loss was observed. The surface area value of sepiolite was 342 m<sup>2</sup> g<sup>-1</sup> at 105 °C, and it increased to 357 m<sup>2</sup> g<sup>-1</sup> at 200 °C. Further increase in temperature caused channel plugging and crystal structure deformation, as a result the surface area values showed a decrease with temperature. The data obtained from adsorption isotherms at different temperatures have been used to calculate some thermodynamic quantities such as the Gibbs energy, heat and entropy of adsorption. The thermodynamic data indicate that acid red 57 adsorption onto sepiolite is characterized by physical adsorption. The dimensionless separation factor ( $R_L$ ) have shown that sepiolite can be used for removal of acid red 57 from aqueous solutions. The sorption capacity of the sepiolite is comparable to the other available adsorbents, and it is quite cheaper.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Adsorption; Dye; Clay mineral; Sepiolite; Langmuir model

### 1. Introduction

Industrial, agricultural and domestic wastes, due to the rapid development in technology and urbanization, are discharged to several receivers. Generally, this discharge is done to the nearest water sources such as rivers, lakes and seas. Control of water pollution has importance for both organisms, which live in water and those who benefit from water. Wastewater treatment includes one or a combination of physical, chemical, and biological purification methods in order

to recover some, or all of the lost water properties due to the several uses and to make the water receivers, in which the wastewater is discharged, not to destroy the physical and ecological properties of the environment. Among several removal technologies, adsorption and ion exchange with natural clays have great importance due to the ease of operation and comparable low cost of application. The removal of dyes from industrial wastewaters is currently of great interest. Different adsorbents have been used for removal of various materials from aqueous solutions, such as dyes, metal ions and other organic materials. These include perlite [1–6], activated carbon [7–11], bentonite [12], silica gels [13], flyash [14–16], lignite [17], peat [18], silica [19] etc. In order to minimize processing costs for these effluents, recent investigations have

\* Corresponding author.

*E-mail addresses:* malkan@balikesir.edu.tr (M. Alkan), ozkan@balikesir.edu.tr (Ö. Demirbaş), mdogan@balikesir.edu.tr (M. Doğan).

### Nomenclature

$C_e$	equilibrium dye concentration in solution ( $\text{mol L}^{-1}$ )
$\Delta G$	Gibbs energy of adsorption ( $\text{kJ mol}^{-1}$ )
$\Delta H$	heat of adsorption ( $\text{kJ mol}^{-1}$ )
$K$	adsorption constant
$K_F$	Freundlich constant ( $\text{mol g}^{-1}$ )
$n$	Freundlich isotherm exponent
$Q_e$	equilibrium dye concentration on adsorbent ( $\text{mol g}^{-1}$ )
$Q_m$	monolayer capacity of the adsorbent ( $\text{mol g}^{-1}$ )
$R^2$	regression coefficient
$R_L$	dimensionless separation factor
$\Delta S$	the entropy of adsorption ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$T$	temperature (K)

focused on the use of cheaper and easily obtainable low cost unconventional adsorbents. It can be said that a suitable candidate can be sepiolite.

Sepiolites, which form an important group of clay minerals, are a magnesium silicate and currently used in a number of different applications such as many industrial, catalytic and environmental applications, most of which are similar to those of the more traditional clays. Because of their structural morphology, sepiolites have received considerable attention with regard to the adsorption of organics on the clay surfaces and to their use as support for catalysts [20]. The abundance and availability of sepiolite mineral reserves as a raw material source and its relatively low cost guarantee its continued utilization in the future, and most of the world sepiolite reserves are found in Turkey. Sepiolite is a good adsorbent for organic species because it exhibits a variety of attractive properties such as high specific surface area, high porosity (50.8%) [21], and surface activity. Sepiolite is therefore used in a spectrum of areas where sorptive, catalytic, and rheological properties are exploited. The sorption ability of sepiolite is mainly ascribed to its high surface area. Thus, it is commonly used in oil refining; wastewater treatment; the removal of odor, drug, and pesticide carriers; paper and detergent; etc. [22]. Investigations on sepiolite have so far focused more on its sorptive properties and attempts have been made to increase its surface area. A number of investigators have studied the interaction of water and various organic reagents with sepiolite. Kara et al. [23] investigated the adsorption of cobalt from aqueous solutions onto sepiolite; Rytwo et al. [24] the adsorption of diquat, paraquat and methyl green on sepiolite; Balcı and Dinçel [25] the ammonium ion adsorption with sepiolite; Molina-Sabio et al. [26] the porous structure of a sepiolite as deduced from the adsorption of  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ ; Akyüz et al. [27] FT-IR spectroscopic investigation of adsorption of 3-aminopyridine on sepiolite and montmorillonite from Anatolia; Sabah et al. [28]

the adsorption mechanism of cationic surfactants onto acid- and heat-activated sepiolites; Rytwo et al. [29] the adsorption and interactions of methyl green with montmorillonite and sepiolite; González-Pradas et al. [30] the adsorption of dilute thiram, an active carbon, as a function of temperature; Shuali et al. [31] the interaction of amines on sepiolite and polygorskite by infrared measurements; González-Pradas et al. [32] the removal of aromatic amines from aqueous solutions by activated sepiolite; Rytwo et al. [33] the access of cationic dye into the structural micropores of sepiolite; Çelik et al. [34] the removal of ammonia by natural clay minerals; Balcı [35] the nature of ammonium ion adsorption by sepiolite; Özdemir et al. [36] the comparison of the adsorption characteristics of azo-reactive dyes on mesoporous minerals. As can be seen above, only a limited number of studies onto the removal of dyes using sepiolite as an adsorbent have been found in the literature. Therefore, the aim of the present investigation is to study the adsorption mechanism of acid red 57 onto natural sepiolite and to understand the way the dye interacts with sepiolite. Towards this aim, the effect of various parameters such as pH, ionic strength and temperature on the adsorption process has been investigated and the equilibrium adsorption isotherms have been reported. The results obtained have been applied to a single batch design for the removal of acid red 57 from aqueous media by using sepiolite. Furthermore, some thermodynamic data have been calculated to interpret the results.

## 2. Material and methods

### 2.1. Material

Sepiolite is a clay mineral with a unit cell formula  $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH},\text{F})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ , and the structure of sepiolite is shown in Fig. 1a [37]. Removal of the structural water causes the sepiolite crystals to fold by rotation of the fibers on axes through the inverted Si–O–Si edge bonds [38], thus, allowing the terminal  $\text{Mg}^{2+}$  to complete their coordination with the oxide surface of the neighboring silica layer (Fig. 1b). The clay used was obtained from Aktaş Lületaşı–Eskişehir regions of Anatolia (Turkey). Acid red 57 was obtained from Setaş and Eksoy Textile Co. (Bursa, Turkey). The molecular structure of acid red 57 used is shown in Fig. 2.

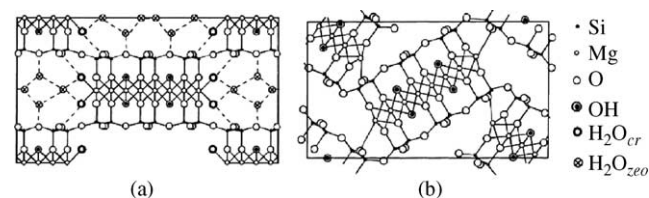


Fig. 1. Schematic representation of (a) the sepiolite structure projected on the plane and (b) the structure of sepiolite anhydride.

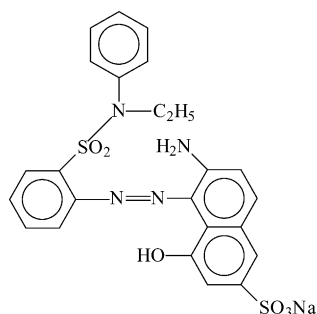


Fig. 2. The molecular structure of acid red 57.

## 2.2. Equipment

The pH measurements were made using a pH meter (Orion 920A). X-ray measurements were performed using a Philips X-ray diffractometer employing nickel-filtered Cu K $\alpha$  radiation. The surface area was measured with Micromeritics Flow Sorb II-2300 equipment. The density of the adsorbent was determined using picnometer method. The chemical constituents of sepiolite were analyzed by XRF. Absorbance measurements were made on a Cary 1E UV–vis spectrophotometer (Varian). The spectrophotometer response time was 0.1 s, and the instrument had a resolution of 0.1 nm. The concentration of acid red 57 was measured with a 1-cm light path cell, with an absorbance accuracy of  $\pm 0.004$  at the maximum wavelength of the dye. The absorbance was found to vary linearly with concentration.

## 2.3. Preparation of sample

The clay was treated before using in the experiments as follows: after cleaning the clay mechanically from the visible impurities, it was ground and sieved to obtain 75  $\mu\text{m}$  size fraction. Then, it was dried at 105  $^{\circ}\text{C}$  for 24 h, and used in further experiments [1–5]. The cation exchange capacity (CEC) of the sepiolite sample was determined by the ammonium acetate method, the chemical analysis determined by XRF, density by the picnometer method, and the specific surface areas measured by BET N<sub>2</sub> adsorption [1]. The results obtained and other some physicochemical properties of sepiolite are presented in Table 1. Furthermore, the chemical analysis of sepiolite are given in Table 2. All chemicals were purchased from Merck.

Table 1  
Physicochemical properties of sepiolite

Parameters	Value	References
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	342	In this study
Density ( $\text{g cm}^{-3}$ )	2.5	In this study
Cation exchange capacity (meg 100 $\text{g}^{-1}$ )	25	In this study
pH of solution	7.8–8.3	In this study
Porosity (%)	50.8	[21]

Table 2  
Chemical composition of sepiolite

Component	Weight (%)
SiO <sub>2</sub>	53.47
MgO	23.55
CaO	0.71
Al <sub>2</sub> O <sub>3</sub>	0.19
Fe <sub>2</sub> O <sub>3</sub>	0.16
NiO	0.43
LOI	21.49

LOI: loss ignition of sepiolite.

## 2.4. Method

Sorption studies were performed by the batch technique to obtain equilibrium data. The batch technique was selected because of its simplicity. Batch sorption studies were performed at different pH, ionic strengths and temperatures to obtain equilibrium isotherms and data required in the design and operation of reactors for the treatment of dye-bearing wastewater. For isotherm studies, adsorption experiments were carried out by shaking 0.5 g sepiolite samples with 50 mL aqueous solution in a series of 100 mL polyethylene flasks. Each polyethylene flask was filled with 50 mL of a dye solution of varying concentrations ( $5 \times 10^{-5}$ – $80 \times 10^{-5} \text{ mol L}^{-1}$ ) and adjusted to the desired pH, ionic strengths and temperature. A known amount of adsorbent was added to each polyethylene flask and agitated for the desired time periods, up to a maximum of about 1 h. Preliminary experiments demonstrated that the equilibrium was established in 1 h. Equilibration for longer times gave practically the same uptake. Therefore, a contact period of 1 h was finally selected for all of the equilibrium tests. At the end of the adsorption period, the solution was centrifuged for 15 min at 3000 rpm and then the concentrations of the residual dye,  $C_e$ , were determined with the aid of a UV–vis spectrophotometer. The measurements were made at the wavelength  $\lambda = 513 \text{ nm}$ , which corresponds to maximum absorbance. Blanks containing no dye were used for each series of experiments. All adsorption experiments were performed at 25  $^{\circ}\text{C}$  and pH 6.0 of acid red 57 solutions except those in which the effects of temperature and pH were investigated. The effect of pH was observed by studying the adsorption of dye over a pH range of 3–9. The pH of the solution was adjusted with 0.1 M NaOH or HCl solution by using a Orion 920A pH-meter equipped with a combined pH electrode. pH-meter was standardized with NBS buffers before every measurement. The sorption studies were also carried out at different temperatures, i.e., 25, 35, 45, and 55  $^{\circ}\text{C}$ , to determine the effect of temperature and to evaluate the sorption thermodynamic parameters. A thermostated shaker bath was used to keep the temperature constant. The amounts of acid red 57 adsorbed were calculated from the concentrations in solutions before and after adsorption [1]. All the experiments were carried out in duplicate. The amount of acid red 57 adsorbed ( $\text{mol g}^{-1}$ ), ( $Q_e$ ), onto sepiolite was calculated

from the mass balance equation as follows [3]:

$$Q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium liquid-phase concentrations of dye solution ( $\text{mol L}^{-1}$ ), respectively;  $V$  the volume of dye solution (L), and  $W$  the mass of sepiolite sample used (g).

### 2.5. Electrokinetic measurements

Zeta potential of sepiolite was measured at  $25 \pm 1^\circ\text{C}$  using a Zeta Meter 3.0 equipped with a microprocessor unit. The unit automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potentials in terms of Smoluchowski equation [39]. A 1 g amount of sepiolite was conditioned in 100 mL of 0.0001 M KCl at various final pH values for 24 h. The suspensions was kept still for 5 min to let the larger particles settle. Each data point is an average of approximately 20 measurements. The pH of the suspension was adjusted using dilute 0.1 M HCl and NaOH. All solutions were prepared using bidistilled water [40].

## 3. Results and discussion

### 3.1. Thermal treatment of sepiolite

The thermal behavior of sepiolite has been the subject of several publications in the literature [39,40]. It has been stated that the structural changes of sepiolite with increasing temperature affect the specific surface area and adsorption capacity. Sepiolite has structurally four water molecules coordinated to magnesium. The loss of these water molecules with increasing temperature will affect specific surface area and adsorption capacity of sepiolite. It has been stated that water molecules coordinated to magnesium lose until  $500^\circ\text{C}$ . After losing of four water molecules coordinated to magnesium, the structure folds. The folding of the structure is associated with a decrease in the adsorption properties since the channels become narrower and the superficial slots sinter. A further increase in temperature produces the dehydroxylation of the structure and leads to the formation of clinoenstatite. The results obtained in order to investigation the changing taking place in the specific surface area of sepiolite in the calcination temperature ranges of  $105\text{--}700^\circ\text{C}$  have been shown in Fig. 3. As can be seen in Fig. 3, the specific surface area of sepiolite has increased until  $200^\circ\text{C}$  calcination temperature, and then continuously decreased with increasing calcination temperature. Thermal treatment produces a maximum specific surface area of  $357\text{ m}^2\text{ g}^{-1}$  at  $200^\circ\text{C}$ . This result is generally in line with the reported literature [23,41]. In this study, the sepiolite was subjected the thermal treatment at  $105^\circ\text{C}$ . The decrease in the specific surface area of sepiolite may be a result of the removal of most of the micropores and the folding of structure due to heating the sample.

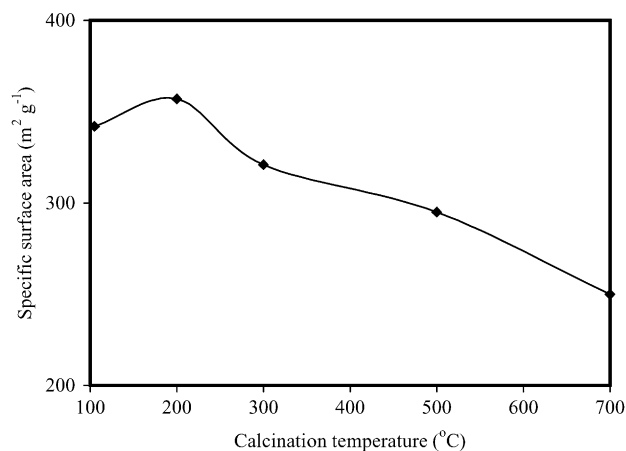


Fig. 3. The changing of specific surface areas against calcination temperatures.

Furthermore, it has been seen from Table 1 that sepiolite has about 21.49% loss on ignition. This result is in a good agreement with Balci's results [35] which used thermal gravimetric analysis (TGA) method to determine the percent weight loss for sepiolite. He said that (i) the removal of hydroscopic water from the external surface and zeolitic water from the voids of the structure was completed up to  $220^\circ\text{C}$  with a 8.7% weight loss for the untreated sepiolite sample, (ii) the first part of the bound water was evolved from the structure with a 5.4% weight loss up to  $450^\circ\text{C}$ , (iii) the remaining part of bound water began to leave the structure at higher temperatures (about  $750^\circ\text{C}$ ) and was accompanied by an 8.5% additional weight loss, (iv) the removal of structural water molecules (hydroxyl groups) was completed at 1.5% weight loss up to  $850^\circ\text{C}$  [42,43]. The X-ray powder diffraction pattern of sepiolite has been given in Fig. 4. By comparing the  $d$  values obtained in this study and taken from JCPDS chart, the results have shown that this structure belongs to sepiolite.

### 3.2. Adsorption parameters

Adsorption of acid red 57 onto sepiolite was systematically investigated by parameters such as pH, ionic strength and temperature.

#### 3.2.1. Effect of pH

The pH is one of the most important factors affecting the adsorption process. In order to study the influence of pH on the adsorption capacity of sepiolite, experiments were performed using various initial solution pH values changing from 3 to 9. Fig. 5 shows the effect of pH on the removal of acid red 57 by sepiolite. The acid red 57 removal by sepiolite decreased with increasing pH. In the discussion of the effect of pH, it is necessary to discuss the zeta potential value of sepiolite. The changing of zeta potential with final pH values of sepiolite–KCl suspensions has been given in Fig. 6. As can be seen in Fig. 6, sepiolite has an isoelectrical point around pH 7.1. In acid medium, the positive charge develops

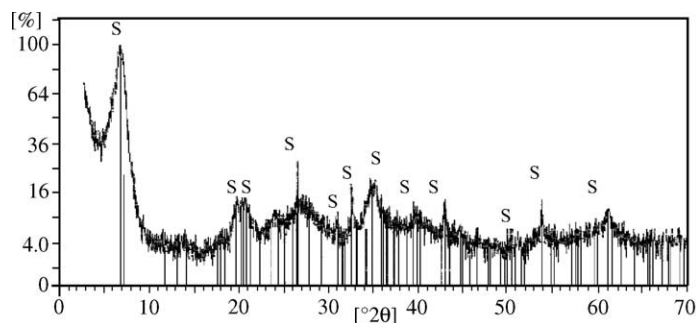


Fig. 4. X-ray diffraction patterns of sepiolite.

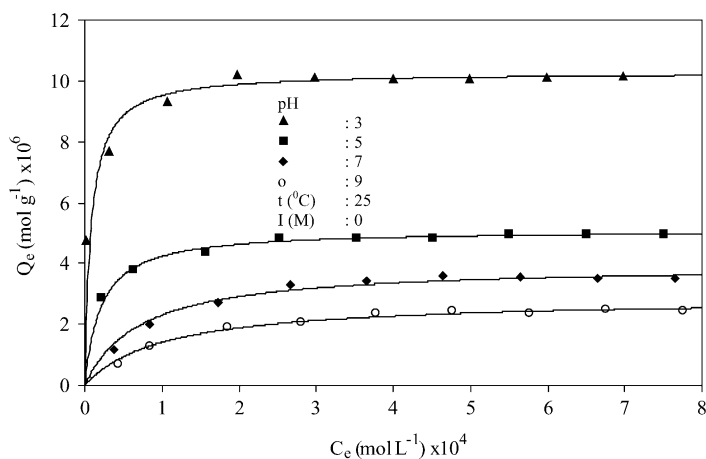
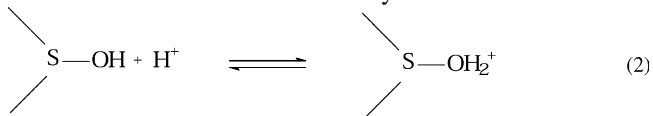


Fig. 5. The effect of pH of the solution on the adsorption of acid red 57 on sepiolite.

on the surface of adsorbent and may be written as:



As can also be seen in Eq. (2), as the pH of the dye solutions becomes lower than pH 7.1, the association of dye anions with more positively charged sepiolite surface because of

increasing  $\text{S—OH}_2^+$  groups could more easily take place. Since the solution is acidified by hydrochloric acid, the outer surface of positively charged interface will be associated with  $\text{Cl}^-$  ions. The chloride ions are exchanged with dye ions

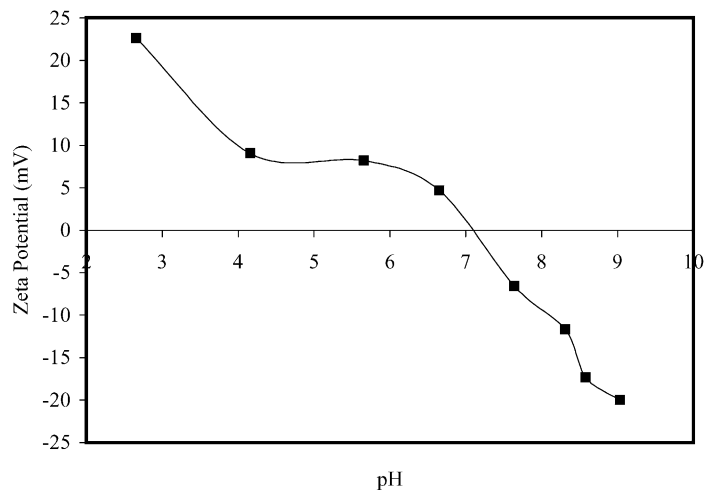
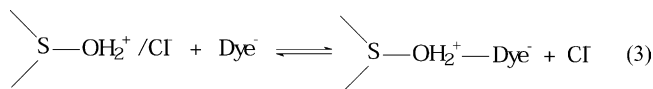


Fig. 6. The electrokinetic behaviour of sepiolite. Conditions: 1.0 g 100 mL<sup>-1</sup> sepiolite, 0.0001 M KCl, Temperature 25 °C.

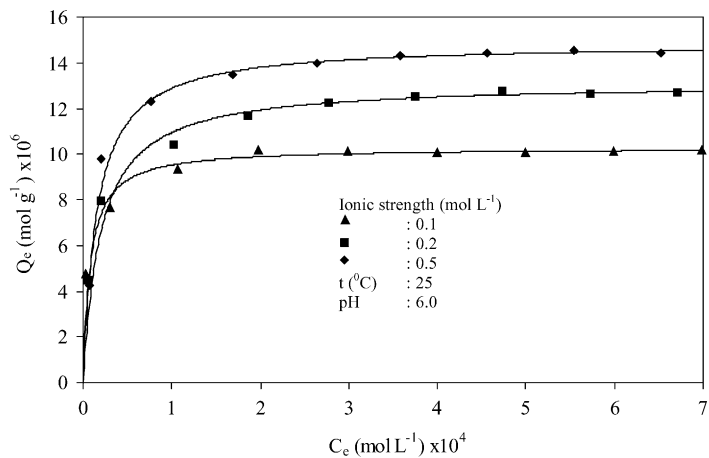


Fig. 7. The effect of ionic strength of the solution on the adsorption of acid red 57 on sepiolite.

With an increase in pH, positive charge at the sepiolite/solution interface decreases since sepiolite has a  $pH_{iep}$  (isoelectrical point) around pH 7.1. Therefore, it can be said that sepiolite sample exhibits a positive zeta potential value in the below of this pH and again, a negative zeta potential value in the above of this pH. At pH above the  $pH_{iep}$  of the adsorbent i.e.  $\sim 7.1$ , the adsorbent surface becomes negatively charged and will be associated with positively charged ions of the solution in the following manner:



Thus, there are no exchangeable anions on the outer surface of the adsorbent at higher pH and consequently, the adsorption decreases. Similar trend was observed in the adsorptions of congo red on red mud [44] and wollastonite [45] and, waste Fe(III)/Cr(III) hydroxide [46]. As a result, it can be said that the decrease in acid red 57 removal as pH increases can be explained on the basis of a decrease in  $H^+$  on the sur-

face sites and by a decrease in positive surface charge, which results in less repulsion of adsorbing dye.

3.2.2. Effect of ionic strength

Ionic strength affects the activity coefficients for  $OH^-$ ,  $H_3O^+$  and specifically adsorbable ions. As seen in Fig. 7, increasing the ionic strength of the solution causes the increase in adsorption of acid red 57 onto sepiolite surface at pH 6.0. It has been stated that increasing in the ionic strength of the solution increases adsorption at pH values below the isoelectrical point and decrease adsorption at pH values above the isoelectrical point [47]. A cause of increasing of adsorption with increasing ionic strength is that increasing in the ionic strength increases the positive charge of the surface below the isoelectrical point, resulting in greater attraction of anions, and increases the negative charge of the surface above the isoelectrical point, resulting in greater repulsion of anions. Kara et al. [23] showed that the positive charge of sepiolite surface increased with increasing ionic strength in the pH ranges of 3.0–6.6. As a result of increasing of the positive

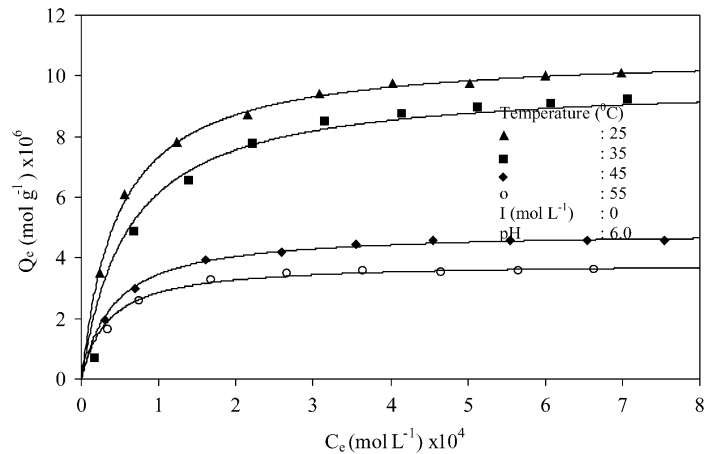


Fig. 8. The effect of temperature of the solution on the adsorption of acid red 57 on sepiolite.



Table 3  
Isotherm constants and the values of removal efficiency for acid red 57 adsorption onto sepiolite

No.	Temperature (°C)	pH	Ionic strength (mol L <sup>-1</sup> )	Langmuir isotherm			Freundlich isotherm			R <sub>L</sub>
				Q <sub>m</sub> × 10 <sup>6</sup> (mol g <sup>-1</sup> )	K × 10 <sup>-6</sup> (L mol <sup>-1</sup> )	R <sup>2</sup>	n	K <sub>F</sub> × 10 <sup>5</sup>	R <sup>2</sup>	
1	25	3	0	10.32	1.17	0.999	3.71	1.64	0.983	0.972–0.108
2	25	5	0	5.42	1.95	0.999	2.21	1.77	0.953	0.707–0.063
3	25	7	0	4.50	0.72	0.997	4.48	3.49	0.945	0.785–0.154
4	25	9	0	2.82	1.27	0.998	3.07	9.68	0.946	0.647–0.092
5	25	6	0.1	8.20	1.63	0.998	4.75	10.10	0.987	0.801–0.080
6	25	6	0.2	11.99	1.01	0.997	2.64	7.02	0.975	0.949–0.128
7	25	6	0.5	13.53	1.95	0.998	4.66	6.33	0.956	0.870–0.072
8	25	6	0	10.98	2.04	0.999	2.78	1.90	0.916	0.765–0.065
9	35	6	0	10.93	1.00	0.997	2.73	2.61	0.936	0.869–0.123
10	45	6	0	5.29	1.10	0.997	2.53	5.05	0.930	0.749–0.107
11	55	6	0	4.30	0.79	0.997	4.65	7.20	0.928	0.789–0.142

charge of sepiolite surface with increasing ionic strength, it can be said that the adsorption capacity of sepiolite increases with increasing ionic strength.

### 3.3. Effect of temperature

The adsorption isotherms were determined for various dye–adsorbent systems. A study of the temperature dependence of adsorption reactions gives valuable information about the enthalpy and entropy changes during adsorption. Greater adsorption is often found at lower temperatures [47]. The removal of acid red 57 has been studied at 25, 35, 45 and 55 °C to determine the adsorption isotherms and thermodynamic parameters. Fig. 8 shows the amount of equilibrium adsorption of acid red 57 on sepiolite at different temperatures. As seen in Fig. 8, adsorption ability of sepiolite decreases with increasing temperature due to the enhancement of the desorption step in the mechanism, indicating the process to be exothermic. Furthermore, the decreasing trend of adsorption with temperature is mainly due to the weakening of adsorptive forces between the active sites of sepiolite and adsorbate species, and also between the adjacent molecules of adsorbed phase. The extent of the decrease in adsorption of solute of definite concentration with increase in temperature depends on the nature of adsorbent–adsorbate system. This type of adsorption is likely classified as reversible adsorption: in this case temperature dependence on adsorption would be comparatively weaker than desorption [48].

### 3.4. Adsorption isotherms

The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. The adsorption curves were applied to both the Langmuir and Freundlich equations. The widely used Langmuir isotherm has found successful application to many real sorption processes and is expressed as in the linear form [1]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m} \quad (5)$$

where  $Q_m$  (mol g<sup>-1</sup>) is the maximum amount of the dye per unit weight of sepiolite to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration  $C_e$ , and  $K$  is the Langmuir constant related to the affinity of binding sites (L mol<sup>-1</sup>).  $Q_m$  represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and assists in the comparison of adsorption performance.  $Q_m$  and  $K$  are calculated from the slopes and intercepts of the straight lines of plot of  $C_e/Q_e$  versus  $C_e$ .

The Freundlich isotherm is given as [1],

$$Q_e = K_F C_e^{1/n}$$

in logarithmic form,

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where  $K_F$  is roughly an indicator of the adsorption capacity and  $(1/n)$  of the adsorption intensity.  $K_F$  and  $(1/n)$  can be determined from the linear plot of  $\ln Q_e$  versus  $\ln C_e$ . Parameters of the Langmuir and Freundlich isotherms were computed in Table 3. As also seen in Figs. 9–11, Langmuir isotherm fits quite well with the experimental data (correlation coefficient  $R^2 > 0.99$ ), whereas the low correlation coefficients ( $R^2 < 0.98$ ) show poor agreement of Freundlich isotherm with the experimental data. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on the sepiolite surface, since the Langmuir equation assumes that the surface is homogenous [1].

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor,  $R_L$ , which is defined as

$$R_L = \frac{1}{1 + K C_e} \quad (7)$$

The value of  $R_L$  indicates the shape of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). Here,  $R_L$  obtained are listed in Table 3. The fact that all the  $R_L$ -values for the adsorption of acid red 57 onto sepiolite are in the ranges of 0.063–0.972 shows that the adsorption process is favourable.

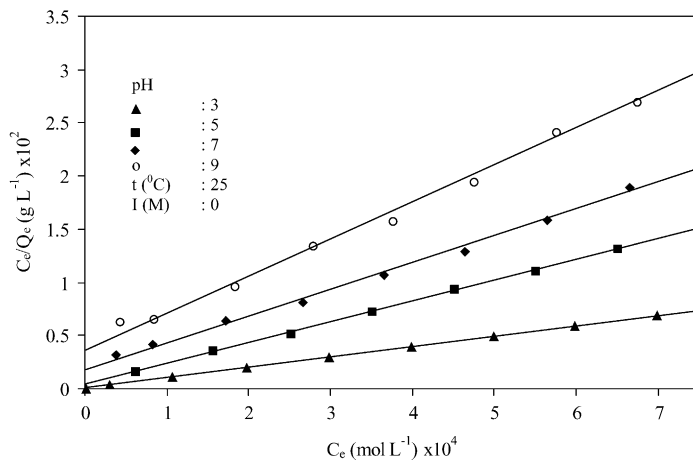


Fig. 9. Langmuir adsorption isotherm for data of Fig. 5.

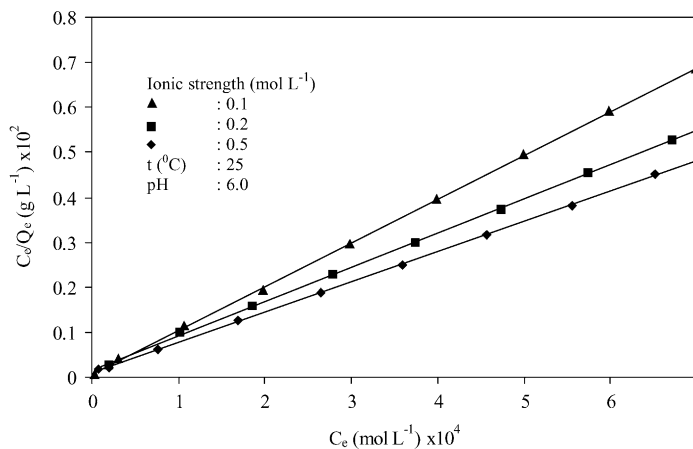


Fig. 10. Langmuir adsorption isotherm for data of Fig. 7.

It is noted that the isotherm data obtained at different temperatures are also well fitted by the Langmuir equation. Temperature dependence of  $K$  can be used to determine the isosteric enthalpy of adsorption,  $\Delta H^0$ . The enthalpy at a fixed

surface coverage ( $\theta = Q_e/Q_m$ ),

$$\left(\frac{\partial \ln K}{\partial T}\right)_\theta = -\left(\frac{\partial \ln C_e}{\partial T}\right)_\theta = \frac{\Delta H^0}{RT^2} \tag{8}$$

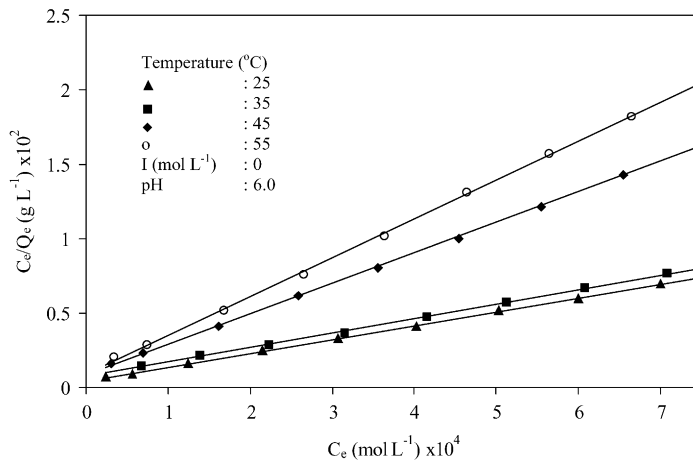


Fig. 11. Langmuir adsorption isotherm for data of Fig. 8.



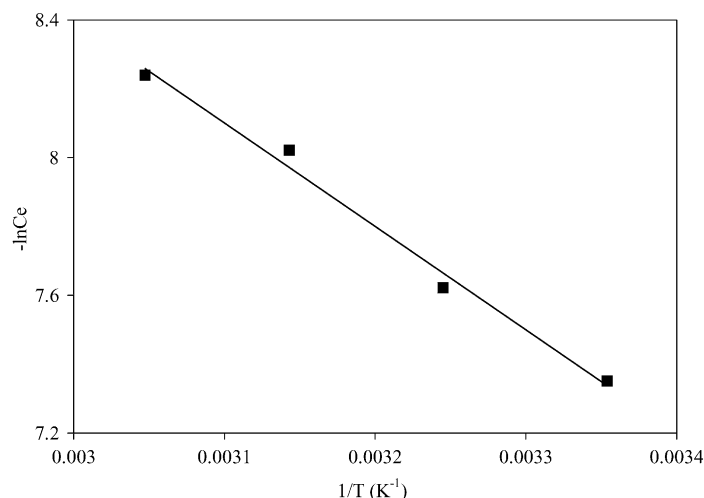


Fig. 12. Plot of  $-\ln C_e$  vs.  $1/T$  for acid red 57 adsorption on sepiolite.

A plot of  $-\ln C_e$  against  $1/T$  should be a straight line. Fig. 12 shows typical isosteres and reveals an approximately linear relationship. The value of  $\Delta H^0$  calculated at a specific coverage fraction of 0.5 is  $-26 \text{ kJ mol}^{-1}$ . The enthalpy change due to chemisorption ( $40\text{--}120 \text{ kJ mol}^{-1}$ ) is larger than that due to physisorption. Thus, the adsorption of the acid red 57 examined on sepiolite is likely due to physisorption. This result shows that the interaction between sepiolite and the dye is mainly electrostatic (Coulombic interactions). The heat of physical adsorption involves only relatively weak intermolecular forces such as van der Waals and mainly electrostatic interactions. Entropy change of the adsorption process, ( $\Delta S^0$ ), has been calculated from the intercept of the line in Fig. 12. Gibbs energy of adsorption, ( $\Delta G^0$ ), can be found from

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

The values of  $\Delta G^0$  and  $\Delta S^0$  were calculated as  $-36.8 \text{ kJ mol}^{-1}$  and  $36.6 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $25^\circ\text{C}$ , respectively. It is expected that  $\Delta G^0$  is negative, indicating that the nature of adsorption process for acid red 57 is spontaneous. The re-orientation or restructuring of water around nonpolar solutes or surfaces is very unfavorable in terms of entropy, since it disturbs the existing water structure and imposes a new and more ordered structure on the surrounding water molecules. As a result of adsorption of acid red 57 onto sepiolite surface, the number of the water molecules surrounding acid red 57 molecules decreases and thus the degree of the freedom of the water molecules increases. Therefore, the positive values of  $\Delta S^0$  suggest the increased randomness at the solid–solution interface during the adsorption of acid red 57 on sepiolite [49].

#### 4. Comparing to other adsorbents

Comparison between the adsorption capacities of sepiolite and other adsorbents is presented in Table 4. When compar-

Table 4

Adsorption capacities of dyes on various adsorbents

Name of the dye	Low-cost adsorbents	$Q_m$ $\times 10^5$ ( $\text{mol g}^{-1}$ )	References
Crystal violet	Wollastonite	0.22	[50]
Methylene blue	Perlite	4.65–8.21	[1]
Rosaniline	Fly ash	1.35	[15]
Methylene blue	hydrochloride or basic fuchsin		
Methylene blue	Activated carbon derived from coconut shell fibers	5.24	[11]
Methyl orange	Activated carbon derived from coconut shell fibers	2.88	[11]
Acid red 57	Sepiolite	1.35	In this study

ing our results for sepiolite with the results of others, it can be concluded that the adsorption capacity of the sepiolite is comparable to those of the other available adsorbents. Again, as seen in Table 4, the  $Q_m$  value obtained for sepiolite-acid red 57 system is at a comparable level to other adsorbent-dye systems. Additionally, if it is considered that the dyes given in the Table 4 are cationic ones, it can obviously be concluded that the  $Q_m$  value for our system is superior to other adsorbents.

#### 5. Conclusions

The removal of acid red 57 with sepiolite obtained from Eskişehir, Turkey, was systematically investigated under various conditions. The adsorption of acid red 57 onto sepiolite as an adsorbent was increased by decreasing pH and temperature, and by increasing ionic strength. Adsorption equilibrium correlated reasonably well by Langmuir isotherm. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such

as Gibbs energy, heat and entropy of adsorption. The results indicate that acid red 57 adsorption onto sepiolite is spontaneous and physical in nature. As a result it can be said that the sepiolite is an effective adsorbent for the removal of acid red 57 from aqueous solution in a commercial system.

## Acknowledgment

The authors thank to BURCAS for zeta potential measurements.

## References

- [1] M. Doğan, M. Alkan, Y. Onganer, Adsorption of methylene blue from aqueous solution onto perlite, *Water Air Soil Pollut.* 120 (2000) 229–248.
- [2] O. Demirbaş, M. Alkan, M. Doğan, The removal of victoria blue from aqueous solution by adsorption on a low-cost material, *Adsorption* 8 (2002) 341–349.
- [3] M. Doğan, M. Alkan, Removal of methyl violet from aqueous solutions by perlite, *J. Colloid Interface Sci.* 267 (2003) 32–41.
- [4] M. Doğan, M. Alkan, Adsorption kinetics of methyl violet onto perlite, *Chemosphere* 50 (2003) 517–528.
- [5] M. Alkan, M. Doğan, Adsorption kinetics of victoria blue onto perlite, *Fresenius Environ. Bull.* 12 (5) (2003) 418–425.
- [6] M. Alkan, M. Doğan, Adsorption of copper (II) onto perlite, *J. Colloid Interface Sci.* 243 (2001) 280–291.
- [7] P. Pendleton, S.H. Wu, Kinetics of dodecanoic acid adsorption from caustic solution by activated carbon, *J. Colloid Interface Sci.* 266 (2003) 245–250.
- [8] W.T. Tsai, C.Y. Chang, M.C. Lin, S.F. Chien, H.F. Sun, M.F. Hsieh, Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by  $ZnCl_2$  activation, *Chemosphere* 45 (2001) 51–58.
- [9] G. McKay, The adsorption of dyestuffs from aqueous solutions using activated carbon. IV. External mass transfer processes, *J. Chem. Tech. Biotechnol.* 33A (1983) 205–218.
- [10] R. Leyva-Ramos, Effect of temperature and pH on the adsorption of an anionic detergent on activated carbon, *J. Chem. Tech. Biotechnol.* 33A (1989) 231–240.
- [11] K.P. Singh, D. Mohan, S. Sinha, G.S. Tondon, D. Gosh, Colour removal from wastewater using low cost activated carbon derived from agricultural waste material, *Ind. Eng. Chem. Res.* 42 (2003) 1965–1976.
- [12] G. Bereket, A.Z. Aroğuz, M.Z. Özel, Removal of Pb(II), Cd(II), Cu(II) and Zn(II) from aqueous solutions by adsorption on bentonite, *J. Colloid Interface Sci.* 187 (1997) 338–343.
- [13] M.M. Mohamed, Adsorption properties of ionic surfactants on molybdenum-modified silica gels, *Colloids Surf., A: Physicochem. Eng. Aspects* 108 (1996) 39–48.
- [14] K.K. Jain, G. Prasad, V.N. Singh, Application of flyash instead of activated carbon for oxalic acid removal, *J. Chem. Tech. Biotechnol.* 29 (1979) 36–38.
- [15] D. Mohan, K.P. Singh, G. Singh, K. Kumar, Removal of dyes from wastewater using fly ash, a low cost adsorbent, *Ind. Eng. Chem. Res.* 42 (2002) 1965–1976.
- [16] V.K. Gupta, D. Mohan, S. Sharma, M. Sharma, Removal of basic dye (Rhodamine-B and Methylene Blue) from aqueous solution using bagasse fly ash, *Sep. Sci. Technol.* 35 (13) (2000) 2097.
- [17] S.J. Allen, G. McKay, K.Y.H. Khader, Equilibrium adsorption isotherms for basic dyes onto lignite, *J. Chem. Tech. Biotechnol.* 45 (1989) 291–302.
- [18] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115–124.
- [19] G. McKay, M.S. Otterburn, A.G. Sweeney, Surface mass transfer processes during colour removal from effluent using silica, *Water Res.* 15 (1981) 327–331.
- [20] R.L. Frost, Z. Ding, Controlled rate thermal analysis and differential scanning calorimetry of sepiolites and palygorskites, *Thermochim. Acta* 397 (2003) 119–128.
- [21] A.A. Gökteş, Z. Misirli, T. Baykara, Sintering behaviour of sepiolite, *Ceram. Int.* 23 (1997) 305–311.
- [22] E. Sabah, M.S. Çelik, Interaction of pyridine derivatives with sepiolite, *J. Colloid Interface Sci.* 251 (2002) 33–38.
- [23] M. Kara, H. Yüzer, E. Sabah, M.S. Çelik, Adsorption of cobalt from aqueous solutions onto sepiolite, *Water Res.* 37 (2003) 224–232.
- [24] G. Rytwo, D. Tropp, C. Serban, Adsorption of diquat, paraquat and methyl green on sepiolite: experimental results and model calculations, *Appl. Clay Sci.* 20 (2002) 273–282.
- [25] S. Balcı, Y. Dinçel, Ammonium ion adsorption with sepiolite: use of transient uptake method, *Chem. Eng. Process.* 41 (2002) 79–85.
- [26] M. Molina-Sabio, F. Caturla, F. Rodriguez-Reinoso, G.V. Kharitonova, Porous structure of a sepiolite as deduced from the adsorption of  $N_2$ ,  $CO_2$ ,  $NH_3$ , and  $H_2O$ , *Microporous Mesoporous Mater.* 47 (2001) 389–396.
- [27] S. Akyüz, T. Akyüz, A.E. Yakar, FT-IR spectroscopic investigation of adsorption of 3-aminopyridine on sepiolite and montmorillonite from Anatolia, *J. Mol. Struct.* 565–566 (2001) 487–491.
- [28] E. Sabah, B. Turan, M.S. Çelik, Adsorption mechanism of cationic surfactants onto acid- and heat-activated sepiolites, *Water Res.* 36 (2002) 3957–3964.
- [29] G. Rytwo, S. Nir, M. Crespin, L. Margulies, Adsorption and interactions of methyl green with montmorillonite and sepiolite, *J. Colloid Interface Sci.* 222 (2000) 12–19.
- [30] E. González-Pradas, M. Villafranca-Sánchez, M. Socias-Viciana, F. del-Rey-Bueno, A. García-Rodríguez, Adsorption of thiram from aqueous solution on activated carbon and sepiolite, *J. Chem. Tech. Biotechnol.* 39 (1987) 19–27.
- [31] U. Shuali, L. Bram, M. Steinberg, S. Yariv, Infrared study of the thermal treatment of sepiolite and palygorskite saturated with organic acids, *Thermochim. Acta* 148 (1989) 445–456.
- [32] E. Gonzalez-Pradas, A. Valverde-Garcia, M. Villafranca-Sanchez, Removal of aromatic amines from aqueous solution by activated sepiolite, *J. Chem. Tech. Biotechnol.* 47 (1990) 15–22.
- [33] G. Rytwo, S. Nir, L. Margulies, B. Casal, J. Merino, E. Ruiz-Hitzky, J.M. Serratos, Adsorption of monovalent organic cations to sepiolite: experimental results and model calculations, *Clays Clay Miner.* 46 (1998) 340–348.
- [34] M.S. Çelik, B. Özdemir, M. Turan, I. Koyuncu, G. Ateşok, H.Z. Sankaya, *Water Science Technology Water Supply* 1 (2001) 81.
- [35] S. Balcı, Nature of ammonium ion adsorption by sepiolite: analysis of equilibrium data with several isotherms, *Water Res.* 38 (2004) 1129–1138.
- [36] O. Özdemir, B. Armagan, M. Turan, M.S. Çelik, Comparison of the adsorption characteristics of azo-reactive dyes on mesoporous minerals, *Dyes Pigments* 62 (2004) 51–62.
- [37] K. Brauner, A. Preisinger, *Miner. Petrol. Mitt.* 6 (1956) 120–140.
- [38] J.L. Ahlrichs, J.C. Serna, J.M. Serratos, *Clays Clay Miner.* 23 (1975) 119–124.
- [39] R.S. Hunter, *Zeta Potential in Colloid Science: Principles and Applications*, Academic Press, London, 1981.
- [40] M. Doğan, M. Alkan, Ü. Çakır, Electrokinetic properties of perlite, *J. Colloid Interface Sci.* 192 (1997) 114–118.
- [41] B.F. Jones, E. Galan, in: S.W. Bailey (Ed.), *Sepiolite and Palygorskite: Hydrous Phyllosilicates*, *Reviews in Mineralogy*, vol 19, Mineralogical Society of America, 1988, 631–674 [Chapter 16].
- [42] E. Galan, Properties and applications of palygorskite-sepiolite clays, *Clay Miner.* 31 (4) (1996) 443–453.

- [43] T. Hibino, A. Tsunashima, A. Yamazaki, R. Otsuka, Model calculation of sepiolite surface areas, *Clays Clay Miner.* 43 (1995) 391–396.
- [44] C. Namasivayam, D.J.S.E. Arasi, Removal of congo red from wastewater by adsorption onto waste red mud, *Chemosphere* 34 (2) (1997) 401–417.
- [45] V.N. Singh, G. Mishra, K.K. Panday, Removal of congo red by wollastonite, *Indian J. Technol.* 22 (1984) 70–71.
- [46] C. Namasivayam, R. Jeyakumar, R.T. Yamuna, Dye removal from wastewater by adsorption on waste Fe(III)/Cr(III) hydroxide, *Waste Manag.* 14 (1994) 643–648.
- [47] F.J. Hingston, in: M.A. Anderson, A.J. Rubin (Eds.), *Adsorption of Inorganics at Solid–Liquid Interfaces*. Ann Arbor Science Publishers Inc., MI, 1981.
- [48] R.S. Juang, F.C. Wu, R.L. Tseng, The ability of activated clay for the adsorption of dyes from aqueous solutions, *Environ. Technol.* 18 (1997) 525–531.
- [49] J.N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed., Academic Press, New York, 1991.
- [50] S.K. Khare, R.M. Srivastava, K.K. Panday, V.N. Singh, Removal of basic dye (crystal violet) from water using wollastonite as adsorbent, *Environ. Technol. Lett.* 9 (1988) 1163.