

Adsorption of Acid Red 57 from aqueous solutions onto surfactant-modified sepiolite

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Abstract

The adsorption of Acid Red 57 (AR57) onto surfactant-modified sepiolite was investigated in aqueous solution in a batch system with respect to contact time, pH and temperature. The surface modification of surfactant-modified sepiolite was controlled using the FTIR technique. The pseudo-first-order, pseudo-second-order kinetic models and the intraparticle diffusion model were used to describe the kinetic data and the rate constants were evaluated. The experimental data fitted very well the pseudo-second-order kinetic model and also followed the intraparticle diffusion model up to 90 min, whereas diffusion is not only the rate controlling step. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. The Freundlich model agrees with experimental data well. The activation energy, change of free energy, enthalpy and entropy of adsorption were also evaluated for the adsorption of AR57 onto surfactant-modified sepiolite. The results indicate that surfactant-modified sepiolite could be employed as low-cost material for the removal of textile dyes from effluents.

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1. Introduction

The environmental issues surrounding the presence of color in effluent are a continuing problem for dyestuff manufactures dyers, finishers and paper-making industry, since increasingly stringent color consent standards are being enforced by regulatory bodies to reduce the quality of color in effluent and water courses [1]. This effluent is also carcinogenic and poses a serious hazard to aquatic living organisms. As a result, many governments have established environmental restrictions with regard to the quality of colored effluents and have forced dye houses to decolorize their effluents before discharging [2].

The treatment of textile waste comprising of dyestuffs and other non-biodegradable organics and inorganic poses con-

siderable problems in the wastewater treatment industry. It is difficult to remove this kind of waste because they are stable to light, heat and oxidizing agents and are biologically non-degradable. Furthermore, conventional biological and chemical processes are insufficient in removing these contaminants, with the majority of the research in this area conducted using adsorption technique [3,4]. This technique is one of the most promising processes of removing pollutant from wastewater. Even though activated carbon is the most widely used adsorbent for the removal of color from textile effluents since it has a high surface area, and high adsorption capacity, its use is limited due to its high cost and a need for regeneration after each adsorption experiment [5,6]. In order to decrease the cost of wastewater treatment, attempts have been made in finding inexpensive adsorbents. Studies indicated that many materials, such as chitosan, bagasse pith, peat, rice husk, fly ash, wood, natural clays including bentonite, montmorillonite, alunite, sepiolite, zeolite, kaolinite and smectite could be used as adsorbents which could effectively remove the dyes from solution [7–13]. A limited

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number of studies were achieved using natural clay of sepiolite as an adsorbent including catalyst support, wastewater treatment, solid wastes, reducing the toxic effect of some heavy metals and pesticides [14] but the adsorption of Acid Red 57 onto surfactant-modified sepiolite has not been found in the literature.

Sepiolite is with $(\text{Si}_{12})(\text{Mg}_8)\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$ [15] as a unit-cell formula is a magnesium hydrosilicate with a micro-fibrous structure and a theoretical high surface area and high chemical and mechanical stability. These characteristics of sepiolite are related to its powerful adsorbent properties and its ability to adsorb organic or inorganic ions. A general structure of sepiolite formed by alternation of blocks and tunnels that grow up in the microfibre direction. Each block consists of by two tetrahedra silica sheets enclosing a central octahedral magnesia sheet but the silica sheets are discontinued and inversion of these sheets that give rise to structural tunnels [14,16–19].

The surface properties sepiolite may be greatly modified with a surfactant by simple ion-exchange reactions to lead van der Waals interaction between organic surfactant cations and adsorbate. The modification of clay surface with surfactant is called as organoclay to cause to transform organophobic to strongly organophilic and therefore the adsorption capacity increases [20]. This kind of surfactant-modified organosepiolite has been used extensively for a wide variety of environmental applications.

The aim of this work is to study the adsorption of Acid Red 57 (AR57) from aqueous solutions onto surfactant-modified sepiolite. The effects of temperature, pH, contact time and concentration were examined and the thermodynamic and the kinetic data were also evaluated.

2. Materials and methods

2.1. Materials

A commercial textile dye AR57 (Nylosan Red EBL) (Fig. 1) was obtained from Clairent-Switzerland and used without further purification. The adsorbent used in this work was provided from Dolsan, Eskişehir-Turkey. It was crushed, ground by a miller and sieved through a $63 \mu\text{m}$ sieve and

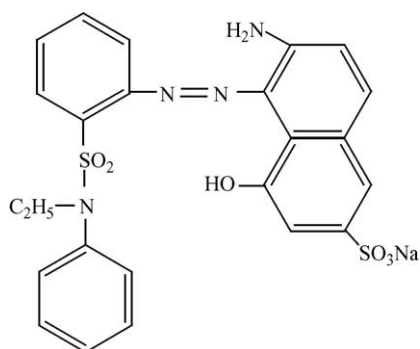


Fig. 1. The structure of AR57.

dried at 110°C in oven for 2 h before use. Sepiolite was characterized with respect to cation exchange capacity (CEC) and the surface area by methylene blue method [21,22]. The CEC and surface area of sepiolite were $544.3 \text{ mmol kg}^{-1}$ and $426.0 \text{ m}^2 \text{ g}^{-1}$, respectively.

2.2. Material characterization

The chemical analysis of natural sepiolite was determined by using an energy dispersive X-ray spectrometer (EDX-LINK ISIS 300) attached to a scanning electron microscope (SEM-Cam Scan S4). The crystalline phases present in the sepiolite were determined by using X-ray diffractometer (XRD-Rigaku Rint 2000) with $\text{Cu K}\alpha$ radiation.

FTIR spectra were recorded (KBr) on a Jasco FT/IR-300E model fourier transform infrared spectrometer to observe surface modification.

2.3. Preparation of surfactant-modified sepiolite

The Na^+ -exchanged form of clay was prepared by stirring samples for 24 h with 1 M NaCl. This was followed by several washings with distilled water and filtered to remove the excess NaCl and other exchangeable cations from the clay. The clay was then resuspended and filtered until a negative chloride test was obtained with 0.1 M AgNO_3 .

A thirty gram of the Na-saturated clay was dispensed in 0.5 L of distilled water. Dodecylethyldimethylammonium (DEDMA) bromide was used as a surfactant. DEDMA-sepiolite was prepared by adding quantities of the respective bromide salts equal to twice the cation exchange capacity of the sepiolite. The clay was then washed with distilled water until free of salts and a negative bromide test had been obtained with 0.1 M AgNO_3 and was used for the adsorption studies [20].

2.4. Adsorption experiments

The pH experiments were undertaken by 50 mL of a 250 mg L^{-1} dye solution with 0.1 g of sepiolite at 25°C and the pH was carefully adjusted between 1 and 11 with adding a small amount of dilute HCl or NaOH solution. The amount of dye adsorbed was measured after periodical stirring for 60 min. The solution was then filtered to remove any organic or inorganic precipitates formed under acidic or basic conditions. Once the optimum pH was determined, the kinetics of adsorption by the sepiolite was conducted at this pH for increasing period of time, up to dye was not remove any more. The concentrations of each solution were measured by spectrophotometer (Shimadzu UV-2101PC) at the respective λ_{max} value, which is 512.5 nm for AR57.

In order to study the adsorption isotherms and kinetics a 0.01 g of surfactant-modified sepiolite were kept in contact with 50 mL of dye solution of various concentrations at equilibrium time to allow attainment of equilibrium at constant temperatures of 20, 30, 40 and 50°C .

3. Results and discussion

3.1. Chemical composition of sepiolite

X-ray diffraction (XRD) analysis together with the chemical analysis of (29.3% SiO₂, 12.4% MgO, 9.09% CaO, and 34.99% CaCO₃) indicates that sepiolite and dolomite are the major components along with traces of Al, K and Fe oxides in the form of impurities.

3.2. FTIR analysis

FTIR spectra of natural sepiolite and surfactant-modified sepiolite were shown in Fig. 2. The band at 3687 cm⁻¹ that corresponds to stretching (ν_{OH}) vibrations of hydroxyl groups (belong to Mg₃OH) attached to octahedral Mg ions located in the interior blocks of natural sepiolite and surfactant-modified sepiolite [16,23]. The band at 3618 cm⁻¹ indicates that assigned to H–O–H stretching vibrations of water molecules weakly hydrogen bonded to the Si–O surface in both of samples. The broad band at 3390 cm⁻¹, observed each samples, is due to H–O–H vibrations of adsorbed water.

A pair of strong bands at 2858 and 2931 cm⁻¹ was observed only with surfactant-modified sepiolite can be assigned to the symmetric and asymmetric stretching vibrations of the methylene group (ν_{CH_2}) and their bending vibrations between 1380 and 1465 cm⁻¹, supporting the intercalation of surfactant molecules between the silica layers, but these stretching bands are not observed in the natural sepiolite [24]. The band at 1652 cm⁻¹ corresponds to the OH deformation of water, because the OH stretching band at 3390 cm⁻¹ suggests the presence of some interlamellar water [25] and the stretching vibrations obtained at 1635, 1612, and 1461 cm⁻¹ could be characteristics of reversibly adsorbed carbonate on the oxide surfaces for both of samples and this result was

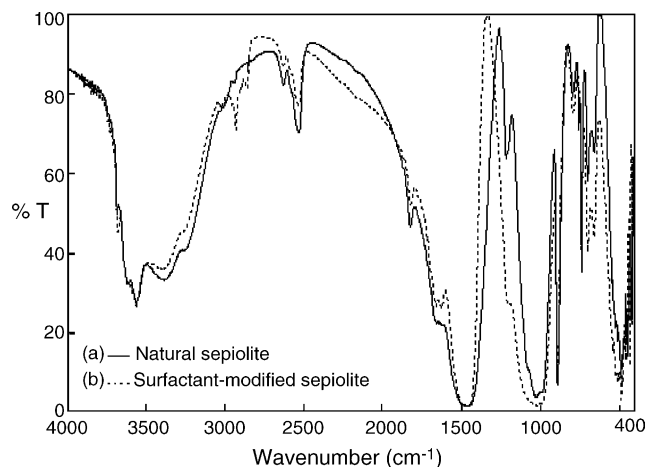


Fig. 2. FTIR spectra of (a) natural sepiolite and (b) surfactant-modified sepiolite.

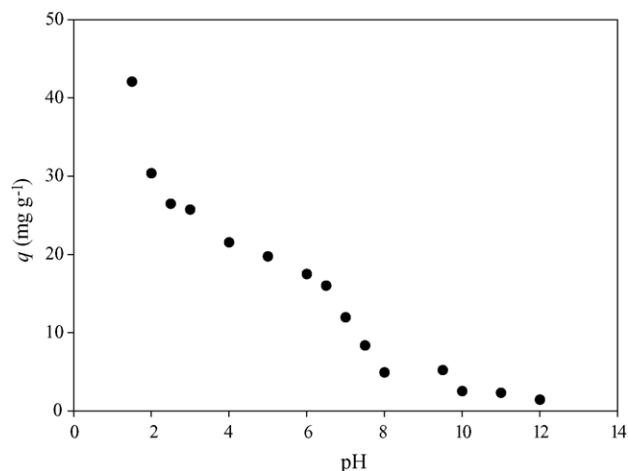


Fig. 3. Effect of pH for the adsorption of AR57 onto sepiolite.

well agreement with the dolomite content of the XRD results [26].

The Si–O coordination bands at 1209, 1078, and 985 cm⁻¹ are observed as a result of the Si–O vibrations. The deep band at 1022 cm⁻¹ represents the stretching of Si–O in the Si–O–Si groups of the tetrahedral sheet [27] and the band at 883 cm⁻¹ conducted with bending vibration of carbonate and two peak at 690 cm⁻¹ is represent the bending vibration of Mg₃OH both of samples. The bands at 530 and 471 cm⁻¹ due to Si–O–Al (octahedral) and Si–O–Si bending vibrations respectively, natural sepiolite and surfactant-modified sepiolite [28].

3.3. Effect of pH

Sepiolite has proved to be an effective adsorbent for the removal of acid dye, AR57, via adsorption from aqueous solution at pH 2 was achieved (Fig. 3). It was observed that the adsorption is highly dependent on pH of the solution which affects the surface charge of the adsorbent and the degree of ionization and speciation of adsorbate. At lower pH more protons will be available, thereby increasing electrostatic attractions between negatively charged dye anions and positively charged adsorption sites and causing an increase in dye adsorption [13]. The high adsorption capacity is due to the strong electrostatic interaction between the $-N^+(C_2H_5)(CH_3)_2$ of DEDMA-sepiolite and dye anions.

When the pH of the solution is increased, the positive charge on the oxide or solution interface decreases and the adsorbent surface appears negatively charged. On the contrary, a lower adsorption at higher pH values may be due to the abundance of OH⁻ ions and because of ionic repulsion between the negatively charged surface and the anionic dye molecules. There are also no exchangeable anions on the outer surface of the adsorbent at higher pH values and consequently the adsorption decreases [29].

3.4. Adsorption isotherms

The analysis of equilibrium data for the adsorption of AR57 onto surfactant-modified sepiolite has been done by the linear forms of the Langmuir [30] and Freundlich [31] equations.

The linear form of Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}, \quad (1)$$

where q_e is the equilibrium dye concentration on the adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in the solution (mg dm^{-3}), q_{\max} is the monolayer capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir adsorption constant ($\text{dm}^3 \text{mg}^{-1}$). The Langmuir adsorption is the monolayer adsorption and the Langmuir equation is applicable to homogeneous adsorption, where the adsorption of each adsorbate molecule onto the surface has equal to adsorption activation energy.

The Freundlich equation is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (2)$$

where q_e is the equilibrium dye concentration on adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in the solution (mg dm^{-3}), K_F is Freundlich constant ($\text{dm}^3 \text{g}^{-1}$), and $1/n$ is the heterogeneity factor. Unlike the Langmuir equation, the Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface, it is not restricted to the formation of the monolayer.

The plot of q_e versus C_e for the adsorption of AR57 onto surfactant-modified sepiolite (Fig. 4) was drawn and fitted to Langmuir and Freundlich isotherms. The values of the Langmuir constant (K_L) and the monolayer capacity of adsorbent (q_{\max}), Freundlich constants (K_F) and (n), the correlation coefficients for Langmuir (r_L^2) and for Freundlich (r_F^2) are listed in Table 1. The Freundlich model yields a much better (0.945–0.981) fit than that of the Langmuir model (0.932–0.975), as reflected by correlation coefficients are compared in Table 1.

One of the Freundlich constants K_F indicates the adsorption capacity of the adsorbent. The values of K_F increases, the adsorption capacity of adsorbent also increases, when the temperature decreases 50–20 °C. The value of n at equilibrium is 1.224 at 20 °C represent favorable adsorption, this would seem to suggest that physical rather than chemical adsorption is dominant when it is used for adsorbing AR57.

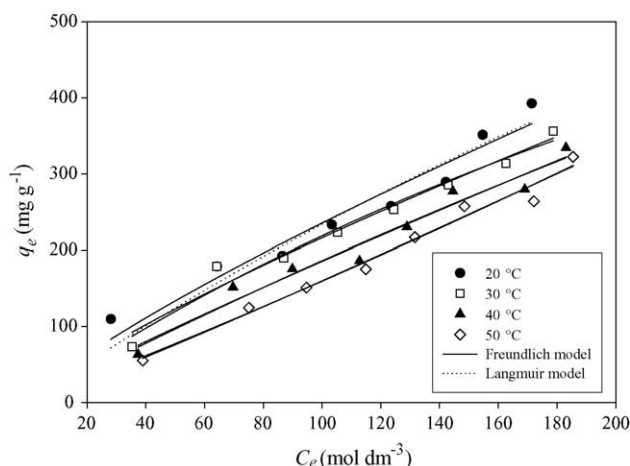


Fig. 4. Adsorption isotherm plots for the adsorption of AR57 onto surfactant-modified sepiolite at various temperatures.

The Freundlich constant K_F and n were influenced by temperature. Increase in temperature from 20 to 50 °C results a decrease in both K_F (from 5.468 to 1.154) and n (from 1.224 to 0.934) indicating the decreasing intensity of adsorption which is in confirmation with Freundlich isotherm constants.

3.5. Adsorption kinetic considerations

The influence of contact time on AR57 removal by surfactant-modified sepiolite was shown in Fig. 5. Based on

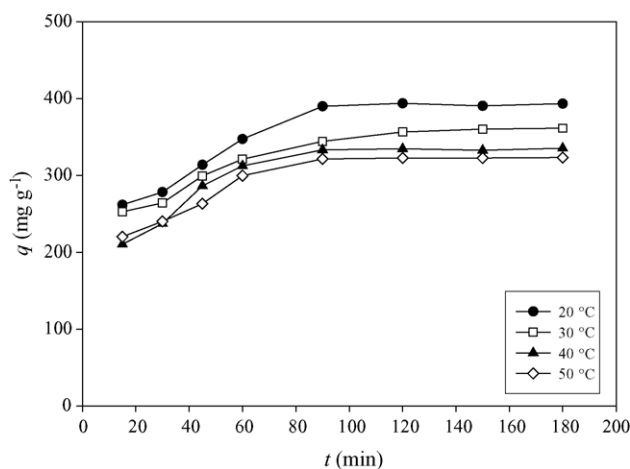


Fig. 5. Effect of contact time for the adsorption of AR57 onto surfactant-modified sepiolite at various temperatures.

Table 1

Langmuir and Freundlich isotherm constants for the adsorption of AR57 onto surfactant-modified sepiolite

t (°C)	Langmuir			Freundlich		
	q_{\max} (mg g^{-1})	K_L ($\text{dm}^3 \text{mg}^{-1}$)	r_L^2	n	K_F ($\text{dm}^3 \text{g}^{-1}$)	r_F^2
20	1.91×10^3	1.40×10^{-3}	0.932	1.224	5.468	0.945
30	1.25×10^3	2.13×10^{-3}	0.975	1.227	5.075	0.975
40	2.48×10^3	8.14×10^{-4}	0.965	1.095	2.767	0.965
50	–	–	–	0.934	1.154	0.981

Fig. 5, the rate of removal of AR57 by adsorption was rapid initially and then slowed down gradually until it attained an equilibrium beyond which there was not significant increase in the rate of removal. The maximum adsorption of AR57 onto surfactant-modified sepiolite was observed at 90 min, and it is thus fixed as the equilibrium contact time.

The equilibrium adsorption capacity of AR57 on surfactant-modified sepiolite was found to decrease with increasing temperature, decreasing from 393.4 mg g^{-1} at 20°C to 323.3 mg g^{-1} at 50°C indicating that the dye adsorption on the adsorbent surface was favored at lower temperatures. This may be due to a tendency for AR57 ions to escape from the solid phase to the bulk phase with an increase in the temperature in the solution and due to a weakening in the van der Waals forces of attraction between AR57 and surfactant-modified sepiolite [32,33]. This effect suggests that an explanation of the adsorption mechanism associated with the removal of AR57 onto surfactant-modified sepiolite involves a physical process.

An increase in the temperature leads to a decrease in the initial adsorption rate, but the adsorption capacities at 90 min are almost the same at 40°C and 50°C . Below and above equilibrium time, the adsorption capacity indicates different trends at various temperatures. Before reaching the equilibrium time, an increase in the temperature leads to an increase in the dye adsorption rate dq/dt and q , which shows a kinetically controlling process. After the equilibrium attained, the uptake slightly decreases with increasing temperature indicating that the adsorption of AR57 onto surfactant-modified sepiolite is controlled an exothermic process [34].

Aiming at evaluating the adsorption kinetics of AR57 onto surfactant-modified sepiolite, the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were used to fit the experimental data, according to the below kinetic model equations.

- The pseudo-first-order rate expression of Lagergren [35,36] is given as:

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

- The pseudo-second-order kinetic model [36] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t, \quad (4)$$

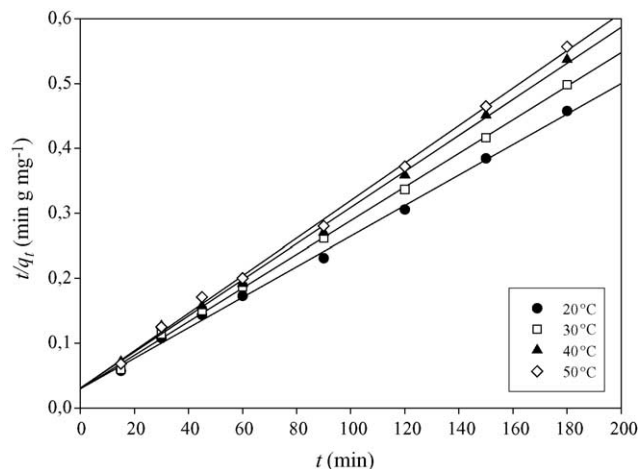


Fig. 6. Pseudo-second-order kinetic plots for the adsorption of AR57 onto surfactant-modified sepiolite at various temperatures.

- The intraparticle diffusion equation [37] can be written by following:

$$q_t = k_p t^{1/2} + C, \quad (5)$$

where q_e is the amount of dye adsorbed on adsorbent at equilibrium (mg g^{-1}), q_t is the amount of dye adsorbed (mg g^{-1}) at various times t , q_e is the maximum adsorption capacity (mg g^{-1}) for pseudo-first-order adsorption, k_1 is the pseudo-first-order rate constant for the adsorption process (min^{-1}), q_2 is the maximum adsorption capacity (mg g^{-1}) for the pseudo-second-order adsorption, k_2 is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), C is the intercept, and k_p is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$). The straight-line plots of $\ln(q_e - q_t)$ versus t for the pseudo-first-order reaction and t/q_t versus t for the pseudo-second-order reaction (Fig. 6) for adsorption of AR57 onto surfactant-modified sepiolite have also been tested to obtain the rate parameters. The k_1 , k_2 , q_e , q_2 , and correlation coefficients, r_1^2 and r_2^2 of AR57 under different conditions were calculated from these plots and are given in Table 2. The correlation coefficients (r_1^2) for the pseudo-first-order kinetic model are between 0.805 and 0.979 and the correlation coefficients (r_2^2), for the pseudo-second-order kinetic model are between 0.997 and 0.999. It is probable, therefore, that this adsorption system is not a pseudo-first-order reaction, it fits the pseudo-second-order kinetic model.

The pseudo-first-order and pseudo-second-order kinetic models cannot identify the diffusion mechanism and the kinetic results were then subjected to analyze by the intra-

Table 2

Kinetic parameters for the adsorption of AR57 onto surfactant-modified sepiolite at various temperatures

t ($^\circ\text{C}$)	k_1 (min^{-1})	q_e (mg g^{-1})	r_1^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_2 (mg g^{-1})	r_2^2	k_p ($\text{mg g}^{-1} \text{min}^{-1/2}$)	C (mg g^{-1})	r_p^2
20	3.97×10^{-2}	296.0	0.805	1.87×10^{-4}	425.0	0.997	23.94	158.7	0.973
30	3.35×10^{-2}	257.5	0.979	2.29×10^{-4}	385.8	0.999	17.58	179.2	0.966
40	3.79×10^{-2}	202.4	0.822	2.51×10^{-4}	359.8	0.998	23.48	119.4	0.961
50	4.44×10^{-2}	258.9	0.933	2.75×10^{-4}	345.8	0.998	19.16	141.2	0.970

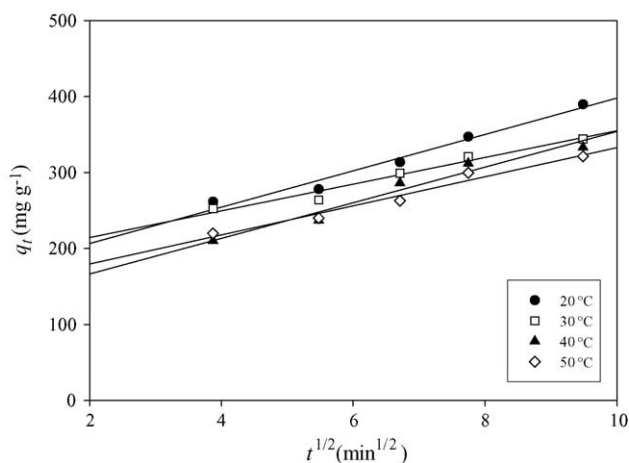


Fig. 7. Intraparticle diffusion plots for the adsorption of AR57 onto surfactant-modified sepiolite at various temperatures.

particle diffusion model. According to this model, the plot of uptake, q_t , versus the square root of time, $t^{1/2}$, (Fig. 7) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step [1,38,39]. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further show that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. The slope of linear portion from the figure can be used to derive values for the rate parameter, k_p , for the intraparticle diffusion, given in Table 2. The correlation coefficients (r_p^2) for the intraparticle diffusion model are between 0.961 and 0.973. This indicates that the adsorption of AR57 onto surfactant-modified sepiolite may be followed by an intraparticle diffusion model up to 90 min.

3.6. Thermodynamic parameters

In any adsorption process, both energy and entropy considerations must be taken into account in order to determine what process will occur spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amount of dye adsorbed at equilibrium at different temperatures is 20, 30, 40 and 50 °C, have been examined to obtain thermodynamic parameters for the adsorption system. The pseudo-second-order rate constant of dye adsorption is expressed as a function of temperature by

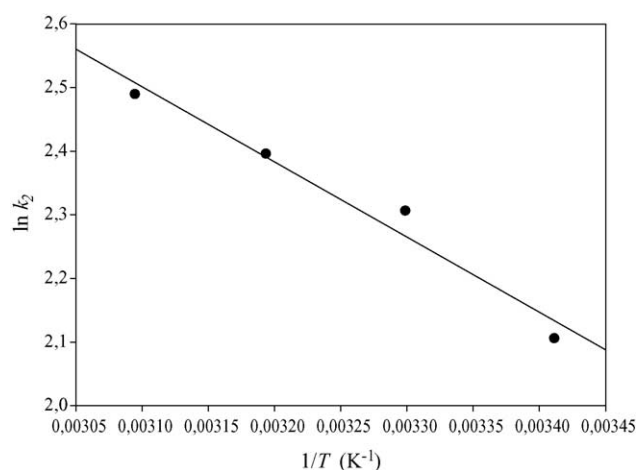


Fig. 8. Arrhenius plot for the adsorption of AR57 onto surfactant-modified sepiolite.

the following Arrhenius type relationship [8]:

$$\ln k_2 = \ln A - \frac{E_a}{RT}, \quad (6)$$

where E_a is the Arrhenius activation energy of adsorption, A is the Arrhenius factor, R is the gas constant and is equal to $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and T is the operated temperature. When $\ln k_2$ is plotted versus $1/T$ (Fig. 8), a straight line with slope $-E_a/R$ is obtained. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. Low activation energies ($5\text{--}40 \text{ kJ mol}^{-1}$) are characteristics for physisorption, while higher activation energies ($40\text{--}800 \text{ kJ mol}^{-1}$) suggest chemisorption [40]. The result obtained is $+9.82 \text{ kJ mol}^{-1}$ (Table 3) for the adsorption of AR57 onto surfactant-modified sepiolite, indicating that the adsorption has a low potential barrier and corresponding to a physisorption.

The other thermodynamic parameters, change in the standard free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were determined by using following equations:

$$K_C = \frac{C_A}{C_S}, \quad (7)$$

$$\Delta G^\circ = -RT \ln K_C, \quad (8)$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (9)$$

where K_C is the equilibrium constant, C_A is the amount of dye adsorbed on the adsorbent of the solution at equilibrium (mg dm^{-3}), C_S is the equilibrium concentration of the dye in

Table 3
Thermodynamic parameters calculated with the pseudo-second-order rate constant for AR57 onto surfactant-modified sepiolite

t (°C)	K_C	E_a (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° ($\text{J K}^{-1} \text{ mol}^{-1}$)
20	0.515	9.82	1.62	-7.87	-32.5
30	0.447		2.03		
40	0.404		2.36		
50	0.382		2.58		

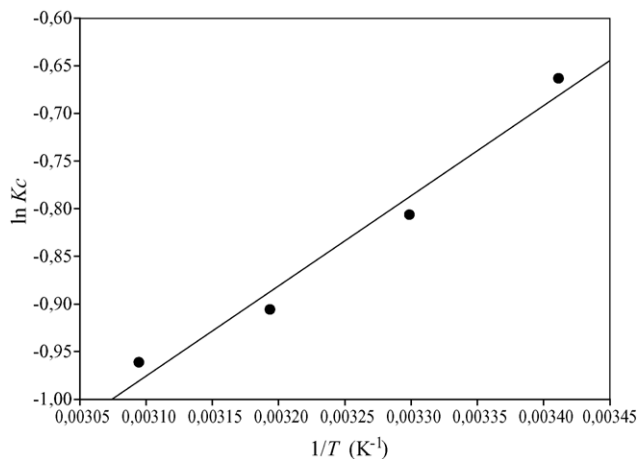


Fig. 9. Plot of $\ln K_C$ vs. $1/T$ for estimation of thermodynamic parameters for the adsorption of AR57 onto surfactant-modified sepiolite.

the solution (mg dm^{-3}). The q_2 of the pseudo-second-order model in Table 2 was used to obtain C_A and C_S . T is the solution temperature (K) and R is the gas constant. ΔH° and ΔS° were calculated the slope and intercept of van't Hoff plots of $\ln K_C$ versus $1/T$ (Fig. 9). The results are given in Table 3.

Generally, the change of free energy for physisorption is between -20 and 0 kJ mol^{-1} , but chemisorption is a range of -80 to -400 kJ mol^{-1} [41]. The results obtained are $+1.62 \text{ kJ mol}^{-1}$ at 20°C , $+2.03 \text{ kJ mol}^{-1}$ at 30°C , $+2.36 \text{ kJ mol}^{-1}$ at 40°C and $+2.58 \text{ kJ mol}^{-1}$ at 50°C (see Table 3), these indicated that the adsorption reaction was not a spontaneous one and that the system gained energy from an external source.

The small negative value of the standard enthalpy change ($-7.87 \text{ kJ mol}^{-1}$) indicate that the adsorption is physical in nature involving weak forces of attraction and is also exothermic, thereby demonstrating that the process is stable energetically. At the same time, the low value of ΔH° implies that there was loose bonding between the adsorbate molecules and the adsorbent surface [42].

The negative standard entropy change (ΔS°) value ($-32.5 \text{ J K}^{-1} \text{ mol}^{-1}$) corresponds to a decrease in the degree of freedom of the adsorbed species.

4. Conclusion

This study investigated the equilibrium and the dynamics of the adsorption of an anionic dye, which is namely Acid Red 57, AR57, onto surfactant-modified sepiolite. The adsorption was found to be strongly dependent on pH, contact time and temperature. A maximum of 425.0 mg g^{-1} AR57 removal could be achieved at pH 2 and at 20°C . The adsorption of AR57 onto surfactant-modified sepiolite was exothermic in nature with the dye removal capacity decreasing with increasing temperature due to increasing mobility of the dye molecules.

The pseudo-second-order kinetic model agrees very well with the dynamic behavior for the adsorption of AR57 onto surfactant-modified sepiolite under different temperatures. However, the evidence is provided that the adsorption of dye onto surfactant-modified sepiolite is a complex process, so it cannot be sufficiently described by a single kinetic model throughout the whole process. For example, intraparticle diffusion (up to 90 min) played a significant role, but it was not the main rate determining step during the adsorption. The experimental data fitted well to the Freundlich adsorption isotherm.

The activation energy of adsorption can be evaluated using the pseudo-second-order rate constants. The positive value of E_a ($+9.82 \text{ kJ mol}^{-1}$) confirms the nature of physisorption of AR57 onto surfactant-modified sepiolite. The enthalpy change (ΔH°) for the adsorption process was $-7.87 \text{ kJ mol}^{-1}$, which did not indicate very strong chemical forces between the adsorbed dye molecules and surfactant-modified sepiolite. The ΔG° values were positive therefore the adsorption was not spontaneous and the negative value of ΔS° suggests a decreased randomness at the solid/solution interface and no significant changes occur in the internal structure of the adsorbent through the adsorption of AR57 onto surfactant-modified sepiolite.

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