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Efficient removal of a reactive textile dye by surfactant/sepiolite one-step process

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ABSTRACT

Removal of a reactive textile dye (Reactive Blue 221) from aqueous solutions was investigated using a one-step process consisting of simultaneous synthesis of organosepiolite and adsorption of dye. The one-step process was using sepiolite as adsorbent which is in contact with the Reactive Blue 221 dye and the cationic surfactant (cetyltrimethylammonium bromide) in the solution simultaneously. The effects of pH, contact time, temperature, adsorbent amount and surfactant amount on the removal of dye were studied. The kinetic data showed that the adsorption process reached equilibrium in 45 min. The rate of adsorption conformed to the pseudo-second-order kinetics. The experimental adsorption equilibrium data were analyzed with Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models and the most suitable adsorption model was found to be Langmuir isotherm. The Langmuir monolayer capacity was calculated as 159.40 mg/g at 25°C. Various thermodynamic parameters such as ΔG°, ΔH° and ΔS° were estimated and the results show the spontaneity of the adsorption. The adsorbent dose of 4 g/L was found to be sufficient for the removal of dye. The adsorption capacity increased to 350 mg/g when the CTAB was added with the amount of three times the cation exchange capacity of sepiolite. In addition, the amount of adsorption in the one-step process was compared with that obtained in the conventional method using the modified sepiolite as the adsorbent. In addition, the XRD, FTIR and SEM-EDS methods were used to characterize the sepiolite, modified sepiolite and dye-loaded samples. The results showed that the one-step process is an effective, easy and cheaper novel technology for the removal of reactive textile dyes from water.

Keywords: Sepiolite; CTAB; Adsorption; One-step process

1. Introduction

In textile industries, huge quantities of chemicals and water are consumed during wet weaving operations. The chemicals used are very diverse in terms of chemical composition ranging from inorganic components to polymers and organic products. As a result, the characteristics of the wastewater are various [1]. Like many other industries, the textile industry also uses dyes to color their products, resulting in wastewaters containing strongly colored organics, where dye loss in wastewaters is up to 50% of the dye [2]. Water pollution control has an increasing prevalence in recent years. Although throwing the dyes is a small part of the water pollution, the dyes obviously seem even in small quantities due to their brightness. Current regulations in this regard force the textile industry to withdraw wastewater to an increasingly higher standard. Dyes do not degrade when they are exposed to many chemical substances, light and water, due to their chemical structure. Dye removal is hard due to its complicated structures and synthetic origins [3]. There are various types of dyes used in the textile industry like reactive, azo, basic, acidic, disperse and metal complexes [1]. Nevertheless, most of the synthetic dyes are in the form of azo-derived dyes and they constitute about 20–40% of the total dyes used for coloring [4,5]. The reactive and acid dyes are the most problematic ones since they tend to pass unaffected by the conventional treatment systems. Depending on the biological activity, the aerobic treatment systems of the municipalities are ineffective in removing these dyes [1]. There are various traditional physical, chemical and

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biological methods for the treatment of textile wastewaters. However, most of the commonly used biological treatment processes are ineffective in color. Since synthetic dyes in wastewaters cannot be effectively removed by conventional methods, adsorption of synthetic dyes on inexpensive and effective adsorbents has gained importance in recent years as a simple, economical and effective method of removing dyes from water and wastewater [1,4]. Various agricultural wastes such as cashew nut shell [6–8], corn pit [9], orange peel [10], and tamarind seeds [11] have been studied for the removal of dye from water. In particular, the use of cheap and abundant clay minerals such as bentonite, sepiolite, etc., as an adsorbent, improves the economical aspect. On the other hand, clays do not perform well for the removal of acidic and reactive dyes although basic dyes have a very good adsorption on the clay minerals. For this reason, the organoclays can be used conventionally as adsorbents for the adsorption of the acidic and reactive dyes. In the first step of the conventional organoclay adsorption process, the organoclay is prepared by using cationic surfactants to modify, and as a second step, the adsorption of acidic and reactive dyes is carried out [3,12–23]. The one-step process is a method involving both organoclay synthesis and adsorption simultaneously [24–27]. In this method, the surfactant is mixed with the wastewater containing dyestuff and then clay is added on it. Thus, the dyes are removed from water [27]. As a result, the organoclay synthesis step, which includes milling of clay, mixing with surfactant, separation, drying and grinding steps, is eliminated. This reduces operating costs by saving material and energy as well as significant savings both in terms of time and labor.

Bentonite was generally used as adsorbent in a one-step process [24–27], but detailed information on the use of sepiolite as adsorbent in this method was not available. The aim of this study is to determine the removal of Reactive Blue 221, a textile dye, from aqueous solutions by one-step adsorption method using sepiolite and a cationic surfactant simultaneously, and to investigate the effects of the variables such as solution pH, temperature, concentration, adsorbent amount and surfactant amount on the adsorption.

2. Experimental

2.1. Materials

The sepiolite sample was taken from Sivrihisar/Eskişehir region in Turkey. The sepiolite was ground, sieved to 200 mesh and dried in an oven at 105°C for 24 h. It was then held in a desiccator until it was used. The cation exchange capacity (CEC) of the sepiolite was determined as 30 meq/100 g sepiolite with methylene blue method.

The commercial textile dye, Reactive Blue 221 (RB221) was taken from a local textile company. It is a metal complex azo reactive dye with molecular formula of $C_{33}H_{24}ClCuN_9O_{15}S_4 \cdot H \cdot 3Na$. A RB221 stock solution (1.0 g/L) was prepared and used in the experiments after dilution to the appropriate concentrations.

A quaternary amine, cetyltrimethylammonium bromide (CTAB) from Merck was used as the cationic surfactant.

The organosepiolite was prepared for using as adsorbent to compare with CTAB/sepiolite in the one step process. A known amount of sepiolite was suspended in deionized water, CTAB was added to the equivalent amount to the cation exchange capacity of the sepiolite, and the mixture was stirred for 1 h. Then, the mixture was shaken in a thermostatic shaker at 25°C for 24 h. The sepiolite was separated from the solution by filtration and washed several times with deionized water until it became bromide free, and then dried at 50°C. The organosepiolite was re-milled and sieved to 200 mesh.

2.2. Adsorption procedure

For studying the adsorption process at one-step, first CTAB (in an amount equivalent to the CEC of the sepiolite) was added into 50 mL of a dye solution at definite concentration (100–700 mg/L) and then a 0.1 g of the sepiolite sample was put into this solution. These mixtures in conical flasks were agitated in a thermostatic shaker at 25°C for 1 h. For comparison, the same experiments were also performed by using raw sepiolite and organosepiolite without CTAB addition.

For studying the effect of pH on the one-step adsorption, the pH values of the dye solutions were maintained in the range of 2–12 by adding dilute HCl or NaOH. The one-step adsorption experiments were also done at various temperatures (25–45°C) and with different sepiolite amounts (1–10 g/L).

In order to determine the adsorption kinetics, 250 mL of a 500 mg/L dye solution containing CTAB (%100 CEC of sepiolite) and 0.25 g of sepiolite were mixed and the mixture was shaken for various time intervals at 25°C.

The effect of CTAB concentrationon adsorption was studied for the concentrations of 100%, 200% and 300% of the CEC of sepiolite. After the end of the contact period, the solutions were centrifuged to separate from the suspensions and the solution concentrations were measured using a UV-Vis spectrophotometer at a wavelength of 615 nm.

The amount of adsorption capacity (q_e, mg/g) and removal percent were calculated using Eqs. (1) and (2).

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

$$\%Removal = \frac{C_0 - C_e}{C_0} 100 \tag{2}$$

where C_0 (mg/L) and C_e (mg/L) are dye concentrations in solution before and after adsorption, respectively. V (L) is the volume of dye solution, and m (g) is the mass of the adsorbent.

2.3. Characterization

The X-ray diffraction (XRD) patterns of the sepiolite, organosepiolite and dye loaded samples were measured with Panalytical Empyrian XRD equipment. The surface morphologies and chemical analyses of the samples were determined by using JEOL JSM 5600 SEM equipped with EDS. The surface chemical characteristics of the samples were analysed by the Fourier transform infrared (FTIR) (Perkin Elmer Spectrum100) spectroscopic method in the range of 4000–400 cm^{-1} with KBr pellets.

3. Results and discussion

3.1. Characterization of the surface

3.1.1. XRD analysis

The XRD spectra of sepiolite, organosepiolite, dye loaded CTAB/sepiolite and dye loaded organosepiolite are given in Fig. 1. When the peaks observed at 2θ = 7.27, 13.32, 19.55, 24.05, 26.50, 28.5, 34.7 and 39.66° were compared to the values reported for sepiolite [28], it was determined that the clay used in this study was mainly sepiolite. A strong diffraction peak at 2θ = 7.27° appears in sepiolite diffraction spectrum. This is characteristic for layered two-dimensional lattice structure minerals and it shows that sepiolite is a kind of layered fibrous structure mineral similar to concentric circles. Its crystal plane spacing is about 12.15Å. The basal spacing of the organosepiolite increase to 12.31Å as a result of modification with CTAB. For the dye loaded CTAB/sepiolite and dye loaded organosepiolite, the basal spacing values are 12.21 and 12.44Å, respectively. The cationic surfactant changed the surface of sepiolite from hydrophilic to hydrophobic,while at the same time increased the basal spacing of the layers, and then promoting the adsorption of organic matters. The XRD results indicated that the presence of organic cation in adsorption had given rise to structural changes in the sepiolite [18].

3.1.2. FT-IR analysis

The FTIR spectra of sepiolite, organosepiolite, dye loaded CTAB/sepiolite and dye loaded organosepiolite are given in Fig. 2. The peak at 3690 cm^{-1} for all samples corresponds to stretching vibrations of Mg-OH [28]. For sepiolite, a broad band was found at 3650–3200 cm^{-1} indicating the O-H stretching vibration of the Si-OH group and HO-H vibration of the water adsorbed silica surface [29]. The absorption band at 1640 cm^{-1} indicated the H-O-H bending vibration and the broad band at 1215–925 cm^{-1} is due to the Si-O stretching vibrations. The peak obtained at 785 cm^{-1} is attributed to O-H bending vibration of Mg-Fe-OH. The peak of Mg-OH bending vibrations was detected at 680 cm^{-1} [28,30]. As a result of Si-O-Si bending vibration, the absorption band was observed at 460 cm^{-1} [28].

As shown in Fig. 2, unlike the sepiolite spectrum, the FTIR spectra of the organosepiolite and dye loaded samples have two peaks at 2930 and 2855 cm^{-1} indicating $-CH_3$ and $-CH_2$ stretching vibrations, respectively. The band at 1470 cm^{-1} is due to the $-CH_2$ deformation peak. These three peaks indicate the intercalation of CTAB molecules between silica layers of sepiolite [29]. The C=C skeleton stretching peak at 1560 cm^{-1} and small peaks at 1430 and 1400 cm^{-1} are present only in the spectra of dye loaded CTAB/sepiolite and dye loaded organosepiolite and these peaks are due to the aromatic ring vibrations of dye molecules [14]. The peaks in the spectra of the dye loaded CTAB/sepiolite and dye loaded organosepiolite were almost overlapped. This situation shows that the adsorption of RB221 on CTAB/sepiolite in one step process gave the same results with the adsorption of RB221 on the organosepiolite.

3.1.3. SEM-EDS analysis

SEM is a useful method for analyzing the surface structure of the materials. The SEM micrographs of the sepiolite, organosepiolite, dye loaded CTAB/sepiolite and dye loaded organosepiolite samples are shown in Fig. 3. It can be seen that the sepiolite surface exhibits a fibrous structure (Fig. 3a) while the organosepiolite surface shows the fragments as a result of intercalation of CTAB (Fig. 3c). In the presence of CTAB, different sizes of pores were observed. These pores could form a crosslinked network, allowing the CTAB/sepiolite to have a high adsorption capacity for removal of dyes from aqueous solution. The images of dye loaded CTAB/sepiolite and dye loaded organosepiolite (Figs. 3e and g) are similar to each other and it seems that the rough structure of the sepiolite before it was coated with the dye disappeared.

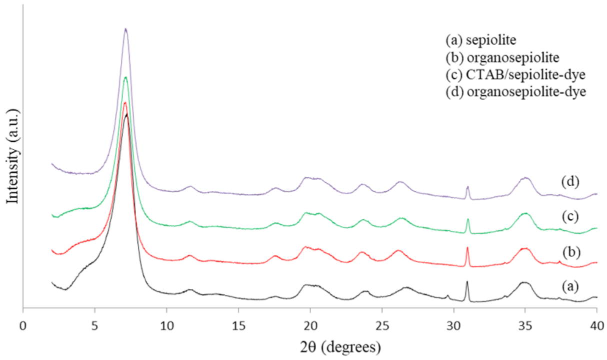

Fig. 1. The XRD spectra of sepiolite, organosepiolite, dye loaded CTAB/sepiolite and dye loaded organosepiolite.

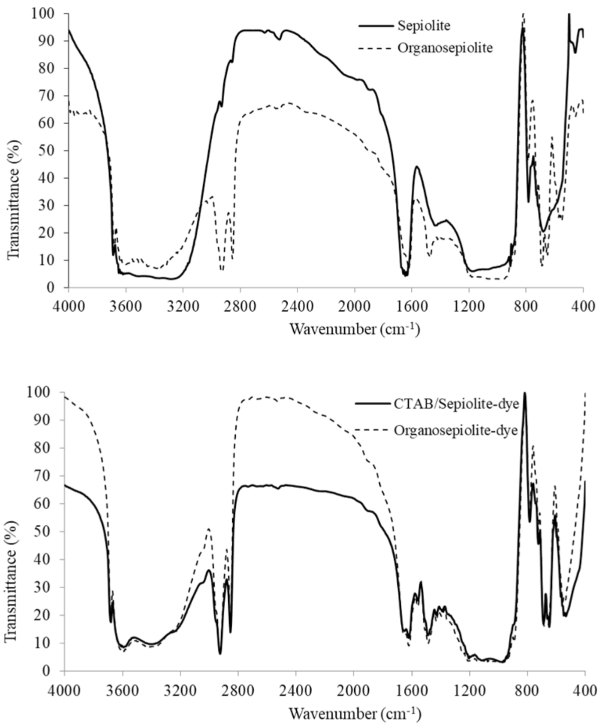

Fig. 2. The FTIR spectra of sepiolite, organosepiolite, dye loaded CTAB/sepiolite and dye loaded organosepiolite.

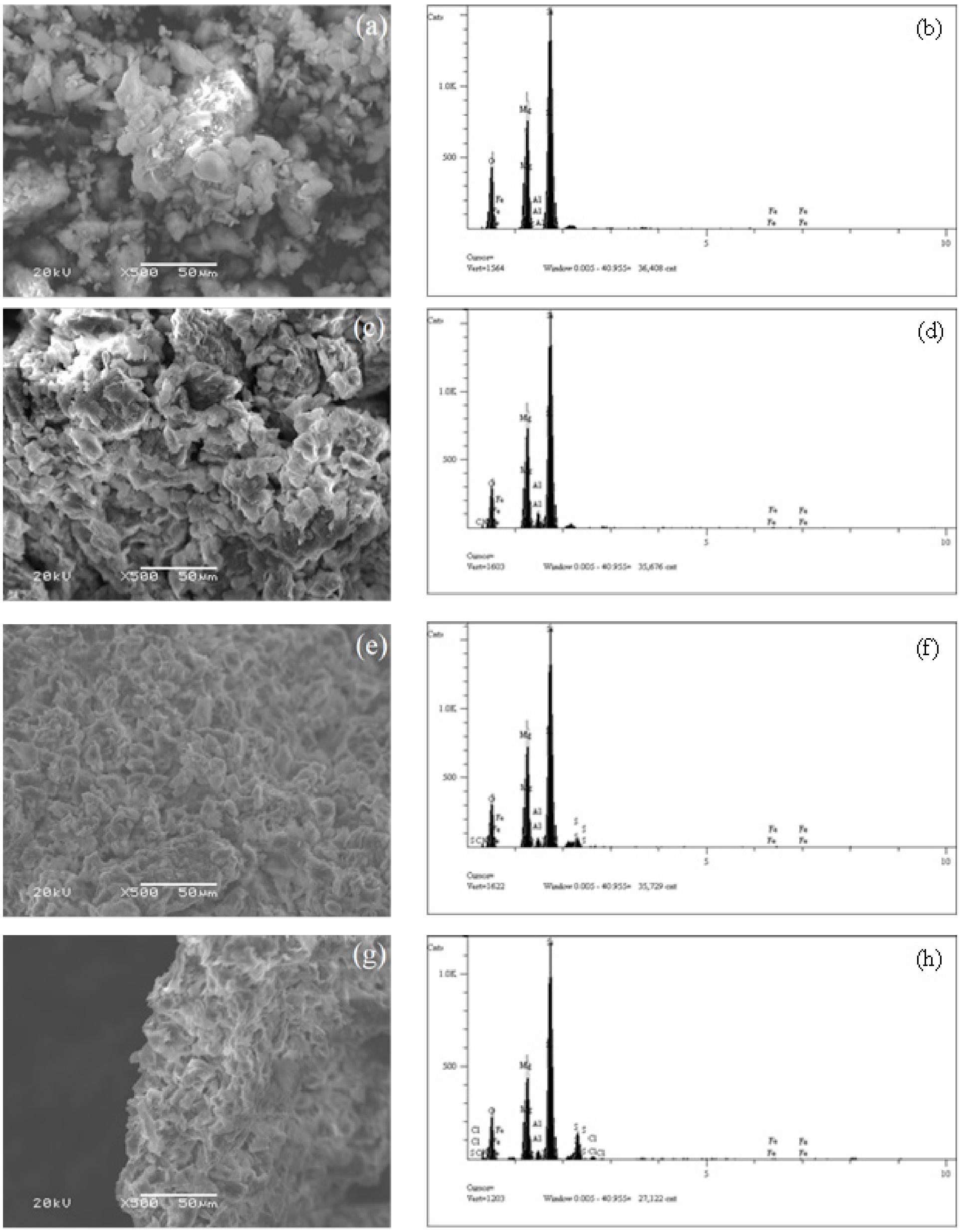

Fig. 3. SEM images and EDS spectra of sepiolite (a and b), organosepiolite (c and d), CTAB/sepiolite-dye (e and f) and organosepiolite-dye (g and h).

The EDS analysis confirms that sepiolite has Si and Mg oxides as major constituents along with traces of Al and Fe in the form of impurities (Fig. 3b). In addition, the analysis indicates the presence of N in organosepiolite and dye loaded samples (Figs. 3d,f and h). This supports the intercalation of CTAB in organosepiolite and dye loaded samples. The presence of S and Cl in dye loaded samples (Figs. 3f and h) confirmed the RB221 adsorption by CTAB/sepiolite and organosepiolite.

3.2. Effect of pH

Solution pH is one of the crucial factors affecting the adsorption behavior between adsorbent and adsorbate. Adsorption usually depends directly on the electrokinetic behavior of the adsorbent. The electrokinetic behavior is determined by the net charge on the particle surface. Fig. 4 shows the zeta potential of sepiolite as a function of pH. Zeta potential was measured by using a Zetasizer Nano ZS. Each sample was measured with three independent determinations, and each determination was repeated for ten times. The point of zero charge of the adsorbent is close to pHpzc = 3 as seen in Fig. 4. The surface is positively charged at pH < pHpzc while it is negatively charged at a higher pH than pHpzc [31].

In order to evaluate the effect of solution pH on the adsorption of RB221 in the one-step process, the adsorption experiments were carried out with initial RB221 concentra-

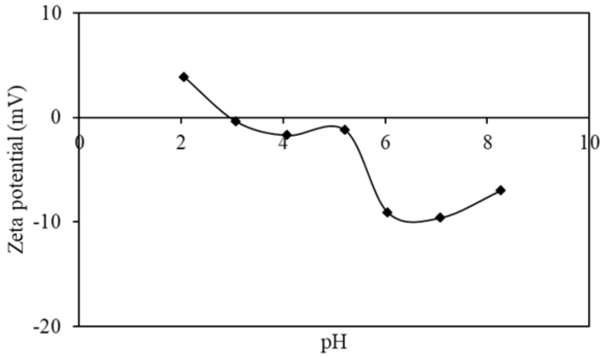

Fig. 4. The zeta potential of sepiolite as a function of pH.

tion of 500 mg/L, sepiolite amount of 0.1 g and CTAB amount of 0.011 g for 50 mL solution volume by varying the pH of the solution over the range of 2–12. The changes in the adsorption amount and removal percent depending on the solution pH during the adsorption of RB221 in the one-step process are shown in Fig. 5. It can be observed that the adsorbed amount of RB221 decreased slightly with the increasing pH from 2 to 12. The maximum adsorption capacity was found as 195 mg/g and the maximum removal percent was found as 78% at pH 2, the minimum adsorption capacity was found as 166 mg/g and the minimum removal percent was found as 66% at pH 12.The anionic dye adsorption is high at pH < pHpzc. At low pH values, the surface of sepiolite becomes positively charged due to the additional protons in the solution. The electrostatic attractions between positively charged adsorption site and anionic dye molecules increase at low pH values, so the dye adsorption increases. As the pH values increased, the surface is negatively charged and the adsorption decreased due to the abundance of OH^- ions. A negatively charged surface site on the sepiolite does not favor the adsorption of anionic dye molecules due to electrostatic repulsion [6]. Furthermore, the decrease may be due to the competition of OH^- ions with dye anions for the adsorption sites [32]. Similar results were reported related to the textile dye adsorption on activated sepiolite [30], modified sepiolite [33] and modified bentonite [14].

3.3. Effect of contact time followed by kinetic models

Determining the adsorption rate is necessary for planning an appropriate adsorption system. For this reason, in order to determine the adsorption rate in this study, the change in the amount of adsorption with respect to the contact time was investigated for the RB221 adsorption in the CTAB/sepiolite one-step process and the obtained results are given in Fig. 6. The rapid adsorption took place within the first 45 min, and then the adsorption rate slowed down and the system reached equilibrium. The adsorption efficiency of RB221 removal was initially higher due to the more number of active sites available for dye adsorption. Beyond the contact time of 45 min,the adsorbed dye forms a monolayer on the surface, so the available active sites are saturated and the capacity of the adsorbent is reduced [7,9]. A rapid adsorption process is preferred because the adsorption rate affects the adsorbate residence time and thus the reactor volume [34].

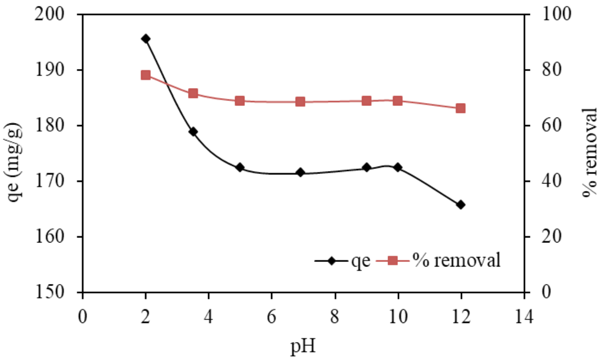

Fig. 5. The effect of solution pH for adsorption of RB221 on CTAB/sepiolite in the one step process.

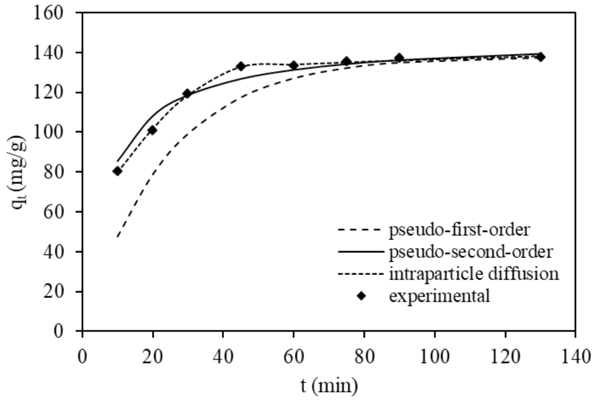

Fig. 6. Effect of contact time on the RB221 adsorption in the CTAB/sepiolite one-step process.

The rate of uptake, which affects the residence time at the solid-solution interface, is related to the adsorption kinetics. In this study, the kinetics of adsorption was analyzed by using the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. The pseudo-first-order rate equation suggested by Lagergren [35] is presented as follows:

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right) \tag{3}$$

where q_e and q_t are the amounts of adsorption (mg/g) at equilibrium and at time t, respectively; and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). Integrating Eq. (3) for $q = 0$ at $t = 0$ and $q = q_t$ at $t = t$ and rearranging it in the linear form yields [36].

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

The pseudo-second-order rate equation is as follows [37,38]:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{5}$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min). Integrating Eq. (5) for the boundary conditions of $q = 0$ at $t = 0$ and $q = q_t$ at $t = t$ and rearranging to obtain a linear form gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

The initial sorption rate, h (mg/g min) is described as $h = k_2 q_e^{\ 2}$.

The intraparticle diffusion model is given as follows [39]:

$$q_t = k_i t^{1/2} + C \tag{7}$$

where k_i is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and C is constant (mg/g) related to the boundary layer thickness [40].

The parameters of the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were calculated from slopes and intercepts of the plots of log ($q_e – q_t$) vs. t, t/q_t vs. t, and q_t vs. $t^{1/2}$ (Fig. 7), respectively. The calculated kinetic parameters and their corresponding R^2 values are given in Table 1. While the kinetic data obtained for RB221 adsorption on CTAB/sepiolite in the one-step process gave poor fits with the pseudo-first-order model, the pseudo-second-order kinetics was well fitted to the data with higher R^2 values. The calculated q_e value for the pseudo-first-order model is 63.39 mg/g and is far from the experimental q_e value (138 mg/g). The calculated q_e value (147.088 mg/g) for pseudo-second-order model close to the experimental q_e indicated that the RB221 adsorption on CTAB/sepiolite in one-step process can be approximated more favorably by the pseudo-second-order model than the pseudo-first-order one. It is seen that the data calculated in this model are very compatible with the experimental data (Fig. 6).

The plots of the intraparticle diffusion model indicated that more than one factors affected the adsorption (Fig. 7b). The first linear section corresponds to the gradual adsorption stage, wherein the intraparticle diffusion controls the adsorption rate. The fact that the plot does not pass through the origin indicates that the rate controlling step is not just intraparticle diffusion but also boundary layer diffusion. The second almost horizontal section of the plot describes the equilibrium stage of the adsorption [40].

3.4. Effect of temperature followed by thermodynamic calculations

The effect of temperature on the removal of RB221 in the one-step process at different initial dye concentrations is shown in Fig. 8. The adsorption for initial dye concentrations of 100–300 mg/L did not change much with temperature. For these concentrations, the effect of temperature was not observed because almost all of the dye in the solution was adsorbed. However, for higher concentrations, as the temperature increases the adsorption capacity increases. When the temperature increased from 25 to 45°C, the adsorption increased from 77% to 90% and 38% to 54% for initial dye concentrations of 400 mg/L and 700 mg/L,respectively. This suggests the endothermic nature of

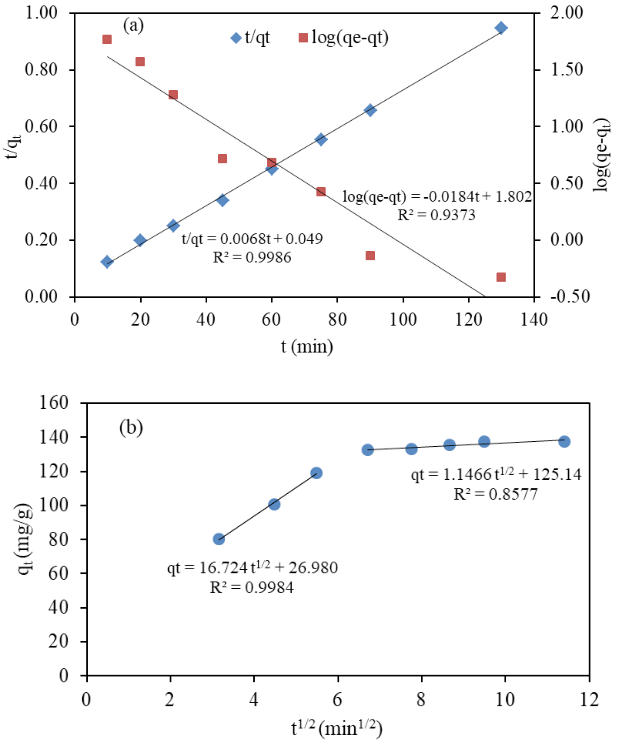

Fig. 7. (a) The pseudo-first-order and the pseudo-second-order kinetics, (b) the intraparticle diffusion plots for the RB221 adsorption onto CTAB/sepiolite in the one-step process.

Table 1
Kinetic parameters for the adsorption of RB221 on CTAB/sepiolite in the one-step process

Model	Parameters		
Pseudo-first-order	q_e (mg/g)	k_1 (min^{-1})	R^2
	63.39	0.0423	0.9373
Pseudo-second-order	q_e (mg/g)	k_2 (mg/g min)	R^2
	147.088	0.000944	0.9986
	h (mg/g min)		
	20.422		
Intra particle diffusion	k_i (mg/g min$^{0.5}$)	C (mg/g)	R^2
	16.724	26.98	0.9984

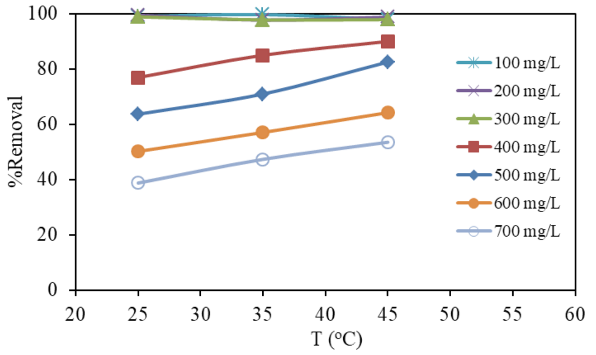

Fig. 8. The effect of temperature on removal of RB221 in the one-step process for different initial dye concentrations.

the adsorption process. As the mobility and diffusion of the adsorbate species increases with increasing temperature, the adsorption capacity may increase.

The nature of the adsorption process such as endothermicity or exothermicity, randomness and spontaneity can be determined by using the thermodynamic parameters [9]. The thermodynamic parameters of the adsorption are usually obtained from the experimental data acquired at different temperatures. The adsorption thermodynamic studies were performed at 25–45°C. The thermodynamic parameters were calculated from the following equations:

$$K_C = \frac{C_{Ae}}{C_e} \tag{8}$$

$$\Delta G^o = -RTlnK_C \tag{9}$$

$$\ln K_C = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{10}$$

where C_{Ae} is the amount of dye adsorbed onto the adsorbent per liter of solution at equilibrium (mg/L), C_e is the equilibrium concentration in solution (mg/L), T is the temperature (K), R is the universal gas constant (8.314 J/mol K) and K_c is the equilibrium constant. The values of ΔH° vs ΔS° were calculated from slope and intercept of the plot of lnK_c vs. $1/T$ (Fig. 9) and are shown in Table 2.

The negative values of Gibbs free energy (ΔG°) indicate the feasibility of the process and the spontaneous nature of the adsorption. Generally, the magnitude of the change in free energy for physical adsorption is between –20 and 0 kJ/mol [12]. The adsorption of RB221 on CTAB/sepiolite in the one-step process could be considered as physisorption according to the obtained values for ΔG°. The positive value of enthalpy change (ΔH°) indicates that the adsorption of RB221 on CTAB/sepiolite in the one-step process was endothermic in nature. The positive value of entropy change (ΔS°) implies enhanced randomness of the solid/solution interface during the adsorption of dye.

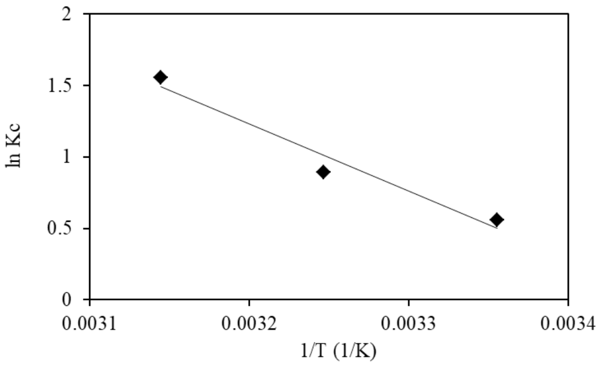

Fig. 9. Plot of ln *Kc* vs. 1/T for the adsorption of RB221 on CTAB/sepiolite in the one-step process.

Table 2
Thermodynamic parameters for the adsorption of RB221 on CTAB/sepiolite in the one-step process

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
298	–1.39	38.93	134.81
308	–2.29		
318	–4.10		

3.5. Effect of initial concentration followed by different adsorption isotherm models

The effect of initial concentration on the adsorption is shown in Fig. 10. The amount of adsorption increased with an increase in the dye concentration from 100 to 300 mg/L. This is due to increase in the driving force of the concentration gradient required to overcome the resistance to the mass transfer of dye between the aqueous phase and the solid phase, as a result of the increase in initial dye concentration [6]. However, when initial dye concentrations were increased to above 300 mg/L, adsorption amounts were almost constant. This may be due to the use of a fixed amount of adsorbent for the different initial dye concentrations. The fixed amount of adsorbent can only adsorb a certain amount of dye molecules from the aqueous solutions. At lower dye concentrations, almost all the dye molecules can be adsorbed onto the adsorbent surface because there are sufficiently the active sites on the adsorbent surface [9]. However, at higher initial dye concentrations, although the amount of dye molecules increased, since the amount of adsorbent was constant, the amount of active sites remained unchanged, which led to the adsorption of dye molecules to remain at almost constant.

To determine the optimum adsorption capacity and dose of the adsorbent to be used for a specific application, it is necessary to obtain experimental adsorption isotherms. To process the adsorption equilibrium data, a suitable isotherm model is first selected and the parameters or constants of the selected model are evaluated [41]. The Langmuir [42], Freundlich [43], Temkin [44], and Dubinin-Radushkevich (D-R) [45] isotherm models were used for analyzing the experimental equilibrium data and their linear forms are given as follows:

Langmuir equation: $$\frac{C_e}{q_e} = \frac{1}{q_m \text{b}} + \frac{C_e}{q_m} \tag{11}$$

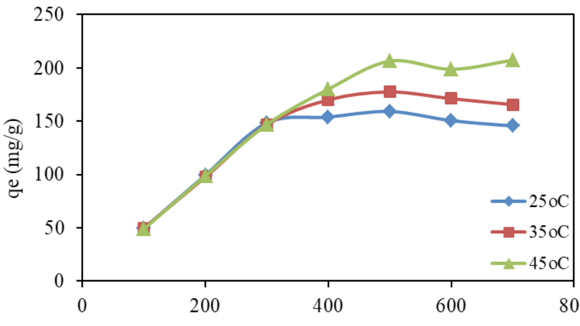

Fig. 10. The effect of initial concentration on adsorption for different temperatures.

Freundlich equation: $\ln q_e = \ln k_f + \frac{1}{n}\ln C_e$ (12)

Temkin equation: $q_e = B_1 lnA + B_1 \ln C_e$ (13)

D-R equations: $\ln q_e = \ln q_s - \beta\varepsilon^2$ (14)

$$\varepsilon = RTln\left(1+\frac{1}{C_e}\right) \quad (15)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbed dye (mg/g), q_m is the monolayer capacity (mg/g) and b is the Langmuir constant related to the energy of adsorption. The k_f and n are the Freundlich constants related with the adsorption capacity and adsorption intensity, respectively. B_1 and A are the Temkin constants. q_s and β are the D-R constants, and ε in the D-R equation can be correlated to Eq. (15) where R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K).

The constants for the used isotherms were calculated from the slopes and intercepts of the plots of C_e/q_e vs. C_e for the Langmuir equation, ln q_e vs. ln C_e for the Freundlich equation, q_e vs. ln C_e for the Temkin equation and lnq_e vs. ε^2 for the D-R equation (figures not shown). The constants and correlation coefficients are given in Table 3. The isotherm model fits were presented in Fig. 11.

The isotherms obtained are L-shaped which is characterized by a higher slope at low C_e indicating vacant adsorption sites. As concentration increases, the isotherm reaches a plateau confirming the monolayer coverage of RB221 on CTAB/sepiolite. Such an adsorption behavior is encountered when the pollutant possesses a high affinity for the material surface.

The Langmuir isotherm with high R^2 values ($R^2 > 0.996$) showed a very good fit to the experimental data for all temperatures. Also, the compatibility of the Langmuir isotherm with the experimental isotherms is shown in Fig. 11. The Langmuir isotherm is a model assuming that monolayer adsorption occurs on a homogeneous adsorbent surface and that there is no interaction between adsorbed molecules [42]. The Langmuir monolayer adsorption capacities were found as 159.40 mg/g for 25°C, 179.56 mg/g for 35°C and 214.94 mg/g for 45°C. The separation factor, R_L, can be defined by using Langmuir equation constant, b and given by

$$R_L = \frac{1}{1+bC_0} \quad (16)$$

where C_0 is the initial RB221 concentration (mg/L). If the R_L values for each initial concentration are in the range of 0–1, it states favorable adsorption. As shown in Fig. 12, for all

Table 3
Adsorption isotherm parameters for the adsorption of RB221 on CTAB/sepiolite in the one-step process

Model	Parameters	25°C	35°C	45°C
Langmuir	q_m	159.40	179.56	214.94
	b	0.772	0.446	0.207
	R^2	0.9997	0.9996	0.9960
Freundlich	k_f	82.44	73.55	61.20
	n	6.998	4.881	7.140
	R^2	0.5296	0.8838	0.7331
Temkin	A	462.77	45.83	4.67
	B_1	14.70	21.13	35.23
	R^2	0.6226	0.9126	0.8791
D-R	q_s	161.91	145.45	190.88
	b	0.272	0.073	1.093
	R^2	0.8300	0.8150	0.9219

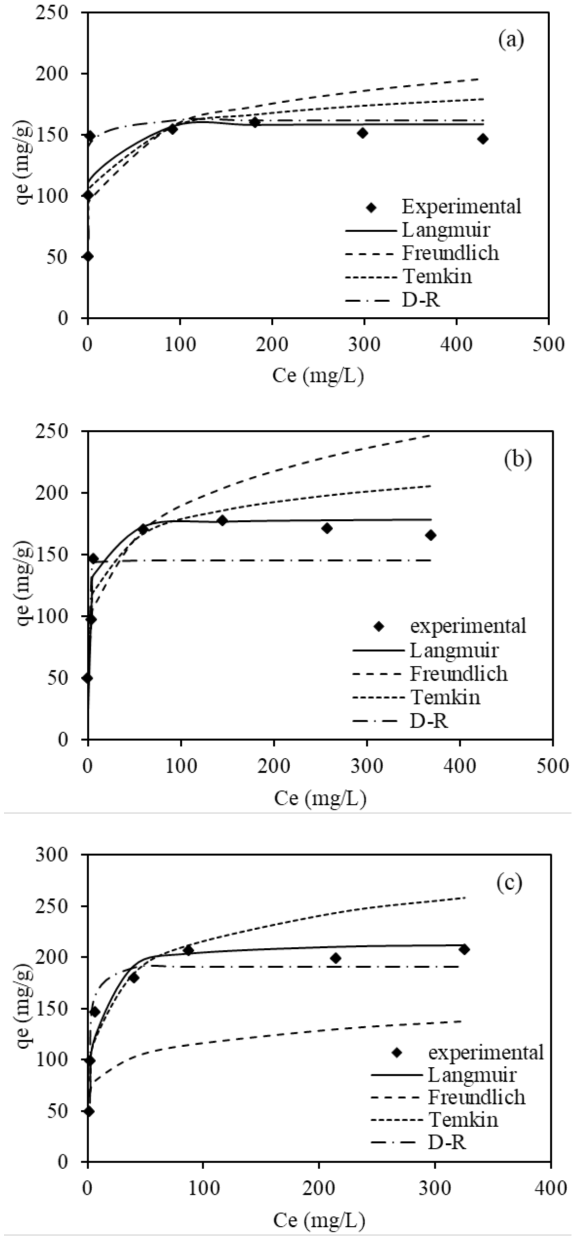

Fig. 11. The adsorption isotherms for RB221 on CTAB/sepiolite in the one-step process at (a) 25°C, (b) 35°C and (c) 45°C.

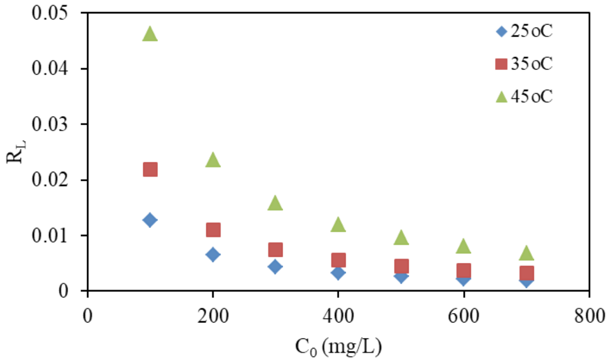

Fig. 12. Separation factors for different initial concentration at various temperatures.

initial concentrations and temperatures, the calculated R_L values were between 0.002 and 0.046 indicating the favorable adsorption of RB221 on CTAB/sepiolite in one step process.

The Freundlich isotherm is based on the fact that the adsorption takes place on an energetically heterogeneous surface. When the value of the exponent n is greater than one, it indicates that the adsorption is favorable and that the process is physical adsorption [43]. The values of n confirmed that RB221 was favorably adsorbed on CTAB/sepiolite in one step process at the applied conditions.

In the Temkin model, B_1 is related to the heat of adsorption. The increase in B_1 as the temperature increases is an indication of endothermic adsorption [46].

The mean free energy of adsorption, E, per molecule of adsorbate as it is transferred to the surface of solid from the solution can be calculated from Eq. (17) by using the constant β in the D-R equation.

$$E = \frac{1}{\sqrt{2\beta}} \tag{17}$$

An E value below 8 kJ/mol indicates that the adsorption type can be considered as physical adsorption [47]. Because E was found to be in the range of 0.676–2.619 kJ/mol, the adsorption of RB221 on the CTAB/sepiolite in the one-step process was defined as physical adsorption.

3.6. Effect of adsorbent dosage

To investigate the effect of sepiolite amount on the adsorption of RB221 on the CTAB/sepiolite in one step process, the amount of sepiolite was changed between 1–10 g/L for 500 mg/L dye solution and CTAB was also added in an amount equivalent to the CEC of sepiolite. The change in the removal percent of RB221 with sepiolite amount in CTAB/sepiolite one step process is shown in Fig. 13. It was observed that the removal percentage of RB221 increased from 22 to 99% with an increase in the sepiolite mass from 1 to 4 g per 1 L solution for 500 mg/L dye concentration. This increase in the removal percentage can be attributed to the increase in number of active adsorption sites available for adsorption. After this point, there was no change with the increase in the amount of sepiolite. This may be due to the reduction in the concentration gradient between the dye solution and the adsorbent surface. Thus, a dosage of 4 g/L sepiolite is sufficient for the removal of RB221.

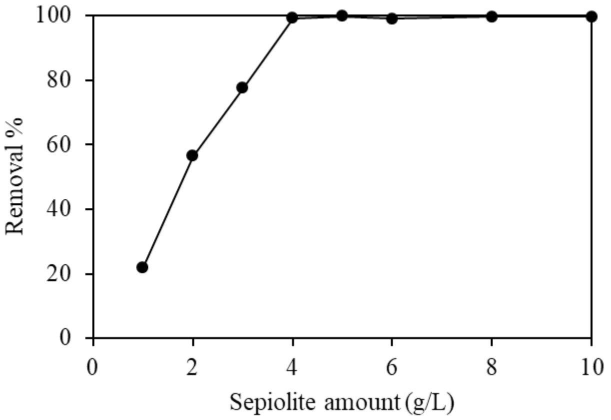

Fig. 13. The effect of the amount of sepiolite on the removal of RB221 in the one-step process.

3.7. Effect of CTAB dosage

To determine the effect of the amount of CTAB on the adsorption of RB221 by applying the CTAB/sepiolite one step process, the amount of sepiolite was kept constant at 0.1 g for each concentration for 50 mL solution and CTAB was added in an amount equivalent to 100%, 200%, and 300% of the cation exchange capacity of sepiolite. The effect of CTAB amount is shown in Fig. 14. The amount of adsorption up to 300 mg /L dye concentration was not affected by the added CTAB concentration and was almost the same for the same concentration. For high dye concentrations, the amount of adsorbed dye increased by increasing the amount of CTAB. The adsorption amount of RB221 increased to 350 mg/g when CTAB was added up to 300% of the CEC of sepiolite, while the adsorbed amount was 130 mg/g when CTAB was added up to 100% of the CEC of sepiolite for 700 mg/L dye concentration. At higher CTAB values, the density of the adsorbed surfactant layer increases, thus the retention of the dye in the surfactant film increases. A synergetic effect occurred in the case of adsorption with higher surfactant amounts than the CEC of the sepiolite [27].

3.8. Comparison of RB221 adsorption capacity of the CTAB/sepiolite (in one-step process) with those of the sepiolite and organosepiolite adsorbents

The RB221 adsorption capacity on the CTAB/sepiolite in one-step process was compared to those of both the raw sepiolite and the CTAB modified organosepiolite in Fig. 15. As shown in the figure, very low adsorption was achieved at 100 mg/L dye concentration for sepiolite. However, no adsorption took place at higher dye concentrations. The adsorption capacities of RB221 in the one-step process and in the organosepiolite process were very close to each other for all concentrations and these values were very high than that of the sepiolite. The high adsorption capacities are attributed to CTAB. The organosepiolite was formed by exchanging CTAB quaternary ammonium cations onto the surface of sepiolite. These cations gave a hydrophobic property to the sepiolite surface. As a result of this situation, the dye anions are attracted by the hydrophobic surface. In CTAB/sepiolite one-step process, the organosepiolite self-assembly and RB221 adsorption can be achieved simultaneously. Thus, the CTAB/sepiolite one-step process reached the same adsorption capacity as the organosepiolite process. As this process does not require the organosepiolite preparation, it simplifies the process considerably compared to the conventional organosepiolite process and saves time, labor and energy.

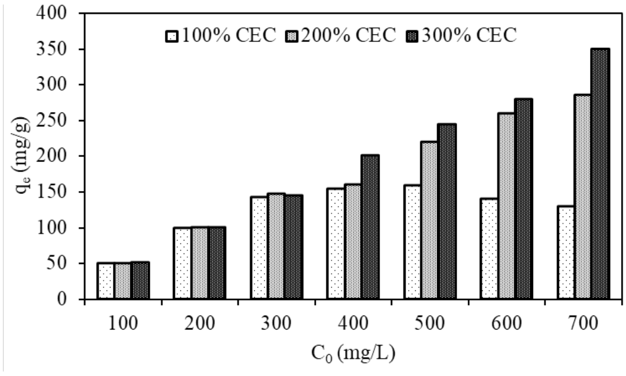

Fig. 14. The effect of amount of CTAB on the adsorption of RB221 in the one-step process.

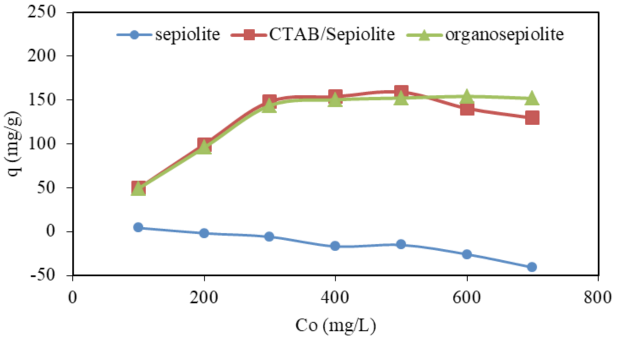

Fig. 15. Comparison of the adsorption amounts of RB221 by CTAB/sepiolite in one-step process, sepiolite and organosepiolite.

The adsorption capacities of various sepiolite samples for some reactive dyes are given in Table 4. According to this table, higher capacities were generally obtained for sepiolite samples modified with surfactant. Nevertheless, the raw sepiolite showed a lower capacity for the adsorption of reactive dyes. The sepiolite used simultaneously with CTAB in the one-step process in this study has a high adsorption capacity and this silicate could be considered as a potential economic adsorbent with the advantage of its large availability.

4. Conclusions

Sepiolite/surfactant one-step process was used for the self-assembly of the organosepiolite and the removal of reactive dye simultaneously. The adsorption of Reactive Blue 221 on sepiolite during the one-step process was found to be dependent on contact time, temperature and pH. The adsorption was higher in low pH, but it decreased as the pH increased. The experimental equilibrium data fitted the Langmuir model and the Langmuir adsorption capacities were found to be 159.40, 179.56 and 214.94 mg/g at 25, 35 and 45°C, respectively. The kinetic results showed that 45 min was sufficient to reach the equilibrium and the pseudo-second order kinetics fitted well to the data. When the CTAB amount was increased in the sepiolite/surfactant one-step process, the adsorption of Reactive Blue 221 increased. The findings of this study showed that the surfactant/sepiolite one-step process is a convenient method for removing reactive textile dyes and simplifies the conventional method by eliminating the organosepiolite preparation step from the process.

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Table 4
The adsorption capacities of various sepiolite samples for some reactive dyes

Adsorbent	Dye	Adsorption capacity (mg/g)	Reference
Modified sepiolite with HTAB	Reactive Black 5	120.5	[47]
Modified sepiolite with HTAB	Red 239	108.8	[47]
Modified sepiolite with HTAB	Yellow 176	169.1	[47]
Thermal activated sepiolite	Remazol Red B	1.46	[30]
Acid activated sepiolite	Remazol Red B	3.37	[30]
Sepiolite	Reactive Blue 21	66.67	[48]
Sepiolite	Reactive Blue 15	31.98	[49]
Sepiolite	Reactive Yellow 138:1	3.23	[50]
Sepiolite	Reactive Orange 86	96.939	[51]
CTAB/Sepiolite in the one-step process	Reactive Blue 221	159.40	This study

References

[1] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol., 77 (2001) 247–255.

[2] M.A.M. Salleh, D.K. Mahmoud, W.A.W.A. Karim, A. Idris, Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review, Desalination, 280 (2011) 1–13.

[3] Ö. Gök, A.S. Özcan, A. Özcan, Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite, Appl. Surf. Sci., 256 (2010) 5439–5443.

[4] E. Forgacs, T. Cserhati, G. Oros, Removal of synthetic dyes from wastewaters: a review, Environ. Int., 30 (2004) 953–971.

[5] B. Armağan, O. Özdemir, M. Turan, M.S. Çelik, The removal of reactive azo dyes by natural and modified zeolites, J. Chem. Technol. Biotechnol., 78 (2003) 725–732.

[6] P. Senthil Kumar, S. Ramalingam, Process optimization studies of Congo red dye adsorption onto cashew nut shell using response surface methodology, Int. J. Ind. Chem., 4 (2013) 17.

[7] P. Senthil Kumar, R.V. Abhinaya, K. Gayathri Lashmi, V. Arthi, R. Pavithra, V. Sathyaselvabala, S. Dinesh Kirupha, S. Sivanesan, Adsorption of methylene blue dye from aqueous solution by agricultural waste: equilibrium, thermodynamics, kinetics, mechanism and process design, Colloid J., 73 (2011) 651–661.

[8] P. Senthil Kumar, R. Vijayakumar Abhinaya, V. Arthi, K. GayathriLashmi, M. Priyadharshini, S. Sivanesan, Adsorption of methylene blue dye onto surface modified cashew nut shell, Environ. Eng. Manag. J., 13 (2014) 545–556.

[9] R. Jothirani, P. Senthil Kumar, A. Saravanan, A.S. Narayan, A. Dutta, Ultrasonic modified corn pith for the sequestration of dye from aqueous solution, J. Ind. Eng. Chem., 39 (2016) 162–175.

[10] P. Senthil Kumar, P. Sebastina Anne Fernando, R. Tanvir Ahmed, R. Srinath, M. Priyadharshini, A.M. Vignesh, A. Thanjiappan, Effect of temperature on the adsorption of methylene blue dye onto sulfuric acid-treated orange peel, Chem. Eng. Comm., 201 (2014) 1526–1547.

[11] P. Senthil Kumar, R. Sivaranjanee, U. Vinothini, M. Raghavi, K. Rajasekar, K. Ramakrishnan, Adsorption of dye onto raw and surface modified tamarind seeds: isotherms, process design, kinetics and mechanism, Desal. Water Treat., 52 (2014) 2620–2633.

[12] A.S. Özcan, B. Erdem, A. Özcan, Adsorption of Acid Blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite, J. Colloid Interface Sci., 280 (2004) 44–54.

[13] J. Ma, B. Cui, J. Dai, D. Li, Mechanism of adsorption of anionic dye from aqueous solutions onto organobentonite, J. Hazard. Mater., 186 (2011) 1758–1765.

[14] A. Tabak, N. Baltas, B. Afsin, M. Emirik, B. Caglar, E. Eren, Adsorption of Reactive Red 120 from aqueous solutions by cetylpryridinium-bentonite, J. Chem. Technol. Biotechnol., 85 (2010) 1199–1207.

[15] A. Kuleyin, F. Aydin, Removal of reactive textile dyes (Remazol Brillant Blue R and Remazol Yellow by surfactant-modified natural zeolite, Environ. Prog. Sustain. Energy, 30 (2011) 141–151.

[16] R. Jian-min, W. Si-wei, J. Wei, Adsorption of crystal violet onto BTEA- and CTMA-bentonite from aqueous solutions, World Academy of Science, Eng. Technol., 65 (2010) 790–795.

[17] N.P. Jovic-Jovicic, A.D. Milutinovic-Nikolic, M.J. Zunic, Z.D. Mojovic, P.T. Bankovic, I.A. Grzetic, D.M. Jovanovic, Synergic adsorption of Pb^{2+} and reactive dye-RB5 on two series of organomodified bentonites, J. Contam. Hydrol., 150 (2013) 1–11.

[18] Z. Huang, Y. Li, W. Chen, J. Shi, N. Zhang, X. Wang, Z. Li, L. Gao, Y. Zhang, Modified bentonite adsorption of organic pollutant of dye wastewater, Mater. Chem. Phys., 202 (2017) 266–276.

[19] P. Huang, A. Kazlauciunas, R. Menzel, L. Lin, Determining the mechanism and efficiency of industrial dye adsorption through facile structural control of organo-montmorillonite adsorbents, ACS Appl. Mater. Interf., 9 (2017) 26383–26391.

[20] A.S. Özcan, B. Erdem, A. Özcan, Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite, Colloids and Surfaces A: Physicochem. Eng. Aspects, 266 (2005) 73–81.

[21] N. Mirzaei, H.R. Ghaffari, K. Sharafi, A. Velayati, G. Hoseindoost, S. Rezael, A. H. Mahvi, A. Azari, K. Dindarloo, Modified natural zeolite using ammonium quaternary based material for Acid Red 18 removal from aqueous solution, J. Environ. Chem. Eng., 5 (2017) 3151–3160.

[22] N. Mirzaei, M. Hadi, M. Gholami, R.F. Fard, M.S. Aminamad, Sorption of acid dye by surfactant modificated natural zeolites, J. Taiwan Inst. Chem. Eng., 59 (2016) 186–194.

[23] D. Karadag, E. Akgul, S. Tok, F. Erturk, M.A. Kaya, M. Turan, Basic and reactive dye removal using natural and modified zeolites, J. Chem. Eng. Data, 52 (2007) 2436–2441.

[24] J. Ma, L. Zhu, Removal of phenols from water accompanied with synthesis of organobentonite in One-Step Process, Chemosphere, 68 (2007) 1883–1888.

[25] L. Zhu, J. Ma, Simultaneous removal of acid dye and cationic surfactant from water by bentonite in one-step process, Chem. Eng. J., 139 (2008) 503–509.

[26] M. Yao, X. Zhang, L. Lei, Removal of Reactive Blue 13 from dyeing wastewater by self-assembled organobentonite in one-step process, J. Chem. Eng. Data, 57 (2012) 1915–1922.

[27] A. Khenifi, B. Zohra, B. Kahina, H. Houari, D. Zoubir, Removal of 2,4-DCP from wastewater by CTAB/bentonite using one-step and two-step methods: A comparative study, Chem. Eng. J., 146 (2009) 345–354.

[28] O. Duman, S. Tunç, T. GürkanPolat, Adsorptive removal of triarylmethane dye (Basic Red 9) from aqueous solution by sepiolite as effective and low-cost adsorbent, Microporous Mesoporous Mater., 210 (2015) 176–184.

[29] H.B. Sentürk, D. Ozdes, A. Gundogdu, C. Duran, M. Soylak, Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: Equilibrium, kinetic and thermodynamic study, J. Hazard. Mater., 172 (2009) 353–362.

[30] M. Uğurlu, Adsoption of a textile dye onto activated sepiolite, Microporous Mesoporous Mater., 119 (2009) 276–283.

[31] T. Ngulube, J.R. Gumbo, V. Masindi, A. Maity, An update on synthetic dyes adsorption onto clay based minerals: A state-of-art review, J. Environ. Manage., 191 (2017) 35–57.

[32] A. Özcan, E.M. Öncü, A.S. Özcan, Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite, Colloids and Surfaces A: Physicochem. Eng. Aspects, 277 (2006) 90–97.

[33] A. Özcan, A.S. Özcan, Adsorption of Acid Red 57 from aqueous solutions onto surfactant-modified sepiolite, J. Hazard. Mater., B125 (2005) 252–259.

[34] Y.S. Ho, Review of second-order models for adsorption systems, J. Hazard. Mater., B136 (2006) 681–689.

[35] S. Lagergren, About the theory of so-called adsorption of soluble substances, KungligaSvenskaVetenskapsakademiens, Handl. Band., 24 (1898) 1–39.

[36] Y.S. Ho, Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometrics, 59 (2004) 171–177.

[37] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[38] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J., 70 (1998) 115–124.

[39] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civ. Eng., 89 (1963) 31–60.

[40] N. Jovic-Jovicic, A. Milutinovic-Nikolic, I. Grzetic, D. Jovanovic, Organobentonite as efficient textile dye sorbent, Chem. Eng. Technol., 31 (2008) 567–574.

[41] W.J. Weber, Adsorption Theory, Concepts and Models, in: F.L. Slejko (Ed.). Adsorption Technology A Step by Step Approach to Process Evaluation and Application, Marcel Dekker Inc.: New York, 1985, pp. 1–35.

[42] I. Langmuir, The constitution and fundamental properties of solids and liquids. I. Solids, J. Am. Chem. Soc., 38 (1916) 2221–2295.

[43] H.M.F. Freundlich, Adsorption in solution, Z. Phys. Chem., 57 (1906) 385–470.

[44] M.I. Temkin, V. Pyzhev, Recent modification to Langmuir isotherms, Acta Physiochim. URSS, 12 (1940) 217–222.
[45] M.M. Dubinin, L.V. Radushkevich, The equation of the characteristic curve of the activated charcoal, Proc. Acad. Sci. USSR Phys. Chem. Sect., 55 (1947) 331–337.
[46] H. Demiral, İ. Demiral, F. Tümsek, B. Karabacakoğlu, Adsorption of chromium(IV) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models, Chem. Eng. J., 144 (2008) 188–196.
[47] O. Ozdemir, B. Armagan, M. Turan, M.S. Çelik, Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals, Dye Pigment, 62 (2004) 49–60.
[48] E. Demirbas, M.Z. Nas, Batch kinetic and equilibrium studies of adsorption of Reactive Blue 21 by fly ash and sepiolite, Desalination, 243 (2009) 8–21.
[49] A. Tabak, E. Eren, B. Afsin, B. Caglar, Determination of adsorptive properties of a Turkish Sepiolite for removal of Reactive Blue 15 anionic dye from solutions, J. Hazard. Mater., 161 (2009) 1087–1094.
[50] A. Rahman, N. Kishimoto, T. Urabe, Adsorption characteristics of clay adsorbents- sepiolite, kaolin and synthetic talk- for removal of Reactive Yellow 138:1, Water Environ. J., 29 (2015) 375–382.
[51] F. Orman, H. Murathan, A. Murathan, Low cost removal of reactive dye from water using sepiolite, Fresenius Environ. Bull., 24 (2015) 2898–2905.