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Adsorption of reactive dyes on calcined alunite from aqueous solutions

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Abstract

An attempt to alleviate the problem caused by the presence of reactive dyes in textile effluents was undertaken. Since alunite is a very abundant and inexpensive, we decided to experiment with it as a potential adsorbent for a certain type of the supracited pollutants used in cellulose fibers dyeing. The adsorption of Reactive Blue 114 (RB114), Reactive Yellow 64 (RY64) and Reactive Red 124 (RR124) by calcined alunite was studied by varying parameters such as the calcination temperature and time, particle size, pH, agitation time and dye concentration. Acidic pH was favorable for the adsorption of RB114 and alkaline pH was favorable to both RY64 and RR124. The equilibrium data fit the Langmuir isotherm. The adsorption capacities were found to be 170.7, 236 and 153 mg dye per gram of calcined alunite for RB114, RY64 and RR124, respectively. The pseudo first- and second-order kinetic models were used to describe the kinetic data, and the rate constants were evaluated. The experimental data were fitted by the second-order kinetic model, which indicates that chemicalsorption is the rate limiting step, inside of mass transfer. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Reactive dye; Calcined alunite; Adsorption kinetics; Isotherm; Adsorption capacity

1. Introduction

Many industries use dyes and pigments to color their final products. Consequently, their wastewater effluents are highly colored and the disposal of these wastes into receiving waters causes damage to the environment as they may significantly affect photo-synthetic activity in aquatic life due to reduced light penetration. They may also be toxic to some aquatic life because they contain metals, chlorides, etc. Color removal from textile effluent is a major environmental problem because of the difficulty of treating such streams by conventional

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physicochemical and biological treatment methods. Many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye-containing effluents [1–5]. The adsorption process is one of the most efficient methods of removing pollutants from wastewater. Also, the adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available [6].

Activated carbon is the most widely used adsorbent for the removal of color from textile effluents because it has a high capacity for organic matter, but its use is limited due to its high cost [3,4,7,8]. This cost problem has led to a search for the use of alternate cheap and efficient materials. Peat, Fuller's earth, wood, chitin, fly ash, clay, various agricultural wastes, neutral alumina, slag, activated bauxite, perlite and alunite have been tried with varying success for color removal [1,4,6-16].

The purpose of this study was to test the possibility of using alunite for adsorption of reactive dyes due to the fact that it is a very abundant and inexpensive material. The effects of calcination temperature and time of alunite, particle size, pH, contact time on the adsorption of reactive dyes onto alunite were investigated. The amounts of adsorbed at equilibrium were measured. The Langmuir and Freundlich isotherm models were tested for their applicability. The batch contact time method was used to measure the adsorption rate. The experimental data were analyzed using the pseudo first- and second-order adsorption kinetic models, and kinetic constants were evaluated.

2. Materials and methods

Alunite exists in substantial deposits in Giresun-Sebinkarahisar, Kütahya-Saphane and Izmir-Foça in Turkey. The deposits in Turkey are estimated to be 37 million tonnes [17]. Alunite used in this study was obtained from the stocks of Dostel Aluminium Sulphate Ltd. in Kütahya-Saphane, Turkey. The analysis of alunite ore was carried out using chemical methods. Original and calcined alunite compositions are reported in Table 1.

Three reactive dyes were used as adsorbates. The dyes used in the experiments were Reactive Blue 114 (RB114, CI 21 620, wavelength at which maximum absorbance occurs

Component	Composition (wt.%)			
	Original alunite	Calcined alunit		
Al ₂ O ₃	22.12	24.89		
SiO ₂	44.86	50.49		
SO ₃	19.19	18.45		
Fe ₂ O ₃	0.11	0.12		
TiO ₂	0.16	0.18		
CaO	0.19	0.21		
MgO	0.10	0.11		
K ₂ O	4.93	5.55		
H ₂ O	8.34	_		

 Table 1

 Chemical composition of original and calcined alunite ore

Table 2

Calcination Temperature (K)		Size range (µm)	BET surface area (m ² /g)	
973	45	90–150	66.0	
		150-250	63.3	
		250-315	44.6	
		315-500	43.6	
		500-710	40.5	

BET surface areas for the different alunite particle size ranges

 $(\lambda_{\text{max}}) = 612$), Reactive Yellow 64 (RY64, CI 29 025, $\lambda_{\text{max}} = 416 \text{ nm}$) and Reactive Red 124 (RR124, CI 17 780, $\lambda_{\text{max}} = 544 \text{ nm}$). All these dyes were commercial grade and were used without further purification. All other chemicals used in the studies were obtained from Merck Chemical Co.

Alunite was prepared by grinding it in a laboratory type ball-mill. The alunite samples were calcined in muffle furnace at the temperature from 373 to 1073 K for 15–120 min. Then it was sieved to give 90–150, 150–250, 250–315, 315–500 and 500–710 μ m size fractions using ASTM standard sieves. The BET surface area was determined from N₂ adsorption isotherms with a sorptiometer (Quantachrome Co., NOVA 2000) and the results are given in Table 2.

The dye solutions were prepared by dissolving the different dyes in distilled de-ionized water at desired concentrations. Adsorption experiments were carried out by agitating 1 g of the calcined alunite with 100 ml of dye solutions of desired concentration and pH at room temperature (approximately 298 K) in a shaker operating at 200 rpm. Prior to measurement for color, the dye solutions were filtered through a 1.25 μ m glass fiber filter. All dye concentrations were measured at the wavelength corresponding to maximum absorbance, λ_{max} , using spectrophotometer (Shimadzu UV-150-02).

The amount of dye adsorbed onto calcined alunite, q_e (mg/g), was calculated by a mass-balance relationship (Eq. (1)):

$$q_{\rm e} = (C_0 - C_{\rm e})\frac{V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of the dye (mg/l), respectively, V the volume of the solution (l) and W the weight of the dry calcined alunite used (g). pH was measured using a pH meter. The affect of calcination temperature and time were studying by calcined alunite at various temperature and time.

Adsorption studies were also conducted at different size fractions. The affect of pH was studied by adjusting the pH of dye solutions using dilute HCl and NaOH solutions. Contact time studies were conducted for increasing periods of time, until no more dye was removed and equilibrium was achieved. The Langmuir isotherm was employed to study the adsorption capacity of the alunite. The procedures of kinetic experiments were basically identical to those of equilibrium tests. The samples were taken at pre-determined time intervals (5, 10, 20, 30, 45, 60, 90, 120, 150 and 180 min), and the concentrations of dyes were measured. Blank runs, with only the adsorbent in 100 ml of de-ionized water; were

conducted simultaneously at similar conditions to account for any color leached by the adsorbent and adsorbed by the glass container.

3. Results and discussion

3.1. Effect of calcination temperature and time

The alunite was calcined at temperatures ranging from 373 to 1073 K for 1 h. The adsorption experiments with these calcined alunites, using aqueous solutions with a dye concentration of 75 mg/l, were run. The results is shown in Fig. 1.

It can be seen on Fig. 1 that the adsorption of dye on calcined alunite changes with alunite calcination temperature and is highest at 973 K for reactive dyes. The adsorption of dyes on the calcined alunite is related to solid phase reactions which occur during calcination. The thermal decomposition of alunite, $K_2O\cdot3Al_2O_3\cdot4SO_3\cdot6H_2O$, occurs in two main stages [18–23]. The first stage is the loss of water vapor, the decomposition pressure reaching one atmosphere at 873 K. The second stage, the decomposition of aluminum sulfate into alumina and sulfur trioxide begins at approximately 973 K. The reaction which occurs during the thermal decomposition of pure alunite can be written as follows:

$$2\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 \rightarrow 2\text{KAl}(\text{SO}_4)_2 + 2\text{Al}_2\text{O}_3 + 6\text{H}_2\text{O}$$
(2)

$$2KAl(SO_4)_2 \rightarrow K_2SO_4 + Al_2O_3 + 3SO_3 \tag{3}$$

 γ -Al₂O₃ which is formed during calcination of alunite up to 973 K begins to change into α -Al₂O₃ at temperatures over 973 K [20,22,23]. Active alumina (porous alumina) used as

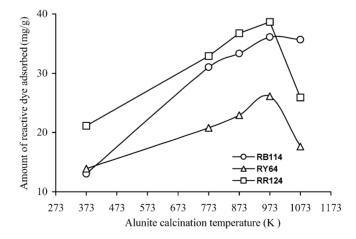


Fig. 1. Effect of calcination temperature on adsorption of reactive dyes by calcined alunite. Conditions: 75 mg/l concentration, $90-710 \,\mu\text{m}$ particle size, $60 \,\text{min}$ calcination, $1 \,\text{g}/100 \,\text{ml}$ dose, $30 \,\text{min}$ agitation, $298 \,\text{K}$ temperature and pH 6.5.

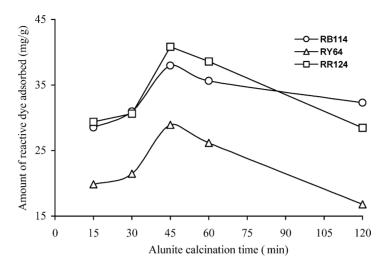


Fig. 2. Effect of calcination time on adsorption of reactive dyes by calcined alunite. Conditions: 75 mg/l concentration, 90–710 μ m particle size, 973 K calcination, 1 g/100 ml dose, 30 min agitation, 298 K temperature and pH 6.5.

an adsorbent is mainly γ -Al₂O₃ [24]. The formation of α -Al₂O₃ is normally associated with a considerable loss of surface area [25].

The maximum adsorption of reactive dyes is reached after decomposition of aluminium sulfate in the alunite at a calcination temperature of 973 K. However, the adsorption of reactive dyes decreased when calcined alunite at temperatures over 973 K was used because of change of γ -Al₂O₃ to α -Al₂O₃.

The alunite was calcined at 973 K for different times. The effect of calcination time on the adsorption of reactive dyes from aqueous solutions on calcined alunite is shown in Fig. 2. The optimum calcination time was found to be 45 min at 973 K for maximum adsorption of reactive dyes (Fig. 2). The calcined amount of alunite depends on calcination time. This time shows varies with respect to chemical composition of alunite. For example, the dehydration time of Pegam alunite is 25–30 min at 793–813 K. The optimum decomposition time of Ping Yang alunite is 10 min at 973 K. The optimum temperature and time for most efficient calcination varies in accordance with the impurities present in alunite ore [20]. It was found that partial sintering was formed in the calcination process at the long time period [20,23]. Also, for the longer time period of heat treatment, the surface area of activated alumina is decreased [25]. Amounts of adsorbed reactive dyes decreased when alunite calcined for more than 45 min was used.

3.2. Effect of particle size

The effect of particle size was studied using three reactive dyes on calcined alunite. Fig. 3 shows the experimental results obtained from a series of experiments performed, using different calcined alunite particle size ranges. It can be seen from Fig. 3, the adsorption capacity for reactive dyes increased with the decrease in the particle size. For a particle size

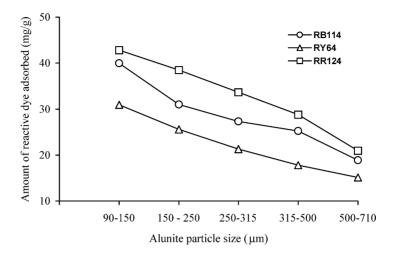


Fig. 3. Effect of particle size on adsorption of reactive dyes by calcined alunite. Conditions: 75 mg/l concentration, 973 K and 45 min calcination, 1 g/100 ml dose, 30 min agitation, 298 K temperature and pH 6.5.

range of $90-150 \,\mu\text{m}$, the values of saturation capacities are 39.97, 30.93 and 42.81 mg dye per gram calcined alunite for RB114, RY64 and RR124, respectively. The adsorption of dye from a solution with a concentration of 75 mg/l increased from 25.2 to 53.3%, from 20.2 to 41.2% and from 28.0 to 57.1% for RB114, RY64 and RR124, respectively, with decrease in particle size of calcined alunite from 500–710 to 90–150 μ m at 298 K and pH 6.5.

The adsorption of dye increases as the particle size decreases, because the surface area increases when the particle size decreases. Such an effect is probably due to the inability of the large dye molecule to penetrate all the initial pore structure of the calcined alunite. A similar phenomenon was reported previously [15,26,27] for the adsorption of certain dyes on alunite, fly ash and Fuller's earth particles.

3.3. Effect of pH

Fig. 4 shows the effect of pH on the reactive dye removal by calcined alunite. Ionic dyes upon dissolution release colored dye anions/cations into solution. The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH [13].

The pH value of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. Any oxide surface creates a charge (positive or negative) on its surface. This charge is proportional to the pH of the solution which surrounds the oxide particles. A convenient index of the propensity of a surface to become either positively or negatively charged as a function of pH is the value of the pH required to give zero net surface charge [2].

The chief constituents of alunite are metal oxides mainly of Al and Si. These metal oxides form metal-hydroxide complexes in solution and the subsequent acidic or basic dissociation of these complexes at the solid-solution interface leads to development of a

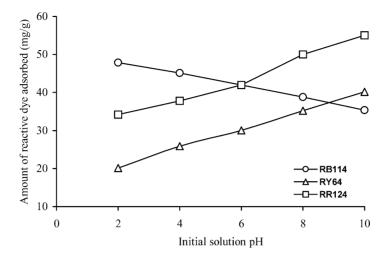


Fig. 4. Effect of pH on the removal of reactive dyes by calcined alunite. Conditions: 75 mg/l concentration, 90–150 µm particle size, 973 K and 45 min calcination, 1 g/100 ml dose, 30 min agitation and 29 K temperature.

positive or negative charge on the surface. As can be seen from Eq. (4), at acidic pH values, the metal oxide in solution tends to form an aqua complex to yield a positively charged surface [27,28].

$$\overset{\circ}{\longrightarrow} M - O + H - O H \xrightarrow{H^+} \overset{\circ}{\longrightarrow} M - O H_2^+ + O H^-$$

$$(4)$$

where M = Al, Si, etc. If hydrochloric acid is used for acidification, then the positively charged surface would be associated with chloride ions, which would subsequently be exchanged for dye anions [27,28], as shown in Eq. (5). As a result, maximum sorption of anionic dye RB114, occurs at the most acidic pH tested (pH 2).

$$\overset{O}{\longrightarrow} M^{-}OH_{2}^{+}/Cl^{-} + Dye^{-} \longrightarrow \overset{O}{\longrightarrow} M^{-}OH_{2}^{+}/Dye^{-} + Cl^{-}$$
(5)

In a similar fashion, when the pH of the solution is increased, the surface tends to become negatively charged and adsorbed cations as shown in Eq. (6) [27,28].

$$\overset{\bigcirc}{\longrightarrow} M^{-O/Na^{\dagger}} + Dye^{\dagger} \longrightarrow \overset{\bigcirc}{\longrightarrow} M^{-O/Dye^{\dagger}} + Na^{\dagger}$$
(6)

Hence, calcined alunite exhibited maximum removals of cationic dyes RY64 and RR124, at the highest pH tested (pH 10).

For RY64 and RR124, the removal increased from 26.9 to 53.6 mg dye and from 45.6 to 73.4 mg dye, respectively, with increase in pH from 2 to 10. Lower adsorption of RY64 and RR124 at acidic pH is due to the presence of excess H^+ ions competing with the dye cations for the adsorption sites. As the pH of the system increases, the number of positively charged

sites decreases and the number of negatively charged sites increases. The negatively charged sites favor the adsorption of dye cations due to the electrostatic attraction. For RB114, the percent removal decreased from 63.8 to 47.2 with increase in pH from 2 to 10. Lower adsorption of RB114 at alkaline pH is due to the presence of excess OH⁻ ions competing with the dye anion for the adsorption sites. As the pH of the system decreases, the number of negatively charged surface sites decreases and the number of positively charged sites increases. The positively charged surface sites on the adsorbent favors the adsorption of dye anions due to the electrostatic attraction [6].

3.4. Effect of contact time

Adsorption isotherms are usually determined under equilibrium conditions. A series of contact time experiments for three reactive dyes have been carried out with a constant initial dye concentration of 75 mg/l, particle size of 90–150 μ m, pH 2 for RB114 and pH 10 for RY64 and RR124 and temperature 298 K. Fig. 5 shows the contact time necessary for reactive dyes to reach saturation is >120 min. As can be seen from Fig. 5, the amount of the adsorbed dye onto calcined alunite increases with time and, at some point in time, reaches a constant value beyond which no more is removed from solution. At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye desorbing from the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions [13].

Calcined alunite exhibited dye removals as high as 84.6, 76.3 and 89.3% for RB114, RY64 and RR124, respectively, with equilibrium times of 120 min. The initial dye

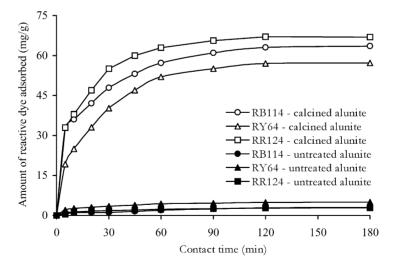


Fig. 5. Effect of contact time on the removal of reactive dyes by calcined and untreated alunite. Conditions: 75 mg/l concentration, $90-150 \mu \text{m}$ particle size, 973 K and 45 min calcination, 1 g/100 ml dose, 298 K temperature and pH 2 for RB114 and pH 10 for RY64 and RR124.

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concentration of dye has little influence on the time of contact necessary to reach equilibrium [27,28].

Similar experiments with untreated alunite were performed and the results are shown in Fig. 5. Untreated alunite adsorbed 2.92, 5 and 2.85 mg/l for RB114, RY64 and RR124, respectively, with equilibrium times of 120 min. The results show that untreated alunite does not have good adsorbent properties. However, calcined alunite has good adsorbent properties because calcining releases H_2O and SO_3 during the calcination process.

3.5. Adsorption Isotherms

Fig. 6 shows the adsorption isotherms of the three reactive dyes (q_e versus C_e) using calcined alunite. Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. These data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. The Langmuir and Freundlich equations are in common use for describing adsorption isotherms at a constant temperature for water and wastewater treatment applications [3–5,16,29,30].

The Langmuir adsorption isotherm has been successfully applied to many adsorption processes and it has been used here to explain the sorption of reactive dyes onto calcined alunite. A basic assumption of the Langmuir theory is that sorption takes place at specific

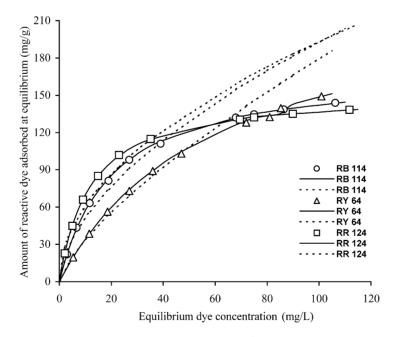


Fig. 6. Adsorption isotherms of reactive dyes by calcined alunite: $(\bigcirc, \triangle, \Box)$ experimental data; (\longrightarrow) Langmuir isotherm; (---) Freundlich isotherm. Conditions: 90–150 μ m particle size, 973 K and 45 min calcination, 1 g/100 ml dose, 298 K temperature and pH 2 for RB114 and pH 10 for RY64 and RR124.

homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. The well-known expression of the Langmuir model is given by Eq. (7):

$$q_{\rm e} = \frac{QbC_{\rm e}}{1+bC_{\rm e}} \tag{7}$$

A linear form of this expression is

$$\frac{1}{q_{\rm e}} = \frac{1}{Q} + \frac{1}{bQ} \frac{1}{C_{\rm e}} \tag{8}$$

where q_e amount of dye adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of dye in solution (mg/l). The constant Q signifies the adsorption capacity (mg/g) and b is related with the energy of adsorption (l/mg).

A plot of $1/q_e$ versus $1/C_e$ yields a straight line of slope 1/bQ and intercept 1/Q.

The values of the Langmuir constants Q and b with the correlation coefficients are listed in Table 3 for the three reactive dye systems and the Langmuir isotherms are plotted in Fig. 6 together with the experimental data points.

The empirical Freundlich equation based on a heterogeneous surface is given by Eq. (9):

$$q_{\rm e} = K_{\rm F} C_{\rm e}^{1/n} \tag{9}$$

where K_F is the Freundlich constant and *n* the Freundlich exponent. A linear form of the Freundlich expression will yield the constants K_F and *n*. Hence,

$$\log q_{\rm e} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e} \tag{10}$$

Therefore, a plot of $\log q_e$ versus $\log C_e$ enables the constant K_F and exponent *n* to be determined. These values together with the correlation coefficients for our work are presented in Table 3 and the theoretical Freundlich equations are shown in Fig. 6.

Based on the correlation coefficient (r^2) shown in Table 3, the adsorption isotherm with calcined alunite can be better described by Langmuir equation. Also, the Langmuir equation yields a better fit of the experimental data than the Freundlich equation (Fig. 6). The applicability of the Langmuir isotherm suggest a monolayer coverage of the three reactive dye on surfaces of calcined alunite.

Langmuir and Freundlich isotherm constants for adsorption of three reactive dyes on calcined alunite

Dye	Langmuir constant			$R_{\rm L}$	Freundlich constant		
	Q (mg/g)	<i>b</i> (l/mg)	r^2		K _F	n	r^2
RB114	170.7	0.050	0.999	0.091	13.72	1.742	0.956
RY64	236	0.017	0.999	0.227	6.28	1.373	0.991
RR124	153	0.084	1	0.056	19.23	1.995	0.974

Table 3

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, $R_{\rm L}$ [2,6], which is defined by

$$R_{\rm L} = \frac{1}{1 + bC_0} \tag{11}$$

where *b* is the Langmuir constant and C_0 the highest initial dye concentration (mg/l). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Under the same conditions, the adsorption capacity decreases in the following manner: RY64 > RB114 > RR124. The R_L values reported in Table 3, show that the adsorption behavior of all reactive dyes was favorable ($R_L < 1$).

3.6. Adsorption kinetics

In order to investigate the mechanism of adsorption and potential rate controlling steps such as mass transfer and chemical reaction, processes were used to test experimental data. Many models such as homogeneous surface diffusion model (also known as pore and diffusion model) have been extensively utilized for batch reactors to describe the transport of solutes inside adsorbent particles; however, the mathematical complexity of there models makes them inconvenient for practical use. Any kinetic or mass transfer representation is likely to be global. From a system design viewpoint, a lumped analysis of kinetic data is hence sufficient for practical operation [3–5,31,32]. The Lagergren's equation, pseudo first-order equation, is given as

$$\log(q_{\rm e} - q_t) = \log q_{\rm e} - \frac{k_1}{2.303}t\tag{12}$$

where q_e and q_t are the amounts of dye adsorbed on adsorbent at equilibrium and at time t (mg/g), respectively, and k_1 is the rate constant of first-order adsorption of dye (min⁻¹). A straight line of $\log(q_e - q_t)$ versus t (Fig. 6) suggests the applicability of this kinetic model to fit the experimental data. The equilibrium adsorption capacity, q_e , is required to fit the data, but in many cases q_e remains unknown due to slow adsorption processes. For this reason, it is necessary to obtain the real equilibrium adsorption capacity, q_e , by extrapolating the experimental data to $t = \infty$ or by using a trial and error method. Also, in many cases, the first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial stage of adsorption processes [3,5,33].

On the other hand, a pseudo second-order equation based on equilibrium adsorption [3,5,31,33] is expressed as

$$\frac{t}{q_{\rm t}} = \frac{1}{k_2 q_{\rm e}^2} + \frac{1}{q_{\rm e}} t \tag{13}$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. If second-order kinetics are applicable, the plot of t/q_t versus t should show a linear relationship. There is no need to know any parameter beforehand and q_e and k_2 can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behavior over the whole range of adsorption and is in agreement with chemical sorption being the rate-controlling

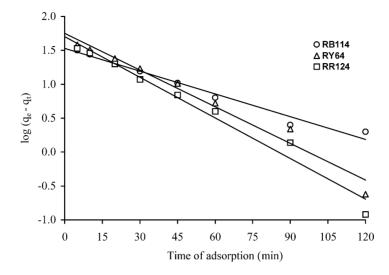


Fig. 7. Plot of the pseudo first-order model for adsorption of reactive dyes on calcined alunite (q_e and q_t are the amounts of dye adsorbed on adsorbent at equilibrium and at time t (mg/g)).

step [5,33], which may involve valency forces through sharing or exchange of electrons between dye anions and adsorbent.

In order to analyze the adsorption kinetics for the three reactive dyes, the pseudo first- and second-order kinetic models were used to analyze the data. Fig. 7 shows a plot of linearised form of the pseudo first-order model at 75 mg/l concentrations of different reactive dyes for the initial 120 min of adsorption. The slopes and intercepts of plots of $\log(q_e - q_t)$ versus *t* were used to determine the first-order rate constant k_1 and equilibrium adsorption density q_e . Table 4 lists the calculated results. A comparison of results with the correlation coefficients is shown in Table 4. The calculated q_e values obtained from the first-order kinetic model do not give reasonable values, which are too low compared with experimental q_e values. This finding suggests that the adsorption of reactive dyes onto the calculate alunite is not a first-order reaction.

The plot of the linearised form of the second-order model at a 75 mg/l concentration of three reactive dyes is shown in Fig. 8. The straight lines in plot of t/q_t versus t show good agreement of experimental data with the second-order kinetic model for all three dyes. The slopes and intercepts of plots of the t/q_t versus t were used to calculate the

Table 4

Comparison of the first- and second-order adsorption rate constants, and calculated and experimental q_e value for three reactive dyes on calcined alunite

Dye	$q_{\rm e,exp}~({\rm mg/g})$	<i>k</i> ₁ (1/min)	q _{e,cal} (mg/g)	r^2	k_2 (g/mg min)	$q_{\rm e,cal}~({\rm mg/g})$	r^2
RB114 RY64 RR124	63.50 57.20 66.90	$\begin{array}{c} 2.58 \times 10^{-2} \\ 4.15 \times 10^{-2} \\ 4.61 \times 10^{-2} \end{array}$	33.89 56.22 50.21	0.978 0.972 0.974	$\begin{array}{c} 1.54 \times 10^{-3} \\ 1.12 \times 10^{-3} \\ 1.85 \times 10^{-3} \end{array}$	67.11 62.50 70.42	0.999 0.998 0.999

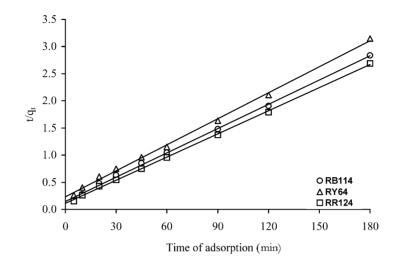


Fig. 8. Plot of the pseudo second-order model for adsorption of reactive dyes on calcined alunite (q_t is the amount of dye adsorbed on adsorbent at time t (mg/g); t is time (min)).

 k_2 and q_e . The values of the parameters k_2 and calculated and experimental q_e and of correlation coefficients are also presented in Table 4. The correlation coefficients for the second-order kinetic model were greater than 0.998 for all dyes. The calculated q_e values also agree very well with the experimental data in the case of pseudo second-order kinetics. These results suggest that each of the dye sorption systems is not a first-order reaction and that the second-order model, based on the assumption that the rate limiting step may be chemisorption. The latter provides the best correlation of the data for each dye. A similar phenomenon was also observed in the adsorption of dye RR189 on cross-linked chitosan beads [5] and in biosorption of dye RB2, RY2 and Remazol Black B on biomass [3,30].

4. Conclusion

In laboratory-scale studies, the data show that calcined alunite has considerable potential for the removal of dyestuff from aqueous solution over a wide range of concentrations. The optimum calcination temperature and time of alunite were found to be 973 K and 45 min, respectively, for adsorption of reactive dyes. The adsorbed amounts of reactive dyes increased with decreasing particle size of calcined alunite. The surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of an adsorbent towards dye ions. Having an excess of negative charge on its surface, calcined alunite has a greater capacity to adsorb RY64 and RR124 compared to RB114. In a similar manner positively charged adsorbent surface, calcined alunite has a greater capacity to adsorb RS114 than RY64 and RR124. The adsorbed amounts of reactive dyes increased with an increase in contact time and reached a maximum at an equilibrium at 120 min. Adsorption followed the Langmuir isotherm. Adsorption capacities were found to be 170.7,

236 and 153 mg dye per gram of calcined alunite for RB114, RY64 and RR124, respectively. The suitability of the first- and second-order kinetic models for the sorption of reactive dyes onto calcined alunite is also discussed. It was clear that the adsorption kinetics of reactive dyes to calcined alunite obeyed second-order adsorption kinetics.

Our study shows that the calcined alunite is an effective adsorbent for the removal of dyes from aqueous solution. Activated carbon, commonly used as an adsorbent, is an expensive material and regeneration is essential, whereas alunite is found in abundance in Turkey, and regeneration is not necessary. Moreover, this adsorbent waste could be used in alumina production. Based on the results, alunite is recommended as an effective adsorbent for dyestuffs removal from textile effluents.

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