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Kinetics and equilibrium studies for the adsorption of Acid Red 57 from aqueous solutions onto calcined-alunite

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Abstract

The adsorption of Acid Red 57 (AR57) onto calcined-alunite was examined in aqueous solution in a batch system with respect to contact time, pH and temperature. The first-order, pseudo-second-order kinetic and the intraparticle diffusion models 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. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were also determined. The equilibrium data are successfully fitted to the Langmuir adsorption isotherm. The Langmuir isotherm constant, K_L, was used to evaluate the changes of free energy, enthalpy and entropy of adsorption for the adsorption of AR57 onto calcined-alunite. The results indicate that calcined-alunite could be employed as low-cost material for the removal of acid dyes from textile effluents.
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Keywords: Alunite; Adsorption; Acid dye; Kinetics; Isotherms

1. Introduction

The main problem facing the textile industry is the cleanup of wastewaters that contain visible concentrations of colored textile effluents. Although dyes are not always toxic, they have a considerable adverse aesthetic effect since they are visible pollutants. The presence of color in water will inhibit aquatic life by blocking the passage of light through the water, resulting in ecological imbalance [1,2].

The removal of color from waste textile effluents has become environmentally important. The most widely used methods for removing color effluents from water include chemical precipitation, ion-exchange, osmosis, ozonation, solvent extraction, adsorption, membrane filtration, etc. but only that of adsorption is considered to be superior to other techniques. This is attributed to its low cost, easy availability of adsorbents, simplicity of design, high efficiency, easy of operation and biodegradability [3].

Activated carbon is perhaps the most widely used adsorbent in the adsorption processes due to its high specific surface area and high adsorption capacity. Unfortunately, it is an expensive and the difficulties involved in its regeneration for re-use [4–6]. Consequently, many researchers have studied the feasibility of using low-cost substances such as agricultural by-products [7], industrial solid wastes (fly-ash [8] and coal [9]), natural clays (bentonite [6,10,11], sepiolite [12,13], smectite [14] and montmorillonite [15]), alunite [16,17], neutral alumina [18], silica [19–21] and slag [22] as adsorbents for the removal of dyes from wastewaters.

The water-soluble anionic dyes, which are one of the most important groups of dyes used in the textile dyeing industries, are used to dye fabrics like wool, nylon and silk. Due to the weak interactions between the negatively charged surface in alunite and anionic dyes, a study on the adsorption of acid dyes has been carried out using alunite as an adsorbent by Ozacar and Şengil [17]. They examined the adsorption of two acid dyes (Acid Yellow 17 and Acid Blue 40) onto calcined-alunite and compared their results with the granular activated carbon. They were also investigated adsorption of

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the first-order kinetics and isotherms. However, any study with calcined-alunite used to determine the kinetics and isotherm models, and thermodynamic parameters for the adsorption of AR57 in aqueous solution has not been found in the literature so far. Alunite ore, $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 4Al(OH)_3$, is one of the minerals of the jarosite group and it is insoluble in water. It forms when volcanic rocks are changed hydrothermally and it occurs with SiO_2 minerals and it contains approximately 50% SiO_2 [23,24]. Alunite exists in substantial deposits in Giresun-Şebinkarahisar, Kütahya-Şaphane and İzmir-Foça in Turkey. The deposits in Turkey are estimated about 37 million tones [23].

The objective of the present work is to study the equilibrium adsorption characteristics as well as the rate of adsorption of AR57 dye from aqueous solutions onto calcined-alunite. Effects of different parameters such as pH, dye concentration, temperature, adsorbent concentration on both equilibrium and the rate of adsorption were studied. The kinetics, isotherms and thermodynamic parameters were calculated to determine the rate and isotherm constants and adsorption mechanism.

2. Materials and methods

2.1. Materials

The dye used in this study is a commercial textile dye AR57 (Nylosan Red EBL), was obtained from Clairent and used without further purification. The chemical structure of AR57 is depicted in Fig. 1. Alunite was provided from Kütahya, Turkey and used as an adsorbent for all experiments. It was crushed, ground and sieved through a 150 μm sieve and samples were collected from under the sieve and calcined in furnace at the temperature from 100 to 900 °C for 3 h. Samples were then preserved in the desiccator for further use. The BET surface area of calcined-alunite (at 900 °C) was determined from N_2 adsorption isotherm with a surface area analyzer (Quantachrome Instruments, Nova 2200e) and the result was $12.28\,m^2\,g^{-1}$.

2.2. Material characterization

The chemical analysis of natural alunite was determined using XRF instrument (ARL FISON 8400/60). Thermogravimetric (TGA) and differential thermal analysis (DTA) of alunite were carried out by a Linseis-L81 Model equipment.
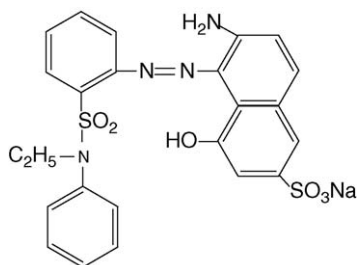

Fig. 1. The chemical structure of AR57.

2.3. Dye adsorption experiments

The adsorption experiments of anionic dye AR57 were carried out in a magnetic stirrer and at ambient temperature using 0.1 g calcined-alunite and 100 mL beaker containing 50 mL dye solutions. The effect of calcination temperature for the adsorption of AR57 onto various calcined-alunite samples was also made to observe the optimum calcination temperature and it was then obtained at 900 °C and used throughout all adsorption experiments. Further experiments were carried out at various pHs (1–11). The solution pH was carefully adjusted by adding a small amount of dilute HCl or NaOH solution by using a pH meter. The optimum pH was determined as 1 and used then throughout all of the adsorption experiments.

Dye adsorption experiments were conducted for various time intervals to determine when the adsorption equilibrium was reached and the maximum removal of dye was attained. A 50 mL of dye solution was used at a range of 0.4–$10.0\,g\,L^{-1}$ adsorbent concentrations to allow attainment of equilibrium at constant temperatures.

Dye adsorption experiments were also accomplished to obtain isotherms at various temperatures (25–55 °C) and at a range of 100–$250\,mg\,L^{-1}$ dye concentrations for 90 min by using a waterbath with a magnetic stirrer.

The solutions were then separated by centrifugation and the amount of adsorbed dye was determined by using a spectrophotometer (UV–vis, Unicam UV2-100) at λ_{max} 512.5 nm.

3. Results and discussion

3.1. Chemical composition of alunite

The chemical composition of alunite obtained by using XRF analysis, given in Table 1, indicates the presence of silica, alumina, sulphur trioxide and potassium oxide as major constituents along with other compounds in the form of impurities. It is, thus, expected that the adsorbate species will be removed mainly by SiO_2 and Al_2O_3.

3.2. Thermal analysis

TGA and DTA thermograms of alunite are illustrated in Fig. 2. This figure exhibits an endothermic peak at 450–600 °C, accompanied by to complete dehydroxilation of alunite. In this stage, mineral was transformed into crystalline $KAl(SO_4)_2$ (alum) and amorphous Al_2O_3 [25,26]. In these temperature ranges, alunite decomposed by losing its structural water accord-

Table 1
Chemical composition of alunite

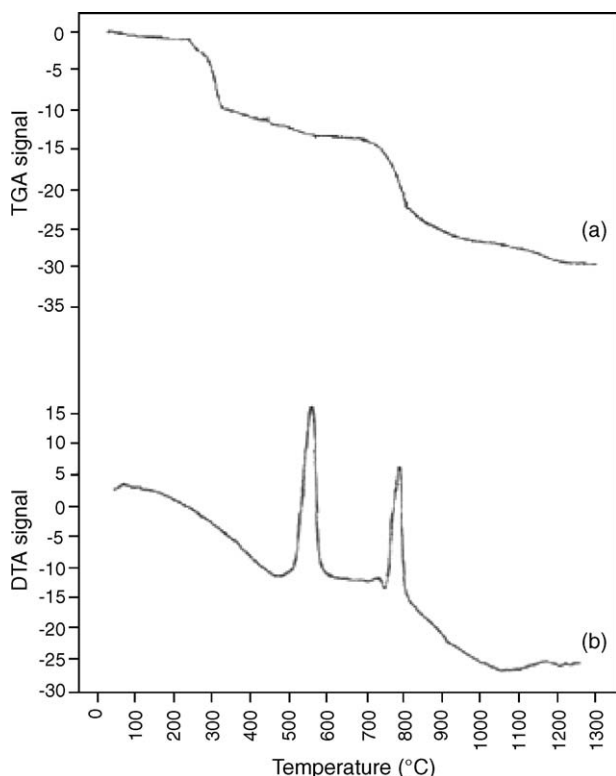| Constituents	Percentage by weight
SiO_2	43.47
Al_2O_3	27.12
SO_3	23.50
K_2O	5.50
Other compounds	0.41

Fig. 2. (a) TGA and (b) DTA thermograms of alunite.

Fig. 3. Effect of calcination temperatures for the adsorption of AR57 onto calcined-alunite. Conditions: $100\,mg\,L^{-1}$ concentration, $2\,g\,L^{-1}$ dose, 60 min agitation, 25 °C and pH 1.

calcination temperature, but this is not occurred in this study and this calcination temperature is close to the literature value. The reason for this phenomenon may be the alunite mineral was collected from the different area. This may also be an increase in the percentages of Si and Al oxides by calcination of alunite.

3.4. Effect of adsorbent concentration

The results of the experiments with varying adsorbent concentrations are shown in Fig. 4. With an increase in the adsorbent concentration, from 0.4 to $2.0\,g\,L^{-1}$ the percentage of AR57 removal increased from 18.82% to 57.00%, as the number of possible adsorbing sites would be increased. It can be concluded that an increase in the adsorbent concentration leads to increase the surface area of calcined-alunite, but the amount of AR57 adsorbed decreased from 47.05 to $28.50\,mg\,g^{-1}$. The optimum amount of adsorbent concentration was determined as $2.0\,g\,L^{-1}$

ing to the following reaction:

$$Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 4Al(OH)_{3(s)}$$

$$\overset{450-600\,°C}{\longrightarrow} Al_2(SO_4)_3 \cdot K_2SO_{4(s)} + 2Al_2O_{3(s)} + 6H_2O_{(g)}$$

The other endothermic peak was observed between 750 and 850 °C in Fig. 2, which refers to the partial desulphatization of alunite by decomposition of alum and loss of 3/4 sulphate as SO_3 [25,27,28] as following reaction:

$$Al_2(SO_4)_3 \cdot K_2SO_{4(s)} \overset{750-850\,°C}{\longrightarrow} K_2SO_{4(s)} + Al_2O_{3(s)} + 3SO_{3(g)}$$
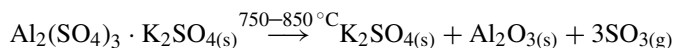
In the range of 1100–1200 °C, it is observed that a final endothermic peak is present, according to the following reaction:

$$K_2SO_{4(s)} \overset{1100-1200\,°C}{\longrightarrow} K_2O_{(s)} + SO_{3(g)}$$
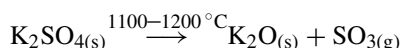
3.3. Effect of calcination temperature

The effect of calcination temperature for various calcined-alunite samples was also made to observe the optimum calcination temperature. The results are shown in Fig. 3.

Although the adsorption of AR57 on calcined-alunite samples does not change until 600 °C, there is a steady increase after this temperature. The highest adsorption of AR57 onto calcined-alunite is obtained at 900 °C and it was used throughout all adsorption experiments. According to the literature [24], partial sintering starts over 800 °C. It is expected to observe a decrease in adsorption of dye onto calcined-alunite after this
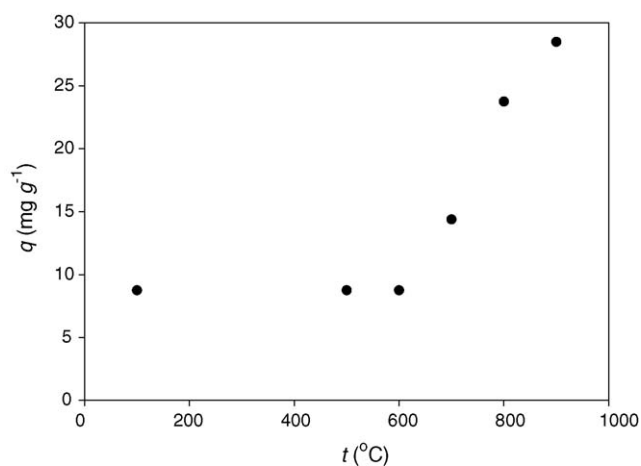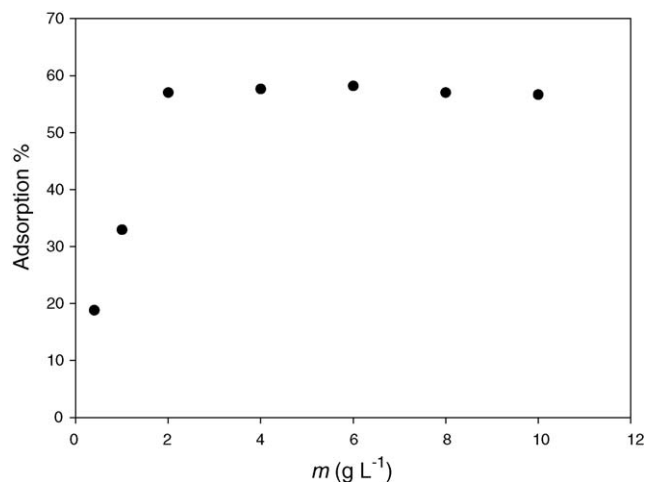

Fig. 4. Effect of adsorbent concentration for the adsorption of AR57 onto calcined-alunite. Conditions: $100\,mg\,L^{-1}$ concentration, 60 min agitation, 25 °C and pH 1.
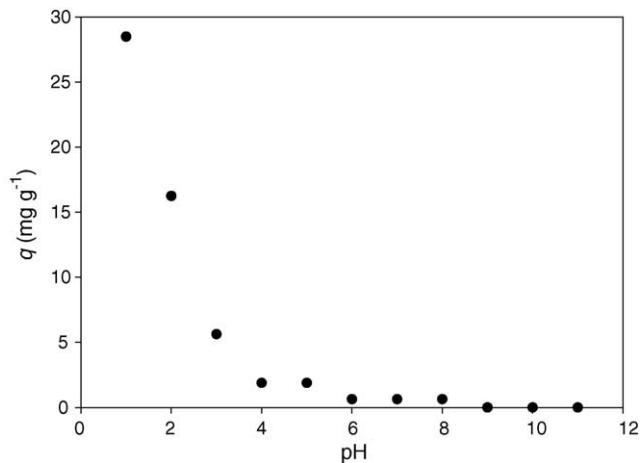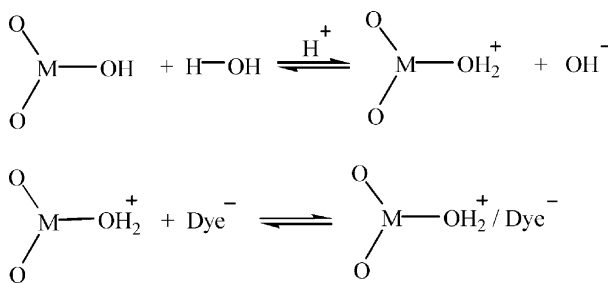
Fig. 5. pH effect for the adsorption of AR57 onto calcined-alunite at 25 °C. Conditions: $100 \, \text{mg L}^{-1}$ concentration, $2 \, \text{g L}^{-1}$ dose and 60 min agitation.

Fig. 6. Effect of contact time for the adsorption of AR57 onto calcined-alunite at various temperatures. Conditions: $100 \, \text{mg L}^{-1}$ concentration, $2 \, \text{g L}^{-1}$ dose and pH 1.

and thus fixed as the adsorbent concentration for further experiments.

3.5. Effect of pH

The effect of pH on the adsorption process was illustrated in Fig. 5. It indicates that the adsorption capacity of AR57 onto calcined-alunite increases gradually with decreasing up to pH 3 and then a sharp increase was observed between pH 3 and 1. The maximum removal of dye for contact time 60 min was determined at pH 1. At strongly acidic pHs, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye.

The chemical composition of alunite mainly consists of Al and Si metal oxides. These metal oxides form metal-hydroxide complexes in aqueous solution. As can be seen from schema, at acidic pH values, the metal oxide in solution tends to form an aqua complex to yield a positively charged surface [16].

where M = Al, Si, etc. Then the electrostatic attraction between positively charged surface and dye anion would be occurred as shown in schema. As a result, maximum adsorption of anionic dye occurs at the lowest pH.

As the pH of the adsorption system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favor the adsorption of dye anions, due to the electrostatic repulsion. Also, lower adsorption of AR57 at alkaline pHs is due to the presence of excess hydroxyl ions competing with the dye anions for the adsorption sites.
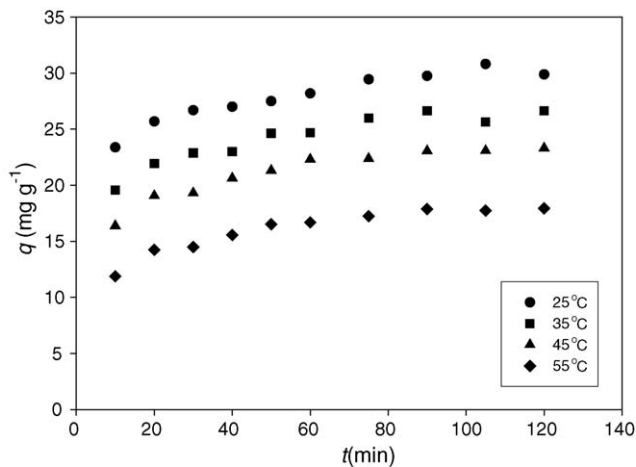
3.6. Adsorption kinetics

The effect of contact time on the amount of AR57 adsorbed onto calcined-alunite was illustrated in Fig. 6. When the contact time was increased, the amount of adsorption was also increased. The maximum adsorption capacity of AR57 onto calcined-alunite was observed at 90 min, beyond which there is almost no further increase in the adsorption capacity, and it is thus fixed as the equilibrium contact time.

The equilibrium adsorption capacity of AR57 onto calcined-alunite was favored at lower temperature. When the temperature increases from 25 to 55 °C at 90 min, the equilibrium adsorption capacity decreases from 30.81 to $17.97 \, \text{mg g}^{-1}$, indicating that the adsorption of AR57 onto calcined-alunite is physical and exothermic process.

Kinetic data were analyzed with the first-order, pseudo-second-order kinetic and intraparticle diffusion equations.

The first-order kinetic model equation [2] is

$$\frac{1}{q_t} = \left(\frac{k_1}{q_1} \right) \left(\frac{1}{t} \right) + \frac{1}{q_1}, \tag{1}$$

where q_1 and q_t are the amounts of the dye adsorbed at equilibrium (mg g^{-1}) and at time t and k_1 is the first-order rate constant (min^{-1}), applied to the adsorption of AR57. Values of k_1 calculated from the slope of the plots of $1/q_t$ versus $1/t$ are given in Table 2 (figure not shown). It was found that the correlation coefficients for the first-order model are lower than that of the pseudo-second-order model. This indicates that the adsorption of AR57 onto calcined-alunite does not follow first-order kinetics.

The pseudo-second-order kinetic model [29–31] is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t, \tag{2}$$

where q_2 is the maximum adsorption capacity (mg g^{-1}) and k_2 is the equilibrium rate constant for pseudo-second-order adsorption ($\text{g mg}^{-1} \, \text{min}^{-1}$). Values of k_2 and q_2 were calculated from

Table 2
Kinetic parameters for the adsorption of AR57 onto calcined-alunite at various temperatures

t (°C)	q_{exp} (mg g^{-1})	k_1 (min^{-1})	q_1 (mg g^{-1})	r_1^2	k_2 (g mg^{-1} min^{-1})	q_2 (mg g^{-1})	r_2^2	k_p (mg g^{-1} min$^{-1/2}$)	C (mg g^{-1})	r_p^2
25	30.81	3.146	30.15	0.899	5.97×10^{-3}	31.47	0.998	0.951	20.97	0.966
35	26.63	3.871	26.60	0.917	6.21×10^{-3}	27.66	0.998	1.064	16.70	0.972
45	23.31	4.715	23.66	0.949	6.23×10^{-3}	24.52	0.999	1.015	13.90	0.951
55	17.94	5.742	18.37	0.957	6.77×10^{-3}	19.09	0.999	0.899	9.680	0.957

the plot of t/q_t against t (Fig. 7). All of kinetic data of AR57 under different temperatures were calculated from plots and were given in Table 2. The correlation coefficients for the pseudo-second-order kinetic plots at all the studied temperatures were above 0.998 (Table 2) and the calculated q_2 values are also agree with experimental q values. These results imply that the adsorption system studied obeys to the pseudo-second-order kinetic model. A similar phenomenon has been observed in the adsorption of acid dyes by acid-activated bentonite [6], surfactant-modified bentonite [10,11], sepiolite [12] and surfactant-modified sepiolite [13].

The intraparticle diffusion equation [32] can be written by following:

$$q_t = k_p t^{1/2} + C, \tag{3}$$

where C is the intercept and k_p is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$). According to this model, the plot of uptake, q_t, versus the square root of time, $t^{1/2}$ (figure not shown), should be linear if intraparticle diffusion is involved in the adsorption system and if these lines pass through the origin, then intraparticle diffusion is the rate-controlling step [2,13,33,34]. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further indicates 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 (figure not shown) can be used to derive values for the rate parameter, k_p, for the intraparticle diffusion, given in Table 2. The correlation coeffi-
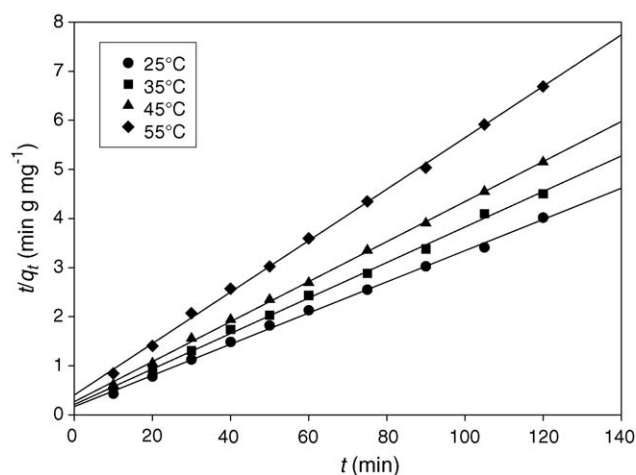

Fig. 7. Pseudo-second-order kinetic plots for the adsorption of AR57 onto calcined-alunite at various temperatures.

cients (r_p^2) for the intraparticle diffusion model are also lower than that of the pseudo-second-order model but this model indicates that the adsorption of AR57 onto calcined-alunite may be followed by an intraparticle diffusion model up to 90 min.

The pseudo-second-order rate constants for AR57 onto calcined-alunite indicate a steady increase from 5.97×10^{-3} to 6.77×10^{-3} g mg^{-1} min^{-1} with temperature is increased from 25 to 55 °C. It may be concluded that the adsorption of AR57 onto calcined-alunite follows a physisorption mechanism; increasing temperature increases the rate of approach to equilibrium [35], but decreases the equilibrium adsorption capacity from 31.47 to 19.09 mg g^{-1}.

3.7. Adsorption isotherms

Two important isotherms are selected in this study, which are namely the Langmuir [36] and Freundlich [37] isotherms.

The Langmuir adsorption isotherm assumes that adsorption occurs at specific homogenous sites within the adsorbent and has found successful application in many adsorption studies of monolayer adsorption. The linear form of the Langmuir isotherm equation is written by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max} K_L}\right)\frac{1}{C_e}, \tag{4}$$

where q_e is the equilibrium dye concentration on the adsorbent (mol g^{-1}), C_e the equilibrium dye concentration in the solution (mol L^{-1}), q_{max} the monolayer adsorption capacity of the adsorbent (mol g^{-1}), and K_L is the Langmuir adsorption constant (L mol^{-1}) and related to the free energy of adsorption. The plots of $1/q_e$ versus $1/C_e$ for the adsorption of AR57 onto calcined-alunite (Fig. 8) give a straight line of slope $\frac{1}{q_{max} K_L}$ and intercept $\frac{1}{q_{max}}$.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. A linear form of the Freundlich equation is

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e, \tag{5}$$

where K_F (L g^{-1}) and n (dimensionless) are the Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. The plots of $\ln q_e$ against $\ln C_e$ for the adsorption of AR57 onto calcined-alunite (Fig. 9) were employed to generate the intercept value of K_F and the slope of $1/n$.
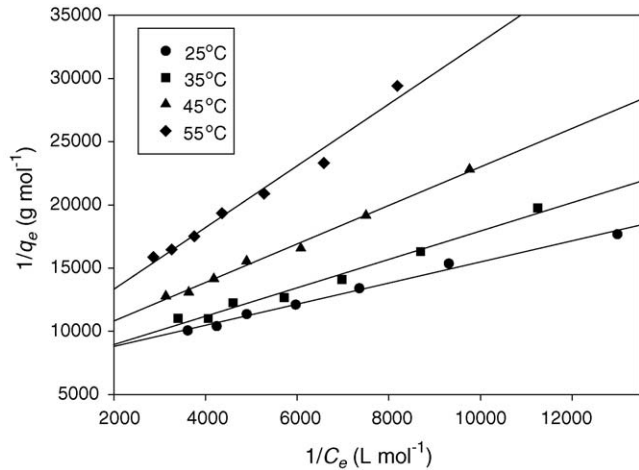
Fig. 8. Langmuir plots for the adsorption of AR57 onto calcined-alunite at various temperatures.
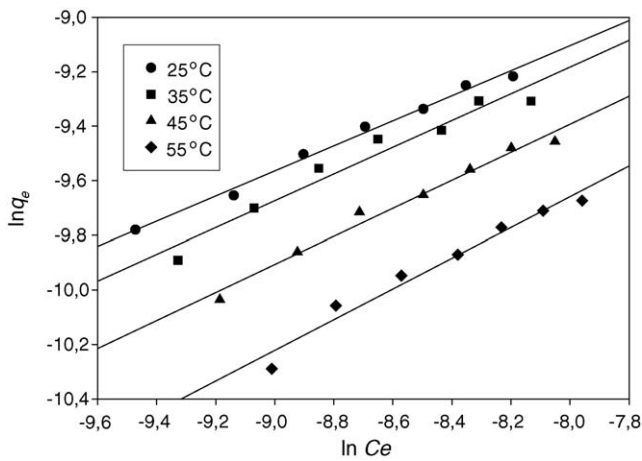

Fig. 9. Freundlich plots for the adsorption of AR57 onto calcined-alunite at various temperatures.

The Langmuir and Freundlich parameters for the adsorption of AR57 are listed in Table 3. It is evident from these data that the surface of calcined-alunite is mostly made up of homogeneous adsorption patches. In other words, Langmuir isotherm model is well fitted than Freundlich isotherm model, when the r^2 values are compared in Table 3.

The effect of isotherm shape has been discussed [38] with a view to predict whether an adsorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation factor or equilibrium parameter R_L is calculated

Table 4
Thermodynamic parameters calculated from the Langmuir isotherm constant (K_L) for the adsorption of AR57 onto calcined-alunite

t (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
25	−22.42	−23.25	−2.774
35	−22.40		
45	−22.37		
55	−22.34		

using the following equation:

$$R_L = \frac{1}{1 + K_L C_0},\tag{6}$$

where C_0 is the highest initial dye concentration (mol L^{-1}). The values of R_L calculated as above equation are incorporated in Table 3. As the R_L values lie between 0 and 1, the adsorption process is favorable [38,39]. Further, the R_L values for the adsorption of AR57 are between 0.198 and 0.378 and therefore, its adsorption is favorable.

One of the Freundlich constants K_F indicates the adsorption capacity of the adsorbent. The other Freundlich constants n is a measure of the deviation from linearity of the adsorption. If a value for n is equal to unity the adsorption is linear. If a value for n is below to unity, this implies that adsorption process is chemical, but a value for n is above to unity, adsorption is favorable a physical process. The highest value of n at equilibrium is 2.174 at 25 °C, represents favorable adsorption at low temperature and therefore this would seem to suggest that physical, which is referred the adsorption bond becomes weak [40] and conducted with van der Waals forces, rather than chemical adsorption is dominant when it is used for adsorbing AR57.

3.8. Thermodynamic parameters

Langmuir isotherm constant K_L, its dependence with temperature can be used to estimate the thermodynamic parameters, such as the changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated to the adsorption process and were determined by using following equations and represented in Table 4:

$$\Delta G^\circ = -RT \ln K_L,\tag{7}$$

$$\ln K_L = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R},\tag{8}$$

The plot of $\ln K_L$ as a function of $1/T$ (Fig. 10) yields a straight line from which ΔH° and ΔS° were calculated from the slope and intercept, respectively.

Table 3
Adsorption isotherm constants for the adsorption of AR57 onto calcined-alunite at various temperatures

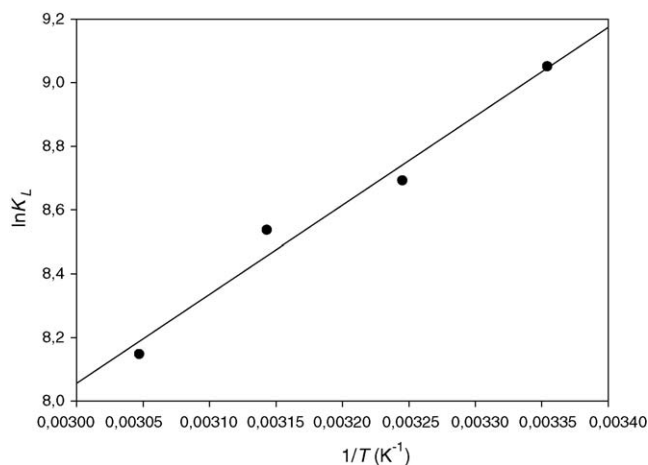| t (°C)	Langmuir				Freundlich		
	q_{max} (mol g^{-1})	K_L (L mol^{-1})	r_L^2	R_L	n	K_F (L g^{-1})	r_F^2
25	1.40×10^{-4}	8.53×10^3	0.991	0.198	2.174	4.41×10^{-3}	0.991
35	1.49×10^{-4}	5.96×10^3	0.982	0.261	2.039	5.20×10^{-3}	0.952
45	1.29×10^{-4}	5.10×10^3	0.994	0.292	1.947	5.08×10^{-3}	0.982
55	1.19×10^{-4}	3.46×10^3	0.979	0.378	1.777	5.76×10^{-3}	0.968

Fig. 10. Plot of $\ln K_L$ vs. $1/T$ for estimation of thermodynamic parameters.

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 overall free energy change during the adsorption process was negative for the experimental range of temperatures (see Table 4), corresponding to a spontaneous physical process of AR57 adsorption and that the system does not gained energy from an external source.

The negative value of the enthalpy change ($-23.25\,kJ\,mol^{-1}$) indicates that the adsorption is physical in nature involving weak forces of attraction and is also exothermic, thereby demonstrating that the process is stable energetically [42]. The negative entropy change (ΔS°) value ($-2.774\,J\,K^{-1}\,mol^{-1}$) corresponds to a decrease in the degree of freedom of the adsorbed species.

4. Conclusion

The present study clearly demonstrated that calcined-alunite is an effective adsorbent for removing AR57 from aqueous solution; it can be represented as a suitable adsorbent and environmentally clean utilization of wastewater.

The adsorption of AR57 onto calcined-alunite follows the pseudo-second-order kinetic model with high correlation coefficients and also fits well the intraparticle diffusion model up to 90 min, but diffusion is not the only rate-controlling step. The high adsorption capacity of AR57 onto calcined-alunite in highly acidic solutions (pH around 1) is due to the strong electrostatic interactions between its adsorption site and dye anion. The adsorption of AR57 onto calcined-alunite obeys the Langmuir adsorption isotherm model.

The enthalpy change (ΔH°) for the adsorption process was indicative of the exothermic nature of adsorption and a physical adsorption. The ΔG° values were negative, therefore the adsorption was 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 calcined-alunite.

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