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Study on removal behavior and separation efficiency of naturally occurring bentonite for sulfate from water by continuous column and batch methods

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ABSTRACT

The removal of sulfate using Jordanian bentonite has been investigated in this study. The surface of the bentonite was modified by calcinations at different temperature. The batch experiments of the equilibrium studies were carried out under different operating conditions. Kinetic modeling for the removal of sulfate ion was investigated using a pseudo-second-order, intraparticle diffusion and Elovich kinetic models to predict the rate constants and equilibrium capacities for this process using column reactor. It was found that intraparticle diffusion of the sulfate ion is the rate limiting step and played an important role in the mechanism of sulfate ion adsorption depending on the obtained activation energy, which was 32.8 kJ/mol. Also, the sorption isotherm analyzed using both the Langmuir and Freundlich models as a function of temperature. The isothermal data found to be fitted Langmuir model rather than Freundlich model. The positive value of ΔH (15.2 kJ/mol) indicated that the adsorption of sulfate ions on the adsorbent was an endothermic process and the positive value of ΔS (22.1 J/mol.K) indicated that the adsorption is favorable with small positive value of the free energy (ΔG).

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1. Introduction

Sulfate is a common constituent of many natural water sources and waste water, and is sometimes present in high concentrations. Sulfate pollutants present commonly in wastewaters, which are produced in many processes such as mining, animal husbandry, food processing, pulp and paper wastewaters, dye and detergent manufacture [1]. Industrial wastewaters are responsible for most anthropogenic emissions. Certain industrial effluents may contain several thousands of mg/L domestic sewage contains typically less than 500 mg/L [2]. The damage caused by sulfate emissions is not direct, since sulfate is a non-toxic compound. However, high sulfate concentrations can unbalance the natural sulfur cycle [3]. Several processes can be applied to promote the removal of dissolved sulfate. Chemical precipitation through the addition of barium or calcium salts is an alternative, mainly applied to the treatment of wastewaters that contain high sulfate concentrations. Using membranes is another alternative. However, the relatively high cost and energy consumption, proportional to the sulfate concentration, should be taken into account. Adsorption is an effective and economical method to treat sulfate-containing wastewaters [4-7].

Many of adverse effects have been reported, e.g. the wastewaters negatively affect the aquatic ecosystem; the reduced products volatilize into the atmosphere and contribute to acid rain; the generated toxic acidic gas raises serious health risks to living beings and is corrosive to materials [2,8]. To date, quite a lot of efforts have been made to treat the sulfate-rich wastewater.

The techniques generally include precipitation, membrane separation and biological methods [9-11]. Chemical precipitation is widely used to remove sulfate from water and wastewater. However, its main drawback is the huge value of accompanying sludge [12].

Using clay material as adsorbent for the removal of sulfate ion is good choice because of its low cost and high efficiency. According to our knowledge, there are few researches that concerned about the investigation of the removal of sulfate ion by clay minerals.

The aim of this work is to examine the sorption of sulfate present in aqueous solution using modified Jordanian bentonite as adsorbent at different parameters like contact time, adsorbent dose, pH and temperature and to study the isothermal and kinetics process for this removal using fixed-bed and continuous methods.

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2. Experimental

2.1. Preparation of sorbent

The bentonite samples were supplied by the Jordanian Natural Resources Authority. The samples were treated by washing them with deionized distilled water many times to remove any fines and other undesirable material; the washing was achieved by soaking bentonite sample in deionized water for 24 h with regular gentle agitation, the washed samples were air dried, these samples were calcinated in the range of 100-900 °C for 8 hours. Finally, the sorbent were crushed then were grounded and sieved to different particle size in average range of 38-125 µm.

2.2. Fixed-bed experiments

Batch adsorption experiments were conducted by introducing exact volume (50.0 mL) with known initial concentration of sulfate into Pyrex glass flasks at an ionic strength of 0.01 M $NaClO_4$ containing accurately weighed amounts (1.0000 g) of the adsorbent. The following parameters were studied, the concentration of the adsorptive solution ranged between 10-100 mg/L. Five different temperatures 25, 35, 45, 55, and 65±0.1 °C and different pH values of in the range of 1-10 were also studied, also the change in the concentration of sulfate was scanning at different time intervals (5, 10, 15, 30 min; 1, 2, 4, 8 and 24 h) until reaching the equilibrium. Also, different particle sizes and different calcinations temperatures were investigated. All of the experiments were done until reaching equilibrium at constant pH which was maintained with 0.1 M NaOH and/or 0.1 M $HClO_4$ solution. The results showed that equilibrium was reached in 4 hours; the adsorbent was then removed from liquid phase by filtration followed by centrifugation. The equilibrium concentration of sulfate was determined was determined by colorimetric method at 420 nm using Diod Array spectrophotometer (S600). All the experiments were carried out in duplicate and only mean values are presented. The isothermal models which are Langmuir and Freundlich were investigated at the optimal conditions at the optimal conditions [13].

2.3. Preparation of reactor column

The adsorbent modified bentonite was packed into glass columns of (37×2.5 cm, id), the column was packed with 2.0000 g, containers which contain the 10 ppm of SO_4^{-2} solution was placed at the top of the columns, the solution was passed through the column by gravity with flow rate 1.5 mL/min using peristaltic pump. The eluate was collected using deionized distilled water for washing purpose, the absorbance of eluate was determined. The eluate was collected at different time intervals (5, 10, 15, 20, 25, 30, ..., 1440 min) with different temperature, while keeping the other optimal parameters constant. The concentration of the residual sulfate ion was determined by colorimetric method at 420 nm using Diod Array spectrophotometer (S600). The amount of sulfate adsorbed was calculated from the concentration in the solution before and after adsorption. All of the experiments were done three times and the average was taken for data analysis.

3. Results and discussion

3.1. Sulfate ion removal by fixed-bed experiments

Experimental studies were done by fixed-bed method to evaluate the effect of calcinations, contact time, solution pH, initial concentration, temperature, and particle size on the removal of sulfate ion.

3.1.1. Effect of contact time

The effect of contact time on sulfate ion uptake using modified bentonite was studied. It is evident from Figure 1A that the removal of sulfate ion increases at the contact time increases. Initially, the rate of uptake is fast. However, equilibrium was attained in one hour as seen from Figure 1A. It is apparent that sulfate ion uptake reached saturation after the initial 60 min, indicating that the kinetics and diffusion are somewhat fast into the intra-particle system to reach this equilibrium which may due to the availability of more adsorption vacant sites at the initial stage [14]. Also, it was noticed that there is no significant change of removal after about 60 min for adsorbents. From Figure 1A, the equilibrium was attained after one hour until reaching four hours.

3.1.2. Effect of calcinations

From Figure 1B, it was seen that the % removal of sulfate ion at the range of temperature 100-300 °C was nearly constant, that means at this range there is no effect of calcination temperature, then at 400 °C it was found that the % removal increased until reaching 600 °C, then at 700 °C the % removal found to be constant. It seems that at 400 °C, the impurities began to be removed, and for higher calcinations temperature the increasing of removal may be due to the change surface area and pore size distribution as well as the morphology of these material [15,16]. It was found that the removal of sulfate ion increases in the range of 100-600 °C, after that the % removal remains constant. All the other experiments were done at the optimum temperature which is 600 °C

3.1.3. Effect of initial sulfate ion concentration

The effect of the initial concentration of adsorbate on the % removal using modified bentonite was investigated; the used initial concentration of sulfate was in the range of 10-100 mg/L. From Figure 1C, we can noticed that as the concentration of the sulfate ion increased the % removal increased, that's may be means the activated sites for adsorption are available for interaction with the sulfate ions [17].

3.1.4. Effect of pH

The pH value of the solution is an important controlling parameter in the adsorption process; it determines the charge of the adsorbent and degree of ionization of the adsorbate. From Figure 1D, the working pH values was 1-10, the maximum removal was found at the range of 2-3. It was seen that as the pH increased the % removal decreased. At pH range 2-3, the degree of protonation was high and the surface of bentonite will have the maximum positive charge for the removal of sulfate anion, because this sulfate ion can make exchanging with the counter ion which attached to the surface of bentonite surface, for higher pH as we can see from the Figure 1D. The negative charge will increase for that it will be a repulsion between the anions and the surface, because the degree of surface protonation decreased and the removal also decreased [7,8]. The pH_{ZPC} for Jordanian bentonite found to be 5.5, that's mean at pH below 5.5, the surface of adsorbent will protonated, while at pH higher than 5.5 the surface of the bentonite will have negative charge. All of the experiments were done at pH = 2.5.

3.1.5. Effect of temperature

As shown in Figure 1E, it was noticed that there was no significant increase in the amount adsorbed of sulfate ions with increase in temperature from 25 to 45 °C, but at the temperatures of 55 and 65 °C the removal increased.

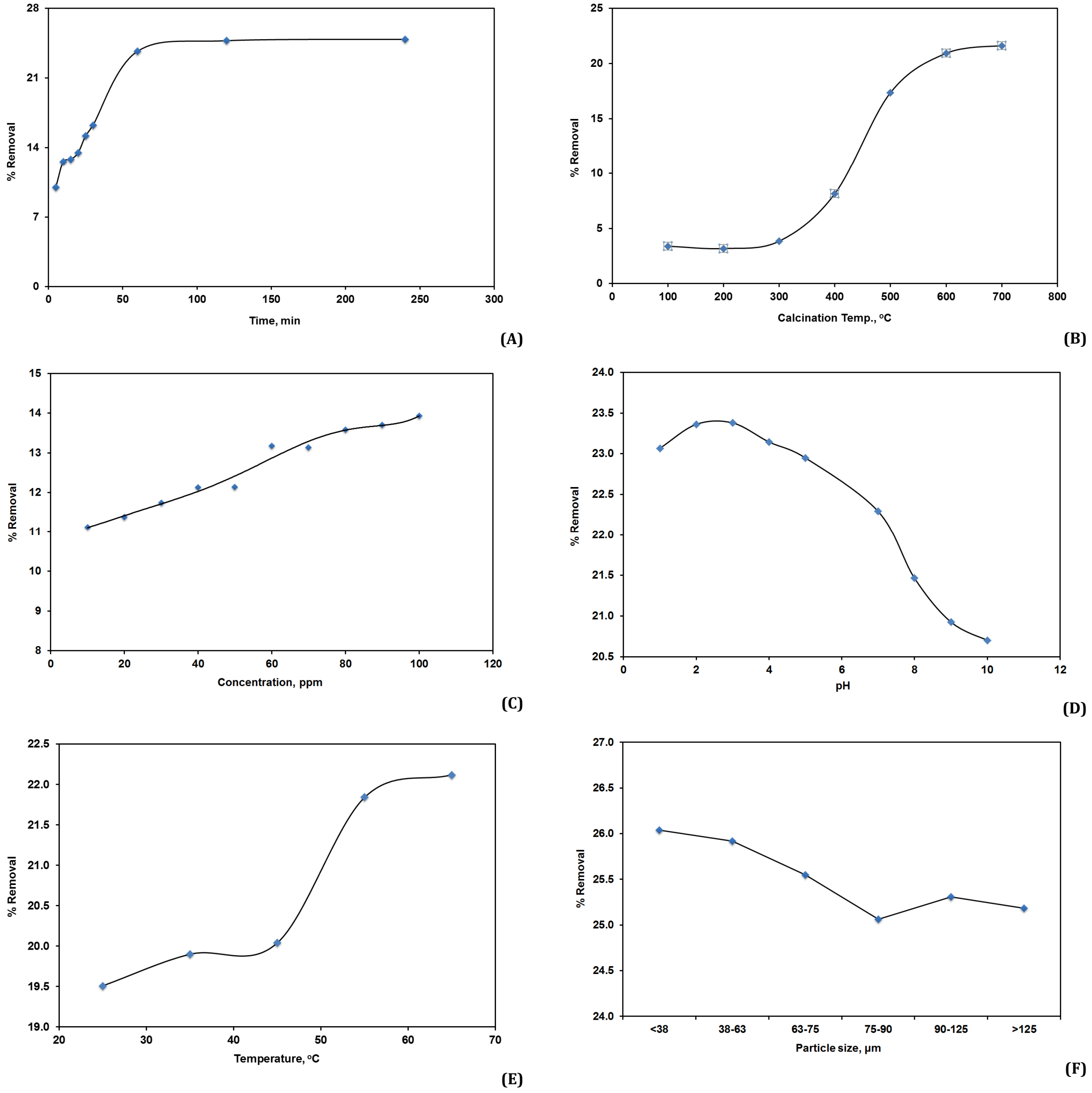


Figure 1. Effect of different variables on the removal of sulfate ion using modified Jordanian bentonite. A: Effect of contact time. B: Effect calcinations. C: Effect of initial concentration. D: Effect of pH. E: Effect of temperature, F: Effect of particle size.

The enhancement of the adsorption capacity when temperature is increased could be due to increased mobility and diffusion of ionic species. Since diffusion is an endothermic process, it would be expected that an increased solution temperature would result in the enlargement of pore size due to 'activated diffusion' causing the micro-pores to widen and deepen and create more surface for adsorption [12]. All of the other experiments were done at 25 °C.

3.1.6. Effect of particle size

The effect of the particle size on the removal of sulfate was investigated as shown in Figure 1F, the higher removal for sulfate ion was found for smaller particle size <38 µm, the gradual decrease in removal was noticed for larger particle size, that means faster adsorption kinetics due to smaller particles. Small particle sizes reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly adsorption capability can be attained) [18]. This is because increasing the external surface area of the bentonite particle exposes more active sites to sulfate molecules and that the anions in modified bentonite of smaller particle size are exchanged much more easily with those in the aqueous solution. All the other experiments were done at the optimum particle size, <38 µm.

3.2. Adsorption isotherm analysis

The isotherm models of Langmuir and Freundlich were used to fit the experimental adsorption equilibrium data of sulfate ion on bentonite adsorbents. These models are represented mathematically as follows.

Table 1. Isotherm parameters obtained using the linear method for removal of sulfate from aqueous solutions on calcinated bentonite various temperatures.

Temperature, °C	Langmuir			Freundlich		
	q_{max} (mg/g)	a_L (L/mg)	r^2	n	K_F (L/g)	r^2
25	31.2	0.030	0.9696	1.36	1.75	0.981
35	32.3	0.041	0.9927	1.96	2.88	0.966
45	40.0	0.044	0.9458	1.80	3.25	0.872
55	64.5	0.027	0.9719	1.51	2.89	0.962
65	76.9	0.029	0.9427	1.50	3.57	0.968

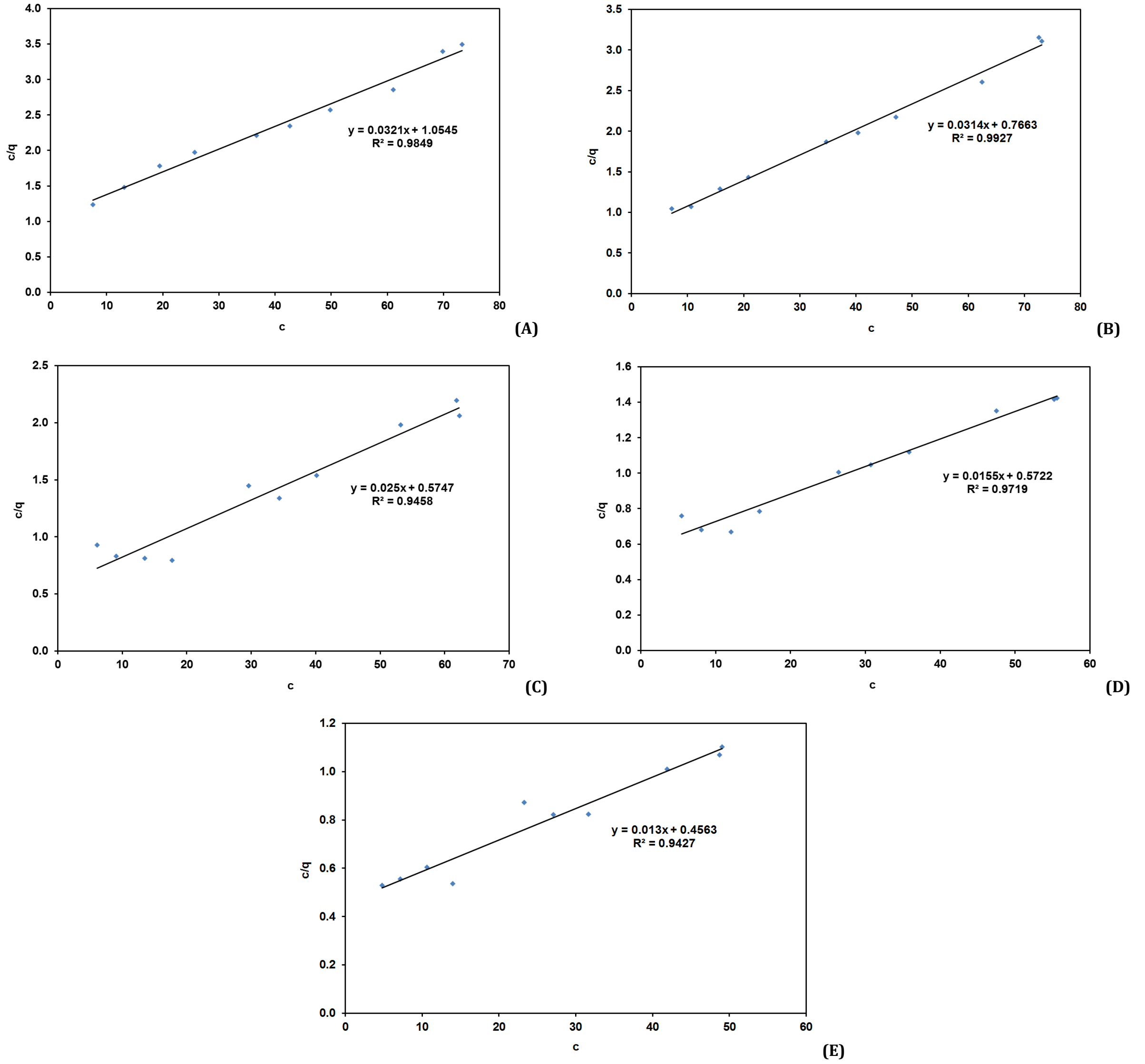


Figure 2. Langmiur isotherm curves obtained using the linear method for removal of sulfate from aqueous solutions on calcinated bentonite at various temperatures. Conditions: pH = 2.5, particle size <8 µm, adsorbent dose 1g. A: 25 °C. B: 35 °C, C: 45 °C, D: 55 °C. E: 65 °C.

The linearized equation for Langmuir model is

$$\frac{C_e}{q_e}=\frac{C_e}{q_{max}}+\frac{1}{K_L q_{max}} \tag{1}$$

The linearized form of the Freundlich isotherm equation is expressed in

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{2}$$

where C_e (mg/ L) is the concentration of sulfate at equilibrium, K_L (L/mg), and q_{max} (mg/g) are the Langmuir constants related to the energy of adsorption and maximum capacity, respectively; K_F and 1/n are the Freundlich constants related to the adsorption capacity and intensity, respectively; and q_e (mg/g) is the mass of sulfate adsorbed per mass of adsorbent [19]. The results of fitting Freundlich and Langmuir equations to isotherm curves which are showed in Figure 2 and 3 are summarized in Table 1. For Langmuir model the regression coefficients (r^2) at different temperature values were larger than 0.94, indicating that this model fit reasonably well with the sulfate adsorption.

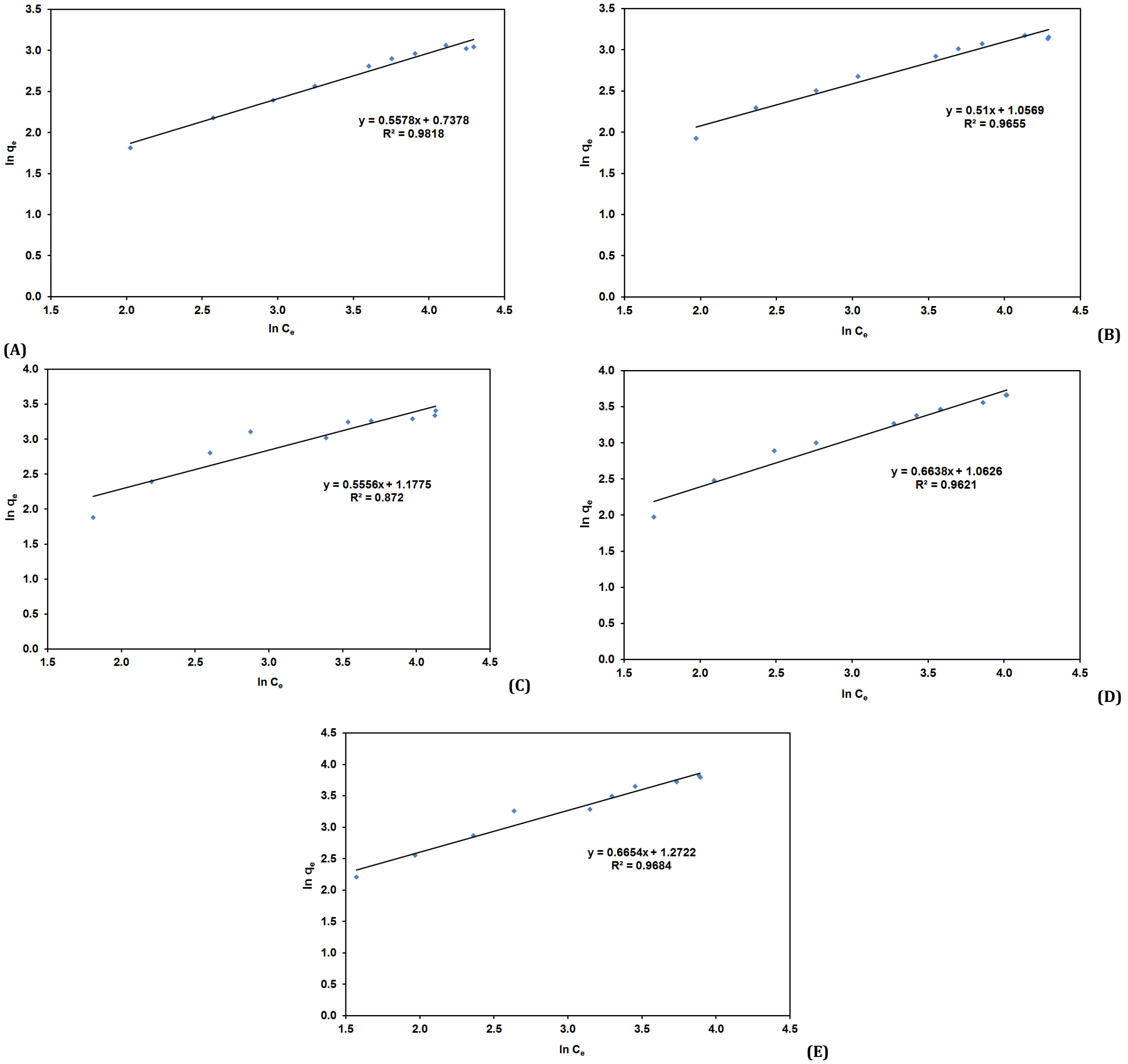


Figure 3. Freundlich isotherm curves obtained using the linear method for removal of sulfate ion from aqueous solutions on calcinated bentonite at various temperatures. Conditions: pH = 2.5, particle size <38 µm, adsorbent dose 1g. A: 25 °C. B: 35 °C, C: 45 °C, D: 55 °C. E: 65 °C.

It was noticed that the maximum monolayer adsorption capacity (q_{max}) increased by increasing temperature, and the constants K_L increased at temperature range of 25 to 45 °C but at temperatures 55 and 65 °C the values of K_L decreased. The value of the regression coefficients (r^2) obtained for Langmuir, are higher than of Freundlich, which means this process is better fit. Although it was found that intensity of adsorption is high according to the values of n which are showed in Table 1, the value of n between 1 and 10 represents a beneficial adsorption process, all the values of n obtained were in the range of 1.36-1.96 which were lied within this range which implies that the modified bentonite has a high affinity for sulfate ions in solution and supporting the favorable adsorption of sulfate on this adsorbent, the r^2 values at different temperatures indicated that the surface of bentonite was not significantly changed when the sulfate ion adsorbed on the surface [20,21].

3.3. Removal kinetic studies using reactor column

Adsorption kinetics is one of the most important characters which represent the adsorption efficiency. Kinetic models was investigated in this study, in order to propose the possible mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process pseudo-second-order. The intraparticle diffusion and Elovich kinetic models were used.

The kinetic equation of the pseudo second- order model is

$$\frac{t}{q_t}=\frac{1}{k_2 q_e^{\,2}}+\frac{1}{q_e}t \qquad (3)$$

where k_2 is the rate constant of pseudo-second-order model (g/mg.min), q_t and q_e are the amounts of sulfate ion sorbed at time t and at equilibrium time (mg/g), respectively [22].

Table 2. Pseudo-second order model for the removal of sulfate from aqueous solutions on calcinated bentonite various temperatures.

Temperature, °C	$q_{e,exp}$	K_2	r^2	q_{cal}	%SSE
25	0.514	0.140	0.981	0.502	0.7095
35	0.823	0.191	0.993	0.808	0.5797
45	1.083	0.748	0.998	1.071	0.3171
55	1.250	0.414	0.999	1.246	0.1596
65	1.349	0.677	0.998	1.346	0.0832

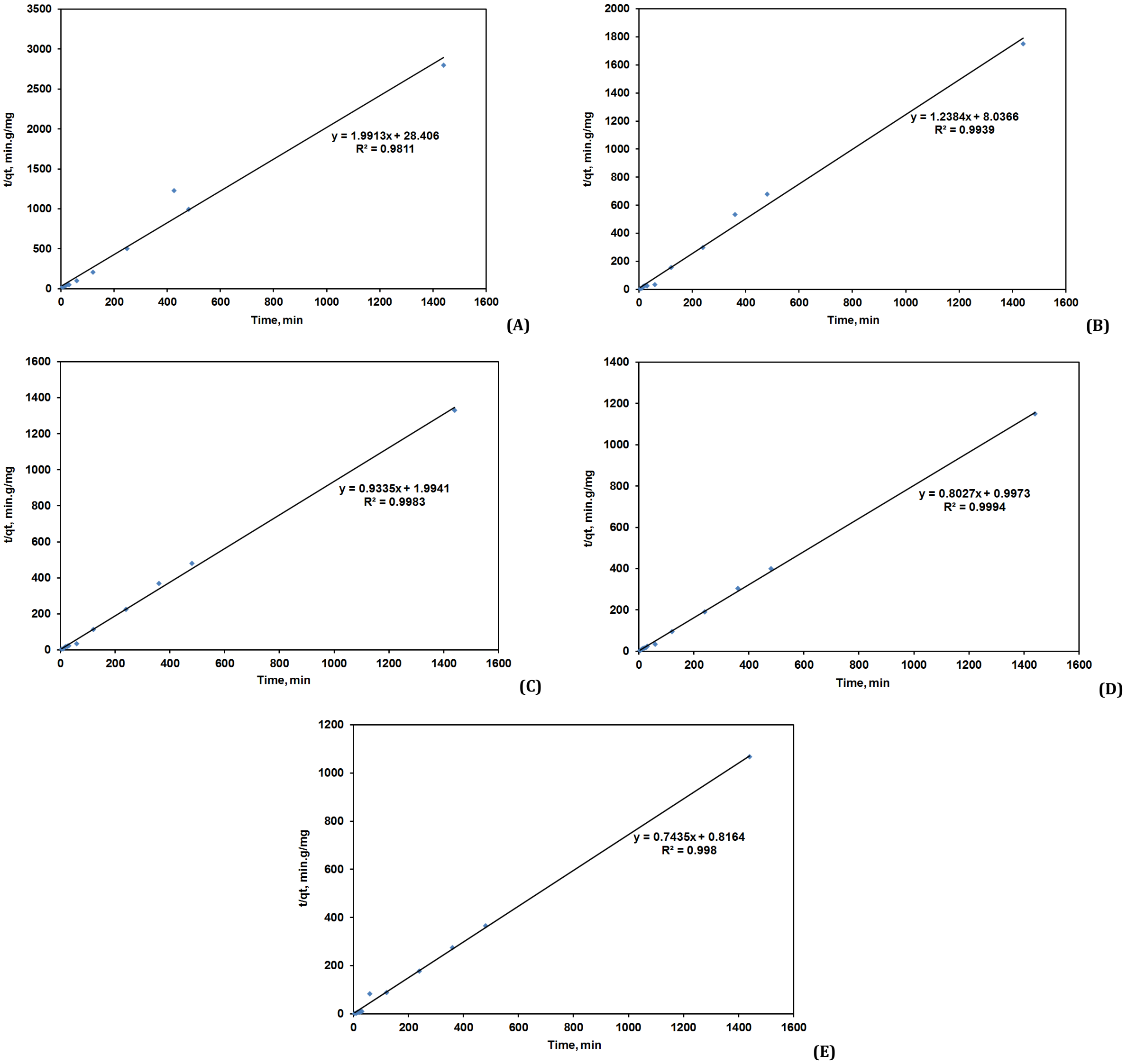


Figure 4. Pseudo-second order model for the removal of sulfate ion aqueous solutions on calcinated bentonite at various temperatures Conditions: pH = 2.5, particle size <38 µm, C_o = 10 ppm, adsorbent dose 2g and flow rate = 1.5 mL/min.; A: 25 °C. B: 35 °C, C: 45 °C, D: 55 °C. E: 65 °C.

The estimated values of q_e and k_2 can be gotten from the slope and the intercept of straight-line plots of t/qt *vs* t. These values are noted in Table 2 and the plots for different temperature of this model were illustrated in Figure 4. As we can see that the values of the correlation coefficients for these plots confirmed that the removal of sulfate by this bentonite could well follow the pseudo-second-order kinetic model at different temperature. Moreover, there is a good agreement between the experimental adsorption capacity and the calculated one at different temperature values indicating the applicability of this model to describe the kinetics of the adsorption process of sulfate ion onto bentonite surface [15].

The intra-particle diffusion is represented by its linearized form of this equation which is given by

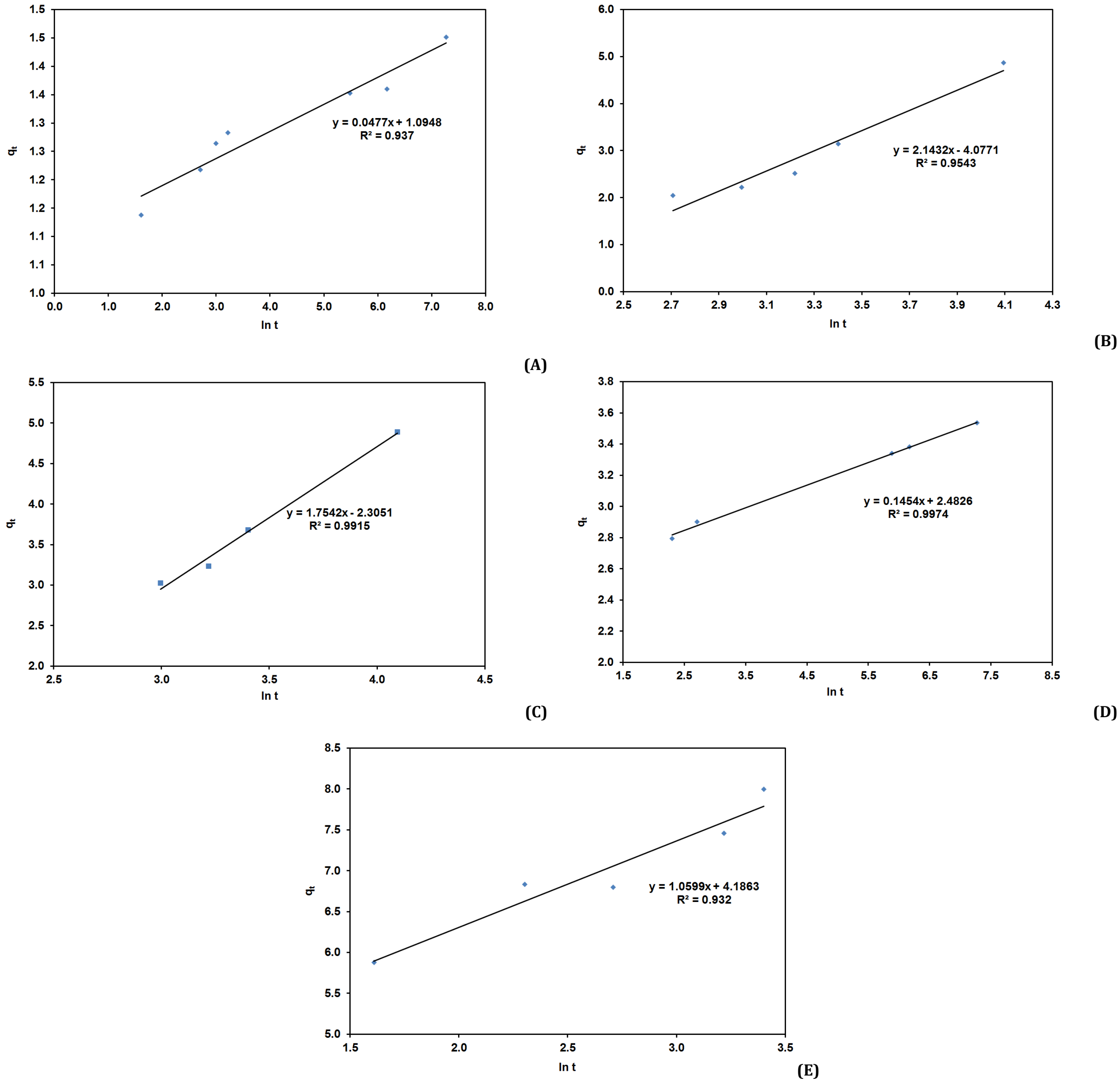
$$\log R = \log k_{id} + \alpha \log(t) \quad (4)$$

where R is the percentage of sulfate ion removal, t is the contact time, α is the gradient of the linear plots, and k_{id} is the intra-particle diffusion rate constant.

From the plots that are illustrated in Figure 5 and results shown in Table 3 at different temperature we can noticed that the plots are almost linear over the whole time range which means nearly this process affected the adsorption, the k_{id} values increase by increasing the temperature. This can be explained by the growing effect of driving force resulted in reducing the diffusion of sulfate species in the boundary layer and enhancing the diffusion in the solid.

Table 3. Intra-particle diffusion model of the removal of sulfate ion from aqueous solution on calcinated bentonite various temperatures.

Temperature, °C	k_{id}	α	r^2
25	64.7	0.04	0.926
35	240.4	0.7	0.975
45	241.5	0.4	0.972
55	248.9	0.3	0.989
65	436.5	0.2	0.939



(A) (B) (C) (D) (E)

Figure 5. Elovich kinetic model: Pseudo-second order model for the removal of sulfate ion aqueous solutions on calcinated bentonite at various temperatures Conditions: pH = 2.5, particle size <38 μm, C_o = 10 ppm, adsorbent dose 2g and flow rate = 1.5 mL/min.; A: 25 °C. B: 35 °C, C: 45 °C, D: 55 °C. E: 65 °C.

It can be observed that the straight lines did not pass through the origin and this further indicates that the intra-particle diffusion is not the only rate-controlling step [23,24].

The linearized equation form of Elovich model is expressed by the following equation

$$q_t = \frac{1}{\beta}\ln(\delta\beta) + \frac{1}{\beta}\ln t \qquad (5)$$

where q_t is the adsorbed amount at time t, δ is the initial adsorption rate (mg/g min), and β is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg). A plot of q_t *vs* ln t gives straight line with slope of ($\frac{1}{\beta}$) and the intercept of $\frac{1}{\beta}\ln(\delta\beta)$ [25]. Figure 6 shows the plots of Elovich model, the values of kinetic constants of β and δ are listed in Table 4 for all adsorbents at different temperature values.

Table 4. Elovich kinetic model of the removal of sulfate ion from aqueous solution on calcinated bentonite various temperatures.

Temperature, °C	β	δ	r^2
25	21.3	6.0×10^8	0.937
35	0.5	0.3	0.954
45	0.6	0.5	0.991
55	6.9	3.9×10^6	0.997
65	0.9	55.2	0.932

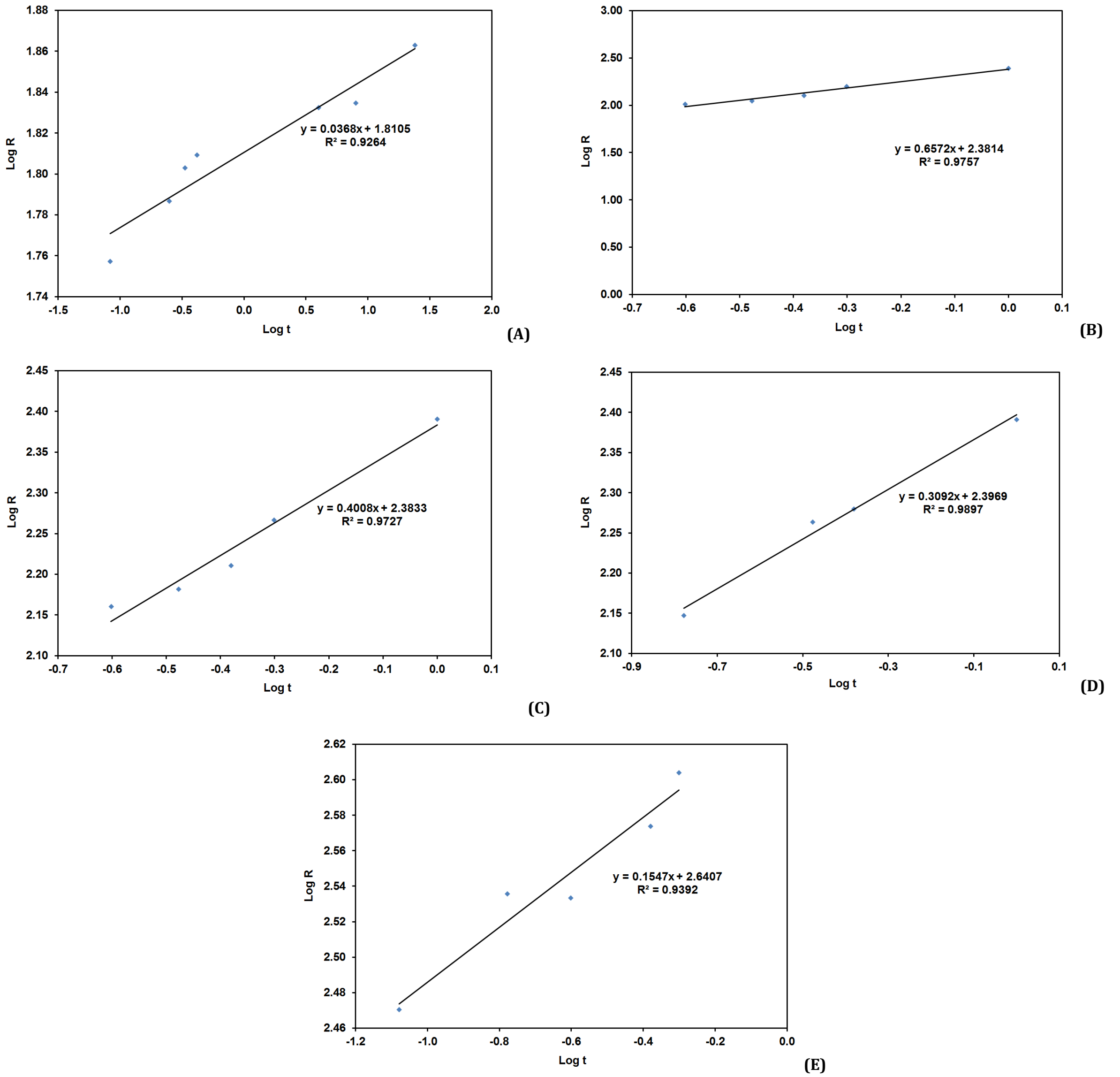


Figure 6. Intra-particle diffusion kinetic model for the removal of sulfate ion aqueous solutions on calcinated bentonite at various temperatures Conditions: pH = 2.5, particle size <38 µm, C_o = 10 ppm, adsorbent dose 2g and flow rate = 1.5 mL/min.; A: 25 °C. B: 35 °C, C: 45 °C, D: 55 °C. E: 65 °C.

From Table 4, it can be seen that in general the values of β had no clear trend by varying the temperature and the constants δ were observed to decrease sharply by increasing temperature in the range of 25-35 °C, then slightly increasing at two temperatures value which are 55 and 65 °C, this may be explain that the kinetic process involves a variation of the energetic of chemisorptions with the active sites are heterogeneous in all of the adsorbents and this would increase the reaction rate. Also, it can be observed that the correlation coefficients for this model are relatively low lying between 0.932 and 0.997, which indicates that this model is not the preferred model for describing the adsorption kinetic of sulfate onto bentonite [15,24].

3.4. Validity of kinetic models

The validity of the three models pseudo-second-order model, intraparticle diffusion and Elovich models was investigated in order to compare the applicability of the models. A normalized standard deviation Δq (%) is calculated using the following equation,

$$\Delta q(\%)=SSE\%=\sqrt{\frac{\sum[(qe,exp-qe,cal)/qe,exp]^2}{(n-1)}}\times 100 \quad (6)$$

where n is the number of data points. The calculated values of SSE% for intraparticle diffusion and Elovich models were found in the range of 32.49 to 36.12%. Table 2 lists the calculated values of SSE% which have the highest values of 0.7% for the pseudo-second-order model which improved the best fitting for this model rather than the other models which have also r^2 lower than the second-order model [26].

3.5. Enthalpy and activation energy

The value ΔH and ΔS were calculated from the slope and intercept of the linear Van't Hoff plot, respectively, using the relation,

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

where K_L is the isotherm constant of Langmuir model, ΔS = Entropy change for the process, ΔH = Enthalpy change for the process, R = Gas constant (8.314 J/mol·K), and T = Absolute temperature.

The calculated value of ΔH, ΔS and ΔG were 15.2, 22.1 and 8.7 kJ/mol, respectively. The positive value of ΔH shows that the adsorption of sulfate ions on the adsorbent is an endothermic process. The value of free energy (ΔG) is positive with small value, which means that the process is not spontaneous one. There is slightly decrease in ΔG value with increasing temperature reveals that adsorption of the ion on the adsorbent becomes favorable at higher temperature [27]. The positive value of ΔS means the increase in randomness at solid solution interface during the fixation of sulfate ions on the active site of the adsorbent. This occurred as a result of redistribution of energy between the adsorbate and adsorbent. The adsorption is classified to be physical one when the magnitude of the enthalpy change is <84 kJ/mol, from the calculated results the removal of sulfate ion using bentonite is a physical one. From the values of K_2, it can be seen that the rate adsorption increases with increasing temperature. The activation energy of this removal estimated using the following equation,

$$\ln K_2 = \ln A - \frac{E_a}{RT} \quad (8)$$

where K_2 is the pseudo-second-order constant, E_a is the activation energy in kJ/mol, R, the gas constant, T, the absolute temperature (K) and A is the frequency factor. E_a was calculated from the slope using the above equation, its value was 32.8 kJ/mol with r^2 of 0.989. The positive value of E_a suggest that increase in temperature favors the adsorption, for that it can be concluded that the adsorption process is an endothermic one. It was written that if the values of E_a are within the range of 8-25 kJ/mol, then the process is physical adsorption, if it is a aqueous diffusion for E_a values less than 24.0 kJ/mol, while if it is pore diffusion, E_a values will be in the range of 20-40 kJ/mol, the estimated value of E_a for our adsorption is lies within the range of pore diffusion, then the rate limiting process is the pore diffusion one [28,29].

4. Conclusions

The results of this study showed that the modified calcinated Jordanian bentonite could be used as a low-cost adsorbent for the removal of sulfate ions from aqueous solution. The removal of sulfate ion was investigated at different variables such as contact time, solution pH, initial concentration, temperature, and particle size using fixed-bed experiment. It was found that the removal of sulfate ion was dependent on all the previous parameters for this adsorbent. The ability of bentonite for removing sulfate ion from aqueous solutions is possible along wide range of pH = 1-10. Adsorption equilibrium for the sulfate ion was reached in about 60 minutes and was endothermic in nature based on the calculated value of ΔH and ΔG that means it depends on temperature. The pseudo-second-order, intra-particle diffusion and Elovich kinetic models were developed using column experiments to predict the rate constants, the equilibrium capacities, the analysis of the kinetic, rate data and the calculated values of SSE% revealed that pseudo-second-order sorption is predominant for removal of sulfate ion. The calculated value of the E_a using pseudo-second-order rate constant indicates that the rate limiting process is the pore diffusion one.

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