Removal of lead from aqueous solutions using Saudi activated bentonite

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Abstract

Raw Saudi bentonite which was obtained from the Khulays bentonite deposit, 95 km north of Jeddah, was ground to -325 mesh (44 μm). Samples of ground bentonite were activated using sulfuric acid in order to increase its adsorptive capacity. The removal characteristics of lead ions from aqueous solution using Saudi activated bentonite were investigated under various operating variables such as shaking time, solution pH and initial metal concentration. The results showed that the sorption of lead ions on Saudi activated clay was very fast and the equilibrium was reached after only 10 min. They also showed that increasing the initial lead concentration decreased lead removal percentage due to the saturation of clay with lead ions. Furthermore, the adsorption of lead increases from 20 to 100% with an increase in solution pH from 1 to 5.0 and then 100% lead was removed when solution pH was from 5 to 11. The adsorption isotherm data were well fitted well with Langmuir better than Freundlich models. Lead adsorption onto Saudi activated bentonite was well represented by the pseudo-second-order kinetic model.

Keywords: lead removal, Saudi activated bentonite, Langmuir isotherm, Freundlich isotherm, Adsorption kinetics.

1 Introduction

Metal industries such as electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining and battery manufacturing use large quantities of water in their processes. Wastewater streams from these processes contain toxic substances, heavy metal, acids, alkalis, and other substances. Removal of

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heavy metals such as lead from aqueous solution is necessary because it can be readily adsorbed by marine animals and directly enters the human food chains, thus presenting a high health risk to consumers [1–3]. Lead contamination is known as a worldwide problem due to its long term and widespread use. It is known to damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages [4, 5].

Montmorillonite mineral, which is known commercially as bentonite or calcium bentonite, is characterized by the presence of exchangeable cations (Na, Ca, and Mg). Montmorillonite can be activated to produce active clay and increase its adsorptive capacity [6, 7]. Bentonite can be utilized as a cost effective sorbets material for the removal of lead from industrial waste water in order to minimize its processing cost and solve its disposal problems in an environmentally sustainable way [8].

The solution pH plays an important role in lead adsorption by bentonite. Mishra and Patel [9] investigated the adsorption of lead on bentonite at different pH. They found no lead was removed at pH lower than 3. It was observed that a gradual increase in adsorption with increase in pH from 3 to 6 and the maximum adsorption was at pH 6. Furthermore, lead adsorption increased gradually with increase in pH from 6 to 10 may be due to the formation of the precipitate of $Pb(OH)_2$. pH 6 was considered as optimum condition for the removal lead from waste water.

Adsorption of lead ions by clay has been the subject of several studies [10–14]. The most important factors which may affect sorption of lead were pH, lead concentration, mixing time and clay dosage.

In this research, removal of lead from aqueous solution will be investigated using Saudi activated bentonite.

2 Materials and methods

2.1 Preparation of Saudi activated bentonite

Saudi bentonite is not active in its natural state. It needs some treatment to modify its adsorptive property. Table 1 shows the chemical composition of Saudi Activated bentonite.

Natural bentonite was activated using sulphuric acid leaching. The apparatus and chemical treatment method with H_2SO_4 which was carried out in this study are similar to what have been described previously [15]. The acid treatment was conducted using a Pyrex glass batch reactor with boiler-reflux condenser and a magnetic stirrer/hot plate. Acid activation was done using the optimum operating variables such as, 45% by weight acid concentration, the temperature of boiling, 15 minutes reaction time, 200 rpm degree of mixing, grain size of -325 mesh (44μm) and water to clay ratio of 5:1.

Table 1: Chemical composition of Saudi activated bentonite [15].

Compound	Chemical composition (%)
Sio_2	66.2
Al_2O_3	11.71
Fe_2O_2	3.0
TiO_2	1.5
MgO	0.73
CaO	<0.05
K_2O	0.48
Na_2O	0.12
MnO	0.05
SO_3	<0.05
P_2O_5	<0.05
L.O.I.(1000°C)	15.3

2.2 Adsorption process

Adsorption of lead with clay is carried out in a batch reactor. Stock solution (1000 mg/L) of lead was prepared by dissolving the appropriate amounts of analytical reagent grade $Pb(NO_3)_2$ in distilled water. The stock solutions were diluted as required to obtain standard solutions containing 20–100 mg/l of a required heavy metal. Known amount of Saudi activated bentonite was placed in a conical flask containing lead solution of known concentration and pH. The resulting mixture was then mixed continuously using horizontal shaker with water bath (JULABO SW 22) for a given time period. 200 rpm shaking and 25°C temperature were applied in the shaker. Afterward, samples were taken out from the shaker and the clay was separated by filtration using filter paper (Whatman No., 42). The filtrate was analyzed for lead concentration by Atomic absorption spectrophotometer (AAS). The effects of several factors such as pH, concentration of solution, clay mass and contact time on lead removal percentage were investigated.

3 Results and discussions

3.1 Effect of shaking time

The time-dependent behavior of lead adsorption was investigated by varying the contact time between the adsorbate and adsorbent in the range of 1-40 min. The initial concentration of lead was ranging from 20 to 100 ppm, while the dose of clay sample was 1.0 g/50 ml and the solution pH was fixed at 3.1. The data showed that the sorption of lead ions on Saudi activated clay was very fast and the equilibrium was reached after only 10 min (Figure 1). As found before [16, 17] the adsorption process is fast at the beginning of the reaction due to the adsorption of lead on the surface sites of clay. The results show that shaking the mixture of different initial concentration for 10 minutes was sufficient to reach

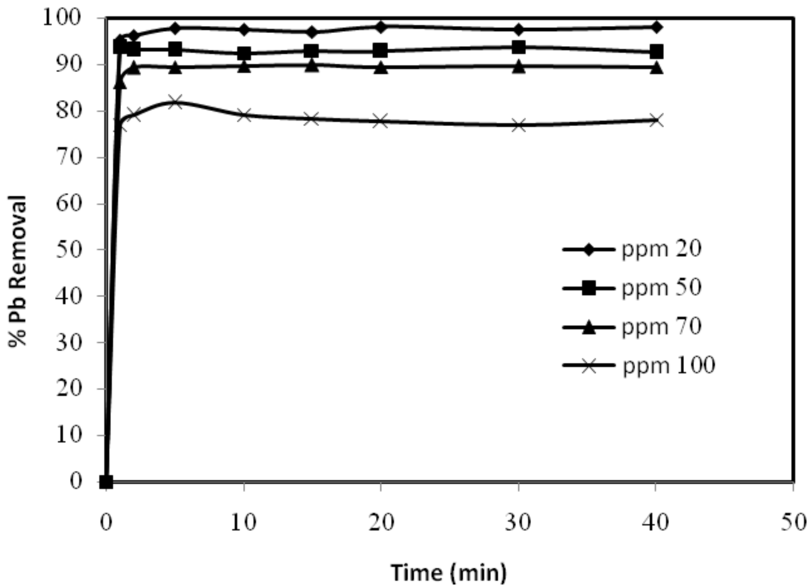

Figure 1: Effect of shaking time on the removal of lead by Saudi activated bentonite. Initial metal concentration varies between 20 and 100 mg/l, clay dosage: 1 g/50 ml, pH = 3.1.

equilibrium. They are also show that increasing the initial lead concentration decreased lead removal percentage due to the saturation of clay with lead ions.

3.2 Effect of pH

The effect of pH on the removal of lead ions by Saudi activated bentonite was investigated. The adsorption of lead was studied in the pH range of 1–11 with a constant clay amount of 1 g/50 ml of lead solution, a shaking time of 10 min and lead concentration of 100 ppm. The pH of the metal ion solution was adjusted by adding required amount of dilute NaOH or HNO3 solution. pH was measured using a pH meter.

The results presented in Figure 2 reveal that the adsorption of lead increases from 20 to about100% with an increase in solution pH from 1 to 5.0 and then about100% lead was removed when solution pH from 5 to 11.

The effect of initial pH on lead removal may be explained as mention before [17], where in the acidic conditions, both adsorbent and adsorbate are positively charged (M^{2+} and H^{+}) and therefore, the net interaction is that of electrostatic repulsion. In addition, the H^{+} ions present in higher concentration in the aqueous medium compete with the positively charged Pb^{2+} ions for the surface adsorbing sites, resulting in a decrease in the removal of lead.

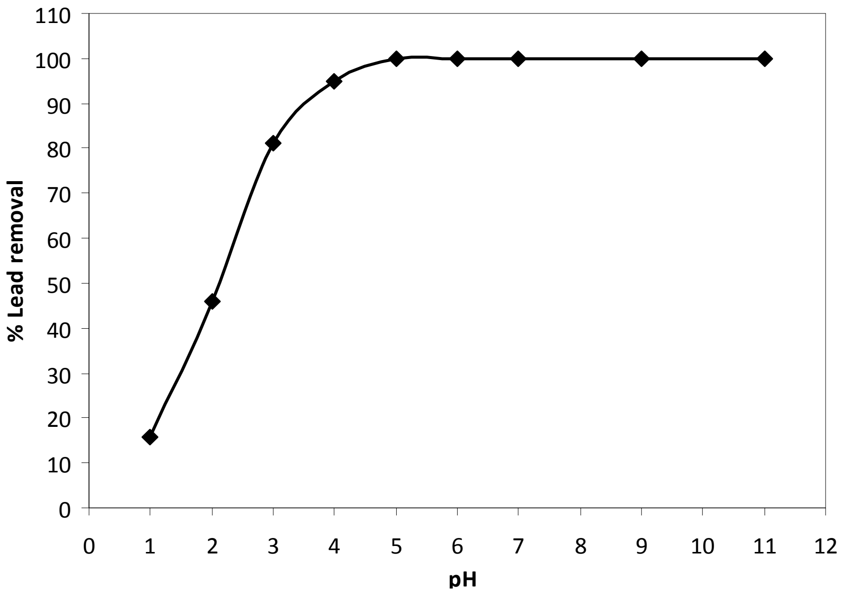

Figure 2: Effect of pH on the removal of lead by Saudi activated bentonite. Initial lead concentrations 100 mg/L, clay dosage: 1 g/50 ml, contact time: 10 min.

3.3 Effect of lead concentration

Figure 3 shows the effect of lead concentration on lead removal when lead concentration varies from 20 to 100 ppm under operating conditions of 10 min shaking time, 1.0 g/50 ml for adsorbent and mixture pH =3.1. The results showed that about 100% of lead was removed when lead concentration was 20 mg/l. Lead removal percentage decreased with increasing lead concentration to about 80% when lead concentration was 100 ppm. Therefore, Saudi activated bentonite removal efficiency needs to be increased by increasing solution pH to 6 to avoid the lead hydroxides precipitation region which it is start at the pH of 6.5 [17].

3.4 Effect of clay dosage

The effect of the amount of Saudi activated bentonite (0.05–0.75 g/100 ml) on lead removal at constant values of initial metal concentration (100 mg/l), contact time (10 min), pH = 6 and temperature (25°C) is shown in Figure 4. The results showed that the removal of lead increased rapidly (98%) until an adsorbent dose of 0.125 g/100 ml and gradually up to 0.25 g/100 ml where about 100% of lead was removed from the solution. However, this result was expected since as the dose of adsorbent increases, the number of adsorbent sites increases. These amounts attach more ions to their surfaces [18]. Similar results were reported where many types of materials were used as adsorbents [19].

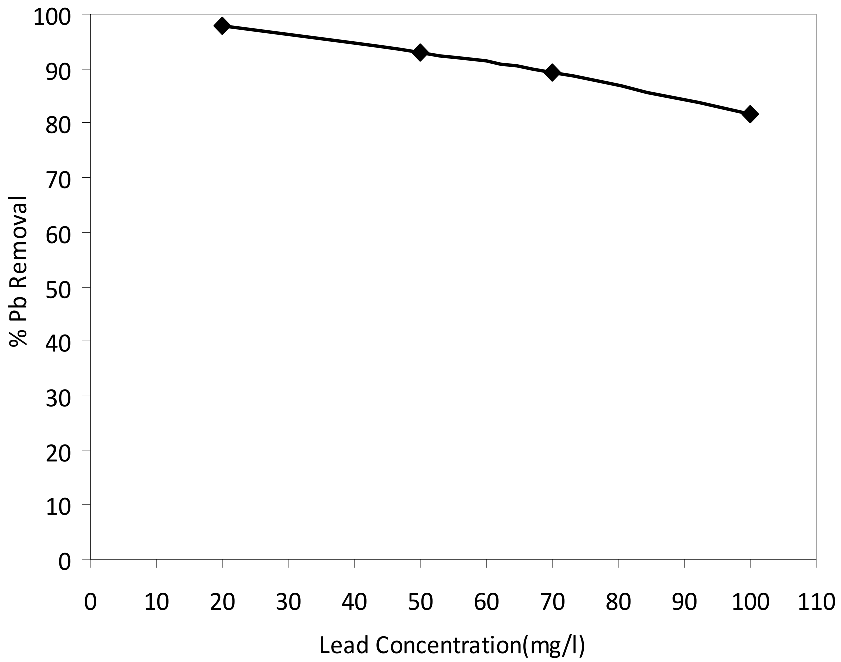

Figure 3: Effect of metal concentration on the removal of lead by Saudi activated bentonite. Clay dosage: 1 g/50mL. pH = 3.1, contact time: 10 minutes.

3.5 Adsorption isotherm

Two different adsorption isotherm models, the Langmuir [20] and Freundlich [21] equations were used to fit the experimental data obtained from this work. These models were tested to determine the maximal capacity of lead removal using Saudi activated bentonite. The quality of the isotherm fit to the experimental data is typically evaluated based on the magnitude of the correlation coefficient for the regression; i.e. the isotherm giving an R^2 value closest to unity is considered to give the best fit. The adsorption isotherms for lead removal were studied using volume of 100 ml at initial metal concentration of 100 mg/l with adsorbent mass ranging from 0.05 to 0.75 g at room temperature (25°C) and solution pH = 6. Afterward, data obtained were fitted to the Langmuir and Freundlich isotherms. The Langmuir equation, in the linear form is written as:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \qquad (1)$$

where C_e is the equilibrium concentration of metal ions (mg/l), q_e is the amount of metal ions adsorbed per unit weight of adsorbent (mg/g bentonite), q_{max} is the maximum adsorption capacity (mg/g), and b is the adsorption equilibrium constant (l/mg).

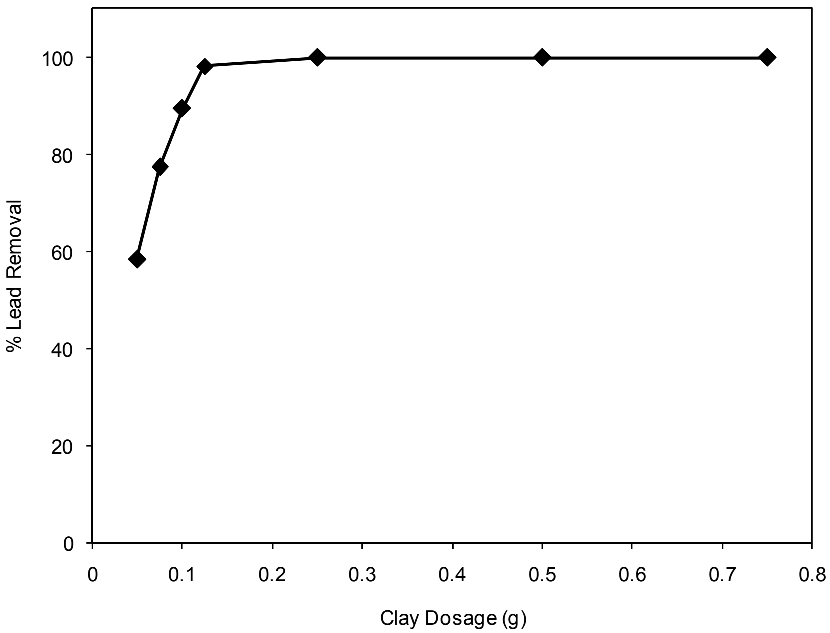

Figure 4: Effect of clay dosage on the removal of lead by Saudi activated bentonite. Initial lead concentrations 100 mg/L, pH = 6, contact time: 10 minutes.

For the Freundlich equation the linear form is written as:

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{2}$$

where k and n are the constant characteristics of the system.

The best estimated values of all the equation parameters are summarized in Table 2. The adsorption isotherm data are well fitted with the linearized

Table 2: The Langmuir and Freundlich equation parameters predicted from adsorption isotherm data of lead ions onto Saudi activated bentonite at pH =6, 25°C and initial lead concentration of 100 mg/l.

Isotherm parameters	Value
Langmuir	
q_{max} (mg/g)	116
b (l/mg)	0.989
R^2	0.9932
Freundlich	
K (mg/g)	47.77
n	3.3
R^2	0.8919

Langmuir better than linearized Freundlich equations and give R^2 = 0.989–0.8919 as shown in figures 5 and 6. The maximum adsorption of Saudi activated clay equals to 116 mg/l.

According to Tryball [22], it has been shown using mathematical calculations that n values of between 1 and 10 for the Freundlich isotherm indicate effective adsorption.

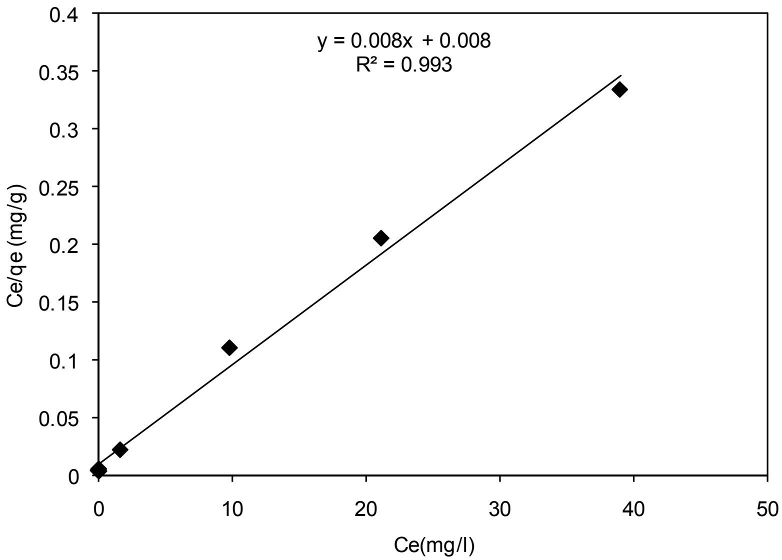

Figure 5: Langmuir plot for the adsorption of lead on Saudi activated bentonite.

3.6 Adsorption kinetic

Kinetics of sorption describing the solute uptake rate is one of the important characteristics defining the efficiency of sorption. The kinetic parameters for the adsorption process were studied on the batch adsorption at room temperature and pH at 3.1. The data were fitted to the first-order Lagergren equation [23],

$$(\log q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

where k_1 ($\min^{-1}$) is the first-order rate constant, q_e (mg /g) is the amount of adsorbed metal ions on the Saudi bentonite at equilibrium and q_t (mg /g) is the amount of lead adsorbed at time t (min). The first-order constants can be obtained by plotting log (q_e–q_t) versus time.

The experimental adsorption kinetics data were analyzed by applying the pseudo-second-order kinetics model, which is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

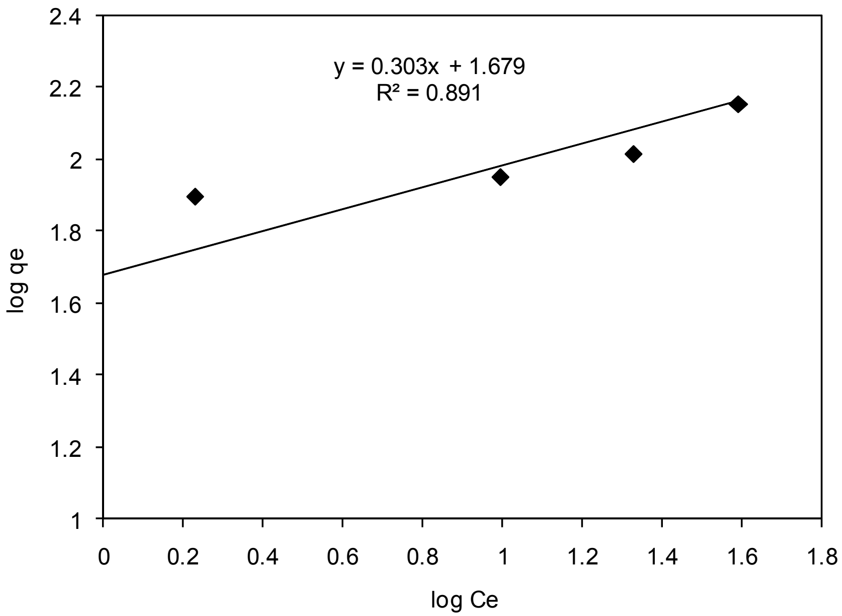

Figure 6: Freundlich plot for the adsorption of lead on Saudi activated bentonite.

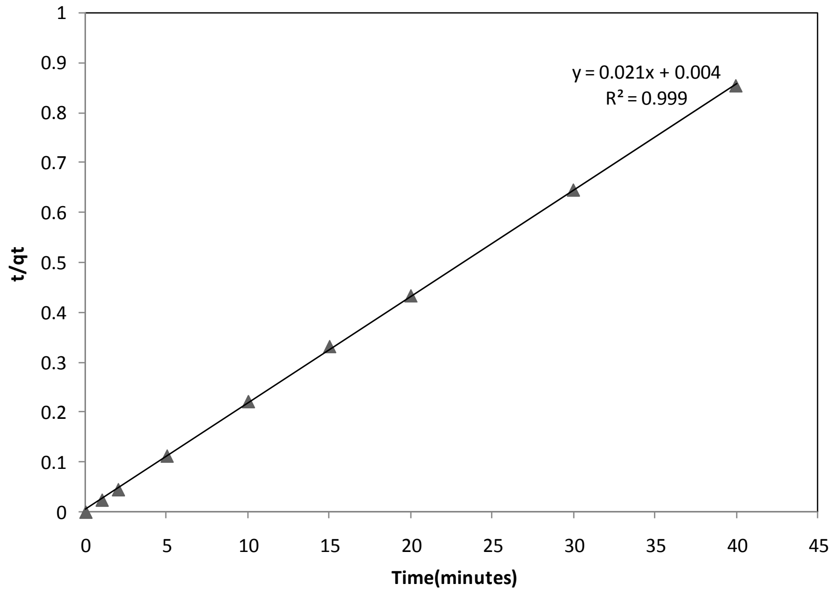

Figure 7: Plot of second order model for lead adsorption by Saudi activated bentonite.

where k_2 (g/(mg/min)) is the pseudo-second-order kinetics constant, q_e (mg /g) is the amount of adsorbed metal ions on the Saudi bentonite at equilibrium and q_t (mg /g) is the amount of lead adsorbed at time t (min). The fit of this model was checked by each linear plot of (t/q_t) versus t as shown in Figure 7.

By comparing to the regression coefficients for each expression, a good agreement of the experimental data with the second order kinetic model was observed. The correlation coefficient for the second order kinetic model is 0.999. Thus, a plot of t/q_t against t should give a linear relationship with a slope of $1/q_e$. These results agree with same results reported before [10, 23].

4 Conclusions

- The sorption of lead ions on Saudi activated clay was very fast and the equilibrium was reached after only 10 min. The results show that shaking the mixture of different initial concentration for 10 minutes was sufficient to reach equilibrium. They are also show that increasing the initial lead concentration decreased lead removal percentage due to the saturation of clay with lead ions.
- Removal of lead ions by Saudi activated bentonite is effected by mixture pH. The adsorption of lead increases from 20 to 100% with an increase in solution pH from 1 to 5.0 and then 100% lead was removed when solution pH increases from 5 to 11.
- Lead removal decreases with increasing lead concentration when lead concentration increases from 20 to 100 ppm.
- The removal of lead increases as the dose of Saudi activated bentonite increases. This is due to increase in the number of adsorbent sites.
- The adsorption isotherm data were well fitted with the Langmuir model better than Freundlich model.
- A batch adsorption kinetic experiment revealed that lead adsorption onto Saudi activated bentonite was well represented by the pseudo-second-order kinetic model. It can be concluded that film diffusion and intraparticle diffusion are simultaneously operating in the whole adsorption process.
- Saudi activated bentonite can be considered as a promising adsorbent for the removal of lead from aqueous solutions.

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