

Treatment of Wastewater Contaminated with Fe(II) by Adsorption onto Saudi Activated Bentonite

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Abstract— The adsorption of Fe(II) from wastewater using Saudi activated bentonite was studied in a batch adsorption system. This study investigates the removal characteristics of Fe(II) ions from wastewater under various operating variables such as shaking time, solution pH, clay amount, initial metal concentration and counter ions. The results showed that the sorption of Fe(II) ions on Saudi activated bentonite was fast and the equilibrium was achieved after only 20 min. The sorption data showed that solution pH was the most important parameter in controlling Fe(II) adsorption onto bentonite. They also showed that increasing the initial Fe(II) concentration decreased Fe(II) removal percentage due to the saturation of clay with Fe(II) ions. Furthermore, the adsorption of Fe(II) ions increased with increasing in solution pH. Increasing solution pH more than 3 causes precipitation rather than adsorption. The adsorption isotherm data were well fitted with the linearized Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models. The maximum adsorption (q_{max}) for Fe(II) on Saudi activated bentonite equals 7.09 mg/g. The value of the mean free energy determined with the D-R equation showed that adsorption process is chemisorptions. Fe(II) adsorption onto Saudi activated bentonite was well represented by the pseudo-second-order kinetic model. Saudi activated bentonite can be considered as a promising adsorbent for the removal of heavy metals from wastewater. Furthermore, Saudi activated bentonite as a cost effective adsorbent is recommended to be an alternate to commercially available activated carbon.

Index Term— Removal of Fe(II), Saudi activated bentonite, adsorption of Fe(II), heavy metals removal, adsorption isotherm, adsorption kinetic.

I. INTRODUCTION

Wastewaters from metal industries such as metal finishing and galvanized pipe manufacturing contain toxic substances, heavy metals, acids, alkalis, and other substances. High concentrations of metals in the effluents can ultimately reach the food chain and thus become a risk factor for human health [1,2]. Fe(II) is among the most common heavy metals in these wastewaters. Although, Fe(II) is essential for human, its presence above a certain level may cause harm to human body. The maximum amount allowed of Fe(II) in drinking

water is 0.3 mg/L. Excessive amount of Fe(II) in public water supplies causes turbidity, unpleasant taste and odor and vomiting. Consequently, the removal of Fe(II) is very important issue in aquatic environments and water pollution control [3,4]. Bentonite as a cheaper and readily available adsorbent can be used to remove Fe(II) from wastewater. Research was conducted to investigate the feasibility of using bentonite to remove Fe(II) from wastewater [5]. It was found that adsorption of Fe(II) onto bentonite using batch techniques was effective to remove Fe(II) from wastewater. The adsorption process was affected by solution pH. Most Fe(II) removal was observed at pH of 3. The kinetics of adsorption developed also support the removal of low concentrations of Fe(II) from wastewater.

Saudi activated bentonite (Khulays bentonite) which is located 95 km north of Jeddah is calcium montmorillonite equivalent to a "Texas bentonite" in the USA or Fuller's earth in the UK. It has reserves ranging from 420 thousand tons (proven) to 28.9 million tons (indicated) and 38.9 million tons (possible) [6]. Saudi activated bentonite was used for the removal of lead and cadmium from aqueous solutions. The results showed that Saudi activated bentonite successfully removed both metals (lead and cadmium) from wastewater. The adsorption process was very fast and the equilibrium was achieved after about 10 and 20 minutes respectively. Moreover, the process was affected by shaking time, solution pH, initial metal concentration and clay dosage.

In this research, the feasibility of using Saudi activated bentonite for the removal of Fe(II) from wastewater will be investigated. The adsorption characteristics will be investigated under operating variables, such as shaking time, solution pH, initial Fe(II) concentration, and clay dosage.

II. MATERIALS AND METHODS

A. Adsorbent

Saudi natural bentonite (Khulays bentonite) was obtained from Khulays bentonite deposit, 95 km north of Jeddah, Saudi Arabia. Saudi bentonite is not active in its natural state where some treatment was required to modify its adsorptive property. Acid treatment was conducted using sulfuric acid to increase its adsorptive capacity. The apparatus and chemical treatment method with H_2SO_4 employed in this study are similar to what have been described previously [7, 8, 9]. Acid activation was done using the optimum operating variables such as 15% by weight acid concentration, the

temperature of boiling, 90 minutes reaction time, grain size of -200 mesh (74 μm) and water to clay ratio of 5:1. After activation process, the surface area of Saudi natural bentonite

was increased from 60 to 299 (m^2/g). Table (I) shows the chemical composition of Saudi activated bentonite [7].

Table I
The chemical composition of Saudi activated bentonite in wt.% (7)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₂	TiO ₂	MgO	K ₂ O	Na ₂ O	L.O.I.
66.2	11.71	3.0	1.5	0.73	0.48	0.12	15.3

B. Chemicals

All chemicals used in this work were of analytical grade reagents and used without further purifications. Fe(II) was obtained from Merck. Stock solution of Fe(II) (1000 mg/L) was prepared by dissolving the appropriate amounts of (FeSO₄·7H₂O), in distilled water. The stock solutions were diluted as required to obtain standard solutions containing 10–130 mg/L of Fe(II). The pH of each experimental solution was adjusted to the required pH value using 1N HCl and 1N NaOH.

C. Batch Adsorption Experiments

Batch adsorption experiments were conducted at room temperature (25 °C) using horizontal shaker with water bath (JULABO SW 22) at 200 rpm. A sample of 50 mL of the diluted solution was added to a group of 100 ml conical flasks. Saudi activated bentonite sample in the range of 0.125–2.0 g were added to each flask under continuous mixing. Afterward, samples were taken out of the shaker at regular contact time intervals and the bentonite was separated by filtration. The filtrate was analyzed for Fe(II) concentration by Atomic absorption spectrophotometer (AAS).

The adsorption capacity was obtained by using a mass equilibrium equation as follows:

$$q = \frac{(C_o - C_e)V}{m} \quad (1)$$

where C_o and C_e being the initial Fe(II) concentration (mg/L) and equilibrium concentration, respectively, V is the

experimental volume of Fe(II) solution expressed in liters, and m is the adsorbent mass expressed in grams. The removal percentage was calculated using the following equation:

$$\text{Heavy metal removal \%} = \frac{C_o - C}{C_o} \times 100 \quad (2)$$

where C is Fe(II) concentration at time t in (mg/L)

III. RESULTS AND DISCUSSIONS

A. Effect of Shaking Time

The effect of shaking time of Fe(II) adsorption on Saudi activated bentonite was studied by varying the contact time between the adsorbate and adsorbent in the range 1 to 60 min. The initial concentration of Fe(II) ranged from 20 to 100 mg/L, while the dose of clay sample was 0.5 g/50 mL, solution pH was 3 and the solution was shaken at 200 rpm. The data showed that the sorption of Fe(II) ions on Saudi activated bentonite was fast and the equilibrium was achieved after only 20 minutes. The adsorption process was fast at the beginning of the reaction due to the adsorption of Fe(II) on the surface sites of clay. The results showed that shaking the mixture of different initial concentration for 20 minutes was sufficient to reach equilibrium as shown in figure (1). They also showed that increasing the initial Fe(II) concentration decreased the removal percentage due to the saturation of clay with Fe(II) ions. Similar result has been reported for the sorption of Fe(II) ions by another type of bentonite clay [10]. The short time needed for adsorption to reach equilibrium could be attributed to the high adsorption efficiency of Saudi activated bentonite.

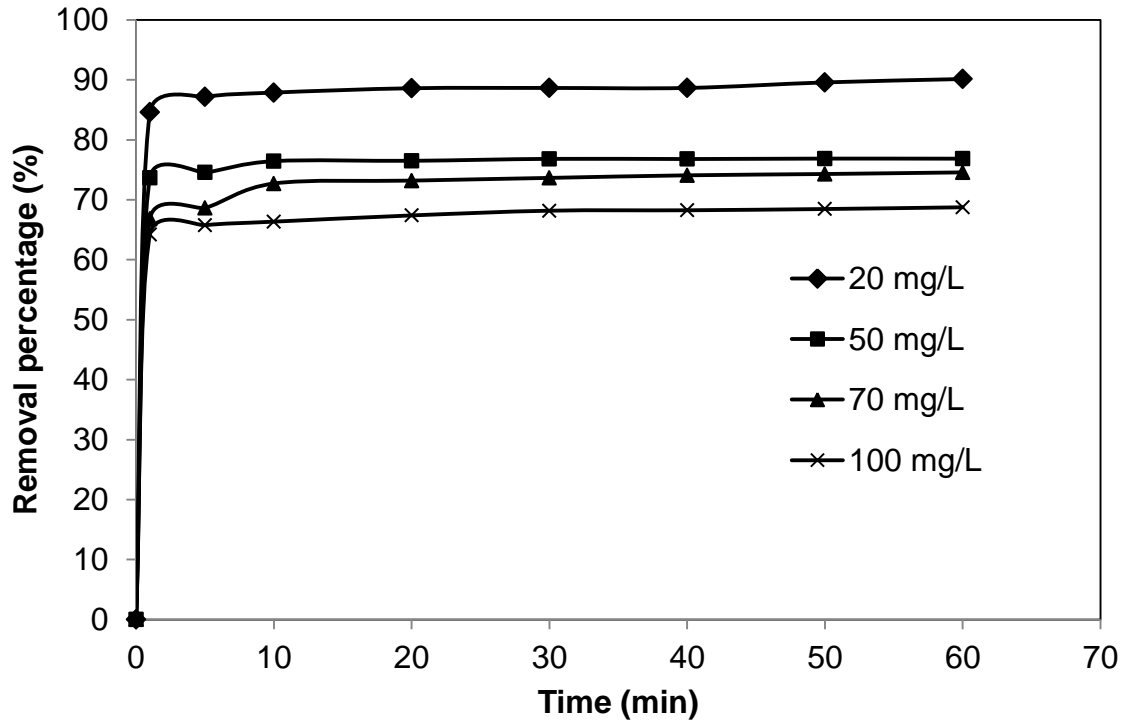


Fig. 13. Effect of shaking time on the removal of Fe(II) by Saudi activated bentonite. Initial metal concentration varies between 20 and 100 mg/L, clay dosage: 0.5 g/50mL, pH= 3.

B. Effect of Solution pH.

The effect of solution pH on the removal of Fe(II) ions using Saudi activated bentonite was investigated and the results are presented in Figure (2). Adsorption of Fe(II) was studied in the solution pH range 1 to 10 with a constant clay amount of 0.5g/50 mL of solution, a shaking time of 20 min at 200 rpm and Fe(II) concentration of 50 mg/L. The results showed that the adsorption of Fe(II) increased from 23 to about 97% when solution pH was increased from 1 to 4. Afterward, 99% of Fe(II) was removed when solution pH was increased from 5 to 10. Therefore, increasing solution pH more than 4 caused Fe(II) to precipitate as ferric hydroxides [11]. Thus, a red color was observed when solution pH was increased above 3.

The effect of pH on the removal of heavy metals may be explained as mention before [12], 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 Fe^{2+} ions for the surface adsorbing sites, resulting in a decrease in the removal of Fe(II). Therefore, in the next experiments, Fe(II) solution pH will be controlled at 3 to study the effect of other variables affecting the removal efficiency of Fe(II) from wastewater solution by adsorption. A similar result was reported before [10].

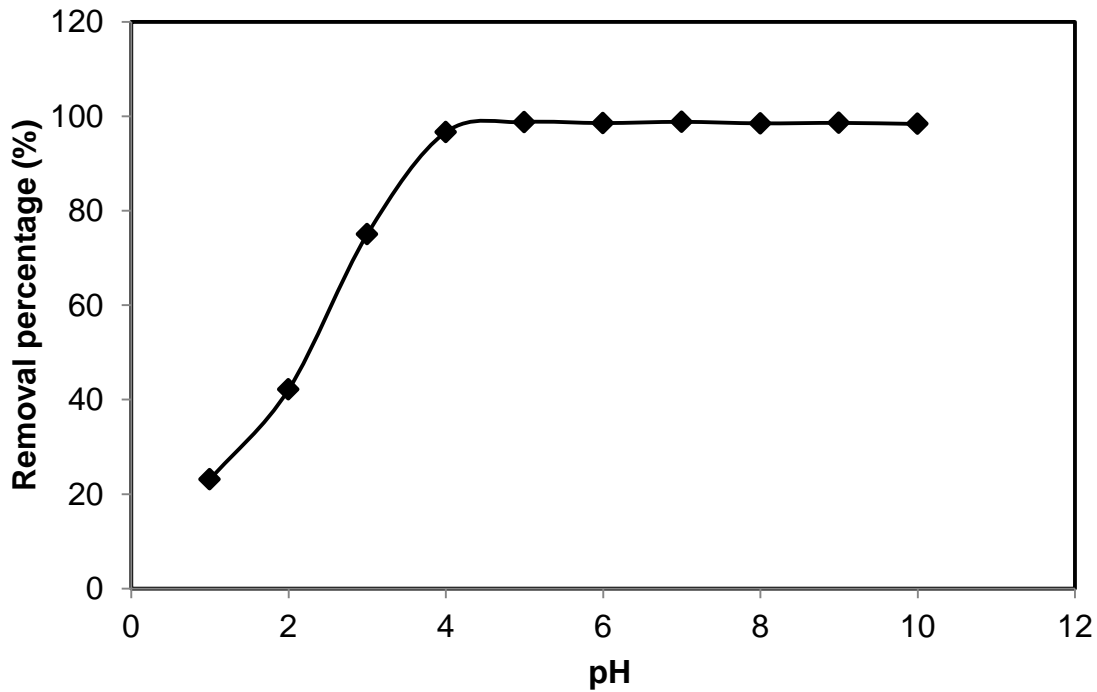


Fig. 2. Effect of solution pH on the removal of Fe(II) by Saudi Activated Bentonite. Initial Fe(II) concentrations of 50 mg/L, clay dosage: 0.5g/50 ml, contact time: 20 min.

C. Effect of Initial Concentration.

The effect of initial concentration on the adsorption of Fe(II) was investigated. Experiments were conducted using Fe(II) initial concentration which varied from 10 to 130 mg/L under operating conditions of 20 min shaking time, 0.5 g/50 mL for adsorbent and mixture pH at 3. Figure (3) shows the results where about 86% of Fe(II) was removed when Fe(II) concentration was 10 mg/L. Fe(II) removal percentage

decreased with increasing Fe(II) concentration to about 46% when Fe(II) concentration increased to 130 mg/L due to the decrease in free clay sites. However, the adsorption percentage decreases with increasing concentration. The results showed that the removal of Fe(II) ions is concentration dependent. At higher initial concentrations, the available adsorption sites of adsorption became fewer and hence the removal of Fe(II) ions depended upon the initial concentration.

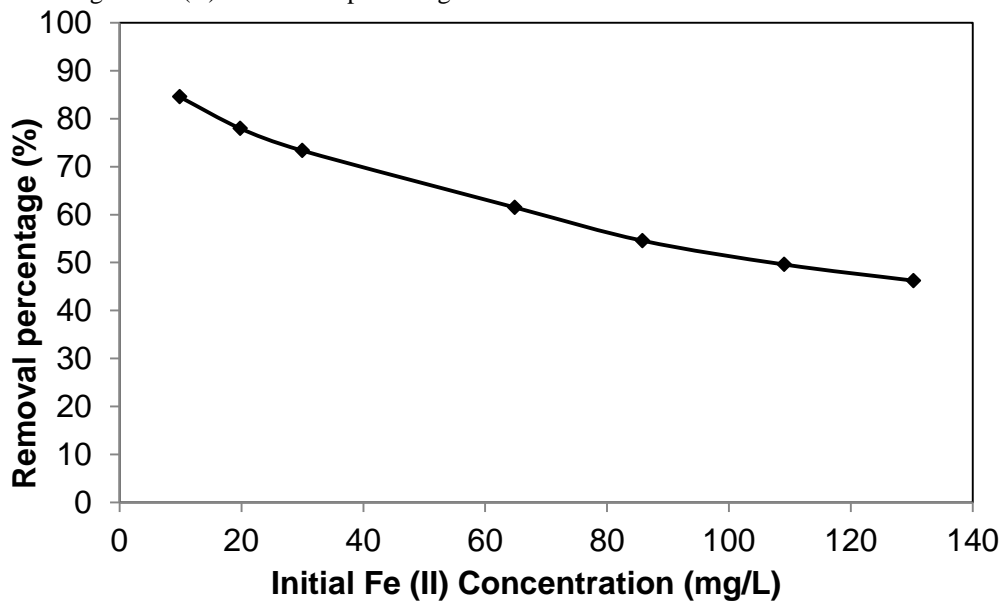


Fig. 3. Effect of initial Fe(II) concentration on the removal of Fe(II) by Saudi activated bentonite. Clay dosage: 0.5 g/50mL. pH = 3, contact time: 20 minutes.

D. Effect of Clay Dosage.

Figure (4) shows the effect of bentonite dosage on the adsorption of Fe(II) from wastewater where the amount of bentonite varies from 0.125 to 2 g. The adsorption process was conducted under operating condition of 50 mg/L initial Fe(II) concentration, 20 min contact time at 200 rpm, solution pH at 3 and temperature of 25°C. The results showed that the

removal of Fe(II) gradually increased from 46% (clay dosage: 0.125) to about 80% when clay dosage increased to 1 g. However, this result was expected since as the dose of adsorbent increases, the number of adsorbent sites increased. Similar results have been reported in the literature [10]. Therefore, 1.0 g of activated bentonite can be considered as enough bentonite dosage for the removal of Fe(II) from wastewater for the same condition.

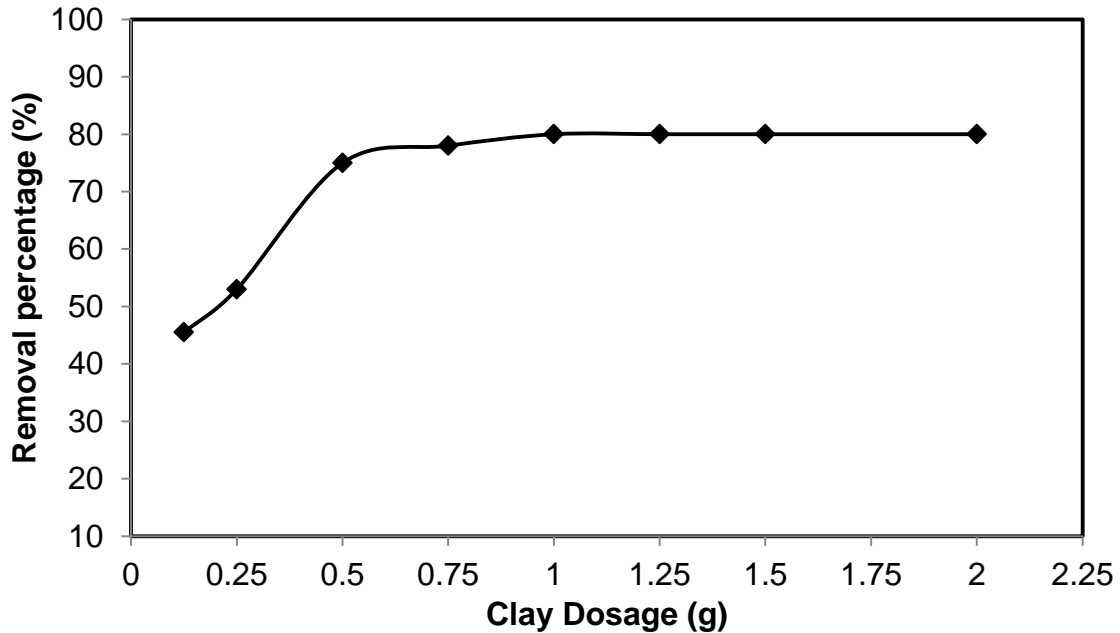


Fig. 4. Effect of clay dosage on the removal of Fe(II) by Saudi activated bentonite. Initial Fe(II) concentrations 50 mg/L, pH = 3, contact time: 20 minutes.

E. Effect of Counter Ions

The effect of counter ions (nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-)) on the removal of Fe(II) from wastewater was investigated using Saudi activated bentonite. Three groups of experiments were conducted. Each group of experiments used Fe(II) solution prepared by dissolving the appropriate amounts of $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ respectively in distilled water. Experiments were conducted using initial Fe(II) concentration which varied from 10 to 130 mg/L under

operating conditions of 20 minutes shaking time at 200 rpm, 0.5 g/50 mL for adsorbent and mixture pH at 3. Figure (5) shows Fe(II) removal in case of the presence of sulfate ions compared to the presence of chloride and nitrate ions. This can be explained by H^+ ions in the solution react with chloride and nitrate ions. These H^+ ions free more adsorbent site which increased Fe(II) ions adsorption from the solution. Furthermore, due to the use of sulfuric acid to activate bentonite, higher sulfate concentration in the solution may hinder the removal efficiency of Fe(II).

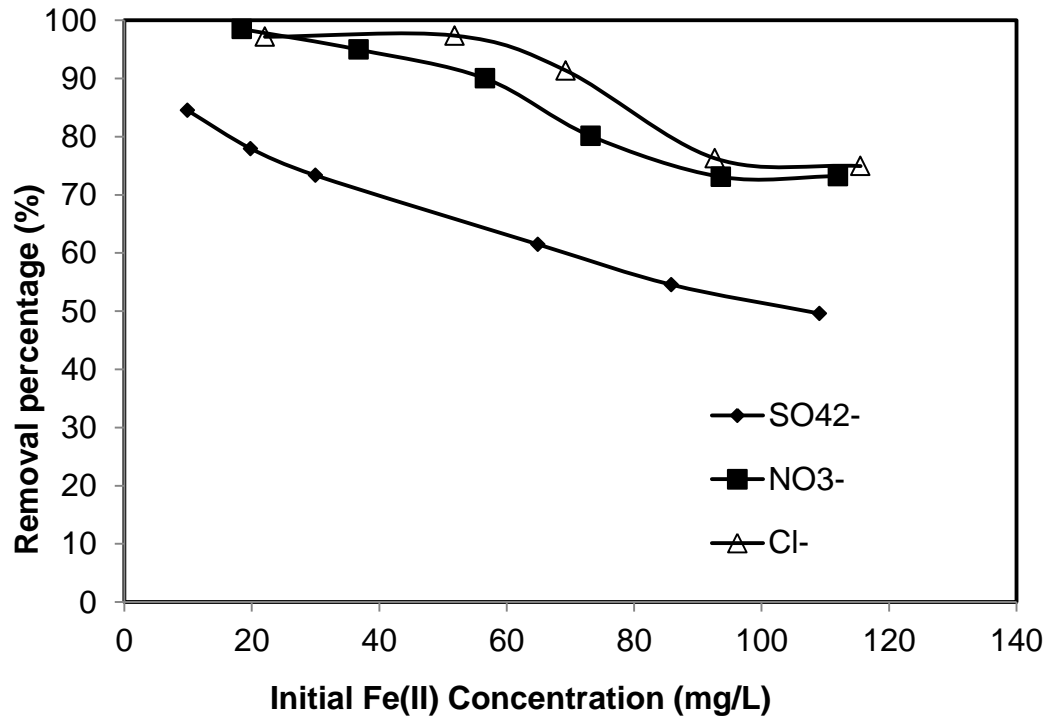


Fig. 5. Effect of counter ions on the removal of Fe(II) by Saudi activated bentonite. Clay dosage: 0.5 g/50mL. pH = 3, contact time: 20 minutes.

F. Adsorption Isotherm

The experimental adsorption data of Fe(II) adsorption onto Saudi activated bentonite was obtained using the well-known three-parameter isotherm models Langmuir [13], Freundlich [14] and Dubinin–Radushkevich (D–R) isotherm [15]. These models were tested to determine the maximal adsorption capacity of Fe(II) onto Saudi activated bentonite. Furthermore, they can be used to estimate the mean free energy and the characteristics of the adsorption process.

The experimental data is considered to give the best fitted isotherm model when the magnitude of correlation coefficient (R^2) is closest to unity. Experimental isotherm data were conducted at an equilibrium time of 20 minute shaking time at shaker speed of 200 rpm, different initial Fe(II) concentrations, adsorbent mass of 0.5 g, room temperature at 25 °C and solution pH at 3. Afterward, data obtained were fitted to the Langmuir, Freundlich and Dubinin–Radushkevich

(D–R) isotherms. The linear form of Langmuir isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

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

The data obtained from linear Langmuir isotherm for the adsorption of Fe(II) onto Saudi activated bentonite is presented in table (II) and plotted in figure (6). The maximum adsorption (q_{\max}) for Fe(II) on Saudi activated bentonite equals to 7.09 mg/g.

TABLE II.

The Langmuir, Freundlich and Dubinin-Raduskevich equation parameters predicted from adsorption isotherm data of Fe(II) ions onto Saudi activated bentonite at pH = 3, 25 °C and initial Fe(II) concentration of 50 mg/L.

Models	Isotherm constants			
	Langmuir	q_{\max} (mg g ⁻¹)	b (L mg ⁻¹)	
7.09		0.06		0.98
Freundlich	K (mg g ⁻¹)	n		R^2
	0.71	1.95		0.995
Dubinin-Raduskevich	q_D (mg g ⁻¹)	B (mol ² kJ ⁻²)	E (kJmol ⁻¹)	R^2
	6.0	5E-5	100	0.91

The logarithmic form of Freundlich equation is written as:

$$\log q_e = \log k + \frac{1}{n} \log C_e \quad (4)$$

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

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data, by plotting $\log(q_e)$ versus $\log(C_e)$. The data obtained from linear Freundlich isotherm plot for the adsorption of Fe(II) onto Saudi activated bentonite is presented in table (II) and plotted in figure (7). The value of n between 1 and 10 shows good adsorption which indicates that Fe(II) is favorably adsorbed by Saudi activated bentonite [16]. The best estimated values of all the equation parameters are summarized in table (II).

D-R isotherm was applied to estimate the porosity apparent free energy and the characteristics of adsorption. The linear form can be represented as:

$$\ln q_e = \ln q_D - B\varepsilon^2 \quad (5)$$

where, B is a constant related to the mean free energy of adsorption ($\text{mol}^2(\text{kJ}^2)^{-1}$) q_D is the theoretical saturation capacity (mg/g), ε is the polyani potential, and calculated as follows:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (6)$$

The slope of the plot of $\ln q_e$ versus ε^2 gives B and the intercept yields the adsorption capacity, q_D . The mean free energy of adsorption (E) (KJmol^{-1}) is calculated from the equation:

$$E = 1/(2B)^{0.5} \quad (7)$$

The calculated value of D-R parameters is given in table (II) and plotted in figure (8). As reported before, the process is considered to be physiosorption processes when the adsorption energies $< 40 \text{ kJ mol}^{-1}$ and above this value sorption follows chemisorption mechanism [17]. As shown in table (II), the calculated value of E shows that the process is chemisorptions. This result is similar to what have been reported before [18, 10].

The adsorption isotherm data in general were well fitted with linearized Langmuir, Freundlich and Dubinin-Radushkevich (D-R) equations and give $R^2 > 0.91$.

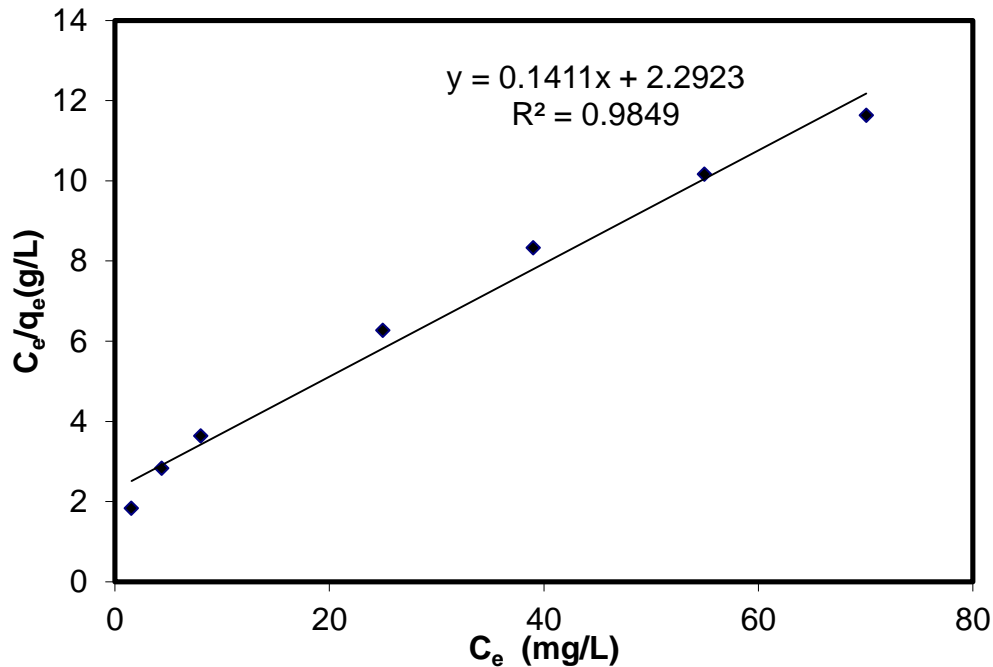


Fig. 6. Langmuir plot for the adsorption of Fe(II) on Saudi activated bentonite.

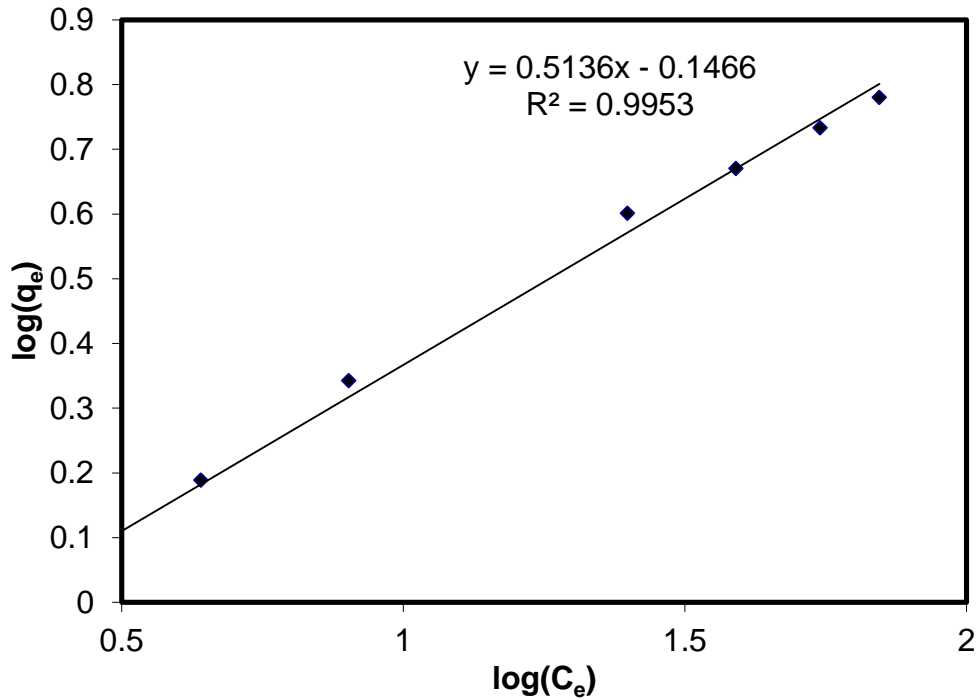


Fig. 7. Freundlich plot for the adsorption of Fe(II) on Saudi activated bentonite.

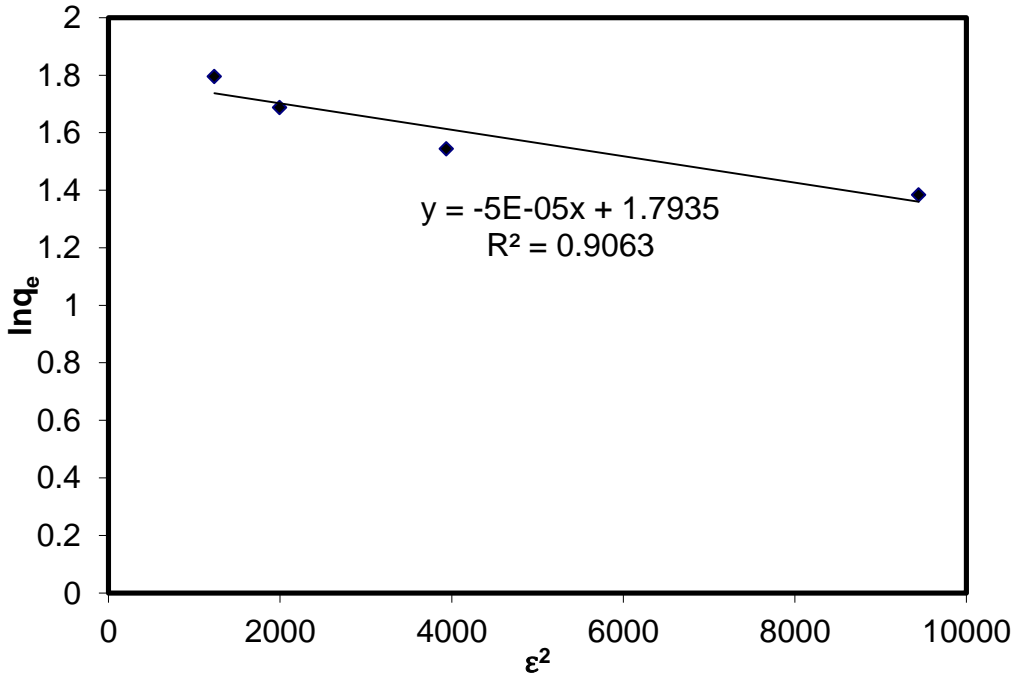


Fig. 8. Dubinin-Raduskevich plot for the adsorption of Fe(II) on Saudi activated bentonite.

G. Adsorption Kinetic

The kinetics study is important for selecting optimum operating conditions for the full-scale batch process (19). The calculated evaluate kinetic parameter gives important information for designing and modeling the processes.

The kinetics of Fe(II) adsorption onto Saudi activated bentonite were investigated using two kinetic models, pseudo-

first-order and pseudo second-order. The kinetics of sorption experiments were conducted to describe the solute uptake rate in order to determine the efficiency of Fe(II) adsorption onto Saudi activated bentonite .

The kinetic parameters for the adsorption process were studied on the batch adsorption using initial Fe(II) concentration of 50 mg/L, pH at 3 and room temperature at

25°C. The data were fitted to the first-order Lagergren equation [20],

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

where k_1 (min^{-1}) is the first-order rate constant, q_e (mg/g) is the amount of adsorbed Fe(II) ions on the Saudi bentonite at equilibrium, and q_t (mg/g) is the amount of Fe(II) adsorbed at time t (min). The first-order constants can be obtained by plotting $\log(q_e - q_t)$ versus time, as shown in Figure (9).

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where k_2 ($\text{g}/(\text{mg}/\text{min})$) 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 Fe(II) adsorbed at time t (min). The fit of this model was checked by the linear plot of (t/q_t) versus t as shown in Figure (10).

The fit of the experimental data obtained from this work showed a good agreement with the second order kinetic model. The correlation coefficients for the second order kinetic model for Fe(II) adsorption was around 1.0. On the other hand, due to lower correlation coefficient, first order rate expression model is not fully valid for the present systems. Thus, a plot of t/q_t against t should give a linear relationship with a slope of t/q_e . Similar studies have also been previously reported [18,21,22].

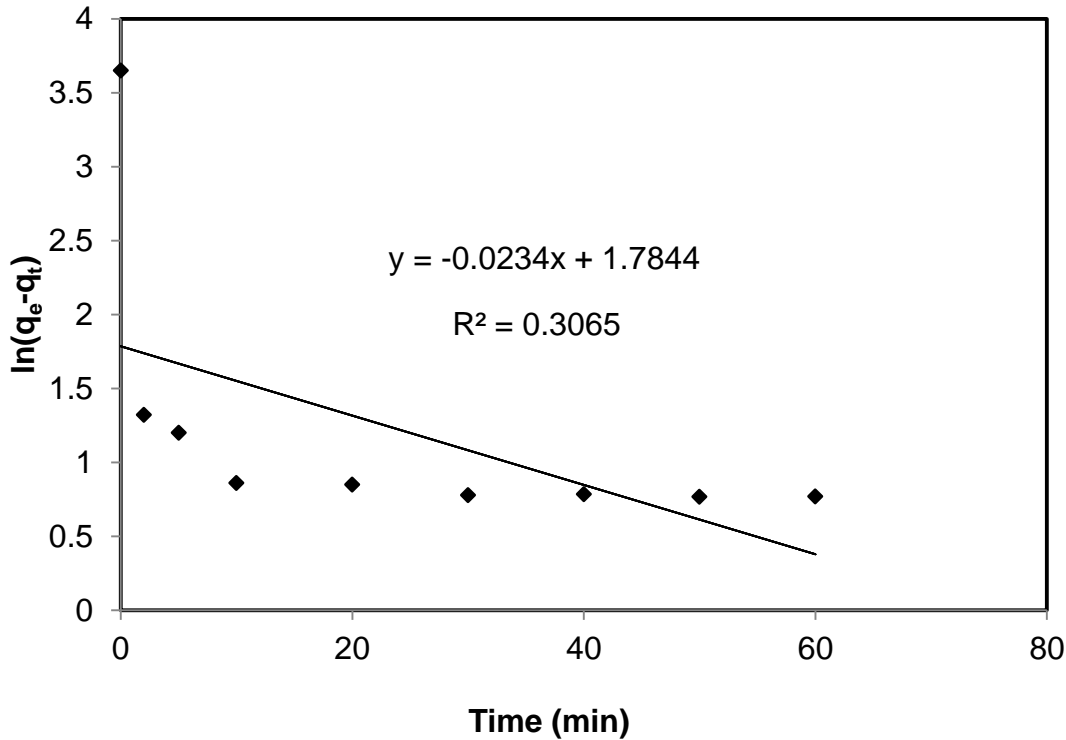


Fig. 9. Plot of first order model for Fe(II) adsorption by Saudi activated bentonite.

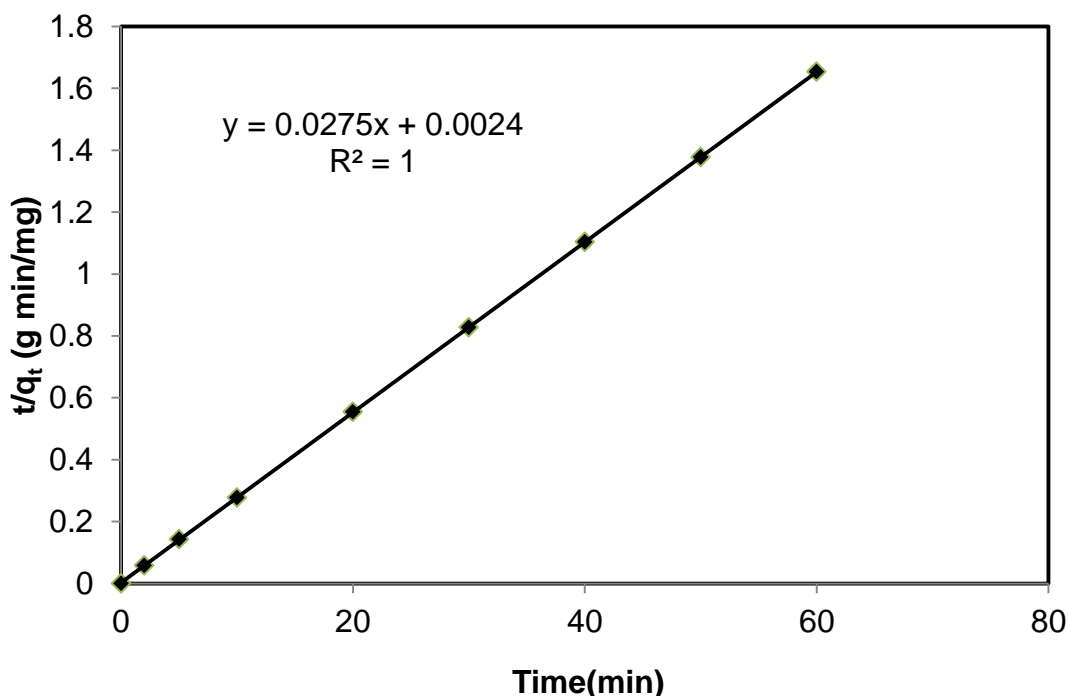


Fig. 10. Plot of second order model for Fe(II) adsorption by Saudi activated bentonite.

IV. CONCLUSIONS

In the present work, Saudi activated bentonite was an effective adsorbent for removing Fe(II) from wastewater. Based on the experimental data, the following conclusions may be drawn. It was found that the sorption of Fe(II) ions on Saudi activated bentonite was fast and the equilibrium was reached after only 20 minutes. The most important factor affecting the removal of Fe(II) ions from wastewater was solution pH. It was found that the increasing of solution pH more than 3 may cause precipitation rather than adsorption. The removal of Fe(II) increases as the dose of Saudi activated bentonite increases. This is due to increase in the number of adsorbent sites. The experimental results were fitted well with Langmuir, Freundlich and Dubinin–Radushkevich (D-R) isotherm models. The maximum adsorption (q_{max}) of Fe(II) on Saudi activated bentonite equals to 7.09 mg/g and the calculated value of E showed that the process is chemisorptions. Furthermore, the data indicate that the adsorption kinetics of Fe(II) follow the pseudo-second-order rate. The present investigation concludes that the Saudi activated bentonite could be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal Fe(II) from wastewater.

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