Removal of cadmium from waste water using Saudi activated bentonite

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Abstract

Application of Saudi activated clay (bentonite) to remove cadmium from wastewater was investigated. Natural local clay which was obtained from Khulays bentonite deposit was selected and activated using sulfuric acid to increase its adsorptive capacity. The removal characteristics of cadmium ions from wastewater were investigated under various operating variables such as contact time, initial metal concentration, clay dosage and solution pH. Batch scale equilibrium adsorption was carried out for a wide range of initial metals concentration. The results showed that the sorption of cadmium ions on Saudi activated clay was relatively fast and the equilibrium was achieved after only 20 min. The sorption data suggests that solution pH was the most important parameter in controlling cadmium sorption onto bentonite. They also showed that increasing the initial cadmium concentration decreased cadmium removal percentage due to the saturation of clay with cadmium ions. Furthermore, the adsorption of cadmium increased with increase in solution pH. The adsorption isotherm data were well fitted with both the linearized Langmuir and Freundlich models.
Keywords: cadmium removal, Saudi bentonite, cadmium adsorption, heavy metals removal, adsorption isotherm, adsorption kinetic.

1   Introduction

Heavy metals wastewaters are directly or indirectly discharged into the environment excessively in many countries. Heavy metals are not biodegradable as organic contaminants and may accumulate in living organisms. Many heavy metal ions are known to be toxic or carcinogenic such as cadmium [1]. Cadmium

is used in many applications such as electroplating, Ni-Cd batteries and paint pigments. Discharge of untreated effluents from such industries is the main source of cadmium pollution. Moreover, mining effluents and geological weathering are also considered as sources of cadmium pollution [2–4].

Cadmium is considered as a probable human carcinogen. Chronic exposure of cadmium results in kidney dysfunction whereas high levels of exposure results in death. The maximum contaminant level (MCL) is 0.005 (mg/l) or 5 parts per billion (ppb) [5].

Cadmium as other heavy metals can be removed from wastewater using activated carbon which is considered as the most used adsorbent, nevertheless it is relatively expensive.

Clay minerals as low-cost and easily available adsorbents have been extensively studied as adsorbents for the removal of heavy metals from aqueous solutions [6–9]. Clays mainly contain aluminosilicate minerals which have negatively charged layered that make them a good cationic adsorbents due to their relatively large surface areas. Heavy metals can be removed by adsorbing on clay surface by ion exchange reactions and by the formation of inner-sphere complexes through SiO^- and AlO^- groups at the clay particle edges [10, 11].

The adsorption capacity of natural clay can often be improved either by intercalation of organic, inorganic, or organometallic molecules in the interlamellar space, or by heat (calcination) or acid treatments according to previous studies [11–15]. These studies found that the removal characteristics of cadmium from aqueous solution by clay minerals can be affected by operating variables such as contact time, solution pH, initial metal concentration and clay dosage. However, solution pH was found as the most important factor controlling the adsorption process.

The Khulays bentonite (Saudi bentonite) which is available in north of Jeddah is calcium montmorillonite equivalent to a "Texas bentonite" in the USA or Fuller's earth in the UK. The estimated reserves are ranging from 420 thousand tons to 28.9 million tons [16].

In spite of the significant resources of Saudi bentonite, few researches were conducted to use bentonite as adsorbent. Al-Shahrani [17] investigated the feasibility of producing Saudi activated bentonite from a local natural occurring bentonite from a technological and economical point view. The results showed that Saudi bentonite is suitable for acid activation. Furthermore, it was proven that Saudi activated bentonite is suitable for bleaching unbleached refined corn oil [18, 19]. Saudi activated bentonite was used for the removal of lead and nickel from aqueous solutions. The results showed that using Saudi bentonite to remove heavy metals from aqueous solutions is promising process [20, 21].

2   Materials and methods

2.1 Chemicals and solutions

All chemicals used in this work were of analytical grade reagents and used without further purifications. Cadmium was obtained from Merck. Stock solution

of Cd(II) (1000 mg/l) was prepared by dissolving the appropriate amounts of Cd(NO3)$_2$•4H$_2$O), in distilled water. The stock solutions were diluted as required to obtain standard solutions containing 20–210 mg/L of Cd(II). The pH of each experimental solution was adjusted to the required pH value using 1N HCl and 1N NaOH.

2.2 Preparation of adsorbent

Saudi natural bentonite which was used in this study comes from Khulays bentonite deposit; 95 km north of Jeddah. It was not active in its natural state where some treatment was required in order to modify its adsorptive capacity. Natural Saudi bentonite samples were received as ungrounded rocks where grinding and sieving processes was conducted before acid activation. The apparatus and chemical treatment method with H_2SO_4 which was employed in this study are similar to what have been described previously [17–19]. 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. The chemical composition of Saudi activated bentonite revealed that SiO_2 is its major (66.2%) constituent and CaO is also present (11.24%) in the adsorbent in significant amount (Table 1). Oxides of other metals are present in small amounts. The surface area of Saudi natural clay was improved from 60 to be 299 m^2/g after activation process.

Table 1:   Chemical composition of Saudi activated bentonite.

Compound	Chemical composition (%)
Sio$_2$	66.2
Al$_2$O$_3$	11.71
Fe$_2$O$_2$	3.0
TiO$_2$	1.5
MgO	0.73
CaO	<0.05
K$_2$O	0.48
Na$_2$O	0.12
MnO	0.05
SO$_3$	<0.05
P$_2$O$_5$	<0.05
L.O.I.(1000°C)	15.3

2.3 Adsorption process

Adsorption experiments were carried out in using batch technique. A certain amount of bentonite and 50 ml of cadmium solution at desired initial concentration were added to 100 ml stoppered conical flasks. The flasks were shaken in a horizontal shaker with water bath at 200 rpm. Stock solution of

Cd(II) (1000 mg/l) was prepared by dissolving the appropriate amounts of Cd(NO3)$_2$•4H$_2$O), in distilled water. The stock solutions were diluted as required to obtain standard solutions containing 20–210 mg/l of Cd(II). pH adjustments were carried out using 1N HCl and 1N NaOH. 200 rpm shaking rate and 25±2°C temperature was applied in the shaker. Samples with clay content in the range of 0.125–2.0 g were taken from the shaker at regular contact time intervals. The sorbent and solution were separated by filtration after each run. The filtrate was analyzed for cadmium concentration by Atomic Absorption Spectrophotometer. The effects of several factors such as solution pH, concentration of solution, clay dosage and contact time on cadmium removal efficiency were examined. The obtained data were employed to calculate the equilibrium metal uptake capacity according to the following equation:

$$q_e = \frac{V(C_O - C_e)}{m}$$
(1)

where q_e (mg/g) is the equilibrium amount of cadmium adsorbed, C_o and C_e are the initial and equilibrium concentrations of metal ion (mg/l) in the aqueous solution, V is the volume of the solution and m is the sorbent dose (g) in the mixture.

3   Results and discussion

3.1   Effect of contact time

Adsorption of cadmium by Saudi activated bentonite was investigated by varying the contact time between the adsorbate and adsorbent in the range of 1-60 min. The initial concentration of cadmium was ranging from 20 to 100 ppm, while the clay dosage was 0.5 g/50 ml and the solution pH was left unchanged at 3.2. The result showed that the amount of cadmium adsorbed increased with increase in the initial concentration and stayed constant after equilibrium as shown in fig. 1. Moreover, the data showed that the sorption of cadmium ions on Saudi activated clay was fast and the equilibrium was reached after about 20 min, which is faster than what was reported before [12, 14, 22]. The results showed that shaking the mixture of different initial concentration for 20 minutes was sufficient to reach equilibrium. After that, contact time has no effect on metal removal percentage. They are also showed that increasing the initial cadmium concentration decreased cadmium removal percentage due to the saturation of clay with cadmium ions. For the rest of experiments, contact time was fixed at 20 min to ensure that adsorption equilibrium was achieved. This finding is in agreement with the results of Ulmanu et al. [23], who investigated heavy metals removal from aqueous solution using peat.
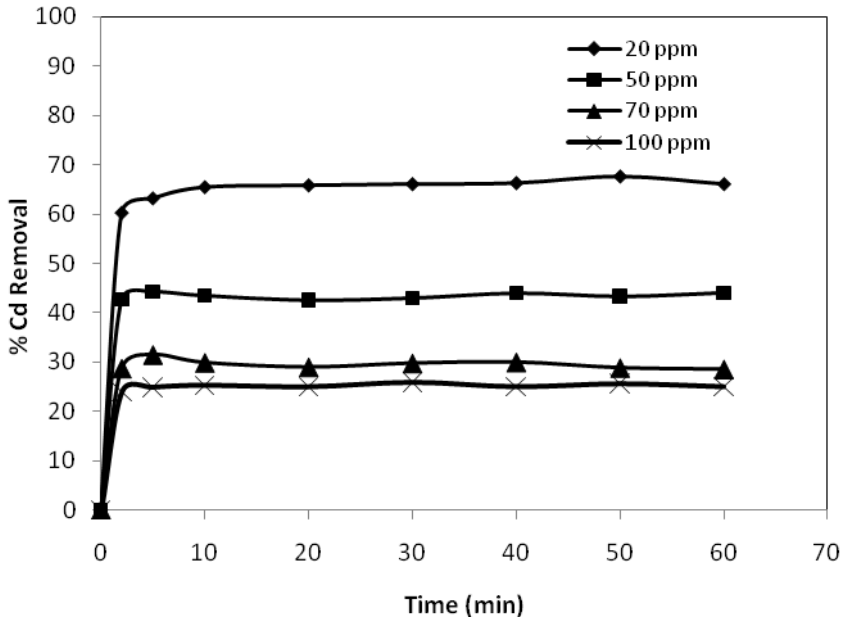
Figure 1: Effect of contact time on the removal of cadmium by Saudi activated bentonite. clay dosage: 0.5 g/50ml, pH= 3.2.

3.2 Effect of solution pH

The effect of solution pH on the removal of cadmium ions by Saudi activated bentonite was investigated. The removal experiments were studied in the pH range 1–10 with a constant clay amount of 0.5 g/50 ml of cadmium solution, a shaking time of 20 min and cadmium concentration of 50 ppm. The results presented in fig. 2 reveal that the adsorption of cadmium increases from 0 to about 100% with an increase in solution pH from 1 to 8. This may be explained by Saudi activated bentonite containing a large number of active sites. Therefore, it may become positively charged at low pH, which increases the competition between H^+ ions and cadmium ions for the adsorption sites. Nevertheless, as solution pH increases, the competition decreases as bentonite surface active sites become more negatively charged, which enhances the adsorption of cadmium ions through electrostatic force of attraction [24, 25]. Beyond pH 8.0, adsorption of cadmium does not change considerably where removal percentage is stayed around 100%. It is known that cadmium hydroxide precipitate occurs when solution pH increases above 8 [26]. Thus, cadmium removal process at pH more than 8 may be caused by precipitation as well as adsorption.
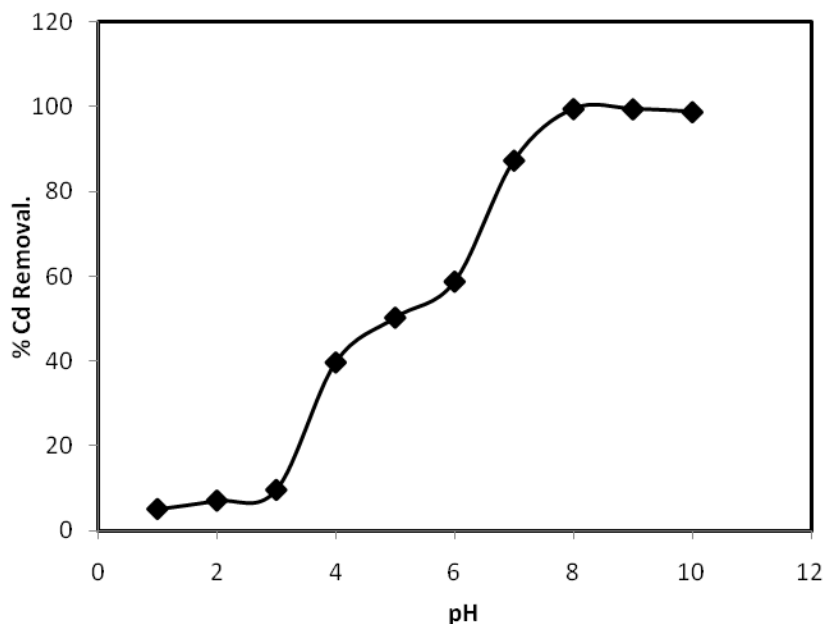
Figure 2:   Effect of solution pH on the removal of cadmium by Saudi activated bentonite. Initial cadmium concentrations 50 mg/l, clay dosage: 0.5g/50 ml, contact time: 20 min.

3.3 Effect of clay dosage

The effect of the amount of Saudi activated bentonite on the removal of cadmium was investigated under the conditions of clay dosage   0.125–2.0 g/ 50 ml, initial metal concentration (50 ppm), contact time 20 min, pH = 7 and temperature (25±2°C). The result is shown in fig. 3 showed that the removal of cadmium increased gradually from 54% at 0.125 g/50 ml up to 95% at 0.75 g/ 50 ml. Afterword, cadmium removal was stayed constant at 95% when clay dosage increased to 2.0/50 ppm. However, this result was expected since as the dose of the adsorbent increases, the number of adsorbent sites increases as a result of increase in adsorbent surface area. These amounts attach more ions to their surfaces [27]. Similar results were reported where many types of materials were used as adsorbents [24, 25].
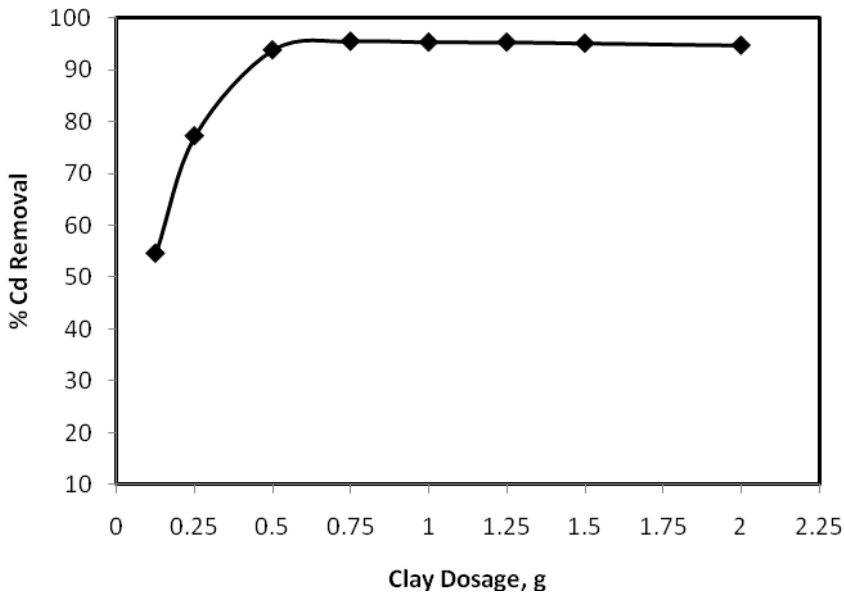
Figure 3:   Effect of clay dosage on the removal of cadmium by Saudi activated bentonite. Initial cadmium concentrations 50 mg/L, pH = 7, contact time: 20 minutes.

3.4 Adsorption isotherm

Two different adsorption isotherm models, the Langmuir [28] and Freundlich [29] equations were used to fit the experimental data obtained from this work. These models were tested to determine the maximal capacity of Cd(II) 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 Cd(II) removal were studied using different initial metal concentrations at adsorbent mass of 0.5 g at room temperature ($25\pm2^{o}C$) and solution pH 7.0. Afterward, data obtained were fitted to the Langmuir and Freundlich isotherms.

The Langmuir isotherm is based on the assumption that it predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent [28]. This model also suggests that there is no lateral interaction between the sorbed molecules.

The Langmuir equation, in the linear form is written as:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \qquad (2)$$

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). The data obtained from linear Langmuir isotherm plot for Cd(II), onto Saudi activated bentonite is presented in Table 2 and plotted in fig. 4. The maximum adsorption (q_{max}) of Cd(II) on Saudi activated bentonite equals to 14.9 mg/g.

Table 2: The Langmuir and Freundlich equation parameters predicted from adsorption isotherm data of Cd(II) ions onto Saudi activated bentonite at pH = 7, 25°C and initial Cd(II) concentration of 50 ppm.

Models	Isotherm constants		
Langmuir	q_{max} (mg/ g)	b (l/ mg)	R^2
	14.9	0.0913	0.969
Freundlich	K (mg/g)	n	R^2
	3.67	3.56	0.981

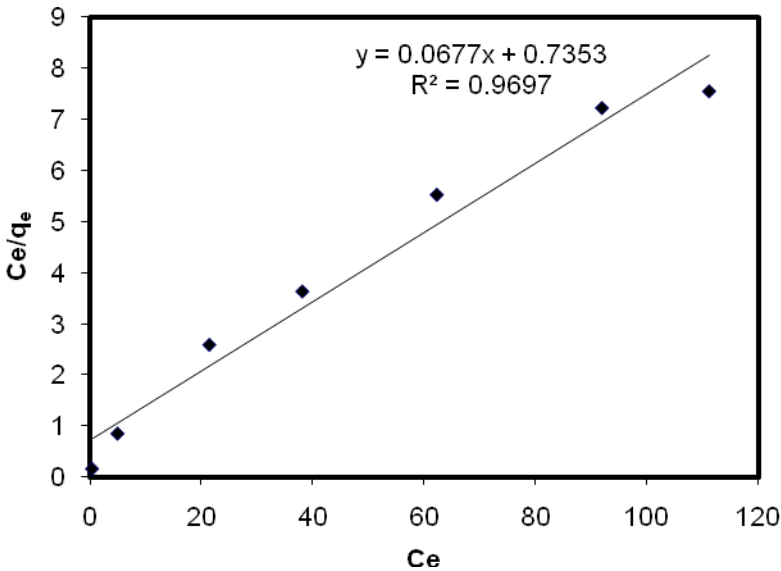
$$y = 0.0677x + 0.7353$$
$$R^2 = 0.9697$$

Figure 4: Langmuir plot for the adsorption of Cd(II) on Saudi activated bentonite.

The Freundlich isotherm is based on multilayer adsorption on heterogeneous surface [29]. Linear form of for the Freundlich equation is written as:

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{3}$$

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 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 is presented in Table (1) and plotted in fig. 5. The value of n between 1 and 10 shows good adsorption which indicating that Cd(II) is favorably adsorbed by Saudi activated bentonite.
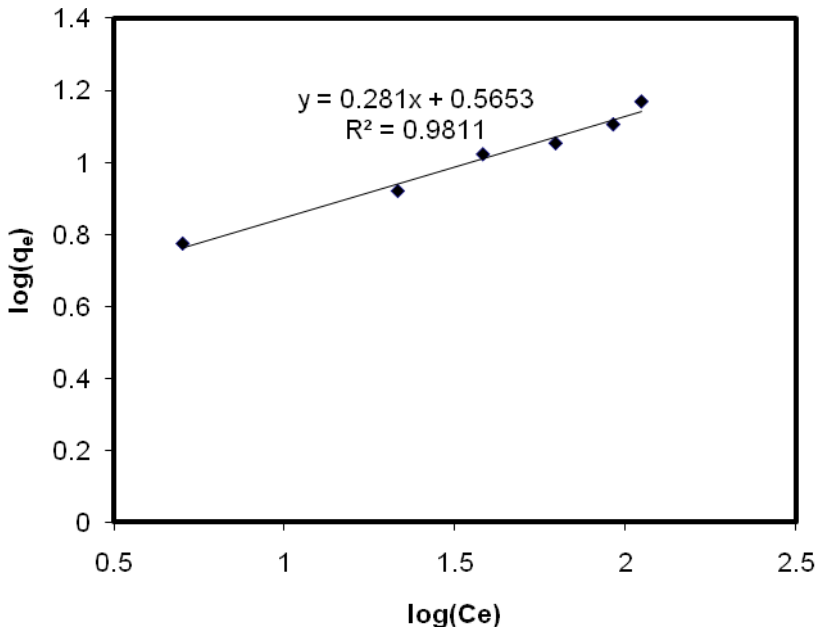

Figure 5:   Freundlich plot for the adsorption of Cd(II) on Saudi activated bentonite.

The adsorption isotherm data in general are well fitted with linearized Langmuir, and Freundlich.

4   Conclusions

Saudi activated bentonite was an effective adsorbent for removing Cd(II) from wastewater. Based on the experimental data, the following conclusions may be drawn:

- The sorption of cadmium ions on Saudi activated clay was fast and the equilibrium was reached after only 20 min.
- Removal of cadmium ions by Saudi activated bentonite is effected by mixture pH. The adsorption of metals increase with an increase in solution pH. Increasing pH more than 7 may cause precipitation rather than adsorption.
- The removal of cadmium increases as the dose of Saudi activated bentonite increases. This is due to increase in the number of adsorbent sites.
- The results of this investigation show that Saudi activated bentonite has a suitable adsorption capacity for the removal of Cd(II) from aqueous solutions.
- The experimental results were fitted well with Langmuir and Freundlich isotherm models.
- The present study concludes that the Saudi activated bentonite could be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal heavy metals from wastewater.

Acknowledgements

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