



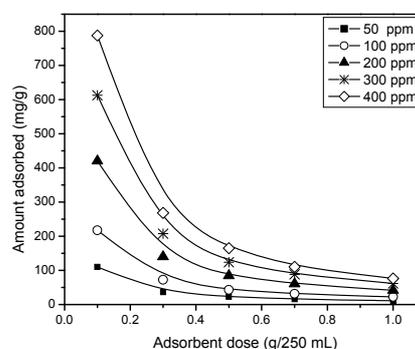
CADMIUM REMOVAL FROM WASTEWATER BY ADSORPTION USING NATURAL BENTONITE

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Cadmium (Cd^{2+}) is a heavy metal which is toxic even at trace level. It is bio-accumulative and persistent in nature. Therefore the adsorption properties of natural bentonite, and the removal of Cd^{2+} from aqueous solution were studied. The results show that the amount of adsorption of Cd^{2+} increases with initial metal ion concentration, contact time and solution PH but decreases with amount of adsorbent and temperatures. The adsorption process has fit pseudo-second order kinetic model. Langmuir and Freundlich adsorption isotherm models were applied to analyze adsorption data and was found to be applicable to adsorption process. Thermodynamic parameters, e.g. ΔG° , ΔS° and ΔH° of the adsorption process was found to be endothermic. Finally, it can be seen that bentonite was found to be effective for removal of Cd^{2+} .



INTRODUCTION

Cadmium removal from the waste water is a very important part of the research carried out in the environmental field.¹ There are several methods such as adsorption, biological methods, electro coagulation, electro dialysis and various membrane separation techniques for its removal from water and wastewater. In recent years, biosorption process has received huge expectations in academic, research, and industries due to its fascinating features.² Heavy metals were extensively known of difficult to eliminate. The biological treatment could not be applied to treat effluent water with metal contaminants due to their inhibitory ability of bacteria in the system.³ The physical and chemical treatment has been used in metal effluent removal. The adsorption method with different types of adsorbent has been used to treat these metals from wastewater.⁴⁻⁷ Many types

of clay have been reports of their high capability in adsorption.⁷ Bentonite clay is alumina-silicate clay mineral, which has been used, in metal absorption because of its physicochemical properties, i.e. large specific area, high cation exchange capacity and strong absorptive affinity with organic and inorganic substances, low cost and low permeability. Many research works have used natural bentonite clay as an adsorbent to eliminate metals from water.

There are many studies on the adsorption of Pb^{2+} , Cd^{2+} and Cu^{2+} . For example, Zou *et al.*⁸ studied the adsorption of Pb^{2+} and Cu^{2+} from aqueous solutions using manganese oxide coated zeolite. Goyal *et al.*⁹ and Chen and Wu¹⁰ investigated the adsorption of Cu^{2+} using activated carbon. In the study of Demirbas *et al.*,¹¹ Amberlite IR-120 synthetic sulfonated resin was used to adsorb Pb^{2+} , Cd^{2+} and Cu^{2+} . However, the use of these adsorbents is restricted due to high costs.

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Therefore, it is relevant to find suitable low cost adsorbent. Hence the presence of heavy metals in natural or industrial wastewaters is a subject of great interest in environmental science which is one of the most serious worldwide environmental problem.^{12,13} Among the different heavy metals, lead is one of the common and most toxic pollutants into the natural waters from various industrial activities such as metal plating, oil refining and battery manufacturing.¹⁴ Cadmium ions are taken into the body via inhalation, ingestion or skin adsorption. As a result, when the body is exposed to cadmium, it can act as a cumulative poison. Thus, the objective of this work is to understand the adsorption capacity of natural bentonite with cadmium metal. The effect of several parameters such as contact time, initial concentration, pH value of the solution, adsorbent dose, volume and temperature were studied. The adsorption isotherm was described by using Langmuir and Freundlich models. The adsorption mechanisms of Cd²⁺ ions onto bentonite evaluated in terms of thermodynamic and kinetic adsorption will be investigated.

EXPERIMENTAL

All chemicals used in this present work were either of analytical reagent or laboratory reagent grade and were used as received. Lead Nitrate supplied by BDH chemicals Ltd. Distilled water was used in all preparations. Lead nitrate and deionized water were used to prepare synthetic cadmium containing wastewater. Bentonite clay was used as an adsorbent and obtained from Egypt. Before the adsorption process, the surface of clay was modified with 1 mol/dm³ hydrochloric acid in a ratio of (1:1) and magnetically stirred for five to six hours at room temperature. It was then filtered by using Whatman 41 filter paper and dried at 70±1 °C in electric oven.

Magnetic hot plate stirrer was used to stir the heavy metal ion solutions with adsorbent bentonite. A definite volume of heavy metal ion solution with a known initial ion concentration was stirred with a definite amount of adsorbent for a certain time at fixed temperature and agitation rate. The pH values of the solutions were measured by digital pH meter (Model i pH system-361, India). The metal ion concentration was measured using atomic-absorption spectrophotometer, AAS, (Model, AA55; Varian Inc., USA).

Experimental procedures

Led Nitrate and redistilled water were used to prepare a stock solution with a concentration of 1000 ppm Cd²⁺ which was diluted for preparation of test solutions. Several solutions with different initial concentrations of potassium dichromate (50, 100, 200, 300 and 400 ppm) were prepared. The required pH was adjusted by drop wise addition of 0.1 N H₂SO₄ depending on the acidity of the sample. All experiments were

carried out at 25 °C by adding different amounts of adsorbents (0.1, 0.3, 0.5, 0.7 and 1.0 g) to different concentrations of 250 mL of heavy metal ion solution. The agitation rate for all experiments was 200 rpm and the residence time were (0, 15, 30, 45, 60, 75, 90 and 120 min). 1 mL of sample was taken from reaction solution and diluted to 10 mL of redistilled water; adsorbents were then separated from the solution by using filter paper (Whatman No. 40) and the residual Cd²⁺ ion concentration in the solution was then determined by atomic-absorption spectrophotometer. The effects of several parameters, such as contact time, initial concentration, adsorbent dose, pH and temperature on the adsorption of Cd²⁺ ions onto bentonite were studied.

Adsorption kinetics

The kinetics study for the adsorption of Cd²⁺ was completed in 2 h for the concentrations (50, 100 and 200 mg/L Cd²⁺ ions onto (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) doses of bentonite at 25°C.

Two kinetic models were considered to investigate the mechanism of cadmium adsorption, as follows:

Lagergren proposed a pseudo-first order kinetic model, the integral form of the model is:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (1)$$

Where q is the amount of lead sorbed (mg/g) at time t (min), q_e is the amount of cadmium sorbed at equilibrium (mg/g), K_1 is the equilibrium rate constant of pseudo-first order adsorption (min⁻¹). This model was successfully applied to describe the kinetics of many adsorption systems. The adsorption kinetics may also be described by a pseudo-second order reaction. The linearized-integral form the model is:

$$t/q = t/q_e + 1/k_2 q_e^2 \quad (2)$$

Where K_2 is the pseudo-second order rate constant of adsorption.

The applicability of the above two models can be examined by each linear plot of $\ln(q_e - q)$ vs. t , and (t/q) vs. t , respectively and are represented in Figs. (1). To quantify the applicability of each model, the correlation coefficient, R^2 , was calculated from these plots. The linearity of these plots indicates the applicability of the two models. However, the correlation, R^2 , showed that the pseudo-second order model, fits better the experimental data ($R^2 > 0.990$) than the pseudo-first order model (R^2 in the range of 0.9108 – 0.986), the kinetic parameters calculated are shown in Table 1.

Effect of contact time

The effect of contact time on the adsorption of Cd²⁺ ions onto bentonite was performed by contacting of (50, 100, 200, 300 and 400 mg/L) of Cd²⁺ concentration at initial pH 5.5 onto (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) of adsorbent dose. The results are depicted in Figs. (2). The Cd²⁺ adsorption rate is high at the beginning of the adsorption because the adsorption sites are open and Cd²⁺ interacts easily with these sites. A larger amount of Cd²⁺ was removed in the first 1 h of contact time, and after that Cd²⁺ increased slowly till equilibrium time (2 h). The relationship between the amount of adsorbed Cd²⁺ ions per gram of adsorbent and contact time in the presence of different amounts of bentonite is illustrated in Figs. (3,4). It can be seen that, q_e increased rapidly with increasing time till the maximum adsorption.

Effect of adsorbent dose

The effect of adsorbent dosage (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) for bentonite on % removal of (50, 100, 200 and 400 mg/L) of Cd^{2+} ions concentrations at 25°C is shown in Figs. (5,6). It is apparent that by increasing the dosage, % removal increased till reaching maximum at 1.0 g dosage of bentonite. The increase in percentage of removal as the dosage was increased due to the increased in the surface of adsorbent. A higher adsorbent dosage also reflects a greater number of available adsorption sites,¹⁵ therefore, more cadmium ions

were able to be adsorbed. On the other hand, the adsorption capacity decreased with the increase in adsorbent dosage for adsorbent Figs. (5,6). It is important to note that the concentration of cadmium was fixed while the adsorbent dosage was increased. Therefore, as the dosage increased, the ratio of number of adsorption sites to the number of heavy metal ions would increase and there would be plenty of unadsorbed adsorption sites. Another possible reason could be due to the particle aggregation, which would lead to a decrease in total surface area of the adsorbent.¹⁶

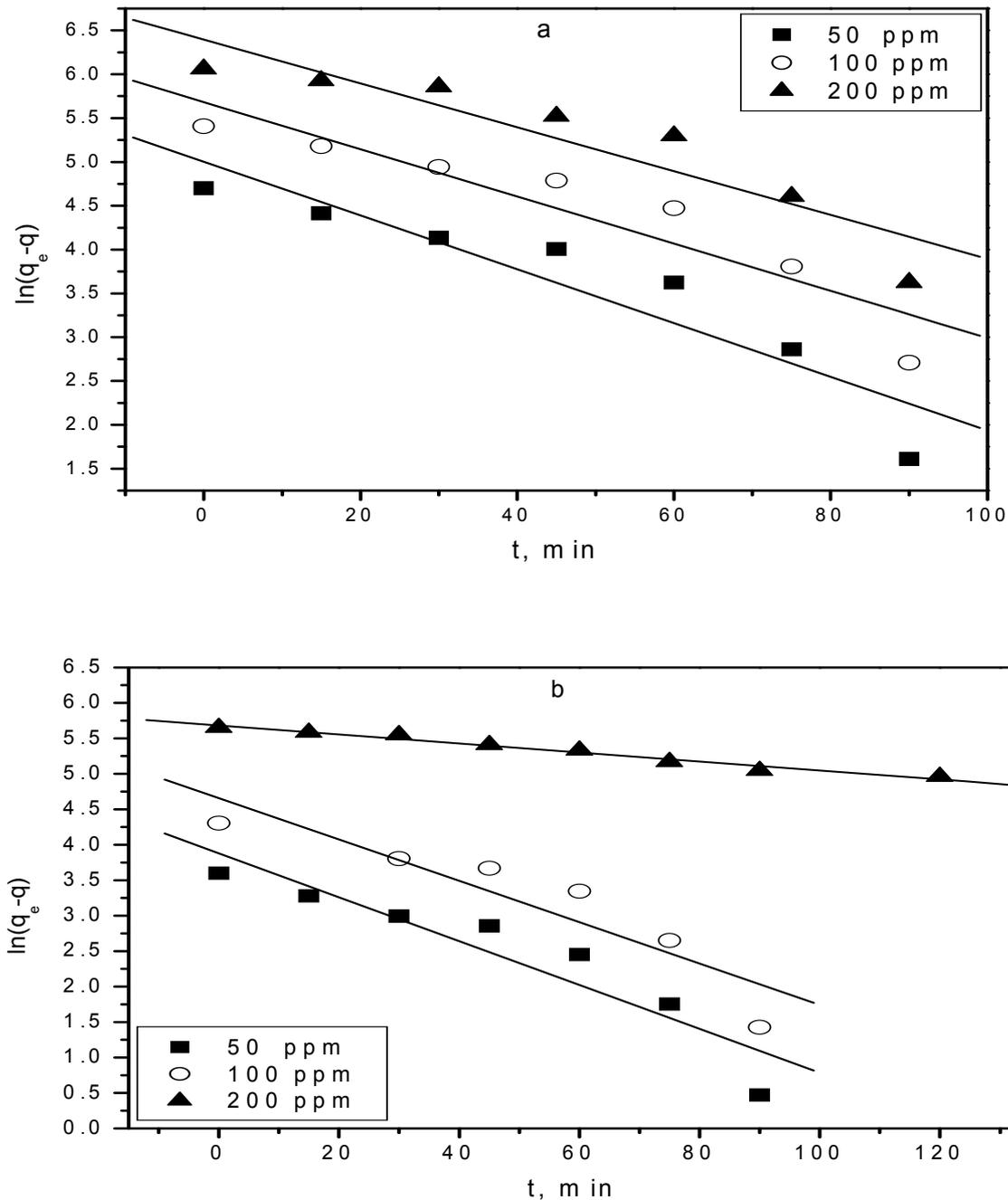


Fig. 1 – Pseudo-first order kinetic plots for the adsorption of different initial concentrations: 50, 100 and 200 ppm Cd^{2+} ions onto different adsorbents doses of bentonite: a) 0.1 g/250 mL and b) 0.3 g/250 mL, (pH: 5.5; agitation speed: 200 rpm; temperature: 25°C).

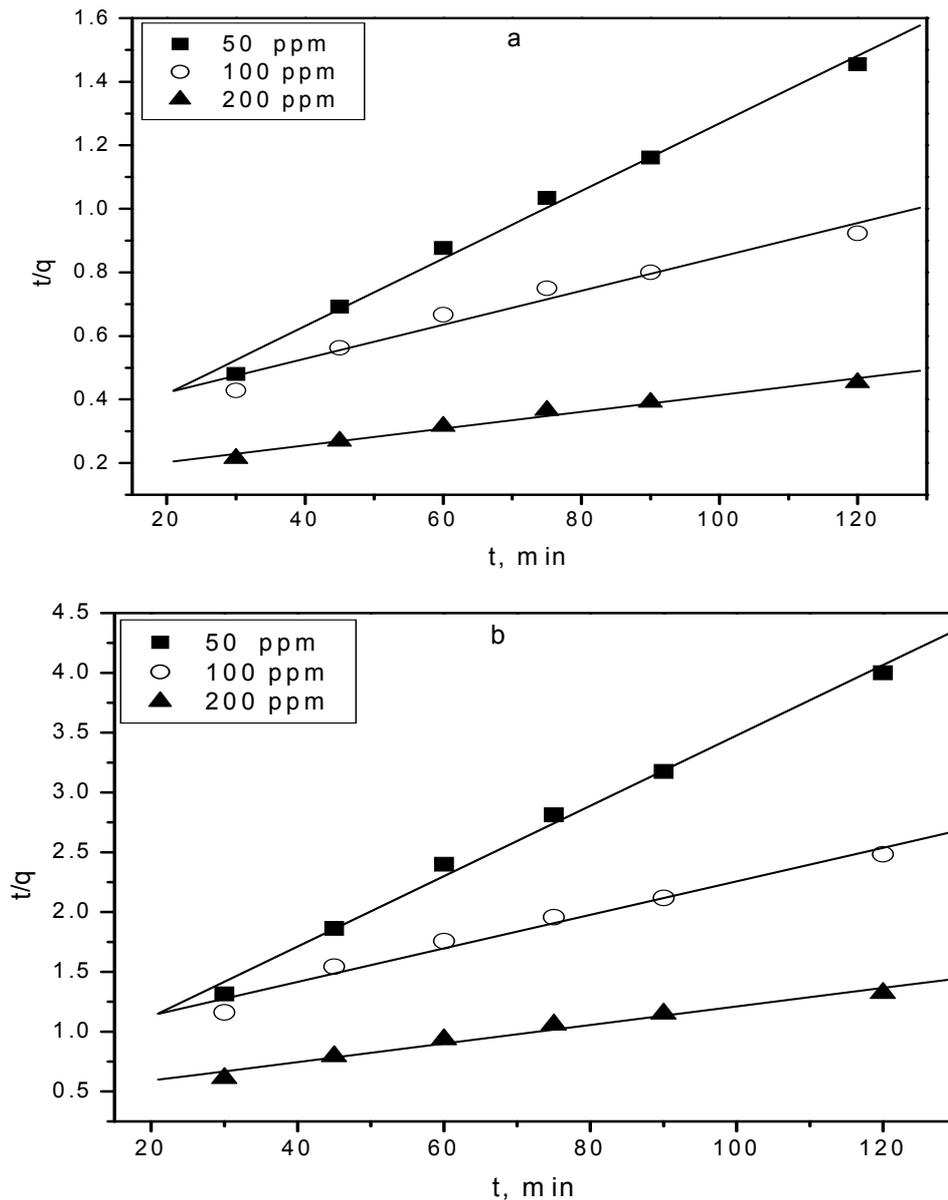


Fig. 2 – Pseudo-second order kinetic plots for the adsorption of different initial concentrations: 50, 100 and 200 ppm Cd²⁺ ions onto different adsorbents doses of bentonite: a) 0.1 g/250 mL and b) 0.3 g/250 mL, (pH:5.5; agitation speed: 200 rpm; temperature: 25°C).

Table 1

The adsorption kinetics model rate constants for adsorption of Cd²⁺ ions onto bentonite at various concentrations and constant temperature 25 °C

Adsorbent (0.1 g)	C ₀ (mg/L)	q _{e, exp.} (mg/g)	Lagergren first order			Pseudo-second order		
			K ₁ (min ⁻¹)	q _{1, theo.} (mg/g)	R ²	k ₂ (gmg ⁻¹ min ⁻¹)	q _{2, theo.} (mg/g)	R ²
Bentonite	50	110	3.1x10 ⁻²	148	0.932	1.1x10 ⁻³	108	0.998
	100	222	2.6x10 ⁻²	293	0.933	1.9x10 ⁻⁴	220	0.995
	200	427	2.5x10 ⁻²	559	0.925	1.3x10 ⁻⁴	420	0.996
Adsorbent (0.3 g)	C ₀ (mg/L)	q _{e, exp.} (mg/g)	Lagergren first order			Pseudo-second order		
			K ₁ (min ⁻¹)	q _{1, theo.} (mg/g)	R ²	k ₂ (gmg ⁻¹ min ⁻¹)	q _{2, theo.} (mg/g)	R ²
Bentonite	50	36	3.0x10 ⁻²	48	0.936	2.0x10 ⁻³	35	0.998
	100	74	2.9x10 ⁻²	105	0.920	3.7x10 ⁻⁴	72	0.996
	200	285	6.3x10 ⁻²	293	0.987	2.9x10 ⁻⁴	283	0.998

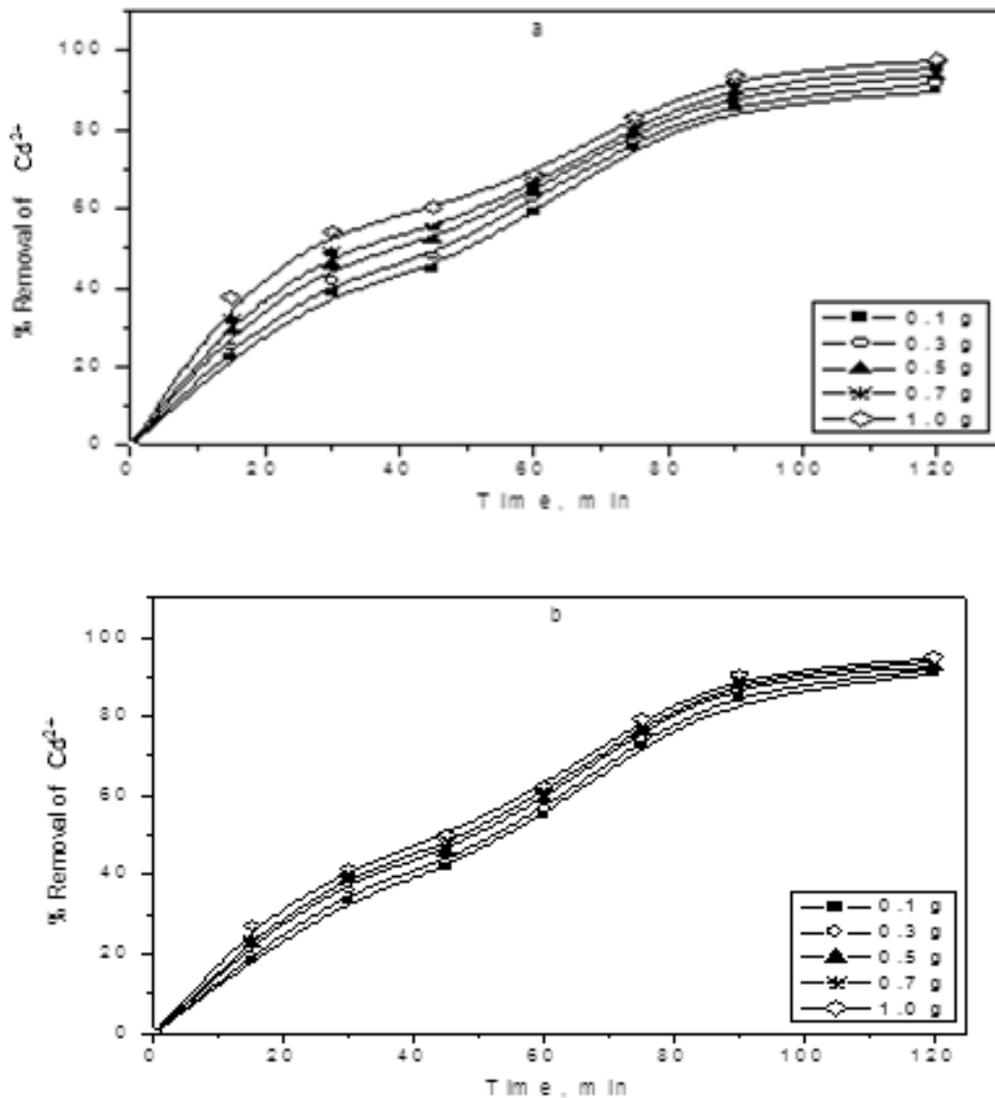


Fig. 3 – Effect of contact time (min) on % removal of Cd^{2+} ions for: a) 50 ppm and b) 100 ppm, in the presence of different amounts of bentonite (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h).

Effect of initial cadmium(II) ion concentration

Figs. (7,8) Show the effect of varying the initial concentration of Cd^{2+} ions from 50 to 400 mg/L on the adsorption under the optimized conditions of pH 5.5 at 25°C and (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) of bentonite. It can be seen from the figures that, with increased Cd^{2+} initial concentration, there was decrease in % removal of Cd^{2+} for both adsorbent. However, the amount of metal adsorbed per unit weight of adsorbent, q , is higher at high concentration as shown in Figs. (7,8) for bentonite. According to¹⁷ the adsorption capacity and percentage of removal are equally important in adsorption experiments because both factors usually take part in deciding the adsorption performance of given adsorbent.

Effect of pH on the uptake of Cd^{2+}

The influence of pH on the adsorption of Cd^{2+} on bentonite examined in the pH range 1-5.5, initial concentration of Cd^{2+} 100 mg/L and adsorbent dose 0.5 g/250 mL for selected adsorbent at 25°C. Figs.(9) shown that for bentonite, %

removal of Cd^{2+} , it can be seen that, there is a decrease in pH 4. This decrease in the adsorption of Cd^{2+} probably reflects a reduction in the quantity of negative surface charges on the clay. At low pH, the silica attracts positively charged adsorbate ions by coulombic forces. This negative charge density on the surface of the adsorbent decrease as the pH increases and this leads to low adsorption of Cd^{2+} from wastewater at high pH. It is therefore evident, that the presence of a negative charge Cd^{2+} on the silica surface sites of the adsorbent over the pH range investigated is the main reason for Cd^{2+} adsorption.

Adsorption isotherm

The equilibrium adsorption isotherms are one of the promising data to understand the mechanism of the adsorption. Various isotherm equations are well known and two different isotherms are selected in this study, which are the Langmuir and Freundlich isotherms.

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful applications in many

adsorption processes of monolayer adsorption. The linearized Langmuir isotherm equation is represented by the following.¹⁸

$$C_e/q_e = 1/(q_{max}b) + (1/q_{max}) C_e \quad (3)$$

where q_{max} is the maximum metal ion uptake per unit mass of adsorbent (mg/g), which is related to the adsorption capacity and b is Langmuir constant (L/mol) which is exponentially proportional to the heat of adsorption and related to the adsorption intensity. Therefore, a plot of C_e/q_e versus C_e for the adsorption of Cd^{2+} ions onto bentonite gives a straight line of the slope $1/q_{max}$ and intercept $1/(q_{max}b)$ as shown in Figs. (10).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The linearized form of the Freundlich isotherm equation is:¹⁹

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (4)$$

where the Freundlich constants K_F and n , which respectively, indicating the adsorption capacity and the adsorption intensity, were calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$ for the adsorption of Cd^{2+} ions onto bentonite as shown in Figs. (11).

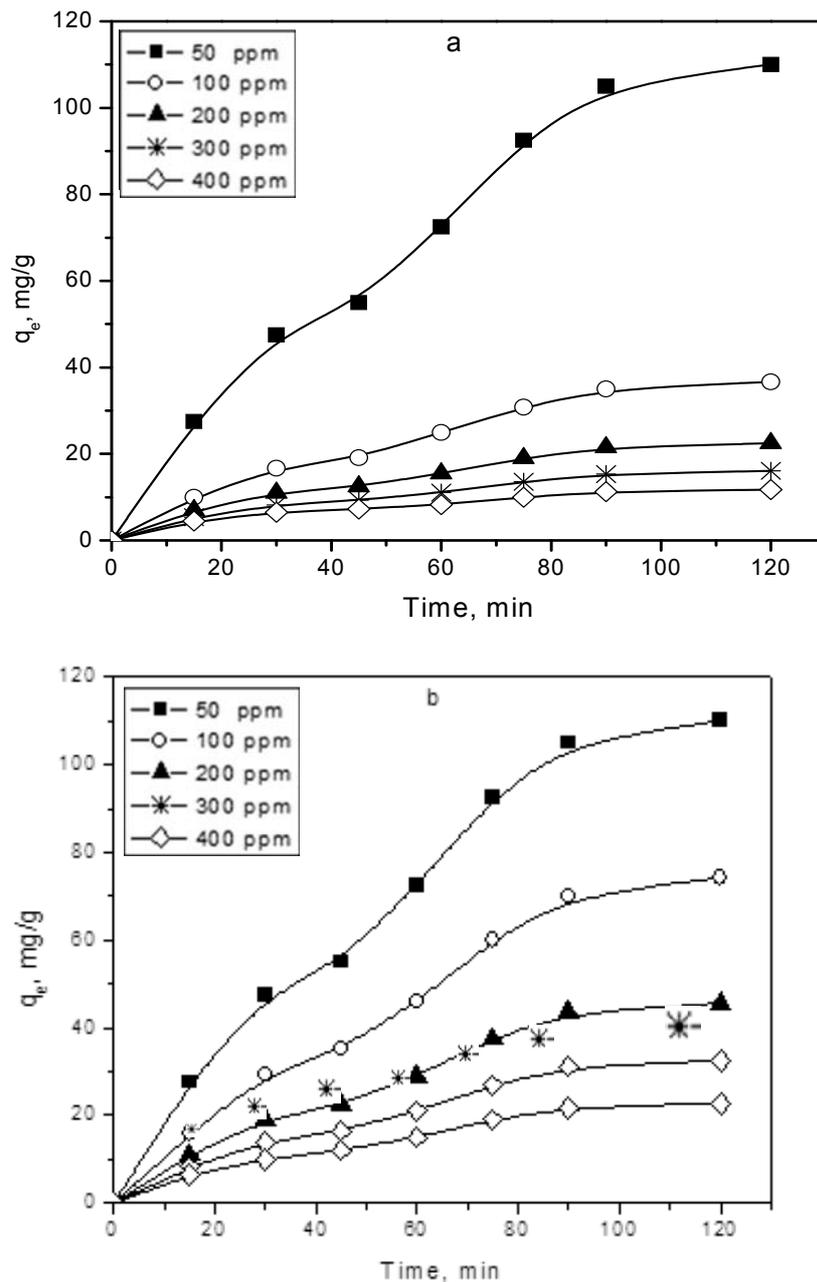


Fig. 4 – Effect of contact time on the adsorbed amount of Cd^{2+} for different concentrations: a) 50 ppm, b) 100 ppm, in the presence of different amounts of bentonite (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h).

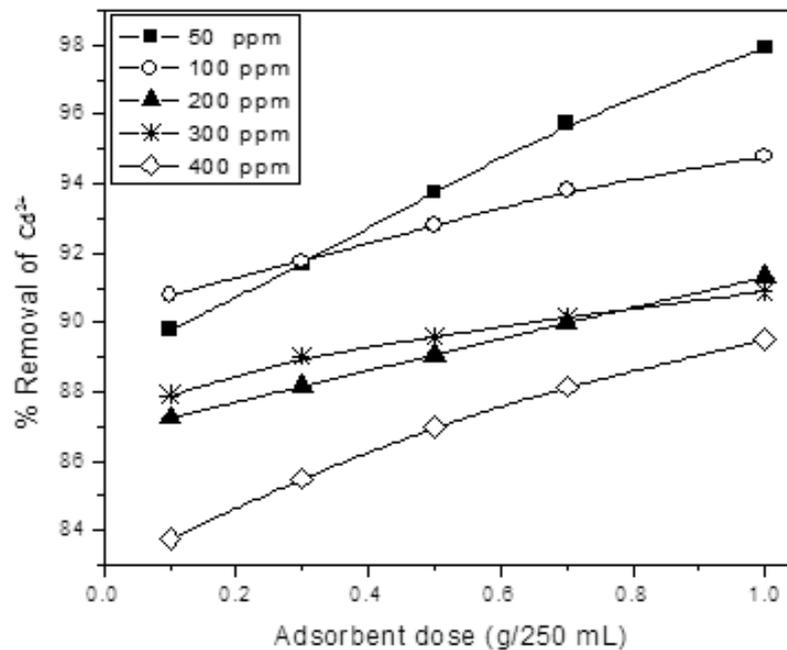


Fig. 5 – The effect of varying bentonite adsorbent doses (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) on % removal for different Cd²⁺ ions initial concentrations solution at 25°C.

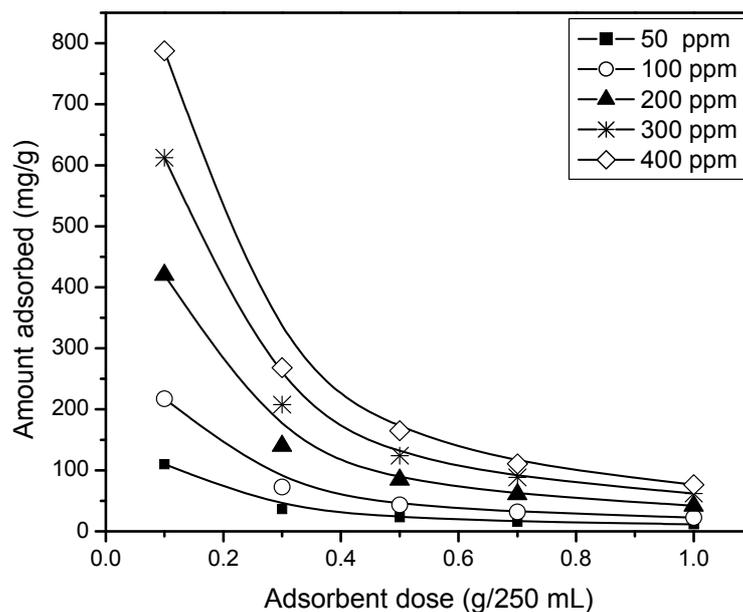


Fig. 6 – The effect of varying bentonite adsorbent doses (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) on the quantity adsorbed for different Cd²⁺ ions initial concentration solutions at 25°C.

The Langmuir and Freundlich parameters for the adsorption of (50, 100 and 200 mg/L) initial concentrations of Cd²⁺ on (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) for bentonite at 25°C are listed in Table 2. In other words, the Freundlich isotherm model fits very well than that of the Langmuir isotherm model when the R^2 values are compared in Table 2 (R^2 values of Freundlich plot > 0.99 were close to unity, indicating isotherm data fitted well to Freundlich model). The Freundlich constant n is the measure of the deviation from

linearity of the adsorption. If a value for n is below unity, this implies that adsorption process is governed by a chemical mechanism, but a value of n is above to unity, adsorption is favoring a physical process. The values of n at equilibrium are between (1.70-1.87), representing favoring adsorption at studied temperatures and therefore this would seem to suggest that a physical mechanism, which is referred the adsorption bond weak,²⁰⁻²⁴ and conducted by Van der Waales forces.

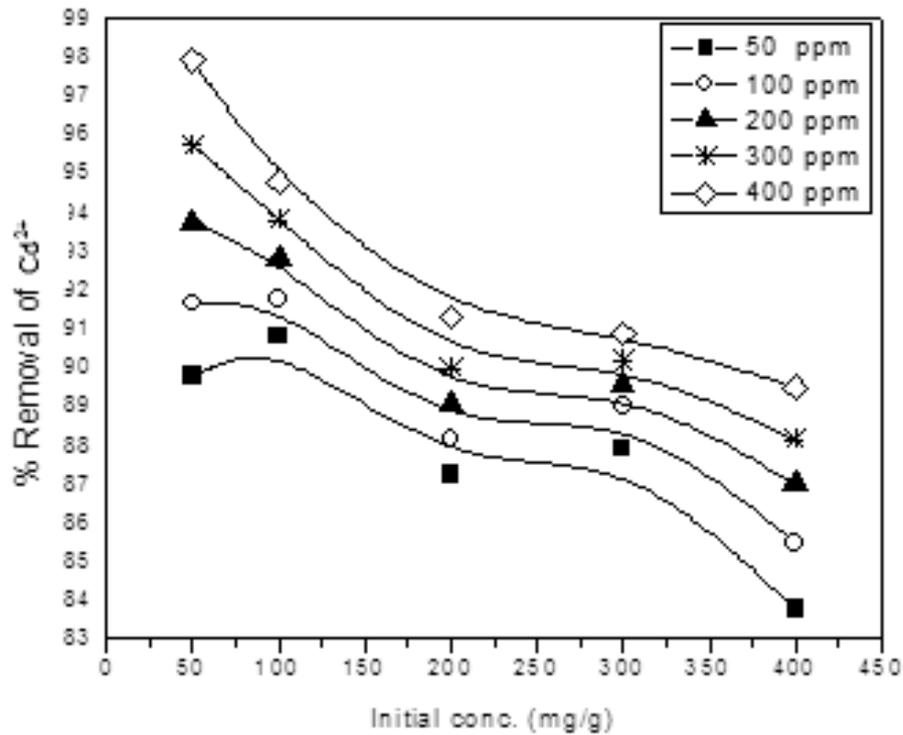


Fig. 7 – The effect of initial concentrations (namely 50, 100, 200 and 300 mg/L) on % removal of Cd^{2+} ions in the presence of different amounts of bentonite (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h).

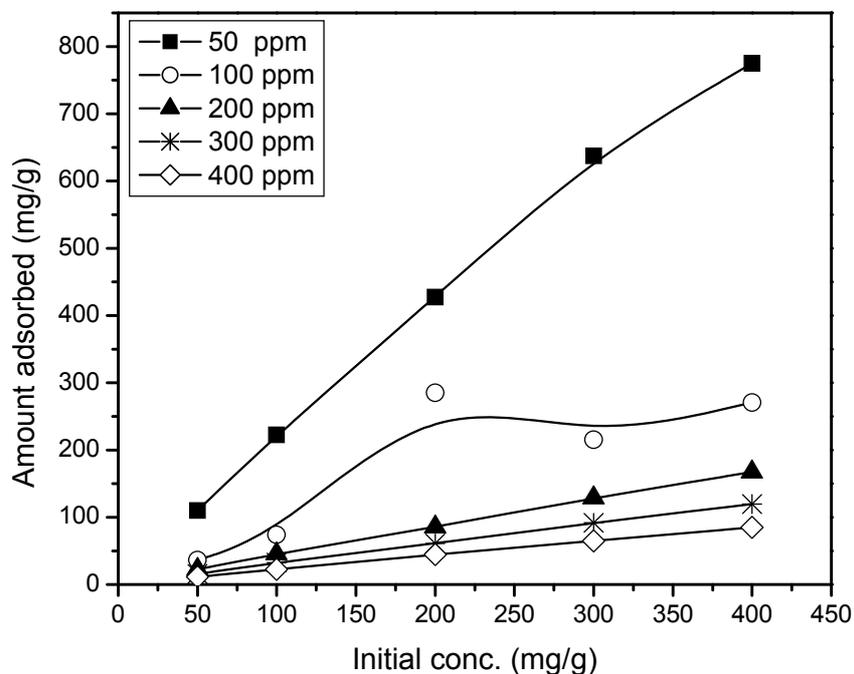


Fig. 8 – The effect of initial concentrations (namely 50, 100, 200 and 300 mg/L) on quantity adsorbed of Cd^{2+} ions in the presence of different amounts of bentonite (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h).

Plots of (q_e) versus (C_e) are represented in Figs. (12), from figures (q_e) increased by increasing (C_e) suggesting a very

strong surface interaction between the metal ions Cd^{2+} and adsorbents (bentonite).

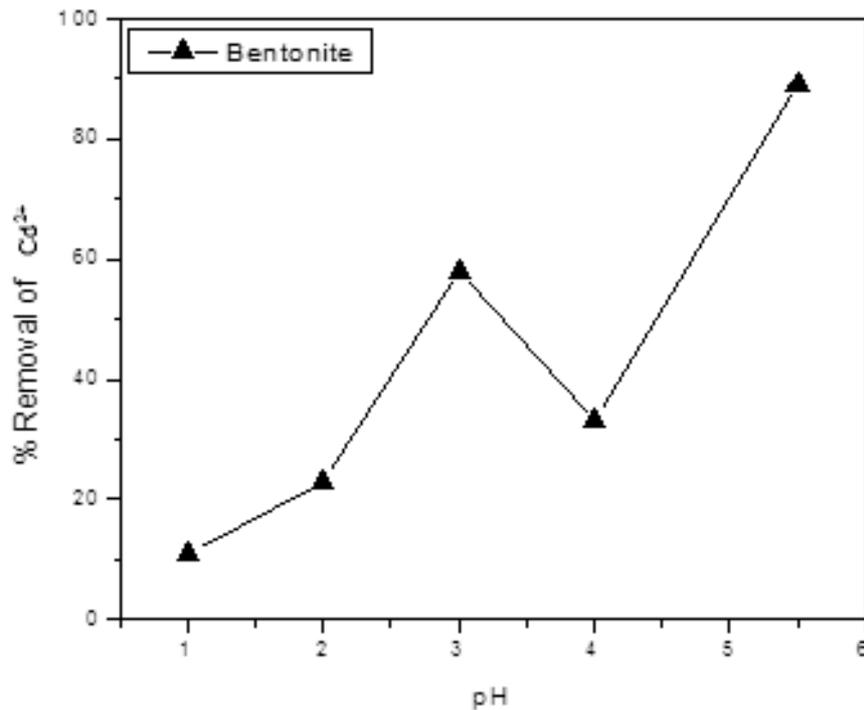


Fig. 9 – Effect of pH value for the adsorption of Cd²⁺ ions onto bentonite (conditions; Cd²⁺ ions initial concentration: 100 mg/L; adsorbent dose: 0.5 g/250 mL; agitation speed: 200 rpm; contact time: 2 h) at 25°C.

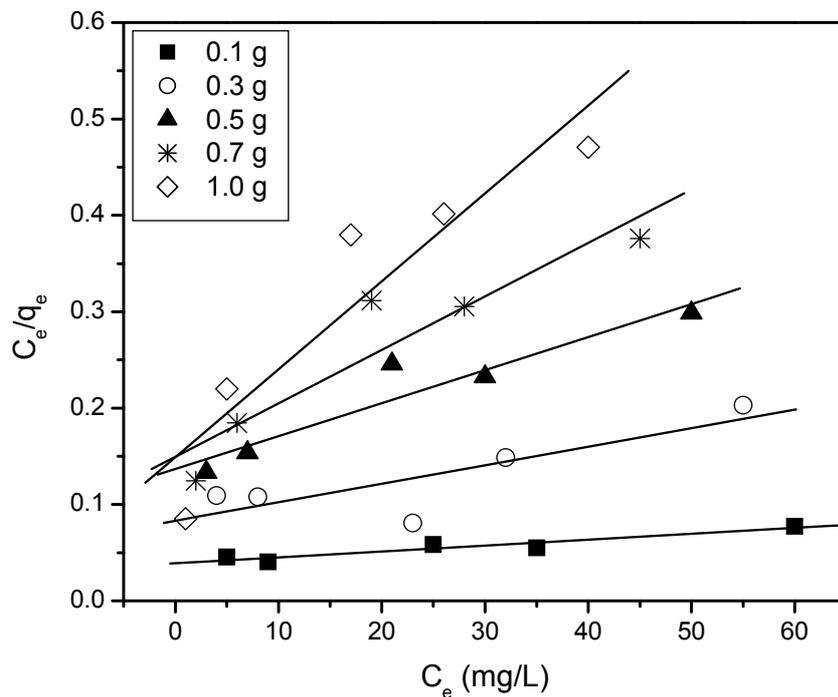


Fig. 10 – Langmuir adsorption isotherm for Cd²⁺ ions adsorption onto different amounts of bentonite at constant temperature 25°C and contact time 2 h.

Thermodynamic parameters

The determination of thermodynamic parameters has a great importance to evaluate spontaneity and heat change for the adsorption reactions. Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes of adsorption can be evaluated from the following equations:

$$K_c = C_{Ae}/C_e \quad (5)$$

$$\Delta G^\circ = -RT \ln K_c \quad (6)$$

where K_c is the equilibrium constant and C_{Ae} and C_e (both in mg/L) are the equilibrium concentrations of solute on the sorbent and in the solution, respectively. The K_c values are

used in Eqs. (5) and (6) to determine the ΔG° , ΔH° and ΔS° , the K_c may be expressed in terms of the ΔH° (kJ mol^{-1}) and ΔS° ($\text{kJ mol}^{-1}\text{K}^{-1}$) as a function of temperature, Eq. (7):

$$\ln K_c = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (7)$$

Thermodynamic parameters such as free energy of sorption (ΔG°), the heat of sorption (ΔH°) and standard entropy (ΔS°) changes during the sorption process were

calculated using Eqs. (6) and (7) on a temperature range of 25-40°C at initial concentrations (50, 100, 200, 300 and 400 mg/L) of Cd^{2+} ions and dose 0.5 g/250 mL for bentonite, (ΔH°) and (ΔS°) were obtained from the slope and intercept of a plot of $\ln K_c$ versus $1/T$ Figs. (13). The values of these parameters were recorded in Table 3.

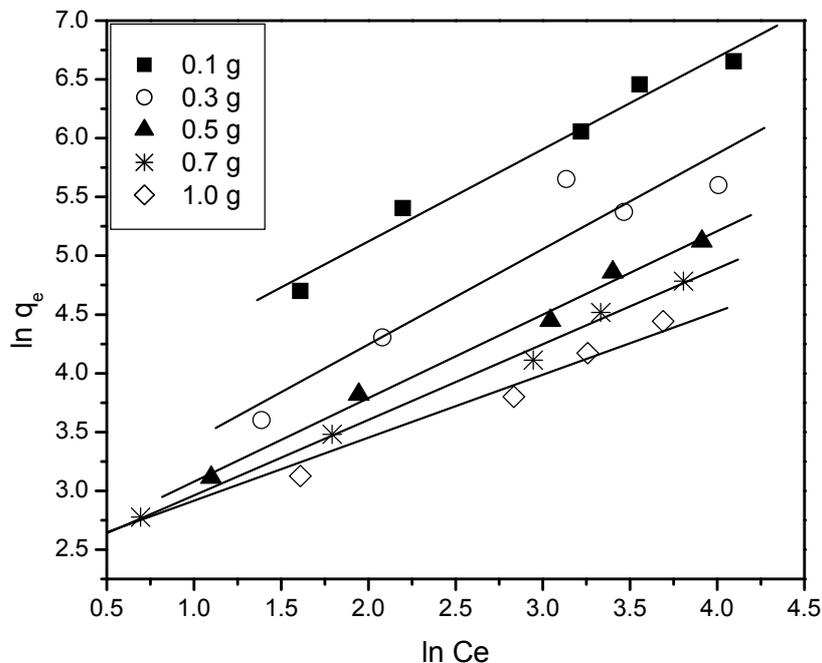


Fig. 11 – Freundlich adsorption isotherm for Cd^{2+} ions adsorption onto different amounts of bentonite at constant temperature 25°C and contact time 2 h.

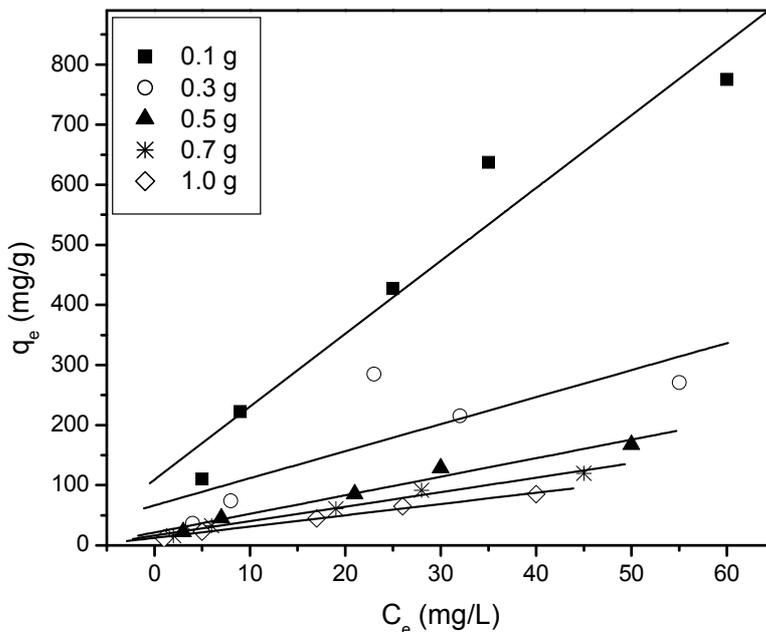


Fig. 12 – Equilibrium isotherm of Cd^{2+} ions adsorption using different amounts of bentonite at constant temperature 25°C and contact time 2 h.

Table 2

Langmuir and Freundlich isotherm for the adsorption of Cd^{2+} ions onto different doses of bentonite at constant temperature (25°C)

Adsorbent (0.1 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q_{max} (mg/g)	b (L/mol)	R^2	K_F (mg/g)	n	R^2
Bentonite	31	1.7×10^{-2}	0.965	35	1.231	0.990
Adsorbent (0.3 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q_{max} (mg/g)	b (L/mol)	R^2	K_F (mg/g)	n	R^2
Bentonite	73	2.3×10^{-2}	0.785	13.730	1.231	0.991
Adsorbent (0.5 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q_{max} (mg/g)	b (L/mol)	R^2	K_F (mg/g)	n	R^2
Bentonite	85	2.5×10^{-2}	0.852	10.68	1.408	0.992
Adsorbent (0.7 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q_{max} (mg/g)	b (L/mol)	R^2	K_F (mg/g)	n	R^2
Bentonite	243	2.7×10^{-2}	0.881	10.17	1.556	0.995
Adsorbent (1 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q_{max} (mg/g)	b (L/mol)	R^2	K_F (mg/g)	n	R^2
Bentonite	110	6.2×10^{-2}	0.886	10.866	1.516	0.990

The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of the adsorption of Cd^{2+} onto bentonite. On the other hand, the more negative value with increase of temperature indicates that a better adsorption is actually obtained at higher temperatures. The positive values of ΔH° confirmed the endothermic nature of adsorption

which was also supported by the increase in value of Cd^{2+} uptake of the adsorbent with the rise in temperature. The positive values of ΔS° showed the increased randomness at solid/solution interfaces during the adsorption of metal ions onto both adsorbents and also reflected the affinity of bentonite toward Cd^{2+} ions under consideration.

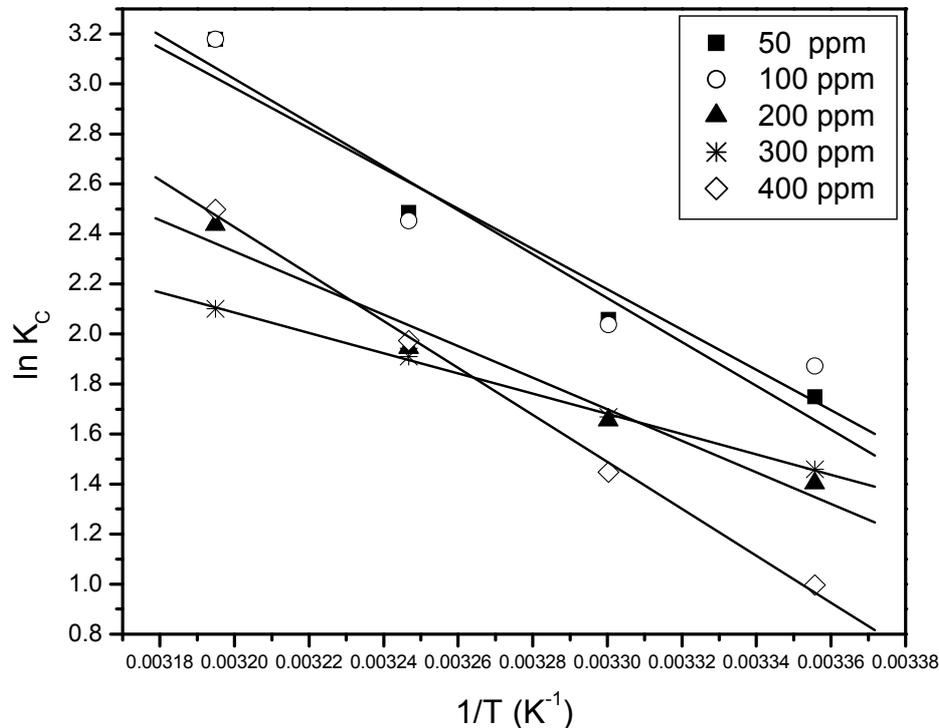


Fig. 13 – A plot of $\ln K_c$ versus $1/T$ for Cd^{2+} ions adsorption onto bentonite for different initial concentrations at constant adsorbent dose: 0.5 g/250 mL.

Table 3

Thermodynamic parameters for different concentrations of Cd²⁺ ions onto bentonite

Adsorbent	C _o (mg/L)	ΔH° (kJ mol ⁻¹)	ΔS° (j mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)			
				25°C	30°C	35°C	40°C
Bentonite	50	72	258	- 3.9	- 5.3	- 6.5	- 7.8
Bentonite	100	67	239	- 4.3	- 5.5	- 6.7	- 7.9
Bentonite	200	52	187	- 3.3	- 4.3	- 5.2	- 6.3
Bentonite	300	34	125	- 3.6	- 4.2	- 4.9	- 5.5
Bentonite	400	78	269	- 2.1	- 3.5	- 4.9	- 6.2

CONCLUSION

The removal of Cd²⁺ from waste water becomes an important issue for environmental study. In this paper, bentonite clay is used to study both kinetics and equilibrium mechanism.

For the kinetic study, the pseudo-second-order model can describe the adsorption kinetic for metal adsorption on the adsorbate quite well while the adsorption isotherm corresponds to that of Langmuir and Freundlich adsorption isotherm models. The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of the adsorption of Cd²⁺ onto bentonite. The results show that the amount of adsorption of Cd²⁺ increases with initial metal ion concentration, contact time and solution PH but decreases with amount of adsorbent and temperatures. Bentonite clays should be a promising material to adsorb the heavy metal from waste water

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