

Thermodynamics and Kinetic Study of Using Modified Clay as an Adsorbent for the Removal of Zn ions from waste water

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Abstract: The present study was carried out to investigate the adsorption capacity of bentonite in the removal of Zn ions from waste water. The study also covered the thermodynamics parameters of the batch adsorption (the Gibbs free energy, entropy, and enthalpy). The results revealed that the amount of adsorption of zinc metal ion increases with increasing contact time from 30 min to 150 min., increasing stirring rate up to 300 r.p.m, solution pH range (2-12), and the optimum pH was 6, and adsorbent dosage from 0.1 to 0.5 g. But decreased with increasing temperature range from 20^o C to 80^o C. The experiments were carried out for the analysis of adsorption equilibrium capacities using a batch equilibrium technique. The process of uptake follows both the Langmuir and Freundlich isotherm models and also the second-order kinetics. The maximum removal of zinc (99%) was observed with initial concentration of 50 mg/L and 0.3 g of bentonite, speed rate of 300 r.p.m. with 30 min time of contact and temperature of 20^oC

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Key words: Adsorption; thermodynamics, heavy metals; isotherms; kinetics; clay; zinc salts.

1. Introduction

Zinc is found naturally at low concentrations in many rocks and soils principally as sulphide ores and to a lesser degree as carbonates. Zinc can be introduced into water naturally by erosion of minerals from rocks and soil, however since zinc ores are only slightly soluble in water [1]. Zinc is only dissolved at relatively low concentrations. High natural levels of zinc in water are usually associated with higher concentrations of other metals such as lead and cadmium. Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissue and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia. Many technologies have been developed to remove heavy metals from contaminated waters, such as chemical precipitation, ion exchange, filtration, solvent extraction and membrane technology [2-5]. These techniques were found not effective due to either being extremely expensive or too inefficient to reduce such high levels of ions from the large volumes of water [6,7]. Therefore, the adsorption is usually used in the water treatment field and the investigation has to be made to determine inexpensive and common available good adsorbent. The utilization of clays as an adsorbent material has been applied for the last few decades [8-12] for the removal of heavy metals. Bentonite is an adsorbent aluminum phyllosilicate and is mainly composed of montmorillonite (smectite) with some other clays and

inorganic minerals [13, 14]. The high specific area and the ability of holding water in the interlayer sites gave clays excellent adsorbent capacity which could be increased by acid activation and/or thermal treatment [15]. Therefore, there are a number of studies that have been reported using clays mainly bentonite to show their effectiveness for removal of metal ions such as Zn⁺², Pb⁺², and Al⁺³, from water [16-19]. The purpose of this study was to investigate the adsorption characteristics of zinc (II) ion on bentonite. A SEM and x-ray diffraction were made to a sample of bentonite which show the morphology study and the chemical characteristics of the clay. The objective of this study is to investigate the effect of various parameters such as the effects of pH, bentonite doses, temperature, and contact time on the adsorption efficiency of removal of zinc from solution. This fundamental study will be helpful for further application in treatment of water containing heavy metal ions beyond their permissible limits.

2. Material and methods

2.1. Chemicals

Experimental solutions of the desired concentrations were obtained by successive dilution with distilled water. Zinc Sulphate ZnSO₄.7H₂O (Merck, USA) was used as a source of zinc salt in the adsorption experiments. A stock solution of zinc sulfates solution was prepared by using an analytical grade chemicals and dissolving them in distilled water. pH measurements were carried out using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH). A digitally calibrated pH-meter (Hanna,

Model pH 211) was used to measure the pH of each solution.

2.2. Physicochemical Characterization of Adsorbent

Bentonite clay was supplied from the Sphinx milling station Company (Alexandria free zone, Egypt). It was characterized by x-ray fluorescence (XRF) using AXIOS PANalytical2005. The analysis was made in Central Metallurgical Research Institute in Alexandria. Table (1) shows the oxides constituents of the studied bentonite clay. A scan electron microscope with different magnification was done on dry base for a sample of clay to specify the morphological features of bentonite as shown in Figure. [1]. This bentonite has low alumina content (16.14%) and contains high silica contents (55.12%). Bentonites show higher distribution of

alkali oxides. There is general agreement between the current obtained values for both major oxide contents and with the calculated values and recorded results previously obtained for Egyptian kaolin and bentonite [20-22].

Table (1), Chemical characterization of bentonite

Oxides	Wt. %
SiO ₂	55.12
Al ₂ O ₃	16.14
Fe ₂ O ₃	8.25
CaO	1.17
TiO ₂	1.18
MgO	2.86
K ₂ O	1.05

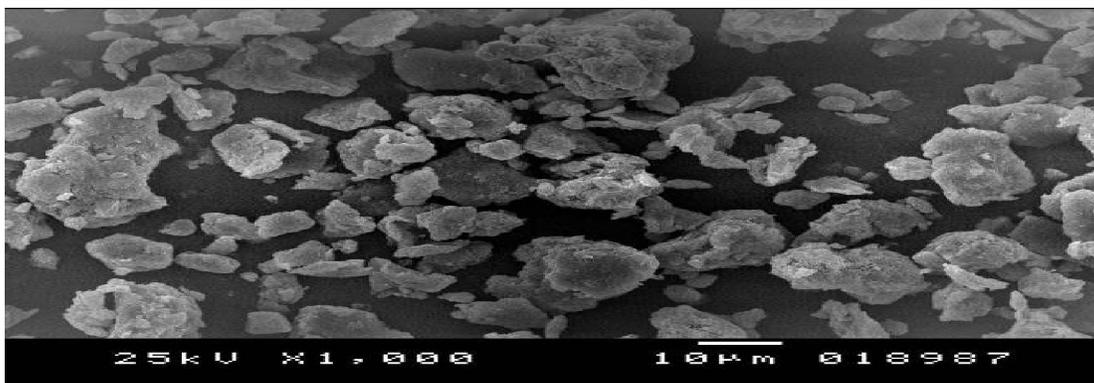


FIGURE 1. Scanning electron microscope (SEM) of dry bentonite

2.3. Adsorption procedure

The required weight of an adsorbent (bentonite) was prepared. Then the stock solution containing 1000 mg of metal ion solutions (Zn.SO₄.7H₂O) were prepared from their stock solutions and then was mixed with different weight of adsorbents. The solutions were then agitated at room temperature or at other experimental temperature to study the thermodynamics of the experiments. After mixing for a time specified according to experimental conditions the samples were filtered using Whatman filter paper and the filtrates were analyzed using flame atomic absorption spectrophotometer (FAAS) (Model ICE 3000, Thermo Fischer-USA). The experiments were conducted using an orbital shaker incubator at 293K under given pH conditions for a known period of time. Adsorption experiments were carried out in flasks of 100mL. The percentage of removal of the heavy metal ions (%R) in solution was calculated using Equation (1):

$$\% \text{ Removal} = \frac{C_0 - C_t}{C_0} * 100 \quad (1)$$

Where:

C₀= Initial concentration of heavy metal (mg/L).

C_t= Heavy metals concentrations (mg/L) at a given time t.

V= Volume of the heavy metals solutions (L).

Calculations were made by using these data and adsorption curves were obtained.

3. Results and Discussion

3.1. Effect of shaking time

In order to study the uptake of adsorption process and to know the kinetics of the adsorption process. The effect of shaking time or contact time was studied as a function of percentage removal of zinc ions. From Fig. (2) it was found that as the contact time between zinc ions and bentonite increased the percentage removal increased and complete removal was observed after 60 mins for 50 mg/L of initial concentration of zinc ions. It was also seen that the rate of adsorption was very rapid at first 30 mins then it was nearly became in equilibrium which can be explained that the available adsorption sites available were sufficient in the beginning. As the process goes on, the adsorption sites became saturated gradually. The uptake rate was controlled by the rate at which the adsorbate is transported from

the exterior to the interior sites of the adsorbent

particles, so the adsorption became much slower [23].

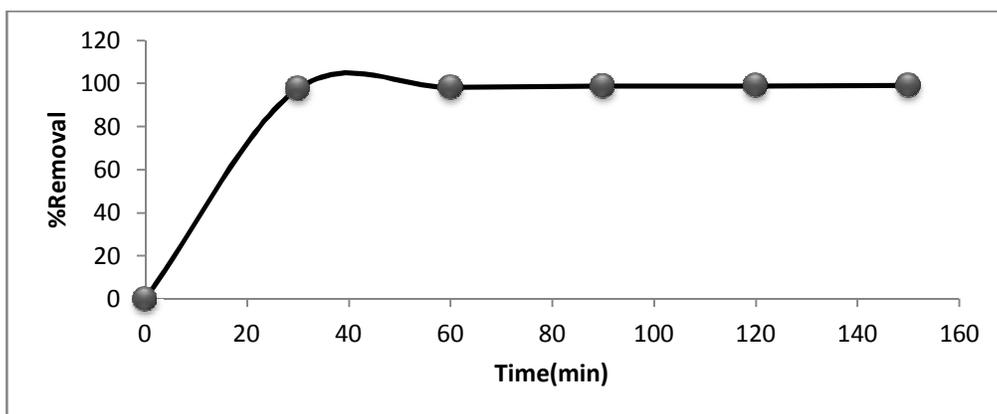


FIGURE.2. Effect of contact time on percentage removal of Zn.
($C_0=50\text{mg/L}$, $\text{pH} = 6$, stirring rate = 300 r.p.m., and Temp. = 25 °C)

3.2. Effect of pH

The effect of pH on the residual concentration and percentage removal of Zn (II) were investigated in Figs(3&4) by using initial concentration of Zn(II) (50 mg/L) and 1 g/L of bentonite .The Figs revealed that as pH of the solutions increased from (2 to 12) the percentage removal of Zn (II) increased from 88.553 % to 98.8005 % and the residual

concentration decreased from 5.7235 mg/L to 0.59975 mg/L .From previous results it was found that the optimum pH for all experiment was 5. The decreased adsorption at low pH is obviously due to stiff competition faced by the metal ion from the large number of available hydrogen ions for adsorption sites on bentonite surface [24,25].

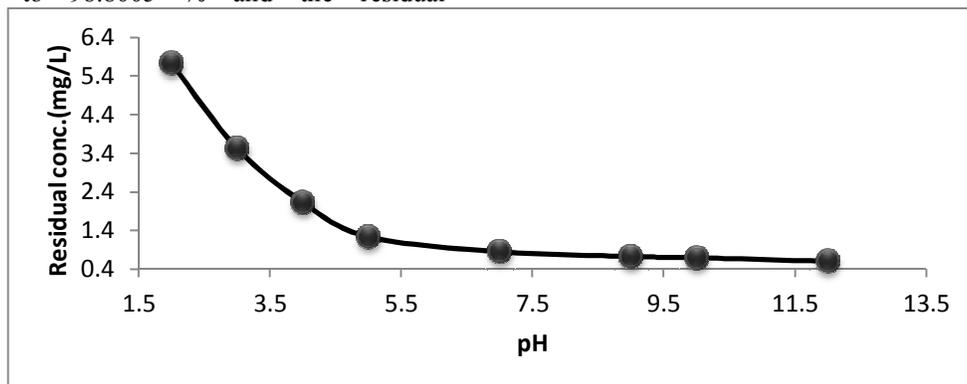


Figure 3. Effect of pH on Residual concentration of Zn

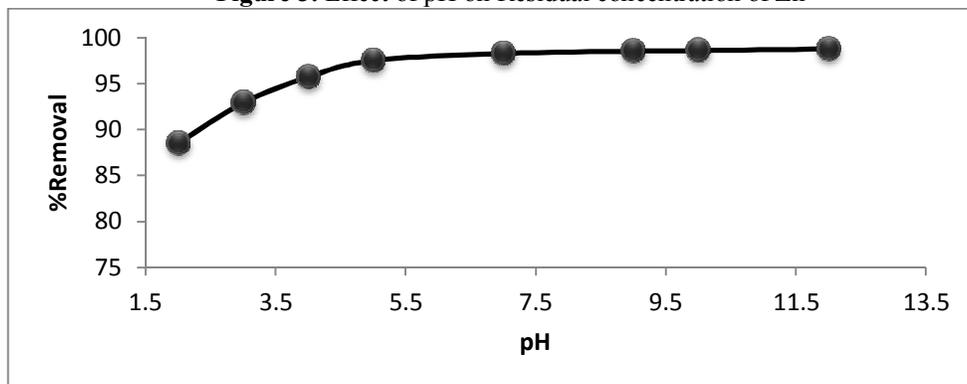


Figure 4. Effect of pH on percentage removal of Zn
($C_0=50\text{mg/L}$, $\text{pH} = 6$, time = 30 min, stirring rate = 300 r.p.m., and temp. = 25 °C).

3.3. Effect of initial metal ion concentration

Figures (5 and 6) indicate the effect of initial concentration of Zn(II) ions on the residual concentration and percentage removal of zinc respectively. It was found that as the initial concentration of Zn (II) increases from 50 mg/L to 100 mg /L, the percent removal of Zn (II) decreases

from 97.54 % to 82.33 % with increasing the residual concentration from 1.232 mg/L to 8.83 mg/L. From figures it was evident that at high concentration, the available sites of concentration adsorption become fewer. This behavior surface and prevent the metal ions from passing deeply inside the bentonite and the adsorption occurs on the surface only [26,27].

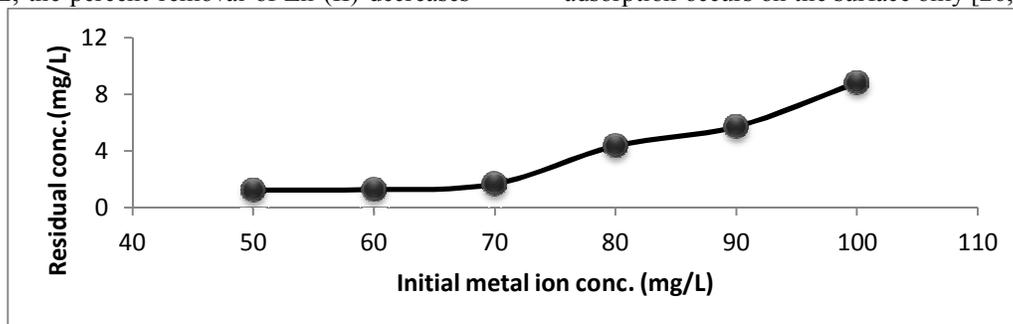


Figure 5. Effect of initial metal ion concentration on Residual concentration of Zn (II).

($C_0=50\text{mg/L}$, pH = 6, time = 30 min, stirring rate = 300 r.p.m., bentonite dosage=0.5g, and temp=25 °C)

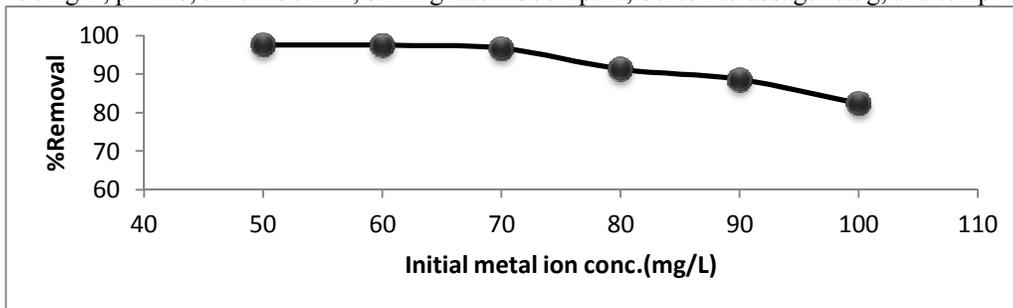


Figure6. Effect Of Initial Metal Ion Concentration On Percentage Removal Of Zn

($C_0=50\text{mg/L}$, pH = 6, time = 30 min, stirring rate = 300 r.p.m., bentonite dosage=0.5g., and temp. = 25 °C).

3.4. Effect of weight of adsorbent

The results of the experiments with varying bentonite dosage were presented in Figs(7 &8) .It was found that as the amount of bentonite increased from 0.1 g to 0.5 g. The percent removal of Zn (II)increased from 74.876 % to 99.156 % and residual concentration decreases from 12.562 mg/L to 0.422 mg/L. From those results it was found that the optimum dosage of bentonite for Zn (II) is 0.3 g.

Other works have observed similar results for adsorption of metal ions [28-29] .The residual concentration of zinc metal decreases as the dosage of bentonite increases. This may be due to those higher amounts of bentonite means availability of a larger surface area or a larger number for adsorption sites [30] and Therefore, higher capacity for adsorption.

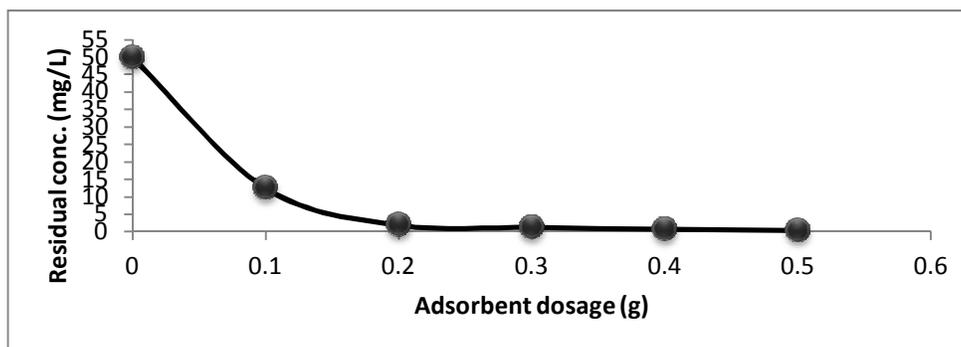


Figure 7. Effect of adsorbent dosage on Residual concentration of Zn

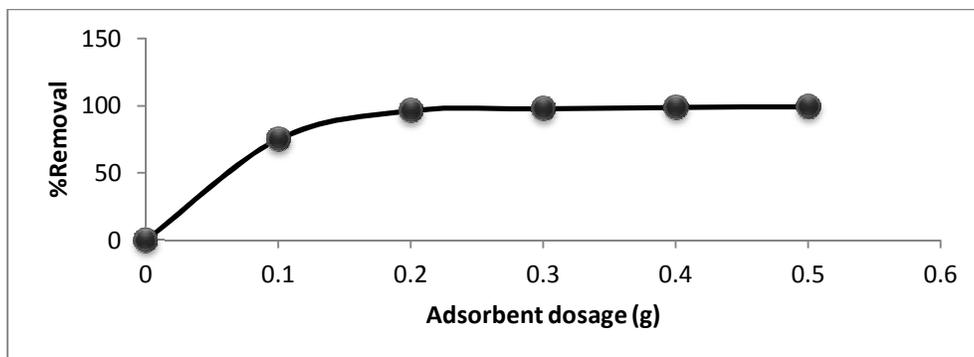


Figure 8. Effect of adsorbent dosage on percentage removal of Zn

3.5. Effect of temperature

The effect of temperature on the removal efficiency and residual concentration of Zn(II) ions from the aqueous solution were shown in figures (9&10). It was found that an increase in temperature

from 20 °C to 80 °C has a little effect on the removal of Zn (II). The percentage removal slightly increased from 97.536 % to 99.37 % and residual concentration decreased from 1.232 mg/L to 0.315 mg/L.

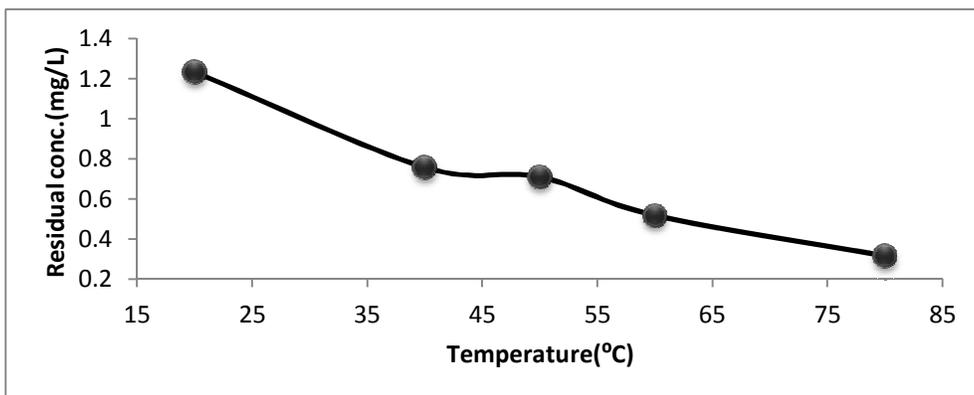


Figure 9 .Effect of temperature on Residual concentration of Zn

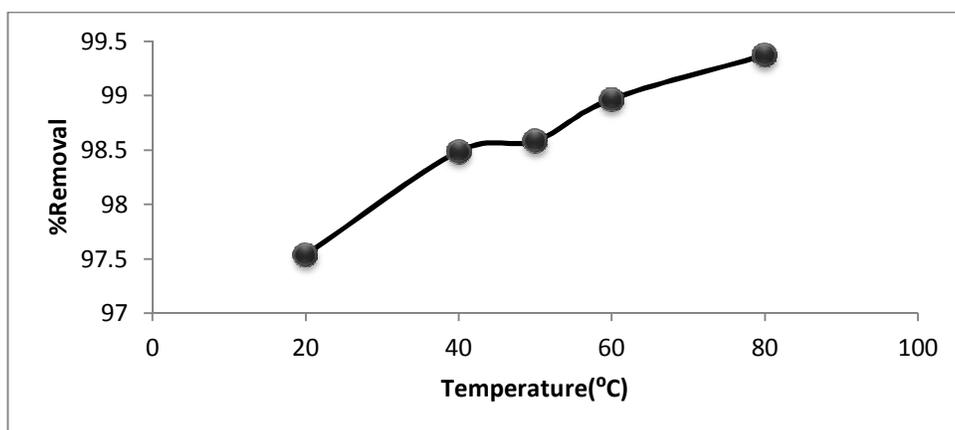


Figure 10. Effect of temperature on % removal of Zn.

3.6. Adsorption isotherm

In order to investigate the adsorption isotherm, the adsorption data can be interpreted and evaluated for Zn (II) molecules on bentonite using Langmuir

isotherm model that suggests that the uptake occurs on the homogenous surface by monolayer sorption without chemical reaction between adsorbent and adsorbate. The linear form of Langmuir isotherm

equation is represented by the following equation[31]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{K_L} * C_e \quad (2)$$

While the Freundlich isotherm describes the adsorption equation for non ideal adsorption and therefore heterogenous adsorption. The linear form of Freundlich isotherm equation is represented by the following equation[31]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

Where K_L , a and K_F , n are the constants for Langmuir and Freundlich models, respectively. In addition to the experimental data, the linearized forms of Langmuir and Freundlich isotherms using the above equation for Zn(II) ion removal by bentonite are given in table (2). The results show that the adsorption process fit both the Langmuir and Freundlich isotherms.

Table 2. Parameters of Langmuir and Freundlich adsorption isotherm models for FZn (II) on bentonite at different temperatures.

Heavy metals	Langmuir isotherm				Freundlich isotherm		
	T (K)	q_m (mg/g)	K_L (L/g)	R^2	$K_f \text{ mg}^{(1-1/n)}$	n	R^2
Zn(II)	293	59.52381	0.377528	0.9942	15.43133	2.081165	0.9806
	313	55.55556	0.743802	0.9969	19.52313	2.437835	0.9594
	323	54.34783	1.005464	0.9925	21.59798	2.675227	0.9567

3.7. Adsorption Thermodynamics

The thermodynamic parameters of the adsorption process that is, the standard enthalpy ΔH^0 , Gibbs free energy ΔG^0 and entropy ΔS^0 were calculated using the equations (4 and 5), [32].

$$\Delta G^0 = -RT \ln K_L \quad (4)$$

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5)$$

Where R is the ideal gas constant ($\text{kJ mol}^{-1}\text{K}^{-1}$), $K_L = k_{\text{ads}} / k_{\text{d}}$ is the Langmuir constant and T is the temperature (K). ΔH^0 and ΔS^0 values can be obtained from the slope and intercept of Van't Hoff plots of $\ln K_L$ (from the Langmuir isotherm) versus $1/T$. The results of these thermodynamic calculations for iron ions are shown in Figure 11 and table (3). From previous results it was shown that Zn (II) adsorption

followed an endothermic path as adsorption capacity decrease with increasing temperature range from 293 to 333 K. Thus, adsorption of Zn (II) on bentonite has to overcome a small activation barrier and increasing energy supply makes it easier for Zn(II) to adsorb to the bentonite surface.

The endothermic interactions between bentonite and metals ions had an average entropy increase of 0.115 and 0.06 $\text{kJ.K}^{-1}\text{mol}^{-1}$, which is therefore responsible for driving the interactions towards equilibrium despite being an endothermic process. The entropy increase is due to increased randomness at the solid-solution interface. This results are in a good agreement with [33].

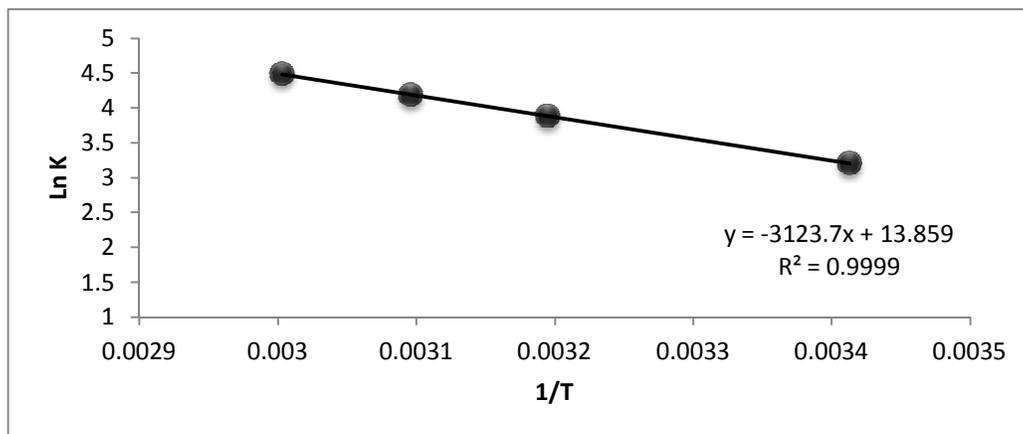


Figure 11. Plot of the Langmuir isotherm constant ($\ln K$) versus temperature ($1/T$) for Zn (II)

Table 3. Thermodynamic constants for the adsorption of Zn (II) at various temperatures.

Zn(II)						
T(K)	1/T (K ⁻¹)	Ln(K _L)(L/g)	ΔG° (KJ.mol ⁻¹)	ΔH° (KJ.mol ⁻¹)	ΔS°(KJ.K ⁻¹ .mol ⁻¹)	Ea(KJ.mol ⁻¹)
293	0.003413	3.200277	-7.82167	26.05634	0.115605	26.05634
313	0.003195	3.878406	-10.1261			
323	0.003096	4.179837	-11.2618			
333	0.003003	4.485515	-12.4595			

3.8. Adsorption kinetics

In the previous sections emphasis were placed on the percentage removal of zinc ions with different parameters. The present section is concerned with the process kinetics. Kinetics of adsorption is one of the most important characteristics to be responsible for the efficiency of the process. In order to clarify the adsorption kinetics of Zn (II) ions onto bentonite, Lagergren's pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data. The linearized form of the pseudo-first order rate equation by Lagergren is given as[34]:

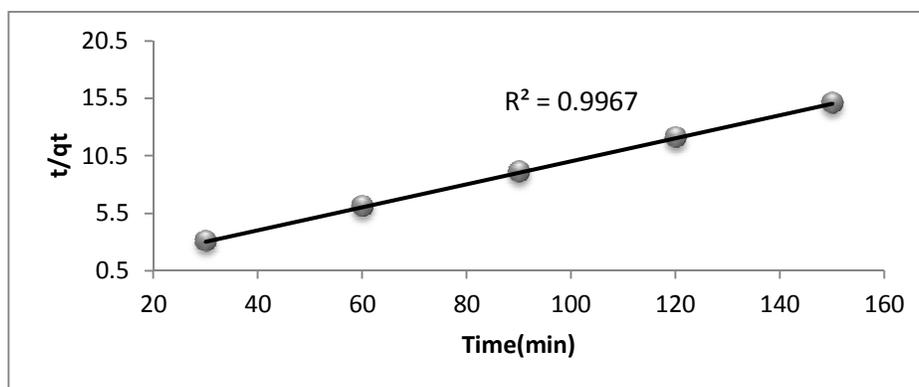
$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (6)$$

Experimental data were also applied to the pseudo-second-order kinetic model, which is given in the following form [35-36]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (7)$$

Where q_t and q_e (mg/g) are the amounts of the metal ions adsorbed at equilibrium (mg/g) and t

(min), respectively and k_1 is the rate constant of the equation (min^{-1}). The adsorption rate constants (k_1) can be determined experimentally by plotting of $\ln(q_e - q_t)$ versus t . The plots of $\ln(q_e - q_t)$ versus t for the Lagergren-first-order model (was not shown here) does not fit a pseudo-first-order kinetic model but it fit the pseudo-second order kinetics as shown in Figure (12). The kinetics data and values of R^2 for the first and second orders kinetics were shown in Tables (3) and (4) From these tables it was shown that correlation coefficient R^2 for the first order pseudo reaction was lower than that correlation coefficient R^2 for the second order pseudo reaction so it was evident that the reaction mechanism of adsorption of Zn is not a first order reaction and it was a second order reaction mechanism. The similar results were found for the adsorption of other metal ions on various adsorbents by several authors [37-38].

**Figure 12.** the pseudo- second-order adsorption kinetics of Zn (II) at different temperatures.**Table 4.** Parameters for adsorption of Zn (II) onto bentonite derived from the first- and second-order kinetic models:

First-order					
Heavy metals	Time (min)	qe(mg/g)	K ₁ (min ⁻¹)	R ²	
Zn (II)	30	11.87221	0.0005	0.6949	
	60	0.657441	0.0019	0.70452	
	90	0.140451	0.0073	0.2954	
Second Order					
Heavy metals	Time (min)	qe (mg/g)	K ₂ (min ⁻¹)	h (mg/g*min)	R ²
Zn (II)	30	38.91051	0.01752	26.5252	1
	60	24.5098	0.047697	28.6533	1
	90	16.6113	0.146131	40.32258	0.9997

4. Conclusion:

The treatment removal of zinc (Zn²⁺) metal ions from waste water by bentonite was studied. The following conclusions can be drawn

- The bentonite clay can be used as an adsorbent for the removal of Zn(II) from waste water .
- The adsorption of Zn(II) was depended on the pH of the solution the best Zn (II) removal efficiency occurs at pH 5.
- Based on the experimental results the optimum dosage of adsorbent is 0.3 g/L.
- The optimum contact time to achieve the maximum efficiency is 30 mins.
- The metal ion adsorption obeyed the pseudo second order model based on the experimental calculated values.
- The experimental data are well fitted to both the linearized Langmuir isotherm and the linearized Freundlich isotherm.
- The thermodynamic parameters are determined at three different temperatures and it has been found that the adsorption process is endothermic because of positive ΔH^0 accompanied by a decrease in entropy change and Gibbs free energy change (ΔG) respectively

5. References

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