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Removal of Zn (II) from Aqueous Solution onto Kaolin by Batch Design

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ABSTRACT

The Algerian kaolin clay was investigated to remove Zn(II) heavy metal ion from aqueous solution. The effect of contact time, initial metal ion concentration, pH and temperature was experimentally studied in batch mode to evaluate the adsorption capacity, kinetic, thermodynamic and equilibrium. The extent of zinc adsorption increased with increasing initial concentration of adsorbat, pH and temperature. The linear Langmuir and Freundlich models were applied to describe equilibrium isotherms and both models fitted well. The monolayer adsorption capacity for Zn(II) ions was 12.23 mg per g of kaolin clay at pH 6.1 and 25˚C. Dubinin-Radushkevich (D-R) isotherm model was also applied to the equilibrium data. Thermodynamic parameters showed that the adsorption of Zn(II) onto kaolin clay was spontaneous and endothermic process in nature. Furthermore, the Lagergren-first-order and pseudo-second-order models were used to describe the kinetic data. The experimental data fitted well the pseudo-second-order kinetic. As a result, the kaolin clay may be used for removal of zinc from aqueous media.

Keywords: Zn(II); Kaolin; Adsorption Isotherm; Thermodynamic; Kinetic

1. Introduction

Heavy metal contamination has become an environmental problem today in both developing and developed countries throughout the world [1,2]. Heavy metals are of considerable environmental concern due to their toxicity, wide sources, non-biodegradable properties and accumulative behaviours [3].

Zinc is considered as an essential element for life and acts as a micronutrient when presented in trace amounts. But too much zinc can be harmful to health. Zn(II) is reported to be toxic beyond permissible limits. Symptoms of zinc toxicity include irritability, muscular stiffness, loss of appetite and nausea [4]. WHO [5] recommended level of zinc in drinking water is 5 mg/L. The metal is further reported to be bioaccumulated into flora and fauna creating ecological problems. In developing countries, metal mining and metallurgy industrial departments produce large quantities of wastewater containing high concentration of Zn(II) [6,7]. It is also present in high concentration in wastewater of pharmaceuticals, galvanizing, paints, pigments, insecticides, cosmetics, etc. that causes serious problem to the environment [8]. Therefore, the heavy metal levels in wastewater, drinking water, and water used for agriculture should be reduced to the maximum permissible concentration. Many methods such as ion exchange, precipitation, membrane processes and reverse osmosis have been used for the removal of toxic metal ions [9-15]. However, these methods have several disadvantages such as incomplete metal ion removal, high reagent and energy requirements, generation of toxic sludge or other waste products, and long desorption time. Adsorption is recognized as an effective and economic method for removal of pollutants from wastewaters. In recent years, many studies have focused on seeking cheap, locally available and effective adsorbents, such as waste biopolymers, clays and clay minerals [16].

Clay minerals are low-cost and readily available materials functioning as excellent cation exchangers, which have often been used to adsorb metallic contaminants.

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They have different adsorption capacities for metal ions, such as mesoporous silica [17] and montmorillonite clay [18,19]. Kaolinite clay is a 1:1 clay mineral including a tight interlayer structure with the ideal formula of $Al_2Si_2O_5(OH)_4$ [20,21]. The sorption properties of this clay are solely determined by the nature of its surface and edges. Kaolinite clay possesses a variable charge that can be related to the reactions between ionisable surface groups located at the edges and the ions present in aqueous solution [20,22]. It has been used as adsorbent material for the adsorption process of various heavy metals [23-26].

The objective of the present work is to study the adsorption characteristics of Zn(II) ions from aqueous solution using Algerian kaolin clay. The influences of adsorption conditions such as contact time, pH changes, initial concentration of Zn(II) ions and temperature effect were investigated. In addition, the evidence for physico-chemical characteristics of Algerian kaolin clay obtained from X-ray diffraction (XRD) and scanning electron microscope (SEM) was investigated to understand the adsorption mechanism. Finally, kaolin clay potentially used to remove Zn(II) metal ion in wastewater was demonstrated.

2. Materials and Methods

2.1. Adsorbent

The kaolin sample used in this investigation was collected from a natural deposit, located in Tabelbala in province Bechar (Algeria). The surface area and CEC of kaolin were measured using methylene blue technique [27]. The sample of kaolin powder was characterized by using infrared (FT-IR), X-ray diffraction (XRD) and scanning electron microscopic (SEM) techniques.

2.2. Reagents

All chemicals used were of analytical grade. Stock standard solution of Zn^{2+} has been prepared by dissolving the appropriate amount of $ZnSO_4 \cdot 7H_2O$ in deionized water. This stock solution was then diluted to specified concentrations. The pH of the system was adjusted using reagent grade NaOH and HCl respectively. All plastic sample bottles and glassware were cleaned, then rinsed with deionized water and dried at 60˚C in a temperature controlled oven.

2.3. Instrumentation

The pH of all solution was measured by a TitraLab Instrument TIM800 Model pH meter. The adsorption experiments have been studied by batch technique using a thermostated shaker bath GFL-1083 Model. A Eppendorf 5702 Model digital centrifuge was used to centrifuge the samples. Zn(II) concentrations of solutions before and after adsorption were measured by using flame atomic absorption spectrophometer (Varian, SpectrAA-100, AAS).

The Fourier transform infrared (FT-IR) absorption spectra was recorded on KBr pressed pellets of the powdered sample in the range 4000 - 400 cm^{-1}, using a Perkine-Elmer FTIR 2000 spectrophotometer.

The X-ray diffraction pattern of powder was recorded on a Phillips-1730 (PAN analytical) X-ray diffractometer using Cu Kα radiation (λ = 1.54Å).

Nanomorphology was characterized by scanning electron microscopy (SEM) witch was carried out using Hitachi S-4800 equipped with energy dispersive spectrometry for chemical analysis (EDS) and operating at 15 kV acceleration voltage.

2.4. Adsorption Procedure

Adsorption measurements were determined by batch experiments. The effect of contact time on the adsorption capacity of Kaolin was studied in the range 1 - 360 min at an initial concentration of 100 mg/L. Adsorption kinetics was studied using an initial concentration of 100 mg/L with the adsorbent dosage of 0.2 g/20 mL at pH 6.1. Adsorption isotherms were studied at various initial concentrations of Zn(II) ion in the range of 10 - 120 mg/L and the experiments were conducted at different constant temperatures in the range 25˚C - 60˚C. The amount of Zn (II) adsorbed per unit mass of kaolin was calculated by using the mass balance equation given in Equation (1) [28].

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

where q_e is the maximum adsorption capacity in mg/g, C_o is the initial concentration and C_e is the concentration at equilibrium of Zn(II) solution in mg/L, V is the volume of the Zn(II) solution in mL and m is the mass of the kaolin in grams.

The percent adsorption of metal ion was calculated as follows Equation (2) [24]:

$$Sorption\% = \frac{C_o - C_e}{C_o} \times 100\% \tag{2}$$

The sorption capacity at time t, q_t (mg/g) was obtained as Equation (3) [24]:

$$q_t = \frac{(C_o - C_e)V}{m} \tag{3}$$

where C_o and C_t (mg/L) are the liquid phase concentrations of Zn (II) at initial and a given time t, V is the solution volume and m the mass kaolin (g).

3. Results and Discussion

3.1. Characterisation of Adsorbent

SEM micrograph of the untreated clay sample suggests a very cohesive material (**Figure 1**). The micrograph confirms that the material is forming micron-size agglomerates. A higher magnification micrograph of the same structure shows that the micro-size particles are composed of individual platelets, which conglomerate into larger size particles.

The X-ray diffraction spectrograph of the kaolin clay is shown in **Figure 2**. Kaolin show three intense diffraction peaks at 2θ value of 12.4˚, 24.8˚ and 26.6˚, less intense peaks at 2θ of 36.7˚, 39.6˚, 48.0˚, 50.1˚ and 60.1˚ and humps at 2θ = 19.8˚ - 21.9˚, 37.8˚ - 39.2˚ and 44.8˚ - 46.9˚, which are all associated with kaolinite (K). Diffraction peaks of quartz (Q) could be found at 2θ values of 20.9˚, 26.4˚, 50.9˚, 62.3˚ and 68.1˚. Illite (I) was also detected at 2θ = 17.9˚, 30.2˚, 35.1˚, 42.4˚ and 55˚.

The FTIR Spectra of the kaolin, in the range of 400 - 4000 cm^{-1} was taken to confirm the presence of functional groups that might be responsible for the adsorption process and presented in **Figure 3**. As may be seen, clay display a number of adsorption peaks, reflecting the complex nature the kaolin clay. The main bonds observed were OH$^-$ stretching, hydroxyl sheet at 3698 cm^{-1} and 3620 cm^{-1}. H_2O stretching was also found at 1636 cm^{-1}. Bands at 1033 cm^{-1} and 984 cm^{-1} were assigned to Si-O bonds in the SiO_4 molecules [29]. The other band at 913 cm^{-1} was attributed to Al^{IV}-OH vibrations [30]. The bands at 798 cm^{-1}, 750 cm^{-1} and 694 cm^{-1} were Si-O symmetric stretching [31]. Absorption at 535 cm^{-1} was assigned as Si-O-Al^{VI}, where the Al is in octahedral coordination [30,31].

The average surface area and CEC (Cation Exchange Capacity) of kaolin which were measured using methylene blue technique [27] were 10.60 m^2/g and 8.01 meq/100 g, respectively.

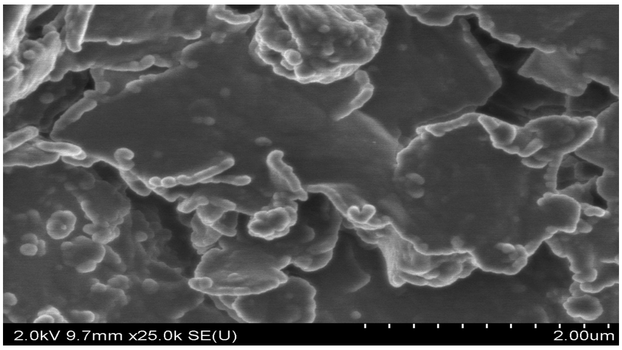

Figure 1. SEM of kaolin clay.

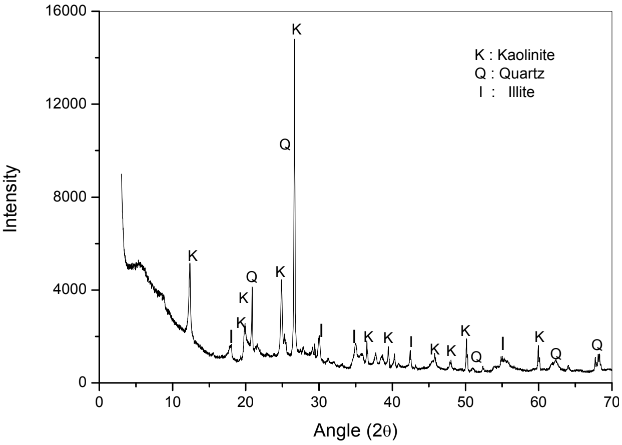

Figure 2. XRD pattern of kaolin.

3.2. Effect of Contact Time

The effect of contact time on the adsorption of Zn(II) ion onto kaolin clay at 25˚C and pH 6.1 is shown in **Figure 4**. It can be seen that the adsorption of Zn(II) occurred very quickly from the beginning of the experiment to the first 12 min. where the maximum adsorption of Zn(II) onto clay was observed; it can be said that beyond this there

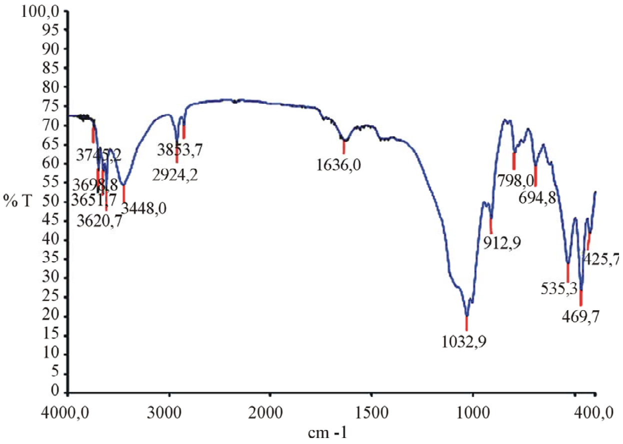

Figure 3. IR spectra of kaolin.

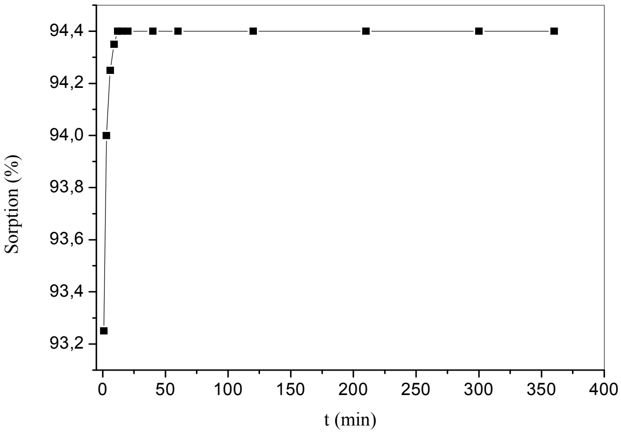

Figure 4. Effect of contact time on adsorption capacity of Kaolin.

was almost no further increase in the adsorption. This was due to the decrease of adsorption sites on the clay which gradually interacted with the metal ion [32]. Therefore, 12 min was selected as the optimum contact time for all further experiments.

In this study, 94.4% of Zn(II), were adsorbed on the Kaolin clay when the equilibrium was reached in just 12 min. On the basis of this result, it can be observed that natural kaolin clay can be used to remove this metal ion.

3.3. Effect of Initial Concentration of Zn (II)

Effect of initial concentration of Zn(II) on adsorption capacity of kaolin was investigated by varying initial concentration of Zn(II) from 10 to 120 mg/L. For this study, pH, temperature, adsorbent dosage and contact time have been fixed as 25˚C, 0.2 g/20 mL and 12 min. The results are presented in **Figure 5**. An increase of Zn(II) concentration accelerates the diffusion of Zn(II) ions from solution to the adsorbent surface due to the increase in driving force of concentration gradient. Hence, the amount of adsorbed Zn(II) at equilibrium increased from 0.98 to 10.44 mg/g as the Zn(II) concentration is increased from 10 to 120 mg/L.

3.4. Effect of pH

Effect of initial pH on the adsorption capacity of kaolin for Zn(II) was studied by varying solution pH from 1.5 to 11 at the adsorbent dosage of 0.2 g/20 mL using an initial concentration of Zn(II) as 100 mg/L. The pH range of 1.5 - 6.1 was chosen, as the precipitation of Zn(II) is found to occur at pH ≥ 7 [16]. Variation of adsorption capacity of kaolin for Zn(II) ions with pH is shown in **Figure 6**. It is evident that the adsorption of Zn(II) ions on kaolin is strongly dependant on the pH of the solution. The adsorption of Zn(II) ions increases steadily with increase in initial pH from 1.5 to 6.1 and the maximum adsorption capacity of 9.4 mg/g is observed at pH 6.1 (natural pH of suspension).

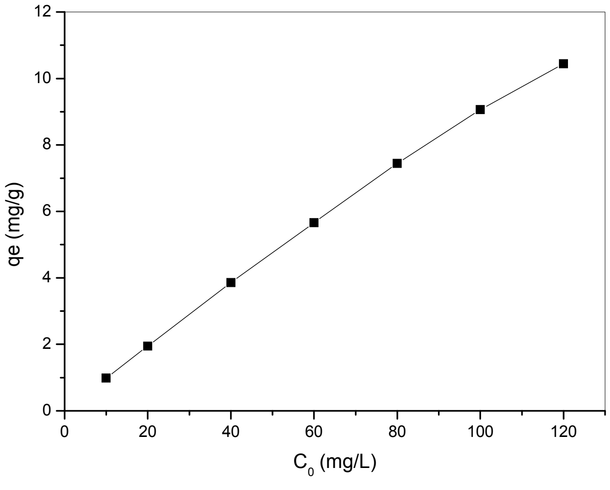

Figure 5. Effect of initial concentration of Zn(II) on adsorption capacity of Kaolin.

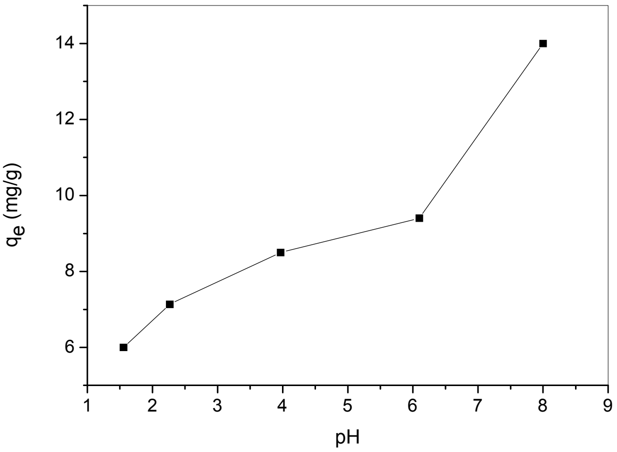

Figure 6. Effect of pH on adsorption capacity of Kaolin.

The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH values (pH 2 - 6), the low adsorption observation was explained due to increase in positive charge (protons) density on the surface sites and thus, electrostatic repulsion occurred between the metal ions (M^{2+}: Zn^{2+}) and the edge groups with positive charge ($Si\text{-}OH^{2+}$) on the surface as follows:

$$-\mathrm{SiOH} + \mathrm{H}^{+} \rightarrow -\mathrm{SiOH}^{2+} + \mathrm{H}^{-} \tag{4}$$

In an alkaline medium (pH > 7), the surface of kaolin clay becomes negatively charged and electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the sorption edges thus resulting in an increase metal adsorption. This mechanism can be shown as follows:

$$-\mathrm{SiOH} + \mathrm{H}^{+} \rightarrow -\mathrm{SiO}^{-} + \mathrm{H}_2\mathrm{O} \tag{5}$$

$$-\mathrm{SiO}^{-} + \mathrm{M}^{2+} \rightarrow -\mathrm{SiOM}^{2+} \tag{6}$$

A similar theory was proposed by several earlier workers for metal adsorption on different adsorbents [6, 33].

3.5. Adsorption Isotherm Models

Three important isotherm models were selected in this study, which are namely the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models.

3.5.1. Langmuir Isotherm Model

Langmuir isotherm model was applied to establish the relationship between the amount of Zn(II) adsorbed onto kaolin clay and its equilibrium concentration in aqueous solution. Langmuir adsorption isotherm [34] is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented in linear form

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (7)$$

where C_e is equilibrium concentration of the metal (mg/L) and q_e is the amount of the metal adsorbed (mg) by per unit of the adsorbent (g). q_m and K_L are Langmuir constant relating adsorption capacity (mg/g) and the energy of adsorption (L/g), respectively. These constants are evaluated from slope and intercept of the linear plots of C_e/q_e versus C_e, respectively (**Figure 7**).

The Langmuir monolayer adsorption capacity of kaolin clay was estimated as 12.23 mg/g (**Table 1**).

Based on the further analysis of Langmuir equation, the dimensionless parameter of the equilibrium or adsorption intensity (R_L) can be expressed by

$$R_L = \frac{1}{1 + K_L C_0} \qquad (8)$$

where C_0 (mg/L) is the initial dye concentration and K_L (L/mg) is the Langmuir constant related to the energy of adsorption. The value of R_L indicates the shape of the isotherms to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The influence of isotherm shape on whether adsorption is favourable or unfavourable has been considered [35].

For a Langmuir type adsorption process, the isotherm shape can be classified by a dimension less constant separation factor (R_L), given by Equation (8). The calculated R_L values as different initial Zn(II) concentrations are shown in **Figure 8**. It was observed that the value of R_L in the range 0 - 1 confirmed the favourable uptake of the Zn(II) process. Also lower R_L values at higher initial Zn(II) concentrations showed that adsorption was more favourable at higher concentration. The degree of favourability is generally related to the irreversibility of the system, giving a qualitative assessment of the kaolin-Zn(II) interactions. The degrees tended toward zero (the completely ideal irreversible case) rather than unity (which represents a completely reversible case).

3.5.2. Freundlich Isotherm Model

The equilibrium data was also applied to the Freundlich adsorption isotherm [36], which is the earliest relationship known describing the adsorption equilibrium and is expressed in linear form by the following equation:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \qquad (9)$$

where K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When lnq_e is plotted against $l\ C_e$, a straight line with slope n and intercept K_F is obtained (see **Figure 9**).

The intercept of the line, K_F, is roughly an indicator of the adsorption capacity and the slope, n, is an indication of adsorption intensity. The values obtained for the Freundlich variables for the adsorption of Zn ions are given in **Table 1**.

A relatively slight slope $n < 1$ indicates that adsorption intensity is good (or favorable) over the entire range of concentrations studied, while a steep slope ($n > 1$) means that adsorption intensity is good (or favorable) at high concentrations but much less at lower concentrations

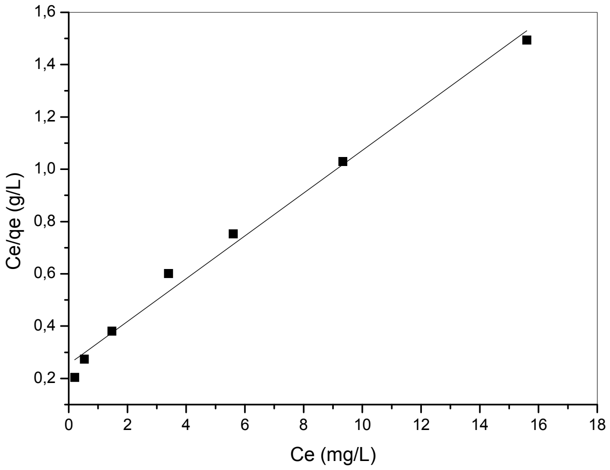

Figure 7. Langmuir isotherm plot for adsorption of Zn(II) on the Kaolin.

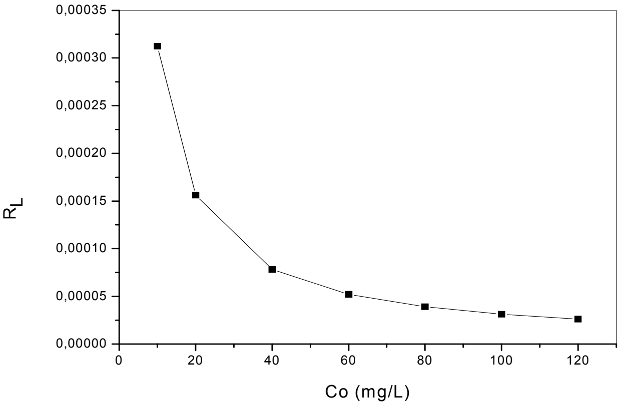

Figure 8. Plot of separation factor versus initial Zn(II) concentration.

Table 1. Langmuir, Freundlich and D-R isotherm parameters for the adsorption of Zn(II) onto Kaolin clay.

Langmuir isotherm constants			Freundlich isotherm constants			D-R isotherm constants		
q_m (mg/g)	K_L (L/g)	R^2	n	K_F	R^2	q_m (mg/g)	E(kJ/mol)	R^2
12.23	0.32	0.988	1.82	2.7	0.981	2.51	2.14	0.80

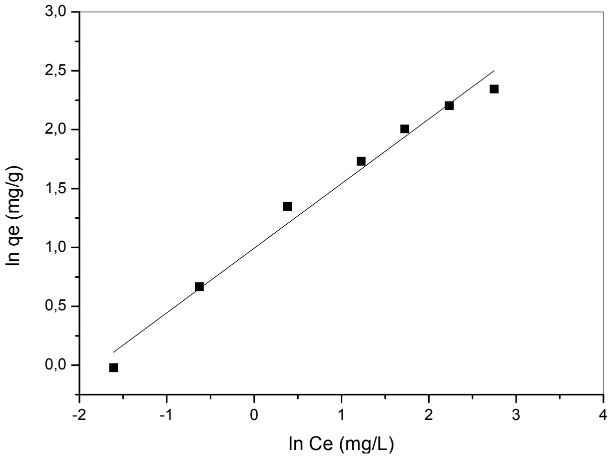

Figure 9. Freundlich isotherm plot for adsorption of Zn(II) on the Kaolin.

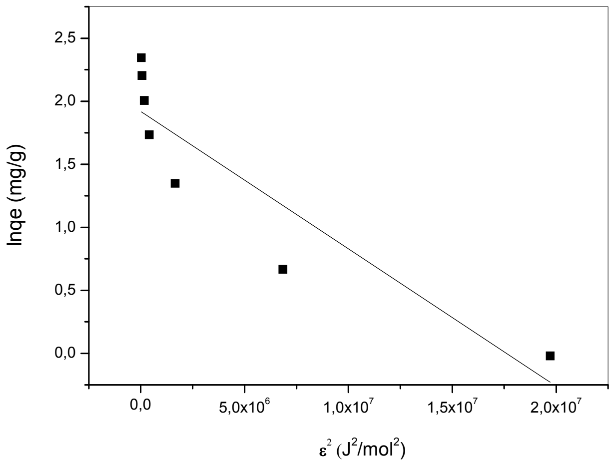

Figure 10. D-R isotherm plot for adsorption of Zn(II) on Kaolin.

[37]. In the present study, the value of *n* (n = 1.82) is greater than 1, indicating that the adsorption process is favourable. The K_F value of the Freundlich equation also indicates that kaolin has a high adsorption capacity for zinc ions in aqueous solutions.

The value of correlation coefficient (R^2 = 0.981) is also good. It can be said that Freundlich model fitted well.

3.5.3. Dubinin-Radushkevich (D-R) Model

The adsorption data was also modeled by D-R isotherm to determinate the adsorption type (physical or chemical). The linear form of this model is expressed by [38-42].

$$ln\,q_e = ln\,q_m - \beta\varepsilon^2 \tag{10}$$

where q_e is the amount of the metal adsorbed onto per unit dosage of the adsorbent (mol/L); q_m, the monolayer adsorption capacity (mol/g); ε, the activity coefficient related to mean sorption energy (mol²/J²) and ε is the Polanyi potential.

$$\varepsilon = RT\,ln\left(1+\frac{1}{C_e}\right) \tag{11}$$

A plot of $ln\ q_e$ against ε^2 is given in **Figure 10**. D-R isotherm constant, q_m, for Kaolin clay was found to be 2.51 mg/g (**Table 1**). The difference of q_m derived from the Langmuir and D-R models is large. The difference may be attributed to the different definition of q_m in the two models. In Langmuir model, q_m represents the maximum adsorption of metal ions at monolayer coverage, whereas it represents the maximum adsorption of metal ions at the total specific micropore volume of the adsorbent in D-R model. Thereby, the value of q_m derived from Langmuir model is higher than that derived from D-R model. The differences are also reported in previous studies [19,38,40].

The mean sorption energy *E* (kJ/mol), can be calculated using the following equation (Equation (12)):

$$E = \frac{1}{\sqrt{-2\beta}} \tag{12}$$

The adsorption is basically a surface adsorption associated with ion exchange when $|E|$ is between 8 and 16 kJ mol^{-1}. Otherwise, for $|E|$ ranging from 1.0 to 8.0 kJ mol^{-1}, the mechanism is physical adsorption [38-42]. The calculated value of *E* is 2.14 kJ/mol for Kaolin, and it is in the range of values for physical adsorption reactions. The similar results for the adsorption of Zn(II) was reported by earlier worker [42-44].

3.6. Adsorption Kinetic Models

In an attempt to present the kinetic equation representing adsorption of Zn(II) onto kaolin clay, two kinds of kinetic models were used to test the experimental data. These are Lagergren-first-order equation and second-order equation.

Lagergren-first-order equation is the most popular kinetics equation. The form is

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1\left(q_e - q_t\right) \tag{13}$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Equation (13) becomes the following [45,46]:

$$ln\,ln\left(q_e - q_t\right) = ln\,q_e - k_1 t \tag{14}$$

where q_t (mg/g) is the amount of adsorption time *t* (min); k_1, the rate constant of the equation (min^{-1}) and q_e is the amount of adsorption equilibrium (mg/g). The adsorption rate constant k_1, can be determined experimentally by plotting of ln ($q_e - q_t$) versus *t* (see **Figure 11**).

The second-order equation is in the following form:

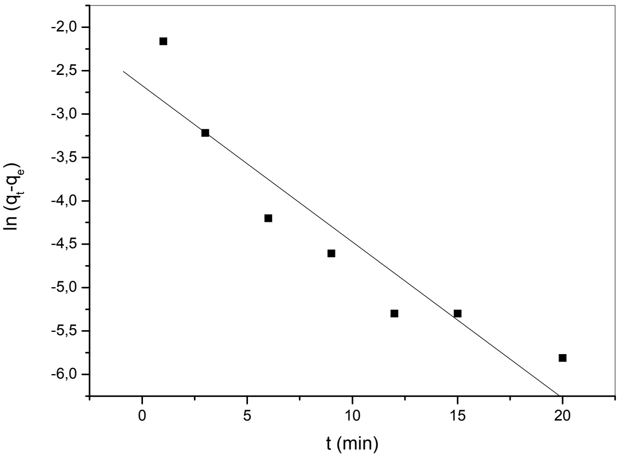

Figure 11. Lagergren pseudo first-order plots for Zn(II) adsorbed on kaolin.

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2\left(q_e - q_t\right)^2 \tag{15}$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Equation (15) becomes the following [47-49]:

$$\frac{t}{q_t} = \frac{1}{2kq_e^2} + \frac{1}{q_e}t \tag{16}$$

where q_t (mg/g) is the amount of adsorption time t (min), k_2 (g/mg min) is the rate constant of the second-order equation and q_e is the amount of adsorption equilibrium (mg/g).

k_2 and q_e can be determined experimentally by plotting of t/q_t versus t (**Figure 12**).

Based on the correlation coefficients presented in **Table 2**, the adsorption of Zn(II) onto Algerian kaolin was best described by the second order equation. A good agreement with this adsorption model was confirmed by the similar values of q_e experimental and q_e calculated. Many studies reported the first-order equation of Lagergren does not fit well to the initial stages of the adsorption processes [42,45,50,51]. The first-order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. In many cases, the second-order equation correlates well to the adsorption studies [43,50].

The best fit to the pseudo-second order kinetic indicated that the adsorption mechanism depended on the adsorbate and adsorbent [52,53].

3.7. Thermodynamic of Adsorption

Adsorption experiments to study the effect of temperature were carried out from 25˚C to 60˚C at optimum pH value of 6.1 and adsorbent dosage level of 0.1 g·L^{-1}. The contact time for adsorption was maintained at 12 min. The variation in the extent of adsorption with respect to temperature has been explained based on thermodynamic parameters viz. free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) which were determined using the following equations [54]:

$$K_d = \frac{q_e}{C_e} \tag{17}$$

$$ln\,K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{18}$$

$$\Delta G = \Delta H - T\Delta \mathrm{S} \tag{19}$$

when lnK_d was plotted against $1/T$, (**Figure 13**), a straight line with the slope of $\Delta H/T$ and intercept of $\Delta S/R$ were obtained. The values of ΔH and ΔS were obtained from the slope and intercept of the Van't Hoff plots. The thermodynamic parameters for the adsorption process are given in **Table 3**.

It is clear that positive value of ΔH suggested the endothermic nature of the adsorption and the negative value of ΔG indicated the spontaneous nature of the adsorption process. Generally, the change in adsorption enthapy for

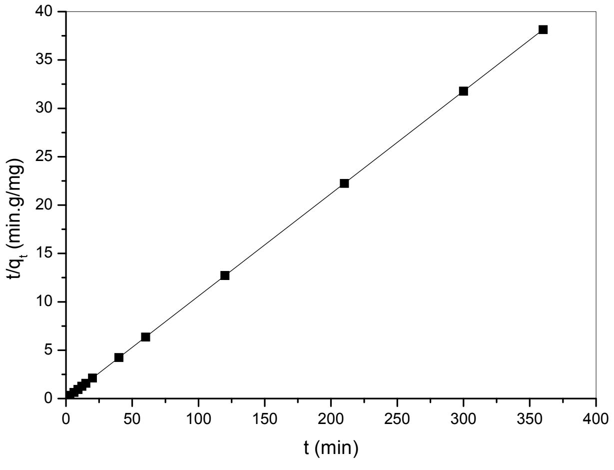

Figure 12. Pseudo second-order plots for Zn(II) adsorbed on kaolin.

Table 2. Comparison of adsorption rate constants, experimental and calculated q_e values for the pseudo-first and second order reaction kinetics for removal of zinc by kaolin clay.

q_e experimental (mg·g^{-1})	Pseudo-first order			Pseudo-second order		
	k_1 (min^{-1})	q_e calculated (mg·g^{-1})	R^2	k_2 (g·mg^{-1}·min^{-1})	q_e calculated (mg·g^{-1})	R^2
9.44	0.18	0.07	0.855	11.33	9.44	1

Table 3. Thermodynamic parameters.

$-\Delta G$ (KJ·mol^{-1})					ΔH (KJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})	R^2
25˚C	30˚C	40˚C	50˚C	60˚C			
0.34	0.94	2.14	3.34	4.54	35.42	0.12	0.96

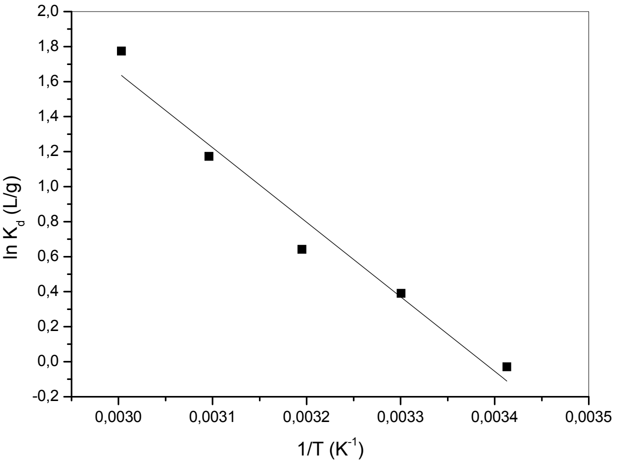

Figure 13. Plot of *lnK$_d$* against 1/*T* for the adsorption of Zn(II) on kaolin.

Table 4. Comparison of adsorption capacity of kaolin clay with various adsorbents for Zn(II) removal.

Adsorbent Adsorption	capacity (mg/g)	Reference
Active carbon	11.24	[60]
Kaolinite	3.05	[60]
Bentonie	9.12	[60]
Penicilliumchrysogenum	11.11	[61]
Tannic acid immobilized	1.23	[62]
Groundnut shells (undyed and dyed with C.I. Reactive Orange 13)	7.62 (undyed), 9.57 (dyed)	[63] [63]
Carbon aerogel	1.183	[64]
Sugar beat pulp	0.176	[65]
Fly ash	11.11	[65]
Low rank Turkish coal	1.66	[66]
Low-grade phosphate	10.32	[67]
Activated alumina	13.69	[68]
Clarified sludge	15.53	[68]
Streptoverticillium	9.15	[61]
Humic acid	6.12	[69]
Amphibolite	11.5	[70]
Granite	8.64	[70]
Zeolite	13.2	[71]
Sawdust	2.58	[72]
Brine sediments	4.85	[72]
kaolin clay	12.23	Present work

physisorption is in the range of −20 to 40 kJ mol^{-1}, but chemisorption is between −400 and −80 kJ mol^{-1} [53,55]. The value of adsorption heat showed that physical adsorption took place in the adsorption of Zn(II) ion on kaolin. Similar results were found for the adsorption of zinc on natural and MnO$_2$ modified diatomite and on crosslinked starch Phosphates [56,57].

The slightly positive ΔS value showed the increased randomness at the solid/solution interface during the adsorption process. The adsorbed water molecules, which were displaced by the adsorbate species, gained more translational energy than was lost by the adsorbate ions, thus allowing the prevalence of the randomness in the system. Enhancement of the adsorption capacity at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface [58, 59].

3.8. Comparison of Kaolin Clay with Various Adsorbents for Zn(II) Removal

The adsorption capacity of the kaolin clay for the removal of Zn(II) was compared with those of other adsorbents reported in literature and the values of adsorption capacities were presented in **Table 4**. The values reported in the form of monolayer adsorption capacity. The experimental data of the present investigation was comparable with the reported values. The kaolin clay had a high adsorption capacity as comparable with that of the other adsorbents. Therefore, considering the low cost of this natural adsorbent, it can be used as an alternative material to minimize the concentration of Zn(II) in wastewater.

4. Conclusions

The results of present investigation show that kaolin, low cost material, has suitable adsorption capacity with regard to the removal of zinc ions from its aqueous solutions. The adsorbed amount of Zn(II) ions increased with increase in initial concentration of adsorbat, pH and temperature. Experimental results were evaluated with Langmuir, Freundich and Dubinin-Radushkevich isotherms. In addition to higher values of correlation coefficients, monolayer capacities (q_m) determined from Langmuir isotherm and adsorption intensity (n) determined from Freundlich isotherm indicate appropriateness of Langmuir and Freundlich isotherms for zinc metal. Pseudo-second-order reaction kinetic has provided a realistic description for removal of Zn^{2+} with similar values of q_e calculated and q_e experimental, whereas in the first order kinetic the difference between these values is large. The correlation coefficient was also higher in pseudo-second-order kinetic.

The enthalpy change for the adsorption process was indicative of the endothermic nature of adsorption. The dimensionless separation factor (R_L) showed that kaolin can be used for removal of zinc ions from aqueous solutions. The results of this research were compared to the published data in the same field, and found to be in agreement with most of them. The batch design may be useful for environmental technologist in designing treatment plants for metal removal from wastewaters.

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