RESEARCH ARTICLE

Kinetics and Thermodynamics of Zinc (II) Ion Adsorption on Flint and Attapulgite Iraqi Clays

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ABSTRACT

In the current work, the adsorption of zinc (II) from synthetic solutions by flint and attapulgite clays as natural adsorbents was studied in batch experiments under various experimental conditions. The effect of temperature, solution pH, clay dosage, and contact time were investigated onto adsorption of metal under studied by flint and attapulgite clays, then perfect conditions were determined and applied on industry waste. The adsorption capacity for zinc ion increased with time, and equilibrium was reached in 90 minutes in both systems, and the maximum capacity was at pH 4. The adsorption results were assessed by two kinetic models (pseudo-first-order and pseudo-second-order) and three isotherms (Freundlich, Langmuir, and D-R). The results revealed which Freundlich isotherm and pseudo-second-order model agreed with the adsorption process. $\Delta G°$ values in both systems were negative and ranged from (-30.7362 to -26.7212) kJ/mol, indicating that both systems' adsorption processes were spontaneous and physisorption. $\Delta S°$ and $\Delta H°$ values in both systems were positive, indicating increasing randomness and an endothermic system. Perfect conditions were applied on the Al-Quds Power Station sample and showed that the removal percentage by attapulgite clay (%R = 99.18) was higher than the removal percentage by flint clay (%R =72.08).

Keywords: Adsorption, Clay, Thermodynamics, Zinc.

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INTRODUCTION

Heavy metals are usually described as metals with densities at least five times that of water. Heavy metals are natural components of the earth's surface, and natural processes like volcanic activity and weathering play a major role in heavy metal contamination. Mining, industrial, agricultural, and smelting contribute to an abundant supply of heavy metal pollution, either by concentrating or releasing it. Heavy metals are used extensively in various manufacturing, agricultural, pharmaceutical, and technical applications.[1-3] Zinc is among the essential heavy metals, and it is used in a variety of industrial fields.

On the other hand, zinc is the most toxic contaminant entering the aquatic environment through industrial effluent. Zinc quantities that are too high cause complications. Migraine, atherosclerosis, and pancreas injury are a few examples.[4] The Health Organization limited the allowed amount of zinc in drinkable water to 4 mg/L.[5,6]

Heavy metal removal processes include adsorption, ion exchange, precipitation, evaporation, flocculation, and membrane separation. Each process has its pros and cons regarding specificity, selectivity, sensitivity, and efficiency.[7,8] Adsorption is popular for its low price, operability, and simple design, particularly its greater removal efficiency from low concentrations.[9]

Clay is a natural, earthy substance made up of many tiny particles of rock layers that have been studied for its ability to absorb trace amounts of metal ions. Clay is primarily composed of grained mineral deposits with elastic properties over a wide range of water content and solidify if dried. Clay deposits may contain organic substances that do not indicate plasticity.[10] Attapulgite is a hydrated magnesium alumino-silicate compound made up of octahedral magnesium and tetrahedral silicon dioxide.[11] It is an excellent potential adsorbent due to its environmental friendliness, excellent mechanical stability, cheap price, and widespread availability.[12] Flint clay is described as a crystalline clay (rock) to sedimentary, microcrystalline consisting mainly of kaolin that breaks with a noticeable conchoidal deformation and resists spilling into water.[13]

This work aimed to assess adsorption capacity of attapulgite and flint clays in having removed zinc ions from

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synthetic solutions and determine optimum conditions using a batch method and applying it to industrial wastewater samples. The adsorption data has been subjected to various adsorption isotherms, including Langmiur, Freundlich, and D-R. The kinetics and thermodynamics for removing zinc ion have been investigated.

METHOD AND MATERIALS

Clays Preparation

The geological survey and mining company (Iraq/Baghdad) provided the flint and attapulgite clays. Flint and attapulgite clays were washed numerous times by distilled water to eliminate soluble substances before drying for 5 hours at (350K) and left at room temperature before being collected in glass containers. Flint and attapulgite clays were ground and sieved with 75 μm size (no. 200) sieves before being collected in glass containers. The composition of flint and attapulgite clays was determined by the Iraq Geological Survey company, as seen in Table 1.

Industry Wastewater Sample Preparation

A sample of industrial wastewater was collected from the Al-Quds Power Station, located northeast of Baghdad. The sample was digested using the method presented by (AL-Shaker and Mohammed).[14] The concentration of zinc ions in an industrial wastewater sample was (63.97 mg/L). After adjusting all of the conditions from the batch experiments on synthetic water, we applied the perfect conditions to the Al-Quds Power Station sample.

Synthetic Wastewater Preparation

By dissolving 2.084 g of $ZnCl_2$ in 1liter deionized water, a standard stock solution of single zinc (II) ions (Conc.1000 mg/L) was obtained. Distilled water was used to dilute the stock solution, which was used to make all operating solutions. Zinc (II) concentrations were determined using an atomic absorption spectrophotometer (AAS 6200). (Shimadzu, Japan).

Devices

The zinc ion concentration was determined using an atomic adsorption spectrophotometer (AAS 6200, Shimadzu, Japan). Adsorbent mass and adsorbate pH were measured using a German electronic balance and a (WTW) pH 7110 digital meter.

Adsorption Studies

The batch method was used to carry out adsorption experiments because of its easiness and dependability. 0.1 and 0.3 g of attapulgite and flint clays were placed in test tubes (100 mL), exposing varying concentrations of 25 mL of synthetic solutions of Zn (II). To achieve equilibrium, the mixes were agitated at 185 rpm for a predetermined time in a thermally controlled automatic shaker at various temperatures. Zinc ion concentrations in synthetic solutions were measured using an atomic absorption spectrophotometer after filtering the suspensions using Whatman no 42 filtrates.

The effects of different process parameters, including contact time 10–120 minutes at temperature 298K, initial concentration 100 mg/L, and pH 7.3, attapulgite and flint clay dosage (0.05–0.9 g) and 0.2–0.8 g, respectively at temperature 298k, initial concentration 100 mg/L, and pH = 7.3, pH of the solutions 1–7 at temperature 298K, and initial concentration 100 mg/L, and temperature (298–328 K) at pH 3, and initial concentration 100 mg/L, on Zn (II) adsorption were investigated. Then, perfect conditions were determined and applied to the industrial wastewater sample. At pH 3, kinetics, thermodynamic, and adsorption isotherms parameters were determined.

The amount of adsorbed qe (mg/g) and percentage removal (% R) for adsorption of Zn (II) ions solutions in equilibrium were determined as below:

$$q_e = \frac{\left(C_0 - C_e\right)V}{m} \tag{1}$$

$$\%R = \frac{\left(C_0 - C_e\right)}{C_e} \times 100 \tag{2}$$

Whereas C0 (mg.L^{-1}) defines the primary concentration of zinc (II), Ce (mg.L^{-1}) defines the concentration of zn (II) at equilibrium, V denotes the solution volume in liters, and m (g) defines the weight of adsorbents.

RESULTS AND DISCUSSIONS

Contact Time Effect

According to experimental data and shapes are seen in Figure 1, the zinc (II) adsorption on flint and attapulgite clays reached equilibrium in 90 minutes. Adsorption was accompanied by a linear increase, corresponding to relatively fast uptake, and then a fixed phase. The fast uptake was caused by zinc ions collecting rapidly on flint and attapulgite clays.[15] Adsorption of zinc ion on flint and attapulgite clay took 90 minutes to reach equilibrium.

Adsorbents Dosage Effect

Figures 2 and 3 show the effect of the amount of flint and attapulgite clays on the adsorption capacity qe (mg/g) of Zn (II) ion at 100 mg.L^{-1} primary concentration. The experimental results revealed that as the quantity of adsorbents increased, the adsorption capacity of zinc (II) ion decreased till a perfect dosage was achieved, after which it stayed

Table 1: The composition of flint and attapulgite clays

	Chemical composition								
Clays	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*CaO*	*MgO*	*SO_3*	*Na_2O*	*L.O.I*	*Total*
Flint Wt%	45.6	35.41	l0.69	0.2	0.1	-	-	13.79	95.51
Attapulgite Wt%	41.54	10.52	5.44	15.45	4.06	l0.17	l0.93	20.04	98.15

unchanged irrespective of adsorbent mass. As anticipated, the equilibrium concentration decreases with increasing clay amount (adsorbents) for a known initial zinc (II) concentration. Perhaps this is caused by rapid increase in surface area and the occurrence of as many adsorption binding sites as when clay amount (adsorbents) was increased.[16] As the weight of the adsorbent materials increases, the curves approach a plateau, as seen in Figures 2 and 3. This plateau value represents the adsorption process's equilibrium. Attapulgite and flint clays have plateaus of 0.1 and 0.4 g, respectively.

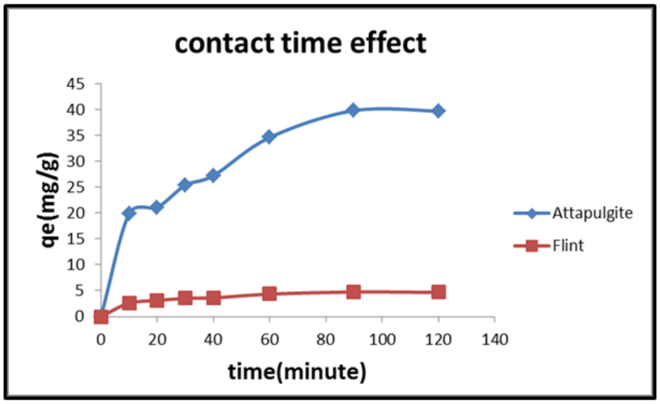

Figure 1: Equilibrium time effect for adsorption of Zn (II) ions on flint and attapulgite at pH ≈ 7.3, flint and attapulgite doses of 0.3g/25 mL and 0.05g/25 mL respectively, C0100 mg/L, temperature 298K, and particle size of 75 µm.

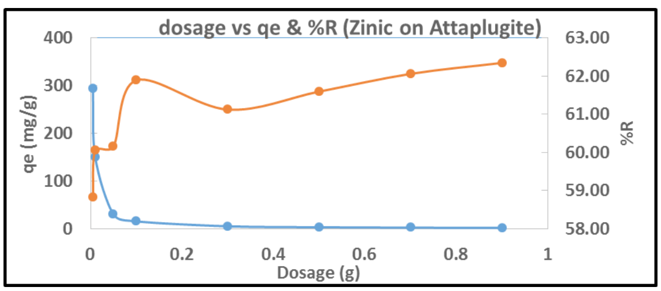

Figure 2: Clay dosage effect of adsorption of Zn (II) ion on attapulgite clay at initial conc. 100 mg/L, pH ≈ 7.3, contact time ≈90minute, temperature 298K, and particle size ≈ 75 µm.

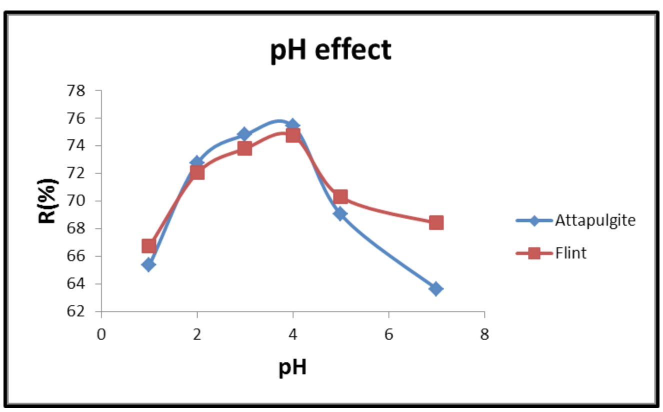

Figure 4: pH effect for adsorption of Zn (II) ions on flint and attapulgite clays at initial conc. 100 mg.L^{-1}, contact time 90 minute,flint and attapulgite doses 0.4g per 25 mL and 0.1g per 25 mL respectively, temperature 298K,and particle size 75 µm.

pH Effect

Adsorption of zinc (II) ion was assessed, and results were dependent on pH, which is directly related to the adsorbent kinds, surface charges, and extent of ionization.[17] Adsorption of zinc (II) ion on attapulgite and flint increased as solution pH rose between 1–4 and then lowered at pH.[5] The increase in pH range 1–4 may be due to reduced competition among both (H^{+1}) ions and zinc (II) ions, whereas the reduction in pH (5) may be caused by increased competition among both (OH^{-1}) ions and zinc (II) ions.[18] Maximum percentage removal for adsorption of zinc ion was at pH (4) as seen in Figure 4. Many experiments also were not produced due to the precipitation of Zn (II) ion in solution at pH (9–11).[19]

Temperature Effect

Temperature effect on the adsorption capacity of zinc (II) ions onto flint and attapulgite clays was investigated at various temperatures (298, 308, 318, and 328K), initial zinc concentration (100 mg/L), pH (3), contact time 90 minute, and flint and attapulgite clays dosage 0.4 and 0.1g respectively. Figure 5 shows the general curves and experimental data of zinc (II) adsorption onto flint and attapulgite clays. The data also revealed which removal efficiency of Zn (II) onto flint and attapulgite clays increases with temperature, showing that the adsorption system is endothermic, possibly due to increased Zn (II) ion diffusion within the crystalline structure of clay with the rise of temperature.[20]

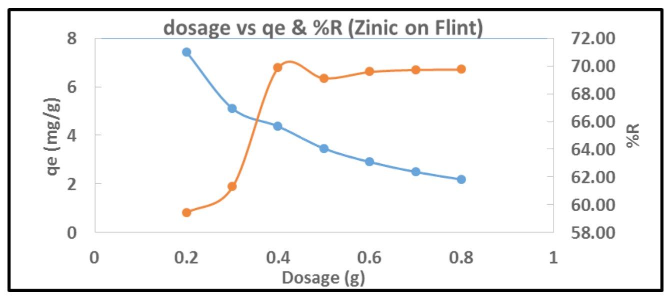

Figure 3: Clay dosage effect of adsorption of Zn (II) ions on flint clay at initial concentration of 100 mg/L, pH ≈ 7.3, contact time ≈90minute, temperature 298K, and particle size ≈ 75 µm.

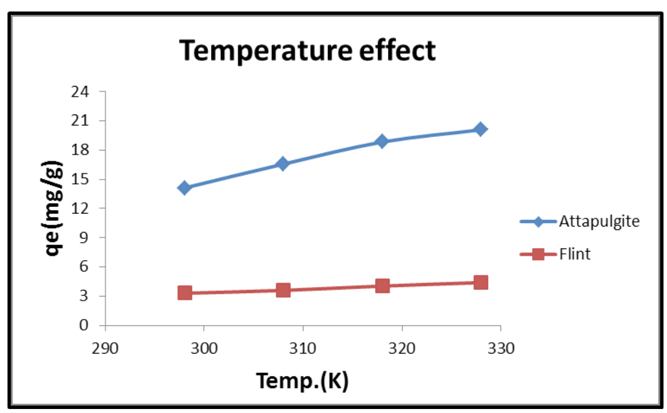

Figure 5: Temperature effect for adsorption of Zn (II) ions on flint and attapulgite clays at initial conc. 100 mg.L^{-1}, contact time of 90 min., flint and attapulgite doses of 0.4 g/25 mL and 0.1 g per 25 mL respectively, pH ≈ 3, and particle size of 75 µm.

Study of Isotherms

The three most important famous adsorption isotherms, Freundlich, Dubinin-Radushkevich, and Langmuir, were used to study adsorption behaviors. Freundlich assumed the Freundlich equation as followsL.[21]

$$\log\log q_e = \log\log K_f + \frac{1}{n}\log\log C_e \quad (3)$$

Whereas Kf (mg/g) denotes Freundlich constant and (1/n) denotes adsorption intensity. The experimental data was fitted with a linear equation by plotting logqe versus log Ce, as shown in Figure 6c–d. Langmuir assumed the Langmuir equation as follows:[22]

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \quad (4)$$

Whereas qe (mg.g^{-1}) means the capacity of adsorption at equilibrium, qmax (mg/g) means maximal capacity of adsorption, KL (mg/L) denotes Langmuir constant related to the adsorption energy and binding sites affinity, and Ce denotes adsorbate concentration at equilibrium. The experimental data was fitted with a linear equation via plotting (Ce/qe) against Ce, as exposed in Figure 6a and b. The main features of Langmuir isotherm could be defined in expressions of equilibrium parameter or factor of separation (RL), which can be computed by relationship.[23]

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (5)$$

Whereas C0 (mg/L) denotes initial concentration. Depending on the value of RL, adsorption kind can be determined as irreversible (RL = 0), unfavorable (RL > 1), linear (RL=1), and favorable (0 < RL < 1). In this study, RL values of adsorption of zinc (II) ion on flint and attapulgite clays were between (0.393-0.600), suggesting that adsorption is favorable.[24] Dubinin assumed the Dubinin equation as follows:[25]

$$\ln\ln \hat{q}\mathring{a} = \ln\ln q_m - \ ^2 \ ln\ lnq_e = ln\ lnq_m - \beta\varepsilon^2 \quad (6)$$

The experimental data were fitted with a linear equation by plotting lnqe versus ε^2, as shown in Figure 6e–f). Whereas qe (mg.g^{-1}) means adsorbate amount at equilibrium, qmax (mg.g^{-1}) denotes maximumal capacity of D-R monolayer, β (mol^{2}kJ^{-2}) denotes constant linked to sorption energy, and ε denotes Polanyi potential linked to equilibrium concentrations that the following relationship can calculate:

$$\varepsilon = RT\ ln\ ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

where R (kJ /K.mol) means gas constant and T (K) means temperature.

The following equation calculates the free adsorption energy (E).[26]

$$E = (-2\beta)^{-0.5} \quad (7)$$

The D-R model is beneficial for defining adsorption mechanism types based on free adsorption energy (E). The Langmuir model suggests that maximum possible adsorption appears to fit for a packed solute monolayer onto the surface of adsorbent materials with no adsorbate-molecule interactions, whereas the Freundlich model applies to heterogeneous surfaces of adsorbate-molecule interactions. Table 3 shows the three isotherms parameters obtained by applying experiment data to isotherm models. The adsorption of zinc (II) ions onto flint and attapulgite clay were fit with the Freundlich isotherm according to R^2 values, as shown in Figure 6a to f. The type of adsorption (physisorption or chemisorption) is determined by the sorption energy (E) value, where (E <16 kJ/mole) indicates physisorption and (E > 16 kJ/mole) indicates chemisorption.[27]

Table 2: Zn (II) ion adsorption capacities on flint and attapulgite clays at two temperatures, pH 3, contact time of 90 minutes, flint and attapulgite doses of 0.4g per 25 mL and 0.1gper25mL, respectively, and particle size of 75 µm

			Temp. (298k)		*Temp.(318k)*	
Metal	*Clays*	*C0 (mg/L)*	*Ce (mg/L)*	*qe(mg/g)*	*Ce (mg/L)*	*qe(mg/g)*
Zinc(II)	Flint	20	6.7455	0.82840625	3.76396	1.0147525
		60	25.198	2.175125	24.09344	2.24416
		100	49.792	3.138	34.42292	4.0985675
		140	83.60875	3.524453125	63.93355	4.754153125
		180	120.4998	3.7187625	94.0612	5.371175
		220	142.0195	4.87378125	119.2701	6.29561875
	Attaplugite	20	3.66432	4.08392	1.82675	4.5433125
		60	26.4277	8.393075	19.0495	10.237625
		100	41.79895	14.5502625	22.12375	19.4690625
		140	71.31392	17.17152	53.9683	21.507925
		180	80.16776	24.95806	66.4277	28.393075
		220	104.7618	28.80955	91.3465	32.163375

Table 3: (Freundlich, D-R, and Langmuir) isotherms parameters for Zn (II) ion adsorption on flint and attapulgite clays at two temperatures, pH 3, contact time of 90 minutes, flint and attapulgite doses of 0.4g per 25 mL and 0.1g per 25 mL, respectively, and particle size of 75 µm.

			Clays			
			Flint		*Attapulgite*	
			Temp. (K)		*Temp. (K)*	
Metal	*Isotherms*	*Parameters*	*298*	*318*	*298*	*318*
Zinc(II)	Langmauir	qmax(mg/g)	5.631	8.026	43.478	40.486
		KL (L/mg)	0.024	0.025	0.013	0.031
		RL	0.457	0.449	0.600	0.393
		R^2	0.9423	0.9205	0.5947	0.8152
	Freundlich	n	1.861	1.867	1.742	1.998
		Kf(L/g)	0.334	0.495	1.712	3.219
		R^2	0.9593	0.9625	0.9364	0.9331
	D-R	qmax(mg/g)	3.507	4.388	17.740	21.042
		$\beta(mol^2/KJ^2)$	13.344	3.820	4.373	1.158
		E(KJ/mol)	0.194	0.362	0.338	0.657
		R^2	0.8727	0.757	0.6634	0.7193

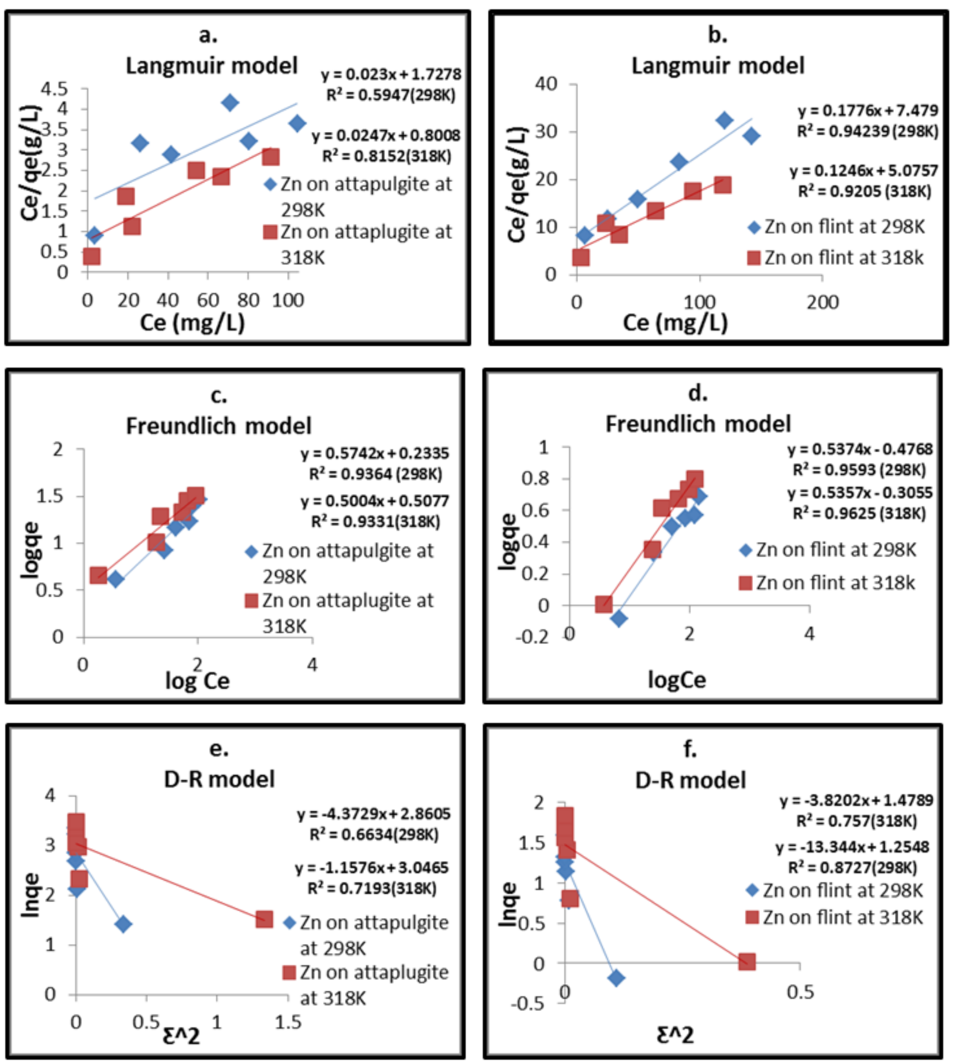

Figure 6a to f: Curves of linearized isotherms, (Freundlich, Langmuir, and D-R) for Zn (II) ion adsorption by flint and attaplugite clays at two temperatures.

The E values in this study ranged from (0.194) to (0.657) KJ/mol, indicating physisorption. Linearized isotherm curves are drawn, and isotherm parameters were calculated using data from Table 2.

Kinetic Models Study

To determine adsorption rate and expected mechanism of zinc (II) ion adsorption on flint and attapulgite clays, pseudo-first order and pseudo-second-order models were applied to adsorption results.

According to Ho and Mckay in 1998, the pseudo-first order model is as next.[28,29]

$$\ln \ln\left(q_e - q_t\right) = \ln \ln q_e - K_1 t \qquad (9)$$

whereas K1 ($min.^{-1}$) denotes pseudo-first-order rate constant, qe($mg.g^{-1}$) represents zinc (II) ion amount which adsorb at equilibrium, and qt (mg/g) represents zinc (II) ion amount which adsorb at the time (t). k1 values and calculated adsorption capacity (qe (cal.)) were caculated from slope and intercept of a linear plot of ln (qe-qt) against (t). Figure 6-a displays pseudo-first-order plots, and also pseudo-first-order features are listed in Table 4. Correlation coefficient values (R^2) listed in table 4 were extremely low, and the calculated adsorption capacity was less than the experimental adsorption capacity, indicating which adsorption did not agree with first-order model.

According to Ho and Mckay in 2000, pseudo second-order model is as follows:[30]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{\,2}} + \frac{t}{q_e} \qquad (10)$$

whereas k2 (g/mg.min) denotes second-order adsorption rate constant. k2 values and calculated capacity of adsorption (qe (cal.)) were determined from the intercept and slope of a linear plot of (t/qt) versus (t). Figure (6b) displays pseudo-second-order plots, and also pseudo-first-order features are listed in Table 4. Correlation coefficient values (R^2) listed in Table 4 were extremely high, and the calculated adsorption capacity was equal to the experimental adsorption capacity, indicating that adsorption agrees with pseudo second-order model (Figure 7a and b).

Parameters of Thermodynamics

Langmuir constant (KL) is connected to energy of the adsorption process. Langmuir model suggests that adsorption is based on a single monolayer. Adsorption from a solution to a solid can be modeled as a perfect two-dimensional solution of solute molecules and solvent, with the solvent and solute competition for active positions on clay surfaces.[31] The equilibrium constant of the adsorption process, K, is related to KL, and the water concentration in the aqueous medium is C (55.56 mole/L), that is stable in dilute solutions. As a result, K could be calculated from the relationship following:[32, 33]

$$K = CK_L \qquad (11)$$

k values can be calculated using the below equation depending on KL (L/mg) values listed in Table 3.

$$\mathrm{K} = 1000 K_L \times M.Wt\ of\ adsorbate \times 55.56 \qquad (12)$$

Parameters of the thermodynamics (ΔG°, ΔH°, and ΔS°) can be calculated by using the listed below thermodynamics relationships:[32, 33]

Table 4: Kinetics parameters for Zn (II) ion adsorption on flint and attapulgite clays at temperature 298K, pH 3, flint and attapulgite doses of 0.4gper2 5 mL and 0.1 g per 25 mL, respectively, and particle size of 75 µm.

			Clays	
Metal	*Kinetic models*	*parameters*	*Flint*	*Attapulgite*
Zinc(II)	Pseudofirst order	q_e (exp.)($mg.g^{-1}$)	3.104643	13.84383
		$K_1 min^{-1}$	0.0158	0.0336
		q_e(cal.)mg.g-1	0.607	4.516
		R^2	0.1202	0.33582
	Pseudosecond order	q_e(exp.)$mg.g^{-1}$	3.104643	13.84383
		K_2 g. $mg^{-1}min^{-1}$	0.05	0.01
		q_e(cal.)$mg.g^{-1}$	3.262	15.456
		R^2	0.999	0.9922

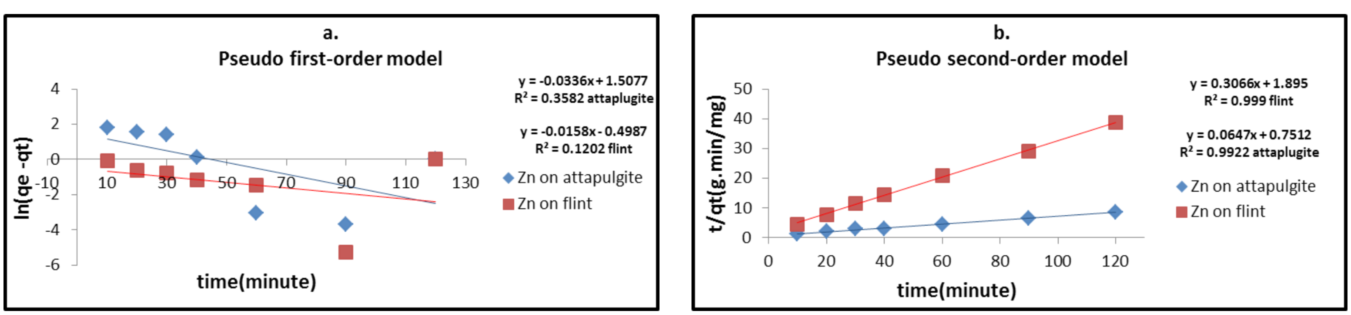

Figure 7(a and b): Curves of linearised kinetic (pseudo first-order and pseudo second-order) of zinc adsorption by flint and attapulgite clay at 298K.

Table 4: Parameters of thermodynamics for Zn (II) ion adsorption on flint and attapulgite clays at two temperatures, pH 3, contact time of 90 minutes, flint and attapulgite doses of 0.4gper25mL and 0.1g per25mL, respectively, and particle size of 75 μm.

		Clays			
		Flint		*Attapulgite*	
		Temperature		*wTemperature*	
Metal	*Thermodynamic parameters*	*298K*	*318K*	*298K*	*318K*
Zinc(II)	1/T	0.003356	0.003145	0.003356	0.003145
	K	86166.28	89075.85	48302.8	111920.8
	lnK	11.36403	11.39724	10.78524	11.62555
	ΔG°(KJ/mol)	-28.1552	-30.1326	-26.7212	-30.7362
	ΔH°(KJ/mol)	1.308228		33.102333	
	ΔS°(KJ/mol)	98.87061		200.7502	

$$\Delta G^\circ = -RT \ln lnK \tag{13}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{14}$$

$$\ln lnK = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{15}$$

In common, chemisorption have a ΔG° change of -80 to -400 $kJ.mol^{-1}$, whereas physisorption has a ΔG° change of -40 to 0 kJ/mol.[34] In this work, ΔG° values were negative and fall between -30.7362 to -26.7212 kJ/mol, indicating which adsorption process in all systems was spontaneous and physisorption. ΔS° and ΔH° values were positive, indicating increasing randomness and an endothermic system.

Apply Perfect Conditions to a Sample of Industrial Wastewater

Applied perfect conditions obtained from batch experiments on synthetic water for zinc ion on Al-Quds Power Station sample. The results showed decreasing zinc ion concentration in an industry sample when using attapulgite clay as adsorbent from 63.97 to 0.521 mg/L at temperature 328K, pH 4, contact time of 90 minutes, and attapulgite dosage of 0.1g (R% =99.18). While decreasing zinc ion concentration in an industry sample when using flint clay as an adsorbent from 63.97 to 17.83 mg/L at temperature 328K, pH 4, contact time of 90 minutes flint dosage 0.4g (R% =72.08).

CONCLUSION

The batch adsorption experiments in this study revealed that flint and attapulgite clays were efficient, low cost, environmentally friendly, and available for removing zinc ion from industrial wastewater. The experiment results showed that zinc ion adsorption capacity increased with contact time and depended on pH, clay dosage, and temperature. The adsorption of zinc (II) ions onto flint and attapulgite clay fits with the Freundlich isotherm and pseudo-second-order model according to R^2 values. ΔG° and free adsorption energy (E) values showed spontaneous adsorption and physisorption in all systems. ΔS° and ΔH° values were positive, indicating increasing randomness and an endothermic system. Perfect conditions were applied on the Al-Quds Power Station sample and showed that the removal percentage by attapulgite clay (R% = 99.18) was higher than the removal percentage by flint clay (R% =72.08).

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