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Removal of Cu (II) and Zn (II) ions from aqueous solution by clay mineral

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Abstract

The ability of a type of clay to adsorb Cu(II) and Zn(II) ions from aqueous solutions was studied and optimized. Different factors affecting adsorption were considered and studied individually. These factors include contact time, pH, initial metal ion concentration, clay dose and temperature. Langmuir, Freundlich and Temkin isotherm models were studied for the adsorption process. Depending on the values of correlation coefficients of the different models, it was concluded that the adsorption of Cu(II) ions was best described by Temkin model (R^2=0.9904), where adsorption of Zn(II) followed both Langmuir (R^2=0.9806) and Freundlich (R^2=0.9840) models. Maximum adsorption capacities according to Langmuir isotherm were 20.08 and 17.60 mg/g for Cu(II) and Zn(II) ions, respectively. The increase of adsorption capacity with temperature for both metal ions indicted endothermic processes.

Keywords: copper, zinc, adsorption, clay, isotherm.

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1. Introduction

The discharge of large amounts of heavy metals-contaminated wastewater into the environment due to urbanization and industrialization has posed a great problem worldwide. Heavy metal contamination exists in aqueous wastes of many industrial sources such as metal plating, mining operations, smelting, alloy industries, tanneries and storage batteries manufacturing [1]. Due to their high solubility in the aquatic environments, heavy metals can be absorbed by different living organisms. The presence of heavy metal ions such as Cd, Cr, Cu, Ni, Pb, and Zn is of major concern due to their toxicity to many life forms if they are ingested beyond the permitted concentration.

Unlike organic pollutants, heavy metal ions do not biodegradable in environment into harmless end products [2]. So, the presence of heavy metal ions in aqueous media leads to accumulate within plants and fish organism and once they enter the food chain, they cause harmful effects to human body. Therefore, it is necessary to treat metal contaminated wastewater prior to its discharge to the environment. The removal of heavy metals from water effluents can be achieved by conventional treatment processes such as chemical precipitation, adsorption, ion exchange, membrane filtration, and electrochemical methods.

In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated water has been of a great importance. Adsorption has become one of the alternative treatments and the search for low-cost adsorbents that have metal-binding capacities has intensified [3]. The adsorbents may be of mineral, organic or biological origin, agricultural wastes, biomass, clay minerals, industrial byproducts, or natural or polymeric materials [4]. Natural clays as the adsorbent with a low cost have received much attention on heavy metals sorption from contaminated water [5-7]. Mineral clays have many advantages over naturally available adsorbents in terms of low-cost, abundant availability, high adsorptivity, non-toxicity and high potential for ion exchange. Many types of locally available clays could bring massive economic and environmental benefits to wastewater treatment as kaolinite [8], perlite [9], sepiolite [10], montmorillonite [11], zeolite [12] and landfill clays [13]. Clay minerals [14] are hydrous aluminosilicates with fine particle size; they are composed of two basic building blocks Silicon–Oxygen Tetrahedron $(Si_2O_5)^{2-}$ and Aluminum Octahedral (Gibbsite Sheet). The chemical composition of the clay mineral is based on a hydroxyl-aluminosilicate framework.

2. Experimental

The effects of some selected reaction parameters on the rate of adsorption of metal ions from aqueous solutions using clay mineral were investigated. The parameters considered included contact time, adsorbent dosage, pH and agitation speed. To study the effect of agitation time on metal adsorption by clay, 50 ml of the aqueous metal solution was transferred into clean glass bottles. 0.1 g of the adsorbent was weighed and added to metal solution and agitated for different contact time (from 5 to 90 min). After each agitated time, the content of each bottle was filtered, and the equilibrium concentration of each of the metals in each filtrate was determined. The effect of adsorbent dosage was studied by adding various amounts of the adsorbent (0.025 – 0.3 g) to 50 ml metal solution (20 mg/l). To determine the effect of pH on the metal removal efficiency, by adjusting the pH to the required value (1.9 – 6.5) and mixing 0.1 g of clay with 50 ml of metal solution (20 mg/l). The final concentration of metal ion was measured after 90 min of continuous agitation. Optimum weight of the adsorbents and agitated at a preset equilibrium time. To study the effect of agitation speed, the optimal adsorbent dosage of the adsorbents was used to adsorb the heavy metals at different agitation speeds by adding the optimal dosages of the adsorbents to 20 mL of electroplating wastewater in different plastic bottles and agitated for 1 h. The agitation speed was adjusted from 150 rpm to 300 rpm and the content of each bottle was then filtered and analyzed.

The amount of metal ions adsorbed was determined by difference between the initial and final concentrations. The sorption efficiency (%) and amounts of adsorbed metal (q_e) by clay were calculated using Eqs. (1) and (2), respectively:

$$Si \qquad ca \qquad (\%) = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

$$q_e = \frac{(C_i - C_e)V}{M} \qquad (2)$$

C_o is the initial metal ion concentration, C_e is the concentration of metal ions in solution (mg/L) at time t in solution, V is the volume of initial metal ion solution used (L) and M is mass of adsorbent used (g).

3. Results and discussion

3.1. Effect of contact time on removal efficiency

The effect of contact time on the removal efficiency (mg/g) of the metal ions was investigated at initial dye concentration 20 mg/L as shown in Fig. 1. The removal efficiency of by the clay was rapid in the beginning due to larger surface area available of adsorbent but its rate gradually decreased with time until it reached equilibrium. The plots reveal that maximum removal of the dye after about 60 min of continuous stirring. After adsorption, the rate of dye uptake is controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent particles. The maximum removal was 9.73 mg/g for Cu(II) and 9.30 mg/g for Zn(II) at the equilibrium time.

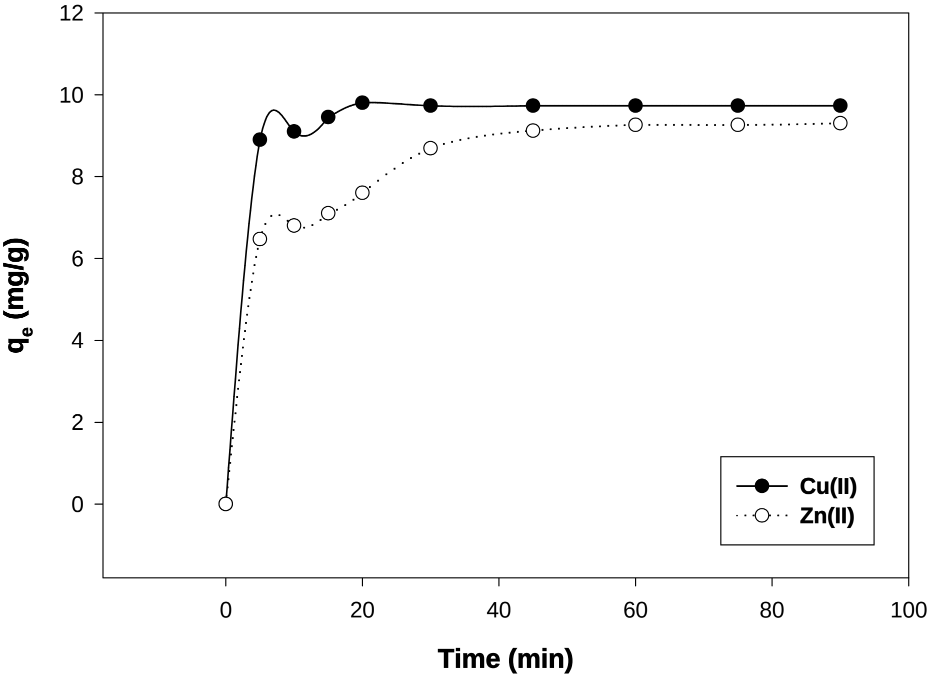

Fig 1: Effect of contact time on Cu(II) and Zn(II) removal

3.2. Effect of pH on removal efficiency

The pH of aqueous solution is one of the major parameters that control the adsorption efficiency of ions at the solid/water interface. In addition, it affects the solubility of the metal ions, concentration of the counter ions on the degree of ionization and the functional groups of adsorbent of the adsorbate during the reaction [15]. The removal of copper and zinc ions by the clay has been studied at different pH values while the other parameters such as the contact time, agitation speed, initial metal ion concentration and the dosage of clay. It is clear that minimum adsorption occurs at acidic solutions while maximum removal is observed at higher pH's. At pH 2.0, 21.40% and 35.35%, while at pH 6.5, 92.30% and 95.27% were removed for Cu(II) and Zn(II), respectively. This behavior is due to the competition between metal ions and hydrogen ions at lower pH values. At higher pH's, the hydrogen ions concentration decreases and this competition decreases allowing the adsorption of metal ions on the clay surface.

Fig 2: Effect of pH on Cu(II) and Zn(II) removal percent.

3.3. Effect of clay dose on removal efficiency

The influence of adsorbent dose on metal ions removal percent by clay is presented in Fig. 3a, while removal efficiency is shown in Fig. 3b. The percentage of removal of the dye increased from 89.94% to 84.85% as the clay dose was increased from 0.5 to 6.0 g/L. The increased removal at high dosages is expected, because of the increased adsorbent surface area and availability of more adsorption sites.

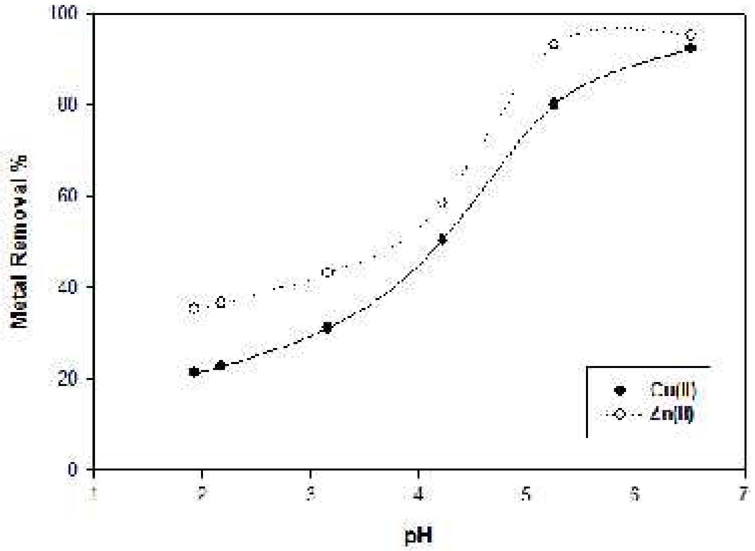

Fig 3(a): Effect of clay dose on Cu(II) and Zn(II) removal percent.

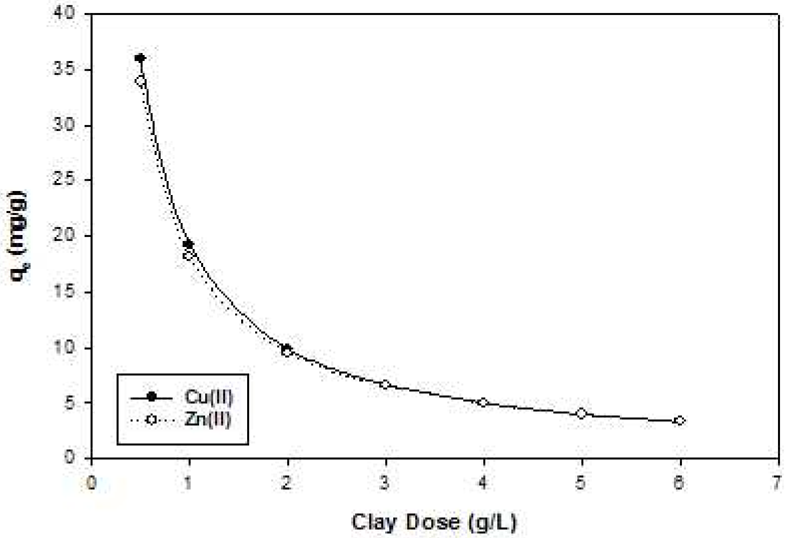

Fig 3(b): Effect of clay dose on Cu(II) and Zn(II) removal efficiency.

3.4. Effect of initial ion concentration on removal efficiency

Fig 4a shows the effect of different concentrations (5 – 50 mg/L) of Cu(II) and Zn(II) ions on the removal percent. The percent removal (%) decreased by increasing metal ions concentration, while the adsorption amount (mg/g) increased (Fig. 4b) with an increase in initial dye concentration. This is because a higher initial concentration enhanced the driving force between the aqueous and solid phases and increased the number of collisions between metal ions and adsorbents [16].

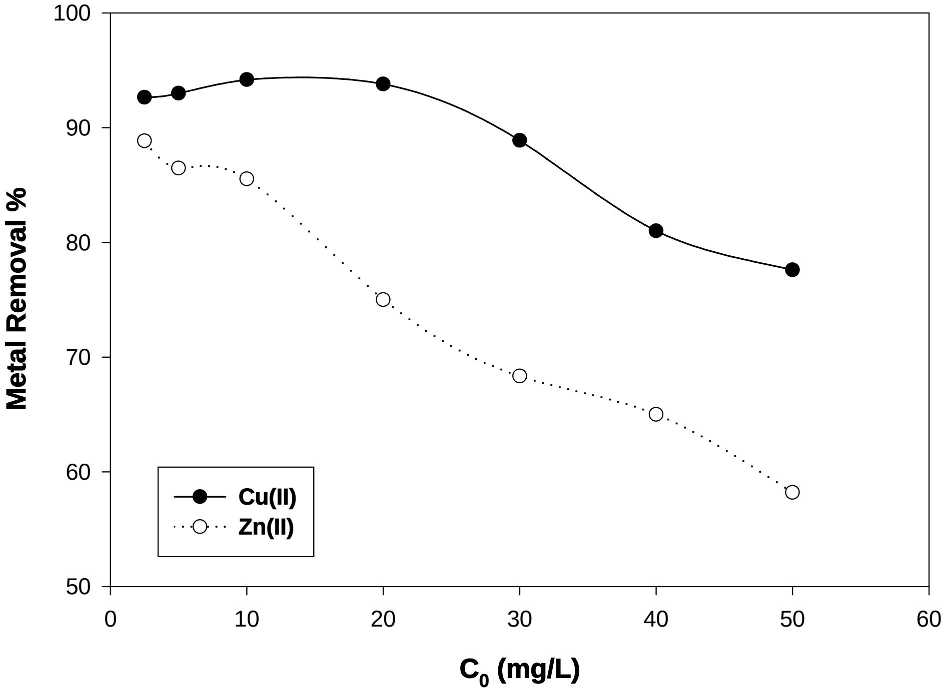

Fig 4(a): Effect of initial metal concentration on Cu(II) and Zn(II) removal percent.

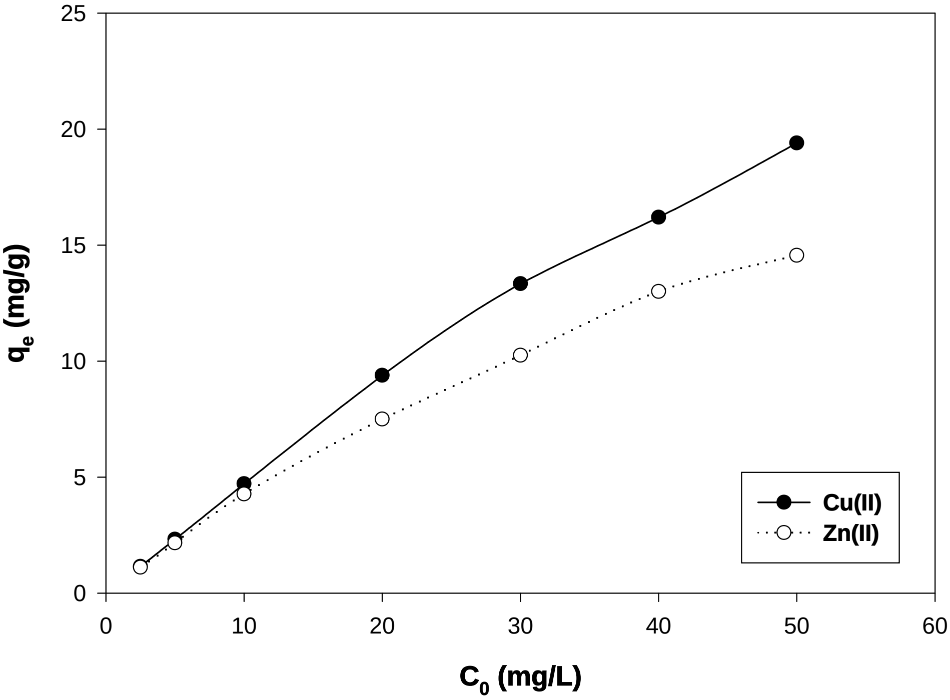

Fig 4(b): Effect of initial metal concentration on Cu(II) and Zn(II) removal efficiency.

3.5. Adsorption isotherm models

Analysis of the equilibrium data is important to develop an equation which accurately represents the results and can be used for the design purposes [17]. Several isotherm equations have been used for the equilibrium modeling of adsorption systems. The sorption data have been subjected to different sorption isotherms, namely; Langmuir, Freundlich, and Temkin.

3.5.1. Langmuir model

An adsorption isotherm is characterized by certain constants which values express the surface properties and affinity of the sorbent and can also be used to find the capacity of different sorbents. Based on ideal assumption of a monolayer, adsorption of adsorbate on adsorbent surface the Langmuir isotherm model [18] is expressed in linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (3)$$

where q_e (mg/g) is the equilibrium adsorption capacity, q_m (mg/g) is the maximum amount of the metal ion per unit weight of Cu(II) or Zn(II) to form a complete monolayer coverage on the surface bound at high equilibrium metal ion concentration C_e (mg/L) and *b* (L/mg) is the Langmuir constant related to the affinity of binding sites. q_m represents the practical limiting adsorption capacity when the surface is fully covered with metal ions. The value of q_m assists in the comparison of adsorption performance for different adsorbents or for different metal ions on the same adsorbent, and *b* indicates the bond energy of the adsorption reaction between metal ion and adsorbing material. Fig. 5, represents the Langmuir isotherm plot for adsorption of Cu(II) and Zn(II).

The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) defined by the relationship [19]:

$$R_L = \frac{1}{1+bC_L} \qquad (4)$$

where C_o is the initial metal ion concentration in (mg/L) and K_L is the Langmuir equilibrium constant (L/mg). The value of the separation factor provides important information about the nature of the adsorption process of metal ions. The adsorption may be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). For the initial metal concentration from 2.5 to 50 mg/L for both metal ions used in this study, the values of R_L ranged from 0.048 to 0.502 for Cu(II) and from 0.134 to 0.756 for Zn(II); this indicates a favorable adsorption process.

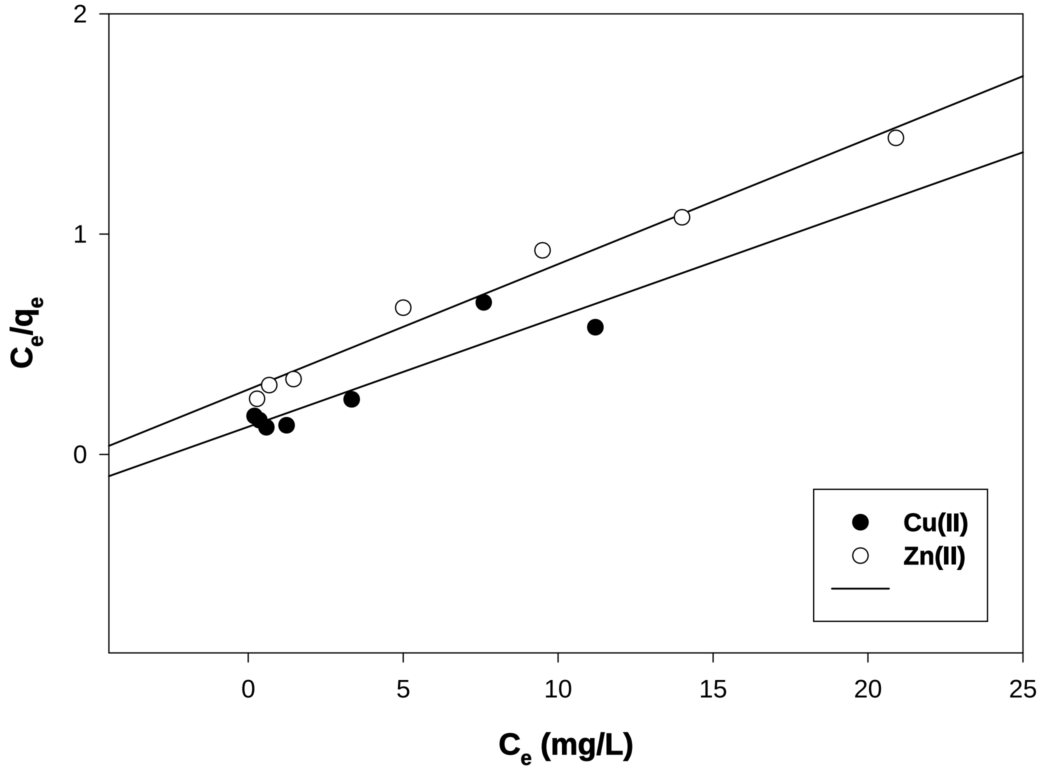

Fig 5: Langmuir isotherm plot for the adsorption of Cu(II) and Zn(II) on clay.

3.5.2. Freundlich model

The Freundlich model is based on the idea that metal ions are infinitely accumulated on the surface of the adsorbent. The Freundlich equation used to obtain the sorption parameters [20]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (5)$$

K_F is a constant related to the adsorption capacity, and n is a constant related to the intensity of adsorption and the spontaneity of adsorption when this value is greater than one.

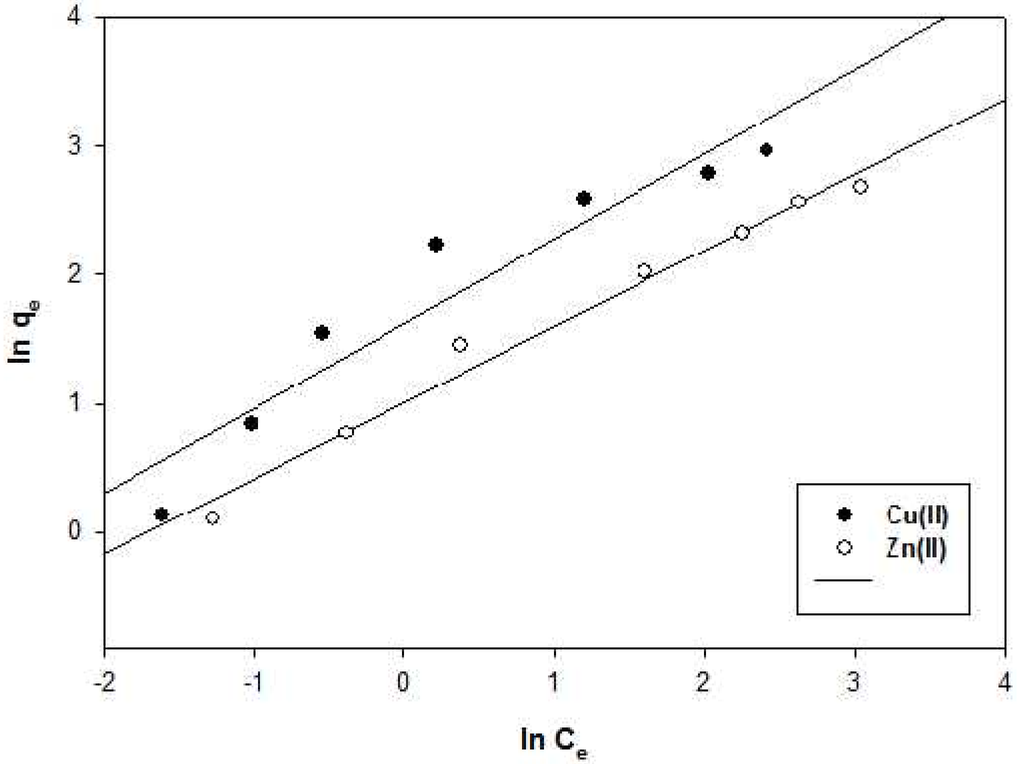

Fig 6: Freundlich isotherm plot for the adsorption of Cu(II) and Zn(II) on clay.

3.5.3. Temkin model

Another model used to evaluated this same equilibrium was the Temkin model [21] which is represented by the following equation:

q_e = B lnA + B lnC (6)

where B is a constant related to the heat of adsorption (J/mol) and A is the Temkin isotherm constant (L/g). B and A could be calculated (Table 1) from the linear plot of ln C_e against q_e. This isotherm assumes that the heat of adsorption of all molecules in the layer decreases linearly with coverage due to the adsorbent–adsorbate interaction. It assumes also that adsorption is characterized by a uniform distribution of binding energies up to some maximum value [22].

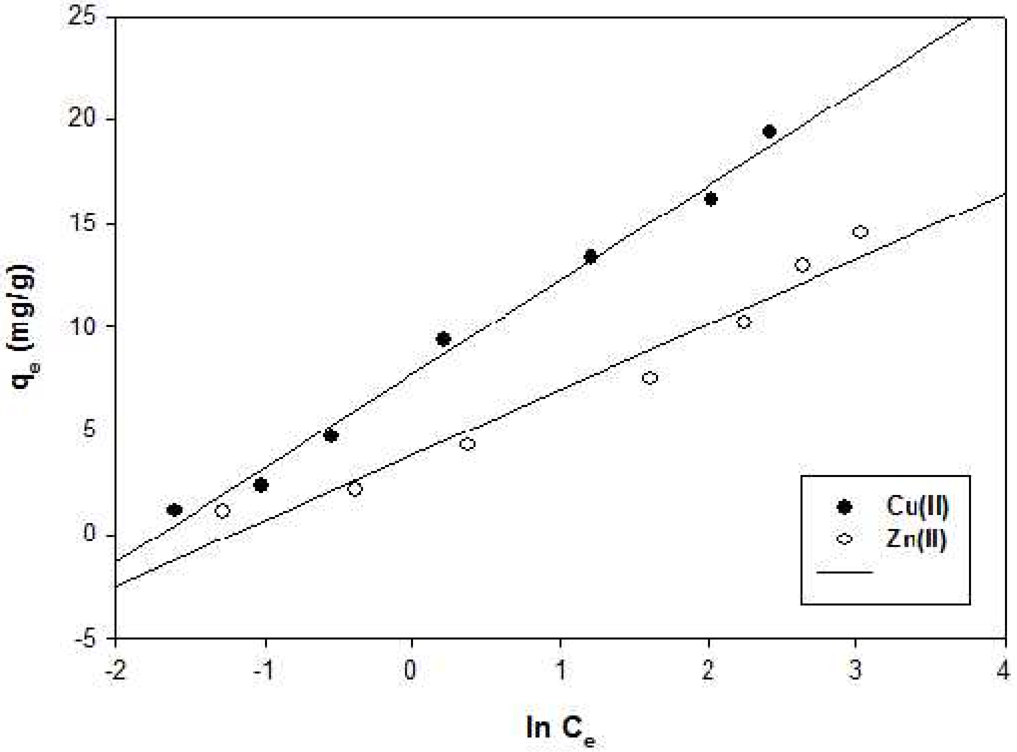

Fig 7: Temkin isotherm plot for the adsorption of Cu(II) and Zn(II) on clay.

Table 1: Isotherm models constants for adsorption of Cu(II) and Zn(II) on clay.

Metal ion	Langmuir model			Freundlich model			Temkin model		
	q_m (mg/g)	*b* (L/mg)	R^2	n	K_F	R^2	A	B	R^2
Cu(II)	20.08	0.396	0.8373	1.51	41.59	0.9096	24.66	5.56	0.9904
Zn(II)	17.60	0.129	0.9806	1.69	10.11	0.9840	16.12	3.16	0.9588

From the data shown in Table (1), it could be concluded that the adsorption process of Cu(II) is best described by Temkin isotherm model (R^2 = 0.9904), while the adsorption of Zn(II) on clay follows both Langmuir (R^2 = 0.9806) and Freundlich (R^2 = 0.9840) models.

3.6. Effect of temperature and thermodynamic parameters

The effect of temperature on Cu(II) and Zn(II) adsorbed by clay has been investigated at four different temperatures (30, 40, 50 and 60 ºC) and is given in Fig 8. The adsorption percent increased from 96.8% to 98.7% for Cu(II) and from 94.0% to 95.9% for Zn(II) at a metal ion equilibrium concentration of 20 mg/L as temperature rises from 30 to 60 ºC. The increase of removal capacity for both metal ions indicates an endothermic adsorption process.

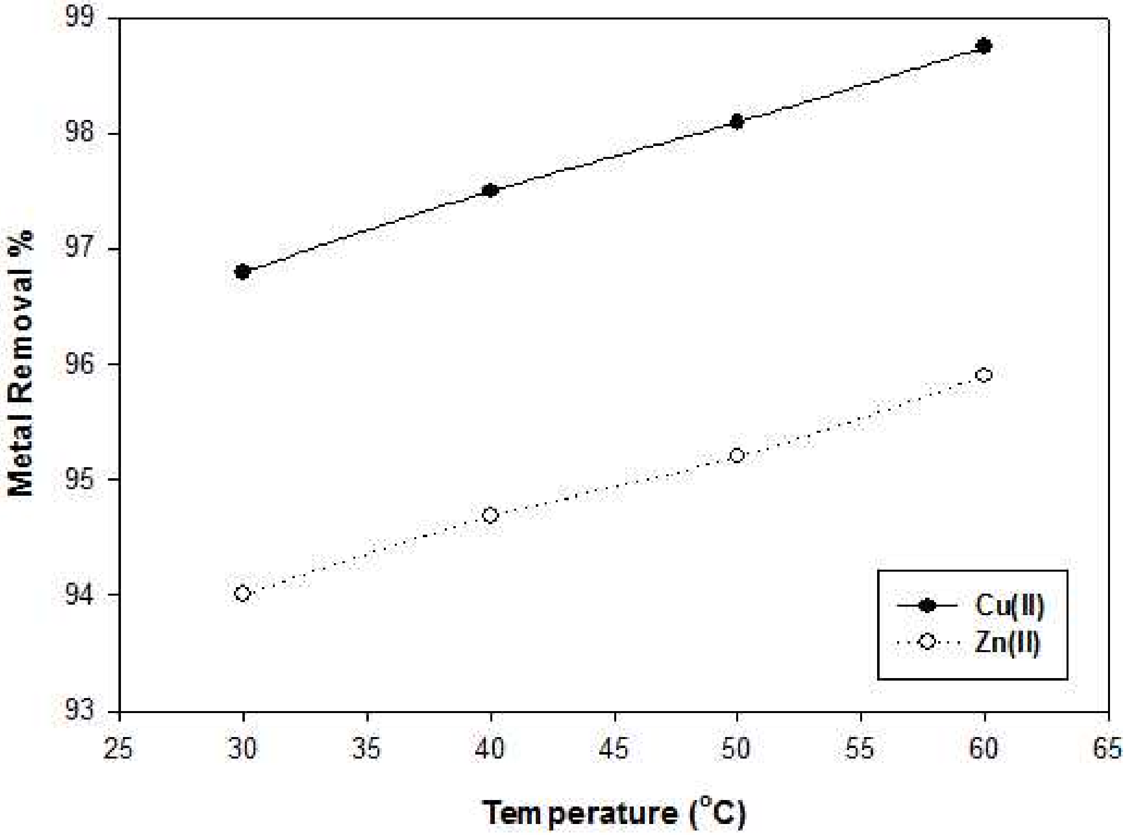

Fig 8: Effect of temperature on the adsorption of Cu(II) and Zn(II) on clay.

Thermodynamic parameters including the change in free energy (*ΔG*), enthalpy (*ΔH*) and entropy (*ΔS*) were used to describe thermodynamic behavior of the adsorption of Cu(II) and Zn(II) ions onto clay. These parameters were calculated from the following equations:

$$\Delta G = -R' \quad K_D \qquad (7)$$

where, *R* is the universal gas constant (8.314 J/mol K), *T* is temperature (K) and K_D (q_e/C_e) is the distribution coefficient.

By applying the following equation, the enthalpy (*ΔH*) and entropy (*ΔS*) of adsorption process were estimated from the slope and intercept of the plot of ln K_D versus 1/*T* yields, respectively (Fig. 9).

$$\ln K_D = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{R}\right) \qquad (8)$$

Table 2: Adsorption values used for estimation of thermodynamic parameters for adsorption of Cu(II) and Zn(II) on clay.

Metal ion	q_e	C_e	q_e/C_e	ln K_D	1/T (x1000)	Slope	Intercept	R^2
Cu(II)	9.68	0.64	15.12	2.716	3.300	-605.7	11.67	0.9561
	9.75	0.50	19.50	2.970	3.144			
	9.81	0.38	25.81	3.250	3.048			
	9.87	0.26	37.96	3.636	3.003			
Zn(II)	9.40	1.20	7.83	2.058	3.300	-591.1	11.34	0.9367
	9.47	1.06	8.93	2.189	3.144			
	9.52	0.96	9.91	2.294	3.048			
	9.59	0.82	11.98	2.483	3.003			

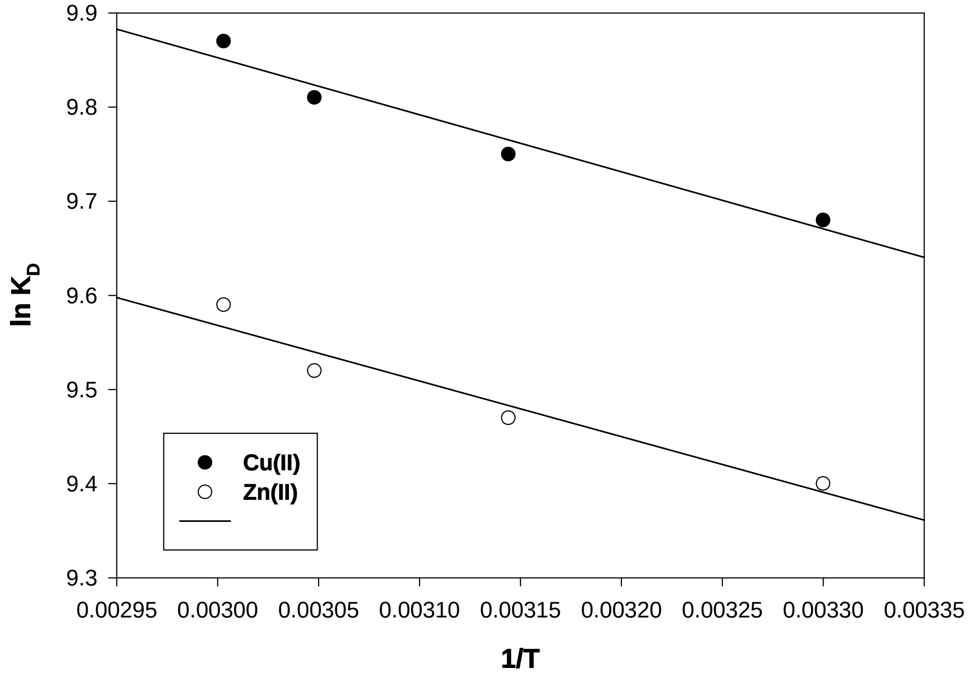

Fig 9: Relation between 1/T and ln K$_D$ for the adsorption of Cu(II) and Zn(II) ions on clay.

The values of Δ*H*, Δ*S* and Δ*G* were calculated and shown in Table 3.

The positive values of Δ*H* indicated endothermic adsorption processes. Positive ΔS reflects the affinity of the clay for Cu(II) and Zn(II) ions and an increased randomness at the solid-solution interface during adsorption, while the negative values of Δ*G* confirm the feasibility of the process and the spontaneous nature of aniline adsorption [23].

Table 3: Thermodynamic parameters of adsorption of Cu(II) and Zn(II) ions on clay.

Metal ion	Temperature K	Thermodynamic parameters		
		Δ*G* (KJ/mol)	Δ*H* (KJ/mol)	Δ*S* (J/mol K)
Cu(II)	303	-6.841	5.035	97.02
	313	-7.728		
	323	-8.727		
	333	-10.066		
Zn(II)	303	5.184	4.914	94.28
	313	5.678		
	323	6.160		
	333	6.874		

4. Conclusion

The ability of a kind of clay mineral was evaluated as adsorbent for Cu(II) and Zn(II) ions from aqueous solutions. Different parameters were evaluated for the adsorption as pH, initial concentration of metal ions, clay dose and temperature. The highest adsorption capacity was observed at about pH 6. Three adsorption isotherm models were examined for the adsorption process. Maximum adsorption capacities according to Langmuir isotherm were 20.08 and 17.60 mg/g for Cu(II) and Zn(II) ions, respectively. The adsorption of the two metal ions was endothermic and occurred spontaneously.

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