

Study of the Factor Affecting the Adsorption of Copper Ion by an Iraqi Clay

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Abstract

In this research work, the efficiency of a local clay (collected from Al-Kadia area of Mosul city in the north part of Iraq) to adsorb the copper (II) ion from aqueous solution was investigated. The experiments were carried out as a batch method. The factors affecting the removal efficiency such as; contact time, initial concentration, initial pH solution and particle size of adsorbent are studied. The results showed that, the increase of initial concentration increases the amount of adsorbed metal ion but decreases the adsorption efficiency. The amount of copper (II) ion increases rapidly with the increase of pH from 2 to 5, however there was little change within the pH range between (5-8). The increase of the surface area (decrease of particle size) was accompanied by increase in removal efficiency.

The adsorption is also conducted at various temperatures (15-55 °C) and at different initial concentration (10-70 mg/L). The thermodynamic functions are estimated.

Kinetic study of adsorption of copper (II) ion on the clay surface is carried out by applying the first order integrated equation of the reversible reaction. The adsorption equilibrium, adsorption and desorption rate constants are calculated at different temperature. The activation energies and the thermodynamic functions of activation of the forward and backward processes are estimated.

Keywords: Iraqi clay, adsorption, copper ion, kinetic study.

Introduction

Pollution of the environment by heavy metals, which are known to be toxic and non-biodegradable, has become one of the most important challenges that the world faces nowadays.

The relatively high cost of technologies employed by the advanced countries for the removal of heavy metals from wastewater such as; ion exchange, chemical precipitation, ultra filtration, or electrochemical deposition, has promoted a demand to look for effective and economic alternatives which are feasible for such industries⁽¹⁾. Adsorption is found to be the most suitable method. Commercial activated carbon has been widely used as an effective material for controlling various pollutants. However, its relatively high cost, especially for the developing countries, created a strong need to develop economical adsorbents. Unconventional adsorbents like sand, saw dust, peat and wood,...etc. have attracted the attention of several researchers groups and adsorption characteristics with varying degree of success⁽²⁾.

According to recent surveys, heavy metals are reported as the most contaminants produced by industrial wastes. In one of these studies, commercial activated carbon, chitosan and agar⁽³⁾ were used as adsorbents for the removal of Mn^{+2} , Fe^{+2} , Ni^{+2} and Cu^{+2} from aqueous solutions. Cigdem et al.⁽⁴⁾ studied the adsorption rate and capacity of the northern Anatolian Smectite for some selected heavy metal ions in the concentration range of (5-900 mg/L) and pH range of 1.0 to 7.0. Competitive adsorption of the metal ions on the Smectite was also investigated. In another study, Kim et al.⁽⁵⁾ examined the adsorption rates and characteristics of Cd, Cr and Zn ions with solutions mixed with red, white, red and white clays and Zeolite under various pH and initial concentrations. Velan et al.⁽⁶⁾ investigated the batch removal of Cu^{+2} ion from aqueous solution under different experimental conditions using *Ulva reticulata*. Abia⁽⁷⁾ studied the rate of adsorption of Zn, Pb and Cd metal ions onto maize cob at optimum pH of 7.5 and temperature of 30 °C. The effect of contact time was also investigated.

The removal of heavy metals by adsorption is still requiring the use of inexpensive adsorbents.

Clay minerals are known to be good adsorbent for cations because of their large specific surface area and their surfaces are negatively charged⁽⁸⁾. These negative charges are commonly due to incomplete ionic exchange. Therefore, electrical neutralization of the clay surface can be achieved by the adsorption of differently charged ions from the outside⁽⁵⁾. For this reason, clays have been widely used as adsorbent especially for the removal of heavy metals from aqueous wastes.

The heavy metal adsorption properties by clay minerals are dependent not only on the physical and chemical characteristics of the clay mineral themselves such as; the existence and amount of organic materials within them, exchangeable cations, amorphous oxides, . . . etc., but also on the chemical compositions and conditions of heavy metal solutions such as; pH, competing cations, ionic strength, and types of ligands⁽⁶⁻¹¹⁾. Generally the adsorption of heavy metal is activated under high pH.

The objective of this study is to investigate the removal efficiency of Cu^{+2} ion from standard solution, with concentration range of 10-70 mg/L and various pHs, by an Iraqi clay. The clay is fairly uniform in its physical and chemical properties and also easily available. The optimum removal conditions by using the clay as adsorbent are determined. The kind and strength of the binding energy of the copper ion to the clay surface is estimated by the calculation of the thermodynamic functions. The rate of adsorption of Cu^{+2} on the clay is also investigated. The thermodynamic parameters of activations as well as the activation energy of adsorption are determined.

Kinetic model

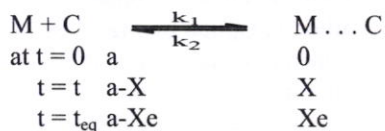
The rate equation of the reversible first order reaction is used to fit the adsorption kinetic data of the studied system. This equation is described as:

$$\ln(X_e - X) = \ln X_e - (k_1 + k_2) t \dots \dots \dots (1)$$

Where X_e and X are the concentrations of the adsorbed metal ion at equilibrium and at definite time respectively,

k_1 and k_2 are the rate constants of the forward and backward processes respectively.

A plot of $\ln(X_e - X)$ versus time gives a straight line of slope equal to $(k_1 + k_2)$. Assuming (a) is the initial concentration of metal ion, the adsorption can be expressed by the following equation:



Since the value of adsorption equilibrium constant (K) can be calculated from the ratio:

$$K = \frac{X_e}{a - X_e} = \frac{k_1}{k_2} \dots \dots (2)$$

Values of k_1 and k_2 can be obtained. The activation energies (E) for both adsorption and desorption processes are calculated using Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT} \dots \dots (3)$$

Where k is the rate constant, A is a frequency factor, R is the universal gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$) and T is the absolute temperature. The value of E is determined from the slope of plotting $\ln k$ versus $1/T$, and A (sec^{-1}) is determined from the intercept. The values of thermodynamic functions of activation (ΔH^* , ΔS^* and ΔG^*) are estimated from the following equations:

$$\Delta H^* = E - RT \text{ (KJ.mol}^{-1}) \dots \dots (4)$$

$$\Delta S^* = R \left[\ln A - \ln \left(\frac{K'T}{h} \right) - 1 \right] \text{ (J.K}^{-1}.\text{mol}^{-1}) \dots \dots (5)$$

Where K' is Boltzman constant (1.38×10^{-23}) J.K^{-1} and h is Planck constant (6.6256×10^{-34}) J. sec^{-1} .

Experimental

1. Preparation of solution

A standard solution of the metal ion with concentration of 1000 mg/L was prepared by dissolving a certain weight of the metal nitrate in 100 ml of deionized water. The desired solution concentrations are then prepared by dilution.

2. Preparation of the clay sample

The raw material was first crushed and washed to remove all impurities, and then dried in oven at 103°C . The clay ground again and a colloidal suspension was made. The heavy particles were discarded by decantation. The suspension was then filtered and the resulting fine particles of the clay were dried at sunlight and then in oven at 103°C and finally ground and sieved into several size fractions in the range of 75-600 μm using standard ASTM sieve series. The fine particles (75 μm) were used as adsorbent for this investigation and the rests were used to test the effect of particle size on adsorption.

3. Effect of contact time

0.1 gm of the clay was put into a 100 ml solution of the metal ion of initial concentration 70 mg/L. Different samples were shaken at time intervals at 90 rpm for 10, 20, 30, 40, 50, 60, 70, 80 and 90 minutes. The samples were filtered rapidly and the metal content of the filtrates determined by atomic absorption spectroscopy (AAS).

4. Effect of pH

The effect of pH is investigated in the range of $\text{pH} = 2-8$ while keeping all the other experimental parameters constant. The pH of the solutions was controlled using NaOH and HNO_3 solutions.

5. Effect of particle size of adsorbent

The study is conducted by using clay with four different particle sizes (75, 150, 300 and 600 μm), and with the same experimental conditions of temperature, pH, etc. The experiments were repeated at seven different initial concentrations (10-70 mg/L).

6. Effect of initial concentration

The effect of initial concentration is conducted at equilibrium conditions within the range of 10-70 mg/L. Seven samples of different concentrations of the tested metal ion (Cu^{+2}) are prepared. 0.1 gm of the clay added to each of them, shaken for 80 minutes, filtered and the amount of adsorbed ion is estimated by AAS. The removal efficiency is expressed in term of adsorption percentage and calculated as follow:

$$\% \text{ Adsorption} = \frac{X}{a} \times 100 \dots \dots (6)$$

Where X is the concentration of the adsorbed ions and a is its initial concentration.

7. Estimation of thermodynamic functions of adsorption

The adsorption equilibrium constant (K) is calculated at various temperatures from the ratio between the adsorbed and free copper ion concentrations. The value of ΔH is estimated from the slope of the straight line ($\Delta H/R$), that resulted from plotting $\ln K$ versus ($1/T$) when applying the Vant Hoff's equation which can be expressed as:

$$\ln K = \ln K_0 - \frac{\Delta H}{RT} \dots \dots (7)$$

Where R is the gas constant, T is the absolute temperature and $\ln K_0$ is the intercept.

Since $\Delta G = \Delta H - T\Delta S$ and ΔG equal to zero at equilibrium, the value of ΔS is equal to ($\Delta H/T$).

The thermodynamic functions of the adsorption system are calculated at various initial concentrations.

8. Kinetic study

The kinetic study is carried out at the natural pH of the copper ion solution of 20 mg/L initial concentration, and within the period of 10-40 minutes. This period was determined from the study of effect of contact time. In this investigation, 0.1 gm of the clay is added into 100 ml of 20 mg/L copper solution. Different samples are shaken for 10, 15, 20, 25, 30, 35, 40 and 80 minutes. The samples are then filtered rapidly and the copper content of the filtrate are determined by AAS. The amount of adsorbed ions is estimated by difference. The above method is repeated at different temperature (25, 35, 45 and 55°C).

Results And Discussion

All the adsorption experiments of the studied system were carried out as a batch method.

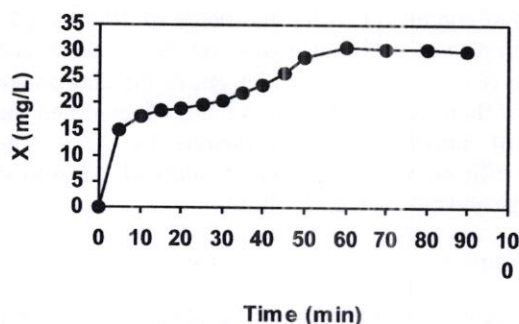
The chemical composition of the raw material (clay) obtained by XRF analysis are listed in Table (1).

Table (1): The chemical composition of the raw material (wt%)

Compos.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ +FeO
Wt%	24.00	0.46	10.00	4.79
Compos.	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
Wt%	20.25	0.42	0.41	0.10
Compos.	MnO	MgO	H ₂ O+CO ₂	
Wt%	0.07	5.73	34.00	

Effect of contact time

A series of batch experiments were carried out to find the optimum time required to reach equilibrium. The results obtained are shown in Figure (1).

**Figure (1): The variation of the amount of adsorbed copper ion with time**

The uptake level of metal ion increases as time increase from zero to 90 minutes. The results indicate that, adsorption process proceeds in two stages; an initial rapid increase between zero and 10 minutes being very sharp, followed by a slower stage in which the uptake rate gradually decreased with time and approached maximum at about 70 to 80 minutes. This time is used in the following steps of this investigation.

Effect of initial concentration

The effect of initial concentration is tested at various concentrations in the range of 10 to 70 mg/L, while keeping all the other parameters constant. The results obtained are listed in Table (2). The adsorption efficiency is calculated as in equation (6).

Table (2): The variation of amount of adsorbed Cu⁺² ions and adsorption efficiency with the initial concentration at 25 °C

Initial conc.	X (mg Cu ⁺² /gm clay)	Adso. efficiency
10	9.577	95.770
20	16.666	83.330
30	23.281	77.603
40	28.480	71.200
50	32.004	64.008
60	29.996	49.993
70	30.249	43.212
70*	64.365	91.950

* adsorption on activated carbon

The results in Table (2) show that, the removal efficiency of Cu⁺² ions by the used clay is highly dependent on the initial concentration of the metal ion. The amounts of adsorbed copper ion increases with the increase of initial concentration while the adsorption efficiency decrease. This could be attributed to the increase of the ionic competition to be adsorbed on a constant number of active sites available for adsorption on a certain amount

of adsorbent. This competition may decrease the binding energy between the copper ion and the solid surface and preclude the adsorption process as a result^(13,14). This result indicates that, this adsorption process is efficient at low concentration which is desired from the economic point of view.

The study also included testing the removal of copper ion on a commercial activated carbon (supplied by Merk) by using exactly the same experimental conditions as those used by the clay adsorption (at initial concentration of 70 mg/L) for comparison. The results obtained are listed in Table (2). Although the adsorption of copper ion by activated carbon is more efficient, the low cost and availability of the used clay make it more favorable.

Effect of particle size of adsorbent

Several experiments were conducted using 175-600 μ m particle sizes clay with different initial concentration for the determination of the effect of particle size on the same amount of adsorbed copper ion on clay. The results are presented in Table (3). The data indicate that, a decrease in particle size from 600 μ m to 175 μ m fraction increases the amount of adsorbed copper ion.

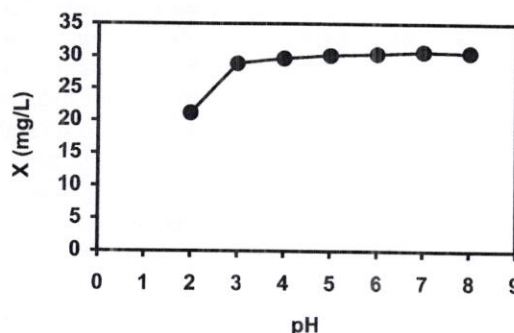
Table (3): The effect of particle size of adsorbent on the adsorption at various initial concentrations

Initial con.	Amount of adsorbed Cu ⁺² ion on clay (mg.gm ⁻¹)			
	75	150	300	600
10	9.577	8.169	6.905	3.690
20	16.334	15.379	12.675	9.477
30	23.281	21.988	19.018	15.278
40	28.480	26.500	23.680	20.013
50	32.004	29.769	26.939	24.000
60	29.996	26.789	24.199	22.789
70	30.249	28.791	27.670	11.680

The metal uptake by clay takes place at sites on the exterior surface of the particles as well as within the particle. However only a fraction of the internal sites is accessible to metal ions due to pore diffusion resistance. Thus, decreasing the particle size increases the surface area, which means increasing the number of available sites for metal uptake.

Effect of initial pH

The effect of varying pH of copper ion solution prior to adsorption when maintaining all other conditions constant is investigated at pH range of 2 to 8. The results obtained are shown in Figure (2).

**Figure (2): The effect of varying pH on amount of adsorbed metal ion at 25 °C and initial conc. 70 mg/L**

It is obvious that the amount of adsorbed metal ion is low at low pH and increases with increasing pH, however,

there were little changes above $\text{pH} = 5$. This can be explained by the competition of protons at low pH with metal ion to occupy the vacant sites on the surface of clay. These results are in agreement with several previous investigations on metal sorption by a variety of materials which revealed that the sorption capacity is low at pH level below 4⁽¹⁵⁻¹⁷⁾.

Effect of temperature

The effect of varying temperature when keeping other factors constant on the removal of copper ion by clay is investigated in the range of 15-55 °C and at different initial concentration (10-70 mg/L). The results obtained are given in Table (4).

Table (4): Amount of adsorbed copper ion at various temperatures

Initial con.	Amount of adsorbed metal ion (mg Cu ²⁺ .gm ⁻¹ clay)				
	15 °C	25 °C	35 °C	45 °C	55 °C
10	9.755	9.577	9.373	9.323	9.113
20	17.213	16.666	16.071	15.872	15.140
30	25.496	23.281	21.743	20.482	19.840
40	29.587	28.480	26.251	24.876	22.760
50	33.306	32.004	28.005	25.599	24.825
60	33.337	29.996	29.789	27.740	27.659
70	37.800	30.249	28.607	27.615	26.759

The study indicated that, the amount of adsorbed metal ion decreases with increasing temperature for all of the initial concentrations. This observation suggests that the adsorption is exothermic and physical in nature in which the increase in temperature increases the desorption process.

Calculation of thermodynamic parameters

The thermodynamic parameters of adsorption are good measure for the determination of the direction of the process, the nature of the forces control it and order of the adsorption system, which occur as a result of the various intermolecular forces between the adsorbate and adsorbent surface.

The estimation of the heat of adsorption is conducted depending on the adsorption isotherm knowledge and various temperatures. The value of adsorption equilibrium constant (K) are determined at different temperature at thermodynamic equilibrium from the ratio between the adsorbed and free Cu²⁺ ions concentrations. The straight lines obtained from plotting $\ln K$ versus $1/T$, (shown in Figure (3)), of Van't Hoff's equation are used to calculate the ΔH values. The values of K, ΔH and ΔS (calculated as mentioned earlier) are listed in Table (5).

Table (5): The values of the equilibrium constant and the thermodynamic parameters of adsorption at various initial concentrations

Initial conc. (mg/L)	Temp.(K)	K	ΔH (J.mol ⁻¹)	ΔS (J.mol ⁻¹ .K ⁻¹)
10	288	39.816	- 25138.21	-87.28
	298	22.640		-84.35
	308	14.999		-81.61
	318	13.771		-79.05
	328	10.274		-76.64
20	288	6.176	- 12680.51	-44.02
	298	4.998		-42.55
	308	4.090		-41.17
	318	3.854		-39.87
	328	3.115		-38.66
30	288	5.666	- 20444.12	-70.98
	298	3.465		-68.60
	308	2.633		-66.37
	318	2.152		-64.28
	328	1.952		-62.32
40	288	2.841	- 15051.66	-52.26
	298	2.472		-50.50
	308	1.909		-48.86
	318	1.644		-47.33
	328	1.320		-45.88
50	288	1.995	- 15060.81	-52.29
	298	1.778		-50.53
	308	1.273		-48.89
	318	1.049		-47.36
	328	0.986		-45.91
60	288	1.250	- 7132.33	-24.76
	298	0.999		-23.93
	308	0.986		-23.15
	318	0.859		-22.42
	328	0.855		-21.74
70	288	1.173	- 5537.45	-19.22
	298	0.761		-18.58
	308	0.691		-17.97
	318	0.651		-17.41
	328	0.618		-16.88

Looking at the results of Table (5), the negative value of enthalpy indicates that, the adsorption process is exothermic and the forces that control it (40 KJ.mol⁻¹) are physical in nature. The negative value of ΔS explained

the increase in order in the adsorption system which resulted from the binding of metal ions to the adsorbent surface. The value of ΔS becomes more positive with the

increase of temperature, which is consistent with the exothermic and physical nature of the adsorption system.

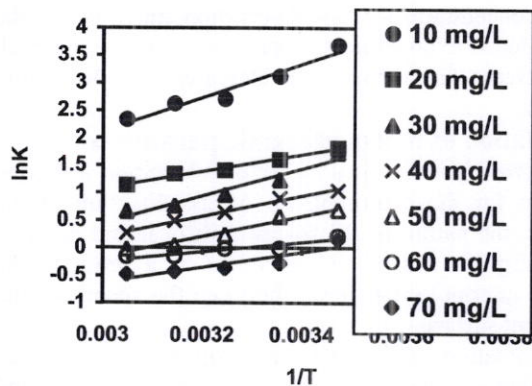


Figure (3): The relation between $\ln K$ versus $1/T$

Kinetic study

The kinetic study of copper ion on clay is conducted as a batch experiments and at initial concentration of 20 mg/L. The investigation is performed at temperature range of 25–55 °C. The rate of uptake was estimated by AAS. Preliminary experiments showed that, the uptake level is very fast with initial increase being very sharp within the first ten minutes, indicating high affinity between the clay surface and the metal ions. The adsorption process is then became slower and the uptake rate gradually decreased with time possibly due to intra-particle diffusion. Finally, saturation is reached beyond which no further adsorption can take place⁽⁷⁾. The results suggest that equilibrium could be reached in about 70–80 minutes. This observation is consistent with other study^(18,19).

This investigation is concerned with studying the rate of adsorption and desorption of copper ion on clay during the period of (10–40) minutes. The work is conducted by using definite amount of clay, natural pH of copper ion solution and different temperature. The reversible first order equation (eq. 1) is applied to fit the experimental data. The values of the equilibrium constant (K), rate of adsorption (k_1) and desorption (k_2) are determined as illustrated earlier. Their values are listed in Table (6).

Table (6): Values of K , k_1 and k_2 at various temperatures and initial concentration of 20 mg/L

Temp. (K)	K	k_1	k_2
298	4.998	0.02334	0.00466
308	4.090	0.02949	0.00721
318	3.845	0.03302	0.00858
328	3.115	0.03922	0.01258

The linear relationships obtained from the plot of $\ln(X_e - X)$ versus time at different temperatures are shown in Figure (4).

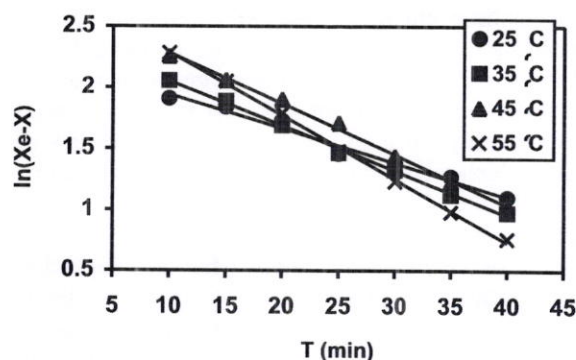


Figure (4): The relation between $\ln(X_e - X)$ and time (min) at 20 mg/L

The Arrhenius equation (eq. 3) is used for the determination of activation energies for the forward and backward processes (Table 7). The straight lines obtained from plotting $\ln k_1$ and $\ln k_2$ versus $1/T$ are shown in Figures (5) and (6) respectively.

Table (7): The thermodynamic parameters of activation of the adsorption and desorption processes at initial concentration of 20 mg/L

Adsorption		Desorption	
Therm. Function	value	Therm. Function	Value
E_1	13511.08	E_2	25494.04
ΔH^* (J.mol ⁻¹)	10937.89	ΔH^*	22891.76
ΔS^* (J.mol ⁻¹ .K ⁻¹)	-183.40	ΔS^*	-269.10
ΔG^* (J.mol ⁻¹)	68343.97	ΔG^*	107122.25

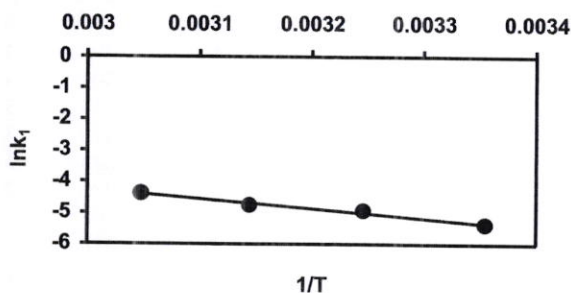


Figure (5): The relation between $\ln k_1$ and $1/T$

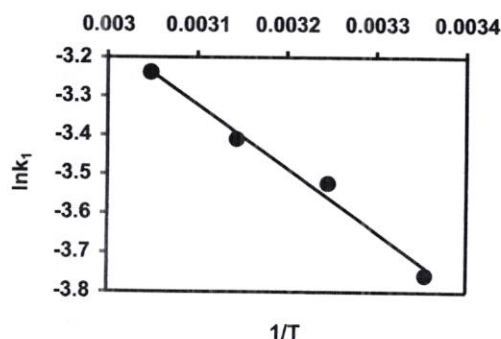


Figure (6): The relation between $\ln k_2$ and $1/T$ at 20 °C

The results of Table (7) show that, the value of activation energy of desorption is higher than the adsorption process, which indicate that, the process occurs in favor

of adsorption direction. The negative value of ΔS^* refers to the increase in order in the intermediate state according to the absolute rate theory⁽¹²⁾. The overall results show a good consistency between the values of

the thermodynamic parameters of activation and activation energies with those of thermodynamically determined ones.

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