



Removal of Copper Ions from Liquid Wastes Using Adsorption Technique

E. Nassef^{1*}; A. Mahmoud²; H. Salah³; Y. El-taweel²

¹Department of Petrochemical Engineering, Faculty of Engineering, Pharos University in Alexandria, Egypt.

²Department of chemical Engineering, Faculty of Engineering, Alexandria University, Egypt.

³Department of Elamriya Petroleum Company, Alexnaria, Egypt.

ABSTRACT

The present study aims to removal of copper ions (Cu^{2+}) as a heavy metal ion from aqueous solution by a high inorganic molecular weight compound. This compound is modified clay (activated bentonite) which is used in oil well drilling, and obtained from local company. The experimental results showed that it is an adsorption reaction that follows Langmuir isotherm model. The maximum removal of copper ions was obtained at low copper ion initial concentration, high adsorbent dosage, low temperature, and high agitation speed. It is clear from the results obtained that the compound within the experimental range investigated cannot be considered as a method for the removal of waste stream within the experimental range investigated as the residual concentration is higher than the limits which are allowed by the environmental limits which are allowed by the low which is 5 ppm. These results may be due to the high initial copper concentration used in this work and low dosage of the compound.

Keywords: Adsorption, heavy metal, wastewater, treatment, copper, clay.

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1. Introduction

Water pollution by heavy metals through the discharge of industrial effluents, is a worldwide environmental problem. Heavy metals are metals of high relative atomic weight (especially one that is poisonous like mercury or lead) and a specific gravity greater than 5.0 [1]. Heavy metal ion pollution is currently of great concern due to the increased awareness of the potentially hazardous effects of elevated levels of these materials in the environment. With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc.

Heavy metals in wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are

* Corresponding author
E-mail: nhadi57@gmail.com
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not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic [2].

Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead, and chromium. Effluent wastewaters from such processes contain toxic substances, metal acids, alkalis, and other substances. High concentrations of metals in the effluents may cause interference with biological treatment processes at sewage treatment plants [3, 4]. Copper does essential work in animal metabolism [5]. But the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death. Many methods that are being used to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies [6, 7]. These techniques were found not effective due to either being extremely expensive or too inefficient to reduce such high levels of ions from the large volumes of water [8, 9]. Effluent wastewaters from such processes also contain toxic substances, metal acids, alkalis, and other substances. High concentrations of metals in the effluents may cause interference with biological treatment processes at sewage treatment plants [10]. In addition, these techniques are not affordable in rural communities of developing countries. Therefore, the effective process must be low cost-effective technique and simple to operate. The wastewater purification processes requires the development of new operations based on low-cost raw materials with high pollutant-removal efficiency. Many toxic heavy metals are being discharged into the environment as industrial wastes, causing serious soil and water pollution [11]. Clay is a natural raw material that has been used for various purposes for ages and its dimension is under 2 mm. Montmorillonite is a member of smectite group clay minerals. Bentonites have a high content of montmorillonite and contain fewer amounts of other clay minerals. Bentonite clay (hydrated aluminum silicate) was shown to be efficient in the removal of many toxic metal ions such as lead, cobalt, nickel, copper, zinc, cadmium and uranium in aqueous solutions [12-16].

The objective of this study is to remove one hazard heavy metal, which is Copper (II). The main objective of this work is to investigate the affecting parameters on the removal efficiency, such as initial metal ions concentration, adsorbent dosage, stirring speed and temperature.

2. Material and Methods

2.1. Chemicals

Synthetic metal ion solutions of the desired concentrations were prepared by successive dilution with distilled water. Copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used as a source of Copper ions in the adsorption experiments. A stock solution of Copper sulfates solution was prepared dissolving an analytical grade of copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water.

2.2. Characterization of Adsorbent

Bentonite clay was supplied from the Sphinx milling station Company (Alexandria free zone, Egypt). Bentonite is brown in color; it was characterized by x-ray fluorescence (XRF) using AXIOS PANalytical2005. The analysis was made in Central Metallurgical Research Institute in Alexandria. Table 1 shows the oxides constituents of the studied bentonite clay. A scan electron microscope with different magnification was done on dry base for a sample of clay to specify the morphological features of bentonite. This was done in laboratory of faculty of science in Alexandria University as shown in Figure 1. Natural bentonite has low alumina content (16.14%) and contains high silica contents (55.12%). Bentonites show higher distribution of alkali oxides. There is general agreement between the current obtained values for both major oxide contents and the high loss on ignition percentage (12-15%) with the calculated values and recorded results previously obtained for Egyptian kaolin and bentonite [17,18]

Table 1. Chemical characterization of bentonite.

Oxides	Wt.%
SiO ₂	55.12
Al ₂ O ₃	16.14
Fe ₂ O ₃	8.25
CaO	1.17
TiO ₂	1.18
MgO	2.86
K ₂ O	1.05
Na ₂ O	1.41
L.O.I	12.35

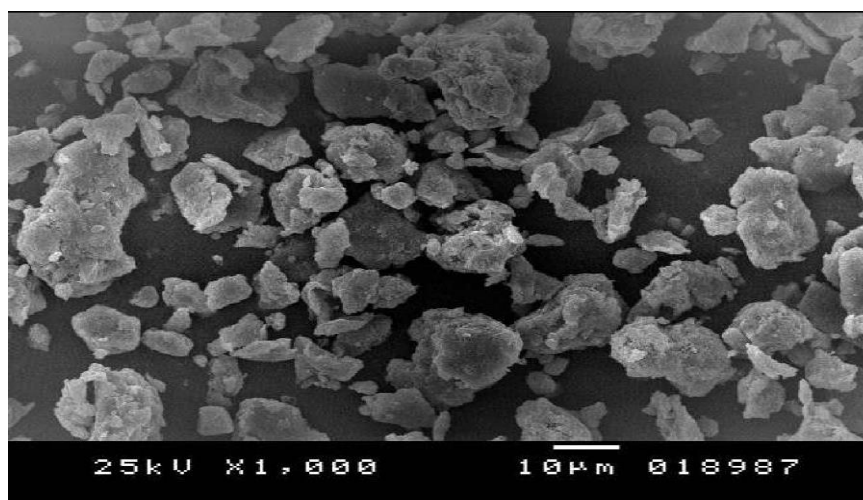


Figure 1. Scanning electron microscope (SEM) of dry bentonite.

2.3. Adsorption Procedure

The removal technique done in this work was adsorption of Copper (II) on the surface of high molecular weight compound was studied. This was sodium carbonate activated bentonite). The required weight of an adsorbent (bentonite) was prepared. Then the stock solution containing 1000 mg/L of metal ions solutions ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were prepared from their stock solutions and then was mixed with different weight of adsorbents. The solutions were then agitated at room temperature or at other experimental temperature, after mixing for a time specified according to experimental conditions the samples were filtered using Whatman filter paper and the filtrates were analyzed using EDTA and Titration method. The experiments were conducted using an orbital shaker for a known period of time. Adsorption experiments were carried out in flasks of 100 mL.

2.4. Adsorption calculations

$$N_{\text{edta}} V_{\text{edta}} = N_{\text{Cu (ii)}} V_{\text{Cu (ii)}} = \text{eq. Cu (II)}, (\text{If } V \text{ is given in L}) \quad (1)$$

$$= m \text{ eq. Cu (II)}, (\text{If } V \text{ is given in mL}) \quad (2)$$

$$= m \text{ eq. Cu (II)}, (\text{if } V \text{ is given in mL}) \quad (3)$$

The mass of Cu equals (eq. Cu (II)) x (equivalent mass of Cu (II)), and

$$\% \text{Cu} = \frac{\text{massCu(II)}}{\text{massCu(II)salt}} \times 100 \quad (4)$$

The concentration of Cu (II) in aqueous solutions before and after adsorption were determined as the following:

$$\text{Original Cu}^{+2} = \frac{\text{initialvolume}}{100} \times 63.5, \quad (5)$$

$$\text{Residual Cu}^{+2} = \frac{\text{remainedvolume}}{100} \times 63.5, \quad (6)$$

$$\text{Adsorbed Cu}^{+2} (q_t) = (\text{original Cu}^{+2} - \text{residual Cu}^{+2}) \times 10^4, \quad (7)$$

(mg Cu^{+2} adsorbed/g adsorbent)

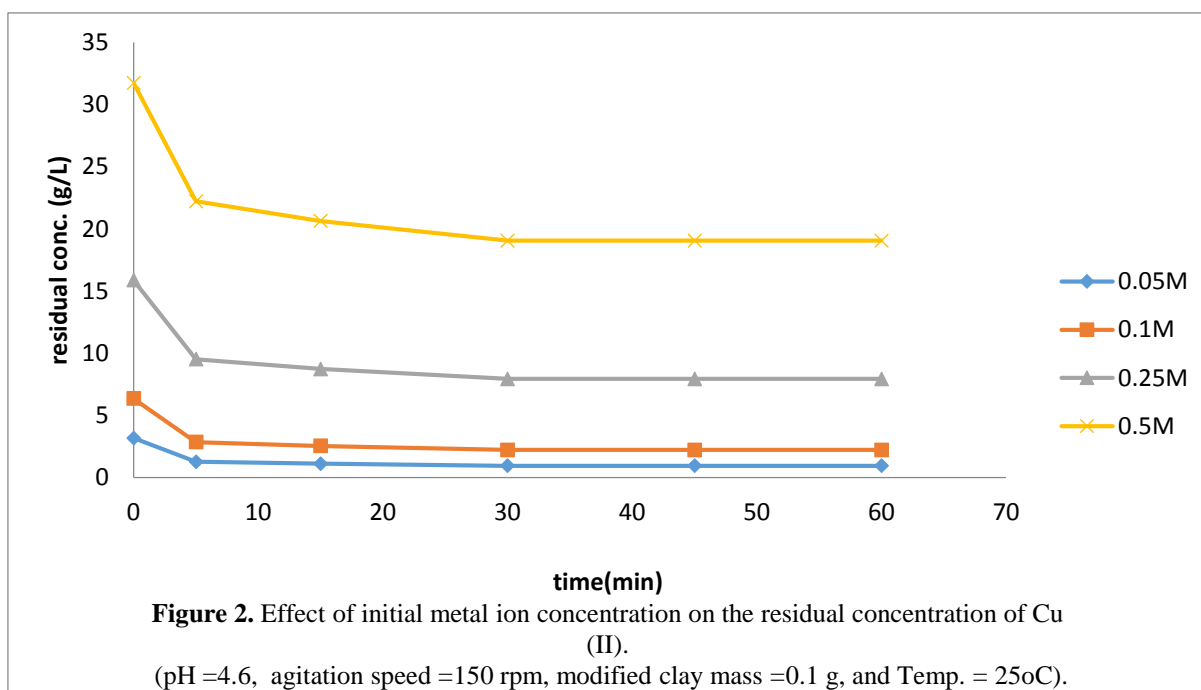
$$\% \text{ removal} = \frac{C_0 - C_t}{C_0} \times 100, \quad (8)$$

Where C_0 = Initial concentration of heavy metal (mg/L), and C_t = Heavy metals concentrations (mg/L) at a given time t. The results were plotted versus t.

3. Results and Discussion

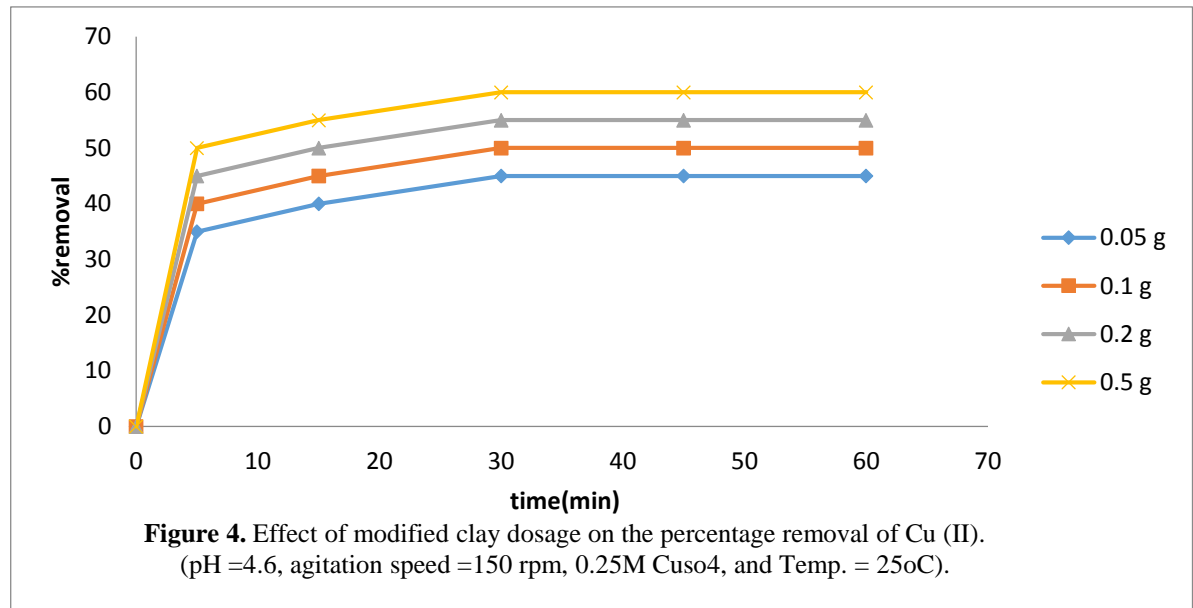
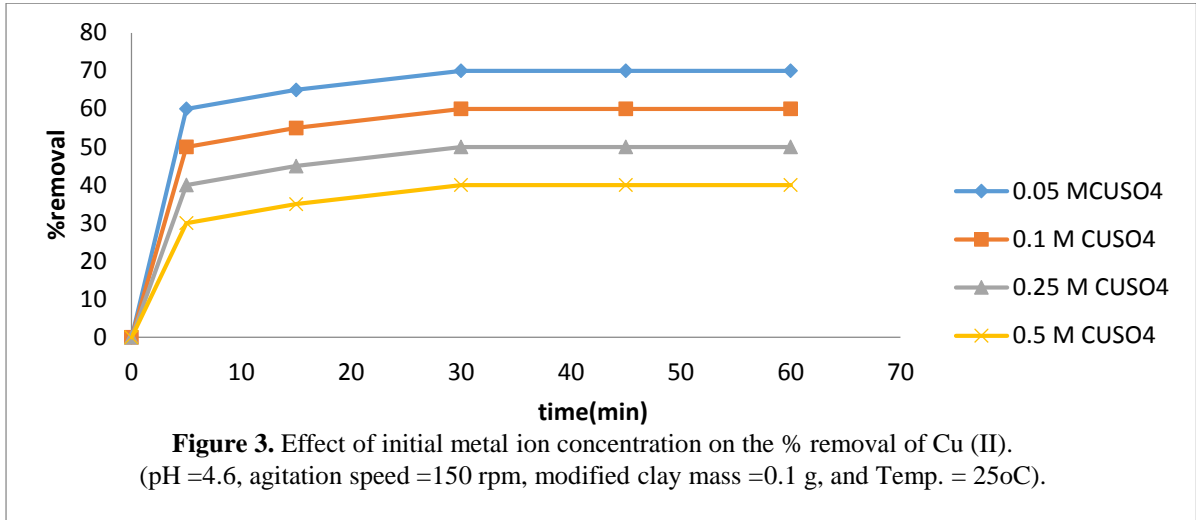
3.1. Effect of Initial Metal Ion Concentration

Figure 2 and 3 indicate that the effect of initial concentration of the Cu (II) ions on the residual concentration and percentage removal respectively. It was found that as the initial concentration of Cu (II) increases the residual concentration increases and the percentage removal decreases. From figures it is evident that at high concentration, the available sites of adsorption become fewer. This behavior is connected with the competitive diffusion process of the Cu (II) ions through the micro-channel and pores in the modified clay. That adsorption of metallic ions will lock the inlet of channel on the surface and prevent the metal ions from passing deeply inside the modified clay. The adsorption occurs on the surface only. Similar results in previous studies using natural zeolite [10] and olive cake [11], in addition to what have been found by karthikeyan et al. [12] confirm this point of view.



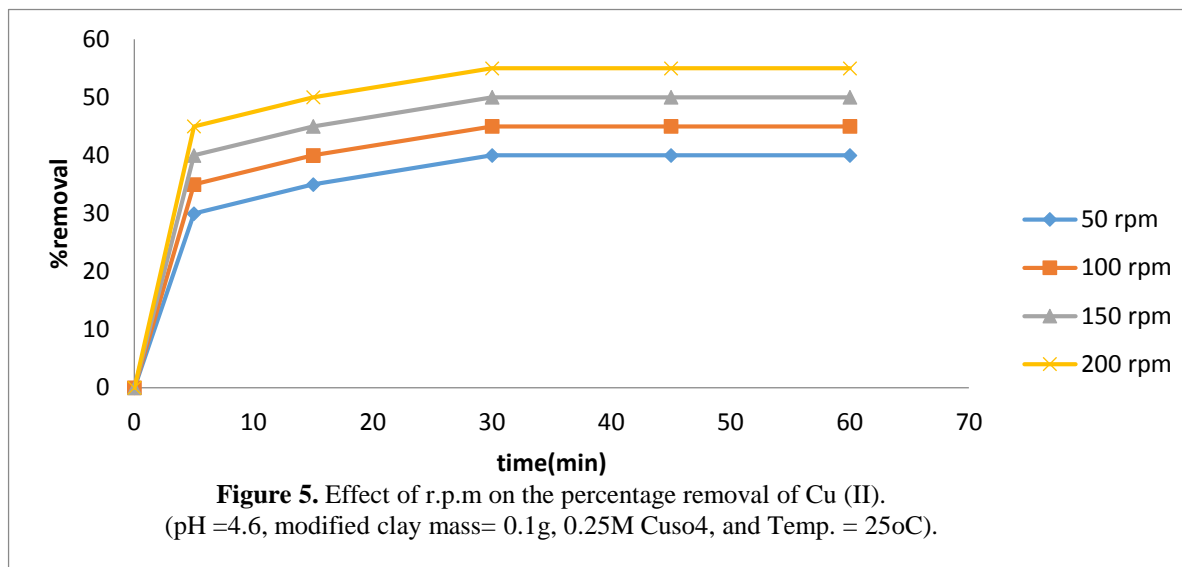
3.2. Effect of Modified Clay Dosage

The effluence of modified clay masses on the percentage removal of Cu (II) is shown in Figure 4. This figure showed that as the amount of modified clay increases the percentage removal of Cu (II) increases. This is may be due to those higher amounts of modified clay means availability of a larger surface area or a larger number for adsorption sites [19-22] and Therefore, higher capacity for adsorption.



3.3. Effect of Shaking Speed (rpm)

Figure 5 indicates the effect of shaking speed on the percentage removal of Cu (II). It was found that as the shaking speed increases the percentage removal increases. The increase in shaking speed resulting to increase in metal ions percentage removal, which was due to the fact that, increase in stirring rate enhanced the metal ions diffusion to the surface of modified clay, and also caused reduction in the film boundary layer around the adsorbent [23], also the increase in efficiency was due to the increase in turbulence and, as a consequence, the decrease in the external mass transfer resistance thickness around the adsorbent particles with increase in mixing speed [24].

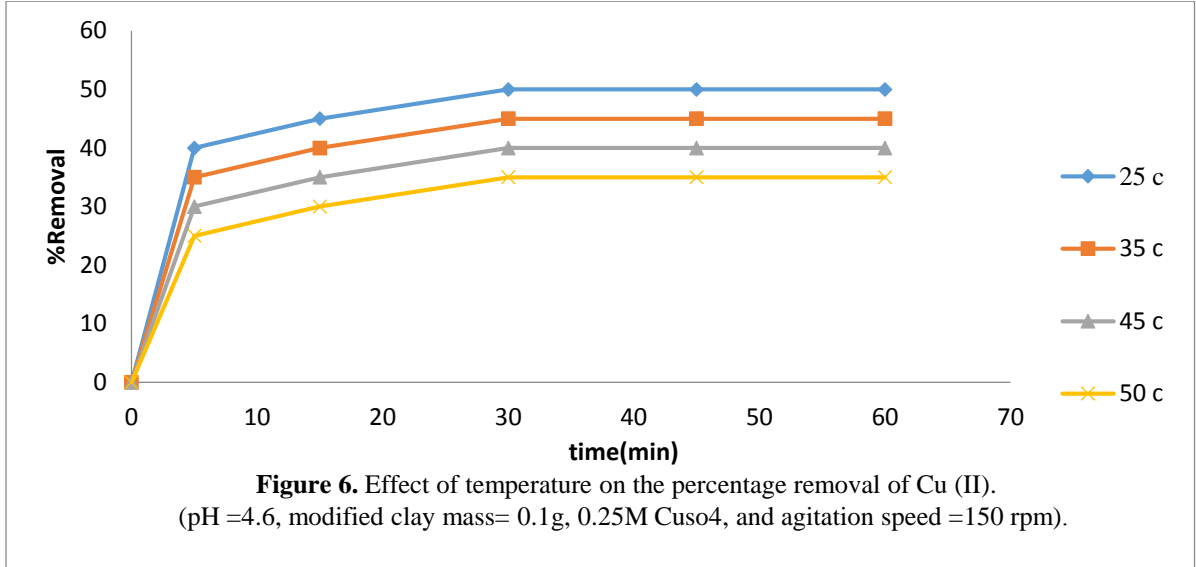


3.4. Effect of Temperature

Figure 6 indicates the effect of temperature on the percentage removal on Cu (II). It was found that as the temperature increases the percentage removal decreases. This was because with increasing temperature, the attractive forces between the adsorbent surface and metal ions are weakened and the desorption decreases. At high temperature, the thickness of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the biomass surface to the solution phase, which results in a decrease in adsorption as temperature increases [25]. As a whole, it is clearly seen that as the temperature increases the loading capacity for the same initial adsorbent concentration decreases. This means that the rate of desorption was more significant than the rate of adsorption, which implies that adsorption in this case is an Exothermic reaction [26-28].

3.5. Adsorption Isotherm Studies

In general, the isotherm studies for solid – liquid systems are carried out by changing CuSO_4 concentration and keeping other conditions, such as: volume of solution, adsorbent size, temperature, solution pH, and r.p.m. as constant. The performance of adsorbent is usually gauged by its uptake. Adsorbents can be compared based on their respective maximum uptake value, which can be calculated by fitting different isotherm models to the actual experiment data if it fits. The adsorption isotherm molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [29, 30]. The analysis of the isotherm data by fitting model that can be used for design purposes. Adsorption isotherm study was carried out on two isotherm models: Langmuir, and Freundlich isotherm models. The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficient, R^2 values.



3.5.1. Langmuir isotherm model

Langmuir's isotherm model suggests that the uptake occurs on homogeneous surface by monolayer sorption without interaction between adsorbed ions. The linear form of Langmuir isotherm equation is represented by the following equation [31, 32]:

$$\frac{c_e}{Q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \quad (9)$$

Where Q^0 is the maximum Cu^{++} ions uptake per unit mass of polymer (mg/g) related to adsorption capacity and b is Langmuir constant (L/mol) related to energy of sorption. Therefore, a plot of (C_e/q_e) versus C_e , gives straight line of slope $1/Q^0$ and intercept $1/(Q^0 b)$. Figure 7 shows the experimental data that were fitted by the linear form of Langmuir model, (C_e/q_e) versus C_e . The values of Q^0 and b were evaluated from the slope and intercept respectively. These values of Q^0 and b are listed in Table 2 with their uncertainty and their determination coefficient, R^2 . The results obtained from the Langmuir model for the removal of Cu^{++} onto modified clay in Table 2 which showed strong positive evidence on the adsorption of Cu^{++} onto modified clay follows the Langmuir isotherm. The applicability of linear forms of Langmuir model modified clay was proved by the high correlation coefficients $R^2 > 0.99$. This suggests that the Langmuir isotherm provides a good model of the sorption system.

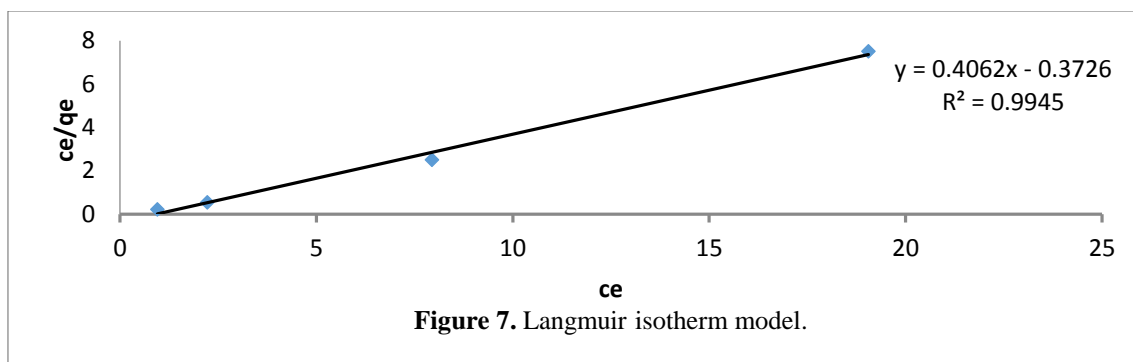


Figure 7. Langmuir isotherm model.

3.5.2. Freundlich isotherm model

Freundlich isotherm describes the adsorption equation for non-ideal adsorption that involves heterogeneous adsorption. This empirical isotherm is expressed by the following equation [32, 33]:

$$Q_e = K_F C_e^{1/n} \quad (10)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

Freundlich constants, K_F and $1/n$, are related to adsorption capacity and intensity of adsorption, respectively. The value of n and K_F can be calculated from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$ derived from Eq. (11). The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption, where values in the range of 2-10 represents good adsorption 1-2 gives moderate adsorption and less than 1 means that the adsorption has poor characteristics [34]. The applicability of the Freundlich sorption isotherm was also analyzed, using the same set of experimental data, by plotting $\log(Q_e)$ versus $\log(C_e)$. The data obtained from linear Freundlich isotherm plot for the adsorption of the Cu^{++} onto modified clay. The correlation coefficients reported in Figure 8.

The equilibrium experimental results of adsorbed modified clay at various initial concentrations of CuSO_4 were compared by using the adsorption isotherm equations, namely Langmuir, and Freundlich models. The temperature was constant throughout the experiments at 25°C . The experimental results were fitted to Langmuir and, Freundlich models were done by linear regression using the statistical analysis package Excel. Figure 7 and 8 show the fitted equilibrium data of Langmuir, and Freundlich respectively. For model comparison accordingly to R^2 which are shown in Table 2 we concluded that Langmuir isotherm is the best model to fit the data.

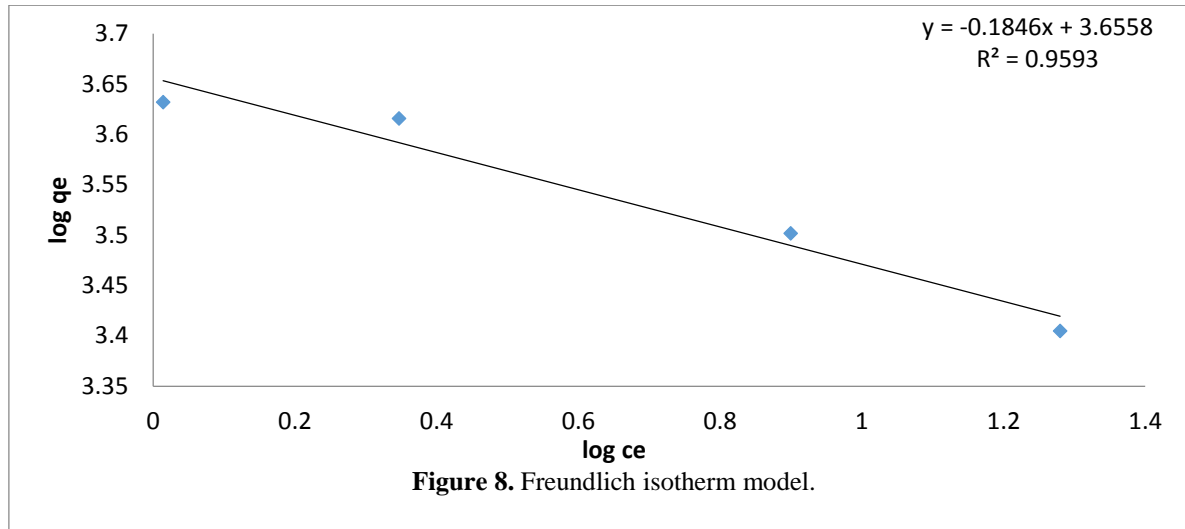


Table 2. Values of Q^0 , b , and R^2 for langmuir and freundlich isotherm models.

Model	Langmuir	Freundlich
R^2	0.9945	0.9593
Q^0	0.4062	-0.1846
B	-0.3726	3.6558

According to R^2 , the higher the value of R^2 the better model, from Table 2, it was concluded that Freundlich model has the least R^2 value (0.9593) while the other model Langmuir isotherm model has the highest value of R^2 which is (0.9945). Therefore, Langmuir isotherm model is the best model to describe the CuSO_4 adsorption system on modified clay. For Freundlich model we found that $1/n = 0.1846$, so that $n = 5.41711809$, therefore it lies in the interval 2-10 and applied good adsorption. The Langmuir model fit the data for metal ions ($R^2 = 0.9945$). Thus, it represents a monolayer sorption process as chemical adsorption. Freundlich model fits the data for metal ions also ($R^2 = 0.9593$). Thus, it describes a heterogeneous system characterized by physical adsorption.

3.6. Kinetic Models Applied

Kinetics of adsorption is one of the most important characteristics to be responsible for the efficiency of adsorption. The adsorbate can be transferred from the solution phase to the surface of the adsorbent in several steps and one or any combination of which can be the rate-controlling mechanism [34]:

- i. Mass transfer across the external boundary layer film of liquid surrounding the outside of the particle.
- ii. Diffusion of the adsorbate molecules to an adsorption site either by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism.
- iii. Adsorption (physical or chemical) at a site on the surface (internal or external) and this step is often assumed to be extremely rapid.

The overall adsorption can occur through one or more steps. In order to investigate the mechanism of process and potential rate controlling steps, the kinetics of Cu^{++} adsorption onto modified clay were analyzed using pseudo-first order [35], pseudo-second-order [36]. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 , values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of Cu^{++} adsorption onto modified clay.

3.6.1. Pseudo-first-order model

The adsorption kinetic data were described by the pseudo-first-order model which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The linear form equation is generally expressed as follows [35]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (12)$$

In order to obtain the rate constants, the values of $\log(q_e - q_t)$ were linearly correlated with t by plot of $\log(q_e - q_t)$ versus t to give a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively as shown in Figure 10. The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process.

3.6.2. Pseudo-second-order model

The pseudo-second-order model may describe the adsorption Kinetic. The linear equation given as follows [36]:

$$\frac{t}{q_t} = \frac{1}{k_2} \frac{1}{q_e^2} + \frac{1}{q_e} t \quad (13)$$

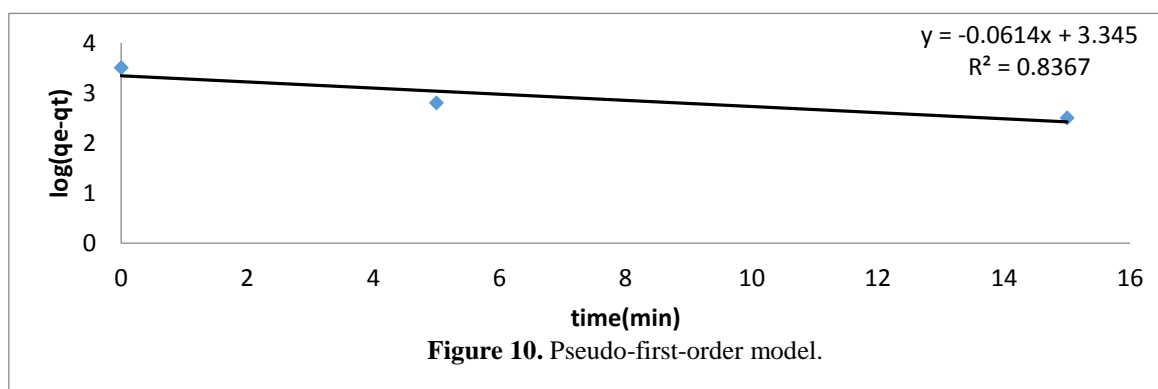


Figure 10. Pseudo-first-order model.

If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots of t/q_t versus t .

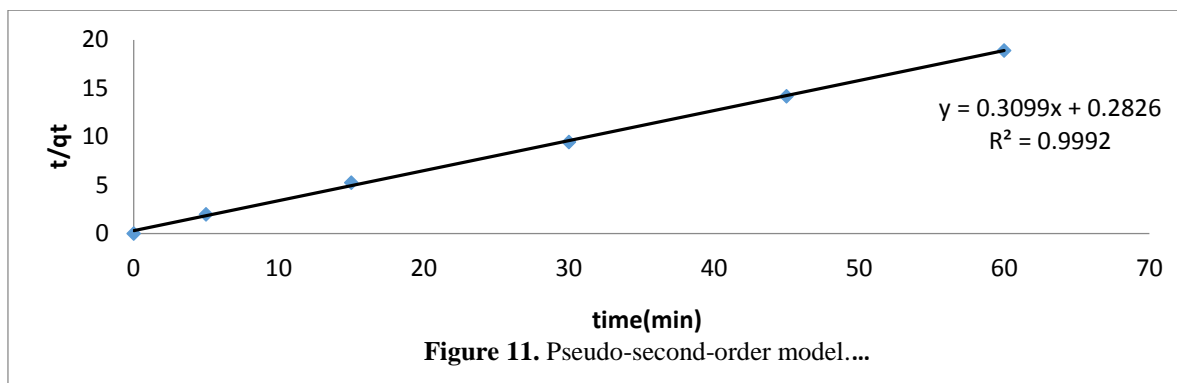


Table 3. Values of R^2 for pseudo-first-order and pseudo-second-order models.

Model	pseudo-first-order	pseudo-second-order
R^2	0.8367	0.9992

According to R^2 , the higher value of R^2 according to pseudo – second order model than pseudo – first-order model as shown in Table 2 confirms that pseudo – first-order model is the best model to fit the data.

4. Conclusions

The removal Cu (II) ions from aqueous solution by modified clay has been investigated. The following conclusions can be drawn based on this investigation:

- I. Modified clay remove Cu (II) from solutions by adsorption, it follows Langmuir isotherm model, and pseudo second order kinetic model.
- II. Maximum percentage removal takes place at low initial metal ion concentration, high shaking speed, low temperature, and high amount of adsorbent dosage.
- III. The results show that the use of modified clay cannot be considered as a waste treatment method for the removal of copper from solution within the experimental range investigated.

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