

## Metal Oxide Nano-particles as an Adsorbent for Removal of Heavy Metals

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### Abstract

In this study, adsorption process performance was assessed using metal oxide nano particles for wastewater treatment containing heavy metals in a laboratory scale reactor. Copper oxide nano-particles were prepared and fully characterized considering their adsorption properties (surface area and pore size distribution) as well as their chemical structure and morphology. The adsorption of heavy metals, including Fe<sup>3+</sup> and Cd<sup>2+</sup> was studied in batch experiments. Various physico-chemical parameters such as pH, initial metal ion concentration, and adsorbent dosage level and equilibrium contact time were studied. The adsorption of Cd<sup>2+</sup> and Fe<sup>3+</sup> ions increased with an increase in pH. The optimum solution pH for adsorption of both metals from aqueous solutions was 6. Adsorption was rapid and occurred within the first 20 min for both metals within different solution concentrations (250, 100, 50 and 25 mg/L). The kinetic of Cd<sup>2+</sup> and Fe<sup>3+</sup> adsorption onto copper oxide nano particles was well fitted by the pseudo-second-order rate equation. The equilibrium adsorption data for Cd<sup>2+</sup> was best fitted by the Langmuir adsorption isotherm model, but for Fe<sup>3+</sup> adsorption, it was found that Freundlich adsorption isotherm model is the best model to describe it. The selectivity order of the adsorbent is Fe<sup>3+</sup>>Cd<sup>2+</sup>. From these results, it can be concluded that the CuO nano particles is a promising adsorbent for the removal of heavy metals from aqueous solutions.

**Keywords:** Heavy metals; Fe<sup>3+</sup>; Cd<sup>2+</sup>; Nano metal oxide

### Introduction

Heavy metal pollution has become one of the most serious environmental problems. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment [1]. With the rapid development of industries such as fertilizer industries, tanneries, metal plating facilities, batteries, paper industries and pesticides, heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries [2]. Also these heavy metals are generally present in refinery and petrochemical wastewaters and are of particular significance as they are potentially toxic to humans and aquatic life, create an oxygen demand in receiving waters, and impart taste and odor to drinking water with even minute concentrations of their chlorinated derivatives [3]. Several techniques have been used to remove heavy metals from industrial wastewater including precipitation [4-6], ion exchange [7-9], membrane filtration [10-13] and adsorption [14-17]. Recently, increasing attention has been focused on metal oxide sorbents such as iron oxide [18-20], aluminum oxide [21-23], titanium oxide [24-26], manganese oxide [27-29], zirconium oxide [30,31]. The nano sized metal oxides are classified as the promising ones for heavy metals removal from aqueous systems [32]. This is because of their large surface areas and high activities caused by the size quantization effect [33,34].

The aim of this work is to study the effect of nano copper oxide particles (CuO) on the removal of some metallic ions such as Cd<sup>2+</sup> and Fe<sup>3+</sup> from wastewater during treatment processes. The removal of these metallic ions will be done by using CuO as a source of inorganic adsorbent. Variables studied on the efficiency of the removal process were removal time for Cd<sup>2+</sup> and Fe<sup>3+</sup> ions, effect of amount of nano CuO on the Cd<sup>2+</sup> and Fe<sup>3+</sup> ions (adsorbent dosage), effect of concentration of Cd<sup>2+</sup> and Fe<sup>3+</sup> ions, effect of pH of the solution during the removal of these metallic ions. Two isotherms were tested (Langmuir, Freundlich) to determine which isotherm the adsorption processes will follow. Kinetic experiments were studied to determine the effect of time on the metal ions removal process. Finally, the removal percentages for the iron and cadmium particles from wastewaters were then calculated under the previous conditions and for different solutions concentrations.

### Materials and Methods

#### Materials

All chemicals used in the experiment are analytic reagent grade. Copper(II) nitrate trihydrate Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, poly ethylene glycol (PEG), cadmium sulfate salt CdSO<sub>4</sub>·8H<sub>2</sub>O, iron chloride salt FeCl<sub>3</sub>·6H<sub>2</sub>O, glacial acetic acid, sodium hydroxide (NaOH), potassium hydroxide (KOH) and hydrochloric acid (HCl). Distilled water was used throughout the experiment.

#### Method used for preparation of nano copper oxide particles

5 g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was dissolved in 250 ml deionized water and then 25 ml of PEG (poly ethylene glycol) was poured into the solution. After PEG uniformly dispersed in the solution, KOH were added. The solution was stirred for 3 hours, then the blue suspension was heated using microwave radiation with power 900 W and temperature reached 800°C for 15 min. After the reaction was completed, all precipitate was filtered, washed with distilled water and finally dried at 110°C for 2 hours.

#### Preparation of cadmium and iron solutions

A Stock solution of cadmium (1000 ml) was prepared by dissolving a 3.14 g of CdSO<sub>4</sub>·8H<sub>2</sub>O in 1 L distilled water, while stock solution of iron was prepared by dissolving a 4.84 g of FeCl<sub>3</sub>·6 H<sub>2</sub>O in 1 L distilled water (Industrial distilled water was used that contains no bacteria and a very little amount of contaminants; with a concentration about 1 ppm, with resistivity of 18.18 MΩ·cm at 25°C).

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## Batch adsorption system procedures

The experiments were performed in a batch reactor at  $(25 \pm 0.5^\circ\text{C})$  with continuous stirring at 150 rpm, 0.1 g of CuO nano particles were left in contact with cadmium or iron solutions of (25, 50, 100 and 250 mg/L) in 250 ml bottles (0.4 g for 1 liter solution), during 210 minutes at the solution default pH (for iron solution pH is 3.5 while for cadmium pH is 6). Then the pH was adjusted by using 0.1N, 1N NaOH and HCl to study the effect of nano CuO adsorbent for the adsorption process within different solution pH (2, 4, 6, 7 and 9) for solution concentrations (50 and 100 mg/L) during 120 minutes. The effect of weight was studied by adding different amounts of nano CuO adsorbent (0.1, 0.2, 0.3 and 0.4 g) to the solution concentration of (50 and 100 mg/L) at the default pH of solutions (3.5 for iron standard solution and 6 for cadmium standard solution) during 120 minutes.

## Batch experiments for isotherms and kinetics determination

Equilibrium isotherms for iron and cadmium were obtained by performing batch adsorption studies at ambient temperature of  $(25 \pm 0.5^\circ\text{C})$ . Solutions ranges from 25, 50, 100 and 250 mg/L concentration were obtained by dilution of the stock solution with distilled water, then 0.1 g of nano CuO was added to each 250 ml bottle (0.4 g for 1 liter solution), at the default solution pH (3.5 for iron and 6 for cadmium). The bottles were exposed to constant rotation of 150 rpm for 210 minutes to reach equilibrium conditions. Sampling was performed by removing aliquots at predetermined time intervals (every five minutes). The samples for iron and cadmium were then filtered and analyzed by atomic absorption spectrometer. The values of  $q$  and  $C_e$  often can be fitted to the two standard isotherms equation Langmuir and Freundlich, to determine which isotherm will better fit the adsorption process. The adsorbed heavy metal amount ( $q$ ) per unit adsorbent mass was calculated at equilibrium as follows:

The adsorbed heavy metal amount ( $q$ ) per unit adsorbent mass was calculated by equation (1):

$$q = \frac{C_i - C_f}{W_t} \times V \quad (1)$$

Where  $C_i$  is the initial heavy metal concentration (mg/L),  $C_f$  is the concentration of heavy metal at equilibrium (mg/L),  $W_t$  is the adsorbent dosage (g) and  $V$  is the solution volume (L).

But samples were drawn at regular time intervals and the concentration of the metal ion was similarly measured to determine the process kinetics. The amount of the metal ion (iron or cadmium) adsorbed by nano CuO at time  $t$ , is  $q_t$  (mg/g), and was calculated by equation (2):

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

Where  $C_0$  is the initial metal concentration at  $t=0$ ,  $C_t$  (mg/L) is metal ion concentration at time  $t$ ,  $V$  is the volume of the solution (L) and  $W$  is the mass of nano CuO adsorbent used (g).

Then  $C_0$ ,  $C_t$ ,  $q_e$  and  $q_t$  are used within the below equations to find out the best isotherm model and the best kinetic rate equation that the adsorption process will follow.

## Isotherms methodology

**Langmuir isotherm:** Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has found successful applications in many other real adsorption processes of monolayer adsorption. Langmuir's model of adsorption depends on the assumption that intermolecular forces

decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a Fe(III) molecule or Cd(II) occupies a site, no further adsorption will take place at that site.

The linear form of Langmuir isotherm equation is represented by equation (3):

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{1}{Q^\circ} C_e \quad (3)$$

Where  $Q^\circ$  is the maximum metal ions uptake per unit mass of adsorbent (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 a straight line of slope  $1/Q^\circ$  and intercept  $1/(Q^\circ b)$ .

**Freundlich isotherm:** Freundlich isotherm describes the adsorption equation for non-ideal adsorption that involves heterogeneous adsorption. This empirical isotherm is expressed by Equation (4):

$$q_e = K_F C_e^{1/n} \quad (4)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as (Equation 5)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Freundlich constants,  $K_F$  and  $1/n$ , are related to adsorption capacity and intensity of adsorption, respectively. The values 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 Equation (5). The magnitude of the exponent  $1/n$  gives an indication of the favorability of adsorption.

The Freundlich adsorption isotherm represents the relationship between the corresponding adsorption capacity  $q_e$  (mg/g) and the concentration of the metal in solution at equilibrium  $C_e$  (mg/L). The plot of  $\log (q_e)$  versus  $\log (C_e)$  for various initial concentrations was found to be linear.

## Kinetics methodology

**First order rate kinetics equation:** The linear form of pseudo-first-order equation is given as (Equation 6)

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (6)$$

Where  $q_e$  and  $q_t$  (mg/g): are the amount of iron or cadmium adsorbed at equilibrium and at time  $t$  (min), respectively,  $K_1$  ( $\text{min}^{-1}$ ): is the pseudo-first-order rate constant. The values of  $\log (q_e - q_t)$  were calculated from the kinetic data and plotted against time ( $t$ ).

**Second order rate kinetics equation:** The kinetics was also described as a pseudo-second-order rate equation (Equation 7)

$$\frac{t}{q_t} = \frac{1}{K_2} \times \frac{1}{q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where  $q_e$  and  $q_t$ : are the amount of iron or cadmium adsorbed (mg/g) at equilibrium and at time  $t$  (min), respectively,  $K_2$  (g/mg min): is the rate constant of pseudo-second-order kinetics. The values of  $t/q_t$  were calculated from the kinetic data and plotted against time ( $t$ ).

## Results and Discussion

### Characterization of adsorbent

**Morphology and particle size:** In order to understand the morphology of the adsorbent SEM analysis of CuO nano powder was

carried out. SEM image with magnification factor 3500 is presented in Figure 1 which shows the rectangular morphology with high surface roughness of the particles. The increase in surface roughness leads to an increase in the surface area of the adsorbent. The particle size distribution for nano particles found to be 33-160 nm. In addition, the surface area is 220 m<sup>2</sup>/g.

**FTIR for CuO nano powder:** The FTIR analysis permits spectrophotometric observation of CuO nano powder in the range 400-4,000 cm<sup>-1</sup> and serves as a direct means for the identification of the functional groups on the surface. Figure 2 shows the Fourier transformed spectrum of CuO nano powders at room temperature. The characteristic peaks of CuO positioned from 984 cm<sup>-1</sup> to 426 cm<sup>-1</sup>. The peaks at 521 cm<sup>-1</sup> and 603 cm<sup>-1</sup> indicated the formation of CuO nanostructure and Cu-O stretching along the 202 direction [35].

### Effect of contact time

**Effect of contact time for the cadmium ions removal:** In order to establish the equilibrium time for maximum uptake and to determine the kinetics of the adsorption process, cadmium adsorption on nano CuO adsorbent was investigated as a function of contact time and the results are shown in Figure 3. Cadmium was rapidly removed by nano CuO (less than 20 min) for the four different solution concentrations (250, 100, 50, 25 ppm).

So that the contact time was maintained for almost three hours to ensure that equilibrium was really achieved as each sample was withdrawn every five minutes time interval. It may be noticed from Figure 3 that time to reach equilibrium is concentration-independent. In the initial stages the removal efficiency of the metal ion by the nano CuO adsorbent increased rapidly due to the abundant availability of active binding sites on the sorbent, and with gradual occupancy of these sites, the sorption became less efficient in the later stages. That means that the equilibrium status can be achieved after 20 minutes to calculate the value of  $q_e$ . This is consistent with the finding of Mansour *et al.* [36], Tu *et al.* [37] and Gutpa *et al.* [38].

**Effect of contact time for the iron ions removal:** In order to establish the equilibrium time for maximum uptake and to determine the kinetics of the adsorption process, iron adsorption on nano CuO sorbent was investigated as a function of contact time and the results are shown in Figure 4. Iron was rapidly removed by nano CuO (less than 20 min) for the four different solution concentrations (250, 100, 50, 25 ppm).

The contact time was maintained for almost three hours to ensure that equilibrium was really achieved. It may be noticed from Figure 4 that time to reach equilibrium is concentration-independent. In the initial stages the removal efficiency of the metal ion by the nano CuO sorbent increased rapidly due to the abundant availability of active binding sites on the sorbent, and with gradual occupancy of these sites, the sorption became less efficient in the later stages. That means that the equilibrium status can be achieved after

20 minutes to calculate the value of  $q_e$ . This agrees with the results of Hodaifa *et al.* [39], and Ostaz *et al.* [40].

### Effect of pH

For the two prepared solutions of, different solutions pH were adjusted by 0.1N sodium hydroxide (NaOH) and 0.1, 1N (HCl), then 0.1 g of nano CuO particles was added to a 250 ml glass bottles at 20 ± 0.5°C, during 120 min. The percentage removal and the metal uptake were then plotted versus the removal the solution pH, to present the strong effect of solution pH on the adsorption process.

**Effect of solution pH for cadmium ions removal:** Hydrogen ion concentration in the adsorption is considered as one of the most important parameters that influence the adsorption behavior of metal ions in aqueous solutions. It affects the solubility of the metal ions in the solution, replaces some of the positive ions found in the active sites and affects the degree of ionization of the adsorbate during the reaction [41]. The effect of initial pH on the sorption of Cd(II) ions onto nano CuO particles was evaluated within the pH range of 2-9. The metal

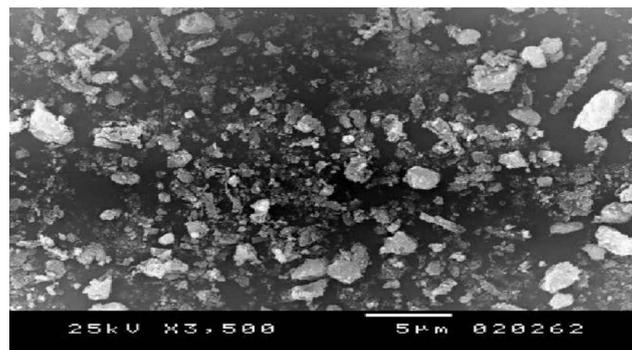


Figure 1: SEM for CuO nano powder.

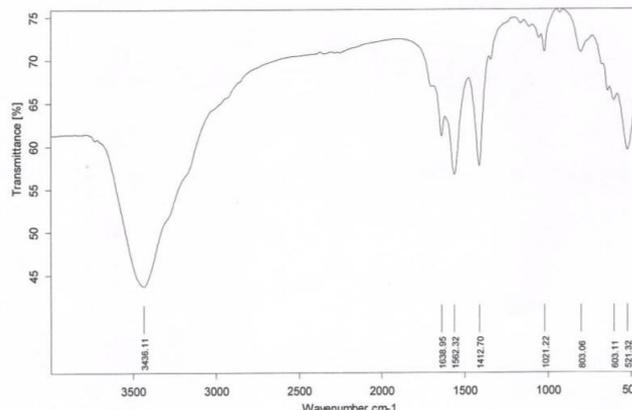


Figure 2: FTIR for CuO nano powder.

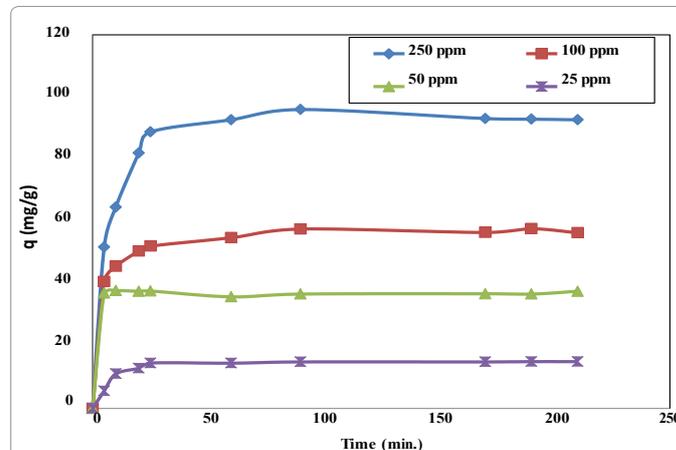
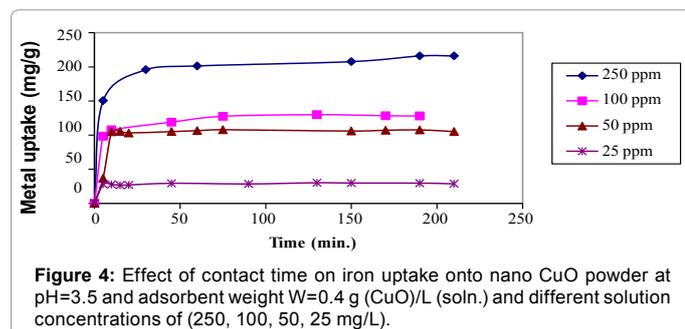


Figure 3: Effect of contact time on cadmium uptake onto nano CuO powder at pH=6, adsorbent weight W=0.4 g (CuO)/L (solution) and different solution concentrations of (250, 100, 50, 25 mg/l).



**Figure 4:** Effect of contact time on iron uptake onto nano CuO powder at pH=3.5 and adsorbent weight W=0.4 g (CuO)/L (soln.) and different solution concentrations of (250, 100, 50, 25 mg/L).

removal from solution at pH beyond 8 would not give accurate results because precipitation of the ions as hydroxides took place, that was the reason the removal curve became high as there were not cadmium ions to be removed (the solution seems to be clear because of the metal precipitation) [42].

The effect of pH on the adsorption behavior of nano CuO for Cd(II) was shown in Figure 5. The initial pH of the solution significantly affected the adsorption capacity of the adsorbent; adsorption capacity was highest when pH was 6 and decreased by either raising or lowering pH under the present range of the experimental condition. At lower values, the metal ion uptake was limited in this acidic medium, this can be attributed to the presence of H<sup>+</sup> ions which compete with the Cd(II) ions for the adsorption sites. Contrarily, the metal ion was about to form metal hydroxide deposition through hydrolysis at higher values of pH [43]. The percentage removal decreased when the pH increased from 6 to 7, as the metal ions started to precipitate as hydroxides so that the solution seemed to be clean after the precipitation and that was the reason that the metal uptake increased at higher pH levels. This is an agreement with the finding of Mansour *et al.* [36], Yao-Jen Tu *et al.* [37], Gupta and Arunima Nayak [38] and Seung-Mok Lee [44].

**Effect of solution pH for iron ions removal:** Hydrogen ion concentration in the adsorption is considered as one of the most important parameters that influence the adsorption behavior of metal ions in aqueous solutions. It affects the solubility of the metal ions in the solution, replaces some of the positive ions found in the active sites and affects the degree of ionization of the adsorbate during the reaction [45]. The effect of initial pH on the sorption of Fe(III) ions onto nano CuO particles was evaluated within the pH range of 2-9. As after that the metal ions started to precipitate as metal hydroxides, the metal uptake was almost stable from the pH of 7 to 9 [46].

The effect of pH on the adsorption behavior of nano CuO for Fe(III) is shown in Figures 6 and 7. The initial pH of the solution significantly affected the adsorption capacity of the adsorbent; adsorption capacity was highest when pH was 6 and decreased by either raising or lowering pH under the present range of the experimental condition. At lower values, the metal ion uptake was limited in this acidic medium, this can be attributed to the presence of H<sup>+</sup> ions which compete with the Fe(III) ions for the adsorption sites. On the other hand, the metal ion was prone to Fe(OH)<sub>3</sub> deposition through hydrolysis at higher values of pH [47]. That was the reason that the metal uptake became almost constant as there were not extra metal ions to be removed after precipitation. This result is different from the normal pH range for iron to obtain the highest removal degree of iron; this can be contributed to the different of the adsorbent nature.

### Effect of adsorbent dosage

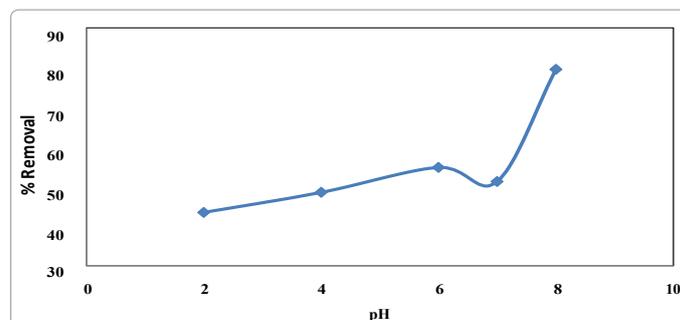
**Effect of the adsorbent dosage on cadmium ions removal:** As shown in Figure 8, with increasing the amount of nano CuO sorbent

(g), the metal uptake (q) will increase too and the percent removal will increase too, this behavior is expected since increasing the amount of sorbent will increase the area available for the adsorption and more metal ion is removed. The high adsorption capacity exhibited by CuO may be explained by its nano-scale particle size giving access to a larger surface area. This is consistent with the results of Meitei *et al.* [48].

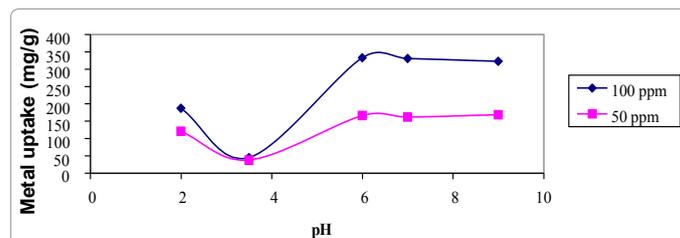
**Effect of the adsorbent dosage on iron ions removal:** As shown in Figure 9, with increasing the amount of nano CuO sorbent (g), the metal uptake (q) will increase too and the % removal will increase too to a limit of (0.3 g) then it decreases again after the dose increases from 0.3 to 0.4, this behavior is expected since increasing the amount of sorbent will increase the area available for the adsorption and more metal ion is removed. The high adsorption capacity exhibited by CuO may be explained by its nano-scale particle size giving access to a larger surface area. This agrees with the finding of Ozer *et al.* [49].

### Modeling of adsorption isotherms

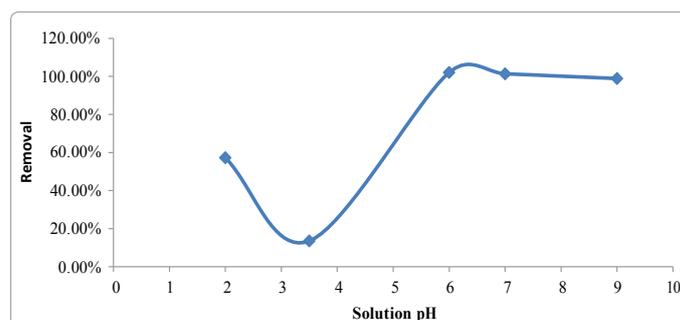
The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for



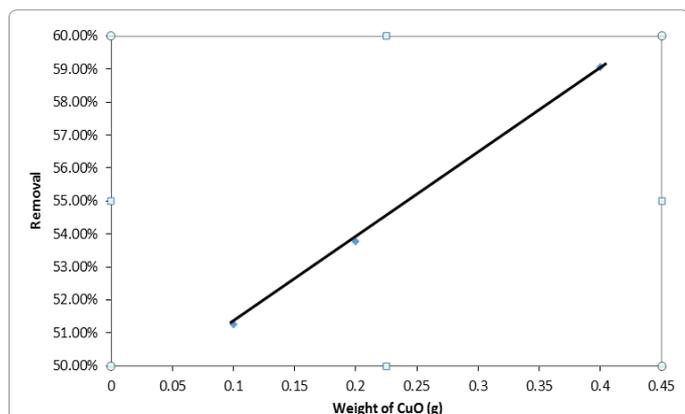
**Figure 5:** Effect of pH on percentage removal of Cadmium ions onto nano CuO powder at adsorbent weight W=0.4 g (CuO)/L (solution) and solution concentration of (50 mg/L) for 2 hours.



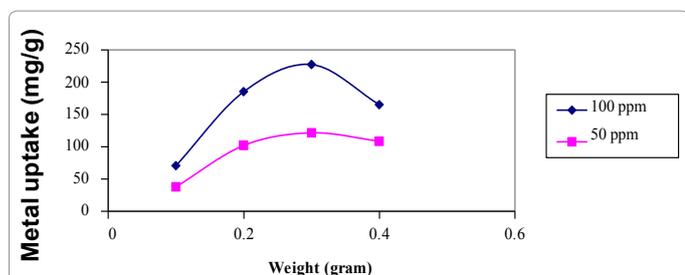
**Figure 6:** Effect of solution pH on Iron uptake onto nano CuO powder at adsorbent weight W=0.4 g (CuO)/L (solution) and solution concentration of (100, 50 mg/L) for 2 hours.



**Figure 7:** Effect of pH on percentage removal of Iron ions onto nano CuO powder at adsorbent weight w=0.4 g (CuO)/L (solution) and solution concentration of (100 mg/L) for 2 hours.



**Figure 8:** Effect of adsorbent weight (Nano CuO) (g) on the percentage removal of cadmium at pH=6 and at solution concentration of (50 mg/L) for 2 hours.



**Figure 9:** Effect of adsorbent dosage on adsorption capacity of Fe ions onto CuO nano powder at pH=3.5 and solution concentration of (100, 50 mg/L) for 2 hours.

design purposes. In order to investigate the adsorption isotherm, the adsorption data can be interpreted using several relationships which describe the distribution of heavy metal molecules between the aqueous and solid phases. In order to investigate the adsorption isotherm, the experimental data of equilibrium isotherms were interpreted using two equilibrium models; the Freundlich and the Langmuir. This modeling permits us to determine the maximal capacity of removal.

**Langmuir isotherm:** 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 (Equation 8) [50]:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \quad (8)$$

Where  $Q^0$  is the maximum metal ions uptake per unit mass of adsorbent (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 a straight line of slope  $1/Q^0$  and intercept  $1/(Q^0 b)$ .

**The Freundlich isotherm:** Freundlich isotherm describes the adsorption equation for non-ideal adsorption that involves heterogeneous adsorption. This empirical isotherm is expressed by the following equation (Equation 9) [51]:

$$q_e = K_F C_e^{1/n} \quad (9)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as (Equation 10)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

Freundlich constants,  $K_F$  and  $1/n$ , are related to adsorption capacity and intensity of adsorption, respectively. The values 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 equation 10. The magnitude of the exponent  $1/n$  gives an indication of the favorability of adsorption.

The applicability of the Freundlich sorption isotherm and Langmuir isotherm were analyzed, using the same set of experimental data. The data are represented in Table 1. The correlation coefficients reported in Table 1 showed strong positive evidence that the adsorption of Cd onto CuO nano powder follow the Langmuir isotherm as shown in Figure 10 while for the adsorption of Fe it follows the Freundlich isotherm. The  $1/n$  is lower than 1.0, indicating that Fe is favorably adsorbed by CuO, as shown in Figure 11.

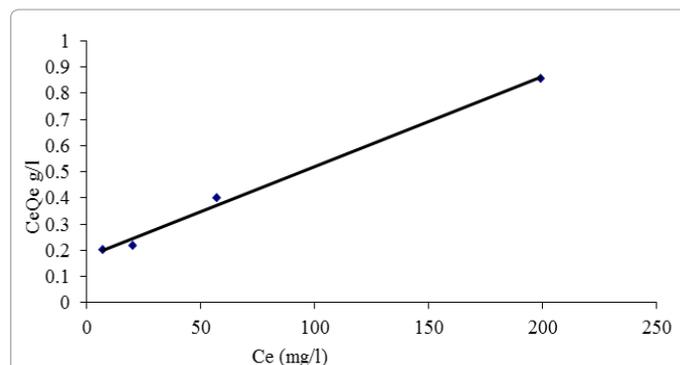
### Kinetic modeling

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: (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; and (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

Isotherm model	Fe	Cd
<b>Langmuir</b>		
$Q^0$ (mg g <sup>-1</sup> )	126.32	84.75
$K_a$ (L mg <sup>-1</sup> )	0.0097	0.0196
No. of parameter estimated	2	2
Data point available	4	4
$R^2$	0.6535	0.9945
<b>Freundlich</b>		
$1/n$	0.549	0.3767
$K_F$ (mg g <sup>-1</sup> )	2.752	2.76
No. of parameter estimated	2	2
Data point available	4	4
$R^2$	0.7539	0.9841

**Table 1:** Langmuir and Freundlich models for the removal of Cd and Fe onto CuO nano powder.



**Figure 10:** Langmuir isotherm for cadmium adsorption onto nano CuO powder at temperature of (25°C).

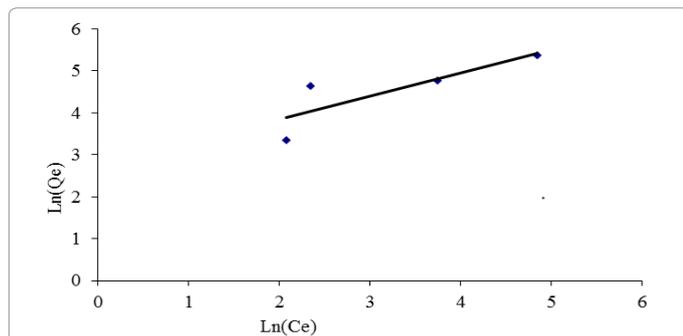


Figure 11: Freundlich isotherm for iron adsorption onto nano CuO powder at temperature (25°C).

controlling steps, the kinetics of Cd and Fe adsorption onto CuO were analyzed using pseudo-first-order [52] and pseudo-second-order [53] kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients ( $R^2$ , values close or equal to 1).

**Pseudo-first-order equation:** The adsorption kinetic data were described by the Lagergren pseudo-first-order model [52] which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The linear form equation is generally expressed as follows (Equation 11):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (11)$$

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.

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.

**Pseudo-second-order equation:** The adsorption kinetic may be described by the pseudo-second order model. The linear equation is generally given as follows (Equation 12):

$$\frac{t}{q_t} = \frac{1}{K_2} \times \frac{1}{q_e^2} + \frac{1}{q_e} t \quad (12)$$

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  $t$ . The linear plot of  $\log(q_e - q_t)$  versus  $t$  show good agreement between experimental and calculated  $q_e$  values (Table 2).

The correlation coefficients for the pseudo second-order kinetic model are greater than 0.98, which led us to believe that the pseudo second order kinetic model provided good correlation for the adsorption of Cd and Fe onto nano CuO as shown in Figure 12 and 13 respectively.

## Conclusion

From the present work the following conclusions have been reached:

- Nano CuO adsorbent removes heavy metal ions as Cd(II) and Fe(III) from wastewater by the main mechanism, which is adsorption.

- Optimal removal conditions were determined from batch experiments.
- Experimental results were evaluated with Langmuir and Freundlich isotherms.
- The adsorption process for Fe(III) follow Freundlich isotherm and for Cd(II) follows the Langmuir isotherm for all solution concentrations, and gives high correlation coefficients  $R^2$  of (0.7539 and 0.9945) for solution concentrations
- 250 ppm for both metals Fe(III) and Cd(III) respectively.
- Adsorption of both metals has reached equilibrium after about (20 minutes).
- Pseudo second order reaction kinetics has provided a realistic description for removal of Fe(III) and Cd(II) with closer experimental  $q_e$ , with high correlation coefficients  $R^2$  of (0.9995, 0.989) for both Fe(III) and Cd(II) respectively.

Kinetics models	Fe	Cd
Pseudo first order kinetics $K_1$ (min)	0.0148	0.184
$q_1$ (mg/g)	22.85	27.74
$R_1$	0.488	0.7343
Pseudo second order kinetics $K_2$ (g/mg min)	0.004	0.0024
$q_2$ (mg/g)	94.34	131.33
$R_2$	0.9995	0.989

Table 2: Kinetic parameters for the adsorption of Cd and Fe onto CuO.

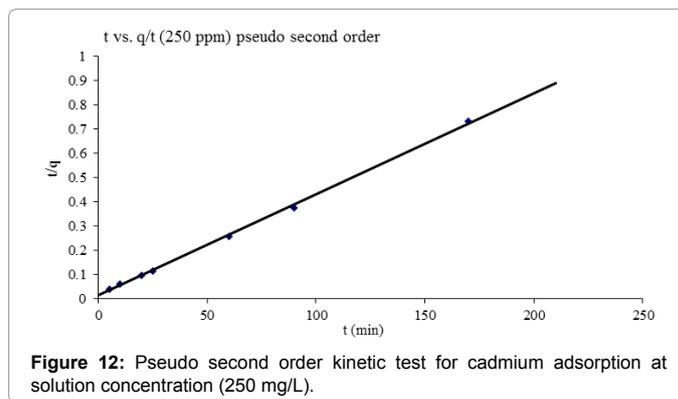


Figure 12: Pseudo second order kinetic test for cadmium adsorption at solution concentration (250 mg/L).

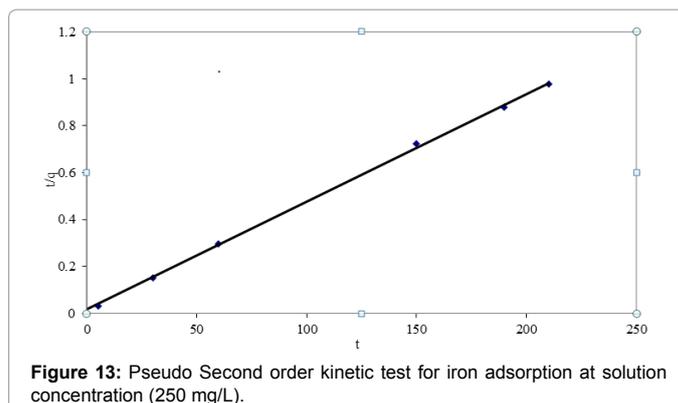


Figure 13: Pseudo Second order kinetic test for iron adsorption at solution concentration (250 mg/L).

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