ADSORPTION STUDIES FOR REMOVAL OF TRACE COPPER METAL IONS FROM AQUEOUS SAMPLES USING MAGNETIC NANOPARTICLES

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Abstract. Fe_3O_4 magnetic nanoparticles (MNPs) synthesized in-housed using co-precipitation method was assessed for the treatment of synthetic aqueous solutions contaminated by Cu(II) ions. Experimental results showed that at 25ºC, the optimum value for Cu(II) removal was pH 6.0 and an adsorbent dose of 60.0 mg. The adsorption capacity of Fe_3O_4 nanoparticles for Cu(II) is 16.28 mg g^{-1}. Adsorption kinetic rates were found to be fast; total equilibrium was achieved after 180 min. Kinetic experimental data fitted very well the pseudo-second order equation and the value of adsorption rate constants was calculated to be 0.0006 and 0.0013 g mg^{-1} min at 5 and 40 mg L^{-1} initial Cu(II) concentrations, respectively. The equilibrium isotherms were evaluated in terms of maximum adsorption capacity and adsorption affinity by the application of Langmuir and Freundlich equations. Results indicate that the Langmuir model fits adsorption isotherm data better than the Freundlich model.

Keywords Fe_3O_4 magnetic nanoparticles; Copper metal ions; Kinetic adsorption; Thermodynamic adsorption; Flame atomic absorption spectroscopy

1.0   INTRODUCTION

Cu(II) is a vital and required micronutrient for several plants and animals at trace levels. Currently the Environmental Protection Agency (EPA) standard for Cu(II) in drinking water is 1.3 mg L^{-1} [1]. However, the increase of dosage of Cu(II) in human body on allowable maximum level could cause damage in liver, kidney and central nervous system [2]. Furthermore, Alzheimer's, Parkinson's, Wilson and Menkes diseases have been found closely related to the disorder of Cu(II) metabolism [3, 4]. Several pollutants sources of Cu(II) ions have been identified in drinking water samples such as the corrosion of pipes, faucets, household plumbing systems [5, 6].

The removal of Cu(II) as inorganic contaminants from environmental and drinking water samples is a well-known process. Various methods, such as ion exchange [7], chemical precipitation [8], membrane processes [9], and electro-dialysis [10] have been developed for the removal of heavy metals from aqueous samples. Among these purification techniques, the adsorption method using suitable adsorbents is considered as one of the most efficient and economical methods from the viewpoint of simple design and facile handling. Numerous adsorbents have been reported for the removal of Cu(II) from aqueous solutions, including zeolite [11], activated carbon [12], kaolinite [13], diatomite [14], functionalized polymers [15], chitosan [16], and alumina [17]. However, most of these adsorbents are not the perfect choices for their unsatisfied adsorption capacity, insufficient adsorption efficiencies, difficulty of separation from the solution, or high fee in application. Currently, the application of nano-materials has appeared as a fast-developing, fascinating area of interest for removal of Cu(II) from industrial wastes because of unique characteristics of nano-materials such as large surface area, a greater number of active sites, and low diffusion resistance for adsorbates. Low-cost materials, including alumina nano-powders [18], carbon nanotubes [19], TiO$_2$ nano-rods [20], etc., have been used for the removal of Cu(II) from aqueous solutions and the experimental results proposed that the adsorption effect was quite well.

In recent years, many studies [21-23] have used Fe_3O_4 MNPs as an adsorbent since Fe_3O_4 MNPs possessed a high surface area and could easily be synthesized. Also, the MNPs have a unique advantage and could be separated easily from solution by an external magnetic field. Thus, an efficient, economic, scalable and non-toxic synthesis of Fe_3O_4 MNPs is highly desired for practical applications and fundamental research. A possible application of this sorbent should start from a thorough analysis of the main parameters influencing the adsorption of heavy metals on magnetite nanoparticles.

In this study, an in-house synthesized Fe_3O_4 MNPs adsorbent was assessed for its feasibility in the adsorption of Cu(II) metal ions from aqueous solutions. Adsorption tests were carried out by isotherm and kinetic Adsorption equations. The Fe_3O_4 MNPs showed high potential application as adsorbents for metal adsorption from wastewater samples.

2.0   EXPERIMENTAL

2.1   Chemicals and Reagents

All vessels were cleaned and soaked in diluted nitric acid for more than 12 h before using. Deionized water (18.2 MΩ) was obtained from a Simplicity 185, Millipore water filtration system from Merck (Darmstadt, Germany) and used for preparation of the standards and sample solutions. Stock solution (1.0 g L^{-1}) of Cu(II) was purchased from Merck (Darmstadt, Germany), ferric chloride 6-hydrate (iron(III) chloride) $Fe_3Cl_3.6H_2O$, ammonium ferrous sulfate hexahydrate $(NH4)_2Fe(SO_4)_2.6H_2O$, concentrated ammonia solution (NH_4OH 28.0%), nitric acid (HNO_3 65.0%) were all purchased from Sigma–Aldrich (St. Louis, MO, USA). Hydrochloric acid (HCl 37.0%) was purchased from Fluka Chemika (Buchs, Switzerland).

2.2   Instrument

Perkin-Elmer AAnalyst 400 flame atomic absorption spectrometer (Waltham, MA USA), equipped with a hollow cathode lamp for copper and with a deuterium lamp for background correction was used to determine the absorption of Cu(II) solution. The hollow cathode lamp was operated at 8.0 mA and the wave length was set at 324.75 nm. The flame composition was operated with an acetylene flow rate of 1.8 L min^{-1} and air flow rate of 10.0 L min^{-1}.

2.3   Adsorption experiments

2.3.1   Adsorption isotherms experiments

Adsorption isotherm experiments were performed in batch-mode. In a typical experiment, 60.0 mg of Fe$_3$O$_4$ nano-adsorbent was weighed into a 500.0 mL glass beaker containing 100.0 mL of Cu(II) metal ion solution. Cu(II) metal ion concentration ranged from 5.0 to 50.0 mg L^{-1}, and the solution pH was adjusted to 6.0 with 0.1 M HCl or 0.1 M NaOH when necessary. The mixture was mechanical shake at 25 ºC for 180.0 min. The adsorbent was gathered by placing an external magnetic field and the supernatant was collected for the determination of Cu(II) by FAAS, when adsorption equilibrium has been reached The equilibrium adsorption capacity of the Fe$_3$O$_4$ MNPs towards Cu(II) was calculated as:

$$q_e = \frac{C_o - C_e}{m} V \qquad\qquad (1)$$

where q$_e$ is equilibrium adsorption capacity (mg g^{-1}), C$_o$ and C$_e$ (mg L^{-1}) are the initial and the equilibrium concentrations of the metal ions, respectively. V (L) is the volume of the solution and m (g) represents the weight of the adsorbent.

2.3.2   Kinetic adsorption experiments

In a typical run, 60.0 mg of Fe_3O_4 MNPs and 100.0 mL of 40.0 mg/L Cu(II) solutions were mechanically shakened at pH = 6.0, 25 ºC under ranged from 30.0 to 360.0 min. The same procedures were followed for the 5.0 mg L^{-1} Cu(II) solutions. Because, the kinetic studies were examined at lower and higher concentration.

3.0   RESULTS AND DISCUSSION

### 3.1   Cu(II) adsorption by Fe_3O_4 MNPs

3.1.1   Adsorption isotherms

The adsorption capacities of as-obtained Fe_3O_4 MNPs were examined at pH 6.0, 25ºC with 60.0 mg of Fe_3O_4 MNPs and varied Cu(II) concentrations from 5.0–50.0 mg L^{-1} (**Figure 3.1**). The adsorption data were analyzed using Langmuir [24] and Freundlich [25] isotherms. These isotherms model were expressed as the following equations, respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (3)$$

where q_e is the amount of Cu(II) adsorbed on the absorbent at equilibrium (mg g^{-1}), q_m denotes the maximum adsorption capacity corresponding to complete monolayer coverage, C_e describes the equilibrium Cu(II) concentration (mg L^{-1}), and K_L is the Langmuir adsorption constant (L mg^{-1}). K_F and n are the Frendlich constants related to the maximum sorption capacity (mg g^{-1}) and the heterogeneity factor (mg^{-1}), respectively.
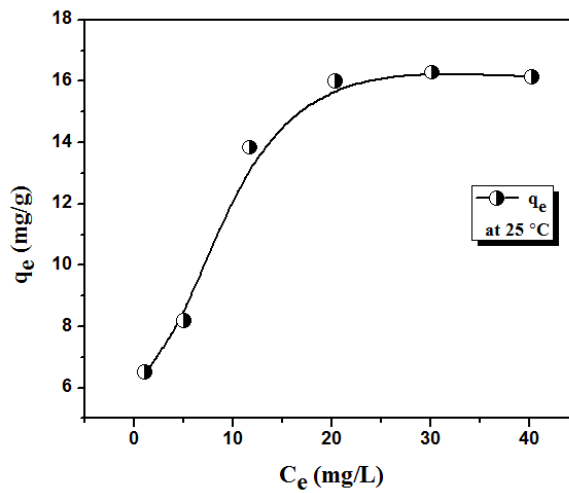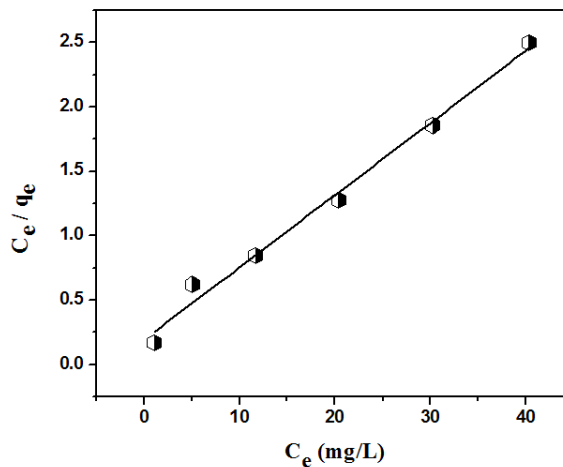
Figure 3.1: Adsorption capacity of Cu(II) on Fe_3O_4 MNPs using 60.0 mg of adsorbent, 100.0 mL of a range of 5.0−50.0 mg L^{-1} as Cu(II) initial concentrations at pH= 6.0, 25 °C and a shaking time of 180.0 min.

In the Langmuir isotherm model, the values of q_m and K_L can be calculated from the slope and intercept of linear plots of C_e/q_e vs. C_e (**Figure 3.2**), respectively. The results are listed in **Table 1**. The type of the Langmuir isotherm can be predicted by a dimensionless constant separation factor ''R_L'', which is defined as $R_L = 1/ (1 + K_L C_0)$. The parameter R_L indicates the type of the isotherm accordingly: RL > 1, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable and $R_L = 0$, irreversible. The calculated R_L values ranged from 0.0604 to 0.2895 for different initial Cu(II) concentrations at 25°C. This indicates that the adsorption of Cu(II) by Fe_3O_4 MNPs is favorable.

Table 1: Isotherm constants for the adsorption of Cu(II) onto Fe$_3$O$_4$ MNPs at 25ºC.
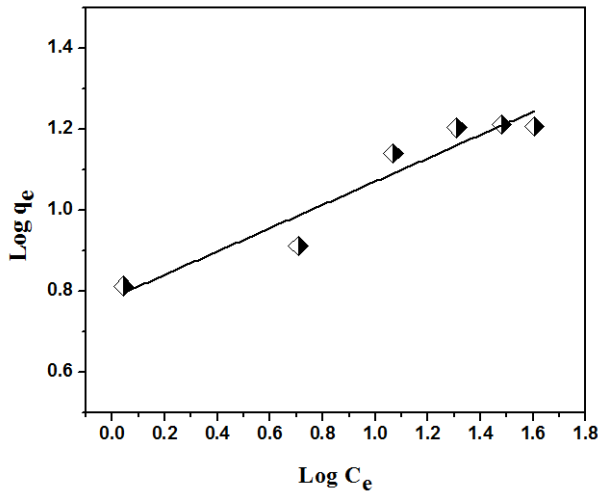
Langmuir isotherm model			Freundlich isotherm model		
q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (L/g)	R^2
17.82	0.29	0.99	3.47	6.07	0.92

Figure 3.2: Langmuir isotherm model of adsorption Cu(II) metal ions on Fe$_3$O$_4$ MNPs using 60.0 mg of adsorbent, 100.0 mL of a range of 5.0−50.0 mg/L as Cu(II) initial concentrations at pH= 6.0, 25ºC and a shaking time of 180.0 min.

The Freundlich isotherm model is used to estimate the adsorption intensity of adsorbent towards the adsorbate (**Figure 3.3**). The values of K$_F$ and n can be obtained from the slope and intercept of the linear plots of log (q$_e$) vs. log (C$_e$), respectively, and the obtained values are shown in **Table 1**. The value of n was 3.474 at 25ºC and this value lies in the range of 1.0−10.0 which reveals that

adsorption is favorable. This is confirmed with the result of Langmuir isotherm model.


Figure 3.3: Freundlich isotherm model of adsorption Cu(II) metal ions on Fe$_3$O$_4$ MNPs using 60.0 mg of adsorbent, 100.0 mL of a range of 5.0−50.0 mg/L as Cu(II) initial concentrations at pH= 6.0, 25 ºC and a shaking time of 180.0 min.

3.2.5   Adsorption kinetics

The adsorption kinetics is essential for describing the solute uptake rate. Kinetics tests were carried out by adding 60.0 mg of Fe$_3$O$_4$ MNPs to 100.0 mL solutions each containing 5.0 and 40.0 mg L^{-1} of Cu(II) at pH 6.0, 25ºC with contact time ranging from 30.0 to 360.0 min. **Figure 3.4** shows that the uptake of Cu(II) is quite effective initially, then slows down with the lapse of time and reaches equilibrium within 180.0 min. The Fe$_3$O$_4$ MNPs have a shorter adsorption equilibrium time and larger adsorption capacity. This rapid adsorption suggests that the adsorption of Cu(II) by Fe$_3$O$_4$ MNPs takes place in a single step, being similar with some previous results [23, 26].
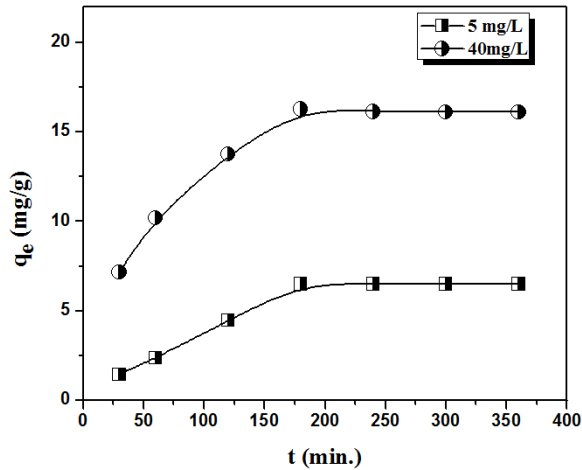
Figure 3.4: Kinetic data for Cu(II) uptake by Fe_3O_4 MNPs from 100.0 mL of 5.0 and 40.0 mg L^{-1} initial Cu(II), 60.0 mg of adsorbent, at pH= 6.0, 25°C.

In order to evaluate adsorption kinetics of Cu(II) onto Fe_3O_4 MNPs, Lagergren pseudo-first order, pseudo-second order [27] kinetics models were applied to fit the experimental data. Both the kinetic equations are shown as the following equations, respectively:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where q_e and q_t are the sorption capacity (mg g^{-1}) at equilibrium and at time t (min), k is the rate constant, h is the initial sorption rate in pseudo-second-order model, and R^2 is the coefficient of determination to express the uniformity between the experimental data and model-predicted values. From the slope of **Figure 3.5**, the Lagergren-first-order rate constants k_1 can be obtained and the coefficients of determination (R^2) are in the range of 0.864−0.906.
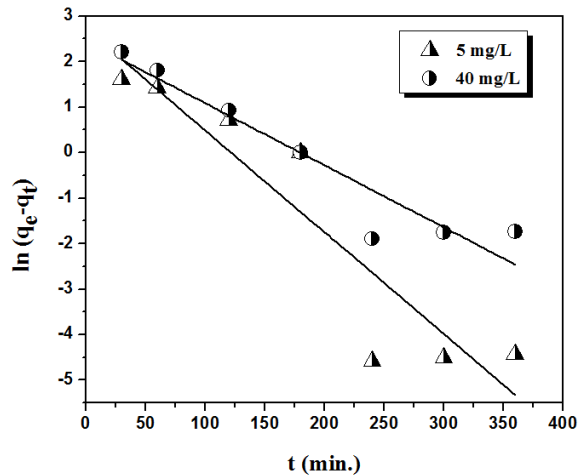
Figurer 3.5: Lagergren pseudo-first order kinetic models for Cu(II) adsorption on Fe_3O_4 MNPs from 100.0 mL of 5.0 and 40.0 mg L^{-1} initial Cu(II), 60.0 mg of adsorbent, at pH= 6.0, 25ºC.

The pseudo-second order kinetic constant k_2 and q_e can be calculated from the intercept and slope of plots of t/q_t vs. t **(Figure 3.6)**. The calculated k_2, q_e (*calc.*), h, and R^2 are presented in **Table 2**. The experimental data are in good agreement with the pseudo-second-order model which suggests that the rate-limiting step in adsorption is controlled by chemical process [28].
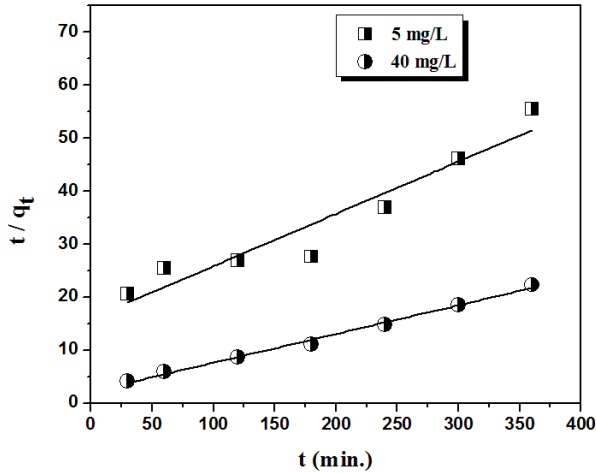
Figurer 3.8: pseudo-second order kinetic models for Cu(II) adsorption on Fe_3O_4 MNPs from 100.0 mL of 5.0 and 40.0 mg L^{-1} initial Cu(II), 60.0 mg of adsorbent, at pH= 6.0, 25ºC.

Table 2: Kinetic parameters of first and second order models fitted to experimental data.

Kinetic models and parameters	Cu(II) C_o (mg /L)	
	5.0	40.0
q_e (exp.)	6.5	16.28
Lagergren pseudo-first order equation		
q_e (calc.)	15.22	11.61
k_1 (min^{-1})	0.0223	0.0136
R^2	0.864	0.906
Pseudo-second-order equation		
q_e (calc.)	10.13	18.41
k_2 (g mg^{-1} min^{-1})	0.0006	0.0013
h (mg g^{-1} min^{-1})	0.0624	0.4453
R^2	0.920	0.993

4.0   CONCLUSION

In this study, the adsorption of Cu(II) from aqueous solution onto Fe_3O_4 MNPs adsorbent prepared with co-precipitation method was successfully studied. The pseudo-second-order model was the most suitable kinetic model, chemical sorption was the rate-limiting step, and Cu(II) adsorption equilibrium was achieved within 180 min. The isotherm analysis indicated that the adsorption data could be well represented by the Langmuir isotherm model and the maximum monolayer adsorption capacity was 16.28 mg g^{-1} at pH 6.0 and 25ºC. The adsorption process was exothermic in nature. Results showed that Fe_3O_4 MNPs had a high stability, which proposed that the Fe_3O_4 MNPs would be a potential candidate as a highly efficient, low-cost and renewable adsorbent for Cu(II) removal from aqueous medium.

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