

Removal of Cu (II) from aqueous solutions using magnetite: A kinetic, equilibrium study

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Abstract. Water pollution means that the physical, chemical and biological properties of water are changing. In this study, adsorption was chosen as the treatment method because it is an eco-friendly and low cost approach. Magnetite is a magnetic material that can synthesize chemical precipitation. Magnetite was used for the removal of copper in artificial water samples. For this purpose, metal removal from water dependent on the pH, initial concentration of metal, amount of adsorbent and effect of sorption time were investigated. Magnetite was characterized using XRD, SEM and particle size distribution. The copper ions were determined by atomic absorption spectrometry. The adsorption of copper on the magnetite was studied in a batch process, with different aqueous solutions of Cu (II) at concentrations ranging from 10 to 50 mg L⁻¹. Optimum conditions for using magnetite were found to be concentration of 10 mg L⁻¹, pH: 4.5, contact time: 40 min. Optimum adsorbent was found to be 0.3 gr. Furthermore, adsorption isotherm data were analyzed using the Langmuir and Freundlich equations. The adsorption data fitted well with the Freundlich ($r^2 = 0.9701$) and Langmuir isotherm ($r^2 = 0.9711$) equations. Kinetic and equilibrium aspects of the adsorption process were studied. The time-dependent Cu (II) adsorption data were described well by a pseudo-second-order kinetic model.

Keywords: adsorption; chemical precipitation; copper; kinetic; magnetite; wastewater treatment

1. Introduction

Heavy metals are toxic because they are present as ions in aqueous systems and can be readily absorbed into the human body. Copper is among those hazardous materials that are most commonly found in industrial wastewater. Even a very small amount can cause severe physiological or neurological damage (Dönmez and Aksu 1999). Bivalent copper (Cu (II)) is a priority pollutant (Sparks 2005), thus its removal is of extreme importance. Copper is a widely used industrial metal whose applications include electrical wiring, plumbing, air conditioning tubing and roofing. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production, the fertilizer industry, etc (Ho 2003). Agricultural chemicals and their by-products are another source of copper waste. However, Cu (II) is known to be one of the heavy metals most toxic to living organisms and it is one of the

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more common heavy metal contaminants of the environment.

A number of techniques have been used to remove the metal ions from wastewater effluents including chemical precipitation, ion exchange process, electrolytic methods, adsorption, and membrane and reverse osmosis processes (Patterson 1985). Most of these methods suffer from some drawbacks such as high capital and operational costs for the treatment and disposal of the residual metal sludge. Therefore, efforts have been made to develop low-cost materials to remove contaminants from aqueous solutions (Jha *et al.* 2004, 2008, Kentish and Stevens 2001).

Magnetite is widely available in nature and recently some researchers have focused on the utilization of nano scale magnetite to remove heavy metals. Magnetic particle sizes from nanometer to micrometer are attractive materials not only in the field of magnetic recording but also in the areas of biological and medical applications (Lida *et al.* 2007).

Interest in magnetite nanoparticles has dramatically increased in the past two decades because of its wide scope of applications (Miller *et al.* 2002, Babes *et al.* 1999). Biomedical applications such as targeted drug delivery (Jain *et al.* 2005) require that the magnetite nanoparticles have high magnetization values, a size smaller than 100 nm, a narrow particle size distribution, and a biocompatible surface coating that allows for a targetable delivery with particle localization in a specific area. In addition, magnetite nanoparticles have been used as adsorbents for the removal of heavy metal cations from wastewater, which also requires low and homogeneous particle size distribution to achieve enhanced efficiency (Lim *et al.* 2008).

One of the more promising particles is the iron oxide nanoparticle of various kinds and derivatives: magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$) (Massart 1981, Kim *et al.* 2001). Magnetite has inverse spinel structure and its unit cell structure represent with $(\text{Fe}^{+3})_A (\text{Fe}^{+3} \text{Fe}^{+2})_B \text{O}_4$ where A and B respectively stand for tetrahedral and octahedral sites coordinated with oxygen ions at face centred cubic array (Racuciu 2009).

Currently there are several methods for synthesizing metal oxide (e.g., magnetite and other ferrites) nanoparticles in solution: chemical co-precipitation (Kang *et al.* 1996), micro emulsion (Liu *et al.* 2004), and decomposition of metal organic salts (Jana *et al.* 2004). Co-precipitation is the least expensive and the simplest approach for making nanoparticles. For example, inexpensive iron salts may be mixed with a precipitating agent such as NaOH to form nanoparticles of iron oxides (Novakova *et al.* 2003, Cheng *et al.* 2005).

The method involves co-precipitation from Fe (II) and Fe(III) aqueous salt solutions by addition of a base. The chemical reaction may be written (Tartaj *et al.* 2003, Cotton and Wilkinson 1988) as follows



According to this reaction, an initial molar ratio of Fe(III):Fe(II) = 2:1 is needed for the production of Fe_3O_4 .

Recently, many researchers have investigated the use of nano scale magnetite to remove heavy metals mainly including Cr (VI) (Hu *et al.* 2004, Peterson *et al.* 1997), Hg (II) (Wiatrowski *et al.* 2009), and As(V)(III) (Bujňáková *et al.* 2013, Dhoble *et al.* 2011). However, very few experimental studies are reported in the literature on the other common heavy metal ions (e.g., Cu(II)) interactions with magnetite (Wang *et al.* 2011, Podzus *et al.* 2012, Chung *et al.* 2012). Consequently, the main objectives of this research were to evaluate magnetite copper adsorption capacity and to investigate sorption kinetics. Moreover, the experimental isotherm data were analyzed using the Langmuir and Freundlich equations as well.

2. Materials and methods

2.1 Materials

All chemicals were obtained from Merck and were of analytical grade and used without any further purification. In this study, ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and ammonia solution (25% vol.) were used to synthesize Fe_3O_4 magnetic particles.

The stock solutions of Cu (II) (1000 mg L^{-1}) were prepared by standard solution. Solution of the selected concentration was prepared using deionized water. Water was purified by passage through a milli-Q water system.

2.2 Experimental procedure

Fe_3O_4 magnetic particles were synthesized by the co-precipitation method at room temperature from an aqueous solution containing iron salts and bases. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were used as iron salts, ammonia solution was used as the base and deionized distilled water as solvent. Sample was prepared by adding a solution containing (150 ml) ferrous chloride (1 M) and ferric chloride (2 M) followed by drop-wise addition of ammonia. Immediately, a dark brown precipitate was formed and the precipitate gradually turned into black. The suspension was vigorously stirred with a magnetic stirrer. A pH value of 11 was maintained by drop-wise addition of ammonia. All the precipitates were filtrated and washed five times with deionized distilled water and then dried to remove water content at ambient temperature (Faiyas *et al.* 2010, Maity and Agrawal 2007).

The batch method was used for removal of Cu (II) in aqueous solutions. The effects of pH, amount of adsorbent, initial metal concentration and contact time were investigated for determination of optimum conditions. The optimal amount of adsorbent was reached with 50 ml of solution containing 10 mg L^{-1} Cu (II) at the optimal time. All the operations were conducted at 400 rpm stirring rate and room temperature. After filtration of the solid phase, the content of copper in the liquid phase was determined by atomic absorption spectrometry.

In order to provide precise data, the samples were analyzed in triplicate, and the averages were reported as results. The removal efficiency of metal was given as C_i/C_0 , where C_0 and C_i (mg L^{-1}) are the initial and remaining metal concentration at given time t .

2.3 Analytical methods

Fe_3O_4 (magnetite) particles were characterized using XRD analyses measurements. X-ray diffraction (XRD) experiments were conducted in a PanalyticalTM X'Pert PRO using the setting of 40 mA and 40 kV at a 2θ range between 0-90.

The particle size distribution analyses of these materials were done using a Malvern, mastersizer 2000 instrument.

Scanning electron microscopy (SEM) investigations were carried out in a CamScan Apollo 300 Field-Emission SEM at 20 kV.

The surface area was determined using the standard single-point method in Quantachrome instrument

A PerkinElmer AAnalyst 200 model atomic absorption spectrophotometer with an air-acetylene flame was used for determination of copper amounts in the aqueous phase. All pH measurements were made with a pH-meter (WTW) and a combination pH electrode.

3. Results and discussion

3.1 Material characteristics

XRD studies

Phase investigation of the crystallized product was performed by XRD and the pattern is shown in Fig. 1. The XRD pattern indicates that the product is iron oxide, Fe_3O_4 and the diffraction peaks are broadened owing to small crystallite size (Xu *et al.* 2005, Langford and Wilson 1978).

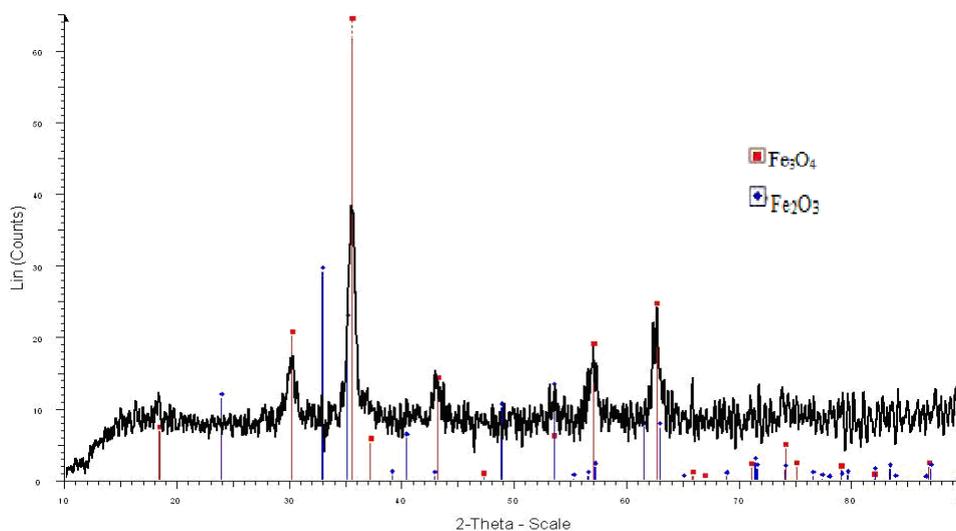


Fig. 1 X-ray diffraction patterns of Fe_3O_4 magnetic particles

Particle size distribution

$d(0.1)$: $2.173 \mu\text{m}$ $d(0.5)$: $26.380 \mu\text{m}$ $d(0.9)$: $83.423 \mu\text{m}$

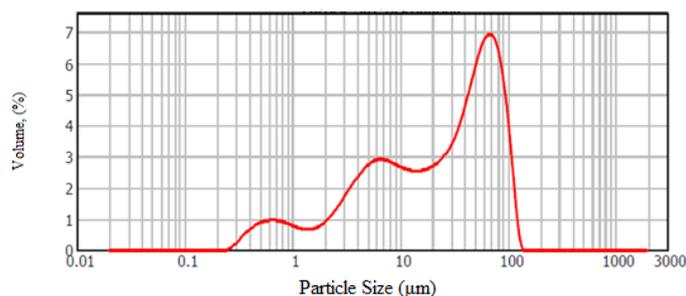


Fig. 2 Particle size distribution histograms for Fe_3O_4 magnetic particles

Fig. 2 shows that the particle size distribution of Fe_3O_4 magnetic particles exhibited narrow distribution of particle size with the average of $2.172 \mu\text{m}$. 50% and 90% of Fe_3O_4 magnetic particles $26.380 \mu\text{m}$ and $83.423 \mu\text{m}$, respectively.

Multi-particle structures are observed. Buzmakaov and Pshenichnikov (1996) demonstrated that the formation of multi particle structure is due to magneto-dipole and van der Waals force between magnetite particles.

SEM studies

SEM micrograph of as-synthesized magnetite particles are shown in Fig. 3.

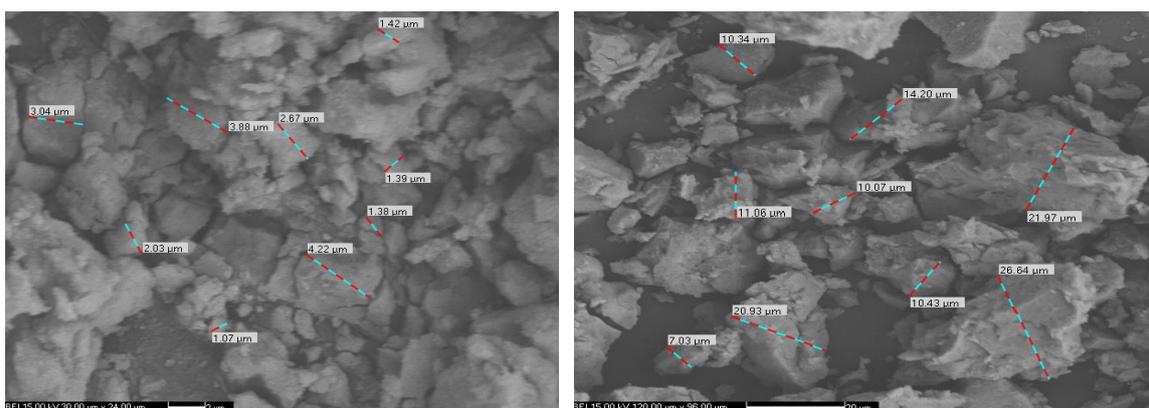


Fig. 3 SEM analysis of Fe_3O_4 magnetic particles

In the study made by Mera Martínez *et al.* (2007), it is explained that there is a decrease in Fe_3O_4 crystal dimension synthesised by decreasing reagent concentration and that spherical shaped crystals are obtained. In this study due to the used mole ratio of $\text{Fe(III):Fe(II)} = 2:1$ micro Fe_3O_4 observed in Fig. 3 is obtained.

Surface area (BET) analysis

The surface areas were determined using the standard single-point method. Samples were analyzed in triplicate. The surface area value of magnetite particles is $90.342 \text{ m}^2 \text{ g}^{-1}$.

3.3 Optimum process conditions

(a) Effect of pH on the retention of copper

It is well known that pH is one of the most important factors that affect the adsorption process. The equilibrium pH of the magnetite (Fe_3O_4)/solution mixture has been shown to be the principal factor controlling the extent of removal of Cu (II) ions from aqueous solutions.

Analyzing the theoretical precipitation curves of metal which is given Fig. 4 Cu (II) is precipitated at about pH 5.5 (Cuppett *et al.* 2006). Thus, experiments were performed to find the optimum pH on the adsorption of Cu (II) ion onto magnetite using different initial pH values changing from 2 to 6.

An experimental condition studied was concentration 10 mg L^{-1} , magnetite amount of 0.3 g L^{-1} and contact time of 40 min.

The higher the proton concentration, the lower the efficiency of the Cu(II) removal. This pH dependency has previously been attributed to the form surface complexes between the functional groups ($\equiv\text{FeOH}$) and the Cu(II) with the possible reaction given as follows (Marmier *et al.* 1999)

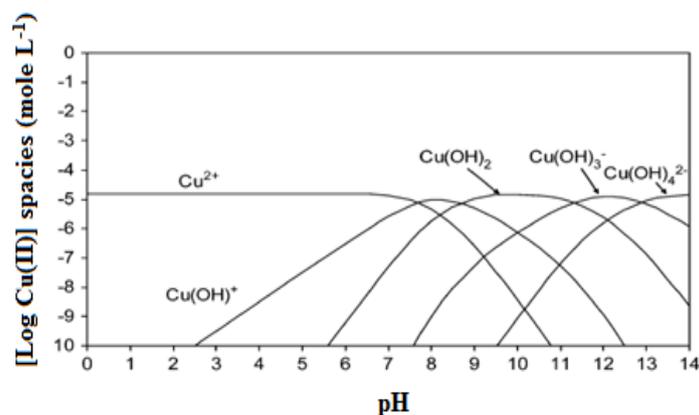


Fig. 4 Theoretical copper speciation for hydroxo complex in pure water for a total copper concentration 1 mg L^{-1} , which is the value for the USEPA aesthetic-based standard

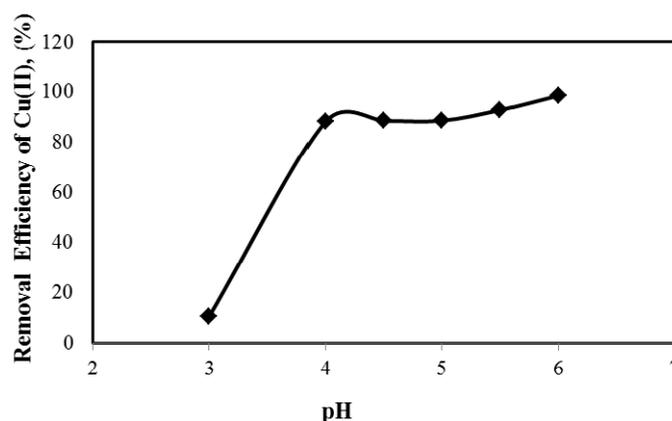


Fig. 5 Effect of pH on the adsorption of Cu(II) removal



where $(\equiv \text{FeO})_q \text{Cu}_r (\text{OH})_s^{(2-q-s)}$ symbolized surface complexes and s , q and r are stoichiometric coefficients.

With an increase in pH, this equilibrium shifts such that a greater number of sites are present in the more reactive deprotonated form, which leads to higher Cu (II) uptake. The species of Cu (II) influences its charge properties and likely uptake by magnetite. As seen from Fig. 4. The theoretical precipitation curves of copper (Cuppert *et al.* 2006), the dominant form of Cu (II) at pH 2.0 is Cu (II) and with an increase in pH from 2.0 to 5.0, other species are formed.

As can be seen in Fig. 5, the highest quantitative retention (88.53%) was obtained for copper at pH 4.5. This situation shows that the adsorption mechanism of Cu (II) on magnetite (Fe_3O_4) is controlled by pH. Similar pH value has been reported for adsorption of Cu (II) from aqueous solutions onto magnetite (Fe_3O_4) (Wang *et al.* 2007, 2011, Chung *et al.* 2012).

(b) Changing of Copper concentration in solution as a function of time

The adsorption of Cu (II) onto magnetite (Fe₃O₄) was monitored for 250 minutes. The data obtained from the adsorption of copper (II) ions on the magnetite showed that a contact time of 40 min. was sufficient to achieve equilibrium and the adsorption did not change with further increases in contact time as can be seen in Fig. 6. Therefore, the uptake and unadsorbed copper (II) concentration at the end of 40 min. are given as the equilibrium values (q_e , mg g⁻¹; C_e , g L⁻¹, respectively). Consequently, equilibrium adsorption time of 10 mg L⁻¹ copper at pH 4.5 was obtained at 40 min. by 0.3 m L⁻¹ of magnetite (Fe₃O₄).

(c) Effect of adsorbent dosage

The influence of adsorbent dosage in percentage adsorption and equilibrium concentration is shown in Fig. 7.

The effect of adsorbent dose by magnetite mass varied from 0.25 to 0.70 g L⁻¹ at pH 4.5 and a fixed initial metal concentration of 10 mg L⁻¹ for 40 min. The general trend indicates that the

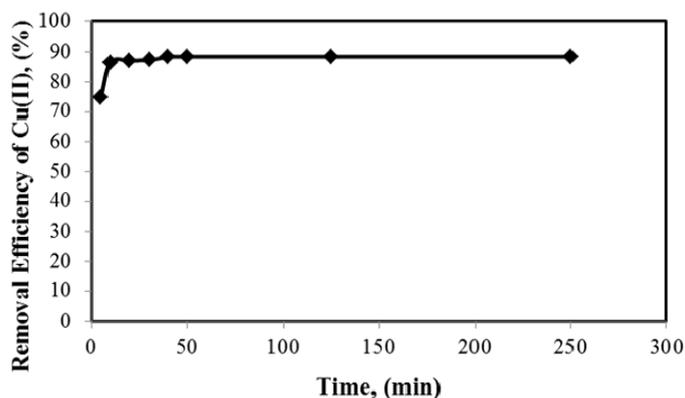


Fig. 6 The effect of contact time on the adsorption of Cu(II) removal

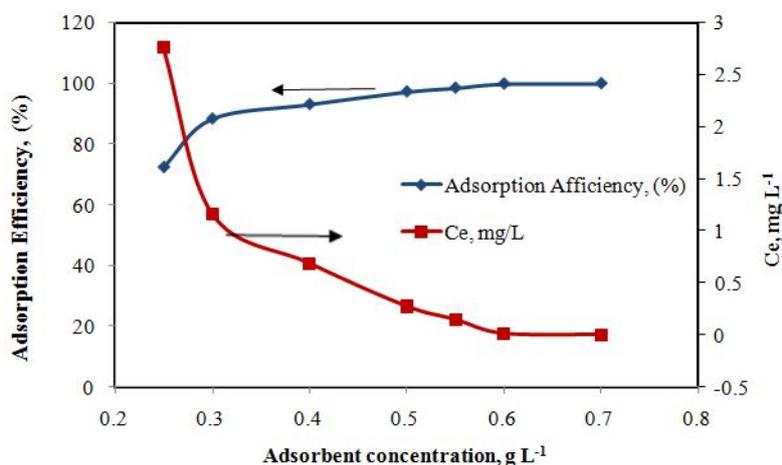


Fig. 7 Influence of adsorbent concentration in percentage adsorption and the equilibrium concentration (conditions 45 ml 10 mg L⁻¹ Cu(II) solution; ambient temperature; contact time 40 min; initial pH 4.5)

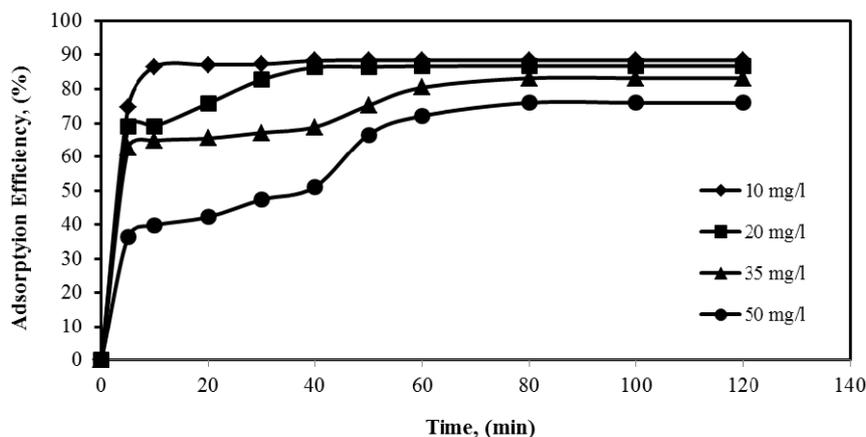


Fig. 8 The change of sorption capacity with time at various the initial Cu(II) concentrations

adsorption of Cu (II) increases with increasing the adsorbent dose from 0.25 to 0.70 g L⁻¹. As seen in Fig. 7, the equilibrium concentration of the Cu (II) in the aqueous solution decreases with the adsorbent dose. Optimum adsorbent was found to be 0.30 g L⁻¹ for Cu (II). The value of sorption Cu (II) was found to be 88.35(%) for 0.30 g L⁻¹ magnetite. At the adsorbent dose of 0.70 g L⁻¹, removal efficiencies of 99.9(%) were observed. The increment of the removal efficiency is due to the increase of adsorbent dose that means increase of the total available surface area of the adsorbent particles.

Moreover, Fig. 7 is examined 88.35% efficiency was obtained by usage of 0.3 mg L⁻¹ adsorbent for 10 mg L⁻¹ Cu (II) initial concentration. The amount of Cu (II) remaining in the solution is 1.165 mg L⁻¹. When the various standards such as WHO, EPA, EC and Turkish standards TS 266 are examined it is observed that this value is compliant with all standards. These standards are drinking and edible water standards. Also it is far below the 3 mg L⁻¹ discharge standard determined for mining wastes. Therefore it is obvious that there is no need for excess adsorbent usage.

(d) Effect of initial concentration on the uptake of Cu (II)

The experiments were carried out at a fixed adsorbent dose (0.30 g L⁻¹) and at different initial Cu (II) concentrations (10, 20, 35 and 50 mg L⁻¹) for different time intervals (5, 10, 20, 30, 40, 50, 125 and 250 min) at ambient temperature as shown in Fig. 8. The contact time required to reach the equilibrium of Cu (II) solution was 40 min at 10 and 20 mg L⁻¹ initial Cu (II) concentration. However, the experimental data were measured up to 120 min to confirm that complete equilibrium was reached. Equilibrium time was determined as 80 min for 35 and 50 mg L⁻¹ initial Cu (II) concentration. It demonstrated that concentration of Cu (II) depends on equilibrium contact time. As a result, Cu (II) uptake is rapid for the first 40 min and thereafter it proceeds at a slower rate and finally attains saturation. At low metal concentrations, vacant surface sites adsorbed the metal more rapidly. One explanation for this observation may be the fact that low metal concentrations are adsorbed very quickly on the outer surface. Further increase in the initial metal concentration led to fast saturation of adsorbent and thus, most of the metal adsorption took place slowly inside the pores by intra-particle diffusion. As the initial Cu (II) concentration increases

from 10 to 50 mg L⁻¹ the equilibrium removal of Cu(II) decreases from 86.38 to 75.99 %.

3.4 The kinetics of Cu (II) adsorption onto the magnetite

The adsorption kinetic data of Cu (II) were analyzed using two kinetics models, which mainly applied pseudo-first-order and pseudo-second-order equations. Lagergren (1898) suggests the pseudo-first-order kinetics rate equation, and integrated the rate equation by applying the initial conditions as below

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \tag{1}$$

Where, q_e and q_t (mg g⁻¹) are the amounts of Cu(II) adsorbed per unit of mass of magnetite at equilibrium and time t , respectively, and k_1 is the pseudo-first-order rate constant (min⁻¹). In other words, q_e represents adsorption capacity. The value for the k_1 was calculated from the slope of the linear plot of $\log(q_e - q_t)$ versus t (Fig. 9). The k_1 values and correlation coefficients r^2 are given in Table 1. As shown in Fig. 9, the pseudo-first-order kinetic model is not satisfactory for the adsorption of Cu (II) onto the magnetite.

The pseudo-second-order reaction rate equation was used by Ho *et al.* (1996) to study the kinetics of adsorption of heavy metals on peat. This model was also applied to assess the kinetics of adsorption of Cu (II) on the magnetite. The pseudo-second-order rate kinetics can be expressed as follows

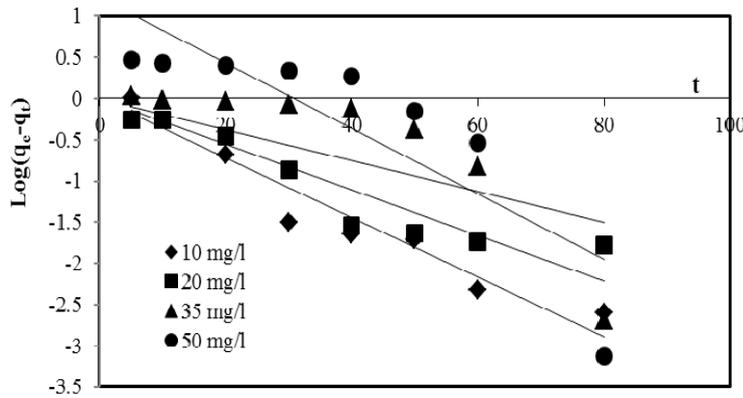


Fig. 9 Kinetics analysis of Cu (II) adsorption by linear plots of pseudo-first-order rate equation at ambient temperature

Table 1 Kinetic parameters for the adsorption of Cu (II) onto bentonite at ambient temperature

Concent. mg/L	Pseudo first-order model			Pseudo second-order model			
	k_1, min^{-1}	q_e, mgg^{-1}	r^2	$k_2, \text{gmg}^{-1}\text{min}^{-1}$	q_e, mgg^{-1}	$h, \text{mgg}^{-1}\cdot\text{min}^{-1}$	r^2
10	0.079	0.8016	0.9269	1.6196	1.334	2.882	1
20	0.056	0.6839	0.8719	0.1864	2.660	1.318	0.9996
35	0.069	3.9829	0.7054	0.0373	4.574	0.780	0.9952
50	2.817	0.9128	0.7022	0.0235	6.544	0.153	0.9712

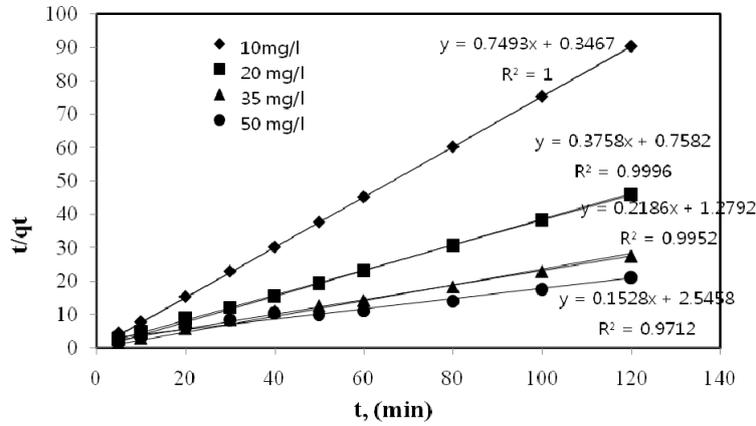


Fig. 10 Kinetics analysis of Cu(II) adsorption by linear plots of pseudo-second-order rate equations

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

Linearized form of Eq. (2) can be described in linearized form as follows

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where, q_e and q_t (mg g^{-1}) are the amounts of Cu (II) adsorbed per unit of mass of the magnetite at equilibrium and time t , respectively, and k_2 is the rate constant of pseudo-second-order adsorption ($\text{g.mg}^{-1}.\text{min}^{-1}$).

The kinetics plots between (t/q_t) versus (t) were plotted for the different initial concentrations (Fig. 10). Slope and intercept values were solved to give the value of pseudo-second-order rate constant (Table 2). Fig. 10 and Table 1 show that the highly significant regression line ($r^2 = 1$) and the data were well fitted only to the pseudo-second-order rate equation (Fig. 10). The straight line was obtained indicating that the process follows pseudo-second-order kinetics for various concentrations of Cu (II). While the initial Cu (II) concentration increases from 10 to 50 mg L^{-1} , the adsorption capacity (q_e), increased from 1.334 to 6.544 mg g^{-1} at ambient temperature. This indicates that the initial Cu (II) concentration plays a key role in determining the adsorption capacity of Cu(II) on the magnetite. It is also observed in Table 1 that when initial Cu (II) concentration increases from 10 to 50 mg L^{-1} , the rate constant, k_2 decreases from 1.6196 to 0.0235 $\text{g mg}^{-1}.\text{min}^{-1}$. Although the adsorption capacity (q_e) increases with increasing the initial Cu (II) concentration, k_2 reduces. The reason is that the adsorption process is slower to reach increased adsorption capacity (q_e) with increasing the initial Cu (II) concentration as seen in Fig. 8. In other words, at the low initial Cu (II) concentrations, while it reaches adsorption capacity in a short time, on the contrary, it takes a long time to reach the adsorption capacity at the higher initial Cu (II) concentrations.

Initial adsorption rates (h , $\text{mg g}^{-1} \text{min}^{-1}$) were also calculated from the data of the pseudo-second-order kinetic model according to the Eq. (4)

$$h = k_2 q_e^2 \quad (4)$$

In addition, the value of initial sorption rate decreased from 2.882 to 0.153 mg g⁻¹.min⁻¹ as can be seen in Table 1.

It is clear that Cu (II) adsorption onto magnetite followed the pseudo-second-order kinetic model. Therefore, it may be concluded that Cu (II) adsorption onto produced magnetite consists of chemical adsorption due to the fact that pseudo-second-order kinetic model suggests that adsorption process involves chemisorption mechanism. Similarly, several researchers have used the pseudo-second-order kinetic model in order to express Cu (II) adsorption onto magnetite or magnetite loaded materials (Wang *et al.* 2011, Podzus *et al.* 2012).

3.5 Adsorption isotherm

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. Isotherm data should accurately fit into different isotherm models to find a suitable model that can be used for the design process. The adsorption of Cu (II) isotherm data at various initial concentrations is presented in Fig. 11. Adsorption isotherms models such as Langmuir and Freundlich were tested to fit the experimental data and are compared in Table 2. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions.

The generalized Langmuir isotherm can be written in the form (Chiron *et al.* 2003)

$$q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \quad (5)$$

The Langmuir equation applied to the linearized equation for adsorption equilibrium of magnetite is described as

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (6)$$

where K_L is the adsorption equilibrium constant related to the affinity of binding sites, q_{\max} the maximum adsorption capacity and q_e the amount of sorbed metal at equilibrium. Based on Eq. (6), the isotherms were fitted to the adsorption data obtained. The Langmuir adsorption exponents for Eq. (6), the q_{\max} , and K_L are determined from the linear plots of C_e/q_e vs. C_e , and the calculated correlation coefficients for these isotherms are shown in Table 2. The values of the Langmuir

Table 2 Langmuir and Freundlich constants for the sorptions of Cu(II) calculated from experimental data

	q_{\max} (mg/g)	K_L (L mg ⁻¹)	r^2
Langmuir isotherm	4.0209	0.3818	0.9711
	K_F (L/g)	n	r^2
Freundlich isotherm	1.550	3.9556	0.9701

constant were calculated from the slopes and intercepts of the plots. The magnitude of Langmuir constant K_L is $0.1599 \text{ (L mg}^{-1}\text{)}$ and the maximum monolayer adsorption capacity (q_{\max}) of the magnetite was determined as 4.0209 mg g^{-1} for ambient temperature.

On the other hand, Freundlich equation is expressed by the following equation

$$q_e = K_F C_e^{1/n} \quad (7)$$

The Freundlich model indicates the heterogeneity of the adsorbent surface and considers multilayer adsorption. This isotherm model shows the relationship between the amount of Cu(II) adsorbed by the magnetite (adsorbent) (q_e , mg g^{-1}) and the equilibrium concentration of Cu(II) (C_e , mg L^{-1}) in solution. The linear form of Freundlich adsorption model is as follows (Huang *et al.* 2007)

$$\log q_e = \log K_F + (1/n) \log C_e \quad (8)$$

Where K_F and $1/n$ are Freundlich constants, related to adsorption capacity and adsorption intensity (heterogeneity factor), respectively. The values of K_F and $1/n$ were obtained from the slope and intercept of the linear Freundlich plot of $\log q_e$ vs $\log C_e$ (Eq. (8)).

Applying the linearized form of Eq. (7) to the experimental data, the Freundlich model constants and r^2 values were obtained and are presented in Table 2. The Freundlich adsorption capacity (K_F) was found to be 1.550, and “ n ” which indicate adsorption intensity was calculated as 3.9556,

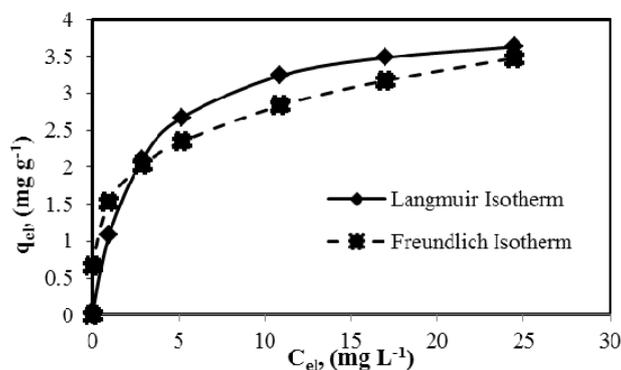


Fig. 11 Adsorption Isotherms at ambient temperature for Cu(II) on magnetite

Table 3 Maximum adsorption capacity of Cu (II) for various adsorbent

Adsorbents	pH	q_m (mg g^{-1})	References
Waste iron okside (α -FeOOH)	6.0	10.58	Huang <i>et al.</i> 2007
Hematite	5.0	7.205	Wang <i>et al.</i> 2008
Amorphous Fe_2O_3	5.0	3.15	Wang <i>et al.</i> 2007
Nano Fe_3O_4	5.0	8.90	Wang <i>et al.</i> 2011
Beidellite	5.0	25.3	Oncel 2008
Micro Fe_3O_4	4.5	4.021	This study

respectively (Table 2). In addition, the Freundlich and Langmuir adsorption isotherms are shown in Fig. 11.

As shown in Table 2 and Fig. 11, the high correlation coefficient (r^2) indicated that the data satisfactorily fitted the Langmuir and Freundlich isotherms.

A comparative evaluation of the uptake capacities (q_m) of various types of adsorbents for adsorption of Cu (II) reported in the literature are given in Table 4. The result indicates the maximum adsorption capacity at ambient temperature obtained in this study compares well with those reported which ranges from 3.15 to 25.3 mg of Cu (II) g^{-1} .

4. Conclusions

Fe_3O_4 was synthesised in micro dimension by co-precipitation method and by selecting the initial mole ratio of Fe(III):Fe(II) = 2:1. No surfactant was used in order to regulate the particle size.

In literature, Fe_3O_4 -magnetite can be easily oxidised so that by using nano sized magnetite which was prepared by modifying the surface by using any material, there are studies related with removal of Cu(II). This study is first. It is clearly observed from XRD analysis that Fe_2O_3 -hematite phase formed due to oxidation is not detected on synthesised Fe_3O_4 surface. The surface of the adsorbent was characterized by XRD and was identified as magnetite (Fe_3O_4). For this reason the fact that structure of Fe_3O_4 synthesized at micro dimension being used in Cu(II) treatment without being subject to oxidation is original.

Additionally, the ability of magnetite adsorbent to bind Cu (II) was investigated with reference to equilibrium kinetics. The magnetite micro particles were applied effectively in the removal of Cu (II) from aqueous solutions due to higher surface area and reactive hydroxyl surface sites. The removal efficiency of Cu (II) strongly depended on pH.

The uptake capacities (q_m) of the magnetite micro particles for adsorption of Cu (II) were obtained as 4.021 ($mg\ g^{-1}$) in this study. Application of a pseudo-second-order model provides much better correlation coefficients. The equilibrium adsorption isotherm is of importance in the design of adsorption systems. The equilibrium data conformed to the Langmuir and Freundlich isotherms very well. The uptake of Cu (II) was by surface complexation adsorption.

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