

Original paper

Synthesis of Fe₃O₄@silica core-shell particles and their application for removal of copper ions from water

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ABSTRACT

The main objective of this study was to synthesize an environmentally friendly nano-structural adsorbent. These nano magnetic particles can be applied to remove heavy metal ions from industrial wastewater because the surface of the particles is covered with SiO₂, and the SiO₂ is inactive and can adsorb heavy metal ions. Tests were then conducted to study the adsorption of Cu(II) ions onto Fe₃O₄@SiO₂ from an aqueous solution for the effect of contact time, adsorbent dose, solution pH and concentration of metal ions in batch systems. The equilibrium data were analyzed using the Langmuir and Freundlich isotherm by nonlinear regression analysis and found that the adsorption isotherm data will better fit by Langmuir model. The maximum adsorption capacities of Cu (II) were 47 mg/g. Fe₃O₄@SiO₂ was regenerated and found to be suitable for reuse in successive adsorption-desorption cycles 5 times without significant loss of adsorption capacity.

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1. Introduction

Nowadays, the excessive and uncontrolled discharge of heavy metal ions becomes a major problem. By means of bioconcentration, bioaccumulation and biomagnification through biologic chain and drinking water, human health will be threatened seriously by heavy metal ions. Copper is widely used in many industries, such as electroplating, paint, metal finishing, electrical, fertilizer, wood manufacturing and pigment industries. Rapid development of these industries has led to accumulation of Cu(II) ions in the environment. Unlike some organic pollutants, copper and some other toxic heavy metals are non-biodegradable and can exist for a long time in natural environment. If the level of Cu(II) ion is beyond the tolerance limit, it will cause serious environmental and public health problems. It is necessary to remove Cu (II) ion from industrial effluents prior to their discharge. Over the past decades, various methods such as precipitation, ion-exchange, and sorption have been employed to remove Cu(II) from large volumes of aqueous solution. Sorption technology is widely regarded as one of the most effective choices for the removal of heavy metal ions from aqueous solution because it is simple and cost-effective. However, most of the common sorbents, such as clay minerals, metallic, oxides and carbon materials usually suffer from either low sorption capacities or sorption efficiencies in the removal of heavy metal ions from aqueous solution. Therefore, the design and development of special sorbents with high sorption capacities for contaminants is critical for pollution management and related applications (Song et al. 2013). Recently, many research groups have explored several nanoparticles for removal heavy metals, because of the ease of modifying their surface functionality and their high surface area to-volume ratio for increased adsorption capacity and efficiency. In the last decade, magnetic nanoparticle (MNP) adsorption has attracted much interest and is an effective and widely used process because of its simplicity and easy operation (Shin et al. 2011). There have been intense interests recently in the fabrication of core-shell particles. Silica has been considered as one of the most ideal materials for protecting Fe₃O₄ MNPs due to its

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reliable chemical stability, biocompatibility and versatility in surface modification. It is anticipated that incorporating silica coating on a magnetic core could attain the advantage of silica and without sacrificing the unique magnetization characteristics of Fe₃O₄. A thin and dense silica layer with a desired thickness was deposited on the surface of magnetic particles in order to protect the iron oxide core from leaching into the mother system under acidic conditions. Compared with nonmagnetic nanoparticles, the silica-magnetite nanoparticles can meet the need of rapid extraction of large volume samples by employing a strong external magnetic field (Liu et al. 2009).

In this study, our aim is to prepare these Fe₃O₄@silica core-shell and check their adsorption capability in removing Cu(II) from aqueous solution. The effects of Cu(II) ions concentration, contact time, and solution pH were studied in order to analyze the adsorption kinetics and determine the equilibrium time. Langmuir and Freundlich isotherms were applied to the experimental equilibrium data in order to explain the adsorption mechanism.

2. Materials and methods

2.1. Synthesis of Fe₃O₄@SiO₂

Magnetic Fe₃O₄@SiO₂ particles were synthesized according to the method reported by Hu et al. The whole synthesis procedure as described following: sodium silicate (1.3 g) was dissolved in deionized water (100 ml) to form a clear solution. Then the prepared Fe₃O₄ nanoparticles (0.3 g) were put into the solution. The pH value of the mixture was adjusted to 6.0 by addition of 1 M HCl and then the mixture was stirred by a nonmagnetic stirrer for 3 h. During the whole process, temperature was maintained at 80 °C. Finally, the formed Fe₃O₄@SiO₂ nanoparticles were thoroughly gathered by an external magnet and washed with deionized water. The final Fe₃O₄@SiO₂ nanoparticles were dried under vacuum at 60 °C for 8h (Hu et al. 2010).

2.2. Characterizations

The size and morphology of the products were characterized by a scanning electron microscope (SEM). Fourier transform infrared spectra (FTIR, 4,000–500 cm^{-1}) were obtained on a Shimadzu FT-IR 8400S. The samples were dried, mixed with KBr and pressed into a thin disc for the FTIR measurements. The concentration of Cu(II) was determined by flame atomic absorption spectrometry using a PHILIPS model PU9400.

2.3. Adsorption equilibrium experiments

The adsorption of Cu(II) ion by the magnetite nanoparticles was investigated in aqueous solution for 1h at room temperature. In general, placing 25 mg $\text{Fe}_3\text{O}_4@\text{SiO}_2$ in 50.0 mL of aqueous solution containing Cu(II) ions (50.0 mg/l), the mixture was adjusted to certain pH (pH=5) with NaOH and stirred at 200 rpm for 1h. When the adsorption process reached equilibrium, the adsorbent was separated using a magnet and the supernatant was collected and the residual concentrations of metal ions in the aliquot were determined by atomic absorption spectroscopy (AAS). The equilibrium adsorbed concentration, q_e was calculated according to the equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where, q_e is the equilibrium adsorption capacity of adsorbent (mg/g), C_0 and C_e are the initial and equilibrium concentrations of the adsorbents (mg/l), respectively, M is the mass of adsorbent (g), and V is the volume of the metal ions solution (l).

The removal efficiency of the metal ions was calculated by the following equation:

$$R = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where, R is the removal efficiency of the metal ions, C_0 the initial concentration and C_t the concentration of the metal ions in mg/l at time.

2.4. Effect of the adsorbent dose

In the batch sorption studies, the effects of the dose of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (10, 15, 20, 25 and 30 mg), adsorbents on adsorption of Cu(II) ion at 50 mg/L were studied. The pH of the working solution was adjusted to 5 by adding 1M HCl. A fresh dilution was carried out for each experiment.

2.5. Effect of the solution pH

A sample of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (25mg) was added to 50.0 mL of 50 mg/L Cu(II) ion solution at different pH value varied from 3 to 6 using 1 M HCl. These samples were stirred for 1h, and then adsorbents were removed by a magnet. The supernatant was also tested by AAS.

2.6. Effect of the temperature

The effects of temperature (15, 25, 35, 45°C) on metal ions adsorption were conducted with 25 mg of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ adsorbent dose in 50.0 ml of 50 mg/l Cu(II) ion solution at pH 5.

2.7. Adsorption Isotherm models

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. Adsorption isotherm is important to describe how solutes interact with the sorbent. Developing an appropriate isotherm model for adsorption is essential to the design and optimization of adsorption processes. Several isotherm models have been developed for evaluating the equilibrium adsorption of compounds from solutions, such as Langmuir, Freundlich, Redlich–Peterson, Dubinin–Radushkevich, Sips, and Temkin (Dąbrowski, 2001). In these study the isotherm data were correlated with the Freundlich and Langmuir models. A study to determine the relationship between the Cu(II) ion adsorbed on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and those remaining in the

aqueous phase was conducted. All experiments were carried out with the various initial Cu(II) concentrations (10, 20, 30, 40 and 50 mg/l) in conditions of: fixed amount of adsorbent 25 mg per 50 ml solution, constant pH 5, room temperature (25 °C) and 200 rpm agitation speed. Contact time was 70 min for all equilibrium conditions. The Langmuir isotherm is based on a monolayer sorption of metal ion on the surface of the adsorbent and is described by the following equation (Sağ and Aktay, 2001):

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

where, q_e is the adsorption capacity of the adsorbent in mg/g and C_e the concentration of metal ion in mg/l at equilibrium. The q_m is the maximum adsorption capacity of the metal monolayer in mg/g, and b the constant that refers to the bonding energy of adsorption in l/mg. The Freundlich isotherm model is considered to be appropriate for describing both multilayer sorption and sorption on heterogeneous surfaces. The Freundlich model can be expressed by the following equation (Hadavifar et al. 2014):

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

where, q_e is the equilibrium adsorption capacity of the adsorbent in mg/g, C_e the liquid phase concentration in mg/l at equilibrium, K_f the constant related to the adsorption capacity of the adsorbent in (mg/g) (l/mg) $1/n$ and n the empirical constant depicting the intensity of adsorption which varies with the heterogeneity of the adsorbent. The greater is the value of n the better its adsorption capacity. The nonlinear regression analysis was carried out with Sigma Plot software (Sigma Plot 12.0. USA) in order to predict both the K_f and the n parameters.

2.8. Adsorption kinetics

The kinetic studies were carried out using 25 mg of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ in 50 ml of different concentrations (10, 20, 30, 40 and 50 mg/l) of Cu(II) metal ion solutions at pH 5. In order to describe the kinetic process between aqueous and solid phase, the pseudo first-order rate was used for surface adsorption of Cu(II) ion on $\text{Fe}_3\text{O}_4@\text{SiO}_2$. This model is presented by Lagergren as follows (Heidari et al. 2009):

$$\text{Log}(q_e - q_t) = \text{Log}q_e - \frac{k_1}{2.303} t \quad (5)$$

The pseudo-second-order rate equation presented by Ho to describe the kinetic adsorption of divalent metal ion onto an adsorbent is expressed as follows (Qiu et al. 2009):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where, q_e and q_t are the amount of adsorbed metal ion in mg/g on the adsorbent, at equilibrium and time t , respectively, while k_1 in min^{-1} and k_2 in $\text{g/mg} \cdot \text{min}$ are the rate constants of first and second-order adsorption, respectively.

2.9. Adsorption thermodynamics

The adsorption experiment was carried out at different temperatures (15, 25, 35 and 45 °C) to evaluate thermodynamic criteria by calculating the Gibbs free energy (ΔG) by the following equation (Hao et al. 2010):

$$\ln k_d = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (7)$$

where, the values of ΔH^0 (change in enthalpy in J/mol) and ΔS^0 (change in entropy in J/mol/K) are obtained from the slope and intercept of $\ln k_d$ vs. $1/T$ plots. T is the temperature in K and R is the universal gas constant (8.314 J/ mol/ K). The distribution coefficient (k_d) is calculated from the initial and the equilibrium concentrations (C_0 and C_e) of the metal ions, where V is the working volume in ml and W is the adsorbent mass in g (Hadavifar et al. 2014):

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{W} \quad (8)$$

The ΔG° is the change in Gibbs free energy in J/mol, calculated according to the following equation (Hao et al. 2010):

$$\Delta G^\circ = -RT \ln K \quad (9)$$

2.10. Batch desorption study

Reusability of $Fe_3O_4@SiO_2$ was determined in five adsorption-desorption cycles. To optimize the concentration of the acid, the experiments were carried out with different concentrations (0.1, 0.2 and 0.3 M) of H_2SO_4 . The mixture was shaken for 1 h to reach desorption equilibrium. Then concentration of acid with more efficiency in desorption of loaded Cu(II) ion on the $Fe_3O_4@SiO_2$ was selected. After each cycle the regenerated adsorbent was washed thrice by deionized water to remove the remainder ion, from the adsorbent and $Fe_3O_4@SiO_2$ nanoparticles were separated magnetically and the supernatant was subjected to Cu(II)

measurements. The metal recovery was calculated by the following equation (Shahbazi et al. 2011):

$$\text{metal recovery} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100$$

3. Results and discussions

3.1. Characterization of adsorbents

FTIR measurements were performed for Fe_3O_4 nanoparticles and $Fe_3O_4@SiO_2$ samples as shown in Fig. 1. Both spectra present absorption peak at 578 cm^{-1} , corresponding to the Fe-O vibration from the magnetite phase (Yamaura et al. 2004). Spectrum of $Fe_3O_4@SiO_2$ present the typical Si-O-Si bands of the inorganic symmetric vibration modes around 786 cm^{-1} , asymmetric stretching vibration around $1033-1100 \text{ cm}^{-1}$ and the band at 964 cm^{-1} is assigned to the Si-O stretch that indicates the silica layer around the Fe_3O_4 (Innocenzi. 2003; Pillay et al. 2013). The morphology of the Fe_3O_4 was analyzed by a scanning electron microscope. A typical image is presented in Fig. 2, which shows many ropelike domains with relatively uniform size of approximately 50 nm.

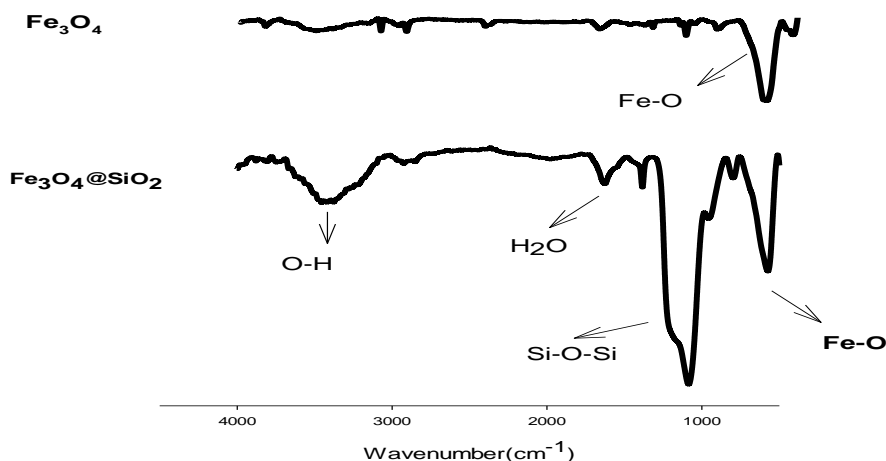


Fig. 1. IR spectrum of $Fe_3O_4@SiO_2$ nanoparticles.

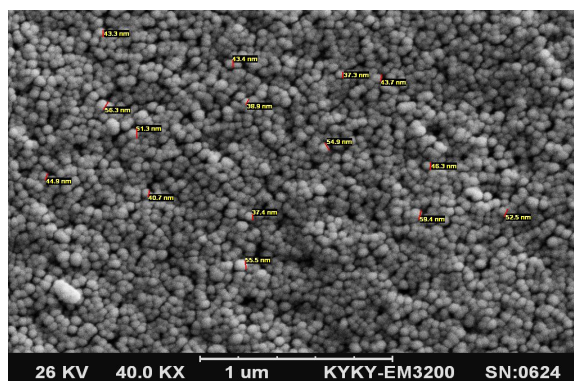


Fig. 2. Scanning electron microscopy of Fe_3O_4 .

3.2. Effect of the adsorbent dose

The effect of the dose of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, adsorbent on removal of Cu(II) metal ion at 50 mg/L has been studied. These results are depicted in Fig. 3. It is clear that the removal efficiency of Cu(II) metal ions increases as the amount of the adsorbent increases owing to the enhanced total surface area of the adsorbent. The results revealed that the metal removal percentage is dependent on the optimal increase of the adsorbent dose, due to a consequent increase in interference between binding sites at the higher dose or an insufficiency of metal ions in solution with respect to available binding sites. The maximum metal ions removal was attained above 25 mg dose of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ for Cu(II).

3.3. Effect of solution pH

The pH of the solution plays an important role on the adsorption of ion metals. In order to determine the effect of pH on the Cu(II) ion removal by $\text{Fe}_3\text{O}_4@\text{SiO}_2$, some experiments were carried out with different pH values while the other parameters were kept constant. Fig. 4 shows the effect of the pH on the removal efficiency of Cu(II) as the function of the solution pH in the range of 3–7, obtained with the initial metal concentration of 50 mg/L and 25 mg $\text{Fe}_3\text{O}_4@\text{SiO}_2$. The metal uptake increases while increasing the pH from 3 till it reaches a maximum of 7. In acidic solution, H^+ can cause the protonation of silanol groups, which means that part of the site occupied by metal ions are replaced by H^+ . Besides, in acidic solution, low pH will restrain the hydrolysis of the metal ion so weaken the adsorption ability of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles.

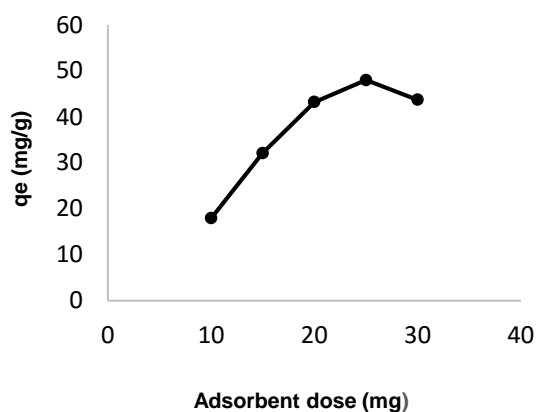


Fig. 3. The effect of adsorbent dose on the Cu(II) removal $\text{Fe}_3\text{O}_4@\text{SiO}_2$: initial Cu(II) concentration 50 mg/l, initial pH value 5, agitation time 60 min at 200 rpm and 25 °C.

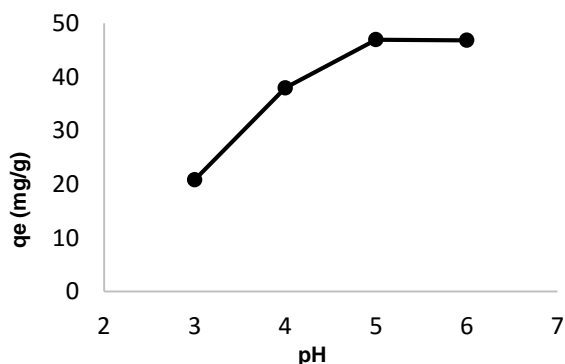


Fig. 4. Effect of pH on Cu(II) removal. Conditions: adsorbent dose 25 mg, initial concentration 50 mg/l, agitation time 60 min at 200 rpm and at 25 °C.

3.4. Adsorption isotherms

To better elucidate the adsorption mechanism of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ the equilibrium experimental adsorption data were fitted by two adsorption models named Langmuir and Freundlich. Fig. 5 display the adsorption isotherms of Cu(II) on the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ under varied initial metal ion concentration. As shown in this figure, the equilibrium adsorption amount depended on the heavy metal ion concentration at equilibrium, and gradually increased with the equilibrium concentration increased. The summary of all the parameters obtained from the curve-fitting results are listed in Table 1. Based on the value of correlation coefficients (R^2), it can be seen that the Langmuir isotherm is more suitable for the experimental data of different heavy metal ions adsorption, suggesting the homogenous distribution of active sites on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$. The maximum adsorption capacity for Cu(II) was 47 mg/g.

Table 1. Isotherm constants for the adsorption of Cu(II) onto $\text{Fe}_3\text{O}_4@\text{SiO}_2$

Langmuir			Freundlich		
q_m	b (L/mg)	R^2	n	k_f (L/g)	R^2
53.17	0.3756	0.9995	4.7	24.75	0.9956

3.5. Adsorption kinetics

Typical kinetic experimental curves for adsorption of Cu(II) on the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ in different ion concentrations showed that ion adsorption increases sharply during a short contact time and slows down gradually to reach equilibrium. In order to describe the kinetics for Cu(II) ion adsorption onto the $\text{Fe}_3\text{O}_4@\text{SiO}_2$, the pseudo-first-order and pseudo-second-order kinetics are applied. The parameters of the kinetic models and the regression correlation coefficients (R^2) are listed in Table 2. The R^2 values clearly indicate the validity of the pseudo-second-order versus pseudo-first-order kinetics which is not fitted logically. As seen in Table 2, when the initial ion concentration increases from 10 to 50 mg/l, the pseudo-second-order constants (k_2) decrease from 0.004 to 0.002 g/mg/min. This indicates that the available active sites on the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ are saturated rapidly by Cu(II) ion, furthermore suggesting the possibility of the formation of a monolayer coverage of Cu(II) onto the adsorbent (Ahangaran et al. 2013).

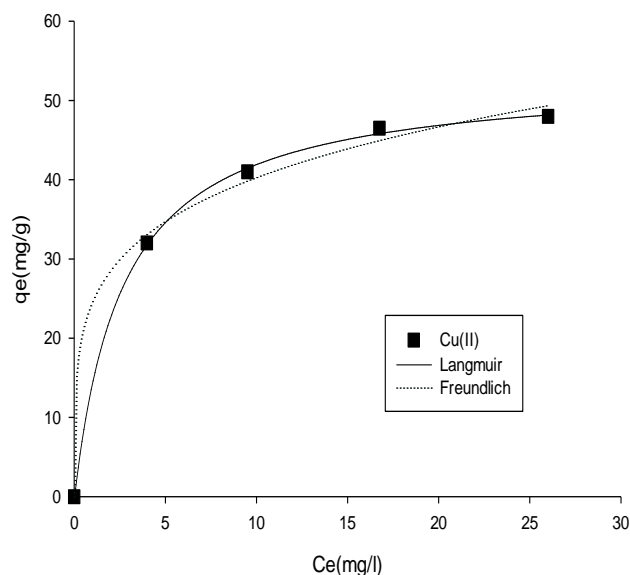


Fig. 5. Langmuir and Freundlich parameters for adsorption of Cu(II) in single solutions onto $\text{Fe}_3\text{O}_4@\text{SiO}_2$.

Table 2. Thermodynamic parameters of Cu(II) adsorption onto Fe₃O₄@SiO₂ at different temperatures.

T(K)	Lnk _d (Lmg ⁻¹)	ΔG (kJ mol ⁻¹)	ΔH ⁰ (kJ mol ⁻¹)	ΔS ⁰ (J(mol k) ⁻¹)
288	0.964	-23.08		
298	1.021	-25.30	3.926	21.65
308	1.073	-27.49		
318	1.118	-29.57		

3.6. Adsorption thermodynamics

The effect of temperature on the adsorption of Cu(II) ions onto Fe₃O₄@SiO₂ is shown by the linear plot of lnk_d versus 1/T in Fig. 6 and the relative parameters and correlation coefficients calculated from Equation 7 are listed in Table 3. The negative values of ΔG confirmed that the adsorption was spontaneous, and the decreasing of ΔG as temperature rises indicated that the adsorption was more favorable at high temperatures. The positive value of ΔH⁰ confirmed

the endothermic nature of adsorption which was also supported by the increase in value of Cu(II) uptake with the rise in temperature.

The positive value of ΔS⁰ suggested the increasing randomness at the solid/liquid interface during the adsorption of Cu(II) ions on Fe₃O₄@SiO₂.

3.7. Desorption

The desorption efficiency of Fe₃O₄@SiO₂ was evaluated by H₂SO₄ acid treatment. The effects of concentrations of sulfuric acid (0.1, 0.2 & 0.3 mol/l) on the stability of the adsorbents and the adsorption of Cu (II) ions were investigated. The 0.1 M H₂SO₄ was more effective than other concentrations of H₂SO₄. The adsorbent was reused in five successive adsorption–desorption cycles as can be seen in Fig. 7. However, the Cu(II) adsorption capacity decreased from 88.25 % in the initial cycle to 81.72 % in the final cycle that revealed a slight loss of adsorption capability (6.6 %).

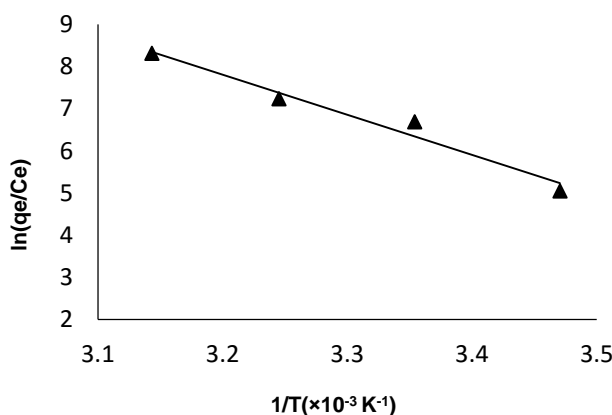


Fig. 6. Plot of ln K vs. 1/T to predict thermodynamic parameters for the adsorption of Cu(II) ion onto Fe₃O₄@SiO₂.

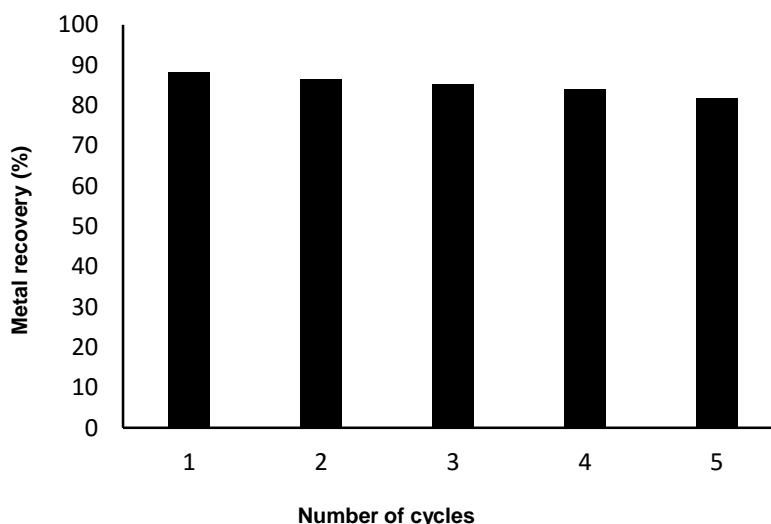


Fig. 7. The number of adsorption–desorption cycle of Cu(II) on Fe₃O₄@SiO₂.

Table 3. The kinetic parameters of different models (for Cu(II) ions adsorption onto Fe₃O₄@SiO₂).

Metal conc.(mg/l)	q _e _{exp}	pseudo-first-order		pseudo-second-order			
		k ₁ (min ⁻¹)	q _{e1} (mg/g)	R ²	k ₂ (g/mg/min)	q _{e2}	R ²
10	19.96118	0.05204	14.2790	0.9862	0.004205	22.7790	0.998
20	32.0305	0.045139	21.7971	0.9908	0.002302	37.03704	0.997
30	41.0003	0.049284	27.2144	0.9912	0.002109	46.72897	0.999
40	46.5064	0.075538	29.0268	0.6773	0.002887	51.28205	0.997
50	47.9934	0.05366	20.3704	0.8518	0.003413	52.08333	0.994

4. Conclusion

Silica core shell magnetic nanoparticles, Fe₃O₄@SiO₂ were successfully prepared for the removal of copper ion from synthetic wastewater. The adsorption experiments revealed that the Fe₃O₄@SiO₂ has a good capability for Cu(II) ion removal from aqueous solution. At desired conditions of the batch system (pH 5 and adsorbent dose of 25 mg/l) the maximum adsorption capacity of Fe₃O₄@SiO₂ for Cu(II) ion removal was achieved at 47.0 mg/g. This maximum capacity is higher than other reports on the magnetic adsorbents as compared in Table 4 (Chang and Chen. 2005; Hu et al. 2006; Rao et al. 2007; Shukla et al. 2009). The adsorption-desorption experiments showed a small loss in the adsorption capacity for Cu(II) after five cycles. Finally, we found out that our new synthesized Fe₃O₄@SiO₂ is a good adsorbent for copper ion removal from wastewater.

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Table 4. Comparison of adsorption capacity of various adsorbents for Cu(II).

Sorbent	Adsorption capacity(mg/g)	Refs.
Maghemite nanoparticle	27.7	Hu et al. 2006
Chitosan-bound Fe ₃ O ₄ magnetic nanoparticles	21.5	Chang and Chen. 2005
Carbon nanotubes	24.49	Rao et al. 2007
Oxidized coir	6.99	Shukla et al. 2009
Fe ₃ O ₄ @SiO ₂	47	this work

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