



Removal of copper by calcium alginate encapsulated magnetic sorbent

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ABSTRACT

In this study, the adsorption performance of copper on calcium alginate encapsulated magnetic sorbent is investigated via equilibrium and kinetics study. Results showed the sorption performance is greatly affected by the initial solution pH, the background ionic strength, the mechanical stirring speed, and the presence of humic acid. The optimum copper sorption was achieved at initial solution pH > 5. The copper uptake is poor in the presence of higher background ionic strength (sodium perchlorate). Langmuir equation can be well used to describe the adsorption isotherm data. The maximum sorption capacity (q_{\max}) and Langmuir constant (b) decrease from 60 to 49 mg g⁻¹ and 1.43 to 0.35 L mg⁻¹ as the ionic strength is increased from 0 to 0.05 M. Kinetics study shows the sorption equilibrium can be obtained within 3 h, and the adsorption kinetics data are well described by the intraparticle pore diffusion model. The mechanical stirring speed greatly enhances the mass transfer rate of copper ions onto the sorbent, and the external mass transfer coefficient (k_f) increases from 2.5×10^{-5} to 2.5×10^{-4} m s⁻¹ when stirring speed is increased from 120 to 220 rpm. The presence of humic acid decreases the k_f from 2.10×10^{-4} to 5×10^{-5} m s⁻¹, and increases the time for copper to attain adsorption equilibrium due to clogging of surface pore which apparently reduce the surface reaction site.

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1. Introduction

Adsorption has been extensively studied as a cost-effective technology for the removal of heavy metals from wastewater during the past decades [1–4]. Sorbent plays a key role in the removal of water contaminants since it determines the performance of treatment technology, including adsorption capacity and post-treatment (separation).

In recent years, the magnetic sorption technology has become one of the emerging technologies in solving environmental problems due to its high efficiency and ease in post-treatment/separation. Some of its applications include iron oxides for desalination [5], magnetic filtration for separation of flocs [6], and iron powder for removal of oil from feathers [7].

The technology has attracted much attention in the area of water treatment [8]. The magnetic sorbents behave similar to or even better than various commercial adsorbents [9]. After the usage, the magnetic sorbent can be easily separated from the solution by simple magnetic force. In the literature, iron oxides have been found to be successfully used as composite materials with host materials in fabricating magnetic sorbent [10–13]. The main advantages of using iron oxides as composite materials with host materials are

the high porosity, magnetic property, and sometimes good settling property [8,9]. Since surface functional group reactions are involved in the sorption processes, higher content of surface functional group sites in a sorbent would greatly lead to higher sorption capacity for removal of contaminants. The host materials to support iron oxides are used to overcome the foregoing problems. The potential host materials are zeolite, alginate, chitosan, clay, and activated carbon [10–13]. Clay–iron oxide magnetic composites and magnetic zeolites were successfully synthesized and used for the removal of metallic contaminants from wastewater and drinking water [10,11]. Some recent studies on cations removal have demonstrated that magnetic chitosan nanoparticles can be good sorbents for gold, Au(III) and cobalt, Co(II) with the maximum adsorption capacities of 59.52 and 27.5 mg g⁻¹, respectively [12,13].

However, few reports are available on the fabrication of composite magnetic sorbent for copper removal. In our recent study, calcium alginate magnetic sorbent was developed to remove metal ions. The resulting magnetic sorbent was able to remove substantial amount of copper [14,15]. In another study in literature, micro-size magnetic polymer adsorbent coupling with metal chelating ligands of iminodiacetic acid was found to be able to load 7.68 mg g⁻¹ of copper ions [16]. These promising findings have laced an alternative solution for the removal of copper from contaminated water using magnetic adsorption technology. Thus, a comprehensive investigation on the sorption behavior of copper on magnetic sorbent is needed.

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This study focused on the investigation of copper ions sorption performances by those fabricated calcium alginate magnetic sorbents. The adsorption behavior of the sorbent was studied from both equilibrium and kinetic viewpoints. The effect of presence of natural organic matter such as humic acid was conducted. Scanning electron microscopy (SEM) was employed to understand the surface microstructure of the sorbent after the copper sorption for both with and without humic substances.

2. Materials and methods

2.1. Materials

The magnetic sorbent used is composed of magnetite (Fe_3O_4) particles coated by calcium alginate. The sorbent was prepared by an approach illustrated in our previous paper [14]. Copper nitrate trihydrate, nitric acid, and sodium hydroxide from Merck (Germany) were used. Sodium perchlorate (used as ionic strength adjuster) and humic acid from Sigma–Aldrich (Singapore) were used. Nitric acid and sodium hydroxide solutions in various concentrations were used for pH adjustments. All chemicals were analytical graded.

2.2. Equilibrium study

Batch equilibrium adsorption experiments were conducted to investigate the characteristics of the copper sorption from aqueous solutions. Copper nitrate solution with various designated concentrations and pH was prepared. The magnetic sorbents were added into the copper solutions at the specific ionic strengths which were adjusted by adding NaClO_4 . During the experiments, the mixtures were shaken on a rotary shaker with the stirring strength of 220 rpm for 48 h. The metal concentrations of final solutions (after 48 h stirring) were analyzed by an inductively coupled plasma optical emission spectrometer (ICP-OES; Perkin-Elmer Optima 3000, U.S.A.). The Experiment were carried out at 293 ± 0.5 K.

In the isotherm experiments, the solution pH for various initial concentrations of copper was adjusted to 5 before the experiments and controlled at the same pH during the whole process. In the pH effect experiments, the initial pH was varied by nitric acid or sodium hydroxide but the initial copper concentration was kept the same.

2.3. Kinetic study

Kinetic experiments with different ionic strength (0, 0.005, and 0.05 M) at initial solution pH of approximately 5 were carried out. The magnetic sorbents (0.5 g L^{-1}) were added into the solutions while being stirred with a speed of 220 rpm at 293 ± 0.5 K. The samples were taken at appropriate time intervals and filtered with $0.45 \mu\text{m}$ filters before analysis for metal ion concentrations. The concentrations of the metal ions were measured by the ICP-ES.

In order to find out the effects of stirring intensity on the adsorption rate, kinetic experiments with different stirring strengths were carried out. Similar kinetic experiments were performed to study the effect of natural organic matters on the sorption of copper. The humic acid was added into the copper solution before adding the magnetic sorbent. Other experimental conditions were similar to those of the kinetic experiments mentioned.

2.4. Scanning electron microscopy

The surface morphology of the magnetic particles was visualized by a scanning electronic microscope (SEM; JEOL, JSM-5600V, Japan). The purpose of SEM study was to characterise the surface microstructure of the sorbents. The SEM was used to identify the

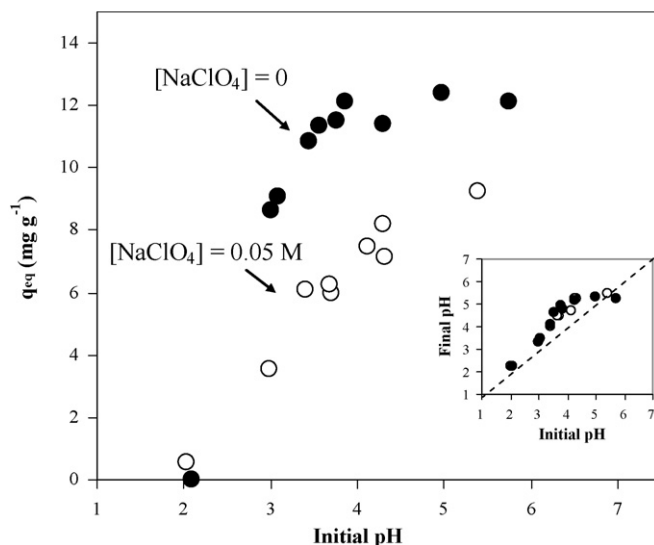


Fig. 1. Effect of solution pH on copper ion sorption. Experimental conditions: $m = 0.5 \text{ g L}^{-1}$, $[\text{Cu}]_0 = 6 \text{ mg L}^{-1}$, $T = 293 \text{ K}$.

surface microstructure of the magnetic sorbent for both before and after copper removal.

3. Results and discussion

3.1. Influence of pH and ionic strength on sorption equilibrium

Batch equilibrium experiments of copper ions at different initial solution pHs are shown in Fig. 1. The copper sorption capacity at equilibrium (q_{eq}) is defined as:

$$q_{\text{eq}} = \frac{V(C_0 - C_{\text{eq}})}{\text{wt}} \quad (1)$$

where V , C_0 , C_{eq} , and wt are volume of solution (L), initial concentration (mg L^{-1}), equilibrium concentration (mg L^{-1}), and weight of adsorbent (g). The results demonstrate that the copper ion sorption is strongly dependent on pH which is quite similar to what was reported on calcium alginate beads, a non-magnetic sorbent [17]. The copper sorption capacity increases when the initial pH is increased. No significant change of q_{eq} was observed when the initial pH was 5 and above. When the initial pH is 5 and above, the q_{eq} is 12.4 and 9.2 mg g^{-1} at sodium perchlorate (as background ionic strength) concentrations of 0 and 0.05 M, respectively. It is therefore concluded that, the optimum copper sorption can be achieved at initial $\text{pH} > 5$. This finding is consistent with the observations reported in the literature [18].

It is observed that the final (equilibrium) solution pH slightly increases from its initial pH as shown in Fig. 1. The adsorbent seems to have a certain buffering capacity. The increase in pH in the absence of ionic strength background is virtually the same as that in the presence of ionic strength background. This indicates that ionic strength does not have a significant impact on the buffering capacity of the magnetic sorbent. This is consistent with our finding that ionic strength does not have significant impact on the acid and base titration curves [15].

Fig. 1 also demonstrates that the adsorption is dependent on the solution ionic strength background. Obvious decrease in the adsorption is observed when the ionic strength background is present. When the initial pH is above 5, q_{eq} is 12.4 and 9.2 mg g^{-1} at sodium perchlorate (as background ionic strength) concentrations of 0 and 0.05 M, respectively. This result is similar to what were reported on biopolymer, natural kaolinite and manganese oxide coated sand [19–21]; however, it is against what were observed on

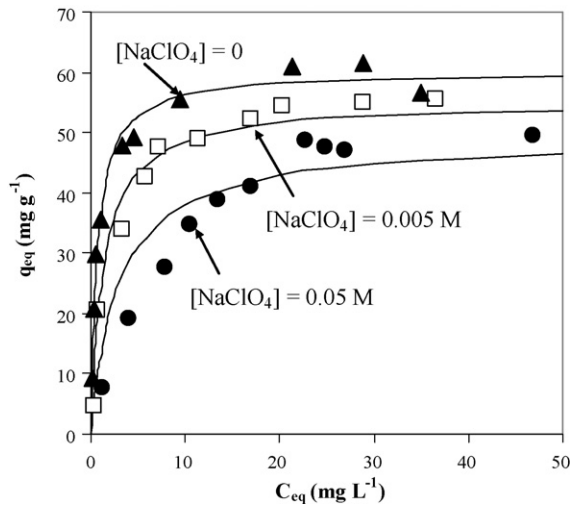


Fig. 2. Adsorption isotherm of copper ion onto calcium alginate magnetic sorbent at different ionic strengths. Experimental conditions: $m = 0.5 \text{ g L}^{-1}$, $\text{pH} = 5$, $T = 293 \text{ K}$. Points represent experimental data, while lines represent Langmuir modeling results.

activated carbons [22]. The cationic substances (sodium ions in this case) could greatly compete with the copper ions for the adsorption sites and thus hinder the copper uptake.

Isotherm experiments at three different ionic strengths background were carried out at the optimum pH of 5 with the result shown in Fig. 2. The equilibrium experiments were investigated over the range of $0\text{--}70 \text{ mg L}^{-1}$ of copper using a dosage of the magnetic sorbent of 0.5 g L^{-1} . The copper removal is greatly dependent upon the solution ionic strength. The experimental data can be described by an adsorption model which considers ion exchange and surface complex formation. However, for sake of easy comparison, the Langmuir equation expressed as follows is used in this study.

$$q_{\text{eq}} = \frac{b q_{\text{max}} C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (2)$$

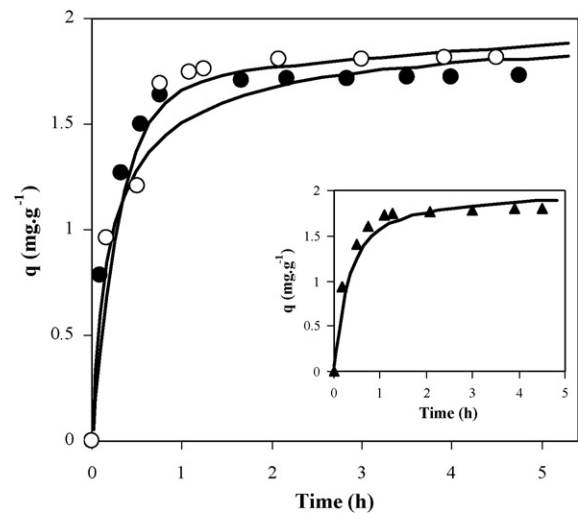
where q_{max} is the maximum sorption capacity (mg g^{-1}), and b is the Langmuir constant (L mg^{-1}), which reflects the affinity between metal ions and sorbent.

As shown in Table 1, the q_{max} and b values decreased from 60 to 49 mg g^{-1} and 1.43 to 0.35 L mg^{-1} as the ionic strength increased from 0 to 0.05 M. The q_{max} values are found higher than the results reported in the studies of Chang and Chen [23] and Banerjee and Chen [24], which were 21.5 and 38.5 mg g^{-1} , respectively. The observation of negative influence on the adsorption by the ionic strength is due to the competition in between Cu^{2+} ions and Na^{+} ions during the adsorption. This is consistent with the observations on other biosorbents such as an alginate gel [25] and protonated *Sargassum* [26].

Table 1
Equilibrium constants for Langmuir model for copper ions sorption by calcium alginate magnetic sorbent.

$[\text{NaClO}_4]$ (M)	q_{max} (mg g^{-1})	b (L mg^{-1})	r^2
0	60 ^a	1.43 ^a	0.9964
0.005	55	0.75	0.9928
0.05	49	0.35	0.9906

^a Lim and Chen [14].



- $[\text{NaClO}_4] = 0$, $D_p = 3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$
- ▲ $[\text{NaClO}_4] = 5 \text{ mM}$, $D_p = 6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$
- $[\text{NaClO}_4] = 0.05 \text{ M}$, $D_p = 9.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$
- Model predictions

Fig. 3. Adsorption kinetics of single-species copper at different ionic strengths. Experimental conditions: $[\text{Cu}]_0 = 1 \text{ mg L}^{-1}$, $m = 0.5 \text{ g L}^{-1}$, $T = 293 \text{ K}$, $\text{pH} = 5$, $k_f = 2.50 \times 10^{-4} \text{ m s}^{-1}$.

3.2. Kinetic study

Adsorption kinetics of copper ion was studied at pH 5. The dependence of the copper sorption capacity against time and ionic strength is shown in Fig. 3. The copper adsorption occurs rapidly in the first hour followed by a slightly slow sorption process. The copper adsorption equilibrium time is 3 h which is compatible with many other sorbents [19].

Thorough modeling analysis of the experimental kinetic data is needed to further understand the characteristic of the process. Surface diffusion model and pore diffusion model are commonly used in the description of adsorption kinetics. In our previous study, it was found that the sorbent was quite porous with a specific surface area of above $300 \text{ m}^2 \text{ g}^{-1}$ [14]. The intraparticle pore diffusion model based on the Fick's law was thus used in this study. The conservative equation for the pore diffusion model is generally written as:

$$\varepsilon_p \frac{\partial c}{\partial t} = \frac{D_p}{r^2} \frac{\partial(r^2(\partial c/\partial r))}{\partial r} - \frac{\rho_p}{m} \frac{\partial q}{\partial t}, \quad 0 \leq r \leq R, t > 0 \quad (3)$$

From the general equation above, the initial and boundary conditions are:

$$\frac{\partial c}{\partial r} = 0 \quad \text{at } r = 0 \quad (4)$$

$$c = 0 \quad \text{at } t = 0 \quad (5)$$

$$D_p \frac{\partial c}{\partial r} = k_f(C - c) \quad \text{at } r = R \quad (6)$$

where c is the local concentration of copper ions within the pores of magnetic sorbent in the solution (mg L^{-1}), q is the local concentration of copper ions in the adsorbed phase (mg g^{-1}), C is the concentration of copper ions in bulk solution (mg L^{-1}), m is the concentration of the magnetic sorbent (g L^{-1}), D_p is the pore diffusion coefficient within the sorbent ($\text{m}^2 \text{ s}^{-1}$), k_f is the external mass transfer coefficient (m s^{-1}), R is the radius of the sorbent (m), and ρ_p is the sorbent's density (g L^{-1}). Eq. (3) with the initial and boundary conditions can be solved by the method developed by Tien [27].

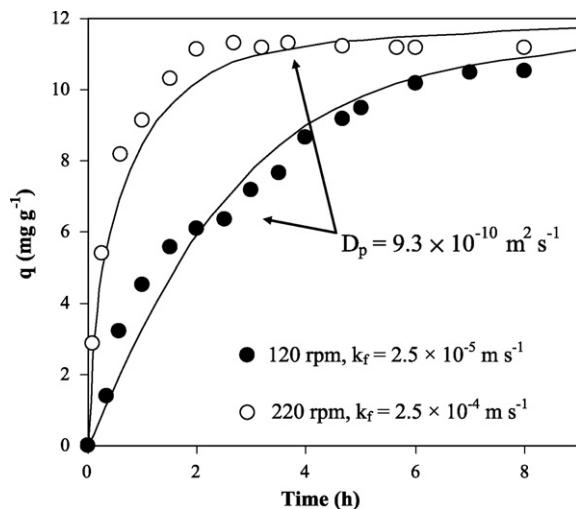


Fig. 4. Effect of stirring strength on copper sorption kinetics. Experimental conditions: $[Cu]_0 = 6 \text{ mg L}^{-1}$, $m = 0.5 \text{ g L}^{-1}$, $T = 293 \text{ K}$, pH 5.

In the pore diffusion model, the D_p and k_f must be known in order to conduct the computation. The k_f can be determined by the forced convection mass transfer analog equation. The sorbent is assumed to be spherical. The mass transfer can be described by the following form:

$$Sh = 2 + 0.60Re^{0.5}Sc^{0.33} \quad (7)$$

Eq. (7) can be computed and solved by the Sherwood number (Sh), Reynolds number (Re), and Schmidt number (Sc) which are defined as below [28]:

$$Sh = \frac{2k_f R}{D} \quad (8)$$

$$Re = \frac{2Rv\rho}{\mu} \quad (9)$$

$$Sc = \frac{\mu}{\rho D} \quad (10)$$

where ρ is the liquid density, D is the ion diffusivity coefficient in bulk solution, v is the superficial liquid velocity, and μ is the viscosity in bulk solution. Thus, the k_f value can be calculated by assuming the typical D value from Nernst–Haskell equation [29]. From the above equations, k_f value of $2.50 \times 10^{-4} \text{ m s}^{-1}$ was determined. The D_p value can then be accurately determined by fitting the modeling results with the corresponding experimental data once the k_f value is obtained.

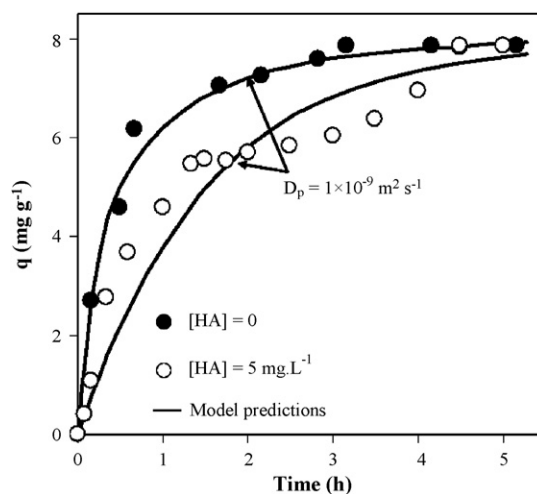


Fig. 5. Effect of humic acid (HA) on copper sorption kinetics. Experimental conditions: $[Cu]_0 = 4.5 \text{ mg L}^{-1}$, $m = 0.5 \text{ g L}^{-1}$, $T = 293 \text{ K}$, pH 5.

The comparison of modeling results with the experimental data is given in Fig. 3. Good fitting for all the three series data is shown; this indicates that the copper sorption process can be controlled by the intraparticle pore diffusion mechanism. Pore diffusivity within the magnetic sorbent slightly increases when the ionic strength is increased. D_p at ionic strength of 0, 5, and 50 mM were found to be 3.0×10^{-10} , 6.0×10^{-10} and $9.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively. The kinetic parameters obtained in this study are within the ranges as reported in literature [30].

A further study was performed in order to confirm the kinetic controlling mechanism. Fig. 4 shows copper sorption kinetic profiles at different stirring strengths. The results demonstrate that the q value increase with an increase in stirring strength. This indicates that mass transfer rate is the controlling mechanism in the copper removal process. Therefore, diffusion model instead of reaction controlled model is appropriate to be used to describe the sorption process.

As shown in Fig. 4, the pore diffusion model provides an excellent representation of the sorption kinetics data. The D_p for both 120 and 220 rpm stirring strengths is found to be $9.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. This clearly demonstrates that the pore diffusivity within the sorbent was not affected much when the stirring strength increases from 120 to 220 rpm. The k_f is higher when the stirring strength is increased to 220 rpm. This shows that the mass transfer rate is significantly influenced by the mechanical stirring.

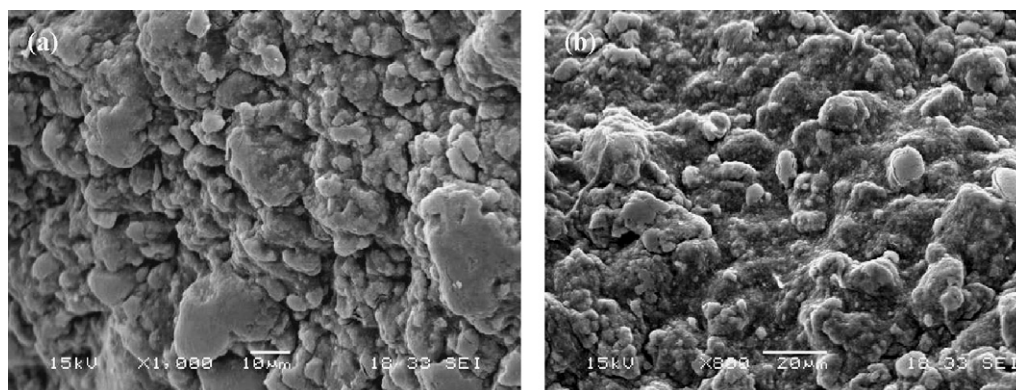


Fig. 6. Scanning electron micrograph of calcium alginate magnetic sorbent after copper sorption: (a) without humic acid and (b) with humic acid.

3.3. Effect of natural organic matter

Fig. 5 presents the effect of humic acid on the adsorption kinetics. The pH was controlled at 5. The presence of humic acid hinders the adsorption kinetics. However, it does not greatly affect the adsorption equilibrium.

The pore diffusion model successfully describes the kinetic profiles in Fig. 5. From the modeling work, the k_f is lower when the humic acid is present, but the D_p is similar for both conditions. Lower k_f value indicates slower mass transfer rate of copper ions onto the magnetic sorbent surface. The lower adsorption kinetics can be explained as follows. The humic acid could cause the blockage in the magnetic sorbent. Secondly, there could be a competition between the humic acid and copper ions during external mass transfer towards the surface of the sorbent.

The results of SEM analysis on the sorbent after copper removal both with and without humic acid support the indication that sorbent's pore are clogged in the existence of humic acid (Fig. 6). This implies that the copper sorption is not favorable in the presence of humic acid as the equilibrium time is significantly extended. A study conducted by Zhang and Bai on humic acid adsorption onto chitosan-coated granules showed that humic acid was attached on the surface site through adsorption reaction [31]. Moreover, the kinetic study also reveals that the adsorption is transport-limited at low solution pH. These observations are also similar to those findings reported by Chen and Wu for copper ions and humic acid adsorption on activated carbon where equilibrium time was also prolonged [32].

4. Conclusions

In this study, the adsorption of copper on calcium alginate encapsulated magnetic sorbent is studied. It was found that the optimum copper sorption can be achieved at initial solution pH > 5. An increase in background ionic strength (sodium perchlorate) diminishes the metal uptake. The adsorption isotherm data can be well fitted by the Langmuir equation, whereas the adsorption kinetics data are described by the intraparticle pore diffusion model. The isotherm study showed that the maximum sorption capacity and Langmuir constant decrease from 60 to 49 mg g⁻¹ and 1.43 to 0.35 Lmg⁻¹ as the ionic strength is increased from 0 to 0.05 M. The kinetics study indicates the copper adsorption equilibrium time can be obtained within 3 h. The mechanical stirring speed greatly enhances the mass transfer rate of copper ions onto the sorbent. When stirring speed was increased from 120 to 220 rpm, the external mass transfer coefficient increases from 2.5 × 10⁻⁵ to 2.5 × 10⁻⁴ m s⁻¹. The presence of humic acid does not significantly affect the adsorption equilibrium, but decreases the external mass transfer coefficient from 2.50 × 10⁻⁴ to 5 × 10⁻⁵ m s⁻¹ and hinders the mass transfer rate of copper ions onto the magnetic sorbent surface.

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