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Biosorption of copper(II) by immobilizing *Saccharomyces cerevisiae* on the surface of chitosan-coated magnetic nanoparticles from aqueous solution

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ABSTRACT

Immobilized *Saccharomyces cerevisiae* on the surface of chitosan-coated magnetic nanoparticles (SICCM) was applied as a new magnetic adsorbent for the adsorption of Cu(II) from aqueous solution. The prepared magnetic adsorbent was characterized by TEM, XRD and FTIR. TEM images indicated that *S. cerevisiae* was immobilized on the surface of chitosan-coated magnetic nanoparticles (CCM) successfully, and conglobation was not observed. The XRD pictures suggested that the Fe_3O_4 nanoparticles were pure Fe_3O_4 with a spinel structure and that the immobilizing process did not result in the phase change of Fe_3O_4. Factors that influence the adsorption of Cu(II) were investigated, which included the initial pH of Cu(II) solution, initial concentration of Cu(II) solution and contact time. The optimum pH for Cu(II) absorption was 4.5. The highest removal efficiency of 96.8% was reached when the initial Cu(II) concentration was 60 mg L^{-1}, and the adsorption capacity was increased with the increase of initial concentration of Cu(II). In particular, SICCM was highly efficient for the fast adsorption of Cu(II) within the first 10 min, and adsorption equilibrium could be achieved in 1 h. Equilibrium studies show that the data of Cu(II) adsorption follow the Langmuir model. The maximum adsorption capacity for Cu(II) was estimated to be 144.9 mg g^{-1} with a Langmuir adsorption equilibrium constant of 0.0719 L mg^{-1} at 301 K.

1. Introduction

Heavy metal contamination of various water resources is of great concern because of the toxic effect to human beings, other animals and plants in the environment. The major sources of heavy metal pollutants are usually from many industries, including mining, metal plating, electric device manufacturing, and so on [1]. Copper, an abundant and naturally occurring element present in municipal wastewater, is one of such heavy metals harmful to human health. The presence of Cu(II) causes serious toxicological concerns, which is usually known to deposit in liver, brain, skin, myocardium and pancreas [2]. In addition, if copper is ingested excessively in human diet, it may result in vomit, cramps, convulsion, and even death [3].

Several technologies have been developed for the removal of Cu(II) from industrial wastewater, such as chemical precipitation, ion exchange, coagulation, electrolysis, reverse osmosis processes and adsorption [4]. These processes are expensive in which some technological problems exist especially when applied to diluted metal solutions. Therefore, the search for clean and competitive technologies is strongly recommended. Biological treatment is usually considered as an effective method and can significantly reduce the quantity of heavy metals in aqueous solutions. Microorganisms have a high surface area-to-volume ratio owing to their small size and therefore, they can provide a large contact interface which could interact with metals from the surrounding environment [5]. The mechanisms of biosorption may involve intracellular uptake and storage via active cationic transport systems, surface binding or some other unidentified mechanisms. The chemical and biological characteristics of these processes of uptake are important for understanding the role of metallic ions in basic cellular functions and also for detoxification of metal-polluted industrial effluents by application of biomass [6]. It has been proved that there is a wide variety of plants and microorganisms (fungi, algae, yeast and bacteria) that are qualified in the uptake of heavy metals from aqueous solution [7,8]. In industrial operation, immobilization is recognized as an effective method used to overcome the incorporating free suspended cells in wastewater treatment. It offers several advantages including minimal clogging in continuous systems [7]. Moreover, cell immobilization can enhance its stability, reusability, mechanical strength and the ease of treatment. The technique has been well used to remove toxic heavy metals from an aqueous solution.

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Several researchers [9–12] have investigated the removal of heavy metals from aqueous streams by immobilizing biomass.

Immobilized biomass, however, has major disadvantages such as cost, cell leakage strengths, instability at low pH, poor mechanical and rate-limitation in diffusion. Several biopolymers such as alginate, agarose, cellulose acetate and gluteraldehyde are widely used as immobilization matrices as they are non-toxic, efficient and inexpensive [13]. A number of studies are available on the use of many different synthetic polymeric agents as a supporting material for the immobilization of microbial biosorbents, but a limited number of studies have been focused on the use of magnetic nanoparticles for the biosorbent immobilization so far. The Fe_3O_4 nanoparticles have been applied in enzyme immobilization by Lee et al. [14]. Yong et al. made use of polymer-grafted magnetic nanoparticles for lipase immobilization [15]. The adsorption of Cu(II) by carboxymethylated chitosan-conjugated Fe_3O_4 nanoparticles was studied by Chang and Chen [16].

More recently, a new adsorbent was developed by immobilizing *Saccharomyces cerevisiae* on the surface of chitosan-coated magnetic nanoparticles (CCM). The excellent adsorption characteristics of CCM for heavy metals can be attributed to (1) high hydrophilicity due to large number of hydroxyl groups of glucose units, (2) presence of a large number of functional groups (acetamido, primary amino, so that it can absorb heavy metal ions in wastewater treatment and/or hydroxyl groups) (3) high chemical reactivity of these groups and (4) flexible structure of the polymer chain [17].

This paper studies the potential of immobilizing *S. cerevisiae* on the surface of chitosan-coated magnetic nanoparticles for adsorption of Cu(II) from aqueous solution. After a batch of experiments, the new magnetic adsorbent exhibited significantly high capability for the adsorption of Cu(II). The biosorption process was studied with regard to the effects of initial pH, initial Cu(II) concentration and contact time. The biosorption equilibrium was also evaluated using the Langmuir model. All the results obtained in this paper would provide a sound basis to the further exploration.

2. Materials and methods

2.1. Reagents

The microorganism *S. cerevisiae* was purchased from Changde Beer Brewery in Hunan province, stored at 277 K in a nutrient medium containing peptone 20.0 g L^{-1}, agar 20.0 g L^{-1}, glucose 20.0 g L^{-1}, yeast extract 10.0 g L^{-1}, agar 20.0 g L^{-1}. The pH of the medium was adjusted to 6.5. $CuSO_4{\cdot}5H_2O$ (Mw = 249.68 g mol^{-1}, purity > 99%) which purchased from Taimao Reagent Factory was used as copper source. Chitosan (90% acetylation degree) was supplied by Sinopharm Chemical Reagent Co., Ltd. Ferric chloride 6-hydrate (purity > 99%) and ferrous chloride-4-hydrate (purity > 99.7%) were purchased from Tianjin Kermel Reagent Co., Ltd. Distilled water obtained from a distilled water system (Shanghai Boxun Co., Ltd, China) was used throughout this study, and was used for the preparation of all the solutions. All chemicals used for the culture medium were of analytical grade and without further purification.

2.2. Preparation of CCM

Firstly, Fe_3O_4 magnetic nanoparticles were prepared by coprecipitating Fe(II) and Fe(III) by ammonia solution and treated under hydrothermal conditions. Ferric and ferrous chlorides (molar ratio 2:1) were dissolved in water at a concentration of 0.3 M irons. Under anaerobic condition (injecting high-purity nitrogen into the mixture), the pH was adjusted to 10 by adding NH_4OH solution with vigorous stirring. The precipitates were heated at 353 K for 30 min, washed three times with ethanol and distilled water, then dried in a loft drier at 343 K, and the powder was prepared after grinding.

For the preparation of CCM, Fe_3O_4 nanoparticles were dispersed in a solution with 20.0 ml of chitosan dissolved in acetic acid with concentration of 5%. The reaction mixture was sonicated in an ultrasonic cleaner for 15 min then atolin and span-80 were added under vigorous stirring at 313 K. After for a while, glutaraldehyde solution was mixed into the reaction solution. During the reaction process, the pH of this mixture was maintained at about 9 using sodium hydroxide solution, and the reaction was further stirred for about 1 h at 333 K. Finally, CCM was recovered from the reaction mixture by placing the bottle on a permanent magnet with a surface magnetization of 5000 G. The magnetic particles settled within 1–2 min, washed with ethyl ether, propanone, ethyl alcohol and distilled water several times, then dried in a loft drier at 328 K.

2.3. Saccharomyces cerevisiae cultivation

The *S. cerevisiae* was enriched in a liquid nutrient medium which contained peptone 30.0 g L^{-1}, glucose 50.0 g L^{-1}, yeast extract 10.0 g L^{-1}, $MgSO_4{\cdot}7H_2O$ 0.5 g L^{-1}, KH_2PO_4 1.0 g L^{-1}, $(NH_4)_2SO_4$ 1.0 g L^{-1}, NaCl 0.5 g L^{-1}, and $ZnSO_4$ 0.01 g L^{-1}. The strain was incubated in flasks stirred at 150 rpm and 301 K. The cultivated cells were harvested after 24 h, then centrifuged at 3500 rpm for 20 min and washed with sterile water and re-centrifuged twice. Afterwards, the active cells were evaporated for 24 h.

2.4. Preparation of SICCM

The CCM was dissolved in the bottle containing phosphate buffer solution (pH = 7) and was kept at room temperature. After 12 h, *S. cerevisiae* which dispersed in sodium chloride solution was added in the bottle, then sharked for 18 h. Finally, SICCM was separated by placing the bottle on a permanent magnet, washed with sodium chloride solution and distilled water several times.

2.5. Characterization of SICCM

The average particle size and morphology of the samples were observed by TEM using a JEOL Model JEM-6700F at 80 kV. The samples for TEM analysis were dissolved in ethanol solution, then sonicated in an ultrasonic cleaner for 20 min. Afterwards, the sample was obtained by placing a drop of magnetic particles dispersed aqueous solution onto a formvar-covered copper grid and evaporated in air at 323 K. XRD measurement was performed using a monochromatized X-ray beam with nickel-filtered Cu Kα radiation (λ = 0.1542 nm). A continuous scan mode was applied to collect 2θ data from 20° to 70°. The SICCM was also characterized by using Fourier-transform infrared spectroscopy (FTIR) (Nicolet, Nexus-670). A background spectrum was measured on pure KBr. The adsorption capacity of SICCM was determined by atomic absorption spectrometer, based on the radiation of copper atoms in 324.8 nm.

2.6. Batch adsorption studies

The adsorption experiments of Cu(II) by SICCM were investigated in aqueous solutions. For each treatment, 0.15 g SICCM was added into 100 mL of copper sulfate solution in 250 ml Erlenmeyer flask. The flasks were agitated in a shaker controlled at 110 rpm and 303 K for an appropriate time. The pH value was adjusted by 1 mol L^{-1} NaOH or 1 mol L^{-1} HCl. In order to mix the Cu(II) solution and SICCM completely and prevent the adsorbents from bonding to the wall of the flask, the prepared $CuSO_4$ solution was injected into the flask by micropipette. The concentrations of Cu(II) were measured using the atomic absorption spectrometer. All media (except

the adsorbents) were autoclaved at 121 °C for 20 min before being used in the experiments.

A batch of experiments to evaluate the effect of pH on Cu(II) adsorption were conducted at the range of pH values from 2 to 7. Experiments to evaluate the effect of initial Cu(II) concentration were conducted in the range of 40–300 mg L^{-1}. The adsorption isotherm experiments were performed with different initial Cu(II) concentration solutions by adding a constant dose of the SICCM of 1.5 g L^{-1}. Further experiments were proceeded to investigate the effect of contact time, during which samples were harvested at 5, 10, 15, 20, 30, 60, 90, 120 and 150 min.

The adsorbed amount of Cu(II) per unit weight of SICCM at time t, $q(t)$ (mg g^{-1}) is calculated from the mass balance equation as

$$q(t) = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 and C_t (mg L^{-1}) are the initial Cu(II) concentration and the Cu(II) concentrations at any time t, respectively; V is the volume of the Cu(II) solution; and m is the weight of the SICCM.

The removal ratio of Cu(II) adsorption from aqueous solution is calculated as follows:

$$\text{Removal efficiency}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

3. Results and discussion

3.1. Particle size and structure of SICCM

It can be seen from Fig. 1(a) and (b) that the pure Fe_3O_4 nanoparticles and CCM are essentially monodisperse and have a mean diameter of 25 nm and 98 nm, respectively. The TEM image of SICCM (Fig. 1(c)) reveals the shapes of SICCM are spherical leading to the bigger size. In comparison with these two TEM images (Fig. 1(a) and (b)), the particle size of the sample had been clearly changed after immobilization (Fig. 1(c)). Moreover, agglomeration is not apparent in the three TEM photos. These findings show that the *S. cerevisiae* was immobilized on the surface of CCM with good distribution. In addition, the surface of the adsorbents has lots of tiny interspaces structure. This could be attributed to reactions occurring on the particle surface, and the heavy metals in the solution can be adsorbed easily by the adsorbents.

3.2. FTIR–ATR spectroscopy

For the CCM (Fig. 2(a)), the wide band around 3365 cm^{-1} is assigned to the stretching of O–H group of macromolecular association [18]. The band at 2925 cm^{-1} is assigned to stretching of $-CH_2-$ bond of methylene groups and the weak band at 2856 cm^{-1} is assigned to –CH– bond of methylene group. It can be estimated to be the characteristic peak of the structure of chitosan. The characteristic absorption 1709 cm^{-1} and 1633 cm^{-1} can be assigned to the absorption peaks of the C=O stretching of carboxyl groups of chitosan. The characteristic absorption bands appeared at 1570 cm^{-1} corresponds to N–H bending vibration. The peak at 1321 cm^{-1} is the typical stretching vibration of the C–N stretching vibration. Besides, the stretch vibration of C–O also can be found at 1065 cm^{-1}, and this may be another reason for the presence of the chitosan polymer of the CCM. The characteristic peak at 586 cm^{-1} relates to Fe–O group, which indicates that chitosan was coated on Fe_3O_4 nanoparticles successfully. Because the surface of iron oxide with negative charges has an affinity toward chitosan, protonated chitosan could be coated on the magnetite nanoparticles by the electrostatic interaction and chemical reaction through glutaraldehyde crosslinking [19].

After immobilizing *S. cerevisiae* on the surface of CCM, the spectrum of SICCM (Fig. 2(b)) shows that the peak 1633 cm^{-1} relating to

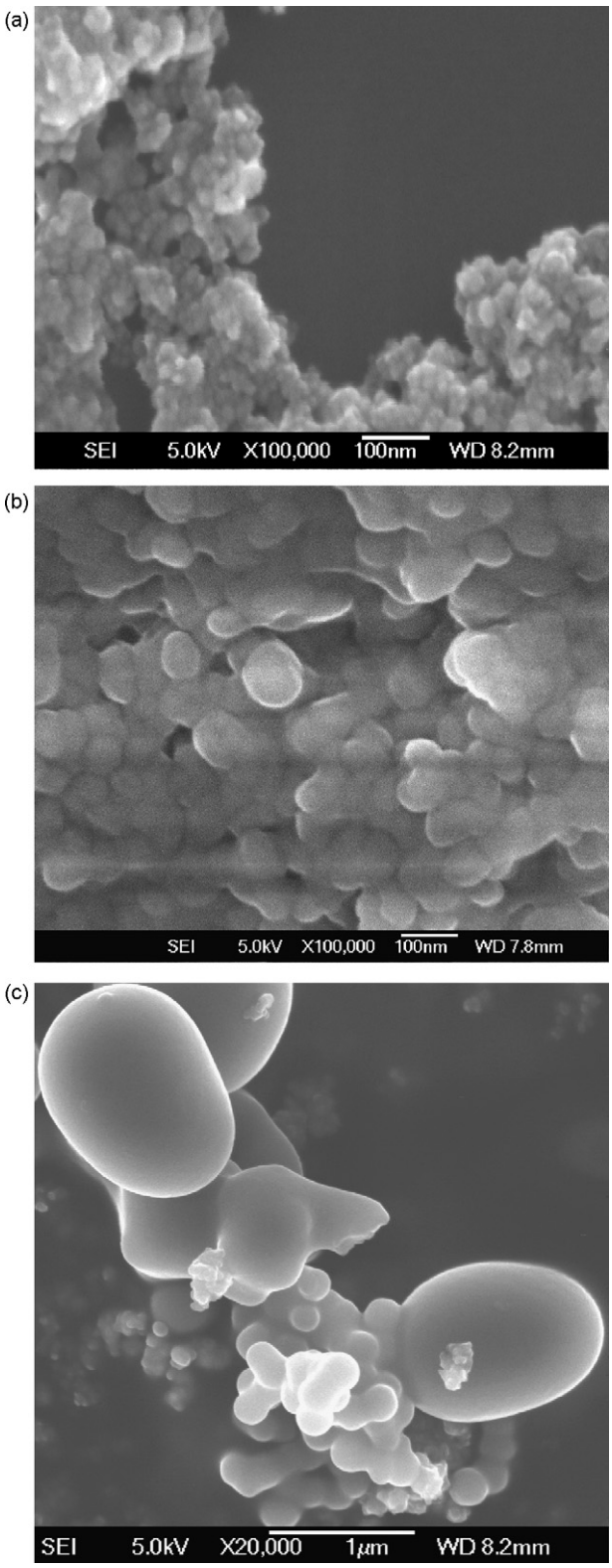

Fig. 1. (a) Transmission electron micrograph of Fe_3O_4 magnetic nanoparticles. (b) Transmission electron micrograph of Chitosan-coated magnetic nanoparticles. (c) Transmission electron micrograph of immobilizing *Saccharomyces cerevisiae* on the surface of chitosan-coated magnetic nanoparticles.

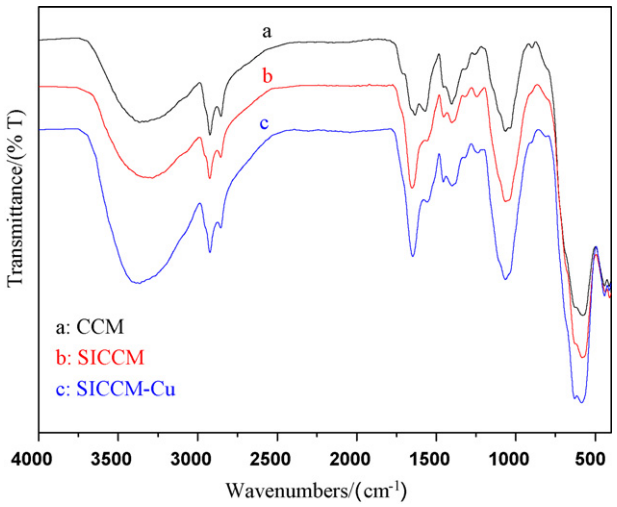

Fig. 2. FTIR spectra for CCM (a), SICCM (b) and SICCM–Cu(II) (c) in the region between 400 and 4000 cm^{-1}.

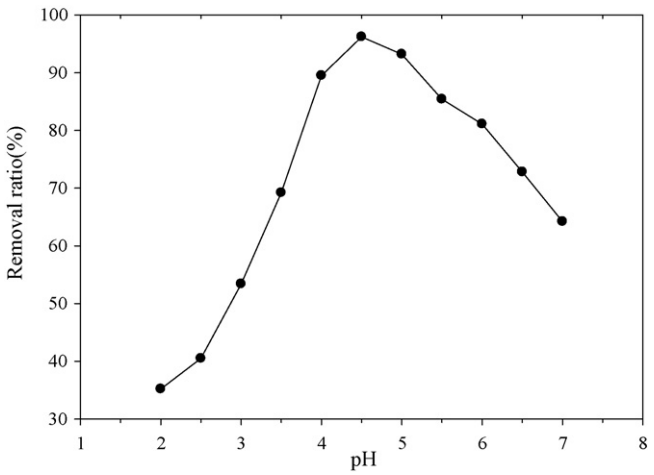

Fig. 4. Effects of pH on adsorption of Cu(II) ions on removal efficiency by SICCM (Initial concentration, 100 mg L^{-1}; absorbent dose, 0.15 g; contact time, 4 h; temperature, 301 K; volume 100 ml).

the stretching vibration of C=O shifts to 1653 cm^{-1}. The characteristic absorption band around 1709 cm^{-1} attributed to the vibration of C=O was not observed. The vibration absorption of N–H bending at 1570 cm^{-1} was weakened. These findings imply that the immobilizing process was accomplished via the reaction of carbonyl group and amine group. The spectrum of SICCM–Cu(II) is shown in (Fig. 2(c)), compared with the spectrum of SICCM (Fig. 2(b)), the peak of O–H stretching vibration increase to 3386 cm^{-1}, indicating that O–H joined in the coordination with Cu(II). The adsorption peak of O–H stretching vibration shifted from 1653 to 1647 cm^{-1} which could help to estimate that these functional groups play an important role in Cu(II) adsorption. The vibration absorption of N–H bending decreased from 1244 to 1238 cm^{-1}, reflecting joining of the N–H in the coordination with Cu(II).

3.3. XRD analysis

From the XRD pictures in Fig. 3(a)–(c), six characteristic peaks of Fe_3O_4 (2θ = 30.1, 35.4, 43.0, 53.5, 57.0 and 62.5) marked by their indices [(2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0)] are observed. These peaks were consistent with the database in MDI Jade 5.0X analyse software and revealed that the resultant nanoparticles were Fe_3O_4 with a spinel structure. Both peaks in the XRD patterns (Fig. 3(b) and (c)) reveal CCM and SICCM are non-crystal structures. The six peaks of the Fe_3O_4 in Fig. 3(c) could be seen for the synthesized adsorbents but the intensity changes a little, which could explain the immobilizing process did not significantly result in the phase change of Fe_3O_4 and CCM. This is in agreement with the results reported in the literature [16,19,20]. By further comparing Fig. 3(a) and (b), the XRD diffraction peaks SICCM (Fig. 3(c)) become lower. It may suggest that *S. cerevisiae* was immobilized on the surface of CCM successfully [21].

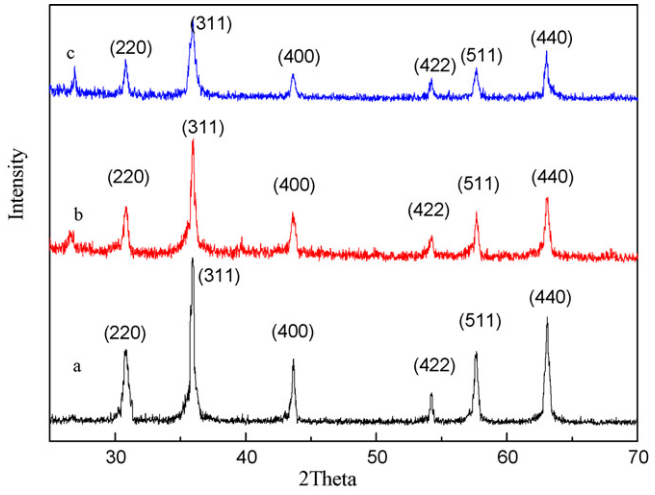

Fig. 3. XRD patterns for Fe_3O_4 magnetic nanoparticles (a), CCM (b) and SICCM (c).

3.4. Adsorption studies

3.4.1. Effects of initial pH on Cu(II) adsorption

According to the experiment results obtained above, it can be noted that pH of the aqueous solution plays a vital role in the adsorption process, because it affects the speciation of copper, the surface charge of the adsorbent, and the degree of ionization of the adsorbent during reaction [22]. This might be because that the pH of solution affects both chemical properties of biosorbates and surface characteristics of biosorbents [23,24]. Fig. 4 illustrates the effect of initial pH on the removal efficiency of Cu(II) on SICCM at the range values of 2–7. When the initial pH was adjusted to 2, a little Cu(II) was removed by the SICCM. On the one hand, the proton of carboxyl, hydroxyl functional group was very difficult to dissociate and the protonation of the amino groups in the protein was increased. On the other hand, a large number of H^+, H_3O^+ in the solution compete with Cu(II) for the adsorption sites. However, the removal efficiency of Cu(II) increases remarkably as the pH increasing from 2 to 4.5, and the maximum capacity of Cu(II) absorption occurs at pH 4.5. That is because the increase of negative charge density on the biomass surfaces offers more metal adsorption sites [25–27]. Within the range of pH values from 4.5 to 7, the removal efficiency of Cu(II) decreases remarkably with increasing pH. Similar trend was also observed with the adsorption of copper from aqueous solution by chitosan crosslinked with a metal complexing agent [28]. It can be explained that high pH plays an important role in dissociating proton of functional groups, resulting in more negatively charged functional groups, and the capacity of combination and probability of reaction between functional groups and Cu(II) can also be enhanced. However, when the pH is higher than a certain value, OH^- itself has a tendency to combine with Cu(II), and it competes with ligand on cytoderm for metal ions, leading to the decrease of the adsorption capacity. This shows the adsorption capacity of Cu(II) is significantly affected with functional groups on

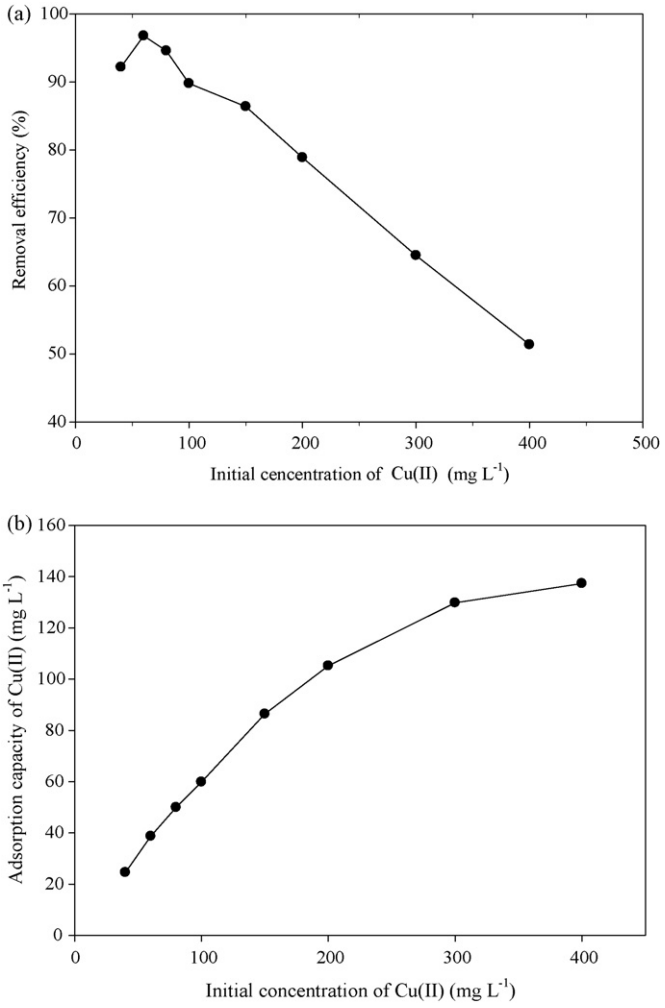

Fig. 5. (a) Effects of initial concentration on adsorption of Cu(II) ions on removal efficiency by SICCM (pH, 4.5; absorbent dose, 0.15 g; contact time, 4 h; temperature, 301 K; volume 100 ml). (b) Effects of initial concentration on adsorption of Cu(II) ions on adsorption capacity by SICCM (pH, 4.5; absorbent dose, 0.15 g; contact time, 4 h; temperature, 301 K; volume 100 ml).

cytoderm. Thus, pH of 4.5 was selected as the optimum pH value of Cu(II) solution for the following adsorption experiment.

3.4.2. *Effects of initial Cu(II) concentration on Cu(II) adsorption*

As mentioned above, SICCM provided good capacity for Cu(II) at pH 4.5 and 301 K. The adsorption isotherm of copper was obtained by varying the initial concentration of Cu(II) at the range values from 40 to 400 mg L^{-1}. It can be observed from Fig. 5(a) that removal efficiency of Cu(II) increases with an increase in initial Cu(II) concentration from 40 to 60 mg L^{-1}, and it reaches a maximum value of removal efficiency 96.8% at the initial Cu(II) concentration of 60 mg L^{-1}. The SICCM exhibited a better performance on Cu(II) removal if the initial Cu(II) concentration was lower than 100 mg L^{-1}. However, the removal efficiency of Cu(II) drops by 45.4% with an increase in initial Cu(II) concentration from 60 to 400 mg L^{-1}. This result may be due to the toxicity effect of Cu(II) on inhibiting the biological activity of SICCM. High concentration of Cu(II) affected cell growth and thus the cells may fail to grow.

Fig. 5(b) shows that the adsorption capacity of Cu(II) grows up with initial Cu(II) concentration increased. When the initial Cu(II) concentration was 400 mg L^{-1}, the adsorption capacity was obtained at 137.3 mg g^{-1}. This may be attributed to immobilization of *S. cerevisiae*, leading to that the absorbents expand the adaptation scope of heavy metals concentrations in solution. Traditionally, biological adsorbents maintain consistent efficiency only when they deal with heavy metals wastewater of low concentrations and achieve low adsorption capacity. Hudson applied polymeric microspheres for heavy metal adsorption, and found that the adsorption capacities were just between 14.4 and 46 mg g^{-1} [29]. Shambhu et al. modified polystyrene by immobilizing polyamines to absorb Cu(II), and obtained the adsorption capacity of 33 mg g^{-1} [30]. Erdal et al. used polyethyleneglycolmethacrylate (PEGMA)-co-vinylimidazole (VI) microspheres as adsorbents and found that its adsorption capacity was only 25 mg g^{-1} Cu(II) [31].

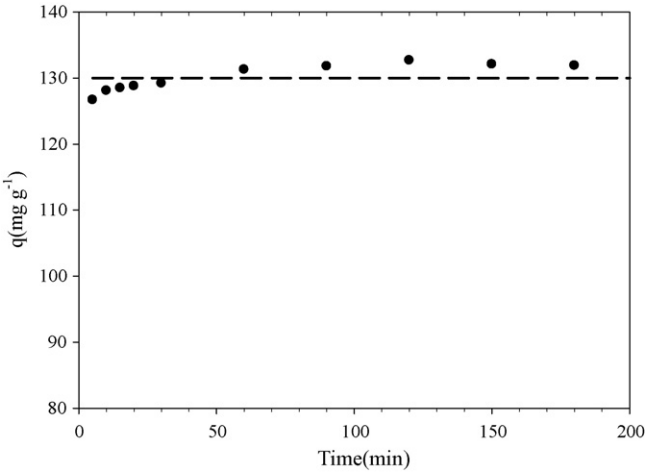

Fig. 6. Effects of contact time on adsorption of Cu(II) ions on adsorption capacity by SICCM (pH, 4.5; initial concentration, 300 mg L^{-1}; absorbent dose, 0.15 g; temperature, 301 K; volume 100 ml).

Compared with the data mentioned above, the SICCM performs better in the treatment of Cu(II) in solution. It can be further indicated that the SICCM have a good potential as adsorbent for the treatment of heavy metals.

3.4.3. *Effect of contact time on Cu(II) adsorption*

Equilibrium time is another important parameter to heavy metals wastewater treatment process. The effect of the contact time for SICCM on the adsorption capacity for Cu(II) is described in Fig. 6. Obviously, SICCM showed a good performance in adsorption during the first 20 min. The time required to achieve the adsorption equilibrium was only 1 h, and there is no significant change from 1 to 24 h. Such a fast adsorption rate could be attributed to the functional groups on SICCM [6]. This is not similar to the previous literatures which have been reported. Murthy and Ryan studied Cu(II) and other heavy metals adsorption on the cellulose dithiocarbamate resin and reported that the maximum adsorption took a very long time [32]. Roozemond et al. investigated copper and cadmium ions adsorption to p-aminomethyl attached 3,5-dimethyl-1-hydroxymethylpyrazole and reported that the adsorption rate was very low and the maximum adsorption value could be reached in 2 days [33]. In latter stages, however, the rate of Cu(II) adsorption becomes slower. It may be attribute to the great decrease of the bonding sites on the surface of SICCM and the aggregation between particulates.

3.4.4. *Adsorption isotherms*

Adsorption equilibrium investigations were conducted at pH 4.5 and an initial Cu(II) concentration with the range of 40–500 mg L^{-1} for 2 h at temperature 301 K. About 0.15 g of SICCM was applied for the equilibrium study. Adsorption isotherm study is important in the treatment of wastewater as it provides valuable information on the pathways of adsorption reactions. Studies of adsorption equi-

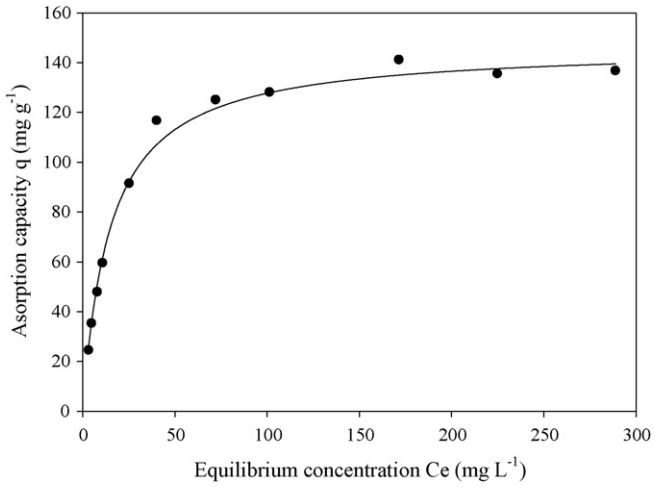

Fig. 7. Equilibrium isotherm for the adsorption of Cu(II) ions on SICCM (pH, 4.5; initial concentration, 40–500 mg L^{-1}; absorbent dose, 0.15 g; contact time, 2 h; temperature, 301 K; volume 100 ml).

librium indicate the capacity of the adsorbent, and the adsorption equilibrium is described by adsorption isotherm which characterized by certain constants whose values express the surface properties [34]. The Langmuir isotherm model is based on the assumptions of a structurally homogeneous adsorbent. The bonding sites on the adsorbent have the same affinity for adsorption of a single molecular layer. The bonding to the adsorption sites can be either chemical or physical but must be strong enough to prevent displacement of the adsorbed molecules [35]. The adsorption data is analysed according to the Langmuir isotherm equation as follow:

$$\frac{C_e}{q} = \frac{1}{kq_m} + \frac{C_e}{q_m}, \quad (3)$$

where C_e is the equilibrium concentration in the solution (mg L^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), q is the amount of Cu(II) adsorbed per unit weight of adsorbents at equilibrium (mg g^{-1}), and k is the Langmuir adsorption equilibrium constant (L mg^{-1}).

From Fig. 7, we can see that the adsorption capacity raises sharply with the increase of equilibrium concentration, and then it grows up slightly, and finally approaches a maximum. The plot of C_e/q vs C_e yields a straight line. According to the slope and intercept of the line, the value of q_m and k can be estimated to be 144.9 mg g^{-1} and 0.0719 L mg^{-1}, respectively. So the maximum adsorption capacity is significantly higher than the value less than 100 mg g^{-1} observed for the chitosan and cross-linked chitosan beads by Wan Ngah [36]. This may be due to the higher value of k for SICCM (0.0719 L mg^{-1}). According to Fig. 8, the value of the correlation coefficient R^2 for the Langmuir equation is 0.9986, which suggests that the adsorption of Cu(II) on SICCM be favourable. These results suggest that the adsorption of Cu(II) on SICCM follow the Langmuir adsorption isotherm. The values of the q_m about adsorption of Cu(II) from similar studies were listed in Table 1. The Cu(II) adsorption capacity observed in this study was superior to the other adsorbents which are shown in Table 1. The outstanding adsorption capacity places SICCM as one of the best adsorbents for the removal of Cu(II) from aqueous solutions.

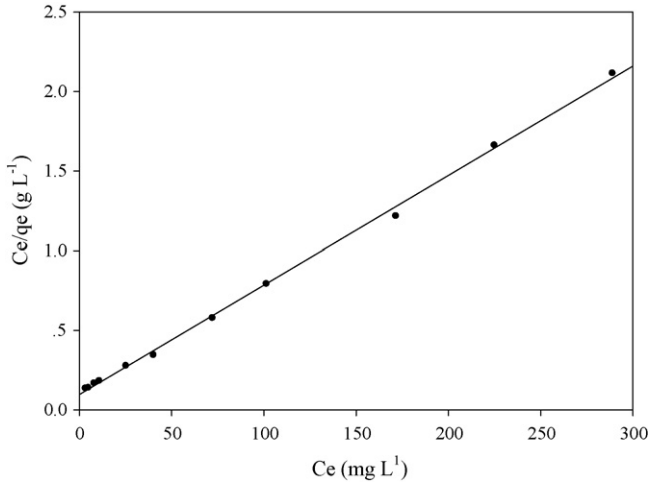

Fig. 8. The linear dependence of Ce/q on Ce (pH, 4.5; initial concentration, 40–500 mg L^{-1}; temperature, 301 K; absorbent dose, 0.15 g; contact time, 2 h; volume 100 ml).

Table 1
Comparison between the Cu(II) adsorption capacity of SICCM with some previously used adsorbents.

Adsorbent	Adsorption capacity (mg g^{-1})	Reference
SICCM	144.9	This study
Chitosan–cellulose hydrogel beads	53.2	[1]
α-Ketoglutaric-acid–chitosan-coated magnetic nanoparticles	96.15	[3]
Chitosan-bound Fe_3O_4 magnetic nanoparticles	21.5	[16]
Chitosan beads	80.71	[36]
Chitosan–glutaraldehyde beads	59.67	[36]
Chitosan–ethylene glycol diglycidyl ether beads	0.94	[36]
Chitosan–epichlorohydrin beads	62.47	[36]
Adapted and growing *Saccharomyces cerevisiae*	2.04–9.05	[38]
Dried yeast biomass	2.59	[39]
Immobilized microorganisms on polyurethane	28.74	[40]
Chitosan-coated perlite beads	104	[41]

4. Conclusions

In this study, SICCM was synthesized and characterized as a novel adsorbent for Cu(II) adsorption from aqueous solution. The new adsorbent was prepared by immobilizing *S. cerevisiae* on the surface of chitosan-coated magnetic nanoparticles. The batch of experiments suggested that the removal efficiency of Cu(II) adsorbed by SICCM was enhanced significantly because of the high specific surface area and the low resistance to internal diffusion of Cu(II). The SICCM was quite efficient as a magnetic adsorbent for the fast adsorption of Cu(II) from aqueous solution at initial pH values from 4 to 6. In addition, more than 90% of Cu(II) was removed within the first 10 min, and the time required to achieve the adsorption equilibrium was only 1 h. The adsorption behavior obeyed the Langmuir adsorption isotherm model with a maximum adsorption capacity of 144.9 mg g^{-1}, which was considerably higher than that of other reported magnetic adsorbents [16,37].

In a word, the batch adsorption experiments tests show that the new adsorbent SICCM will have broad applications in the removal of heavy metals from wastewater, and it can be competitive with conventional adsorbents. In addition, the studies are still continuing, and more detailed results will appear in a forthcoming paper.

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