

Soybean hull functionalized by phosphoric acid for sorption of copper from aqueous solution

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Abstract—One kind of potentially biodegradable cationic sorbent, which bears hydroxyl groups of phosphoric acid as its functional groups, with high sorption capacity of copper was prepared by thermochemically esterifying phosphoric acid (PA) onto soybean hull. Sorption of Cu(II) from aqueous solution onto modified soybean hull (MSH) was investigated in a batch system. The sorption experiments were performed under various conditions such as different initial pH, copper concentration, MSH dosage, and contact time. The maximum copper sorption was obtained when initial solution pH \geq 3.5. The isothermal data of copper sorption fitted the Langmuir model and the sorption process could be described by the pseudo-first-order kinetic model. The maximum sorption capacity (Q_m) of MSH for Cu(II) was 31.55 mg/g. For 100 mg/l of Cu(II) solution, a sorption ratio above 91% could be achieved by 5.0 g/l of MSH. The equilibrium of Cu(II) sorption was reached within 50 min. The foreign cation and chelator in Cu(II) solution caused decline of Cu(II) sorption.

Key words: Sorption, Copper, Esterification, Phosphoric Acid, Soybean Hull

INTRODUCTION

Enhanced Industrialization during recent decades in China has led to the discharge of unprecedented volumes of heavy metal wastewater into the aquatic environment. Heavy metals are highly toxic and therefore pose a serious threat to public health and wildlife. Once being absorbed into living organisms, heavy metals can bind to vital cellular components, such as structural proteins, enzymes and nucleic acids, and interfere with these components' functions. Public concern over heavy metal pollution has grown steadily since the outbreak of Minamata disease caused by mercury in Japan [1]. People's awareness of the hazards of heavy metals now covers a wide spectrum of heavy metals such as lead, mercury, cadmium, chromium, copper, zinc, nickel and arsenic.

The removal and recovery of heavy metals from wastewater is important in the protection of the ecological environment and human health. A number of techniques such as chemical precipitation [2], solvent extraction [3], flotation [4], electro dialysis [5], membrane separation [6], reverse osmosis [7], ion exchange [8], and sorption [9] have been employed to remove heavy metals from wastewater. But strict environmental protection legislation, public environmental concerns and high expense of conventional disposal methods have provided incentive for inventing novel techniques for heavy metal wastewater treatment.

The use of biomaterials for removing heavy metals from contaminated wastewater has emerged as a potential alternative method to conventional techniques [10]. In recent years, considerable attention has been devoted to the study of removal of heavy metals from wastewater by sorption using crude or modified agricultural wastes such as apple residue [11], wheat straw [12], corn cob [13], peanut

hull [14], cassava waste [15], wheat bran [16], carrot residues [17], mustard oil cake [18], Juniper bark [19], coir fiber [20], rice husk [21], and rice bran [22].

Copper, a widely used metal in industry, is an essential mineral element for human health when in trace quantity, but its excess amount in the body can be toxic. Doses of copper above 50 mg/kg body weight can be lethal. The World Health Organization's guideline for copper concentration in drinking water is 2 mg/l [23]. When its aqueous concentration exceeds 5 mg/l, copper imparts clear color and undesirable taste to water.

Soybean (*Glycine max* (L.) Merr.), an annual crop belongs to the *Leguminosae* family, sub-family *Papilionoideae*, is widely cultivated in many countries as oil seed crop. Soybean hull, representing about 8 to 10% of the weight of soybean grain, is a lignocellulosic agricultural waste containing cellulose (14 to 25%), hemicellulose (14 to 20%), pectin (10 to 12%), protein (9 to 12%), uronic acid (7 to 11%), ash (4 to 5%) and lignin (3 to 4%) [24]. China's annual output of soybean hull exceeds 1.6 million tons. Besides as animal feed, the redundant soybean hull in large quantity needs to be disposed of every year. In this work, we attempted to utilize phosphoric acid (PA) thermochemically esterified soybean hull as a cationic sorbent for the sorption of copper from aqueous solution by batch system. The objective of this work was to develop a new economical technique for soybean hull exploitation and utilization and to enhance the treatment of industrial wastewater and reduce the cost of wastewater treatment.

MATERIALS AND METHODS

1. Preparation of Soybean Hull and Esterifying Agent

Soybean hull, supplied by a local vegetable oil factory, was washed with tap water to remove soil and dust, and then dried overnight at 50 °C. Dried soybean hull was ground and sieved to retain the 420-

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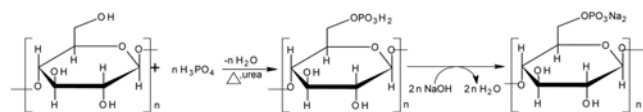
850 μm fractions for further chemical modification.

For preparing the esterifying agent, 1.67 g of urea was dissolved in 1 l of 0.5 mol/l PA, and then the pH value of above solution was adjusted to 3.5 with NaOH.

2. Modification of Soybean Hull

The chemical modification of soybean hull was carried out according to the following method: Ground soybean hull was mixed with esterifying agent at the ratio of 1 : 12 (hull : esterifying agent, w/v) and stirred for 30 min. The esterifying agent/hull slurry was placed in a stainless steel tray and dried at 50 °C in a forced air oven. After 24 h, the thermochemical reaction between PA and soybean hull was performed by raising the oven temperature to 120 °C for 90 min. After cooling, the PA-modified soybean hull was extensively washed to neutral pH with double-distilled water. After filtration, the PA-modified soybean hull was suspended in 0.1 mol/l NaOH at suitable ratio and stirred for 60 min, followed by washing thoroughly with double-distilled water to remove residual alkali, and then the wet PA-modified soybean hull was dried at 50 °C until constant weight and preserved in a desiccator as sorbent for further use.

The chemical modification of soybean hull can be schematically expressed by equation:



3. Preparation of Copper Solution and other Reagents

Stock solution of copper (II) was prepared by dissolving accurately weighed amount of analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck) in double-distilled water to the concentration of 500 mg/l. The experimental solutions were obtained by diluting the copper stock solution in accurate proportions to different initial concentrations (25–250 mg/l).

Ammoniacal buffer (pH 10.0) was prepared by adding 54 g NH_4Cl to 350 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ and diluting with double-distilled water to 1,000 ml.

Screening agent was prepared by dissolving 50 g of EDTA and 200 g of triammonium citrate in double-distilled water and adding double-distilled water to 1,000 ml.

4. Sorption Experiments

Sorption experiments were conducted in a rotary shaker at 150 rpm and ambient temperature (20 ± 2 °C) by using 250 ml shaking flasks containing 100 ml different concentrations and initial pH values of copper solution. The initial pH values of the solution were previously adjusted with 0.1–0.5 mol/l HNO_3 or NaOH with a pH meter. Different doses of MSH were added to each flask, and then the flasks were sealed up to prevent change of volume of the solution during the experiments. After the flasks were shaken for predetermined time intervals, the samples were withdrawn from the flasks and the sorbent was separated by filtration through a membrane filter (0.45 μm). The concentration of residual Cu(II) in filtrate was determined spectrophotometrically.

The experiments were conducted in duplicate and the negative controls (with no sorbent) were simultaneously carried out to ensure that sorption was by sorbent and not by the container.

5. Copper Analysis

Into a suitable aliquot of sample solution containing lower than 100 μg of copper ions, 2.0 ml of ammoniacal buffer (pH 10.0), 4.0 ml of screening agent, 2.0 ml of 2% (v/v) OP emulsifying agent, and 1.0 ml of 1% (w/v) sodium diethyl dithiocarbamate solution was added, respectively with gentle shake, and then the solution was diluted to 25 ml with double-distilled water. After thorough mixing and placing in ambient temperature (20 ± 2 °C) for 10 min, the absorbance of the yellow-brown colored solution was measured at 460 nm against a blank of the reagents with a 752 W Grating Spectrophotometer (Shanghai, China) and copper concentration was computed from the calibration curves.

RESULTS AND DISCUSSION

1. Effect of Initial Solution pH on Cu(II) Sorption

The amount of Cu(II) sorption as the function of initial pH was shown in Fig. 1. As initial solution pH increased, the amount of Cu(II) sorption increased and the sharpest increase was observed between pH 1.5 and 2.5. At around pH 3.0 a plateau was reached. When pH was higher than 5, the precipitation of insoluble copper hydroxide affecting the Cu(II) sorption experiment took place. These results showed the strong pH dependence of Cu(II) sorption by MSH. For the above reason, pH 4.5 was selected for the subsequent experiments.

2. Influence of Initial Cu(II) Concentration on its Sorption

The influence of initial Cu(II) concentration on its sorption was estimated. As shown in Fig. 2, when the initial Cu(II) concentration was increased from 25 to 250 mg/l, the percentage of Cu(II) sorption obviously decreased from 94.75 to 58.75%. However, with increasing initial Cu(II) concentration, the absolute amount of Cu(II) sorption per unit mass of MSH sharply increased from 4.74 to 29.38 mg/g at optimum pH value.

With the data in Fig. 2, the Langmuir equation was employed as

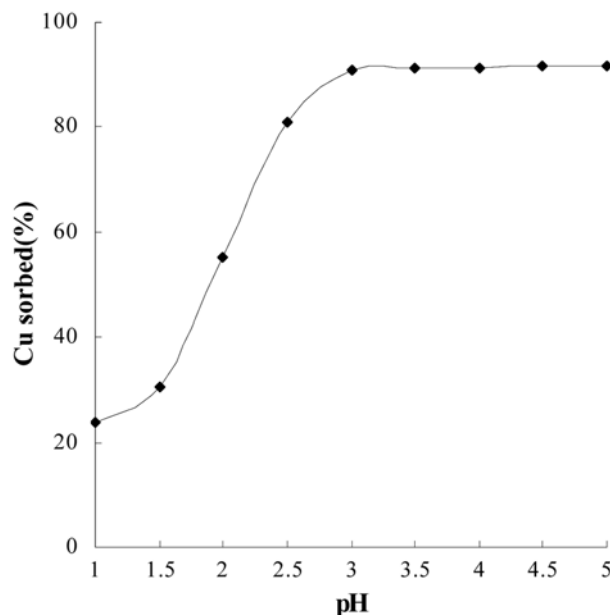


Fig. 1. Effect of initial solution pH on Cu(II) sorption by MSH (Cu (II) concentration: 100 mg/l; MSH dose: 5 g/l; contact time: 1 h).

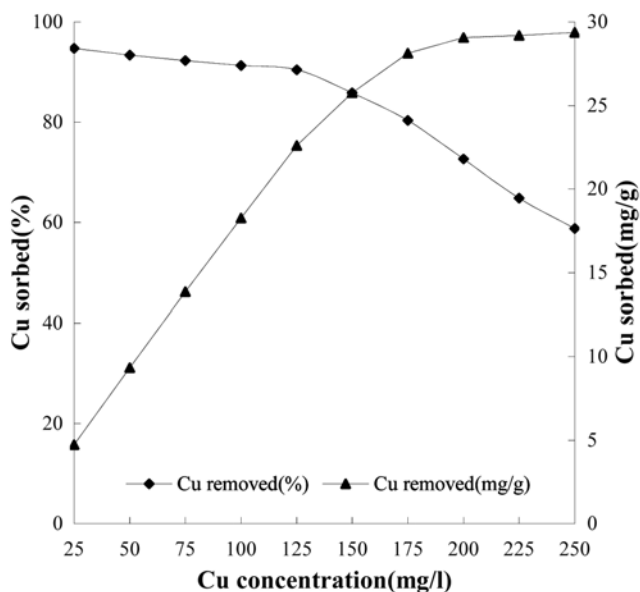


Fig. 2. Influence of initial copper concentration on Cu(II) sorption by MSH (MSH dose: 5 g/l; contact time: 1 h; pH: 4.5).

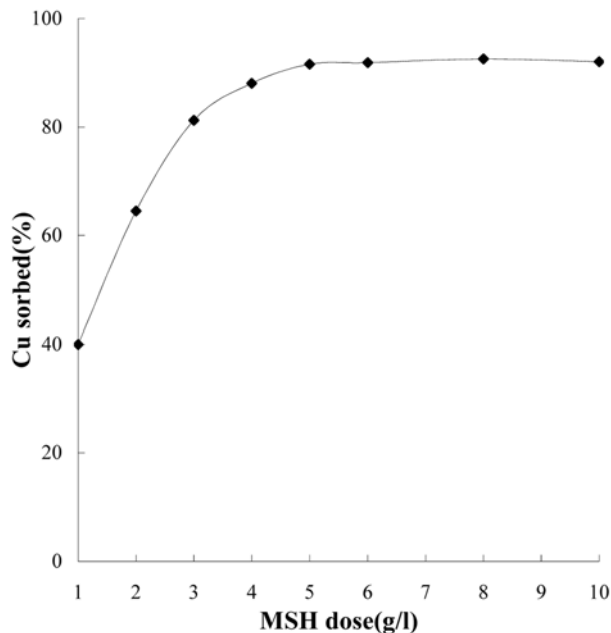


Fig. 4. Effect of MSH dosage on Cu(II) sorption by MSH (Cu(II) concentration: 100 mg/l; contact time: 1 h; pH: 4.5).

the mathematical model of the sorption isotherm to describe the Cu(II) sorption by MSH and to estimate the maximum capacity of Cu(II) sorption.

The linear Langmuir equation was shown as follows:

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m \tag{1}$$

where C_e (mg/l) is the concentration of the Cu(II) solution at equilibrium, q_e (mg/g) is the amount of Cu(II) sorbed by per unit sorbent at equilibrium, Q_m is the maximum sorption capacity and represents a practical limiting sorption capacity when the sorbent surface is fully covered with monolayer sorbate molecules and a is Langmuir constant. The Q_m and a values can be obtained from the slope

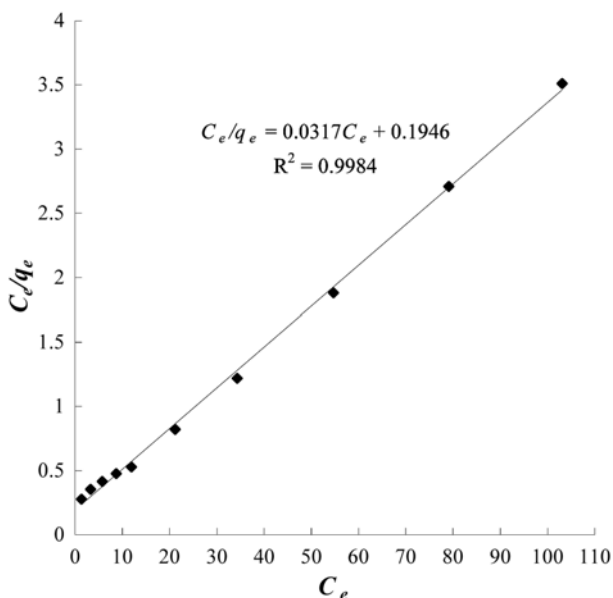


Fig. 3. The Langmuir plot of Cu(II) removed by MSH.

($1/Q_m$) and intercept ($1/aQ_m$) of the linear plot of C_e/q_e versus C_e .

The Langmuir sorption isotherm of Cu(II) removed by MSH is given in Fig. 3. The experimental result indicated that the sorption isotherm of Cu(II) removed by MSH followed the Langmuir model ($R^2=0.9984$). The maximum sorption capacity (Q_m) of MSH for Cu(II) was 31.55 mg/g.

3. Effect of MSH Dosage on Cu(II) Sorption

The effect of MSH dosage on the sorption ratio of Cu(II) is shown in Fig. 4. For the Cu(II) solution at 100 mg/l initial concentration, the percentages of Cu(II) removed increased from 40.01 to 91.56% with increasing the MSH dosage from 1 to 5 g/l. Above 5 g/l of sorbent dose, the sorption equilibrium was reached and the sorption ratio of Cu(II) held almost no variety. Thus, the MSH dosage of 5 g/l was chosen for subsequent experiments.

It is to be expected, for a fixed initial solution concentration, that increase of sorbent dosage provides a greater surface area (or sorption sites). So, before the sorption equilibrium, the percentage of Cu(II) removed increased along with increase of sorbent dosage; after the sorption equilibrium, the sorption ratio of Cu(II) kept constant. But the absolute amount of Cu(II) sorption per unit mass of MSH obviously decreased along with the increase of sorbent dosage.

4. Influence of Contact Time on Cu(II) Sorption

Fig. 5 illustrates the influence of contact time on Cu(II) sorption by MSH. The sorption rate of Cu(II) was very rapid during the initial stage of the sorption process. It was only 2 minutes that the percentage of Cu(II) removed had reached 43.13%. After a very rapid sorption, Cu(II) uptake rate slowly declined with lapse of time and reached equilibrium value at about 50 min. The sorption ratio of Cu(II) increased from 43.13 to 91.81% with the passage of time from 2 to 50 min; after that, the sorption ratio of Cu(II) had almost no variety. The three phases of Cu(II) sorption could be attributed to boundary layer diffusion sorption, intraparticle diffusion sorption and sorption equilibrium, respectively.

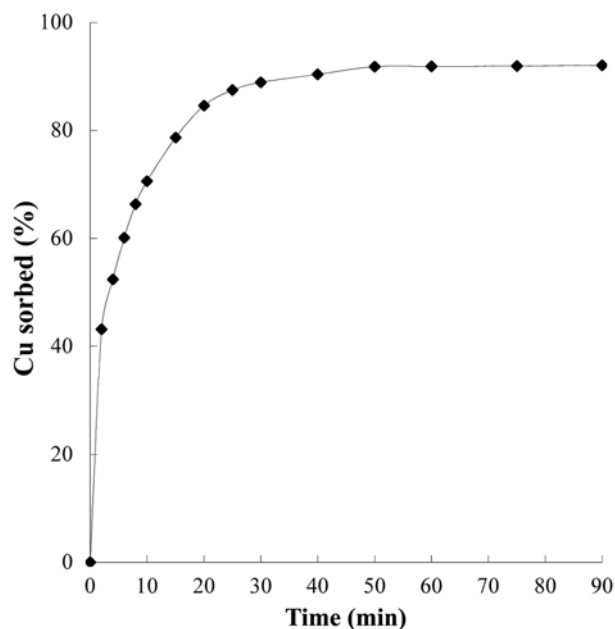


Fig. 5. Influence of contact time on Cu(II) sorption by MSH (Cu(II) concentration: 100 mg/l; MSH dose: 5 g/l; pH: 4.5).

The above Cu(II) sorption mechanism may be assumed to involve the following sequential steps:

- Migration of Cu(II) from bulk of the solution to the boundary layer of the sorbent,
- Diffusion of Cu(II) through the boundary layer to the surface of the sorbent,
- Intraparticle diffusion of Cu(II) into the interior pores of the sorbent particle, and
- Sorption of Cu(II) at an active site on the exterior or interior surface of sorbent.

The kinetic data in Fig. 5 were treated with the following Lagergren's pseudo-first-order rate equation:

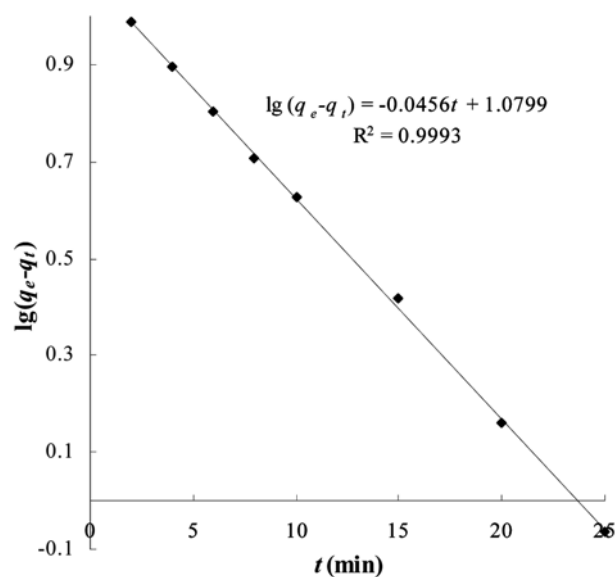


Fig. 6. The Lagergren plot of Cu(II) removed by MSH.

$$\lg(q_e - q_t) = \lg q_e - k_{ad}t/2.303 \quad (2)$$

where q_e and q_t (mg/g) refer to the amount of Cu(II) removed at equilibrium and time t (min), respectively, and k_{ad} is the rate constant. The rate constants k_{ad} could be calculated from the slope of the linear plot of $\lg(q_e - q_t)$ versus t . The Lagergren plot of Cu(II) removed by MSH is shown in Fig. 6. The high value of correlation coefficient showed that the data conformed well to the pseudo-first-order rate kinetic model.

The kinetic data in Fig. 5 were also treated with the following intraparticle diffusion rate equation:

$$q_t = k_{id}t^{1/2} + C$$

where q_t (mg/g) is the amount of Cu(II) sorbed at time t (min), k_{id} is the intraparticle diffusion rate constant, and C is the intercept. When the line passes through the origin ($C=0$), the intraparticle diffusion will be the sole rate control step.

The linear intraparticle diffusion rate plot of Cu(II) sorbed on MSH is shown in Fig. 7. It can be seen that the plot exhibits a good linear portion. The deviation of the line from origin ($C \neq 0$) implies that intraparticle diffusion is not the only rate controlling step.

5. Effect of Foreign Matter on Cu(II) Sorption

The effect of Na^+ ion on Cu(II) removed by MSH was tested by the addition of sodium chloride to the Cu(II) solution. As seen in Fig. 8, the percentage of Cu(II) sorption decreased from 91.54 to 74.38% with increasing NaCl concentration from 0 to 0.5 mol/l. This may be due to the following two reasons: a) The addition of NaCl reduced the electrostatic interaction between MSH and Cu(II) ion. b) The adding Na^+ ion competed against Cu(II) ion for the active sites of MSH.

The further experiments indicated that K^+ , Ca^{2+} , or Mg^{2+} ion caused more decline of Cu(II) sorption than Na^+ ion, because these cations had bigger atomic radius and more electric charge. Because of its chelation, EDTA also had obvious effect on Cu(II) sorbed on MSH.

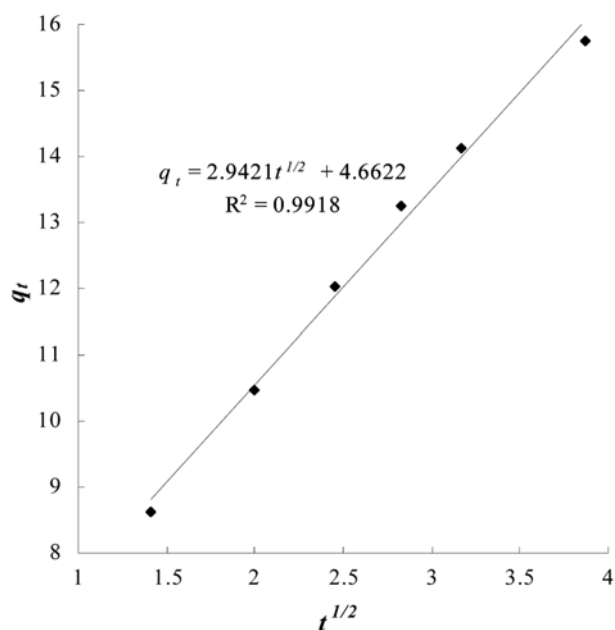


Fig. 7. The intraparticle diffusion rate plot of Cu(II) removed by MSH.

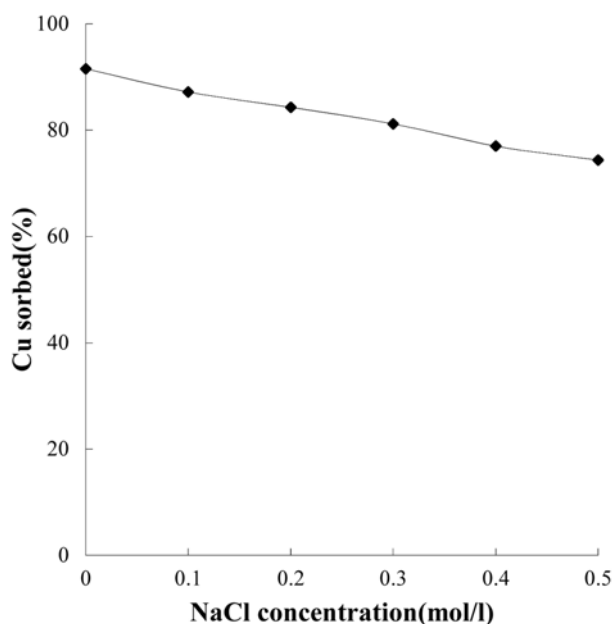


Fig. 8. Effect of NaCl on Cu(II) sorption by MSH (Cu(II) concentration: 100 mg/l; MSH dose: 5 g/l; contact time: 1 h; pH: 4.5).

6. Influence of MSH Reuse

After sorption experiment, 10 ml of 1 mol/l hydrochloric acid as eluant was added to the shaking flask containing exhausted MSH, and then the flask was sealed up and shaken for 60 min. After the eluant was removed, MSH was washed to neutral with double-distilled water, and then 0.1 mol/l NaOH at suitable ratio was added and stirred for 60 min, followed by washing thoroughly with double-distilled water to remove residual alkali. Finally, regenerative MSH

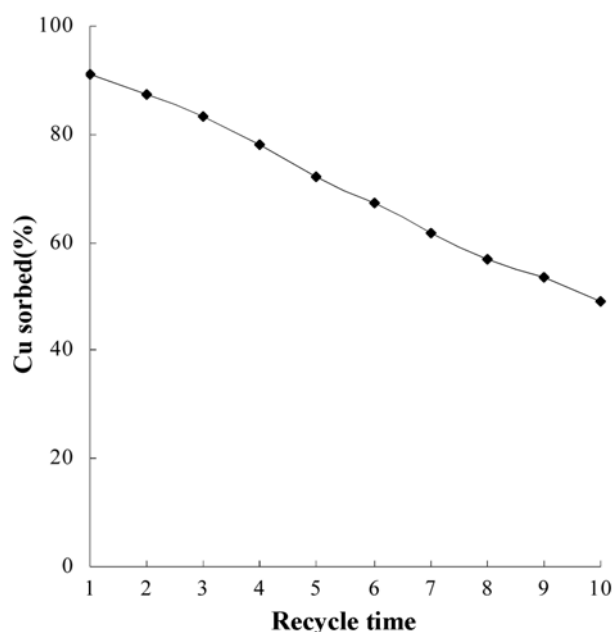


Fig. 9. Influence of MSH recycle on Cu(II) sorption by MSH (Cu(II) concentration: 100 mg/l; MSH dose: 5 g/l; contact time: 1 h; pH: 4.5).

was separated by filtration for its reuse.

To investigate the stability and potential recyclability of MSH, ten sorption-desorption cycles were carried out. The result in Fig. 9 indicated that the Cu(II) sorption capacity of MSH gradually decreased from 91.25% to 48.94% with the increase of recycle time. It was maybe caused by the loss of MSH itself and the decrease of its sorption capacity.

CONCLUSIONS

The batch tests conducted in the present study indicated that MSH is a promising sorbent for removing Cu(II) from its aqueous solution. The main conclusions could be stated as follows:

1. The Cu(II) sorption by MSH was influenced by various experimental parameters such as solution pH, Cu(II) concentrations, contact time, MSH dosage and foreign matter.
2. The Cu(II) sorption came up to the maximum value in the range of pH 3.0-5.0.
3. The maximum sorption capacity (Q_m) of MSH for Cu(II) was determined from Langmuir equation to be 31.55 mg/g.
4. The equilibrium of Cu(II) sorption was reached within 50 minutes.
5. The foreign cation and chelator, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} ion and EDTA, in Cu(II) solution caused decline of Cu(II) sorption.
6. The Cu(II) sorption capacity of MSH decreased with the increase of its reuse time.

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