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# Study on adsorption of Cu(II) by water-insoluble starch phosphate carbamate

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**Abstract**

Crosslinked starch phosphate carbamates were prepared and used to adsorb Cu(II) ions from an aqueous solution. Scanning electron microscopy (SEM) was used to investigate the changes in the starch granule structure before and after adsorption. Batch adsorption experiments were carried out as a function of adsorption time, adsorbents dose, pH, substitute groups' content, initial Cu(II) ions concentrations, and temperature. The results reveal that 20 min of adsorption time is sufficient for reaching the adsorption equilibrium, the adsorption of Cu(II) ions on crosslinked starch phosphate carbamate is endothermic in nature, and the adsorption equilibrium data correlate well with the Langmuir isotherm model with the maximum adsorption capacity of 1.60 mmol/g. Moreover, the adsorbed Cu(II) ions can be desorbed by treating with HCl solution and the desorption percentage reached above 96% when desorbing with 1 N HCl solution for 1 h.

*Keywords:* Adsorption; Crosslinked starch phosphate carbamate; Cu(II) ions

## 1. Introduction

Heavy metals such as copper, lead and cadmium are of environmental concern due to extensive use and toxicity to human and natural wildlife. Although a great understanding of the magnitude of their toxicity and environmental cycling is slowly being realized, there is not a satisfying method to remove and recover heavy metals. Among all the treatments proposed, adsorption is a commonly used technique for the separation and recovery of heavy metals.

Recently, adsorbents based on starch deserved particular attention because of an increasing interest in the synthesis of new cost-effective adsorbents. Xu and coworkers studied the adsorption process of Cr(VI), Cu(II), and Pb(II) by crosslinked amphoteric starch with quaternary ammonium and carboxymethyl groups (Xu, Zhang, Lu, Yang, & Cui, 2003; Xu, Feng, Yue, & Wang, 2004; Xu, Feng, Peng, Wang, & Yushan, 2005); Zhang and Chen investigated crosslinked starch graft copolymers containing amino groups as the adsorbents for Pb(II) and Cu(II) (Zhang & Chen, 2002); Chan reported the adsorption of Cu(II) onto insoluble amphoteric starch containing quaternary ammonium and phosphate groups (Chan & Wu, 2001); Starch after crosslinking with $POCl_3$ and carboxymethylation was proposed by Kim and Lim as adsorbents for the removal of heavy metal ions (Kim & Lim, 1999).

Starch phosphate carbamate is new amphoteric starch containing phosphate groups and amino groups (Heinze, Klemm, Unger, & Pieschel, 2003). Heinze et al. found starch phosphate carbamate has high adsorption capacity for Cu(II) and pointed out it may act as super absorbents in various applications. But there is no paper to give the further investigation on the adsorption between this modified starch and heavy metal ions.

The aim of this paper is to prepare crosslinked starch phosphate carbamates using a dry process and study the adsorption between this modified starch and Cu(II) ions. Batch experiments were conducted to study the main parameters such as treatment time, adsorbent dose, initial pH, initial Cu(II) ions concentration, and substitute groups' content of adsorbents. The adsorption isotherm, thermodynamics and desorption were also investigated.

## 2. Experimental

### 2.1. Materials

Corn starch (food-grade) was dried at 105 °C before it was used. $Cu(SO_4)\cdot 5H_2O$ (analytic reagent grade) was used to prepare the adsorbate solution. Urea, phosphoric acid, and all other commercial chemicals were analytic reagent grade and

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Table 1
Adsorbents with the different content of phosphate and carbamate groups

| Sample | CSPC1 | CSPC2 | CSPC3 |
|---|---|---|---|
| Content of phosphate groups (mmol/g) | 1.51 | 2.55 | 3.10 |
| Content of carbamate groups (mmol/g) | 1.03 | 1.21 | 1.40 |

used without further purification. All solutions and standards were prepared using deionized water.

### 2.2. Preparation of adsorbents

100 g corn starch was slurried in 150 mL water in a stirred glass kettle. Then, 1.5 g sodium chloride and 10 mL epichlorohydrin were added. To this, potassium hydroxide solution (8 g KOH in 40 mL water) was added over 15 min, and the mixture was stirred for 16 h at 25 °C. Later on, the mixture was adjusted to pH 6 with acetic acid. The slurry was subsequently washed with distilled water and 95% ethanol and then filtered. The prepared crosslinked starch was dried and used for further chemical modification.

Crosslinked starch phosphate carbamates (CSPC) were prepared according to the method of Heinze (Heinze et al., 2003). Crosslinked starch was mixed with urea and phosphoric acid to give a homogeneous paste. The mixture was heated for 4 h at 140 °C in a vacuum oven. After cooling to room temperature, the product was washed three times with deionized water and one time with ethanol. The product was then dried at 50 °C in vacuum.

### 2.3. Analysis of adsorbents

Phosphorus content of adsorbents was determined according to spectrophotometry (GB/T 12092-1989); Nitrogen content, and hence the content of carbamate groups in the adsorbents, were measured with the Kjeldahl method (GB/T 12091-1989). The contents of phosphate and carbamate groups of the Adsorbents are shown in Table 1. With the aim to study the effect of substitute groups' content on adsorption, other adsorbents were also prepared (Tables 2 and 3).

Scanning electron micrographs (SEM) were obtained using a KYKY-2800B scanning electron microscope (made in China).

### 2.4. Adsorption experiments

Adsorption experiments were carried out by batch method. The desired dose of CSPC was added to 50 mL of aqueous $CuSO_4$ solution in a series of 100 mL glass-stoppered Erlenmeyer flasks. The suspension was stirred on a magnetic stirrer at a uniform speed of 120 rpm in a constant temperature bath. After certain adsorption time, the suspension was filtered and the concentration of Cu(II) ions in the aqueous phase was analyzed by complexometric titration method (John, 1995). pH was adjusted to the desired values by adding either 0.1 N HCl solution or 0.1 N NaOH solution before adding the adsorbent.

Table 2
Adsorbents with the same content of phosphate groups and the different content of carbamate groups

| Sample | C1 | C2 | C3 |
|---|---|---|---|
| Content of phosphate groups (mmol/g) | 0.15 | 0.15 | 0.15 |
| Content of carbamate groups (mmol/g) | 0.55 | 0.92 | 1.27 |

Table 3
Adsorbents with the different content of phosphate groups and the same content of carbamate groups

| Sample | P1 | P2 | P3 |
|---|---|---|---|
| Content of phosphate groups (mmol/g) | 0.84 | 1.23 | 1.73 |
| Content of carbamate groups (mmol/g) | 0.77 | 0.77 | 0.77 |

The adsorption capacity was calculated from the following expression:

$$Q = \frac{(C_i - C_t)V}{m}.$$

where $Q$ (mmol/g) is the adsorption capacity of the adsorbent, $C_i$ and $C_t$ (mol/L) are the initial and terminal concentrations of the Cu(II) ions in the adsorption solution, respectively, and $V$ (mL) and $m$ (g) are the volume of the adsorption solution and the dose of the adsorbent, respectively.

### 2.5. Desorption experiments

Batch desorption experiments were carried out by stirring 0.1 g of Cu(II)-loaded adsorbent with 50 mL 1 N HCl solution for 1 h at 20 °C.

## 3. Results and discussion

### 3.1. Scanning electron micrographs

Fig. 1 shows the scanning electron micrographs of corn starch, crosslinked starch, CSPC, and CSPC adsorbed Cu(II) ions. There is no evident change between before and after crosslinking (Fig. 1(a)–(d)). However, the different surface morphology of crosslinked starch and crosslinked starch phosphate carbamate is clearly visualized in the scanning electron micrographs. Crosslinked corn starch (Fig. 1(c) and (d)) after reacting with Urea and phosphoric acid under high temperature shows the appearance of large holes (Fig. 1(e) and (f)). These holes increase the surface of granules. When crosslinked starch phosphate carbamate had adsorbed Cu(II) ions, the large holes became small (Fig. 1(g) and (h)).

### 3.2. Effect of treatment time

To establish an appropriate treatment time between CSPC and Cu(II) ions solution, adsorption capacities of Cu(II) were measured as a function of time. As shown in Fig. 2, Cu(II) ions are rapidly removed by CSPC (less than 10 min) and the adsorption process reaches equilibrium in about 20 min. In general, there are three main steps involved in Cu(II) ions adsorption onto solid adsorbent: (i) the transport of the Cu(II) ions from the bulk solution to the adsorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the adsorbent particle (Crini, 2005). Because the adsorption is a chemical process, step (ii) is fast. On the other hand, CSPC was prepared using a solid-state technique, so most of the active groups are on the particle surface, which makes step (iii) rapid. So the whole adsorption process reaches equilibrium rapidly. For the following experiments, the treatment time was maintained for 20 min to ensure that equilibrium was really achieved.

### 3.3. Effect of pH

The adsorption of Cu(II) ions on CSPC is highly pH-dependent, as can be observed in Fig. 3. The amount of Cu(II) ions adsorbed increases with increase in pH. Fig. 3 further shows that below pH 2.0 or so, the adsorption capacity is negligible. This is due to the fact that at low pH values the high concentration of the $H^+$ in solution makes the phosphate and amino groups exist in the form of $-PO(OH)_2$ and $-NH_3^+$, respectively, and they prevent the adsorption of Cu(II) ions onto CSPC. This implies that the active groups are protonated. As the pH increases from 2.0 to 6.0, the active sites become increasingly ionized and the Cu(II) ions become adsorbed because of the ion-exchange on the phosphate groups and chelation on the amino groups. At pH 6.0, there is an inflection point for CSPC1. The presence of the inflection point suggests a change in the mechanism for Cu(II) ions removal. Beyond pH 6.0, therefore, adsorption becomes masked by precipitation. At $pH > 6.0$, therefore, both ions adsorption and $Cu(OH)_2$ precipitation jointly contribute to Cu(II) ion removal from solution.

### 3.4. Effect of substitute groups' content

Sample C1, C2, C3, P1, P2 and P3 (Tables 2 and 3) were used to examine the effect of active groups' content of CSPC on the adsorption capacities of Cu(II) ions. As shown in Fig. 4, the adsorption capacity of Cu(II) ions increases with increase in the content of substitute groups, but phosphate groups contribute much more to Cu(II) ions removal from solution than carbamate groups. This phenomenon may be attributed to

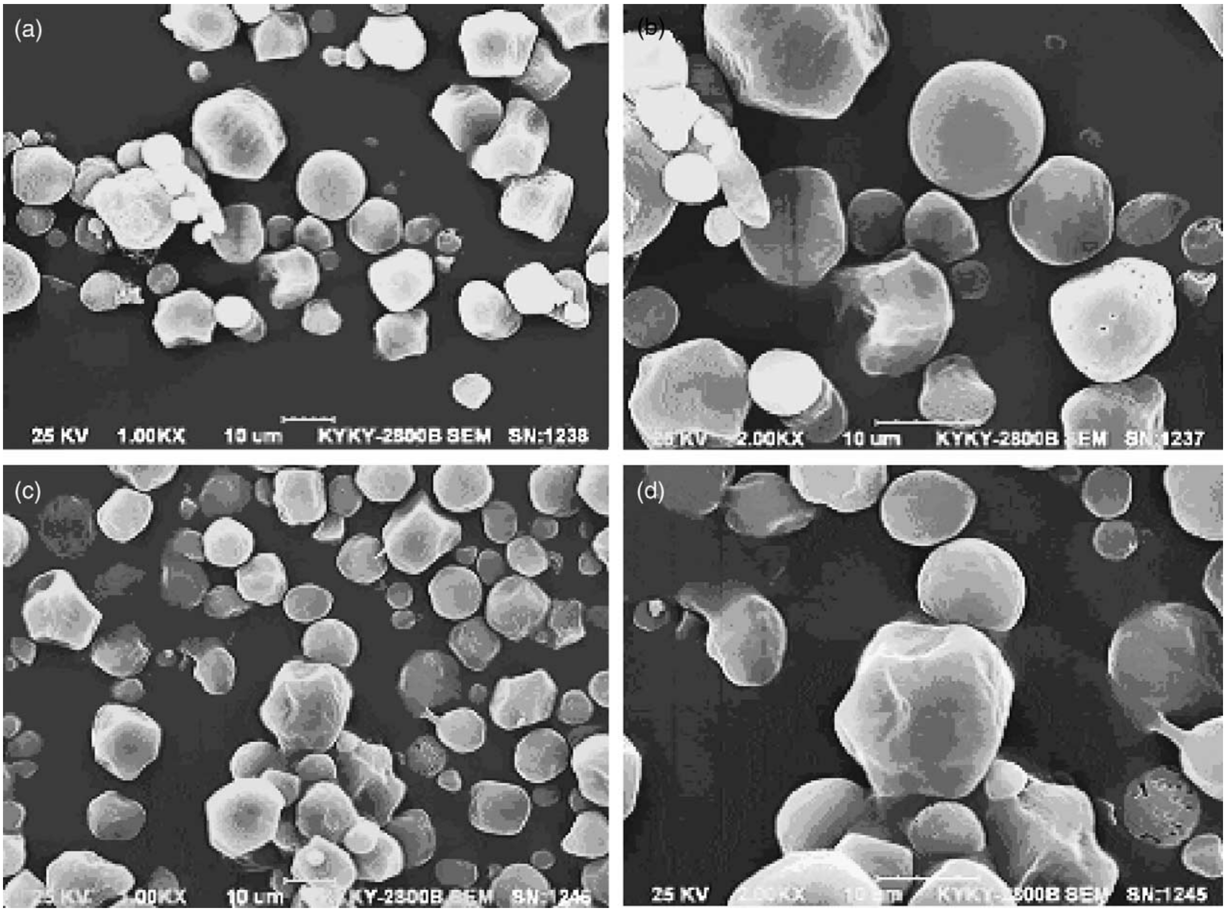

Fig. 1. SEM pictures of different starch granules ((a), (b): corn starch; (c), (d): crosslinked starch; (e), (f): CSPC3; (g), (h): CSPC3 adsorbed Cu(II) ions, $Q = 1.40$ mmol/g).

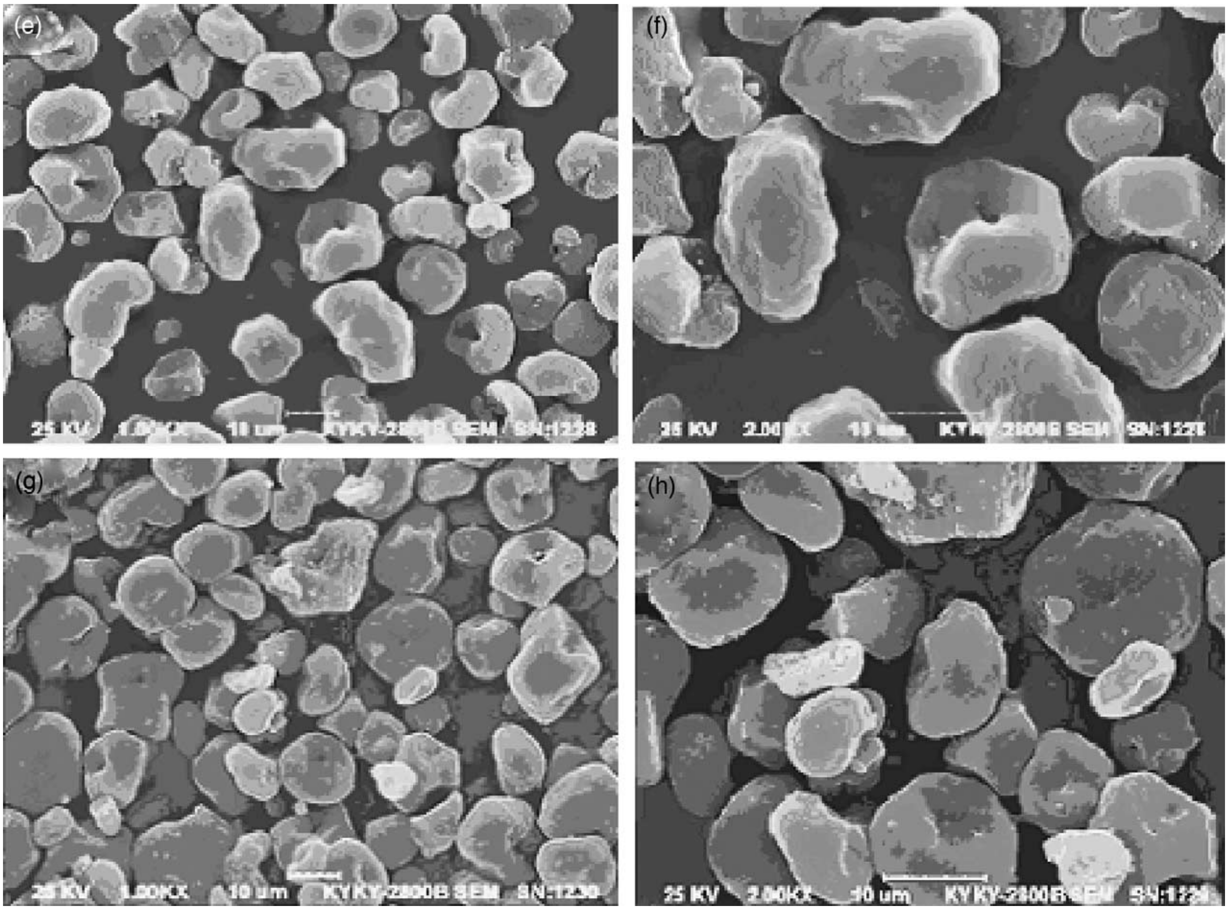

Fig. 1 (*continued*)

the difference in the mechanism for Cu(II) ions removal. Adsorption of Cu(II) ions on the phosphate groups is an ion-exchange process, and one mole of phosphate group can bind the same amount of Cu(II) ions in theory. Cu(II) ions removal by carbamate groups is a chelation process on the amino groups. The amide groups are weak ligands and several mole of amino group can bind only one mole of Cu(II) ions, which was also found by Khalil et al. in their study on utilization of some starch derivatives containing amide groups in heavy metal ions removal (Khalil & Farag, 1998). Undeniablely, some amino groups may cooperate with phosphate groups to adsorb Cu(II) ions.

### *3.5. Effect of the initial Cu(II) ions concentration*

The equilibrium adsorption capacity of CSPC for Cu(II) ions increases with a rise in the initial Cu(II) ions concentration, as shown in Fig. 5. Adsorption process is highly concentration dependent. When the initial Cu(II) ions concentration was increased from 1.5 mmol/L up to 3.0 mmol/L, the adsorption capacity of CSPC1, CSPC2, and CSPC3 increased from 0.88 to 1.01 mmol/g, 1.14 to 1.41 mmol/g, and 1.21 to 1.58 mmol/g, respectively. This increase in adsorption capacity of CSPC with relation to Cu(II) ions concentration is probably due to a high driving force for

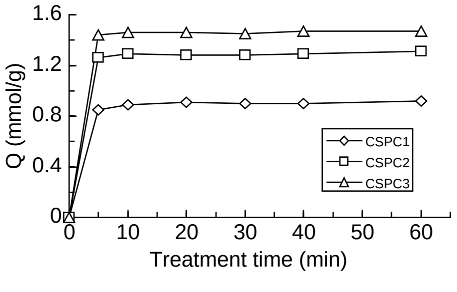

Fig. 2. Effect of the treatment time on the adsorption capacities of Cu(II) ions ([Cu$^{2+}$]=2 mmol/L; $T$=20 °C; pH, 4.28; dose of CSPC, 60 mg).

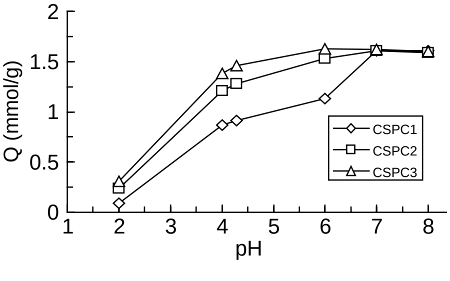

Fig. 3. Effect of pH on the adsorption capacities of Cu(II) ions ([Cu$^{2+}$]= 2 mmol/L; $T$=20 °C; Treatment time, 20 min; dose of CSPC, 60 mg).

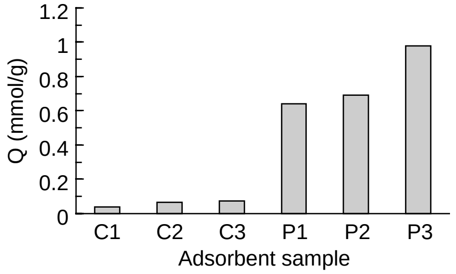

Fig. 4. Effect of substitute groups' content of CSPC on the adsorption capacities of Cu(II) ions ($[Cu^{2+}]=2$ mmol/L; $T=20$ °C; pH, 4.28; Treatment time, 20 min; Dose of CSPC, 60 mg).

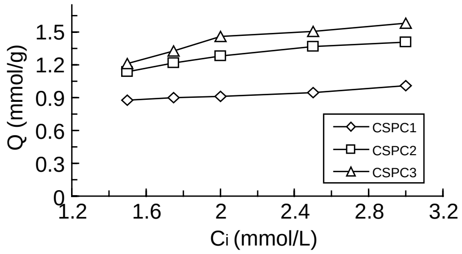

Fig. 5. Effect of the initial Cu(II) concentration on the adsorption capacity ($T=$ 20 °C; pH, 4.28; treatment time, 20 min; dose of CSPC, 60 mg).

mass transfer. In fact, the more concentrated the solution is, the better the adsorption is.

### 3.6. Adsorption isotherm

Langmuir equation was applied to quantify adsorption capacity and is given as follows:

$$\frac{C_e}{Q}=\frac{1}{Q_m b}+\frac{C_e}{Q_m}$$

where $C_e$ and $Q$ are equilibrium Cu(II) ions concentration (mmol/L) and equilibrium adsorption capacity (mmol/g), respectively; $Q_m$ and $b$ the Langmuir constants representing maximal adsorption capacity (mmol/g) and energy of adsorption (L/mmol), respectively. The straight lines were given by plotting $C_e/Q$ versus $C_e$, as shown in Fig. 6, which give the values of $b$ and $Q_m$ in Table 4 according to the intercept and slope of these lines, respectively. The maximum adsorption capacities of CSPC1, CSPC2, and CSPC3 are 1.06, 1.46, 1.60 mmol/g, respectively.

Table 4
Langmuir parameters for the adsorption of Cu(II) ions on CSPC at 20 °C

| Absorbents | $Q_m$ (mmol/g) | $b$ (L/mmol) | Correlation coefficient |
|---|---|---|---|
| CSPC1 | 1.06 | 8.53 | 0.9982 |
| CSPC2 | 1.46 | 19.48 | 0.9997 |
| CSPC3 | 1.60 | 38.04 | 0.9997 |

pH, 4.28; treatment time, 20 min; dose of CSPC, 60 mg.

### 3.7. Thermodynamic studies

Thermodynamic parameters such as change in Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) were determined using the following equations (Donat, Akdogan, Erdem, & Cetisli, 2005; Tahir & Rauf, 2003):

$$K_D=\frac{Q}{C_e}$$

$$\log K_D=-\frac{\Delta H}{2.303\ \mathrm{RT}}+\frac{\Delta S}{2.303R}$$

$$\Delta G=\Delta H-T\Delta S$$

where $K_D$ is the distribution coefficient, $Q$ (mmol/g) and $C_e$ (mmol/L) are the adsorption capacity and the Cu(II) concentration at equilibrium, respectively, $T$ is temperature in Kelvin and $R$ is the gas constant. $\Delta H$ and $\Delta S$ were obtained from the slope and intercept of the plots of log $K_D$ versus $1/T$ (Fig. 7.). Table 5 shows the calculated values of the thermodynamic parameters. The negative values of $\Delta G$ at various temperatures indicate the spontaneous nature of the adsorption process. The decrease in $\Delta G$ with the increase temperature shows that the adsorption is more favorable at high temperatures. The positive value of $\Delta S$ indicates that there is an increase in the randomness in the system solid/solution interface during the adsorption process. In addition, the positive value of $\Delta H$ indicates that the adsorption is endothermic.

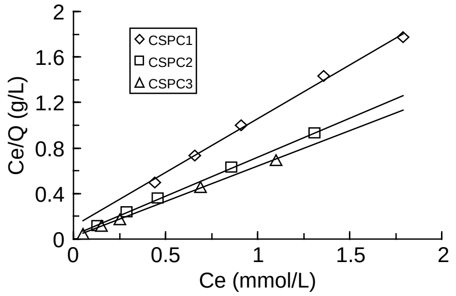

Fig. 6. Langmuir adsorption isotherms for the adsorption of Cu(II) ions on CSPC ($T=20$ °C; pH, 4.28; treatment time, 20 min; dose of CSPC, 60 mg).

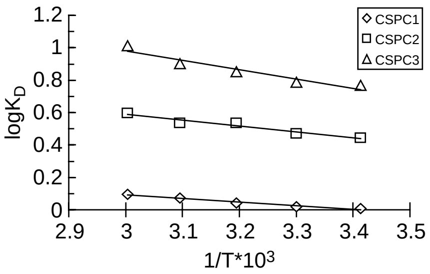

Fig. 7. The plots of log $K_D$ versus $1/T$ for the adsorption of Cu(II) on CSPC ($[Cu^{2+}]=2$ mmol/L; pH, 4.28; treatment time, 20 min; dose of CSPC, 60 mg).

Table 5
Thermodynamic parameters for the adsorption of Cu(II) onto CSPC

| Sample | Temperature (°C) | $Q$ (mmol/g) | $\Delta G$ (kJ/mol) | $\Delta H$ (kJ/mol) | $\Delta S$ (J/mol K) |
|---|---|---|---|---|---|
| CSPC1 | 20 | 0.92 | −0.01 | 4.23 | 14.47 |
| | 30 | 0.93 | −0.15 | | |
| | 40 | 0.95 | −0.30 | | |
| | 50 | 0.98 | −0.44 | | |
| | 60 | 1.00 | −0.59 | | |
| CSPC2 | 20 | 1.28 | −2.48 | 6.87 | 31.90 |
| | 30 | 1.30 | −2.80 | | |
| | 40 | 1.34 | −3.11 | | |
| | 50 | 1.34 | −3.52 | | |
| | 60 | 1.38 | −3.75 | | |
| CSPC3 | 20 | 1.46 | −4.15 | 11.16 | 52.25 |
| | 30 | 1.47 | −4.67 | | |
| | 40 | 1.49 | −5.19 | | |
| | 50 | 1.51 | −5.72 | | |
| | 60 | 1.54 | −6.24 | | |

$[Cu^{2+}]=2$ mmol/L; pH, 4.28; treatment time, 20 min; dose of CSPC, 60 mg.

Table 6
The desorption percentages of CSPC

| Sample | CSPC1 | CSPC2 | CSPC3 |
|---|---|---|---|
| $Q$ (mmol/g) | 0.93 | 1.41 | 1.55 |
| Desorption percentage (%) | 97.8 | 96.3 | 97.7 |

Desorption agent, 1 N HCl; treatment time, 60 min; $T=20$ °C.

### *3.8. Desorption studies*

An important characteristic of adsorbents is the desorption efficiency. The recovery of Cu (II) from CSPC was studied by utilizing desorption agents 1 N HCl. Table 6 gives the desorption percentages of CSPC. The desorption percentages of CSPC1, CSPC2, and CSPC3 are all greater than 96%. When the acidic solution makes contact with the loaded adsorbent, the $H^+$ has more affinity with the active groups so the Cu(II) ions is released. On the other hand, most of the active groups are on the particle surface, which makes the desorption process fast and complete.

## 4. Conclusions

Crosslinked starch phosphate carbamates were prepared by a solid-state technique. Their adsorption behavior toward Cu(II) ions from aqueous solutions was investigated by a batch technique under various conditions. The results show that adsorption reaches equilibrium in about 20 min. Moreover, adsorption capacity is strongly dependent on the initial Cu(II) ions concentration, pH of solution, and CSPC dose. The adsorption is endothermic in nature, and Adsorption equilibrium can be simulated by Langmuir isotherm with the maximum adsorption capacity of 1.60 mmol/g.

Preparation of CSPC is simple and low cost, and the materials can be biodegradable as used up to be favorable for environmental protecting. By raising the amount of substitute groups, Cu(II) adsorption activity of this modified starch could be increased up to the level required for industrial applications.

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