

Selective sorption and preconcentration of tartaric acid using a copper(II)-bound polymeric ligand exchanger

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Received 7 June 2007; received in revised form 24 July 2007; accepted 27 July 2007

Abstract

The current study reports a potential process to selectively separate and preconcentrate tartaric acid from its simulated industrial effluent. It was achieved by sorption onto a tailored polymeric ligand exchanger. The polymeric ligand exchanger is essentially a copper(II)-bound specialty chelating polymer (denoted D-Cu). Effect of solution pH and competing sulfate on tartaric acid sorption onto D-Cu was also included in the study. Compared to a weakly basic anion exchanger D-301, D-Cu exhibits more favorable sorption of tartaric acid from aqueous media coexisting with Na_2SO_4 at a high level. The exhausted D-Cu was amenable to an entire regeneration by the diluted NaCl solution. Results of column sorption tests further demonstrated the feasibility of D-Cu for selective separation and preconcentration of tartaric acid from the simulated wastewater for its further recovery.

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Keywords: Tartaric acid; Selective sorption; Preconcentration; Polymeric ligand exchanger; Cu(II)

1. Introduction

Fatty acids are widely used in food processing and pharmaceutical industry. During the manufacture process of fatty acids a great amount of waste streams are always generated rich in fatty acids and inorganic salts such as Na_2SO_4 . For example, industrial waste stream from the manufacture of tartaric acid, which is always present as an acidulant compound in soft drinks or as an additive in medicines and cosmetics, contains about 1–3 g/L tartaric acid as well as Na_2SO_4 at ~5 mass%. Currently, the stream is not suitable for reuse due to the relatively low concentration of tartaric acid and must be pretreated to minimize its negative environmental impact if disposal into the receiving body. However, high content of Na_2SO_4 makes the traditional treatment processes such as biological degradation less effective and of high cost [1]. On the other side, previous studies indicated that separation and preconcentration of tartaric acid from its industrial effluent is a potential choice for waste recovery [2–6], and some techniques such as solvent extraction [2,3], electrodialysis [4], chemical precipitation [5], membrane separation [6] and

evaporation could be useful to preconcentrate the tartaric acids from the waste stream.

As a simple operational technique, adsorption by activated carbon or polystyrene adsorbents is widely used for removal of organic compounds from aqueous media [7–10]. However, it is not suitable for the current purpose due to the strong hydrophilic interaction between tartaric acid and water. Use of polymeric anion exchanger is understandable for possible removal of organic acids [11–13], however, sulfate coexisting at concentration several order greater of magnitude results in a fast exhaustion due to the competitive effect. In recent years ligand exchangers bound with transitional metal ions such as Cu(II) and Fe(III) have been demonstrated for selective sorption of organic acids (always in anionic form) from solutions of high salinity [14–17], where the targeted acids can be regarded as ligands owing to the moiety of carboxylic and/or phosphate group. Typically, such sorbent is composed of a supporting matrix (a polymer) and a transition metal (Lewis acid) that is firmly immobilized on the matrix and serves as the functional group. Its preference towards organic anions is attributed to the concurrent electrostatic and Lewis acid–base interaction [14–16]. However, we have little knowledge of any studies involving the separation behavior of tartaric acid from its industrial effluent by such type of sorbent.

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In the current study we aimed to explore the feasibility of Cu(II)-bound polymeric ligand exchanger for selective separation and preconcentration of tartaric acid from the simulated wastewater. Batch sorption tests including effect of pH, isotherm, kinetics, competitive sorption as well as column sorption runs were performed to achieve the goal.

2. Materials and methods

2.1. Materials

Tartaric acid, CuSO₄ and Na₂SO₄ were of reagent grade and purchased from Shanghai reagent station (China) and solutions were prepared by double-distilled water. The chelating resin Dowex M-4195 was purchased from the Dow Chemical (USA) and D-301, a macroporous weakly anion exchanger (in chloride form), was kindly provided by Langfang Electrical Resin Co. Ltd. (Hebei, China). Prior to use the chelating resin Dowex M-4195 was packed within a glass column (30 mm diameter and 200 mm length) and rinsed by five-bed volume (BV) of 1 M HCl and 1 M NaOH solution in turn, finally washed with double-distilled water until the neutral pH of the effluent.

2.2. Preparation of the Cu(II)-bound polymeric ligand exchanger

The Cu(II)-bound polymeric ligand exchanger (denoted D-Cu hereafter) was prepared by passing CuSO₄ solution (containing 3200 mg/L Cu²⁺) through a glass column (30 mm diameter) packed with 100 g of Dowex M-4195 beads until the complete breakthrough of Cu(II) ion [15,16]. Then the sorbent particles were conditioned by rinsing with double-distilled water until reaching the neutral pH of the effluent. Finally, D-Cu particles were dried under vacuum at 40 °C before use.

2.3. Batch sorption and regeneration runs

Batch sorption tests were carried out in 250-mL glass flasks. To start the experiment, 0.100 g of D-Cu particles were introduced to a 100-mL solution with known solute concentration. The flasks were then transferred to a G25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.) and shaken under 200 rpm for 24 h at desired temperature to ensure the equilibrium sorption process, as indicated by the preliminary kinetic study. Hydrous sulfate or sodium hydroxide was used to adjust the solution pH throughout the experiment and Na₂SO₄ was introduced into the flask before sorption when necessary. 0.5-mL solution at various time intervals was sampled from the flasks to determine sorption kinetics. The D-Cu beads exhausted by tartaric acid during sorption runs were transferred to another flask after filtering and 50 mL of 2% NaCl solution at pH 2 was used for regeneration tests.

The amount of solute loaded on the sorbent particles is determined by conducting a mass balance on the solute before and after the test.

2.4. Column sorption test

Column sorption runs were carried out with a glass column (12 mm diameter and 230 mm length) equipped with a water bath to maintain a constant temperature. About 5 mL D-Cu beads (wet volume) were packed in the column for test use. A Lange-580 pump (China) was employed to assure a constant flow rate. The column sorption run was performed under the hydrodynamic conditions: the superficial liquid velocity (SLV) and the empty bed contact time (EBCT) were identical and equal to 0.10 m/h and 60 min, respectively. After sorption NaCl solution (8%, pH 2) was employed for regeneration of the exhausted sorbent particles.

2.5. Analysis

Tartaric acid in aqueous solution was determined by TOC analysis using the TOC-5000 analyzer (Shimuda, Japan). BET surface area and pore volume of all the related sorbents were obtained by N₂ physisorption using Micromeritics ASAP-2010C automatic analyzer (Australia). Cu(II) bound to the M-4195 beads was extracted by digesting the D-Cu beads using HClO₄ solution and determined by using an atomic absorption spectrophotometer (Hitachi Z-8100, Japan).

3. Results and discussion

3.1. Characterization of D-Cu

Some important properties of D-Cu are identified and shown in Table 1 by comparison with the host material M-4195 and a weakly basic anion exchanger D-301. It can be seen that Cu(II) has been successfully immobilized on the M-4195 beads as inferred from its content variation before and after loading. It is noteworthy to mention that the host sorbent undergoes a distinctive color change from dark brown to blue upon Cu(II) binding (in Fig. 1). In viewpoint of theory, the immobilized Cu(II) ions can interact with tartaric anions not only through electrostatic interaction, but also through Lewis acid–base interaction, where Cu(II) ions can be regarded as Lewis acid and tartaric anions as ligand (Lewis base) [14–16].

3.2. Effect of solution pH

Effect of solution pH on tartaric acid sorption by D-Cu was examined and the results are presented in Fig. 2. Tartaric acid uptake onto D-Cu increased as the solution pH increased to ~5,

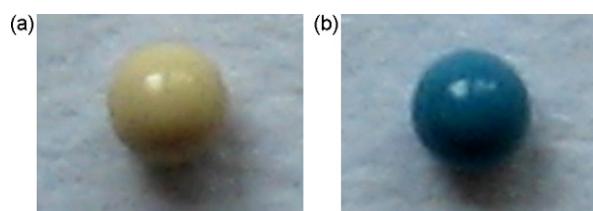
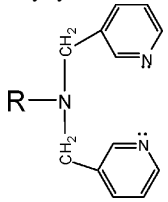
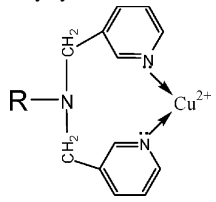
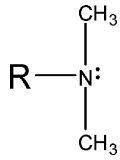


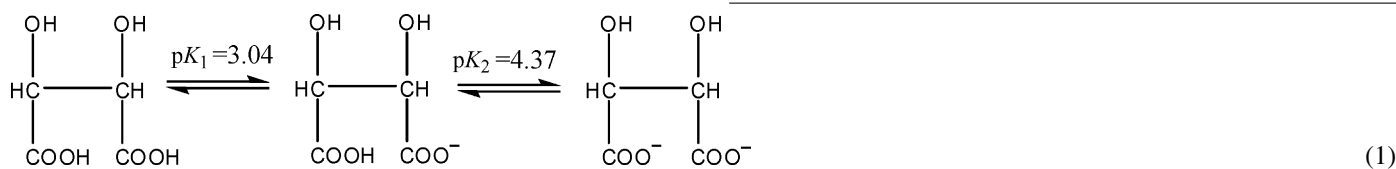
Fig. 1. Micrograph of Dowex 4195 and its Cu(II)-bound derivative D-Cu.

Table 1
Properties of Dowex M-4195, its Cu(II)-bound derivative D-Cu and a weakly basic anion exchanger D-301

Designation	Dowex M-4195	D-Cu	D-301
Matrix structure	Polystyrene	Polystyrene	Polystyrene
Structure			
BET surface area (m ² /g)	20.4	18.6	31.8
Average pore diameter (nm)	78.4	86.0	16.6
Pore volume (cm ³ /g)	0.078	0.095	0.125
Cu content (mg/g)	0	83.4	0
Particle size (mm)	0.6–1.0	0.6–1.0	0.5–1.2

and negligible variation of capacity was observed when solution pH ranged from 5 to 8. Further increase of solution pH results in a marked drop of the uptake of tartaric acid, and the capacity even approaches to zero at solution pH of 12.

In general, tartaric acid will be dissociated as



and only the negatively charged tartaric anions can be effectively bound to the D-Cu beads through electrostatic interaction and ligand interaction [14–17]. Expectedly, when the solution pH increases from 1 to about 5, the tartaric acid will be gradually dissociated into anionic form negatively charged with one or two electrons (in A⁻ or A²⁻ form). Consequently, the electrostatic interaction between tartaric acid and D-Cu results in an increase of tartaric acid uptake, as seen in Fig. 2. The deep drop in uptake capacity within pH 8–12 is mainly caused by the firmly

binding of Cu²⁺ with OH⁻ from aqueous solution. Under such conditions, Cu(II) ions bound on the polymeric matrix will be transferred into the neutral Cu(OH)₂ and cannot effectively interact with tartaric anions through electrostatic or Lewis acid–base interaction.

3.3. Sorption isotherms

The sorption isotherms of tartaric acid onto D-Cu at 298 K are illustrated in Fig. 3. The isotherms were then correlated by Langmuir and Freundlich models [18–20].

$$q_e = \frac{bq_0C_e}{1 + C_e} \quad (2)$$

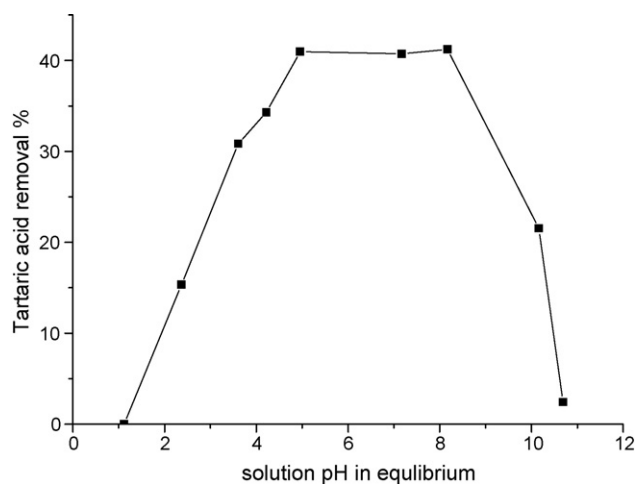


Fig. 2. Effect of solution pH on tartaric acid sorption onto D-Cu at 25 °C (0.1 g D-Cu was added into 100-mL solution containing 100 mg/L tartaric acid and 1% Na₂SO₄).

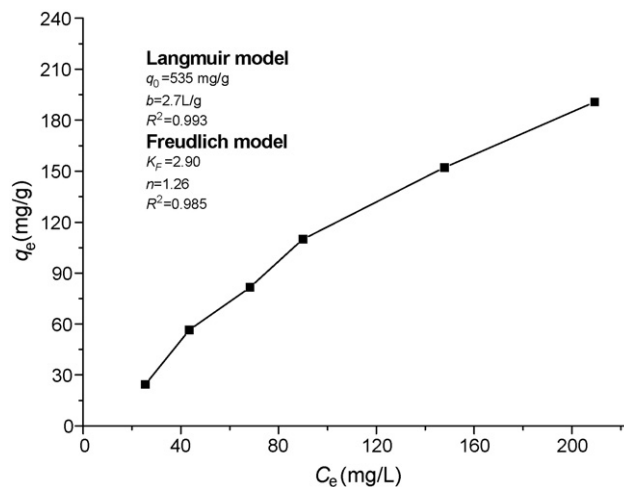


Fig. 3. Sorption isotherms of tartaric acid onto D-Cu at 25 °C (solution pH 6.7–7.0).

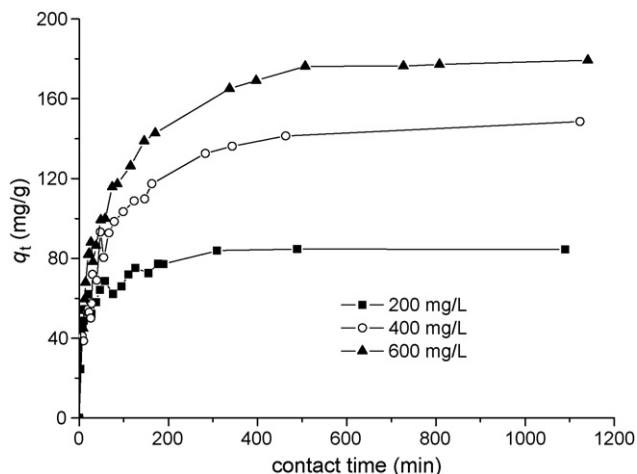


Fig. 4. Sorption kinetics for tartaric acid sorption onto D-Cu at different initial concentrations at 25 °C (2 g D-Cu particles were added into 1000-mL solution; pH 6.5–7.0).

$$q_e = K_F C_e^{1/n} \quad (3)$$

where q_e is the equilibrium solute uptake on the sorbent (mg/g), C_e the equilibrium solute concentration in solution (mg/L), q_0 the monolayer sorption capacity of the sorbent (mg/g), b the Langmuir constant (L/mg) related to the free energy of sorption; K_F and n are the Freundlich constants to be determined. It can be seen in Fig. 3 that Langmuir model can represent tartaric acid sorption onto D-Cu more reasonably, as indicated by their different correlation coefficient values (R^2).

3.4. Sorption kinetics

Fig. 4 depicts the plots of tartaric acid uptake onto D-Cu versus contact time at different initial concentration of tartaric acid. It can be seen that the sorption equilibrium was achieved within 400 min. Kinetic data was then represented by the pseudo-second-order model [18–20].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e and q_t are the amount of tartaric acid loaded (mg/g) at equilibrium and at time t (min), k_2 is the pseudo-second-order rate constant (g/(mg min)). Higher correlation coefficients and the calculated q_e values (Table 2) close to the experimental data indicated that tartaric acid uptake onto D-Cu can be approximated favorably by the pseudo-second-order model. Also, the second-order rate constants decrease with increasing initial concentration. Similar results were reported elsewhere

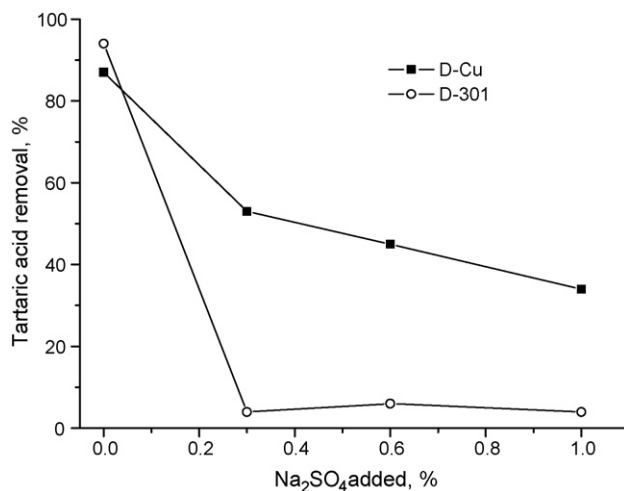


Fig. 5. Effect of initial Na_2SO_4 concentration on tartaric acid sorption onto D-Cu and D-301 at pH 6.7 and 25 °C (0.10-g D-Cu or D-301 beads were added into 100-mL solution containing 100 mg/L tartaric acid).

for sorption of dyes onto sepiolite [18] or mesoporous hybrid xerogel [20].

Based on the pseudo-second-order model, the initial sorption rate (u) and half-sorption time ($t_{1/2}$) are also calculated in Table 2 according to the following equations [19,20]:

$$u = k_2 q_e^2 \quad (5)$$

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (6)$$

Half-sorption time is the time required for the sorption to take up half as much tartaric acid as its equilibrium value. This time is an indicator for the sorption rate.

3.5. Effect of Na_2SO_4

Taken into account that Na_2SO_4 coexist with tartaric acid in industrial wastewater, effect of Na_2SO_4 on tartaric acid sorption onto D-Cu was examined by comparison with a weakly basic anion exchanger D-301. The weakly basic anion exchanger has been demonstrated for effective removal of organic acids from aqueous media through electrostatic interaction [11–13,20–22]. Results in Fig. 5 indicated that high removal of tartaric acid is readily achieved by D-Cu or D-301 when Na_2SO_4 was absent in solution. However, Na_2SO_4 added in solution markedly decrease the capacity of tartaric acid onto D-301 and the capacity even approaches to zero in the presence of Na_2SO_4 at 0.3 mass%. For D-Cu beads, Na_2SO_4 also plays a negative role on tartaric

Table 2
The pseudo-second-order kinetics parameters for tartaric acid sorption onto D-Cu at 25 °C

C_0 (mg/L)	q_e (mg/L)		k_2 ($\times 10^{-4}$ g/(mg min))	u (mg/g min)	$t_{1/2}$ (min)	R^2
	Calculated	Experimental				
200	85.5	82.3	8.59	0.22	18.6	0.999
400	153.6	150.2	1.55	0.31	47.5	0.999
600	184.2	182.3	1.51	0.30	51.7	0.999

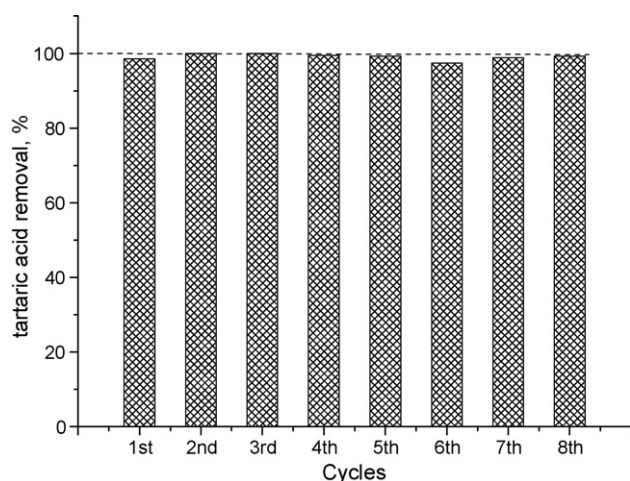


Fig. 6. Results of continuous batch sorption–regeneration cycles at 25 °C (Sorption: 0.10-g D-Cu, 100 mL solution containing 100 mg/L tartaric acid, 25 °C; Regeneration: the identical D-Cu beads exhausted in sorption runs, 50 mL 2% NaCl solution (pH 2), 30 °C).

acid sorption, but it still exhibits more favorable sorption than D-301 under the identical conditions. Such different behavior is attributed to their different sorption mechanism for tartaric acid. For D-301 anion exchange is the sole mechanism for sorption of organic acid, while the concurrent electrostatic and Lewis acid–base type interaction is responsible for tartaric acid sorption onto D-Cu particles.

3.6. Continuous batch sorption–regeneration cycles

To further test the applicability of D-Cu beads, we next carried out a continuous batch sorption–regeneration cycle experiment and the results are presented in Fig. 6. The removal efficiency of tartaric acid is kept constant during the cycle experiments, and the regeneration efficiency of the exhausted sorbent is all about 100% (data not shown). At the end of the experiment we determined the Cu(II) content of the sorbent (83.2 mg/g),

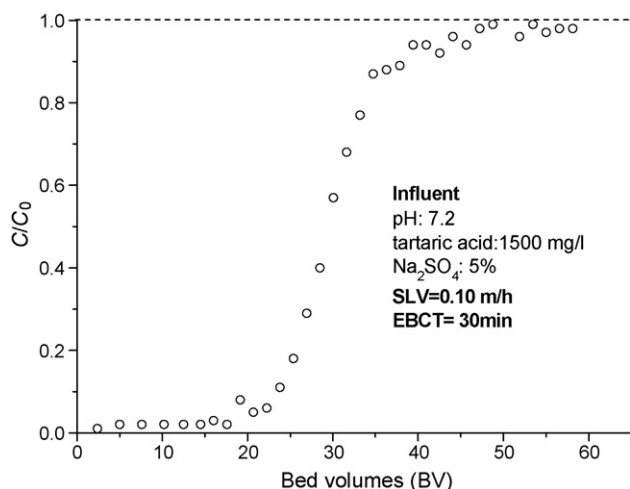


Fig. 7. A complete breakthrough curve of tartaric acid sorption onto D-Cu at 25 °C.

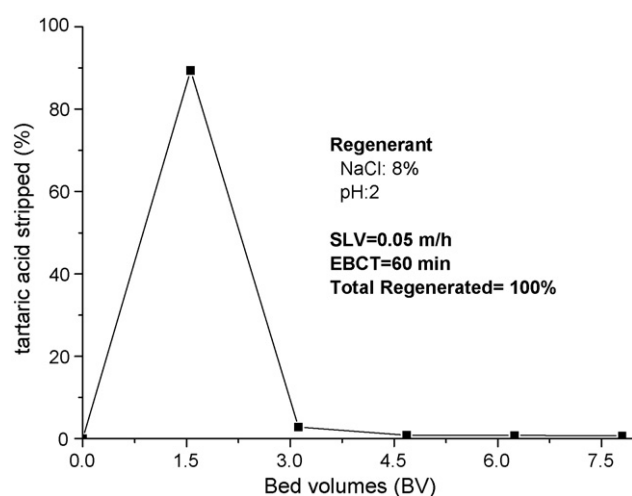


Fig. 8. A regeneration curve of the D-Cu beads exhausted by tartaric acid at 30 °C.

which indicated the negligible leaching of Cu(II) during the cycle runs. Such satisfactory performance further implied that Cu(II) is firmly bound to the polymeric ligand exchanger and the hybrid sorbent is suitable for continuous runs such as in field application.

3.7. Column sorption run

Fig. 7 illustrated an effluent history of a separate fixed-bed column packed with D-Cu for simulated industrial effluent containing tartaric acid and competing Na₂SO₄ at 5%. Satisfactory breakthrough results observed is consistent with its excellent performance described above. The regeneration results in Fig. 8 indicated that the exhausted D-Cu was amenable to an entire regeneration and the tartaric acid loaded on D-Cu can be completely rinsed within two to three bed volumes. Taken into the fact that significant breakthrough only occurred after 20 or more bed volumes during the sorption run (Fig. 7), preconcentration of tartaric acid is therefore realized through regeneration of the exhausted sorbent particles, which is significant for potential recovery of tartaric acid from its industrial wastewater.

4. Conclusion

In the present study, a hybrid sorbent (namely D-Cu) was prepared by binding Cu(II) onto a polymeric ligand exchanger Dowex M-4195. The sorbent exhibited satisfactory performance for tartaric acid sorption from aqueous media even coexisting with Na₂SO₄ at a high level. Moreover, the exhausted sorbent particles are amenable to an entire regeneration by using NaCl solution as the regenerant. Continuous sorption–regeneration cycle runs indicated that Cu(II) is firmly bound onto the polymeric ligand exchanger. Column sorption and regeneration tests suggested that sorption onto D-Cu is a potential alternative for selective removal and preconcentration of tartaric acid from aqueous media, which is of significance for recovery of tartaric acid from its industrial effluent.

Acknowledgments

The study was financially supported by Natural Science Funding of China (20504012) and Jiangsu NSF (BK2007717/2006129).

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