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Adsorption of tartaric acid–cadmium complex by imprinted chitosan biopolymer

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ABSTRACT

In this study, cross-linked imprinted chitosan polymer (ICP) was synthetized from chitosan (CS), using tartaric acid–cadmium complex (TA–Cd) as template, and glutaraldehyde as the cross-linker. The parameters of influence of the sorption process were studied: solution pH, oscillating time and temperature. Results suggest that the most important factor affecting the effectiveness of sorption is pH and oscillating time. The second-order kinetics model was more suitable to describe the sorption kinetics on CS than the first-order kinetics model. Furthermore, the TA–Cd–ICP could be regenerated using 0.1 M HCl solutions and could be reused for seven times with about 12.30% regeneration loss.

Keywords: Chitosan; Molecular imprinting; Tartaric acid–cadmium complex; Biopolymer

1. Introduction

Cadmium in the environment is concerned increase because of known toxicities of it to human beings [1], and cadmiun mainly exist in water, soil, and air. However, there is no chelation therapy for cadmium toxicity approved for clinical use in environment. Under this situation, environmental and food scientists have done a great many of works to solve those problems through removing heavy metals from soil, water, sea product, and other materials. It is well known that the mineral acids and metal chelating agents, like tartaric acid [2], citric acid [3], ethylene diamine tetraacetic acid, [4] and dilute sulfuric acid [5] have already been reported to remove Cd from contaminated soil and sea food waste.

Since it is necessary to remove Cd ions before discharge the leaching liquid, an economical process for removing low levels Cd ions from such a large volume of organic acid leaching liquid was significant. Precipitation, oxidation and reduction, ion exchange, filtration, reverse osmosis, electro-chemical removal, and evaporative can be used to treat industrial effluents for recovery metals [6,7]. However, these methods are all inefficient such as ion exchange and membrane separation which require high operation cost, and precipitations are unfavorable especially when dealing with large volumes of matter that

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Presented at the 2012 Qingdao International Desalination Conference June 26–29, 2012, Qingdao, China contains heavy metal ions in low concentration [8]. Magnesia is a good precipitating agent for Cd ions, which reach high pH ranges (10–11) in any other solution [9], but its precipitates are difficult to be separated with their own characteristics [10].

For economic and effective reasons, metal bios option by biomass materials have been well established [11]. For instance, Chitosan (CS) and its derivates could bind heavy metal ions strongly and could be used for heavy metals absorption, such as Cu(II), Ni(II), Zn(II) [12–14], Fe (II) and Fe (III) [15], and Cd (II) [16] with lower specific recognition.

At present, molecularly imprinted polymers have aroused rapid attention and been widely applied in many fields, such as solid-phase extraction, chemical sensors, and artificial antibodies owing to their desired selectivity, physical robustness, thermal stability, as well as low cost and easy preparation, its recognition is based on the specificity of the ligand, on the coordination geometry, the coordination number, the charge, and the size of metal ions [17]. So far, many metal ion-imprinted polymers have been prepared, including uranium [18]. Cu, Zn, Ni, and Pb [19–22], as well as Cd from aqueous solution [23]. However, there are seldom investigations reported in the literatures on the removal of citric acid–cadmium complex by tartaric acid–cadmium complex–imprinted chitosan polymer (TA–Cd–ICP) from aqueous solution.

In this study, we attempted to research the removal efficiency of less-researched TA–Cd complex from dilute solutions by molecular imprinted biosorbents. Experiments were performed as a function of different pH, oscillating time, and temperature. Then, the adsorption kinetics, isotherm, and selectivity were carried out to investigate the mechanism of TA–Cd adsorption onto TA–Cd–ICP.

2. Experimental

2.1. Materials

CS (degree of deacetylation = 92%, and Mw = 5.0 $\times 10^5$) was purchased from Haihui Bioengineering Co., Ltd. (Qingdao, China). Metal ions standard were all obtained from National Steel Material Test Center (Beijing, China). Cadmium chloride, glutaraldehyde, and all the other reagents used in this study were of analytical grade and used as received without further purification, all reagents were prepared in Millipore milli-Q deionized water (DW).

2.2. Preparation of biosorbent polymer

The experimental procedure for the preparation of the new biosorbent polymer (TA–Cd–ICP) was as follows: Cadmium chloride was dissolved in 50 ml 0.1 M tartaric acid to give a Cd (II) solution of 20 mg/L as the complex of TA–Cd. Then the pH was adjusted to be 7.0, and 1.0 g CS (dry weight) was added into above solution, and the mixture was stirred for 12 h. Then, the mixture was recovered by filtration through filter paper and washed with DW until Cd (II) could not be detected, and the CS composite was dried in a vacuum oven at 323 K for 4 h.

Afterwards, amount of CS composite was added in 50 ml DW, and the pH value was adjusted to 7.0 with NaOH/HCl (0.1 M), and glutaraldehyde as a cross-linking agent was added in the system, stirred for 4–6 h at 333 K. Then, the mixture was recovered by filtration, and the residue was rinsed with ethanol and DW for three times at least.

Eventually, the template TA–Cd complex was removed from the polymer using 0.1 M HCl by monitoring with sodium sulfide, and the procedure was repeated several times until the Cd(II) could not be detected. The polymer was added into 0.1 M sodium hydroxide aqueous solution for 4–8 h to active amino group and dried in vacuum oven at 323 K for 4 h. Not molecular imprinted polymers (NIMIPs) was similarly synthesized in the absence of TA–Cd complex.

2.3. Adsorption experiments

2.3.1. Effect of pH

The pH is one of the most important parameter affecting adsorption of metal ions on adsorbents. The experiments were performed at controlled pH (2–12), and 303 K by shaking 0.1 g of dry polymer with 25 ml (20 mg/L) TA–Cd solution for 12 h at 160 rpm, and the solution pH was adjusted to the desired value by NaOH/HCl (0.1 M). After equilibration, the residue concentration of TA–Cd was determined with a flaming atomic absorption spectrophotometer (AA-6800, Shimadzu Ins.) at 228.8 nm wave numbers.

2.3.2. Effect of oscillating time

Oscillating time affects adsorption of TA–Cd at different time intervals was obtained by shaking 0.1 g of biopolymer in a flask containing 25 ml (20 mg/L) TA–Cd solution at pH 8.0 under 160 rpm and 303 K. One milliliter of sample was taken at time interval to determine the residual metal concentration in the residue solution.

2.3.3. *Effect of temperature*

The uptake of TA–Cd complex at different temperature was obtained by placing 0.1 g polymer in a series of flasks containing 25 ml (20 mg/L) at pH 8.0, the flasks were agitated on a shaker at 160 rpm for 12 h. After equilibration, the uptake value of TA–Cd complex was calculated.

2.3.4. *Adsorption kinetics*

Adsorption kinetics was performed by 0.1 g biopolymer in 25 ml metal solution (20 mg/L) at pH 8.0 and the flasks were agitated at 160 rpm under different time. One milliliter of samples was taken at time intervals for the analysis of residual TA–Cd complex concentration and the uptake value was obtained.

2.3.5. *Adsorption isotherm*

Complete adsorption isotherms of TA–Cd complex was obtained by placing 0.1 g biopolymer in the flasks containing 25 ml of TA–Cd complex at definite concentration (2.5–20 mg/L) at pH 8.0. The flasks were agitated on a shaker at 160 rpm for 12 h while keeping the temperature at 293, 303, 313, or 323 K. After equilibration, the residual concentration of TA–Cd was determined.

2.3.6. *Adsorption selectivity*

The selectivity adsorption behavior was measured by the uptake between TA–Cd and TA–Zn with TA–Cd–ICP, and place 0.1 g biopolymer with 25 ml metal ions solution (20 mg/L) in a series of flasks at pH 8.0 and 303 K for interval time.

2.3.7. *Desorption and reuse after desorption*

Desorption experiments were carried out using 0.1 M HCl solutions. After having adsorbed the TA–Cd complex, the TA–Cd–ICP (0.1 g) was washed with DW several times and transferred into flasks. Then, 25 ml of the desorption agent (0.1 M HCl) was added and shaken at room temperature (298 K) for 1 h. Afterwards, the concentration of TA–Cd released from TA–Cd–ICP into aqueous phase. The TA–Cd–ICP after desorption was reused in adsorption experiment, and the process was repeated for seven times.

3. Results and discussion

3.1. *Influence of pH*

As well known, the adsorption process of metal ions was sensitive to pH at low pH [24]. The adsorption of TA–Cd complex ions on the investigated resins as a function of pH is shown in Fig. 1. The highest uptake value was observed at pH 8.0 for TA–Cd–ICP compared with NIMIPs. At lower pH (<6.0), the active sites on biopolymer become protonated and their ability for interaction with TA–Cd decreases. It can be attributed to the competitive binding of H^+ and TA–Cd complex to amino group. Hence, pH 8.0 was chosen as the optimal pH in the following experiments.

3.2. *Effect of oscillating time*

Fig. 2 shows the change in the uptake of TA–Cd complex by the given adsorbent as a function of time. The kinetic curves for TA–Cd complex showed that the adsorption was initially rapid and reached equilibrium after approximately 120 min. The fast uptake in the beginning can be attributed to the greater concentration gradient and more available sites for interaction. The fast adsorption equilibrium in the case of TA–Cd–ICP is probably attributed to high complexation and geometric shape affinity between TA–Cd and cavities in the TA–Cd–ICP structure. As well known, when the template was removed from the biopolymeric matrix leaving cavities of imprinting sites, specific space, or chemical functionality to the template [25]. The adsorption data were treated according to kinetic models of first-order kinetics, Eq. (1) [26] and second-order kinetics, Eq. (2) [27].

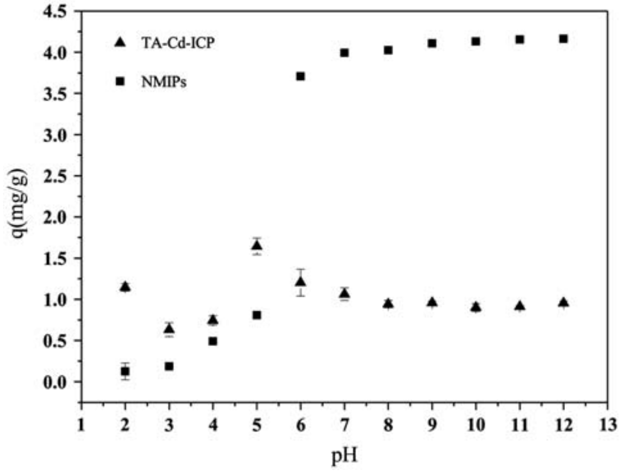

Fig. 1. Effect of pH on the uptake of TA–Cd by TA–Cd–ICP and NIMIPs (initial concentration 20 mg/L, adsorption dose 0.1 g, contact time 12 h, shaking rate 160 rpm, 303 K).

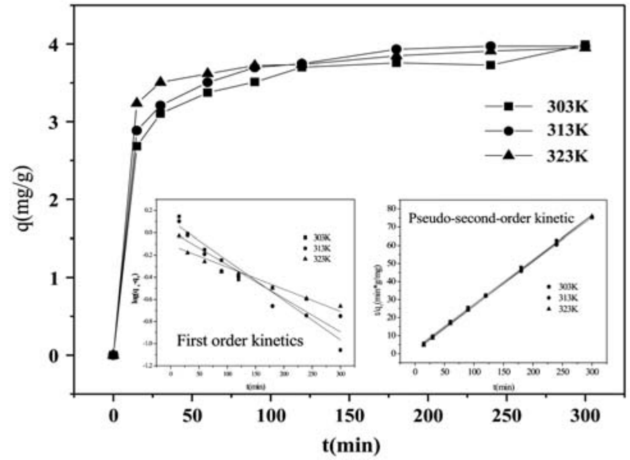

Fig. 2. Effect of adsorption time on the uptake of TA–Cd by TA–Cd–ICP (initial concentration 20 mg/L, solution pH 8.0, adsorbent 0.1 g, shaking rate 160 rpm, 303 K) and the first-order kinetics (the left insert figure), second-order kinetics (the right insert figure).

$$\log(q_e - q_t) = \log q_e - \frac{\circ K_1 t}{2.303} \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where t is the contact time (h), q_t and q_e are the amount of TA–Cd complex adsorbed at an arbitrary time and at equilibrium (mg/g), and K_1 (min^{-1}) or K_2 (g/mg min) is the rate constant, respectively (Table 1).

3.3. Effect of temperature and adsorption isotherms

The adsorption isotherms of TA–Cd complex on the investigated biopolymer at different temperatures are shown in Fig. 3. The adsorption of TA–Cd complex increases with the increase in the initial TA–Cd complex concentration. The Freundlich equation is an empirical equation employed to describe heterogeneous systems. In addition, the Freundlich equation describes reversible adsorption and is not restricted to the formation of the monolayer. In this work, Freundlich model is employed to analyze the data.

Freundlich isotherm equation [28]:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K \tag{3}$$

where q_e is solid-phase sorbate concentration in equilibrium (mg/g), C_e is liquid-phase sorbate concentration in equilibrium (mg/L). K is Freundlich constant ($L^{1/n}$ mg$^{1-1/n}$/g) and $1/n$ is the heterogeneity factor.

As shown in Fig. 3 and Table 2, the Freundlich constant of the TA–Cd on TA–Cd–ICP decreased with increasing temperature when the temperature was higher than 313 K. This might be attribute to the fact that the interaction between the TA–Cd complex and the active groups of TA–Cd–ICP was weaker at higher temperatures. Furthermore, It is evident from those data that Freundlich isotherm model is well fitted ($R^2 > 0.98$). In other words, it predicts that the TA–Cd concentrations on the adsorbent will increase so long as there is an increased in the TA–Cd concentration in the aqueous solution.

3.4. Evaluation of the selective adsorption

As seen from Fig. 4, the selective uptake studies were carried out under the optimum conditions. It can be seen that the adsorption capacity of TA–Cd is higher than TA–Zn complex with increasing oscillating time. This result is attributed to the specific recognition cavities for TA–Cd created in TA–Cd–ICP,

Table 1
Kinetic parameters for TA–Cd adsorption by TA–Cd–ICP

First-order model

T/K	Regression equation	K_1 (min^{-1})	q_e (mg/g)	R^2
303	log (q_e–q_t) = 0.1104–0.00359t	0.0083	1.29	0.93542
313	log(q_e–q_t) = 0.0171–0.00304t	0.0071	1.04	0.8927
323	log(q_e–q_t) = −0.1078–0.00200t	0.0046	9.89	0.9257

Second-order model

T/K	Second-order model	K_2 (g/mg min)	q_e (mg/g)	R^2
303	$t/q = 0.2461t + 2.7846$	0.061	4.06	0.9986
313	$t/q = 0.2481t + 2.1082$	0.062	4.03	0.9997
323	$t/q = 0.2502t + 1.4253$	0.063	4.00	0.9997

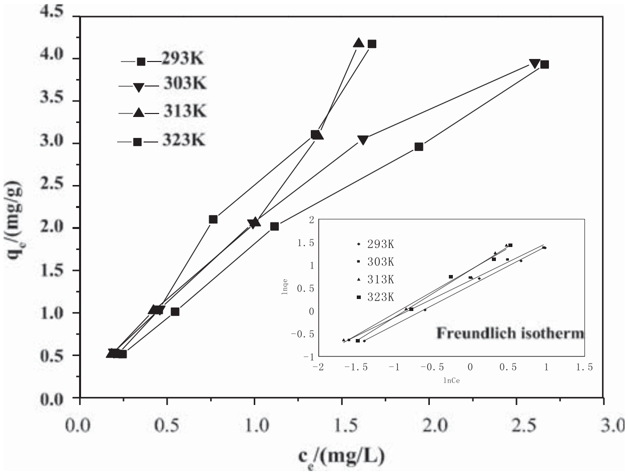

Fig. 3. Adsorption isotherms of the uptake of TA–Cd by TA–Cd–ICP (initial concentration 2.5–20 mg/L, solution pH 8.0, adsorbent 0.1 g, shaking rate 160 rpm, 293–323 K), the Freundlich isotherm (the insert figure).

Table 2
Freundlich isotherm constants for the adsorption of TA–Cd on TA–Cd–ICP

T (K)	Freundlich isotherm equation	K ($\mathrm{L}^{1/n}\,\mathrm{mg}^{1-1/n}/\mathrm{g}$)	R^2	n
293	$\ln q_\mathrm{e} = -0.5443 + 0.8590 \ln C_\mathrm{e}$	3.5	0.9982	1.16
303	$\ln q_\mathrm{e} = -0.6663 + 0.8085 \ln C_\mathrm{e}$	4.6	0.9957	1.24
313	$\ln q_\mathrm{e} = -0.8911 + 0.9518 \ln C_\mathrm{e}$	7.9	0.9842	1.05
323	$\ln q_\mathrm{e} = -0.8885 + 1.0336 \ln C_\mathrm{e}$	7.7	0.9920	0.97

which are developed by ion complex imprinting. Based on the above results, it is evident that TA–Cd–ICP has a strong ability to adsorb TA–Cd complex from other organic acid–metal complex present in aqueous solutions.

3.5. Desorption and regeneration studies

Regeneration of the adsorbent was carried out using 0.1 M HCl. The reusability of TA–Cd–ICP for TA–Cd adsorption was shown in Fig. 5. It was revealed that the adsorption capacity of TA–Cd–ICP for TA–Cd decreased slightly from 3.63 to 2.39 mg/g with increasing the times of reuse. TA–Cd–ICP could be reused for seven times with about 34.43% regeneration loss, which indicated that TA–Cd–ICP had a good reusability.

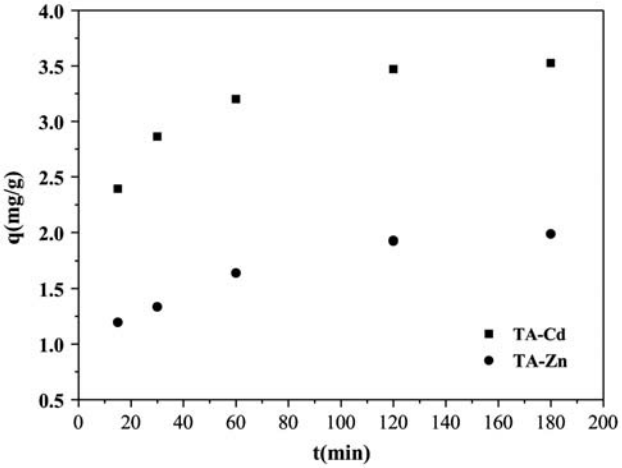

Fig. 4. Evaluation of the selective adsorption by TA–Cd–ICP (initial concentration of TA–Cd and TA–Zn are 20 mg/L, solution pH 8.0, adsorbent 0.1 g, shaking rate 160 rpm, 303 K).

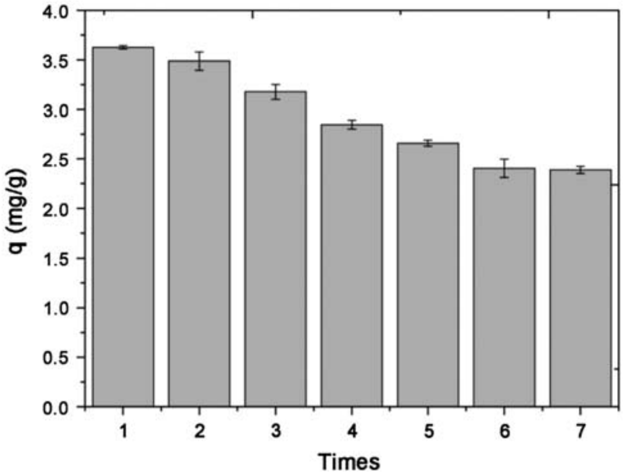

Fig. 5. Relationship between the times of reuse and adsorption capacity of TA–Cd (adsorption conditions: initial concentration of TA–Cd is 20 mg/L, solution pH 8.0, adsorbent 0.1 g, shaking rate 160 rpm, 303 K).

4. Conclusions

In this study, the new job of imprinted TA–Cd complex on chitosan biopolymer was prepared successfully. Further, adsorption of TA–Cd onto TA–Cd–ICP fitted the Freundlich adsorption isotherms, and the kinetics of adsorption followed a pseudo second-order rate equation well. An overall selectivity for TA–Cd was observed showing that TA–Cd–ICP can be used effectively to remove and recover TA–Cd from aqueous solutions. In addition, it was also suggested that TA–Cd–ICP could be reused for seven times with 12.30% regeneration loss.

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