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Fabrication of modified porous starch for the removal of vanadate from aqueous solutions

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ABSTRACT

The dithiocarbamate-modified porous starch (DTCPS) was synthesized. It is a cheap sorbent with super adsorption ability for V(V) ions removal from aqueous solutions. Surface structure of DTCPS was confirmed by using SEM, Fourier transform infrared spectra and TGA. The DTCPS has many micropores, which favours the adsorption of V(V) ions. Adsorption results indicate that mechanism is predominately based on electrostatic attraction. The adsorption of V(V) ions on DTCPS was largely dependent on the pH value, and the optimal pH was 3.0. In such solution, the decavanadate $V_{10}O_{26}(OH)_2^{4-}$ and $V_{10}O_{27}(OH)^{5-}$ are main species. They adsorbed to DTCPS following the pseudo-second-order equation and Langmuir isotherm.

Keywords: Modified porous starch; Synthesis; Characterization; Vanadate; Adsorption

1. Introduction

With a large number of applications of chemical technology in human daily lives, as well as in various industries, various emerging contaminants are continually being found. Heavy metals, such as copper, zinc, and vanadium, are often observed in discharged effluents [1]. It is necessary to remove the harmful metal ions from industrial effluents before they are discharged into the environment. Especially, vanadium (V) having strong toxicity is widely used in various industries, such as ceramic, glass, and textile [2]. The adsorption of vanadium (V) on various adsorbents is considered to be an important issue [3,4]. It has long been studied and recognized as one of the most important techniques [5]. Proper selection of adsorbent using in the adsorption procedure will yield high-quality-treated effluents. Many materials, such as chitosan [6], and aluminum-pillared bentonite [7], have been used for the removal of vanadium ions from aqueous solution.

Among these materials, starch as abundant, inexpensive, renewable and fully biodegradable natural raw material has demonstrated its superiority [8]. In our previous studies, a new kind of crosslinking starch was developed as copper, nickel and chromate fixation agents [9–11]. However, they could not fix the vanadium (V) effectively. Low specific surface area of

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starch limited its application in the engineering, even the modified starch. The appearance of porous starch (PS) has attracted much attention due to higher specific surface area. Many biodegradable starches have been developed for a variety of applications, such as drug delivery [12] and desiccants [13]. However, there is no report on the recovery of vanadium (V) from aqueous solution using starch and its derivates. In this context, new PS is designed for vanadium (V) fixation.

The main enzyme involved in starch hydrolysis is α-amylase that catalyses the hydrolysis of α-1,4-glycosidic linkages of starch to maltose and dextrins, reducing the molecular size of starch [14]. It was also shown that α-amylase was even able to degrade chemically modified starch. In this paper, we obtained a PS by hydrolysis of starch using α-amylase. Furthermore, its vanadium (V) fixation ability was investigated. Such observations provided new insights into vanadium (V) interacting with PS.

2. Experimental

2.1. Materials

Food-grade quality of corn starch, glucoamylase, α-amylase, ammonium vanadate and other routine reagents were purchased from the Shanghai Reagents Company.

2.2. Techniques

Thermogravimetric analysis was performed with STA 409PC/4/HLux at a heating rate of 10℃ per minute under N_2 atmosphere. Fourier transform infrared spectra (FT-IR) were recorded on a PE Spectrum One spectrometer with KBr pellets in the 4,000–450 cm^{-1} region. The total vanadium contents were determined by inductively coupled plasma atomic emission spectroscopy on POEMS-2. Specific surface area was determined by TRISTAR3000 BET determinator and obtained by equation of Brunauer–Emmett–Teller (BET).

2.3. Preparation of PS

The PS was first synthesized as reported previously [15]. About 30 g corn starch was immersed in the buffer solution (sodium citrate/disodium hydrogen phosphate, pH 5.0) with stirring to form a starch suspension. Next, 1.0 g admixture of glucoamylase and α-amylase (5:1, w/w) was added to the suspension. The mixture was stirred for 20 h at 45℃, and the precipitate was separated from the solution by washing five times with deionized water. The acquired PS was kept in a vacuum oven for 1 d.

2.4. Preparation of dithiocarbamate-modified PS

The crosslinked porous starch (CPS) was synthesized by react 100 g PS with 0.8 mL epichlorohydrin (ECH) in 200 mL dilute NaOH solution (0.16 mol L^{-1}) under 25℃. After 18 h, the pH was adjusted to 6–7, and the CPS was separated from solution. Then, the intermediate, 3-chloro-2-hydroxypropyl crosslinked porous starch (CHCPS) was prepared from 25 g of dried CPS with 15 mL ECH in the presence of 60% $HClO_4$. The dried CHCPS further reacted with ethylenediamine to produce ethylenediamine-modified cross-linked porous starch (CAPS) in basic solution under 80℃ for 12 h. Then, 10 g dried CAPS further reacted with 5 mL CS_2 in alkaline solution. The mixture was warmed up to 40℃. After 12 h, the precipitation was separated and washed with deionized water, dilute HCl solution, dilute NaOH solution and acetone in sequence. The acquired dithiocarbamate-modified porous starch (DTCPS) was kept in a vacuum oven for 1 d and stored in desiccators. The procedure was depicted in Fig. 1.

2.5. Sorption experiments

Adsorption studies were performed using a batch technique. The effect of solution pH on the adsorption of vanadium ions onto DTCPS was investigated at 25℃. The effect of pH was observed by studying the adsorption of vanadium over a pH range of 2−10. Each flask was filled with 50 mL of a V(V) solution for a concentration of 80 mg L^{-1} at different pHs. The flasks were shaken for 12 h in a shaking thermostatic bath to reach equilibrium and the concentrations of vanadium were measured. The amount of vanadium

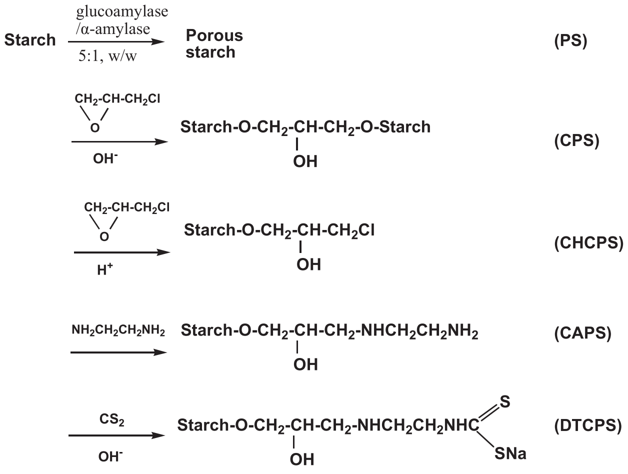

Fig. 1. Synthesis of DTCPS.

sorbed onto unit mass of DTCPS (sorption capacity, mg g^{-1}) was calculated from:

$$q_e m = (c_0 - c_e)V \tag{1}$$

where q_e is the vanadium concentration in the solid phase (adsorbent) at equilibrium (mg g^{-1}), m is the mass of DTCPS used (g), c_0 is the initial vanadium concentration in the liquid phase (mg L^{-1}), c_e is the vanadium concentration in the liquid phase at equilibrium (mg L^{-1}), and V is the total volume of solution used (L).

The adsorption kinetics was studied with the initial vanadium concentration of 80 mg L^{-1}, and the volume of solution was 50 mL. The solution pH value was kept at 3.0 by the measurement. The concentration of vanadium was measured at different time intervals up to equilibrium. For the equilibrium adsorption studies, 0.05 g of DTCPS was weighted into 50 mL V(V) solution with a known amount concentration (varying from 30 to 150 mg L^{-1}), pH value maintained 3.0 and agitated for 24 h at 25℃. The models of the kinetics and isotherms were fitted to experimental data using a nonlinear method, with the nonlinear fitting facilities of the Microcal Origin 7.0 software.

3. Results and discussion

3.1. Characterization of DTCPS before and after adsorption of V(V)

It is well-known that surface morphology of the adsorbent can affect its adsorption performance. Fig. 2 shows the SEM images obtained for DTCPS before and after adsorption of V(V). As is clearly seen here, the beads have dent but the surface is smooth surface. The presence of pores within the bead interior is clearly seen in this photograph. Such pores are helpful not only for the increase in specific surface area but also for the mass transfer of ions [16]. After the adsorption of V(V), the surface of the DTCPS-V became rougher and aggregation together simultaneously due to the adsorption of ions. It can be considered that the micropores reduce the diffusion resistance and facilitate mass transfer because of their high internal surface area.

The different FT-IR spectra of DTCPS before and after the adsorption of the V(V) (DTCPS-V) also indicated the interactions (Fig. 3). The DTCPS shows a broad vibration of δH_2O and δN–H at 1,657 cm^{-1}. The v(S–C$\overset{\cdots}{\underline{}}$N) and v(S$\overset{\cdots}{\underline{}}$C–N) appeared at the 1,372 and 1,240 cm^{-1}, respectively [17]. After adsorption of V(V) ions, δN–H shifted to 1,639 cm^{-1} suggested the protonation of NH groups and the interaction with V(V) anions. The v(S–C$\overset{\cdots}{\underline{}}$N) and v(S$\overset{\cdots}{\underline{}}$C–N) shifted to 1,381 and 1,256 cm^{-1} attributed to the interaction with V(V) anions. A new peak of V=O appeared at 849 cm^{-1} for DTCPS-V [18].

When the V(V) ions interacted with DTCPS, the thermal stability of DTCPS-V enhanced. As can be seen from Fig. 4, at least three weight loss stages can be distinguished from the TGA curves. For DTCPS, weight loss in the 60–150℃ attributed to the release of adsorbed water, following in the 220–360℃ range, weight loss is due to the breakdown of the dithiocarbamate and partial hydroxyl groups. After adsorption occurred, the DTCPS-V complex formed. The decomposition temperature of DTCPS-V rose to 260℃. Furthermore, the DTCPS-V shows lower decomposition rate than that of DTCPS. It can be attributed to the formation of DTCPS-V complex, which enhances the stability of modified PS.

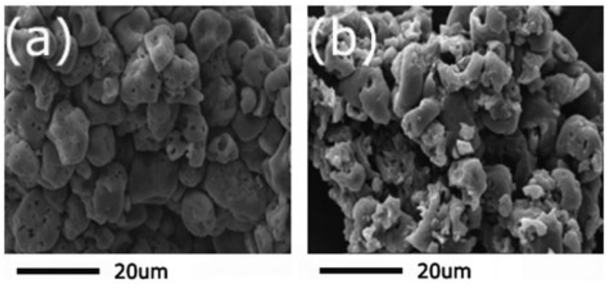

Fig. 2. SEM images of DTCPS before (a) and after (b) adsorption of V(V) ions.

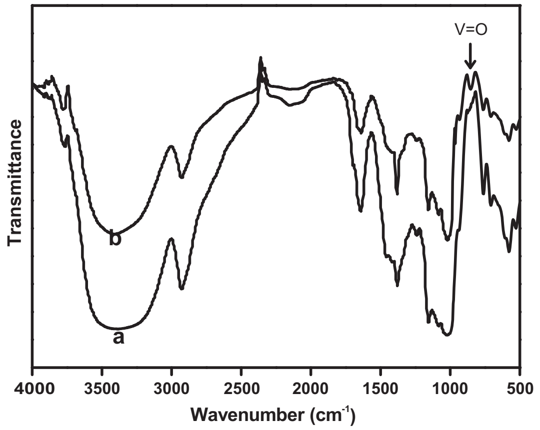

Fig. 3. FT-IR spectra of DTCPS (a) and DTCPS-V (b).

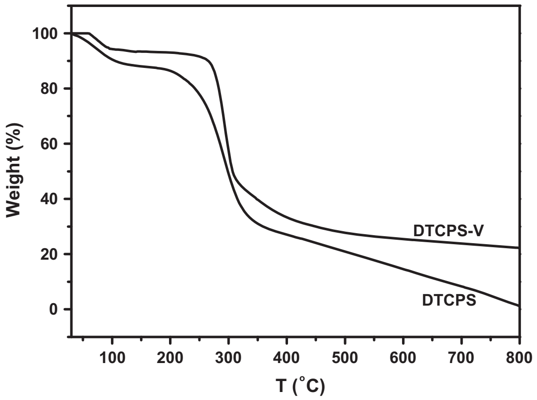

Fig. 4. TGA of curves of DTCPS and DTCPS-V.

3.2. *Adsorption behaviours and characteristics*

There are many factors controlling the adsorption of the V(V) onto DTCPS, such as pH, the driven force, vanadium species and isotherm equation. The effect of pH value on the adsorption capacity is observed in Fig. 5. The influence of solution pH was observed in a pH range of 2–10. The adsorption of V(V) was pH dependent, and adsorption capacity decreased with the increase in pH value (pH > 3). The effect of pH on the sorption of V(V) onto DTCPS can be interpreted with the help of surface charge of the sorbent in acidic/basic medium. In acidic medium, positive surface charge is developed due to the protonation of amine and dithiocarbamate which increases with the increase in H^+ (decrease in pH): Then, the anionic V(V) species can be adsorbed via the electrostatic attraction. It is well-known that vanadium is present in solution under more than 10 different species [19]. In most cases, regardless of the pH, two or three species represent more than 95% of total metal concentration. In the optimum pH 3.0 for vanadium sorption, the most representative vanadium species are $V_{10}O_{26}(OH)_2^{4-}$ and $V_{10}O_{27}(OH)^{5-}$. That is why sorption of negatively charged vanadium ions is expected to increase with decreasing pH. In basic medium, base abstracts the H^+ of dithiocarbamate group, which makes the surface of DTCPS negative. Due to electrostatic repulsion, the sorption ability decreases with increase in pH and almost negligible sorption occurs at pH 10. The sorption efficiency for V(V) decreased about 83% from pH 3–8. Interestingly, the dithiocarbamate-modified starch (DTCS) untreated by enzymes showed low capacity (no more than 5 mg g^{-1}) for V (V). The DTCS has a specific surface area of 0.5302 m^2/g, whereas the DTCPS has 1.2645 m^2/g. Since the vanadium species predominately are decavanadate, their diameters are higher than those of many metal ions. Therefore, the porous structure favours the adsorption of decavanadate.

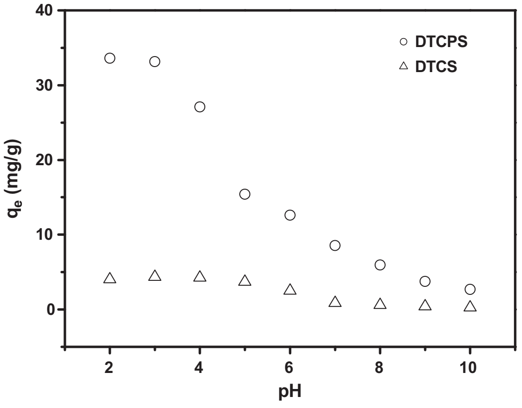

Fig. 5. Influence of pH on V(V) uptake by DTCS and DTCPS.

To evaluate the effectiveness of the adsorbate and sorption equilibrium, the study of contact time was showed in Fig. 6. The V(V) uptake has two stages. It can be found that 70% of removal occurs within the first hour of contact in the first stage and the rates of uptake of V(V) are rapid. The equilibrium obtains after 4 h. Two kinetic models, that is, pseudo-first- and pseudo-second-order, were tested to investigate the adsorption process. The pseudo-first-order [20] and pseudo-second-order equations [21] were used in this work. The pseudo-first-order rate expression is generally expressed as follows:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

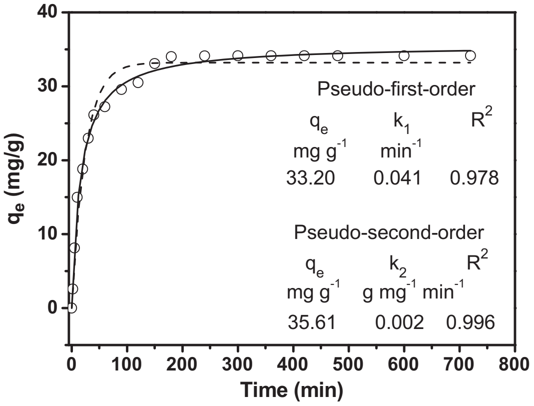

Fig. 6. Effect of contact time on adsorption of V(V) by DTCPS in pH 3.0 solution. Real line represents modelled results using the pseudo-second-order equation, and the dash line represents modelled results using the pseudo-first-order equation.

The pseudo-second-order equation is also based on the sorption capacity of the solid phase. If the rate of sorption is a second-order mechanism, the pseudo-second-order equation is expressed as follows:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

where q_t is the amount of V(V) on the sorbent (mg g^{-1}) at any time t (min), q_e is the amount of vanadium absorbed at equilibrium (mg g^{-1}), k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and k_2 is the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The kinetic parameters of the models were calculated and discussed as showed in Fig. 6. The results suggest that the best fit model is the pseudo-second-order equation.

Furthermore, the Langmuir [22] and Freundlich [23] equations were tested in this work. In the Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. This equation can be written as follows:

$$q_e = \frac{abc_e}{1 + bc_e} \tag{4}$$

Another isotherm is represented using Eq. (5) known as the Freundlich equation which describes heterogeneous systems, that is, surfaces with nonenergetically equivalent sites. It is an empirical equation and can be written as follows:

$$q_e = K_f c_e^{1/n} \tag{5}$$

where q_e is the adsorbed amount of the vanadium at equilibrium (mg g^{-1}), c_e is the adsorbate concentration at equilibrium in aqueous solution (mg L^{-1}), a and b are the Langmuir isotherm parameters, K_f is the Freundlich constant being indicative of the extent of sorption, $1/n$ is the heterogeneity factor being an indicator of sorption effectiveness. The experiment results are showed in Fig. 7. The Langmuir isotherm showed satisfied fit for V(V) adsorption. Such behaviors are similar to the V(V) adsorption to chitosan by electrostatic attraction [24]. It agrees with the above observations.

4. Conclusions

In this study, the DTCPS was synthesized and characterized by spectrometric methods. Its adsorption behaviour for V(V) removal was investigated. The adsorption is pH-dependent, and the optimal solution pH is 3.0. The experimental data for the adsorption of V(V) best fitted Langmuir isotherm. Such facts indicate a mechanism of electrostatic attraction. The amine and dithocarbamate groups of DTCPS was protonated and then attracted the decavanadate, $V_{10}O_{26}(OH)_2^{4-}$ and $V_{10}O_{27}(OH)^{5-}$. The thermogravimetric analyses showed that the thermal stability of DTCPS enhanced after binding vanadate. Such understanding provides new insights as how to optimize the use of porous dithiocarbamate-modified starch.

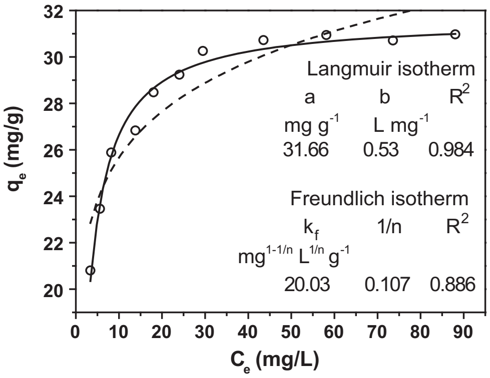

Fig. 7. Adsorption isotherms fitted to Langmuir model (the real line) and Freundlich equation (the dash line).

Acknowledgments

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