Studies of Adsorption Behavior of Crosslinked Chitosan for Cr(VI), Se(VI)

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ABSTRACT: In this work, it was found that crosslinked chitosan (CCTS) had strong adsorption ability for some anions under certain conditions. Cr(VI) and Se(VI) existed in anion forms in aqueous solution, and their adsorption rates by CCTS were 97% for Cr(VI) at pH 3.0 and 95% for Se(VI) at pH 4.0. In addition, the adsorption balance time and isotherm of CCTS for Cr(VI) and Se (VI) were discussed and adsorption mechanism was explained. This research will be useful for designing CCTS-based adsorption for metallic toxin removal and preconcentrating Cr(VI) and Se(VI) in their trace analysis.
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Key words: crosslinked chitosan; adsorption properties; Cr(VI); Se(VI); anion

INTRODUCTION

Chitosan (CTS) is a deacetylation product of chitin and can effectively remove toxic metals in wastewater because of its strong adsorption.[1] However, CTS can be dissolved in acid media, which is one disadvantage in application.

Crosslinked chitosan (CCTS) synthesized by reaction chitosan with crosslinking agents can overcome the disadvantage of CTS and still keep good adsorption properties for many metal ions. Qu et al. studied the adsorption properties of CCTS prepared by the reaction of CTS with polyethylene glycol (PEG) bisglycidyl ether for Cu(II), Ni(II), and Co(II).[2] Wang et al. synthesized two novel chitosan derivatives, crosslinked chitosan dibenzo-16-*c*-5 acetate crown ether (CCTS-1) and crosslinked chitosan 3,5-di-tert-butyl dibenzo-14-*c*-4 diacetate crown ether (CCTS-2), and studied their adsorption and selectivity properties for Pb(II), Cu(II), Cr(III), and Ni(II).[3] But to date, all studies were focused only on adsorption behavior of CCTS to cationic forms,[4–7] and their behavior for adsorption of anions has not been reported.

In this paper, we studied the adsorption properties of CCTS synthesized by the reaction of CTS with epichlorohydrin for Cr(VI), Se(VI) that existed in anionic forms in aqueous solution. Experimental results showed that the adsorption rates of CCTS were 97% for Cr(VI) at pH 3.0 and 95% for Se(VI) at pH 4.0. Therefore, CCTS can be used to design metallic toxin removal and to preconcentrate Cr(VI) and Se(VI) in their trace analysis.

EXPERIMENTAL

Materials

The raw material of chitin was obtained from the shell of crabs.[8] Chitosan (Yuhuan Organisms Ltd. Co., Hangzhou, Zhejiang, China) was prepared by deacetylizing reactions from the raw materials of chitin.[9] Stock solutions (1000 mg L^{-1}) of Cr(VI) and Se(VI) were prepared by dissolving $K_2Cr_2O_7$ and Na_2SeO_4 in distilled deionized water and 2 mol L^{-1} HNO_3, respectively. Standard solutions of lower concentrations were prepared after serial dilution of the stock solutions. HCl, HNO_3, and

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NaOH were reagent grade, and distilled deionized water was used throughout.

Synthesis of Crosslinked Chitosan

Chitosan (6.0 g) was dissolved in 320 mL of 1% (v/v) acetic acid. To this, 6 mL of epichlorohydrin was slowly added with rigorous stirring, and then 50 mL of 5% (w/v) NaOH was added in drops. After reacting for about 18 h at room temperature, a white solid was precipitated. The resulting precipitate was filtered off, washed thoroughly with water and then with a little propanol, and dried *in vacuo*. Panmilled and sieved (200 mesh), it was ready for use in the experiments.

Apparatus

The pH values were measured with a Model DF-180 PH/MV meter. Cr(VI) and Se(VI) were determined by a Hitachi 180–80 atomic absorption spectrometer with hydride generator. Infrared spectra were taken with a Perkin–Elmer 683 spectrometer.

Procedure

A measure of 30 mL of an aqueous solution containing 100 μg Cr(VI) or Se(VI) was add to a beaker of 50 mL and adjusted to desirable pH value by 0.1 mol L^{-1} HCl or NaOH. The solution was then transferred to a flask containing 20 mg CCTS and vibrated for 30 min at room temperature and filtered. The filtrate was diluted to 50 mL with distilled deionized water in the volumetric flask. Residual Cr(VI) or Se(VI) concentration in the filtrate were then determined by atomic absorption spectrometry (AAS) or hydride generation atomic absorption spectrometry (HG-AAS). Three samples were run in each group and repeated four times. The relative standard deviations are 3.6% for Cr(VI) and 4.8% for Se(VI).

RESULTS AND DISCUSSION

Effect of pH

According to the procedure mentioned above, after 2 mg L^{-1} Cr(VI) and Se(VI), respectively, were adsorbed by CCTS at different pH values, their concentrations were determined and adsorption rates were obtained. Figure 1 shows the effect of pH on adsorption rate. The optimum pH values for maximum adsorption were 3.0 for Cr(VI) and 4.0 for Se(VI), at which the adsorption rates of CCTS for Cr(VI) and Se(VI) were 97 and 95%, respectively.

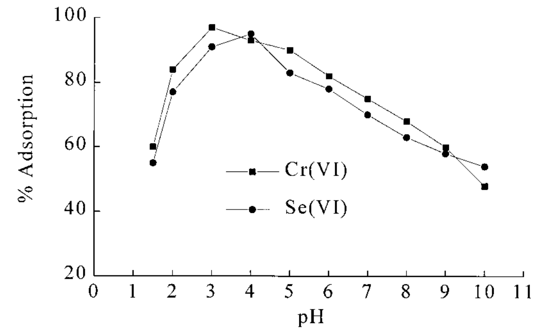

Figure 1 Effect of pH on Cr(VI) and Se(VI) adsorption by CCTS.

Cr(VI) and Se(VI) exist in acid solution in the forms of $HCrO_4^-$, $Cr_2O_7^{2-}$ and $HSeO_4^-$, SeO_4^{2-}, respectively. The adsorption of CCTS with positive charges for $Cr_2O_7^{2-}$ and SeO_4^{2-} is stronger than that of $HCrO_4^-$ and $HSeO_4^-$. By increasing the pH value from 3 to 4, the proportion of SeO_4^{2-} increases, whereas the proportion of $Cr_2O_7^{2-}$ decreases. Therefore the optimum pH value for maximum adsorption of CCTS for Se(VI) is higher than that of Cr(VI).

Adsorption Balance Time and Desorption

After 2 mg L^{-1} Cr(VI) and Se(VI), respectively, were adsorbed by CCTS at different adsorption times, their concentrations were measured. The adsorption balance times were 8 min for Cr(VI) and 20 min for Se(VI). After absorption, Cr(VI) and Se(VI) could be quantitatively eluted off from CCTS with 0.1 mol L^{-1} NaOH and 1.0 mol L^{-1} HCl, respectively. The desorption rates were 98% for Cr(VI) and 95% for Se(VI).

Effects of Foreign Ions

The effects of 14 foreign ions on adsorption rate of Cr(VI) were tested and the results indicated that no interferences were observed when Na^+ (1100 mg), Mg^{2+} (150 mg), K^+ (40 mg), Ca^{2+} (45 mg), Fe^{2+} (1 mg), Hg^{2+} (40 mg), Pb^{2+} (50 mg), Cu^{2+} (50 mg), Zn^{2+} (50 mg), Mn^{2+} (50 mg), CO_3^{2-} (3 mg), NO_3^- (2 mg), SO_4^{2-} (300 mg), and Cl^- (2000 mg) were added to 100 mL of solution containing 2 mg L^{-1} of Cr(VI).

The effects of 20 foreign ions on adsorption rate of Se(VI) were tested and the results indicated that no interferences were observed when Cd^{2+}

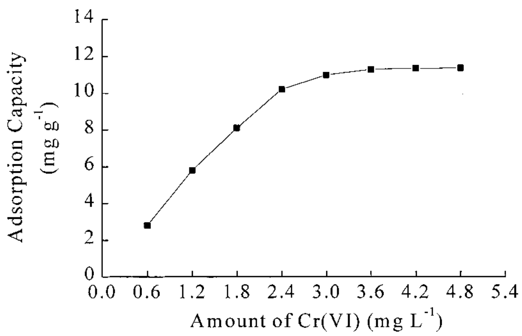

Figure 2 Adsorption isotherm of Cr(VI).

(20 mg), Ca^{2+} (30 mg), Al^{3+} (13 mg), Ba^{2+} (10 mg), Mg (100 mg), Na^{+} (100 mg), K^{+} (100 mg), Cu^{2+} (2 mg), Ag^{+} (5 mg), Ni^{2+} (5 mg), Mn^{2+} (5 mg), Fe^{3+} (5 mg), Co^{2+} (5 mg), Sn^{2+} (5 mg), CO_3^{2-} (50 mg), SO_4^{2-} (38 mg), Pb^{2+} (2 mg), I^{-} (2 mg), and Cl^{-} (1550 mg) were added to 50 mL of solution containing 2 mg L^{-1} of Se(VI).

Adsorption Behavior of Cr(VI) and Se(VI)

The isotherm is frequently used to describe adsorption behavior. To obtain the adsorption capacity of Cr(VI) or Se(VI) by CCTS, 10 mg of CCTS were added to 75 mL of a serial standard solution containing different concentrations of Cr(VI) or Se(VI), and the pH values of the solutions were adjusted to 3.0 for Cr(VI) or 4.0 for Se(VI). The concentrations of Cr(VI) and Se(VI) were determined after adsorption of 20 min. The adsorption capacities were calculated as

$$Q = V(C_0 - C)/W$$

where Q is adsorption capacities of CCTS [mg Cr(VI) or Se(VI)/g adsorbent], V is the volume of solution (mL), C_0 is concentration of Cr(VI) or Se(VI) before adsorption (mg mL^{-1}), C is concentration of Cr(VI) or Se(VI) after adsorption (mg mL^{-1}), and W is the weight of CCTS (g).

The adsorption isotherms of Cr(VI) and Se(VI) for CCTS can be constructed and saturated adsorption capacity was estimated at 11.3 and 34.5 mg g^{-1}, respectively, from Figures 2 and 3. The adsorption isotherms of Cr(VI) and Se(VI) were fitted with the Langmuir equation as follows

$$X/M = abc/(1 + ac)$$

where X is the adsorption amount (mg/g), M is the amount of CCTS (g), a, b are constants, and c is the balance concentration (mg mL^{-1}). The results showed that the adsorption isotherms of Cr(VI) and Se(VI) are in accord with the Langmuir equation.

Mechanism of Adsorption CCTS for Cr(VI) and Se(VI)

The free amino group (—NH_2) in CCTS exists due to the following balance in aqueous solution

$$\mathrm{CTS-NH_2 + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} CTS-NH_3^+ + OH^-}$$

It is evident that the amino group is protophilic and becomes NH_3^+ in acid media. CCTS with positive charges can adsorb anions by charge neutralization. The stronger the attraction between positive and negative charge, the stronger the adsorption is.

In addition, CTS has a straight-chain structure; crosslinking reactions of CTS with epichlorohydrin mainly take place between hydroxyl and amino groups or between hydroxyl groups. Crosslinks can occur between different parts of the same straight chain or between different straight chains. Therefore, a space net structure is formed in CCTS and each mesh has a certain space volume. Anions that have the proper volumes can be adsorbed by CCTS. The larger the volume of the anion that can get in the meshes, the stronger the adsorption is.

Cr(VI) and Se(VI) exist in acid solution in anion group forms. Their volumes are moderate for adsorption, hence, Cr(VI) and Se(VI) can be strongly adsorbed by CCTS. Figure 4 shows the IR spectrum of CCTS after adsorption of Cr(VI). The characteristic absorption peaks of amino and hydroxyl are at 3387 cm^{-1}, carbonyl of amide at 1724 and 1662 cm^{-1}, and secondary alcohol and

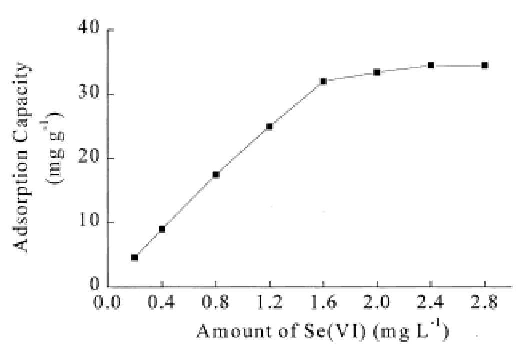

Figure 3 Adsorption isotherm of Se(VI).

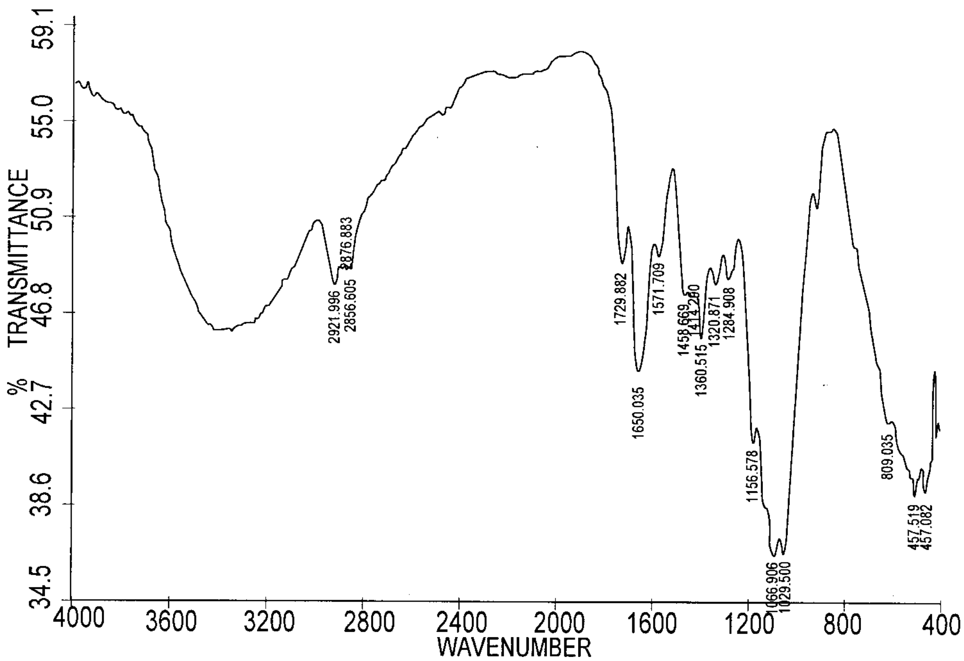

Figure 4 The FTIR spectrum of CCTS after adsorption for Cr(VI).

primary alcohol at 1067 and 1025 cm^{-1}. Compared with the IR spectrum of CCTS before adsorption,[3] it can be seen that the main absorption peaks of CCTS have not changed. The IR spectrum of CCTS after adsorption for Se(VI) is similar to that of Cr(VI). The results display that actions between CCTS and Cr(VI), Se(VI) are physical adsorption, not complexing reaction. This fact is further demonstrated from the isotherms of Cr(VI) and Se(VI) that are in accord with the Langmuir equation and the properties that adsorption speed is quick and desorption easily takes place.

CONCLUSION

CCTS has adsorption ability for some anions. pH value is an important factor on the adsorption. At a specific pH value, the adsorption rates of CCTS for Cr(VI) and Se(VI) that exist in aqueous solution in anion group forms can reach 97 and 95%, respectively, and the adsorption speed is rather quick. The interactions between CCTS and Cr(VI), Se(VI) are mainly physical adsorption.

REFERENCES

1. Yan, J. Chin Chem Bull 1984, 11, 26–31.
2. Qu, R. J.; Liu, Q. Environ Chem (Chinese) 1996, 15, 41–45.
3. Tan, S. H. Y.; Wang, Y. T.; Peng, C. H. H. J Appl Polym Sci 1999, 71, 2069–2074.
4. Ohga, K.; Kurauchi, Y.; Yanase, H. Bull Chem Soc Jpn 1987, 60, 444–446.
5. Huang, J. M.; Jing, X. R. Chem J Chinese Univ 1992, 13, 535–536.
6. Wang, Y. T; Cheng, G. Environ Pollut Control (Chinese) 1998, 20, 1–3.
7. Wang, Y. T.; Peng, C. H. H.; Tang, Y. R. Environ Chem (Chinese) 1998, 17, 349–353.
8. Muzzarelli, R. A. A. Chitin; Pergamon Press: Oxford, 1977; p 16.
9. Chen, S. H. Q. Chem World (Chinese) 1993, 34, 389–491.