Studies of Adsorption Properties of Crosslinked Chitosan for Vanadium(V), Tungsten(VI)

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ABSTRACT: In this article, the adsorption properties of crosslinked chitosan (CCTS) for V(V) and W(VI) were studied. Experimental results showed the adsorption rates of CCTS for V(V) and W(VI) were closely related to the acidity of solution. The adsorption rates were 97% for V(V) at pH 4.0 and 96% for W(VI) at pH 4.5. The adsorption balance times, adsorption capacities, and adsorption mechanism were explored. This research is of significance for removal of V(V) and W(VI) in industrial wastewater and their preconcentration in trace analysis. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1584–1588, 2004

Key words: vanadium(V); tungsten(VI); adsorption; chitosan; crosslinking; adsorption

INTRODUCTION

Chitin, whose chemical name is (1,4)-2-acetamide-2-deoxy-β-D-glucosamine is a natural biomacromolecule compound. Chitosan (CTS) is its deacetylated derivative. CTS contains two kinds of functional groups, an amino group and a hydroxy group. Muzzaralli's[1] study showed that through the hydroxyl group and amino group, CTS can form stable chelate compounds with many metal ions, such as Cu^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}. Because of its strong adsorption, CTS has been used to remove toxic metals in wastewater[2] and to preconcentrate and analyze some elements.[3] However, CTS can be dissolved in acid media and its applications are limited.

Crosslinked chitosan (CCTS) is a product synthesized by reaction CTS with crosslinking reagents. It is not dissolved in acid and we found that it has strong adsorption ability for some ions existing in anion form in solution of acidity, such as Cr(VI) and Se(VI).[4] We reported the studies of the adsorption behavior of CCTS for Cr(VI) and Se(VI). Their adsorption rates by CCTS were 97% for Cr(VI) at pH 3.0 and 95% for Se(VI) at pH 4.0. Furthermore, we investigated the adsorption of Mn(VII) and Mn(II) by CCTS. Results showed that at pH 3.0, the adsorption rate of CCTS for Mn(VII) existing in MnO_4^- was 98%, whereas Mn(II) was not adsorbed. So, CCTS was used successfully to preconcentrate and separate Mn(VII)/Mn(II) in water samples.[5]

Vanadium and tungsten are the metal elements of high melting point. They are widely used in industrial production, such as steel, aerospace, and electronics industries.[6] Vanadium and tungsten are also essential trace elements that have good function to man and animals. For example, vanadium can take part in various enzyme systems as an inhibitor and a cofactor.[7,8] Tungsten can increase the absorption ability for oxygen of animals. However, vanadium and tungsten are harmful at high concentrations. An overdose of chemical compounds of vanadium will injure breathing, nerves and hemopoietic systems of the body. Of all compounds of vanadium, the toxicity of vanadium(V) is the highest. Excessive tungsten has inhibition for activity of some kinds of enzymes in organisms, such as nitrogennase and nitrate reductase. Therefore, it is necessary to analyze vanadium and tungsten and treat their pollution.

In this work, the adsorption properties of CCTS synthesized by the reaction CTS with epichlorohydrin for V(V) and W(VI) were studied. The outcomes displayed that the adsorption rates of CCTS were 97% for V(V) at pH 4.0 and 96% for W(VI) at pH 4.5. In addition, it was found that CCTS had quite high adsorption capacity for W(VI). The saturation capacity of adsorption was 364.8 mg g^{-1}. This research is of significance for removal of V(V) and W(VI) in industrial wastewater and their preconcentration in trace analysis.

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EXPERIMENTAL

Apparatus

V(V) was determined by a 180-80 spectrometer with a Zeeman effect background correction system (Hitachi

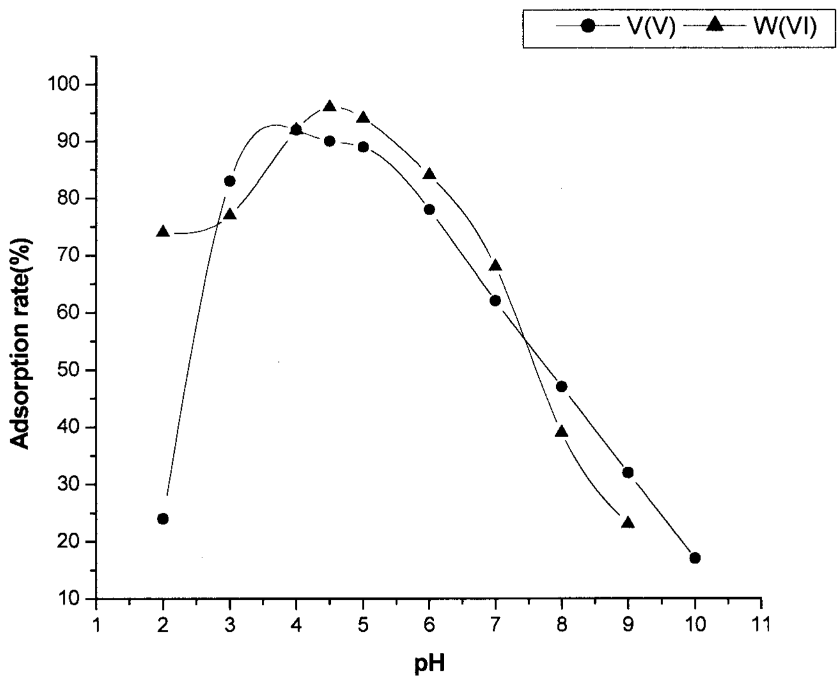

Figure 1 Effects of pH on V(V) and W(VI) adsorption by CCTS.

Corp., Osaka, Japan). W(VI) was determined by a UV-1601 UV-visible spectrophotometer (Shimadzu Corp., Osaka, Japan). The pH values were measured with a Delta 320-s pH meter (Mettler-Toledo, Greifensee, Switzerland). The infrared spectra of CCTS was taken with a Model 170-SX infrared spectrometer (Nicolet, Madison, WI, USA).

Material and reagents

The CCTS (200 mesh) was synthesized by literature.[1] Stock solutions of V(V) (1.000 g L^{-1}) were prepared by dissolving ammonium metavanadate (2.3000 g) in 100 ml of 4.5 mol L^{-1} H_2SO_4 and diluting to 1000 ml with distilled deionized water. W(VI) (1.000 g L^{-1}) was prepared by dissolving WO_3 (0.6306 g) in 20 ml of 20% (W/V) KOH and diluting to 500 ml. Working standard solutions of lower concentration were prepared by appropriate dilution of the stock solution. Mg $(NO_3)_2$ $6H_2O$, NH_4SCN,$TiCl_3$, and HCl were reagent grade, and deionized-distilled water was employed throughout.

Procedures

A measure of 25 ml of an aqueous solution containing 15 μg V(V) or 500 mg W(VI) was add to a beaker of 50 ml and adjusted to a desirable pH value by 0.1 mol L^{-1} HCl or NaOH. The solution was transferred to a flask containing 30 mg CCTS, vibrated for 60 min at room temperature, and filtered. The filtrate of V(V) was diluted to 50 ml with distilled deionized water in the volumetric flask. Residual V(V) was detected by graphite furnace atomic spectrometry (GFAAS) at a wavelength of 318.4 nm. The filtrate of W(VI) was diluted to a colorimetric tube of 50 ml, then 5 ml HCl, 3 ml $TiCl_3$ (0.75%), 3 ml NH_4SCN(50%) were added in turn. After 15 min, W(VI) of this solution was determined by a UV-visible spectrophotometer at a wavelength of 402.2 nm.

RESULTS AND DISCUSSION

Effect of pH

According to the procedure mentioned above, after 300 μg L^{-1} V(V) and 10 mgL^{-1} W(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 V(V) and W(VI) adsorption by CCTS. The optimum pH values for the maximum adsorption were 3.0 for V(V) and 4.5 for W(VI), at which the adsorption rates of CCTS for V(V) and W(VI) were 92 and 96%, respectively.

Effect of time on V(V) and W(VI) adsorption by CCTS

For the adsorption of 300 μg L^{-1} V(V) at pH 4.0 and 10 mg L^{-1} W(VI) at pH 4.5; Figure 2 shows the adsorption efficiency reached a maximum value when the adsorption time was 60 min.

Effects of coexistent ions

The effects of 13 diverse coexistent ions on the V(V) and W(VI) adsorption by CCTS were tested in 200 ml

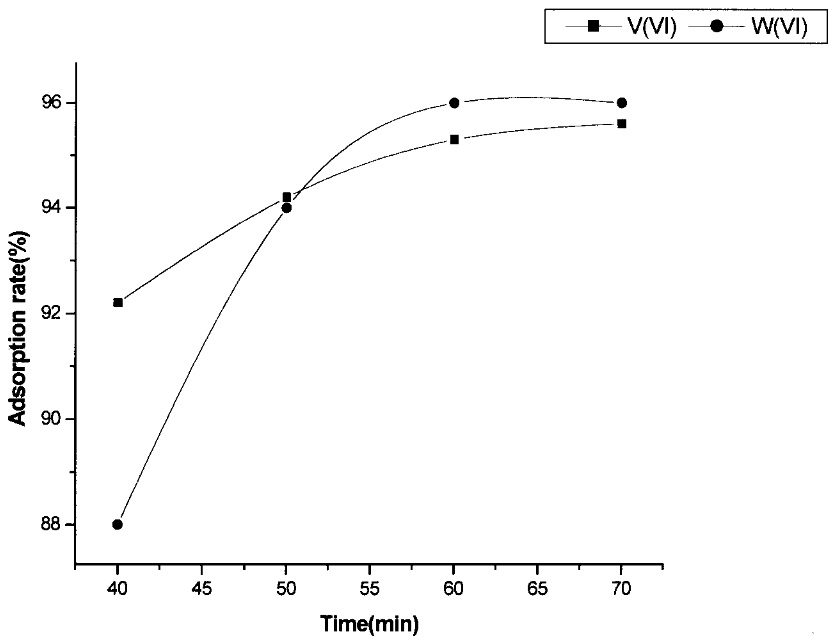

Figure 2 Effects of time on V(V) and W(VI) adsorption by CCTS.

solutions containing 0.51 μg V(V) or 5 μg W(VI). The results indicated that no influences were observed from Na^+ (2.15 g), K^+ (79.8 mg), Mg^{2+} (256 mg), Ca^{2+} (82.4 mg), Zn^{2+} (0.95 mg), Fe^{3+} (185 μg), Al^{3+} (187 μg), Br^- (13.4 mg), Cl^- (3.88 g), Cr^{6+} (0.25 mg), PO_4^{3-} (10.4 mg), NO_3^- (201 mg), and SO_4^{2-} (542 mg).

The saturation capacity of adsorption

Serial standard solutions containing different concentrations of V(V) and W(VI) were prepared. Their concentrations were determined after adsorption for 1 h by 10 mg CCTS at pH 4.0 for V(V) or pH 4.5 for W(VI). The adsorption capacities were calculated as

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

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

Figures 3 and 4 describe the relations of the adsorption capacities of CCTS for V(V) and W(VI) with their original concentrations, respectively. The saturation capacities of V(V) and W(VI) adsorption by CCTS were estimated at 6.27 and 364.8 mg g^{-1}, respectively.

Adsorptive mechanism of CCTS for V(V) and W(VI)

It is well known that in acid media, the free amino group ($—NH_2$) in CCTS is protonized ($—NH_3^+$)

$$CCTS—NH_2 + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} CCTS—NH_3^+ + OH^-$$

where $CCTS—NH_3^+$ can adsorb some anions by electrostatic forces.

When the concentration of V is lower than 10^{-4} mol L^{-1}, the reaction balance of V(V) exists in aqueous solution as follows[9]:

$$VO_4^{3-} + H^+ \leftrightarrows HVO_4^{2-}$$

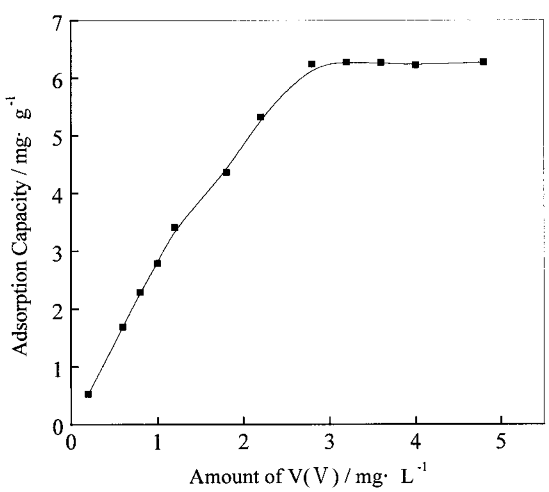

Figure 3 Adsorption capacity of V(V).

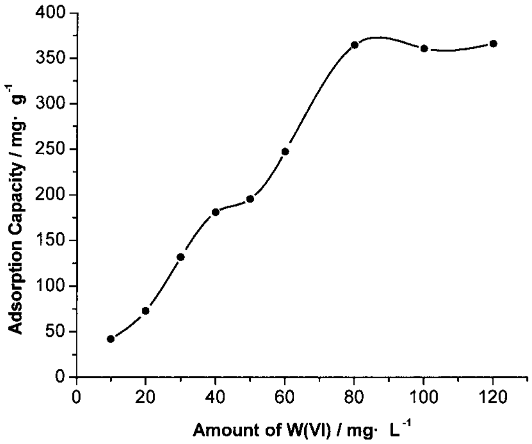

Figure 4 Adsorption capacity of W(VI).

$$HVO_4^{2-} + H^+ \rightleftharpoons H_2VO_4^-$$

$$H_2VO_4^- + H^+ \rightleftharpoons H_3VO_4$$

$$H_3VO_4 + H^+ \rightleftharpoons VO_2^+ + 2H_2O$$

It is evident that the pH values of solution effect the existing form of V(V) and its adsorption by CCTS. At pH 4.0, V(V) exists in VO_4^{3-} and HVO_4^{2-}; by decreasing pH values, the proportion of VO_4^{3-} and HVO_4^{2-} decreases and the adsorption rate of CCTS for V(V) reduces. Hence, the optimum pH value for maximum adsorption is 4.0. The pH value of W(VI) maximum adsorption by CCTS is 4.5, at which, W(VI) mainly exists in $HW_6O_2^{5-}$ and $W_{12}O_{41}^{10-}$.[9] Therefore, CCTS with positive charges can strongly adsorb them by charge neutralization.

Figures 5 and 6 show the IR spectrum of CCTS after adsorption of V(V) and W(VI). Compared with the IR spectrum of CCTS before adsorption,[10] it can be seen that the adsorption peaks of active groups—NH_2 and —OH in CCTS at 3424 cm^{-1} have not changed.

According to these mentioned above, we calculate that the adsorptions of CCTS for V(V) and W(VI) mainly are physical adsorption, just as Cr(VI), Se(VI), and Mn(VII). We will use other means to study further the adsorptive mechanism.

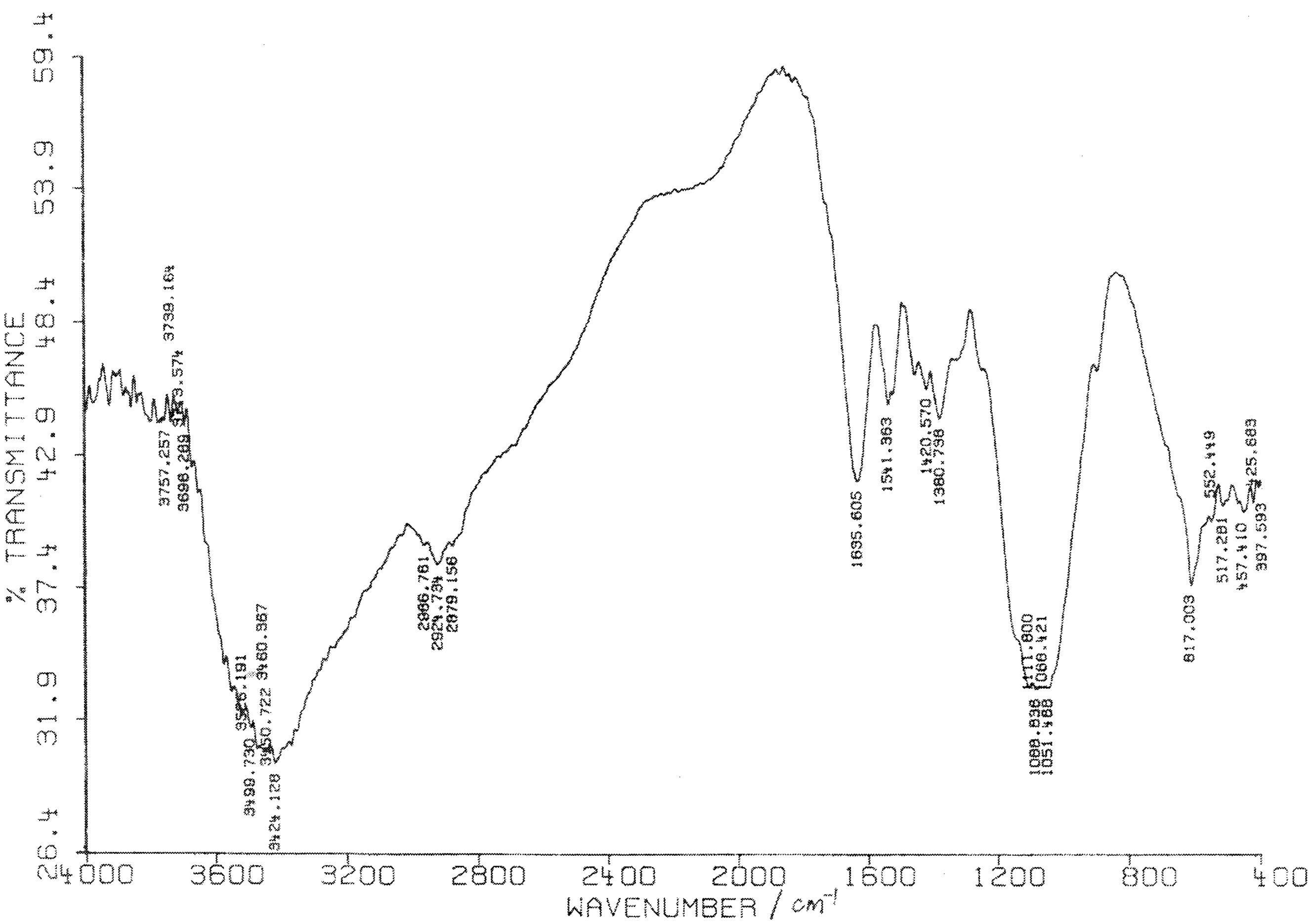

Figure 5 The FTIR spectrum of CCTS after adsorption of V(V).

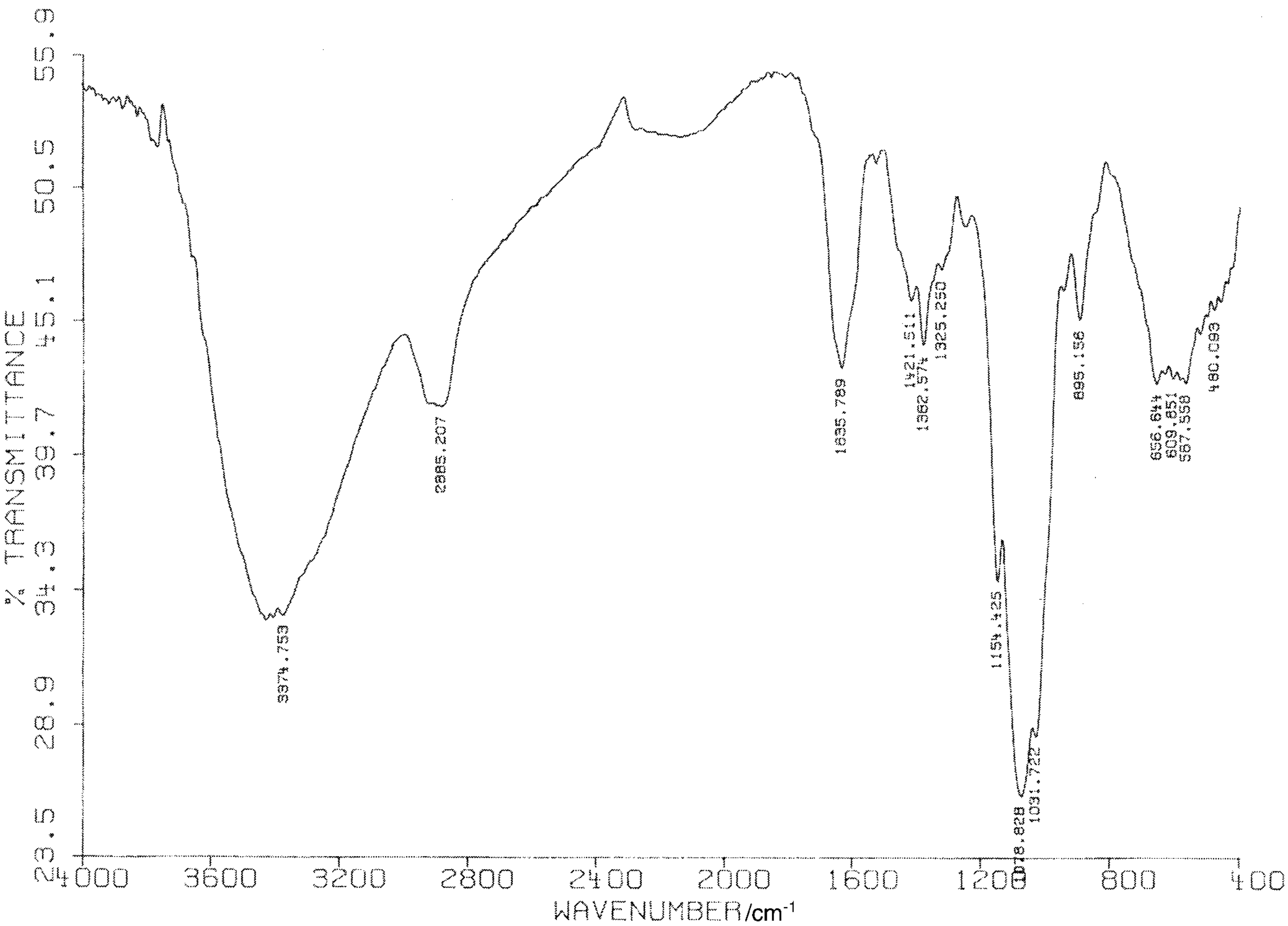

Figure 6 The FTIR spectrum of CCTS after adsorption of W(VI).

CONCLUSION

CCTS has stronger adsorption ability for V(V) or W(VI) in acidity solution. The pH values of V(V) and W(VI) maximum adsorption by CCTS are 4.0 and 4.5, respectively. The interactions between CCTS and V(V) or W(VI) are mainly physical adsorptions.

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