Application of Crosslinked Chitosan in the Analysis of Ultratrace Mo(VI)

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ABSTRACT: In this work, the adsorption properties of crosslinked chitosan for Mo(VI) were studied. The adsorption rate of Mo(VI) by CCTS was 97% at pH 3.0. Adsorption balance time, elution conditions, the effect of coexisting elements, and the adsorption mechanism were investigated. A novel method of ultratrace Mo(VI) preconcentration with CCTS and determination by graphite furnace atomic absorption spectrometry was found. The detection limit (3σ, $n = 10$) of the method was 0.040 μg L^{-1}, and the relative standard deviation was 2.98% at 1.00 μg L^{-1}. The method has been applied to the determination of Mo(VI) in environmental water samples, with satisfactory results. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 432–435, 2006

Key words: adsorption; chitosan; crosslinking

INTRODUCTION

Molybdenum, one of the necessary microelements in body, has indispensable functions. But, the over-ingestion of molybdenum will result in molybdenum poisoning. Some argue that the incidence of gout is related to excessive molybdenum. In addition, excessive molybdenum may disturb the metablization of Ca and P, and cause osteoporosis and articular abnormity. In conclusion, the analysis on the content of molybdenum is of great importance for human health.[1,2]

The molybdenum in natural water exists in the form of MoO_4^{2-}(Mo (VI)),[3] whose concentration is very low. The average concentration of molybdenum in sea water and river is about 10 μg L^{-1} and 1.5 μg L^{-1}, respectively,[4]so that the graphite furnace atomic absorption spectrometry method cannot detect it directly, thus the preconcentration of molybdenum before its detection is needed.

Crosslinked chitosan (CCTS), a kind of macromolecule polymer with reticulate structure, is synthesized by the crosslinking reaction of chitosan and crosslinking agent. It retains the good adsorbing ability of chitosan to some kinds of metal ions, and on the other hand, overcomes the shortcoming that the dissolving of chitosan will lead to its loss in acidic solution, which makes CCTS's application is more extensive. In recent years, we studied the adsorbing abilities of CCTS to some ions, such as Cr(VI), Se(VI),[5] Mn(VII), V(V), W(VI),[6] Pt(IV), and Au(III). We found that under acidic condition the ion's adsorption rates can reach more than 97%. On the basis of the results, we developed the analytical methods for trace Mn,[7] Pt,[8] and Au[9] in environmental water samples, i.e., the preconcentration by CCTS and the detection by atomic absorption spectrometry.

In this study, the adsorbing ability of CCTS to Mo(VI) is studied. And, results show that, when pH is 3 and adsorption time is 20 min, the adsorption rate of CCTS to Mo(VI) can reach 97%. On the basis of this, we built the method of using CCTS to enriching extreme-trace Mo(VI), and the enriching multiple is about 100. It is simple and fast. When this method is used together with the graphite furnace atomic absorption spectrometry (GFAAS), to detect extreme-trace Mo(VI), the detection limit is about 0.040 μg L^{-1}, which will be satisfactory for environment water samples.

EXPERIMENTAL

Materials

Chitosan was purchased from Yuhuan Organisms Ltd. Co., Hangzhou, Zhejiang, China. The stock solution 1000 mg L^{-1} of Mo(VI) was prepared by dissolving 0.1840 g $NH_4M_{07}O_{24} \cdot 4H_2O$ in subboiling distilled water, adding 1 mL NH_4OH, and diluting to 100 mL. The working standard solutions were prepared by gradient diluting the stock solution. HNO_3 and NaOH were high-purity reagents. Subboiling distilled water was used throughout the study.

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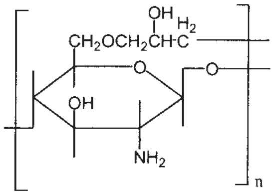
TABLE I
Furnace Operating Conditions

Step	Temp (°C)	Ramp time (s)	Hold time (s)	Argon flow (mL min^{-1})
Dry	80–120	30	10	200
Ash	1000	0	30	200
Atomization	2700	0	7	0
Clean	2800	0	3	200

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, dried in vacuo, panmilled, and sieved (200 mesh).The main structure of CCTS is as follows:



Apparatus

Mo(VI) was determined by a Hitachi 180−80 atomic absorption spectrometer with Zeeman effect background correction system, and molybdenum hollow cathode lamp and the pyrolytic-coated graphite tubes(Hitachi corp, Osaka, Japan) were used. The spectral bandwidth and analysis wavelength of molybdenum were set to 1.3 and 313.3 nm, respectively. The lamp current was 12.5 mA, and the sampling volume was 20 μL. The operation conditions of graphite furnace and the heating procedures are presented in Table I. The pH values were measured with a Delta 320-s pH meter (Mettler-Toledo, Greifensee, Switzerland). A magnetic stirrer (Nanhui telecommunications equipment factory, Shanghai, China) and a CHA-S thermostatic shaker (Changzhou Guohua Electric Appliance Co., Changzhou, China) were used in this experiment.

Procedure

Adsorption and determination of Mo(VI)

An aqueous solution of about 30 mL containing 5 μg Mo(VI) was adjusted to desirable pH value by using pH meter. The solution was then transferred to a flask containing 20 mg CCTS and vibrated for 20 min at room temperature and filtered. The liquid phase was transferred to 50 mL volumetric flask, supplemented it with water until the surface reached scale, and was detected by GFAAS to get the resident value of Mo(VI) in the solution. Compared with the concentration of Mo(VI) before adsorption, the adsorption rate of CCTS for Mo(VI) was gained.

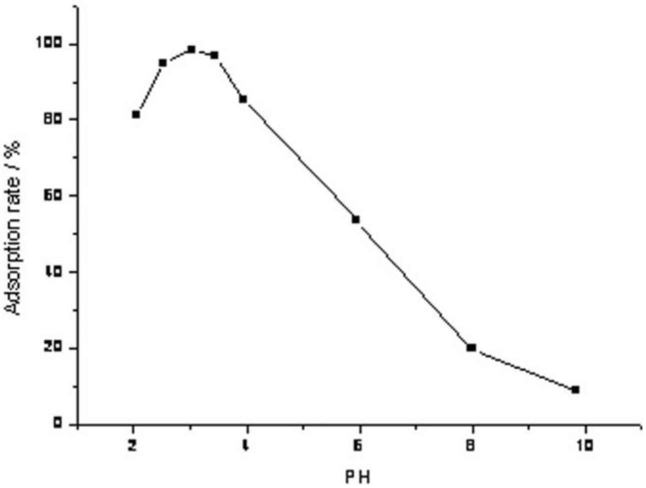


Figure 1 Effect of pH on Mo(VI) adsorption by CCTS.

Preconcentration and determination of Mo(VI)

The pH value of a 100 mL aqueous solution containing Mo(VI) was adjusted to 3.0. After the solution was adsorbed by CCTS according to above-mentioned procedures and filtered, the residue was washed with 1 mL of 0.1 mol L^{-1} NaOH. The Mo(VI) in this eluent was determined by GFAAS.

RESULTS AND DISCUSSION

Effect of pH on adsorption

Figure 1 shows the effect of pH on adsorption rate of CCTS for 50 mL of 100 μg L^{-1} Mo(VI) standard solution.

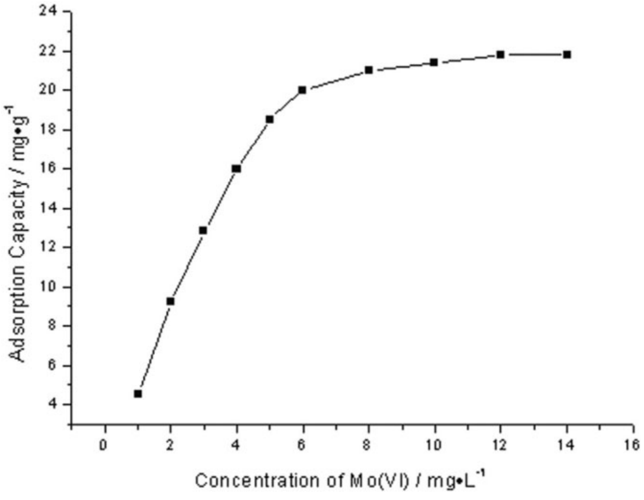


Figure 2 Adsorption capacity of CCTS for Mo(VI).

TABLE II
Analytical Results of Environmental Water Samples and Recovery Tests (μg/L, $n = 6$)

Samples	Mo added	Mo found	Recovery (%)
East lake[a]	0.00	0.46	–
	1.00	1.46	100
East lake[b]	0.00	0.64	–
	1.00	1.65	101
Tap water	0.00	ND	–
	1.00	0.99	99

ND, not detected.
[a] Sampled in site a.
[b] Sampled in site b.

At pH 2.5–4.0, adsorption rates were more than 90%. The optimum pH value for maximum adsorption was 3.0, at which the adsorption rate of CCTS for Mo(VI) was 97%.When pH values went beyond 2.5–4.0, the adsorption rates were reduced. The causes would be discussed in the study of adsorption mechanism.

Adsorption balance time and desorption

100 μg L^{-1} Mo(VI) standard solution was adjusted to pH 3.0 and adsorbed by CCTS at different adsorption times. The adsorption balance time was 20 min. On the basis of the adsorption curve in Figure 1, NaOH solutions of different concentrations and volumes were used to elute the Mo(VI) adsorbed by CCTS. The results displayed that the maximum desorption rate (93%) was obtained with 1 mL of 0.1 mol L^{-1} NaOH.

Adsorption capacity of CCTS for Mo(VI)

According to the procedure of Mo(VI) adsorption and determination to examine the adsorption capacity of CCTS for a series of Mo(VI) solutions with different concentrations, the results are shown in Figure 2. It can be seen that the saturation capacity is 21.4 mg g^{-1}.

Effect of coexistence ions

The effects of 17 diverse coexisting ions on 1.00 ìg L^{-1} Mo(VI) in 100 mL aqueous solution were tested according to the procedure of preconcentration and determination of Mo(VI). No interferences were observed from K^+(1000 mg L^{-1}), Na^+(2380 mg L^{-1}), Ca^{2+}(660 mg L^{-1}), Mg^{2+}(540 mg L^{-1}), NO_3^-(800 mg L^{-1}), SO_4^{2-}(680 mg L^{-1}), Cl^-(3940 mg L^{-1}), PO_4^{3-}(40 mg L^{-1}), Zn^{2+}(380 mg L^{-1}), Al^{3+}(750 μg L^{-1}), Fe^{3+}(740 μg L^{-1}), Cr^{6+}(18 μg L^{-1}), Cu^{2+}(280 μg L^{-1}), Sr^{2+}(45.8 μg L^{-1}), As^{5+}(10 μg L^{-1}), Br^-(200 μg L^{-1}), and Se^{6+}(8.7 μg L^{-1}). It is thus evident that this method has the ability of antiinterference.

Detective ability of the method

Enriching 100 mL 1.00 μg L^{-1} Mo(VI) standard solution for 10 times and determining, we could gain the detection limit (3σ, $n = 10$) and the relative standard deviation, which were 0.040 μg L^{-1} and 2.98%, respectively. The detection limit was about 100 times lower than that before preconcentration.

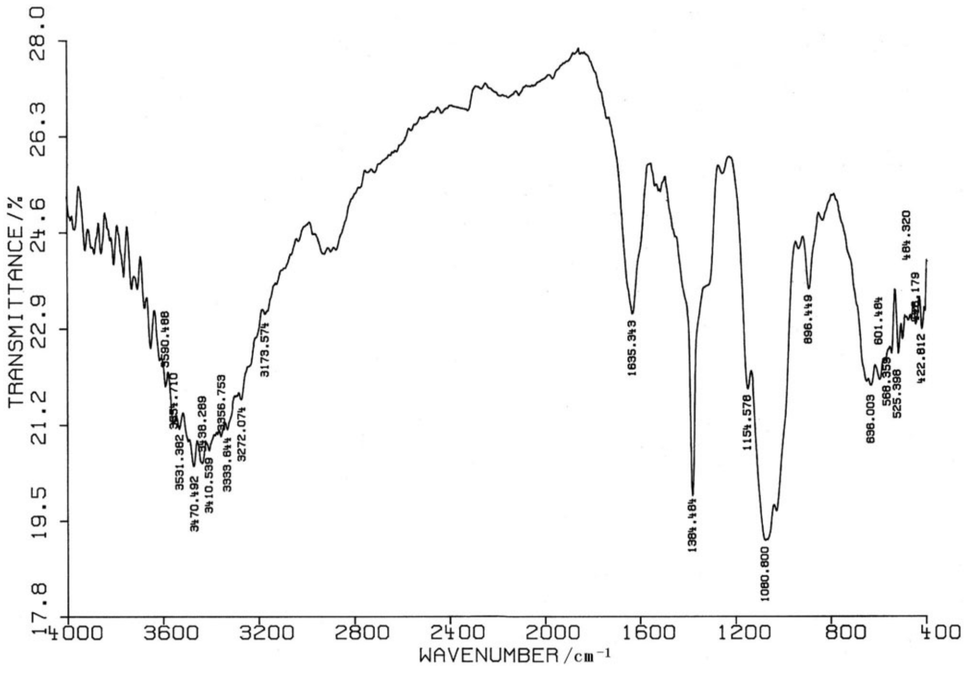


Figure 3 FTIR spectrum of CCTS after adsorption of Mo(VI).

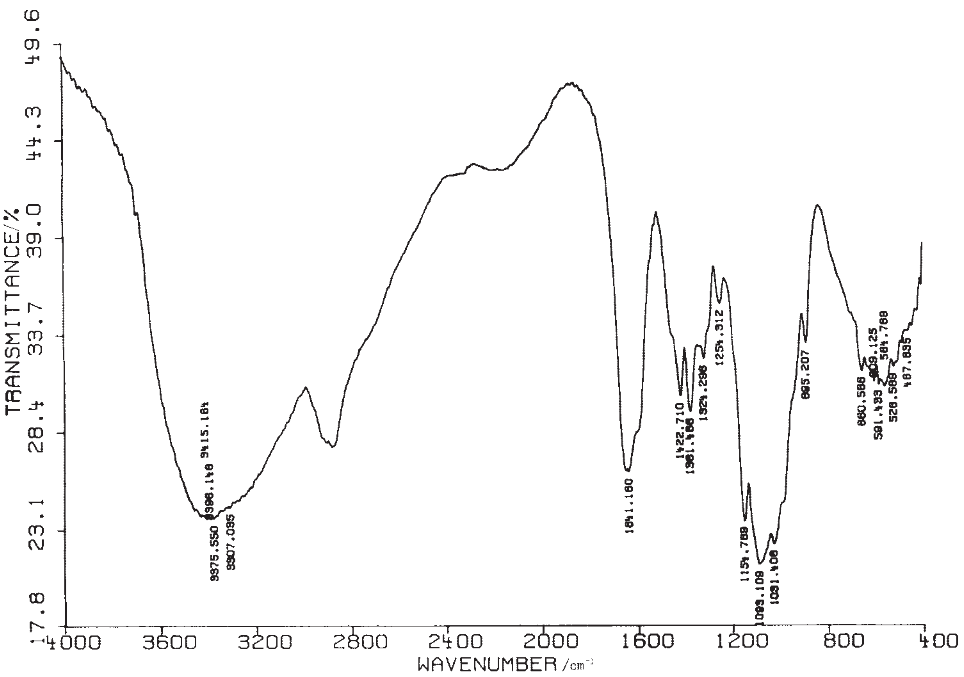


Figure 4 FTIR spectrum of CCTS.

Analytical application

A water sample was filtered through a membrane of 0.45 μm to exclude insoluble particles. Following above-mentioned procedure, the Mo(VI) of 100 mL water sample was preconcentrated and detected. The results, including the recovery test, are listed in Table II, which indicate that the method is reliable.

Mechanism of adsorption of Mo(VI) by CCTS

The IR spectrum of CCTS after adsorption for Mo(VI) is shown in Figure 3. Compared with the IR spectrum of CCTS before adsorption (Fig. 4), it can be seen that the main adsorption peaks ($-NH_2$ and $-OH$) of CCTS have not changed. Hence, we think that the adsorption of CCTS for Mo(VI) is mainly physical adsorption as Cr(VI), Mn(VII), and Se(VI).In the solution of pH 2.5–4, the primary forms of Mo(VI) are polymerization anion,[4] such as $Mo_7O_{24}{}^{6-}$ and $Mo_8O_{26}{}^{4-}$.The free amino group ($-NH_2$) in CCTS is protolized and becomes $-NH_3{}^+$. CCTS can adsorb polymerization anion of Mo(VI) by static electricity gravitational force. Because at pH < 2.5, Mo(VI) becomes cation, such as $MoO_2{}^{2+}$, and the adsorption rates are decreased.

CONCLUSIONS

The method has the advantages of short-enriching time, high-enriching capability, multiple, low-detection limit, very antiinterferential, fine accuracy, and precision. This technique can be applied to detect ultratrace Mo(VI) in environmental water samples.

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