



Adsorption of molybdate on molybdate-imprinted chitosan/triethanolamine gel beads



Liang Zhang^{a,*}, Juanqin Xue^b, Xingwen Zhou^c, Xiang Fei^a, Yang Wang^a, Yuanzhen Zhou^a, Lvling Zhong^a, Xuanli Han^a

^a College of Science, Xi'an University of Architecture and Technology, Xi'an, Shaanxi, 710055, China

^b College of Metallurgy Engineering, Xi'an University of Architecture and Technology, Xi'an, Shaanxi, 710055, China

^c Technical Center of Jin Dui Cheng Molybdenum Co., Ltd, Xi'an, Shaanxi, 710077, China

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ABSTRACT

Mo (VI)-imprinted chitosan (CTS)/triethanolamine (TEA) gel beads (Mo (VI)-ICTGBs) (ICTGBs = imprinted chitosan triethanolamine gel beads) were prepared by using ion-imprinted technology, in which TEA and molybdate solution were used in coagulation bath. The spectrum of FT-IR implies that bonding are formed between TEA and the primary hydroxyl of CTS, and ion gel reaction happen between CTS and molybdate; XRD patterns also prove the change among CTS, TEA and molybdate. SEM images and N₂ adsorption show that the surface area increases obviously after eluting Mo (VI) ions. The adsorption isotherm of Mo (VI)-ICTGBs imply that the adsorption process is according with Freundlich model. Adsorption kinetics suggests that the pseudo-second order adsorption mechanism is predominant for this adsorbent system of Mo (VI)-ICTGBs. The Mo (VI)-ICTGBs show high adsorption capacity and good selectivity for Mo (VI) anions in the coexistence system at pH = 6.0. The Mo (VI)-ICTGBs have a good application prospect, because it is with a simple and rapid technique and good durance.

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1. Introduction

The recycling of Mo becomes very important due to the increasing demand for Mo in the industrial field. Many technologies have been applied in the recycling field of Mo at present, i.e. biological, chemical and physical treatments. Adsorption is a simple and facile technique used in molybdate treatment. Different adsorbents, such as pyrite, synthetic schwertmannite, kaolinite, organo-bentonite, goethite, natrolite, titania, iron oxide, and aluminum oxide, have been used for molybdate removal from aqueous solutions (Antelo et al., 2012; Atia, 2008; Xu and Washington, 2006). In addition, new adsorbing materials, including resins, solvent-impregnated resins (Atia, 2008), carbon base materials (Afkhami and Conway, 2002; Namasivayam and Sangeetha, 2006) or biomass, have attracted some interest. Removal and preconcentration of Mo (VI) from water and wastewater solutions has been investigated using carminic acid modified anion exchanger (Asem, Ahmed, & Haytham, 2008). Magnetic resins derived from glycidyl methacrylate and crosslinked with divinylbenzen or *N,N*-methylenebisacrylamide have been also prepared (Rojas et al., 2005). However, the above treatment for

Mo is not recycling, but rather removal. Therefore, in order to reach the aim of recycling for Mo, the selective adsorption for molybdate is necessary.

CTS is a well-known biopolymer, whose high nitrogen content confers not only remarkable ability for the sorption of metal ions from dilute effluents, but also the sorption of metal anions from dilute effluents (Vold et al., 2003; Muzzarelli, 2011). CTS have been used for removing Cr (VI), arsenic, Mo (VI), etc. (Chassary, Vincent, & Guibal, 2004; Dambies, Vincent, Domard, & Guibal, 2001; Guibal, Milot, & Tobin, 1998; Guibal, Milot, & Roussy, 2000; Muzzarelli & Rocchetti, 1973). The study also shows that CTS is effective for removing molybdate with high sorption capacities (Guibal et al., 1998, 2000). Some researchers have further proved that the gel bead could be formed self-rembulately by CTS and Molybdate (Dambies et al., 2001; Draget, Vårum, Moen, Gynnild, & Smidsrød, 1992). This new gel technique leads to a structure different from that produced during alkaline coagulation of a CTS solution. According to the self-rembulate propriety of CTS solution and Molybdate, the crosslinking CTS has been prepared by ion gel reaction. The ion gel of CTS formed by CTS and molybdate is suitable for adsorbing other anions, such as As (V) (Chen et al., 2008; Dambies, Vincent, & Guibal, 2002). The above CTS material is still shortcoming in specific and reusability. Some researchers have prepared crosslinked metal complexed CTS by using a metal ion as template, and then removed

* Corresponding author. Tel.: +86 2982201469.
E-mail address: z198z1@hotmail.com (L. Zhang).

the template ion to overcome the above problem. The resins have good selectivity and show maximum adsorption capacity (Varma, Deshpande, & Kennedy, 2004). When the ion imprinted technology was applied for the ion gel formed by CTS and molybdate by using molybdate anion as template, the imprinted material became powder and a loss after eluting molybdate from the ion gel. Therefore, it is necessary to add a crosslinking agent for the stability of the Mo (VI) imprinted material. Zhang et al. have reported that TEA has coagulating function for CTS solution (Zhang et al., 2012). The similar study also shows that amino functions are involved in the sorption mechanisms, together with carbonyl sites in adsorption anion (Guibal, Milot, Etteradoss, Gauffier, & Domard, 1999). So TEA is a suitable coagulating agent for forming the imprinted material considering adding adsorption site and stability of gel.

The subject of this work is to prepare Mo (VI)-ICTGB by ion imprinted technique and ion gel reaction between CTS and molybdate, and utilizing the material for selective adsorption of Mo (VI). SEM and N₂ adsorption, FT-IR and XRD were used to characterize the material to study the mechanism of forming gel beads. Static equilibrium and kinetics were performed to explore adsorption mechanism of the material. The Mo (VI)-ICTGB were applied into a mixed solution containing molybdate, chromate, vanadate and arsenate was used to perform a study of competitive adsorption in this work. The Mo (VI)-ICTGB were applied to the factual wastewater.

2. Materials and methods

2.1. Materials

All reagents used in this work were of analytic grade. Chitosan (CTS, ≥90% deacetylation) were purchased from Sinopharm Chemical Reagent Co. Ltd. Ammonium molybdate were obtained from Shanghai ShenBo Chemical Co. Ltd. Triethanolamine (TEA) were obtained from Tianjin Tianli Chemical Reagent Co. Ltd. Other chemicals were purchased from Xi'an Chemical Reagent Factory.

2.2. Analytical instrumentation

IR Fourier transform infrared spectrometer (FT-IR, Shimadzu, co., Japan) was used to characterize and analyze the forming mechanism of the composite beads. X-ray diffraction (XRD) analysis was carried out by a PerkinElmer PHI-5400 diffract meter, employing Cu K α radiation of wavelength 1.54. The data were taken in the range of 3–90° (2 θ), with a step size of 0.02°. The N₂ adsorption–desorption isotherms were measured at –196 °C using a Micromeritics ASAP 2020-Physisorption Analyzer. Prior to the characterization, samples were degassed for 5 h at 100 °C. The specific surface area was calculated according to the BET (Brunauer–Emmett and Teller) model, while the pore size and pore volume were calculated using the Barrett–Joyner–Halenda (BJH) formula. The surface morphology of the bead was examined using FEI Quanta 200 scanning electron microscope (SEM). The absorbance of Mo (VI) was detected by GFS97 graphite furnace atomic absorption spectrophotometer (GFAAS, Thermo co., USA).

2.3. Preparation of Mo (VI)-ICTGB

The process of preparing Mo (VI)-ICTGBs has been described by Fei, Zhang, Zhong, Chen, and Ma (2012), and a flow chart of the preparation of Mo (VI)-ICTGB was shown in Fig. S1 (seen in Supporting Information). CTS-acetate solution was prepared by dissolving the powder of CTS (0.20 g) in 10.0 mL of 2% (v/v) acetic acid at room-temperature till the solution became homogeneous. After deaeration, the casting solution was slowly dropped into 200 mL of 11% (v/v) of TEA with syringe (needle, Φ 0.4 mm), and

stirred for 4 h to form the non-imprinted CTS/TEA gel beads. After being washed and dried, the beads were labeled as NICTGBs (non imprinted CTS/TEA gel beads). According to the same procedure, the casting solution was dropped into 200 mL of ammonium molybdate solution (8.0 g L⁻¹) to form the CTS/Mo (VI) beads (labeled as CMOBs). The CTS/TEA/Mo (VI) beads (CTMOBs) were prepared by the same procedure in the mixed solution of 11% (v/v) of TEA and ammonium molybdate solution (8.0 g L⁻¹).

The CTMOBs were soaked and stirred in 50 mL of 8.0 g L⁻¹ NaOH solution about 1.5 h to remove Mo (VI) ions, and the procedure was performed for three times. The Mo (VI)-ICTGBs were obtained by rinsing repeatedly with deionized water. The Mo (VI)-ICTGBs (Φ 1–1.5 mm) were soaked in deionized water.

2.4. Adsorption capacity testing

All the adsorption experiments were carried out at room-temperature. Adsorbent concentration was kept constant at 0.0400 g in 20.00 mL solution, and the initial pH of solution was adjusted to 6.0 with 0.1 M sulphuric acid. The concentration of Mo (VI) in the filtrate and initial concentration were determined by using GFAAS. Adsorption capacity could be calculated by Eq. (1) (Ren et al., 2013; Vold, Vårum, Guibal, & Smidsrød, 2003).

$$Q = (C_0 - C) \times V/m \quad (1)$$

Where Q is the adsorption capacity (mg g⁻¹); C_0 and C are the initial and equilibrium concentrations of Mo (VI) (mg L⁻¹), respectively; m is the dry mass of Mo (VI)-ICTGBs (g); V is the volume of adsorption solution (L).

2.5. Adsorption selectivity experiments

The mixed solution (100.0 mg L⁻¹ for each element) prepared by solving molybdate, chromate vanadate and arsenate was used to perform an experiment of competitive adsorption. Cr (VI), As (V) and V (VI) ions were chosen as similar anions to prove the specificity of Mo (VI)-ICTGBs for Mo (VI) in this work. The concentration of each ion in the remaining solution was measured with GFAAS after adsorption equilibrium. Distribution coefficients (K_d) of Cr (VI) ion, As (V) ion and V (VI) ion with respect to Mo (VI) were calculated by Eq. (2) (Ren et al., 2008; Naja & Volesky, 2011).

$$K_d = Q_e/C_e \quad (2)$$

Where K_d is the distribution coefficient; Q_e is the equilibrium adsorption capacity of metal ions (mg g⁻¹); C_e is the equilibrium concentrations of metal ions (mg L⁻¹).

Selectivity coefficient (k) for the binding of Mo (VI) in the presence of competitor species can be calculated by Eq. (3).

$$k = K_{\text{template metal}}/K_{\text{interferent metal}} \quad (3)$$

2.6. Column adsorption studies

Column flow adsorption experiments were performed in a glass column of about 1.2 cm internal diameter and 25 cm length. The column was filled with Mo (VI)-ICTGBs (Φ 1–1.5 mm). The Mo (VI) ion solution (100 mg L⁻¹) was allowed to flow through the column at a constant flow rate (2 mL min⁻¹) throughout the experiment. The pH of the inlet solution was adjusted to 6.0 at the start of the experiment. The effluent solution was collected at 5 min intervals and the concentration of Mo (VI) ion in the effluent solution was monitored by GFAAS. The solutions were diluted to detection range for Mo (VI) prior to analysis.

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