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Removal of Mo(VI) as oxoanions from aqueous solutions using chemically modified magnetic chitosan resins

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ABSTRACT

Chitosan was cross-linked using glutaraldehyde in the presence of magnetite. The resin obtained was chemically modified through the reaction with tetraethylenepentamine followed by glycidyl trimethylammonium chloride to produce chitosan bearing amine (R1) and chitosan bearing both amine and quaternary ammonium chloride moieties (R2), respectively. The removal of Mo(VI) as molybdate anions from aqueous solution was studied using batch and column methods. R1 works efficiently towards the removal of molybdate in acidic medium. Whilst R2 works efficiently in all pH ranges (acidic/neutral/basic). The nature of interaction of the resins obtained with molybdate was clarified. The resins showed a higher affinity towards the uptake of Mo(VI). Kinetics and thermodynamic parameters of the uptake process were obtained. Breakthrough and regeneration curves for the removal of Mo(VI) were also studied. The adsorbed molybdate anions were found to be effectively eluted from the investigated resins.

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1. Introduction

Molybdenum naturally occurs in various ores, especially molybdenite (MoS_2) (Namasivayam and Sangeetha, 2006). Molybdenum also represents the most abundant trace element in see water, in part due to its stability and weak adsorption (Bostick et al., 2003). Molybdenum compounds are used primarily in the production of metal alloys (Bei et al., 2007). Water soluble molybdate anions cause an environmental problem if their concentration exceeds 5 ppm (Moret and Rubio, 2003). The degree of toxicity of molybdenum and/or molybdate compounds ranks between those of Zn(II) and Cr(III) compounds (Wu et al., 2001). So, pollution by molybdate oxoanions in groundwater represents a serious issue in the field of drinking water that is obtained from wells (Smedley et al., 2002). Therefore, the search for suitable methods for water/wastewater treatment against toxic oxoanions becomes very interesting subject (Sabarudin et al., 2007). Among these methods are coprecipitation (Mamtaz and Bache, 2001) and reverse osmosis (Al-Wazzan et al., 2003; Zhaoa et al., 2005) that generally need various and complicated equipments and reagents. Simple adsorption techniques have also been reported for the removal of toxic pollutants of oxoanions using activated carbon (Kubota et al., 1998; Bostick et al., 2003), polymers (Yokoi et al., 2004), soils components (Sabine and Forster, 1998), iron minerals (Zhang et al., 2005; Xu et al., 2006), and alumina (Wu et al., 2000; Al-Dalama et al., 2005). On the other hand, chelating and chelating magnetic resins represent also an important category of promising adsorbents. They are highly selective, efficient and easily regenerable relative to other types of adsorbent materials (Utkelov et al., 1991). Rorrer et al. synthesized porous magnetic chitosan Beads for removal of Cd(II) ions from waste water (Rorrer et al., 1993). Recently, we reported on the use of chelating and chelating magnetic resins for the removal of some metal ions from aqueous solutions (Donia et al., 2006a,b; Atia et al., 2005). These magnetic resins is easily collected from aqueous media using an external magnetic field and displayed higher uptake capacity compared to the magnetic particles-free resin.

The ultimate goal of this study is the development of a new magnetic resins based on chitosan for the removal of molybdate oxoanions from aqueous solutions. The factors affecting the removal behavior will be studied. Thermodynamic as well as kinetic properties of the removal process will also clarified.

2. Experimental

2.1. Chemicals

Chitosan with deacetylation degree (DD) of 82.1%, glutaraldehyde, tetraethylenepentamine (TEPA) and glycidyl trimethylammonium chloride (GTMAC) were Aldrich products. All other chemicals were Prolabo products and were used as received. Ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot{}_2O$) was used as a source for Mo (VI) oxoanions. $FeSO_4\cdot 7H_2O$ and $FeCl_3\cdot 6H_2O$ were used for preparing magnetite particles.

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2.2. Preparation of magnetite

Magnetite was prepared using the modified Massart method (Sun et al., 2004; Donia et al., 2007). A 250 mL (0.2 M) of $FeCl_3$ solution was mixed with 250 mL (1.2 M) of $FeSO_4$ solution. A 200 mL (1.5 M) of NH_4OH solution was added to the above solution of $FeCl_3/FeSO_4$ under vigorous stirring. A black precipitate was formed which was allowed to crystallize for another 30 min under magnetic stirring. The precipitate was filtered off and washed with deoxygenated water through magnetic decantation until the pH of the suspension became below 7.5.

2.3. Preparation of modified magnetic chitosan resins

The process of preparation takes place through subsequent steps (Scheme 1).

(i) Preparation of the magnetic chitosan gel

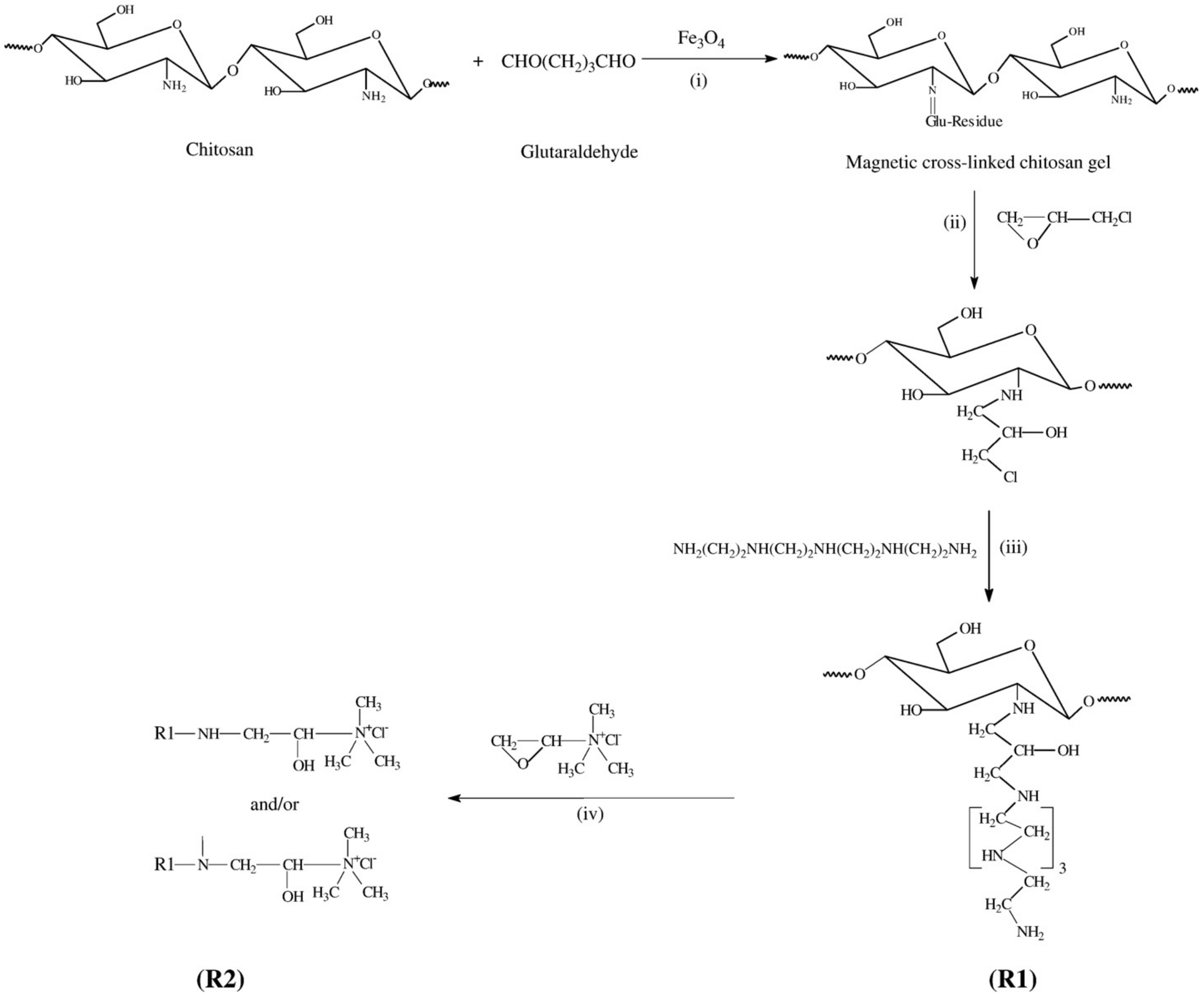
Three grams of chitosan was dissolved in 20% aqueous solution of acetic acid. One gram of magnetite was added to chitosan solution and stirred until the solution became homogenous. Then 2 mL of glutaraldehyde solution (25%) was added and the solution was stirred with heating until gelatinous product was obtained. The gel obtained was washed with distilled water several times and kept for use.

(ii) Reaction with epichlorohydrine

The cross-linked chitosan gel obtained in the above step (i) was suspended in 70 mL isopropyl alcohol. Then 7 mL epichlorohydrine (62.5 mmol) dissolved in 100 mL acetone/water mixture (1:1 v/v) was added. The above mixture was stirred for 24 h at 60 °C. The solid product obtained was filtered off and washed several times with water followed by ethanol.

(iii) Reaction with tetraethylenepentamine (TEPA)

The product obtained in the step (ii) was suspended in 100 mL ethanol/water mixture (1:1 v/v) and then treated with 5 mL TEPA. The reaction mixture was stirred at 60 °C for 12 h. The product obtained was washed with water followed by ethanol. The produced chitosan/pentamine resin was dried in air and sieved where the particle size fraction (−0.5/+0.4) mm was used in this study, and referred by (R1). The amine content in R1 was estimated using volumetric method of HCl according the early reported method (Atia et al., 2003) and was found to be 4.9 mmol/g.



Scheme 1. Preparation of modified magnetic chitosan resins.