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Uptake of U(VI) from aqueous media by magnetic Schiff's base chitosan composite

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ABSTRACT

Schiff's base chitosan composite with magnetic properties has been prepared and investigated. The modification process took place through the reaction between chitosan and polymeric Schiff's base of thiourea/glutaraldehyde in the presence of magnetite. The sorption characteristics of the composite towards UO_2^{2+} at different experimental conditions were carried out by means of batch and column methods. The composite showed high affinity and fast kinetics for the sorption of UO_2^{2+} ions, the sorption capacity reached 2.32 mmol/g at 25 °C. Various parameters such as pH, agitation time, UO_2^{2+} concentration and temperature had been studied. The kinetics and thermodynamic behavior of the sorption reaction were defined. These data indicated an exothermic and spontaneous sorption process, and kinetically followed pseudo-second order model, Fickian diffusion low and Elovich equation. The uptake of UO_2^{2+} was slightly influenced by the increase of ionic strength. Breakthrough curves for the removal of UO_2^{2+} were studied at different flow rates and bed heights. The critical bed height for the studied column was found to be 0.656 cm at flow rate of 4 mL/min. Hydrochloric acid (0.2 M) was used for desorbing UO_2^{2+} from loaded composite: desorption yield as high as 97% was obtained.

1. Introduction

Reducing carbon emissions need rapid development of nuclear power industry. But excessive amounts of uranium have entered into environment through the activities of nuclear industry (Manter et al., 2013). In the past decades, many cases of environmental contamination have resulted from overuse of uranium at industrial and military sites. Generally, uranium exists in solution as aqueous uranyl ions (UO_2^{2+}) (Wei et al., 2014). Uranium disposed into the environment can eventually reach the top of the food chain and be ingested by humans (Sussa et al., 2013; Montaña et al., 2013). The carcinogenic impacts of uranium ingestion are well documented and exposure of human beings to uranium can cause acute toxicological effects and harmful diseases such as lungs, pancreatic and liver cancer (Zhang et al., 2011). The U. S. Environmental Protection Agency (1996) has set up the tolerance level for U(VI) in drinking water as 0.02 mg/L (U.S. EPA, 1996). The permissible discharge level of uranium for nuclear industries ranges from 0.1 to 0.5 mg/L (U.S. EPA, 1996). As per the standards of World Health Organization, the U(VI) concentration in water should not exceed 0.05 mg/L (WHO, 1993). The recovery of uranium from natural sea water and industry wastewater is a challenging problem for scientists because uranium is one of important resources to secure energy. Nuclear power is derived from uranium, which has no significant commercial use other than as a fuel for electricity generation (Jacobson, 2009). In view of the extensive usage of uranium for various industrial purposes and potential risks presented by radionuclides for humans and the environment, comprehensive knowledge of the behavior of wastewaters has been used to develop various processes for their decontamination treatment such as: chemical precipitation (Nejad et al., 2013), membrane separation (Zhang et al., 2013), ion exchange (Rahmati et al., 2012), electrodialysis (Pombo and Dutra, 2013), photocatalysis (Gao et al., 2013), flotation (Tripathi et al., 2013) and adsorption procedures (Ilaiyaraja et al., 2013). Adsorption of uranium onto various solids is important from purification, environmental, and radioactive waste disposal points of view (Muzzarelli, 2011). Sorption is by far the easiest way for removing radioactive ions from aqueous media. Various types of materials have been used for uranium sorption, for example functionalized carbon (Wang et al., 2012), magnetic composite (Hritcu et al., 2012), clay (Xiao-yu et al., 2013), chitin and chitosan (Muzzarelli, 2011). There

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is fervent research activity on alternative sorbents especially polysaccharides that are abundant, renewable and biodegradable (Schleuter et al., 2013). Among them chitosan plays a prominent role (Wang et al., 2009; Oshita et al., 2009; Sureshkumar et al., 2010; Wang et al., 2011). Chitosan is a poly-N-glucosamine species obtained by the deacetylation of chitin, the most abundant amino-polysaccharide existing in the environment (Elwakeel, 2010). It is highly hydrophilic and is characterized by a flexible polymer chain and by a large number of hydroxyl and amino groups that represent potential adsorption sites (Elwakeel et al., 2012). Moreover, it can be considered a low-cost sorbent because it requires little processing, is abundant in nature and represents a by-product of fishery industry (Yang et al., 2012; Zhao et al., 2012). Grafting of new functional groups and chemical crosslinking increases its sorption capacity and selectivity towards metal ions in solution through the formation of different chelates.

Previously, magnetic chitosan functionalized with schiff's base of thiourea and glutaraldehyde moieties was prepared (Atia et al., 2008). Magnetic sorbents are easily collected from aqueous media using an external magnetic field and displayed higher uptake capacity compared to the magnetic particles-free sorbent. The sorption behavior of the magnetic chelating composite towards Ag(I), Au(III) and Hg(II) in aqueous solution at different experimental conditions was studied (Atia et al., 2007). Magnetic separation techniques offer several advantages. The most attractive one for radioactive wastewater treatment is its good performance in difficult-to-handle samples. By using the magnetic separation techniques rather than centrifugation or filtration, it will reduce the chances of contacting with radiations. However, so far only limited knowledge exists concerning the removal of radioactive substances by magnetic separation method, especially uranium removal by magnetically modified chitosan, which is meaningful from the purification, environmental and radioactive waste disposal point of view.

To address this objective in this study we use chitosan modified with magnetite and schiff's base of thiourea and glutaraldehyde for UO_2^{2+} removals from aqueous media. Uranium(VI) sorption onto the prepared magnetic chitosan was investigated, including a pH optimization, and the determination of sorption isotherms, kinetics and column parameters.

2. Materials and methods

2.1. Chemicals

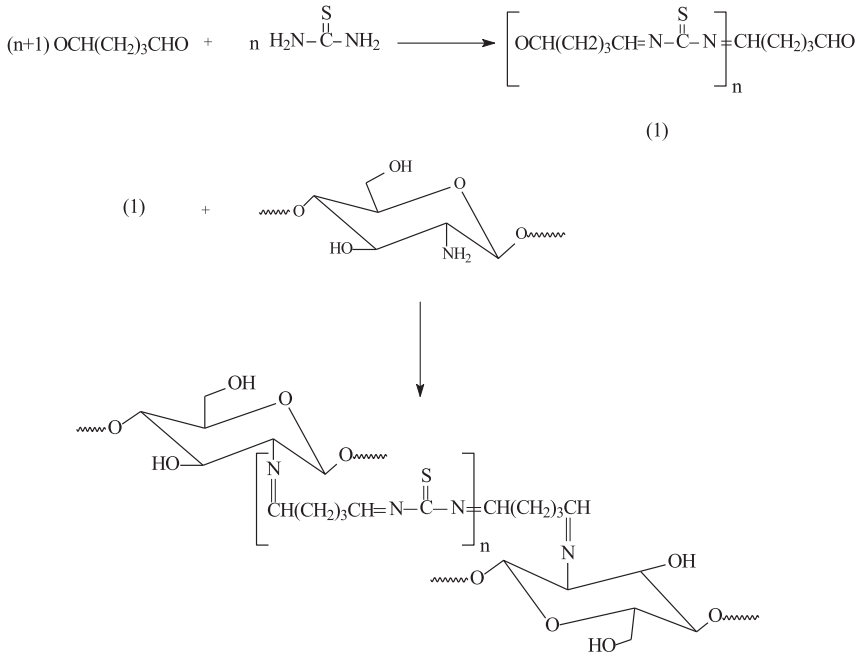
Chitosan (M.W. 190,000–310,000 Da), glutaraldehyde, thiourea were Sigma–Aldrich products. Arsenazo-III (M.W. 892.4) was procured from Himedia (Mumbai, India). All other chemicals were Prolabo products and were used as received. Uranyl chloride and Yttrium chloride were used as source of UO_2^{2+} and Th^{4+} ions, respectively. Stock solutions of rare earth ions (La^{3+}, Eu^{3+} and Yb^{3+}) were prepared from their oxides by dissolution in concentrated hydrochloric acid. Thorium nitrate and Cesium nitrate were used as sources of Th^{4+} and Cs^{+}, respectively. $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$ were used for preparing magnetite particles as reported earlier using modified Massart method (Qu et al., 1999).

2.2. Preparation of Schiff's base modified magnetic composite

Schiff's base modified magnetic composite was prepared according to the previously reported method (Scheme 1) (Atia et al., 2008). One gram of chitosan was dissolved in 50 mL of 25% aqueous acetic acid solution. Three grams of thiourea (39.47 mmol) were dissolved in 100 mL distilled water. 18 mL (25%) glutaraldehyde solution (46.8 mmol) was added to thiourea solution in a round flask. The mixture was heated on a water bath for 5 h at 50 °C. After completion of the reaction, magnetite (1.0 g) was added while stirring. The contents of the flask were then added to the chitosan solution and stirred until the solution become homogenous then heated up to 70 °C for 6 h. A large quantity of gel was formed, washed repeatedly with 0.5 NaOH solution then water and dried at 70 °C for 8 h. The dried gel (6.85 g) was then grinded and sieved where the particle size fraction (−0.6/+0.5) mm was used in this study.

2.3. Preparation of solutions

A stock solution (2×10^{-2} M) of uranyl chloride was prepared in distilled water. The desired concentrations were then obtained by dilution. HCl (0.5 M) and NaOH (0.5 M) were used to change the acidity of the medium. 0.2 M of HCl was used for elution UO_2^{2+} from



Scheme 1. Suggested structure of the magnetic Schiff's base chitosan composite.