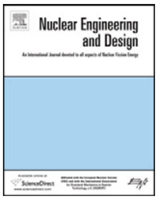
Nuclear Engineering and Design 242 (2012) 452–457

Contents lists available at SciVerse ScienceDirect

Nuclear Engineering and Design

journal homepage: www.elsevier.com/locate/nucengdes



The characteristics and mechanism of Co(II) removal from aqueous solution by a novel xanthate-modified magnetic chitosan

Yuwei Chen[a], Jianlong Wang[a,b,*]

[a] Laboratory of Environmental Technology, INET, Tsinghua University, Beijing 100084, PR China
[b] Beijing Key Laboratory of Fine Ceramics, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

Article history:
Received 9 September 2011
Accepted 7 November 2011

ABSTRACT

A novel xanthate-modified magnetic chitosan (XMCS) was prepared, characterized and applied for Co(II) removal from aqueous solution, and compared with magnetic chitosan (MCS). The characteristics and mechanism of Co(II) sorption was investigated. The experimental results showed that the introduction of thiol group on magnetic chitosan greatly increased the adsorption capacity for Co(II). The kinetics of Co(II) sorption could be described by pseudo second-order equation, and the adsorption isotherm followed the Langmuir model for both MCS and XMCS. The maximum adsorption capacity was found to be 18.5 mg/g and 2.98 mg/g, respectively from the Langmuir isotherm for XMCS and MCS. The mechanism of Co(II) adsorption onto XMCS was tentatively proposed through FTIR and XPS analysis.

1. Introduction

Radioactive waste is an inevitable residue from the use of radioactive materials in industry and medicine sector as well as from research and nuclear establishments. The presence of radionuclide and their fission products, even at low concentrations, can pose serious chemical and radiological toxicity threats to lower and higher living organisms. Therefore, the management and disposal of radioactive waste is a significant issue to almost all countries (Sheha and Metwally, 2007). In the aspect of radiological safety, strontium, cobalt and cesium are major radioactive isotopes because of their relatively long half-lives (Coughtrey and Thorne, 1983).

The main techniques that have been used for the removal of radioactive waste include precipitation, membrane separation, ion exchange and adsorption (Gűrboga et al., 2006; IAEA, 2003). Among them, adsorption is regarded as a promising one for the removal of these substances. The natural biopolymer and their derivates can be utilized as economical and environmental-friendly materials for removal of heavy metals and radionuclides from aqueous solution with high efficiency (Wang and Chen, 2006, 2009). Using low-cost biosorbents may be an alternative technology for the removal of heavy metals and radionuclides from aqueous solutions. For example, the waste biomass of *Saccharomyces cerevisiae* produced from a brewery was used for sorption of Pb^{2+}, Ag^{+}, Cs^{+}, Sr^{2+} from aqueous solution (Chen and Wang, 2008, 2010).

Recently, many researchers have reported the application of magnetic chitosan for removing metal ions (Chen and Wang, 2011; Huang et al., 2009; Zhou et al., 2009a,b). Magnetic chitosan have several advantages. This material has strong metal chelating capability due to presence of the amine and hydroxyl groups in chitosan chain. Also, it can easily be separated from the sorption system using magnetic field due to magnetic properties. However, to our knowledge, there have been a few reports on treatment of radioactive waste by magnetic chitosan. Furthermore, to improve the adsorption capacity, we modified magnetic chitosan using xanthate. The addition of thiol group on xanthate-modified magnetic chitosan (XMCS) may enhance the interaction with Co(II) in solution and increase the adsorption ability of XMCS for Co(II). Also, there is an urgent need to investigate the mechanisms of XMCS during the removal of radioactive waste.

Therefore, the main objectives of our research are (1) to compare the adsorption capacity of un-modified magnetic chitosan (MCS) and xanthate-modified magnetic chitosan (XMCS) for Co(II); (2) to investigate adsorption kinetics and equilibrium of Co(II) by MCS and XMCS; (3) and to identify the possible adsorption mechanisms, using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Chemicals and materials

Chitosan flakes (85% deacetylated) used in the experiments were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All other reagents used in this work were of analytical

---

* Corresponding author. Tel.: +86 10 62784843; fax: +86 10 62771150.
E-mail address: wangjl@tsinghua.edu.cn (J. Wang).

0029-5493/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.nucengdes.2011.11.004

grade. $CoCl_2 \cdot 6H_2O$ was used as source for Co(II) ions. Stock solution (1000 mg/L) of the studied ions was prepared in distilled water.

2.2. Preparation of magnetic chitosan (MCS)

Chitosan flakes were added into 100 mL 3% (v/v) acetic acid in a beaker to obtain chitosan solution and the mixture placed overnight. $FeSO_4$ and $FeCl_3$ were dissolved in 1:2 molar ratio and the resulting solution was dropped into 30% (w/v) sodium hydroxide, mechanically stirred for 3 h. The beads were collected and washed with DI water until reaching neutrality. Then the magnetic chitosan beads were cross linked with glutaraldehyde (Wan Ngah et al., 2002). The wet beads were suspended in 0.05 M glutaraldehyde solution to obtain a ration of 1:1 with chitosan. The chitosan beads in resulting glutaraldehyde solution were left standing for 24 h at room temperature. After 24 h the cross-linked magnetic chitosan beads were intensively washed with distilled water, filtered and dried in vacuum at 70 °C. The newly formed beads were ground to a constant particle size (<84 μm) before use.

2.3. Modification of magnetic chitosan with xanthate (XMCS)

Grafting of thiol groups was carried out according to the procedure described by Kannamba et al. (2010) with chitosan flakes. The cross-linked magnetic chitosan (2 g) were treated with 100 mL of 14% NaOH solution and 1 mL of CS_2. The mixture was stirred at room temperature for 24 h. The product was washed thoroughly with DI water, dried in vacuum at 70 °C and used in all the experiments.

2.4. Characterization of XMCS

Fourier transform infrared spectroscopy (FTIR) spectra of XMCS before and after adsorption of Co(II) were recorded using FTIR spectrometer (Spectrum GX, Perkin-Elmer) connected with a computer. Samples were prepared in KBr disks. The scanning range was 400–4000 cm^{-1}. X-ray photoelectron spectra (XPS) of XMCS before and after Co(II) adsorption were obtained using PHI Quantera SXM XPS spectrometer. Computer deconvolution was applied to detect the elemental peaks present in the XMCS.

2.5. Co(II) uptake experiments using batch method

Experiments were carried out by mixing sorbent with 15 mL of an aqueous solution of Co(II). The mixture was agitated at 150 rpm in a temperature controlled shaker to reach the equilibrium. The solution pH was adjusted to 5.0 with 0.1 N HCl or 0.1 N NaOH aqueous solution without any further adjustment during the sorption process.

For MCS, adsorption kinetics was studied using an initial concentration of 10 mg/L with the sorbent dosage of 20 mg/15 mL at 30 °C. During the kinetics experiment, aliquots of samples were withdrawn at fixed intervals and the concentration of the Co(II) ions in each of the samples was determined. Adsorption isotherms were studied at various initial concentrations of Co(II) ion in the range of 5–50 mg/L with the sorbent dosage of 20 mg/15 mL.

However, for XMCS, when the initial concentration of Co(II) was 10 mg/L and the XMCS dosage was 20 mg/15 mL in adsorption kinetics study, there was no residue Co(II) detected even the contact time was 5 min. In equilibrium study, when the initial concentration of Co(II) was at 5–20 mg/L and the XMCS dosage was 20 mg/15 mL, there was also no residue Co(II) detected. So, for XMCS adsorption experiments, adsorption kinetic was studied using an initial concentration of 20 mg/L with the sorbent dosage of 10 mg/15 mL. Adsorption isotherms were studied at various initial concentrations of Co(II) ion in the range of 10–100 mg/L with the sorbent dosage of 10 mg/15 mL.

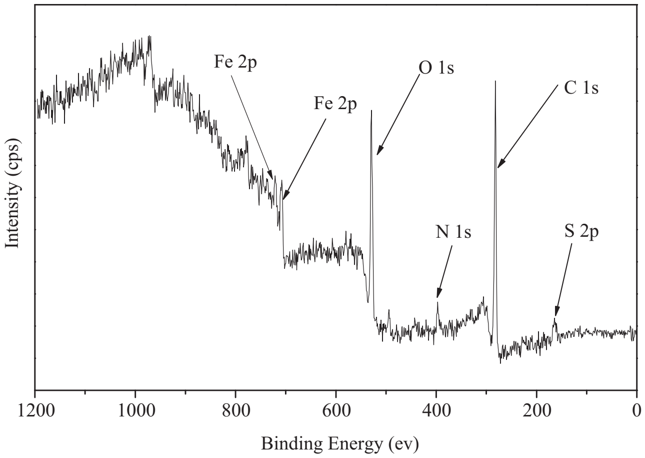


Fig. 1. XPS spectrum of XMCS.

The Co(II) concentrations were determined by atomic absorption spectrometric method with flame atomization (AAS 6 Vario). All experiments were conducted three times.

The adsorbed amount of Co(II) ion per unit weight at time t, q_t (mg/L) was calculated from the mass balance equation as

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where C_0 and C_t (mg/L) are the initial Co(II) ion concentration and the Co(II) ion concentration at any time t, respectively; V is the volume of the Co(II) ion solution; and m is the weight of MCS or XMCS.

3. Results and discussion

3.1. Characterization of XMCS

Amine groups of chitosan are the potential functional groups, which complex with toxic metal ions during the adsorption process. In the present study, a new thiol group was introduced and cross-linked with glutaraldehyde in order to improve the adsorption capacity and resistance to solubility in acid media. XMCS was characterized by XPS spectra analysis.

XPS spectra are widely used to distinguish the different forms of the same element and to identify the existence of a particular element in a material (Sankararamakrishnan and Sanghi, 2006). The XPS spectrum of XMCS is presented in Fig. 1. It shows the peaks corresponding to carbon, nitrogen, oxygen, iron and sulphur. The characteristic peaks of C 1s (285 eV), N 1s (399 eV) and O 1s (532 eV) was observed for XMCS. The Fe 2p spectrum shows two broad peaks at 710 eV and 724 eV representing Fe 2p3/2 and Fe 2p1/2 respectively, according well with the dual oxidation states (Fe(II) and Fe(III)) of iron oxide (Lee et al., 2010). Fe(II) and Fe(III) are components of Fe_3O_4. Fe_3O_4 has magnetic properties and can be used for the magnetic separation. A peak at 164 eV infers the presence of sulphur on the surface of XMCS (Castner, 1996). From the XPS spectrum, we could see that the magnetic chitosan has been successfully modified by xanthate.

3.2. Adsorption kinetics

Fig. 2 gives a typical result for Co(II) adsorption on MCS and XMCS. Both for MCS and XMCS, the plots were characterized by a monotonous increasing trend with the steep climb at the beginning of sorption being succeeded by a more gradual rise, then reaching equilibrium at 6 h (XMCS) or 8 h (MCS). Obviously, the adsorption capacity of XMCS was quite higher than MCS.