Journal of Environmental Management 92 (2011) 3121–3129

Contents lists available at ScienceDirect

Journal of Environmental Management

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

P(4-vinyl pyridine) hydrogel use for the removal of UO_2^{2+} and Th^{4+} from aqueous environments

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ARTICLE INFO

Article history:
Received 3 August 2010
Received in revised form
13 June 2011
Accepted 2 August 2011
Available online 24 August 2011

Keywords:
Magnetic composite hydrogels
Uranium and thorium removal
Smart materials
4-Vinyl pyridine
2-Hydroxyethylmetacrylate

ABSTRACT

4-vinyl pyridine (4-VP) based hydrogels with 2-hydroxyethylmetacrylate (HEMA) and magnetic composites were prepared and tested for use in the removal of UO_2^{2+} and Th^{4+} ions from aqueous environments. It was found that the absorption of these metal ions from aqueous environments decreased with an increase in the amount of HEMA contained within p(4-VP-co-HEMA) hydrogels between 0.498 mmol for pure p(4-VP) and 0.027 mmol for pure p(HEMA). The characterization of the hydrogels was determined by swelling experiments, FT-IR and thermal analysis. The effects of initial metal ion concentration, hydrogel amount and the temperature of the medium on absorption of the ions were investigated. Langmuir and Freundlich isotherms were constructed for the absorption of UO_2^{2+} and Th^{4+}. Both isotherms demonstrated that these metal ions complied with monolayer absorption kinetics.

1. Introduction

Toxic metal ions (whether radioactive or not) contaminate the environment and are released by many industrial activities and mining plants (James et al., 2009; Akkaya and Ulusoy, 2008). A great many studies have been carried out on removing metal ions from various media by different polymer-based adsorbents (Pekel et al., 2004). Metal ions are not biodegradable and they have high toxicity; some are carcinogenic in living organisms. In addition to reverse osmosis, electrochemical treatments, hyper filtration, membrane separation, evaporation, coagulation, bio-sorption processes, and extraction (Akkaya and Ulusoy, 2008; Ozay et al., 2009, 2010; Karadag et al., 2007; Saraydin et al., 2001; Singh et al., 2010), some metal ions can be removed from aqueous media by using low-cost polymeric sorbents.

Uranium (U) and thorium (Th) are among the most important metal ions (Akperov et al., 2009) that threaten the environment with both toxic and radioactive effects (Denizli et al., 2004; Ulusoy and Akkaya, 2009; Han et al., 2007). With the development of the nuclear industry, including power plants and the weapons industry, the amount of UO_2^{2+} and Th^{4+} discharged to the environment has increased progressively (Donia et al., 2009; Kundakci et al., 2009; Boonchayaanant et al., 2009). UO_2^{2+}, $UO_2(OH)^+$, $UO_2(OH)_2^0$ and $UO_2(OH)_3^-$ from natural sources (soil, rock, etc.) can exist and create different problems. Solution properties such as the pH of the medium and the presence of other ions (Atun and Ortaboy, 2009; Karadag et al., 2007; Han et al., 2007) affect the solubility of metal ions.

Hydrogels are capable of swelling up to a hundred times, in some cases even thousands of times, more than their dry mass in aqueous environments by imbibing large amounts of water due to the hydrophilic groups (−OH, −COOH, NH_2, $-CONH_2$, $-SO_3H$) in their polymeric networks. These unique properties give hydrogels many advantages for their use in applications as broad as bioengineering, pharmaceuticals, medicine, food industry, water purification, sensors and so on (Ozay et al., 2009, 2010; Uzum et al., 2007; Sahiner and Singh, 2007; Barakat and Sahiner, 2008). Environmental factors, such as pH, ionic strength, temperature, and use of some molecules as a signal for hydrogels, can produce responses accordingly. There are many investigations into the removal of toxic metal ions by hydrogels (Akkaya and Ulusoy, 2008; Pekel et al., 2004; Ozay et al., 2009, 2010; Uzum et al., 2007; Saraydin et al., 2001; Denizli et al., 2004; Ulusoy and Akkaya, 2009). Especially as some hydrogels can be modifiable, able to adopt additional

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doi:10.1016/j.jenvman.2011.08.004

characteristics such as magnetic properties; they are very important in the struggle against toxic contamination (Ozay et al., 2009; Barakat and Sahiner, 2008; Pekel et al., 2001; Liu et al., 2010).

4-vinyl pyridine (4-VP) is an interesting material that can complex with metal ions by means of its nitrogen atom, can be further employed to create charge and hydrophobic groups, and additionally can be readily polymerized (Fares et al., 2003). In this study, p(4-VP), p(2-hydroxyethylmetacrylate) p(HEMA), and p(4-vinyl pyridine-c-2-hydroxyethylmetacrylate) (p4-VP-c-HEMA) hydrogels were synthesized via a redox polymerization technique. The synthesized polymeric, pH sensitive, hydrogels were characterized by thermal analyzer and FT-IR spectroscopy. Furthermore, p(4-VP)-based hydrogels with magnetic properties were prepared as a composite material and used in absorption experiments of UO_2^{2+} and Th^{4+} ions in aqueous media. Langmuir and Freundlich adsorption isotherms were applied to the removal of these toxic metal ions and both isotherms resulted in a reasonably good fit.

2. Experimental

2.1. Materials

4-vinyl pyridine (95%, Acros) and 2-hydroxyethylmetacrylate (99%, Acros) as monomers, N, N′ methylenebisacrylamide (MBA) (99%, Sigma) as crosslinkers, ammoniumpersulfate (APS) (98%, Aldrich) as an initiator, and N, N, N′, N′-tetramethylethylenediamine (TEMED) (Across) as an accelerator were used in the hydrogel preparation. Uranyl nitrate hexahydrate (98%, Sigma) and thorium nitrate pentahydrate (99%, Merck) were used as metal ion sources for the absorption experiments. $FeSO_4.7H_2O$, and $FeCl_3$ (Fluka) were used as metal ion sources for magnetic particle synthesis. All the reagents were of analytical grade or highest purity available, and used without further purification. The DI water was 18.2 MΩ cm (Millipore Direct-Q3 UV) and was used throughout the absorption experiments. The pH measurements were performed using a Sartorius Documenter pH meter.

2.2. Synthesis of p(4-VP)-based hydrogels

The hydrogels p(4-VP), p(HEMA) and p(4-VP-c-HEMA) were synthesized via a redox polymerization technique. Briefly; in a certain amount of 4-VP, 0.125 mol % MBA (with respect to monomer) as a crosslinking agent was dissolved by mixing thoroughly using a vortex mixer and to this solution 100 μl TEMED was added and mixed thoroughly using a vortex mixer. Finally, the initiator solution APS (1 mol % with respect to monomer) in 1 ml water was added to this hydrogel precursor. After mixing meticulously, the solution was injected into plastic straws with 5 mm diameter and allowed to polymerize and crosslink for 12 h to complete the reaction. Then, hydrogels were removed from the plastic straws, cut into 6 mm long cylinders and cleaned by placing in DI water for 72 h. The hydrogels were washed by replenishing the wash water every 12 h to remove unreacted species (monomer, polymer, crosslinker, and initiator). After the cleaning procedure, hydrogels were dried in a vacuum oven at 40 °C to a constant weight and kept in sealed containers for absorption experiments and swelling studies.

2.3. Preparation of hydrogel composites

Insitu magnetic p(4-VP)-based hydrogels were prepared according to the literature with some modification (Ozay et al., 2009, 2010; Sahiner, 2006). In brief, a known amount of dried and cleaned p(4-VP)-based hydrogel was placed in nitrogen-purged 0.5 M Fe(II) and 1 M Fe(III) mixture for 24 h (total volume 100 mL). At the end of this metal ion loading time, hydrogels were kept in DI water for a day to remove the unbound or physically absorbed metal ions. After cleaning, the metal-ion-absorbed hydrogels were transferred into nitrogen-purged 0.5 M 100 mL sodium hydroxide solution for *in situ* reduction of absorbed iron ions by keeping them in a water-shaker for 12 h. Hydrogel composites were cleaned by placing them in distilled water for another 6 h at ambient temperature. The cleaned composite hydrogels were separated and dried in vacuum oven at 40 °C and stored in a sealed container for further use.

2.4. Characterization and swelling behavior of hydrogels

To investigate the thermal behavior of the hydrogels and composite hydrogels thermogravimetric analysis (TGA) was carried out by using a thermal analyzer (SII TG/DTA 6300 model) heating up to 50–850 °C under N_2 with 100 mL/min flow rate at 10 °C/min heating rate. The samples weighed 4 mg. The FT-IR spectra of hydrogels were obtained from a Perkin Elmer Spectrum 100 instrument using ATR apparatus with 4 cm^{-1} resolution between 4000 and 650 cm^{-1}. Swelling studies of hydrogels were performed in triplicate with distilled, tap and sea water (Dardanelles Strait, Canakkale, Turkey) to observe possible utilization of these absorbents in different media. The mass increase was measured by weighing the hydrogels at certain times after wiping with filter paper to remove the superficial water, and then placing back into the same swelling media. Hydrogels were kept in swelling medium for 24 h to determine the maximum swelling values, % S. The % S values can be calculated by subtracting the dry weight of the hydrogel from the water swollen weight at time t and dividing by dried weight and then by multiplying the overall result by 100. Swelling characterization was also studied as a function of pH between 2 and 12 by adjusting the pH of the solutions with 0.1 M HCl and 0.1 M NaOH. Again hydrogels were kept 24 h in acidic and basic solutions to determine the effect of medium pH on the swelling behavior.

2.5. Absorption studies from aqueous media

The absorption experiments of UO_2^{2+} and Th^{4+} ions from aqueous media were carried out in a water-shaker bath at 30 °C. The effects of metal ion concentration on the absorption performance were investigated by placing 0.25 g hydrogel (p(4-VP),

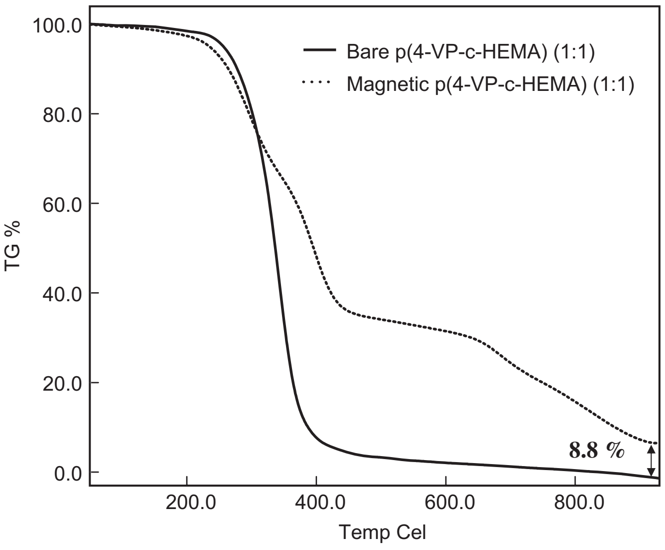

Fig. 1. The thermogram of bare and magnetic p(4-VP-c-HEMA) (1:1) hydrogels.