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Radiation synthesis of a new amidoximated UHMWPE fibrous adsorbent with high adsorption selectivity for uranium over vanadium in simulated seawater

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HIGHLIGHTS

- GMA and MA were grafted on UHMWPE fiber by radiation graft copolymerization.
- The nitrile groups were immobilized onto grafted UHMWPE fiber via chemical method.
- This new AO-based fibrous adsorbent has good adsorption selectivity of uranyl ion.

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ABSTRACT

A new kind of highly efficient adsorbent material has been fabricated in this study for the purpose of extracting uranium from seawater. Ultra-high molecular weight polyethylene (UHMWPE) fiber was used as a trunk material for the adsorbent, which was prepared by a series of modification reactions, as follows: (1) grafting of glycidyl methacrylate (GMA) and methyl acrylate (MA) onto UHMWPE fibers via ^{60}Co γ-ray pre-irradiation; (2) aminolyzation of UHMWPE fiber by the ring-opening reaction between of epoxy groups PGMA and ethylene diamine (EDA); (3) Michael addition of amino groups with acrylonitrile (AN) to yield nitrile groups; (4) amidoximation of the attached nitrile moieties by hydroxylamine in dimethyl sulfoxide–water mixture. Modified UHMWPE fibers were characterized by means of attenuated total reflectance-Fourier transformed infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) to confirm the attachment of amidoxime (AO) groups onto the UHMWPE fibers. The results of X-ray diffraction (XRD) and single fiber tensile strength verified that the modified UHMWPE fiber retained excellent mechanical properties at a low absorbed radiation dose. The adsorption performance of the UHMWPE fibrous adsorbent was evaluated by subjecting it to an adsorption test in simulated seawater using a continuous-flow mode. The amount of uranium adsorbed by this AO-based UHMWPE fibrous adsorbent was 1.97 mg-U/g after 42 days. This new adsorbent also showed high selectivity for the uranyl ion, and its selectivity for metal ions was found to decrease in the following order: U > Cu > Fe > Ca > Mg > Ni > Zn > Pb > V > Co. The adsorption selectivity for uranium is significantly higher than that for vanadium. In addition, preparation of this modified adsorbent consumes much smaller amounts of the toxic acrylonitrile monomer than the conventional preparation methods of AO-based polyethylene fibers.

1. Introduction

Recovery of uranium from seawater has become a hot research topic recently, arousing great interest of scholars because of the heavy demand for uranium used as nuclear fissile fuel and also due to the large quantity of uranium deposited in seawater (Sun et al., 2013a). The total amount of uranium in seawater is about

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4.5 billion tons, which is about one thousand times more than the amount found in mineral ores on land (Davies et al., 1964; Rao, 2011). Although there is an enormous amount of uranium in seawater, its concentration is extremely low (only about 3.3 ppb) while other metal ions in seawater have relatively high concentrations (Kobuke et al., 1990; Takeda et al., 1991). Therefore, the development of an excellent adsorption material with high adsorption capacity and selectivity for uranyl ion in seawater is one of the most important issues in uranium extraction from seawater.

Extensive investigations have been carried out over the years to develop adsorbents capable of recovering uranium from seawater and aqueous solutions. In the early 1980s, German researchers conducted systematic screening studies of about 200 adsorbents for collection of uranium from seawater and found that the amidoxime (AO) functional group was the most promising adsorbent candidate (Kim et al., 2013; Rao, 2011; Schenk et al., 1982). Since then, Japanese researchers have prepared adsorption materials for extraction of uranium from seawater by carrying out radiation graft polymerization of acrylonitrile onto polyethylene (PE) nonwoven fabric, chosen as trunk polymer, and converting the cyano groups of grafted polyacrylonitrile (PAN) chains into AO groups (Tamada, 2009). In later years, various copolymeric adsorbents imparted different hydrophilic monomers were prepared in order to enhance the selectivity for uranyl ions by some other groups (Oren et al., 2000; Pekel et al., 2000a, 2000b, 2001). Polymer fibrous materials have gained considerable interest as uranium adsorbents since they have high specific surface area compared to common non-woven fabrics and resins. Some other AO-based fibrous adsorbents have also been prepared via radiation-induced graft polymerization (RIGP) (Chi et al., 2013; Xing et al., 2013a, 2013b), and RIGP–ATRP (atom-transfer radical polymerization) hybrid approach (Saito et al., 2014). These previous works have contributed significantly to the research of uranium recovery from seawater. However, for the preparation of AO-based adsorbents, a large amount of acrylonitrile is typically used in the grafting polymerization process in order to enhance the grafting yield and obtain high AO group density. Acrylonitrile is a highly toxic, explosive and volatile chemical; thus special care and handling are required during the grafting polymerization of acrylonitrile.

In this work, ultra-high molecular weight polyethylene (UHMWPE) fiber was selected as a substrate for the preparation of AO-based fibrous adsorbent due to its high specific modulus and strength, as well as excellent corrosion and impact resistance. Moreover, the alkyl radicals trapped in the UHMWPE fiber have long lifetimes, which is helpful for the pre-irradiation induced graft polymerization step (Zhao et al., 2011). The nitrile groups can be anchored onto the UHMWPE fiber by a combination of radiation graft polymerization and a series of chemical modifications, as listed below: (1) introduction of epoxy groups via pre-irradiation induced graft copolymerization of GMA and MA; (2) aminolyzation via the ring-opening reaction between the epoxy group and EDA; (3) immobilization of acrylonitrile using Michael addition reaction (de Souza et al., 2009; Worner and Mulhaupt, 1993). The final step involves amidoxination of the immobilized nitrile moieties with hydroxylamine, to yield the AO-based fibrous adsorbent material. Compared with conventional radical polymerization, these processes have some advantages, such as flexible operation, mild reaction condition and convenient post-processing. More importantly, the consumption amount of acrylonitrile can be reduced significantly via cyclic utilization of residue acrylonitrile monomer and the density of nitrile groups onto UHMWPE fiber can be quantitatively controlled via adjustment of experimental parameters. In this paper, the kinetics of graft polymerization of GMA with the aid of MA are discussed as well as the variation of the density of nitrile groups on fiber with reaction time. Chemical structure, surface morphology, thermal stability and tensile strength of modified fibers were systematically characterized. The adsorption performance of these UHMWPE fibrous adsorbents was evaluated by subjecting them to adsorption tests in simulated seawater with uranium concentration of 3.3 ppb and other metal ions, approximately equal to that of real seawater. This investigation is expected to provide a new approach to the preparation of uranium adsorption fiber with outstanding performance. More importantly, we have found this fiber adsorbent has very good adsorption selectivity of uranyl ion over vanadium in the simulated seawater.

2. Experimental

2.1. Materials

UHMWPE fiber with a linear density of 3.6 Denier, was purchased from Beijing Tongyizhong Advanced Material Company. Glycidyl methacrylate purchased from Sigma Co. Ltd., was used without further purification. Other reagents, purchased from Sinopharm Chemical Reagent Company, were of analytical grade. A 5 (w/w) % solution of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) was prepared using 50/50 (v/v)% water/dimethyl sulfoxide as the solvent, and its pH was adjusted to 7 using solid Na_2CO_3. Nitrogen (99.99%) was supplied by Loutang Special Gases of Shanghai.

2.2. Preparation of UHMWPE fiber adsorbent

Preparation of UHMWPE fiber adsorbent containing graft chains with functional AO groups requires four procedures as illustrated in Fig. 1. (1) Grafting of GMA and MA onto UHMWPE fibers by pre-irradiation induced graft copolymerization; (2) modification of GMA moieties with ethylene diamine in 1, 4-dioxane; (3) reaction of AN with amine group using a Michael addition reaction to obtain graft chains containing nitrile groups; (4) amidoximation of nitrile groups on the grafted chains using hydroxylamine hydrochloride.

UHMWPE fibers (6 cm in length, 0.12 g) were bound into sheaves and wrapped with aluminum foil for irradiation. The samples were irradiated via γ-ray (dose rate: 1.67 kGy/h) in air at room temperature (about 25 °C) with different absorbed doses from 5 to 50 kGy, since radiation generated radicals in UHMWPE fiber can be stable in air for a long time. The irradiated fiber was immersed in a flask containing GMA/MA/methanol solution. The solution was bubbled with nitrogen for 20 min to remove the oxygen before graft polymerization. The graft polymerization was conducted in a water bath at 55 °C for 3 h. Afterwards, the grafted samples were extracted with acetone in a Soxhlet apparatus for 24 h to remove homopolymer and residual monomer, and then dried at 60 °C in vacuum oven. After drying to a constant weight, the degree of grafting (Dg) was calculated as follows:

$$Dg\,(\%) = W_1 - W_0/W_0 \times 100 \quad (1)$$

where W_o and W_1 represent the weights of the initial and grafted fibers, respectively. The amount of epoxy groups of UHMWPE-*g*-P (GMA-*co*-MA) fiber was measured by titration using hydrochloric acid and acetone (Tang et al., 2013).

The UHMWPE-*g*-P(GMA-*co*-MA) fiber was modified with 50% (v/v) of EDA in 1,4-dioxane at 80 °C for 3 h. The modified sample was washed several times with fresh ethanol and deionized water to remove the residual EDA, and then dried in a vacuum oven at 60 °C. UHMWPE-*g*-P(GMA-*co*-MA)-EDA fiber was further immersed in 50% (v/v) of AN in ethanol solution at 40 °C for different time periods to obtain various conversions. The resulting fiber was washed several times with ethanol and deionized water to remove