



Preparation of a novel electrospun polyvinyl alcohol/titanium oxide nanofiber adsorbent modified with mercapto groups for uranium(VI) and thorium(IV) removal from aqueous solution

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HIGHLIGHTS

- ▶ The synthesized novel adsorbent was characterized by FTIR, SEM and BET analysis.
- ▶ The sorption affinity of metal ions was Th(IV) > U(VI) for both utilized systems.
- ▶ We observed physical sorption mechanism and endothermic sorption for both metal ions.
- ▶ The U(VI) and Th(IV) sorption onto the nanofiber did not change after five cycles.
- ▶ In the binary system, the inhibitory effect of Th(IV) ion was greater than U(VI) ion.

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ABSTRACT

A novel polyvinyl alcohol (PVA)/titanium oxide (TiO₂) nanofiber adsorbent modified with mercapto groups was synthesized by electrospinning. The adsorbent was characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) and Brunauer–Emmett–Teller (BET) analysis. The influence of several variables such as TiO₂ and mercapto contents, adsorbent dose, pH, contact time, initial concentration of U(VI) and Th(IV) ions and temperature were studied in batch experiments. The results showed that the sorption capacities of both metal ions for the modified PVA/TiO₂ nanofibers were remarkably greater than those of the unmodified nanofibers. The kinetic data were described with pseudo-first-order, pseudo-second-order and double-exponential models. Three isotherm models, namely Freundlich, Langmuir and Dubinin–Radushkevich were used for analysis of equilibrium data. The maximum sorption capacities of U(VI) and Th(IV) by Langmuir isotherm are estimated to be 196.1 and 238.1 (mg/g) at 45 °C with pH of 4.5 and 5.0, respectively. Calculation of ΔG° , ΔH° and ΔS° showed that the nature of both metal ions sorption onto the nanofiber was endothermic and spontaneous and was favored at higher temperature. The sorption capacity did not change remarkably after five cycles of sorption–desorption. The selectivity order of uranium and thorium sorption onto the adsorbent was Th(IV) > U(VI). The inhibitory effect of competitive Th(IV) ion on the U(VI) sorption was greater than the inhibitory effect of competitive U(VI) ion on the Th(IV) sorption in the binary systems. Also the inhibitory effect was increased with increase of concentration of metal ions.

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1. Introduction

Radioactive waste originates from the nuclear industrial activities and some human activities such as exploitation of ores [1]. The appraisal of water pollution, which depends on the presence of radionuclide in the ground, is of major environmental concern [2]. Uranium and thorium are the poisonous radioactive elements. The toxic nature of these radionuclides has been a serious health problem

for many years [1]. For example, these elements affect the human health by creation such diseases as the lung and liver cancers [3,4]. In addition, the recovery and removal of uranium and thorium is a principal purpose for industry and saving clean water resources [1,5]. Solvent extraction [6], chemical precipitation [7,8], reverse osmosis and membrane separation [9], ion exchange [10], electro-floation [11], coagulation [12] and sorption processes [13] are some techniques for removing heavy metal ions from aqueous solution. Sorption and ion exchange are the most popular methods for the removal of heavy metal ions from aqueous solution. High efficiency, simple operation and environmental compatibility are some of the

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advantages of sorption process [14]. Certain properties such as high mechanical and thermal stability and high sorption capacity should be considered for the adsorbent. For these reasons, the choice of suitable materials for sorption of heavy metal ions from aqueous solution is very important. Some adsorbents have been utilized as materials for the sorption of heavy metal ions and radioactive elements including zeolites [1], polymers [15], metal oxides [16] and polymer/metal oxides [17]. For example, the maximum sorption capacity of uranium ions onto the PVA/TEOS/APTES hybrid nanofiber membrane is found to be 168.1 mg/g with the optimum pH of 4.5 and at the optimum temperature of 45 °C [4]. Nano-sized titanium oxide (TiO₂) has been investigated as an adsorbent for removal of heavy metal ions due to its physical and chemical stability, nontoxicity and high specific surface area. But, in the field of water treatment, powdered nanoporous material is not suitable for recycling [18]. Separation of TiO₂ from aqueous solution is very difficult, specially, when particle size is on a nano-scale. Currently, researchers are focusing on ways of applying nano-powder metal oxides for removal of heavy metal ions. One of the ways is to add nanoparticles to an organic material such as polymer matrix for their immobilization. Polymer nanofibers improve mechanical and thermal properties of the adsorbent [19]. Electrospinning is a simple, reliable and convenient technique for generating nanofiber materials [20]. Both polymer and inorganic materials can be electrospun to fibers [21]. Removal efficiency of heavy metal ions increases after nanofiber adsorbents are modified with -NH₂, -SH, -HSO₃, tetrazine and phosphoric functional groups, which can react with the metal ions [5,17,19]. After modification, electrospun nanofibers with long length and high specific surface area have found general applications for removing heavy metal ions from aqueous solution [21]. Recently, TiO₂ nanofibers were fabricated successfully by electrospinning [18]. Most of the studies have been focused mainly on synthesis, structural characterization and morphology [19,21]. Little attention has been paid to the sorption properties based on TiO₂ nanofibers [18].

In this study, at first, the TiO₂ nanoparticles surface was modified by -SH functional group of 3-mercaptopropyltrimethoxysilane (TMPTMS). Then, the novel mesoporous PVA/TiO₂/TMPTMS composite nanofibers were synthesized via electrospinning method. The aim of this study was the sorption of uranium and thorium on polyvinyl alcohol (PVA)/TiO₂/TMPTMS nanofiber adsorbent. The structure of the prepared nanofiber was characterized using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR). Specific surface area of PVA/TiO₂/TMPTMS nanofiber adsorbent was measured by the Brunauer-Emmett-Teller (BET). Also the effects of both TiO₂ and TMPTMS contents, pH, contact time, initial concentration, adsorbent dose and temperature on the sorption process were investigated. Also, the inhibitory effect of the initial Th(IV) and U(VI) ions concentrations on the sorption capacity was investigated in the binary (U(VI)-Th(IV)) system.

2. Experimental

2.1. Materials

Nano-sized TiO₂ powder was purchased from Aldrich Co. with average particle sizes of 10–20 nm. PVA polymer (99% hydrolyzed, average MW = 72000), TMPTMS and acetone were provided by Sigma-Aldrich. The solutions of thorium and uranium ions were prepared by dissolving weighed amounts of thorium nitrates and uranyl nitrates (Aldrich) in deionized water, respectively. Deionized water was utilized throughout this experiment.

2.2. Surface modification of TiO₂ nanoparticles

The nanoparticles were dried at 400 °C for 8 h before surface modification. Then 0.2 g of TiO₂ nanoparticles was added into

20 mL acetone. After that, 5, 10, 15 and 20 weight percentages of silane coupling agent (TMPTMS) were dissolved in 20 mL distilled water. Then the mixture of nanoparticles and TMPTMS was sonicated for 2 h. The reaction mixture was centrifuged and washed with distilled water two times to remove the unattached coupling agent molecules. Finally, the modified TiO₂ nanoparticles were dried for 4 h. The presence of organic groups on the surface of modified nanoparticles was confirmed by FT-IR spectrum.

2.3. Preparation of PVA/TiO₂ and PVA/TiO₂/TMPTMS nanofibers

For preparation of PVA/TiO₂ solution, first, aqueous 10 wt% PVA solutions were provided by dissolving 1 g of PVA in 10 mL deionized water, after that, different amounts of unmodified TiO₂ nanoparticles (5, 7, 10, 15, 20, 25, 30 wt% of TiO₂) were dispersed in PVA solution and then sonicated for 12 h (solution A). For preparation of PVA/TiO₂/TMPTMS solution, first, different amounts of modified TiO₂ (0.2 g of TiO₂ with 5, 10, 15, 20 wt% of TMPTMS) were dispersed in PVA solution and then sonicated for 12 h (solution B). Then the prepared solutions (solutions A and B for preparation of PVA/TiO₂ and PVA/TiO₂/TMPTMS nanofibers, respectively) were put into 10 mL plastic syringe with a 0.5 mm diameter capillary tip. A variable high voltage generator was used for the electrospinning process. The positive terminal of a high voltage generator was connected to the metallic syringe tip while the negative terminal was connected to an aluminum foil. The applied voltage was 17.5 kV. The electrospun fibers were collected on a aluminum foil coiled on a metal cylinder rotating at 200 rpm. The distance between the tip and the collector was 15 cm and the flow rate of the spinning solution was 0.3 mL/h.

2.4. Adsorbent characterization studies

The fibers were characterized by Fourier Transform Infrared spectroscopy (FTIR) (Vector22-Bruker Company, Germany) in the range of 400–4000 cm⁻¹ and Scanning Electron Microscopy (SEM, JEOL JSM-6380). Specific surface area was measured by the Brunauer-Emmett-Teller (BET) method. Total pore volume and pore size were calculated on the basis of BJH (Brrett-Joyner-Halenda) method. The point of zero charge (PZC) was investigated for finding of the surface charge of PVA/TiO₂/TMPTMS nanofiber adsorbent. The point of zero charge (pH_{pzc}) shows a pH at which the total number of negative and positive charges on its surface becomes zero. The pH_{pzc} for the adsorbent was determined by the following method. 0.1 M NaCl was prepared and its initial pH was adjusted between 1 and 6 by using 0.1 M HCl and/or 0.1 M NaOH solution. Then, 50 mL of 0.1 M NaCl was transferred in series of 100 mL flasks, and 0.1 g of adsorbent was added to each solution. After that, the solutions were shaken for 2 days at 25 °C. Finally, the values of the final pH were plotted versus their related initial pH values. pH_{pzc} of adsorbent was determined on the basis of the points where the initial pH equals the final pH.

2.5. Batch adsorption studies

In a single component, adsorption experiments were performed by adding 0.05 g of adsorbent to 50 mL of solution with an initial U(VI) and Th(IV) ions concentration of 30 mg/L in a flask (except optimizing of adsorbent dose). The effect of TiO₂ and TMPTMS weight percentages on sorption of metal ions was studied with an adsorbent dose of 1 g/l and at temperature, pH and contact time of 25 °C, 5 and 5 h, respectively. The effect of pH on sorption of U(VI) and Th(IV) ions was studied in the range of 1–6, at a temperature of 25 °C and contact time of 5 h. The effect of contact time was investigated by varying the time from 10 to 360 min, at a temperature of 25 °C and with an optimum pH. The effect of adsorbent

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