Niobate nanofibers for simultaneous adsorptive removal of radioactive strontium and iodine from aqueous solution

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ABSTRACT

Radioisotopes pose a potential mass threat to public heath if accidently released into the environment. To mitigate the consequences, effective methods must be developed for removal of radioactive ions from the environment. In this study, we show that nanofibers of sodium niobate with negatively charged layers and readily exchangeable sodium ions between the layers can efficiently remove radioactive Sr^{2+}. The exchange of Sr^{2+} ions with the interlayer Na^+ ions can cause structural deformation of layers, trapping the Sr^{2+} in the nanofibers. Furthermore, silver oxide (Ag_2O) nanocrystals can be firmly anchored on the surface of niobate nanofibers via coherent interfaces between Ag_2O and niobate phases. I^- anions in fluids can easily access the Ag_2O nanocrystals and be efficiently trapped by forming an AgI precipitate that firmly attaches to the adsorbent. This bi-functional absorbent can be arranged to remove Sr^{2+} and I^- ions simultaneously by optimizing the Ag_2O loading and Na^+ content of the niobate nanofibers. It can provide high adsorption capacity for both ions in basic media, unlike other adsorbents that can be used in acid or neutral media. The maximum adsorption capacities of Sr^{2+} and I^- for Ag_2O anchored sodium niobate nanofibers were found to be 148.92 and 296 m^2 g^{-1} respectively. Furthermore, the niobate adsorbents can be readily dispersed in liquids and easily separated after purification due to their fibril morphology, which significantly enhances their adsorption efficiency and reduces separation costs. This study demonstrates that Ag_2O anchored sodium niobate nanofibers with fibril morphology, negatively charged thin layers and readily exchangers are potential sorbent for the simultaneous uptake of cations and anions.

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1. Introduction

Radioactive ^{90}Sr and ^{131}I are products of nuclear fission; they easily dissolve in water. Thus, accidental release to the environment of these radionuclides during an accident at a nuclear reactor poses a serious threat to the health of a large part of population [1–8]. Such incidents have already occurred at Chernobyl in 1986, at Three Mile island in Pennsylvania in 1979, and in 2011 at Fukushima, Japan. Especially after the nuclear accident at Fukushima, concerns about nuclear waste leakage have risen globally, the main worry being that such radionuclides with high mobility will move into soils via contaminated water [9]. This will lead to them entering the human food chain via plants. Recently, high levels of radiostrontium (^{90}Sr) and radioactive iodine (^{131}I) have been found in the groundwater at the devastated Fukushima nuclear facility. It is clear that development of effective techniques for separation of such radionuclides from radioactive liquid waste is of great practical significance.

The key requirements in the development of such a technology are to devise materials which are able to adsorb radioactive ions irreversibly, selectively, and efficiently. Inorganic layered ion exchangers, such as metal phosphates [10], synthetic micas [11,12], clay minerals [13], magadites [14], titanates and niobates [15–19], have the advantages of higher selectivity for target cations, and higher resistance to radiation and temperature compared to organic resins. Furthermore, in some metastable layered materials, a structural collapse occurs during ion exchange, resulting in tight immobilization of target cations in the interlayers, causing ion exchange to be irreversible [19]. This is significant given the desire for complete removal of target cations from wastewater, and allows safe disposal of entrapped hazardous cations without worries that they will leach from ion exchangers. However, layered ion exchangers are ineffective for adsorbing anionic radionuclides such as iodine species, because they have both a permanently negatively charged surface like other aluminosilicate minerals, and a pH-dependent negative surface charge caused by deprotonation of

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the surface hydroxyl group under high pH conditions [20,21]. It is thus challenging to develop bi-functional adsorbents which can remove both ^{90}Sr cations and ^{131}I anions at the same time.

I[-] anions can readily react with silver oxide (Ag_2O) to form insoluble silver iodide (AgI). However, the direct use of Ag_2O or another silver compound to precipitate iodine species is impractical because the capacity and adsorption dynamics of the removal mainly depend on the specific surface area of Ag_2O particles [21]. Recently, Ag_2O grafted layered nanomaterials, such as Ag_2O grafted layered titanate [22], and Ag_2O grafted layered sodium vanadate [23], have shown better removal ability for radioactive Cs^+ and I[-]. These findings initiated a new direction of grafted synthesis of adsorbents for simultaneously capturing radioactive cations and anions from wastewater.

Inorganic materials used as supports must possess some useful features. They should be formed of negatively charged thin layers, have readily exchangeable Na^+ ions located between the layers, have the ability to firmly bind Ag_2O nanocrystals on their surfaces, and demonstrate good resistance to radiation, heat, and chemicals. Although some Ag_2O-based absorbents have displayed high adsorption capacity and selectivity for radioactive iodide ions, the supports displayed poor ion exchange abilities for radioactive cations (^{90}Sr, ^{137}Cs). Furthermore, ^{90}Sr may exist in basic radioactive wastewater, while some support structures are unstable in basic media, losing their ion exchange abilities for radioactive cations. Thus, it is an urgent requirement to find new absorbents with high capacities to remove radioactive cations and anions in basic conditions.

Niobate nanofibers (with chemical formula $Nb_2Na_2O_6 \cdot H_2O$) may be obtained from pentaethoxyl niobium solution by simple hydrothermal treatment. They are stable under a wide range of pH conditions and exhibit excellent resistance to radiation. This material possesses a layered structure composed of [NbO_6] and [NaO_6] octahedral units [19], which endow these materials with abundant microporous structures, open tunnels and relatively high surface area. These layers carry negative charges, and Na^+ ions remain between the layers. The Na^+ ions are easily exchanged with other cations. In our work, nanofibers of a layered niobate to which Ag_2O nanocrystals were anchored were prepared by a simple method; they possessed many exchangeable sodium cations located in the interlayers of the structure. This absorbent exhibited excellent simultaneously removal abilities for radioactive Sr^{2+} and I[-] from basic aqueous solutions.

2. Experimental

2.1. Synthesis

The 1D sodium niobate nanofibers (SNF) were prepared using a simple hydrothermal method, as follows. First, 1 g Nb_2O_5 and 60 mL of 10–12 mol L^{-1} NaOH solution were mixed by stirring at room temperature. Subsequently, the mixture was transferred into a 100 mL Teflon-lined autoclave and allowed to react at 180 °C for 2 h, the autoclave then cooling naturally. The final products were collected by glassware, washed with deionized water three times, and dried in air at 80°.

Ag_2O nanocrystals were anchored to the sodium niobate nanofibers (Ag_2O-SNF) by simple chemical deposition: 0.2 g $Nb_2Na_2O_6 \cdot H_2O$ were dispersed in 200 mL pure water. The pH value of the suspension was adjusted to about 11 by dropwise addition of dilute NaOH solution. The nanoparticles were collected by centrifuging and then dispersed in 200 m L 0.01–0.03 mol L^{-1} silver nitrate aqueous solution (at varying Na/Ag mole ratios between 0.01 and 0.03). After stirring vigorously for 24 h, the precipitate was collected and washed with deionzed water three times, and then dried at 80 °C for 24 h.

2.2. Characterization

The crystalline structure of the samples was characterized using X-ray diffraction (PXRD, X'Pert PRO, PANalytical, Almelo, Netherlands) with Cu-Ka radiation ($\lambda = 0.15406$ nm at 40 kV and 45 mA). The morphology of prepared samples were observed using a field emission scanning electron microscope (FE-SEM Philips XL30 FEG, Eindhoven, Netherlands) and a transmission electron microscope (TEM, JEM200CX, 120 kV). The chemical compositions of the sorbents were determined by energy dispersive X-ray spectroscopy (EDX) technique using the attachment to the same microscope. The composition and chemical state were determined by X-ray photoelectron spectroscopy Fourier transform infrared (FT-IR) spectra of the samples were obtained on a Perkin-Elmer1730 infrared spectrometer in the range of 400–4000 cm.[-1]

2.3. Adsorption test

The equilibrium uptake capacities of the Ag_2O grated sodium niobate absorbents for Sr^{2+} and I[-] ions were measured through batch experiments implemented using a series of concentrations of NaI or $SrCl_2$ solutions ranging from 50 ppm to 1000 ppm. All experiments were equilibrated for over 48 h at room temperature with magnetic stirring. Afterwards the solids and solutions were separated by centrifugation. The concentrations of Sr^{2+} and I[-] in supernatants were analyzed by atomic absorption spectroscopy (AAalyst800, PerkinElmer, USA) and ultraviolet spectrophotometry (UV−vis), respectively.

3. Results and discussion

3.1. Adsorption isotherms of Sr^{2+} and I[-] ions

[90]Sr cations dominate basic radioactive waste by dissolution of irradiated uranium targets. To decrease the radioactive intensity of waste and to recover ^{90}Sr, the absorbent materials must retain its abilities in basic media. The influence of pH on the capture of Sr^{2+} ions by the sodium niobate absorbent was investigated in the pH range 2−11. As shown in Fig. 1a, the percentage of Sr^{2+} removal remained very high (90%) over a wide pH range, 5−11, and the adsorption equilibrium is obtained when pH is over 4. This indicates that sodium niobate has better performance under basic conditions compared to other ions exchangers [24,25]. It also confirms that sodium niobate nanofibers are stable under basic conditions.

After the absorption of Sr^{2+} ions, the used absorbents were investigated by XRD and TEM techniques. TEM images confirm that the fibril morphology is maintained after uptake of Sr^{2+} ions (Fig. 1S). The absorbents can be easily separated from liquid suspensions after absorption because of their fibril morphology. However, the absorption of Sr^{2+} ions casued a significant transformation of the sodium niobate structure, as confirmed by XRD (Fig. 1b). XRD shows that the diffraction peaks of the prepared sodium niobate are associated with the octahedral phase of niobate, which has a formula of $Na_2Nb_2O_6 \cdot H_2O$. the diffraction peak (510) move to a high angle after absorption of Sr^{2+}, resulting in the contraction of the crystal lattice of sodium niobate and further leading to substantial structural changes within the fibers; the Sr^{2+} ions were firmly trapped between the layers due to the irreversible structural change of the sodium niobate nanofibers. This property is an advantage for safe disposal of the immobilized radioactive ions. In addition to the decrease in the interlayer spacing, the Sr^{2+} ions absorption also resulted in substantial decrease in the intensity of