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Synthesis and metal ion sorption properties of peroxide-modified sodium titanate materials using a coprecipitation method

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ABSTRACT

Peroxide-modified sodium titanate is synthesized by a coprecipitation method that uses titanium isopropoxide and sodium hydroxide precursors, with hydrogen peroxide as a mineralizer to modify the titanate to enhance actinide sorption. The mechanism and microstructure of the peroxide-modified titanate, synthesized using hydrogen peroxide at various pH values, and the effect on the sorption capacity of metal ions were studied. In the pH range of 8–9, the product experiences a highest weight loss of 34%, as well as the smallest sodium content and ion exchange capacity. In contrast, in the pH range of 6–7, the highest metal ion exchange ability is noted, up to 170 mg/g. The pH value is crucial for the synthesis of peroxide-modified titanate materials.

1. Introduction

The metallurgy, electrolysis, electroplating and the dye industries generate a large amount of industrial wastewater that contains heavy metal ions that can flow into the surrounding environment. Pollutants such as heavy metals and radioactive waste are not biodegradable or destructible, so when released into the environment, they cause long-term pollution. In addition, the progressive depletion of precious metals due to excessive exploitation by industry has resulted in more recycling. There are many methods for wastewater treatment and recycling precious metals, such as chemical precipitation, ion exchange, reverse osmosis, membrane filtration and adsorption of heavy metal ions [1–3].

In recent years, sorbent materials were developed for metal ion removal based on monosodium titanate (MST), which is the baseline material for the removal of ^{90}Sr and alpha-emitting radionuclides [4–6]. MST exhibits high selectivity for many metallic ions in both acidic and alkaline waste solutions, including those containing strontium and several actinides [5,6].

MST was first prepared by Lynch *et al.* using a sol–gel method [4] that mixed a methanol solution of NaOH with an isopropanol solution of titanium isopropoxide ($Ti(OC_3H_7)_4$), followed by the addition of water. MST has strong adsorption and ion exchange properties for most metal species in aqueous solution [5]. Template assistance [7], self-assembly [8], anodic oxidation [9], the hydrothermal method [10] and precipitation [11] are all used to prepare titanate nanostructures. The precipitation method in alkaline solution for producing nanometric-sized MST is developed with potential because the merits of high metal ions' sorption efficiency and low cost, which are the most important requirements for the sorbent materials for diminution of high-level radioactive waste.

MST has a high chemical affinity for actinide ions in the presence of a high sodium salt matrix that has a free hydroxide concentration in excess of one molar [12]. Metal ions form strong inner spherical complexes using the oxygen atoms of titania [13], so this material is an excellent sorbent/ion exchange medium for the separation of radionuclides (*e.g.*, ^{90}Sr, ^{239}Pu, ^{237}Np and ^{238}U) from waste solutions that emanate from spent nuclear fuel reprocessing operations [14].

Titanate materials, such as crystalline silicotitanate (CST), monosodium titanate (MST), and peroxo titanate (PT), are widely used and commercially available. Recently, Nyman *et al.* studied a series of peroxotitanates (PTs) to significantly improve the sorption ability for strontium and actinides in comparison with MST [15]. These PT materials were prepared by adding hydrogen peroxide either during the synthesis of MST or through a post-synthesis treatment. Peroxotitanates show remarkably improved sorption ability with respect to the separation of actinides and strontium from Savannah River Site (SRS) nuclear waste stimulants [16]. Furthermore, Nyman et al. [15] also indicated that peroxo-titanate sorbents prepared or modified with hydrogen peroxide are universally superior to titanates prepared without hydrogen peroxide. However, to the best of our knowledge, studies of the MST formation mechanism, microstructure of peroxo-titanate—synthesized using hydrogen peroxide to modify titanate in various pH-value conditions—and the effect on the sorption capacity of the metal ions have seldom been reported.

In this study, peroxide-modified sodium titanate was prepared at various pH values using a co-precipitation method. The optimal

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preparation conditions were also identified and used to simulate ion exchange for heavy metal ions, actinide metal ions and lanthanides. The treatment of wastewater that contains metal ions and radioactive waste is expensive, so the synthesis of titanate materials that are highly adsorbent (ion exchange) was studied to simplify the synthesis process and significantly reduce costs.

2. Experimental methods

2.1. Reagents

All chemicals used were of analytical grade and used as received. Ti(O-iC_3H_7)$_4$ (purity 98%, Fluka), NaOH (purity ≥ 96%, Showa), HNO_3 (purity 65%, Showa), $NaNO_2$ (purity 98.5%, Showa), H_2O_2 (purity 35%, HSE) and lanthanide metal (Merck, 99%) were used for the ion exchange experiments.

2.2. Instrumentation

All glassware was soaked in concentrated HNO_3 for 12 h and then thoroughly washed in tap water and double-distilled water. The glassware was then dried overnight in a hot-air oven at 50 °C. The crystal structures of the samples were characterized by X-ray diffraction (PANalytical, X Pert PRO X-ray diffractometer, CuK_α radiation) and micro-Raman spectroscopy (Dimension-P2 Raman). A Micromeritics ASAP 2020 Analyzer was used for BET analysis. Thermogravimetry analysis (TGA) was performed in air on a model TA, SDT-Q600, using 8–10 mg powder and a heating rate of 10 °C min^{-1}, up to a maximum temperature of 800 °C. The morphologies of the samples were investigated by field emission scanning electron microscopy (FESEM, JEOL JSM-7401F) at 5 kV. An energy-dispersive spectrometer (EDS) (Philips, XL-40) was used to determine the elemental composition. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer, ELAN 6000 model) was used to detect trace metals.

2.3. Preparation of peroxide-modified sodium titanate

The preparation process for peroxide-modified sodium titanate is shown in Fig. 1. First, 0.6 g of $NaNO_2$ was dissolved in a 100-mL solution of 1 M HNO_3 and this mixture was placed in a stirring vessel. Then, Ti(O-iC_3H_7)$_4$ was slowly added to the acidic solution, and the solution was agitated using a magnetic stirrer for 30 min. NaOH was subsequently added using a reflux condenser. After the mixture was stirred, a white precipitate was produced, and then, H_2O_2 was added. Titanate forms quickly from the precipitate. After precipitation, the nanoparticle suspension was kept in a stirred vessel to disperse the agglomeration. To mineralize the surface and control the chemical precipitation reaction, different synthesis temperatures and pH ranges were used. The final pH was obtained by adding 0.1 M nitric acid until the desired pH was achieved. The nanoparticles were separated from the solution by washing several times with DI water until the pH reached approximately 7. Finally, the titanate was dried by natural drying and ground into powder. The lanthanide metal ions were analyzed using ICP to determine the relationship between the adsorption (ion exchange) values and these variables to determine the optimal conditions for the synthesis of peroxide-modified titanate materials.

For the accuracy of this study, each experiment was carried out at least three times or more. The data error must be less than 5%; the arithmetic mean value of data is applied. If the error is higher than 5%, the data is discarded, and re-examined again. Particularly, the preparation of sample at pH = 8–9 is treated carefully for a good reproducibility.

2.4. Ion exchange of metal ions from peroxide-modified titanates

To measure ion adsorption, a 100-mL of simulated solution containing of metal ions with an initial concentration each of 50 ppm of Ce^{2+}, Co^{2+}, Eu^{2+}, Gd^{3+}, La^{3+}, Nd^{3+}, Sm^{3+}, Sr^{2+}, Y^{3+} and other ions was provided by the Institute of Nuclear Energy Research in Taiwan. During the adsorption, the metal was conducted in room temperature and stirred. Moreover, Every 15 min, the metal ion concentration was measured using ICP-AES.

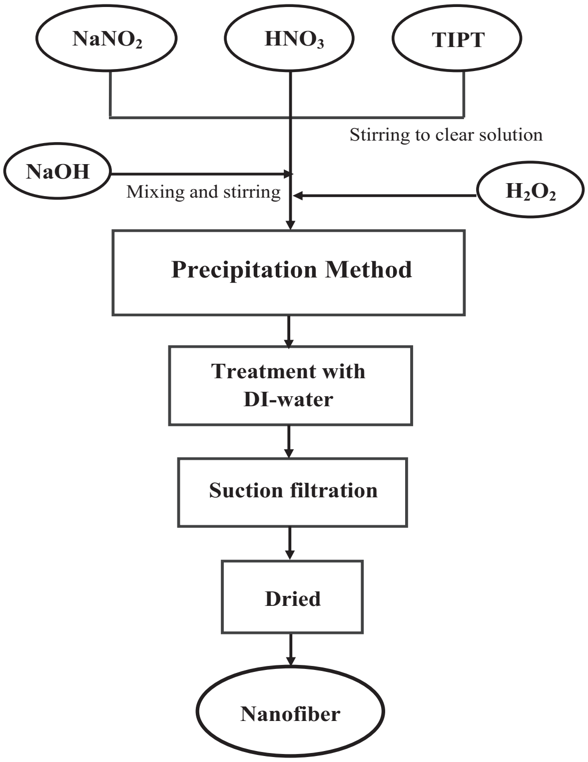

Fig. 1. Flow chart for the synthesis of peroxide-modified sodium titanate materials using coprecipitation method.

3. Results and discussion

3.1. The characterization of peroxide-modified titanate materials

All the peroxide-modified titanates were milky yellow in color, indicating that the titanium-peroxo species is protonated or associated with water protons [17]. Moreover, deeper yellow–orange slurries were observed for peroxide-modified titanate obtained at acidic conditions. In contrast, the titanate materials precipitated under alkaline conditions are light yellow in color. Furthermore, more peroxide-modified titanate can be obtained in an acidic condition, whereas lower yields were prepared in an alkaline condition because of the partial dissolution of the product [18]. Thus, a decreasing yield of peroxide-modified titanate was prepared at higher pH values.

The results of the initial TGA analyses, with a heating rate of 10 °C min^{-1}, are shown in Fig. 2 for samples prepared at different pH ranges and a synthesis temperature of 60 °C. Weight loss was classified into two types. The first type, observed in samples (A), (B) and (D) and shown in Fig. 2(A), (B) and (C), has a large fraction of weight loss below 200 °C. This loss is attributed to the removal of adsorbed water and the –OH group from the peroxide-modified titanate structures. The weight loss changes of the samples is small for 200–600 °C because of the loss of by-products H_2O_2, O_2^{2-}, HO_2^-, which were produced in the treatment of hydrogen peroxide. A smaller fraction of the weight is lost between 600 and 700 °C; XRD indicated that the conversion of trititanate ($Na_xH_{2-x}Ti_3O_7$) into hexatitanate ($Na_yH_{2-y}Ti_6O_{13}$) took place in this temperature range.