Research Article

Effect of Hydrogen Peroxide Content on the Preparation of Peroxotitanate Materials for the Treatment of Radioactive Wastewater

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The modification of peroxotitanate using hydrogen peroxide significantly improved the ion-exchange capacity of titanate materials as sorbents for metal ions contained in a radioactive waste simulant solution. The effects of hydrogen peroxide content (hydrogen peroxide/titanium isopropoxide molar ratios, hereafter expressed as H/T) on the properties of as-prepared titanate synthesized at 130°C and at pH of 6–7, followed by freeze-drying, were investigated. The peroxotitanate materials thus obtained were characterized by XRD, BET, SEM, TEM, EDX, ICP, and Raman spectroscopy. At an H/T ratio of 2, peroxotitanate predominantly exhibited an amorphous structure, with a clearly observed tubular or fibrous structure. Furthermore, peroxotitanate modified at an H/T ratio of 2 exhibited the best ion-exchange capacity of 191 mg g^{−1} for metal ions contained in a radioactive waste simulant solution. Hence, these peroxotitanate materials are suitable for removing metal ions from wastewater, especially lanthanide ions (Ln³⁺) and Sr²⁺.

1. Introduction

Heavy metals and radioactive waste are not biodegradable or destructible and can persist in the natural environment, which in turn indirectly affect human health. Currently, chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and heavy metal adsorption are employed for the treatment of precious-metal-containing wastewater [1–3].

Derived sodium titanate exhibits high selectivity for several metal ions in both acidic and alkaline waste solutions, including those containing strontium and several actinides [4, 5]. In recent years, researchers have investigated the use of derived sodium titanate as adsorbent materials for metal ions, which is the baseline material for the removal of ⁹⁰Sr and alpha-emitting radionuclides [6, 7].

Previously, several studies have investigated and reported the synthesis of various forms of titanate materials, such as titanate nanofibers, hydrogen titanate nanowires, and titanate nanostructures [8–10]. The most common chemical formula for the sodium titanate crystal is Na₂Ti_nO_{2n+1} ($n = 3$ or

6); the structure with $n = 3$ is more common as (Ti₃O₇)₂[−] and Na⁺ bind together, affording a layered structure. The sodium matrix Na₂Ti₃O₇ is reported to exhibit the highest ion-exchange capacity [11]. On the other hand, depending on the extent of exchange between sodium and protons, chemical formulae of Na₂Ti₃O₇· n H₂O, Na_{2− x} H _{x} Ti₃O₇· n H₂O, and H₂Ti₃O₇· n H₂O have been proposed for titanate nanotubes [12].

The mechanism of the adsorption of lanthanide ions (Ln³⁺) on sodium trititanate nanofibers is believed to occur as follows: Na⁺ occupies the space between the interlayers parallel to the crystal axis, followed by the exchange of Na⁺ with Ln³⁺. When Ln³⁺ enters the structure, a stable three-dimensional crystal structure of Ln³⁺-titanate salts is formed, followed by the removal of Ln³⁺ [13]. Trititanate nanofibers exhibit very good and unique properties with respect to the ion exchange and adsorption of lanthanide metals, attributed to the number of Na⁺ or H⁺ between the layers.

Nyman and Hobbs have investigated a series of peroxotitanates by the addition of hydrogen peroxide, which results

in the significant improvement of the sorption ability for strontium and actinides [14]. Furthermore, peroxotitanate sorbents prepared via modification with hydrogen peroxide are more superior to titanates prepared without hydrogen peroxide [15]. Titanate materials that are synthesized in the presence of H_2O_2 and undergo modified postsynthesis of sodium titanate with H_2O_2 demonstrate good radionuclide sorption selectivity, kinetics, and capacity [7, 16]. A methodology to modify the synthesis of sodium titanate for producing materials, which achieve significantly improved strontium and actinide removal and increased capacity and sorption kinetics, was proposed in an earlier study [17]. However, to the best of our knowledge, studies on the effect of hydrogen peroxide content on as-prepared peroxotitanate materials for the treatment of radioactive wastewater have seldom been reported.

In this study, peroxo-modified sodium titanate was prepared by the hydrothermal method using hydrogen peroxide at different titanium/hydrogen peroxide molar ratios. Effects of different titanium/hydrogen peroxide molar ratios on the properties of peroxotitanate materials were determined. The high adsorption efficiency of peroxotitanate for the treatment of stimulant wastewater was confirmed.

2. Experimental

2.1. Reagents. Analytical-grade chemicals were used as received, without any further purification. $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$ (98% purity, Fluka), NaOH ($\geq 96\%$ purity, Showa), HNO_3 (65% purity, Showa), NaNO_2 (98.5% purity, Showa), H_2O_2 (35% purity, HSE), and lanthanide metal (Merck, 99%) were used for ion-exchange experiments with compounds such as $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and ultrapure water (purity $\geq 98\%$).

2.2. Preparation of Peroxotitanate Materials. Figure 1 shows the flowchart of the synthesis of peroxotitanate materials. First, 0.6 g of NaNO_2 was dissolved in 100 mL of 0.1 M HNO_3 and added to a vessel. Second, $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$ was slowly added to an acetic acid solution, which was stirred using a magnetic stirrer for 30 min and heated to 130°C in an autoclave for 3 h. Third, NaOH was slowly added to the vessel using a reflux condenser for achieving pH of 6-7. After uniform stirring, a white precipitate was observed, and then an appropriate amount of H_2O_2 was added to the system. The titanate rapidly formed from the titanium precipitate. Peroxotitanate materials were also synthesized at various hydrogen peroxide/ $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$ molar ratios (H/T molar ratios). The solution gradually became transparent and bright yellow, further forming a yellow peroxotitanate precipitate. After the reaction was complete, the precipitates were cooled and washed several times with DI water until the pH reached approximately 7. Finally, the resulting precipitate was freeze-dried (<0.1 torr and -45°C), followed by grinding, affording peroxo-modified titanate material. Table 1 summarizes the H/T molar ratios utilized for the synthesis of peroxotitanate under different experimental conditions.

TABLE 1: Molar ratios of hydrogen peroxide and titanium isopropoxide utilized for the synthesis of peroxotitanate materials under different experimental conditions.

Sample	Reaction temp. ($^\circ\text{C}$)	pH	Drying	Ti : H_2O_2
H1	130	6-7	F	1 : 1
H2	130	6-7	F	1 : 2
H3	130	6-7	F	1 : 3
H4	130	6-7	F	1 : 4

FIGURE 1: Flowchart of the synthesis of peroxotitanate materials by the hydrothermal method.

2.3. Instrumentation. The glassware used for the experiments was soaked in concentrated HNO_3 for 12 h and then thoroughly washed using tap water and double-distilled water, followed by drying overnight in a hot-air oven at 50°C . The crystal structures of the samples obtained were investigated by X-ray diffraction (XRD; PANalytical, X'Pert PRO XRD, CuK_α radiation) and micro-Raman spectroscopy (Dimension-P2 Raman). A Micromeritics ASAP 2020 analyzer was employed for BET analysis. TEM measurement was performed using a CM-200 TEM system (Philips) operating at 200 kV. Before TEM analysis, the samples were sonicated in ethanol for 15 min, followed by the deposition of 2-3 drops of the sample on a thin carbon film supported on a perforated copper grid; the samples were then dried overnight at 60°C . Fourier transform infrared (FTIR) spectra were recorded on a spectrometer (Perkin Elmer). UV-vis diffuse reflectance spectra were recorded between 300 and 800 nm on a Jasco V-600 UV-vis spectrophotometer, which was employed to measure the red shift in samples. All absorbance measurements were recorded on a UV-vis spectrophotometer (Hitachi, U-2800) equipped with a quartz cell of 1 cm. Thermogravimetry/differential thermal analysis (TGA/DTA) was performed

in air on a TA SDT-Q600 instrument using 8–10 mg of powder at a heating rate of 10°/min and a maximum temperature of 800°C. The composition of elements in the samples was investigated by energy-dispersive X-ray spectrometry (EDS) (Philips, XL-40). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Perkin Elmer, ELAN 6000) was employed for the detection of trace metals.

2.4. Adsorption of Metal Ions on Peroxotitanate Materials. The radioactive waste simulant solution at pH 5–6, provided by the Institute of Nuclear Energy Research in Taiwan, contained an initial concentration of 50 ppm for each of Ce^{2+} , Co^{2+} , Eu^{2+} , Gd^{3+} , La^{3+} , Nd^{3+} , Sm^{3+} , Sr^{3+} , Sr^{2+} , Y^{3+} , and other anions.

First, the as-prepared peroxotitanate was added to the radioactive waste simulant solution for permitting ion exchange, which removed metal ions. Second, 100 mL of the simulant solution was added to a 250 mL beaker and stirred at room temperature. The resultant solution was subjected to analysis for determining the relationship between adsorption time and efficiency.

In experiments, 0.05 g of the as-prepared peroxotitanate material was dispersed in 100 mL of the radioactive waste simulant solution, followed by stirring at room temperature and atmospheric pressure. After every 15 min, the solution was tested for the presence of metal ions by ICP-AES for determining the ion-exchange capacity of the as-prepared peroxotitanate materials. Furthermore, surface analyses of the as-prepared titanates were performed using a V.G. Instruments X-ray photoelectron spectrometer (XPS). The adventitious C 1s signal at 284.6 eV was used to calibrate the charge-shifted energy scale.

3. Results and Discussion

3.1. Characterization of the As-Prepared Peroxotitanate Materials. XRD patterns of the as-prepared peroxotitanate materials synthesized at different calcination temperatures at an H/T ratio of 2 are shown in Figure 2. The as-prepared peroxotitanate exhibiting weak diffraction peak is amorphous and poorly crystalline. The powder was still amorphous if calcined at temperature below 500°C, but the powder has a trace of anatase at 600°C. However, the sample calcined at 700°C exhibited characteristic peaks 2θ at around 28.4° and 47.5°, which are attributed to $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ structure with the crystal diffraction plane of (111) and (020), respectively (JCPDS 31-1329). Nevertheless, the powder is also accompanied with few TiO_2 (rutile phase). Furthermore, the diffraction peaks are observed at $2\theta = 11.8, 14.1, 24.5$, and 30.1 (JCPDS 73-1398). These are attributed to the $\text{Na}_x\text{H}_{2-x}\text{Ti}_6\text{O}_{13}$ structure of diffraction crystal plane peaks of (200), (201), (110), and (203), respectively. The XRD studies were in good agreement with the previous studies [18]. Kim et al. [19] reported Raman spectra of the titanate powders with Na content (Na/H-Ti Nanotube), taken at temperature of 700°C for 3 hours in air. They also showed that it is a mixture of H-Ti Nanotube, $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$, and TiO_2 (anatase).

FIGURE 2: XRD pattern of the as-prepared peroxotitanate materials synthesized at different calcination temperatures at an H/T ratio of 2.

When the calcination temperatures were at 900°C, most of the $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ structure peaks disappear and other diffraction peaks of the $\text{Na}_x\text{H}_{2-x}\text{Ti}_6\text{O}_{13}$ structure were examined.

Furthermore, in this study, the authors used titanium isopropanoxide as raw material. These peroxotitanates included $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ that may transform to TiO_2 in high temperature. Also, the synthesis is entirely different from conventional titanate synthesis, using TiO_2 powder in NaOH atmosphere. Nyman and Hobbs [14] indicated that titanium isopropanoxide reacts with methanol in sodium hydroxide solution to become monosodium titanate, shown as follows:

Figure 3 shows the Raman spectra for the peroxotitanates prepared at various H_2O_2 /titanium molar ratios. As seen from this figure, these broadened peaks of titanates indicate that the crystallinity is low, in accordance with the XRD measurements (not shown). The Raman spectra of the as-prepared materials have the bands characteristic around 285, 455, 710, and 910 cm^{-1} , which are identified to be titanate phase [20]. Furthermore, Raman spectra of the titanates prepared at H/T ratios of 2 and 3 ((c) and (d) in Figure 3) have a broader band in the range of $600\text{--}720\text{ cm}^{-1}$ than the Raman spectra of the titanate obtained at lower H/T ratios of 0 and 1 ((a) or (b) in Figure 3). It can be explained that the titanates prepared at higher H/T ratios contain a higher fraction of H-Ti-NT structure. Therefore, the greater broadening of the Raman bands in H-Ti-NT may be related to the greater water content in these titanate materials [21].

Typically, the Raman shifts for titanate obtained at H/T ratio of 2 were 153, 185, 269, 283, 386, 450, 693, and 828 cm^{-1} ((c) in Figure 3). The observed Raman shifts are in good agreement with those reported by Korosi et al. for $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ [20]. However, the three most intense

FIGURE 3: Raman spectra of sodium titanates prepared at different hydrogen peroxide molar ratios. (a) H/T ratio of 0, (b) H/T ratio of 1, (c) H/T ratio of 2, and (d) H/T ratio of 3.

bands, at 269, 283, and 450 cm^{-1} , are also characteristic of $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot \text{H}_2\text{O}$.

Figure 4 shows the nitrogen adsorption-desorption isotherms of the sodium titanate synthesized before and after modification using hydrogen peroxide. As per BDDT classification, all samples exhibit type IIb isotherms with H3-type hysteresis loops, with no indication of a plateau at high P/P_0 [20, 21]. The inset of Figure 4 shows the pore size distribution of all samples; the sample with no added hydrogen peroxide (Figure 4(a)) exhibits a wider pore size distribution (approximately 10–60 Å), while that prepared at an H/T ratio of 2 exhibits a relatively narrow pore size distribution (approximately 10–40 Å).

The pore size distribution of nanotubes (H/T = 2) at 10–100 nm is narrower than that without peroxide (H/T = 0). Owing to the decomposition of peroxotitanate during the process of adding hydrogen peroxide, therefore, it exhibits less aggregation of the nanotubes, demonstrating a more uniform distribution of pore sizes. This is consistent with the studies of Kim et al., who considered the morphological examination of the nanotubes, where the smaller pores (<10 nm) may correspond to the pores inside the nanotubes and the diameters of these pores are equal to the inner diameter of the nanotubes, while the larger pore (10–100 nm) can be attributed to the aggregation of the nanotubes [19]. Hence, the titanate prepared by adding hydrogen peroxide produces a more uniform pore size distribution.

Table 2 and Figure 5 show the results obtained for specific surface area, pore volume, and average pore diameter. With increasing $\text{H}_2\text{O}_2/\text{Ti}$ molar ratio, the specific surface area gradually decreases, reaching the minimum at an H/T ratio of 2. With further increase in the H/T ratio, the specific surface area slightly increases.

TABLE 2: BET analysis of peroxotitanate materials synthesized at different molar ratios of hydrogen peroxide and titanium isopropoxide.

Properties	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore size (Å)
H/T = 0	123.7	0.56	18.3
H/T = 1	46.8	0.22	19.0
H/T = 2	21.8	0.11	20.6
H/T = 3	36.4	0.19	20.6
H/T = 4	38.1	0.20	21.0

Figure 5 shows the TEM images of the titanates synthesized at different molar ratios of hydrogen peroxide and titanium isopropoxide. At an H/T ratio of 1 (Figure 5(a)), the tubular or fibrous structure is not clear. On the other hand, with increasing hydrogen peroxide content (H/T = 2), the tubular or fibrous structures with a diameter of approximately 10 nm are clearly observed. As can be observed in Figure 5(d), another nanostructure predominates over the nanotubes or nanofibers, apparently nanosheets, possibly explaining the increase in surface area (at similar dimensions, nanosheets exhibit a surface area greater than that of nanotubes or nanofibers). Furthermore, with increasing hydrogen peroxide content, the density of nanotubular or nanofibrous structures tends to increase, attributed to the addition of excess hydrogen peroxide, which makes the reaction more intense; hence, binding with O_2 between the crystal layers is accelerated, prevailing in the formation of nanosheet structures.

Figure 6 shows the SEM images of the peroxotitanate materials prepared at an H/T ratio of 2 at different calcination temperatures. At a calcination temperature of 600°C , the sample nanostructure still retains the tubular or fibrous form and is clearly observed. However, with increasing calcination temperature to 700°C , rod-like nanotubes or nanofibers coexist. Moreover, from 700°C , the nanotubes or nanofibers decrease, attributed to their condensed tunnel structure, and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ exhibits an ion-exchange capacity significantly less than that of its counterpart with an open layered structure [15]. At 800°C , because of the high-temperature effect, the sample exhibits a short rod-like structure, the diameter of which increases with calcination temperature.

The sodium ion content was measured by EDS. The specific surface area (Table 2) and content of sodium ion in the samples are combined to construct a correlogram between specific surface area, content of sodium ion in peroxotitanate materials, and different hydrogen peroxide and titanium isopropoxide molar ratios, as shown in Figure 7. At an H/T ratio of 0 (sample not modified by H_2O_2), the sample exhibits the highest specific surface area of $123.7\text{ m}^2/\text{g}$ and the lowest sodium content of 5.4%. Moreover, with increasing hydrogen peroxide content, specific surface area decreases, and sodium content increases gradually. In fact, at an H/T ratio of 2, the sample exhibits the lowest specific surface area of $21.8\text{ m}^2/\text{g}$ and the highest sodium content of 7.3%. With further increase in the hydrogen peroxide content, the content of sodium in the titanates gradually decreases, attributed to the fact that

FIGURE 4: Nitrogen adsorption-desorption isotherms of sodium titanate materials synthesized before and after modification by hydrogen peroxide: (a) H/T ratio of 0 and (b) H/T ratio of 2.

FIGURE 5: TEM images of the peroxotitanates prepared at different hydrogen peroxide and titanium isopropoxide (H/T) molar ratios of (a) 1, (b) 2, (c) 3, and (d) 4.

FIGURE 6: SEM images of peroxotitanate materials prepared at H/T ratios of 2 at different calcination temperatures.

FIGURE 7: Correlagram for the hydrogen peroxide and titanium isopropoxide molar ratio, specific surface area, and content of sodium ions in the as-prepared peroxotitanates.

modification with hydrogen peroxide leads to an increase in the number of oxygen-containing functional groups on the surface and also improves the protonation of the surface; hence, the substitution of Na^+ by H^+ increases, which in turn results in the reduction of sodium content. The H/T ratio of 2 is possibly the optimal amount that permits coprecipitation; hence, the sodium content is optimal in the layered structure of the peroxotitanate materials.

The atomic ratios measured by XPS were utilized to reveal the surface properties of the as-prepared peroxotitanate. Table 3 shows Ti/O atomic ratios by XPS of the peroxotitanate prepared at different H/T molar ratios. From this table, the Ti/O molar ratio decreases as the H/T ratio increases up to 2 and then slightly increases as the H/T ratio increases above 2 during the synthesis of peroxotitanate. The attacking of functional groups containing O_2^{2-} , HOO^- , or H_2O_2 , and so

TABLE 3: Atomic ratios by XPS of the peroxotitanate prepared at different H/T molar ratios.

Sample	Atomic percentage (%)				
	Ti	O	Na	C	Ti:O (atomic ratio)
H/T = 0	19.5	55.2	5.5	19.5	1: 2.83
H/T = 1	18.7	55.6	6.7	19.0	1: 2.97
H/T = 2	17.1	58.2	7.6	17.1	1: 3.40
H/T = 3	18.1	56.8	7.3	17.8	1: 3.14
H/T = 4	18.3	57.2	7.0	17.5	1: 3.13

forth, to form a Ti-peroxospecies is explained; therefore, the as-prepared peroxotitanate contains a relative higher fraction of oxygen on the surface.

3.2. Adsorption of Metal Ions Contained in the Radioactive Waste Simulant Solution. First, 100 mL of the radioactive waste simulant solution, with an initial concentration of 50 ppm of each of Ce^{2+} , Co^{2+} , Eu^{2+} , Gd^{3+} , La^{3+} , Nd^{3+} , Sm^{3+} , Sr^{2+} , and Y^{3+} , was provided by the Institute of Nuclear Energy Research (Taiwan). ICP-AES was employed to analyze the concentration of these metal ions. Ion-exchange capacity is calculated using formula (1) for determining adsorption capacity: $\text{ion-exchange capacity (mg/g)} = (C_1 - C_2) \times (V/W)$, C_1 is the initial concentration (ppm), C_2 is the concentration after adsorption (ppm), V is solution volume (L), and W is the adsorbent weight (g).

The peroxotitanate materials prepared at different molar ratios of hydrogen peroxide and titanium isopropoxide were tested for the adsorption of the metal ions contained in the simulant solution. Figure 8 plots ion-exchange capacity versus time. Treatment with hydrogen peroxide during synthesis results in the attack of the titanate by different oxygen-containing functional groups (e.g., peroxoligand can exist as O_2^{2-} , HOO^- , or H_2O_2) in the surface structure, affording a

FIGURE 8: Plot of ion-exchange capacity versus time for the as-prepared peroxotitanate materials prepared at different hydrogen peroxide molar ratios.

peroxommodified sodium titanate complex in the presence of a protonated or hydrated Ti-peroxospecies [22]. Generally, this aforementioned species is expressed by the following chemical formula: $H_vNa_wTi_2O_5 \cdot (xH_2O)[yH_zO_2]$ ($(v+w) = 2$, $z = 0-2$) [23]. Hence, more negative charges are present on the surface structure, which contribute to the significant increase in ion exchange with metal ions by electrostatic attraction. The lowest ion-exchange capacity is about 40 mg/g after 45 min for the titanate obtained at an H/T ratio of 0, without the treatment of hydrogen peroxide, because the structures are newly formed and short (by TEM, not shown), making it less attractive to Na^+ . On the other hand, the highest ion-exchange capacity is observed at an H/T ratio of 2 (191 mg/g after 45 min), followed by gradual decrease with further increase in the hydrogen peroxide content. As shown in Figure 7, an H/T ratio of 2 affords the highest sodium content.

Figure 9 shows the comparison of the ion-exchange capacities of peroxotitanate materials prepared at an H/T ratio of 2 for various metal ions. The results indicated that the as-prepared peroxotitanate material exhibits the best ion-exchange capacity for Nd^{3+} and the lowest ion-exchange capacity for Co^{2+} .

Figure 10 plots the ion-exchange capacities for metal ions contained in the radioactive waste simulant solution using peroxotitanate synthesized at an H/T ratio of 2 at different calcination temperatures. The result indicated that the ion-exchange capacity decreases with increasing calcination temperature. At high calcination temperatures of 800°C and 900°C, the ion-exchange capacity significantly decreases. At calcination temperatures of 300°C and 900°C, the highest and lowest ion-exchange capacities of 104.4 mg/g and 49.3 mg/g, respectively, are observed. At high temperatures,

FIGURE 9: Removal efficiencies for different lanthanide metal ions by the as-prepared peroxotitanate materials synthesized at an H/T ratio of 2.

FIGURE 10: Plot of ion-exchange capacities of the as-prepared peroxotitanate materials synthesized at an H/T ratio of 2 at different calcination temperatures for various metal ions.

the morphological structures of the as-prepared peroxotitanate possibly change; as a result, heat stress and aggregation are observed. Eventually, $Na_2Ti_3O_7$ is transformed into the nanorod $Na_2Ti_6O_{13}$ structure, as previously shown (see the XRD pattern in Figure 2 and the SEM image in Figure 6), which results in the decrease of ion-exchange capacity.

Nyman and Hobbs [14, 23] developed peroxide modified sodium titanates to improve the sorption capacities for nuclear waste treatment. Peroxotitanates show remarkable and universal improved sorption behavior with respect to separation of actinides and strontium from Savannah River Site (SRS) nuclear waste simulants. They also indicated that the enhancement in sorption kinetics can potentially result in as much as an order of magnitude increase in batch processing throughput.

However, in this study, similar peroxotitanate materials were prepared by the postperoxide adding process. The modification by H/T ratio of 2 can enhance the ion-exchange capacity 4~5 times more than without the peroxide. Perhaps, further enhancement of sorption performance will be achieved by processing, storing, and utilizing the peroxotitanate as aqueous slurry rather than as a dry powder, which will be explored in the future [23].

4. Conclusions

In this study, peroxotitanate nanomaterials are synthesized by the hydrothermal method at 130°C and pH of 6-7, followed by modification with different molar ratios of hydrogen peroxide and titanium isopropoxide. In addition, the properties of the as-prepared peroxotitanate materials are characterized.

The structure of the as-prepared peroxotitanate is found to be amorphous. By calcination at 700°C, it is a mixture of H-Ti nanotube, $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$, and TiO_2 . With the calcination temperature of 900°C, most of the $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ structure peaks disappear and convert to $\text{Na}_x\text{H}_{2-x}\text{Ti}_6\text{O}_{13}$ structure.

At an H/T ratio of 1, peroxotitanate does not exhibit a tubular or fibrous structure; however, at an H/T ratio of 2, the tufts of nanostructures with a diameter and length of approximately 10 nm are clearly observed. With increasing hydrogen peroxide content, the nanofiber length decreases. Moreover, at an H/T ratio of 2, the sample exhibits a relatively narrow pore size distribution (approximately 10–40 Å) and the smallest specific surface area of 21.8 m²/g.

Modification with hydrogen peroxide significantly increases the ion-exchange capacity of the peroxotitanate materials for metal ions. The as-prepared peroxotitanate synthesized at 130°C and at pH of 6-7, followed by freeze-drying and modification with H/T at a molar ratio of 2, exhibits the best ion-exchange capacity of 191 mg/g for metal ions. Hence, these peroxotitanate materials are suitable for removing metal ions from wastewater, especially lanthanide ions (Ln^{3+}).

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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