



Strontium ion (Sr^{2+}) separation from seawater by hydrothermally structured titanate nanotubes: Removal vs. recovery



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HIGHLIGHTS

- Titanate nanotubes (TiNTs) were synthesized by a simple hydrothermal reaction.
- The sorption of strontium (Sr) on TiNTs rapidly occurred, achieving Sr uptake 97 mg/g.
- Na had little effect on Sr sorption despite the sorption mechanism of the Na exchange.
- Ca significantly hindered Sr sorption on TiNTs among co-existing cations in seawater.
- TiNTs could be easily regenerated by acid treatment and reused for repeated cycles.

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ABSTRACT

Strontium ion (Sr^{2+}) separation from seawater has attracted attention for radioactive pollutants removal and for Sr^{2+} recovery. Herein, we synthesized titanate nanotubes (TiNTs) via a simple hydrothermal reaction, characterized their physicochemical properties, and systematically evaluated Sr^{2+} sorption behavior under various reaction conditions corresponding to seawater environments. The synthesized TiNTs exhibited a fibril-type nanotube structure with a high specific surface area (260 m^2/g). Sr^{2+} adsorption on TiNTs rapidly occurred following a pseudo-second-order kinetic model and was in good agreement with the Langmuir isotherm model, indicating a maximum adsorption capacity of 97 mg/g. Based on the Sr^{2+} uptake and Na^+ release with a stoichiometric balance, the Sr^{2+} sorption mechanism on TiNTs was ion exchange between Na^+ in the TiNT lattice and Sr^{2+} in the solution phase, as confirmed by XRD and Raman analysis. Among the competitive ions, Ca^{2+} significantly hindered Sr^{2+} sorption on TiNTs, whereas Na^+ only slightly affected Sr^{2+} sorption, despite the Na^+ exchange sorption mechanism. The effect of Ca^{2+} on Sr^{2+} sorption was evaluated by introducing a distribution coefficient (K_d) as a critical factor in determining the selectivity, which revealed a slightly higher selectivity for Sr^{2+} . The Sr^{2+} adsorption-desorption test in a real seawater medium enabled the determination of K_d and the concentration factor (CF) for co-existing matrix ions in seawater; these values were evaluated for Sr^{2+} removal and recovery from seawater. TiNTs were regenerated by acid treatment and reused through consecutive adsorption-desorption experiments. While most studies addressing Sr^{2+} sorption using TiNTs aimed for extraction from wastewater and radioactive wastewater, this study elucidated Sr^{2+} sorption behavior under seawater conditions and provided insights into developing the removal and recovery processes from seawater.

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1. Introduction

Recently, the removal of strontium ions (Sr^{2+}) from seawater has received substantial attention from an environmental perspec-

tive after the Fukushima plant accident, which released a large amount of radioactive Sr (^{90}Sr) and Cs (^{137}Cs) [1,2]. The ^{90}Sr isotope is a beta-emitter that genetically affects seawater organisms and ultimately causes harm to humans [3]. Accordingly, the efficient separation of radioactive elements released to seawater has become a critical technological requirement, along with their removal from radioactive wastes.

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Seawater contains various types of mineral resources with different concentrations depending on the elements. In the case of strategically valuable resources, such as lithium and uranium, seawater is the most attractive resource due to its large reserve, despite the very low concentrations. If the practical problem of process cost could be addressed, then extraction of these metals from seawater would be promising and beneficial compared with typical land mining [4]. Strontium, which has many industrial applications, such as ferrite magnets, ceramics, and fire-works, exists in seawater with a concentration of approximately 7 mg/L [5]. In a previous report estimating the economic potential of the recovery of various elements from seawater in terms of their commercial values and concentrations in seawater [6], Sr^{2+} was located above the approximate break-even line, implying that Sr^{2+} recovery from seawater can potentially be profitable. Nevertheless, research on the recovery of Sr^{2+} from seawater has received limited attention.

The separation of Sr^{2+} from aqueous media by various methods has previously been introduced, including solvent extraction [7], adsorption by solid materials [8,9], and ion exchange [10]. Among these methods, the adsorption technique using solid adsorbents is of great interest in selectively separating Sr^{2+} from seawater, allowing for the concentration level of Sr^{2+} . Many studies have been conducted to investigate Sr^{2+} adsorption on metal oxides, such as hydrous manganese dioxide and sodium nonatitanate, and clays, such as zeolite and titanosilicate [11–13]. However, only a few studies have reported the extraction of Sr^{2+} from seawater using a liquid membrane [14], commercial resin-type sorbents [15], and an alginate-based biosorbent [16,17].

Titanate-based materials have been widely investigated, primarily for the removal of heavy metals and radioactive pollutants from aqueous media due to their chemical stability and facile synthesis [18–20]. Most studies addressing Sr^{2+} adsorption using titanates aimed for extraction from aqueous media, such as wastewater and radioactive wastewater [12,18,21]. Similar to the cases of other adsorbents, the understanding of Sr^{2+} sorption behavior on titanates in a seawater medium remains insufficient. The systematic investigation of Sr^{2+} sorption behavior under seawater conditions is necessary to provide insights into developing new sorbent materials for the removal and recovery processes from seawater.

Herein, we report Sr^{2+} separation from seawater using titanate nanotubes (TiNTs), focusing on an evaluation of the effect of seawater matrix ions on Sr^{2+} sorption behavior. This is the first study reporting Sr^{2+} sorption behavior on TiNTs in detail for the purpose of removing and simultaneously recovering Sr^{2+} from seawater. Hydrothermally structured TiNTs were prepared and systematically characterized using XRD, SEM, TEM, and BET. The overall performance of TiNTs was comprehensively evaluated in terms of the Sr^{2+} adsorption isotherm, adsorption kinetics, and competitive adsorption of co-existing cations in seawater. The Sr^{2+} sorption test in a real seawater medium provided the strategy to increase the efficiency depending on the purpose of removal and recovery. Finally, the regeneration and reusability of TiNTs were examined for practical applications and for the simultaneous recovery of Sr^{2+} from seawater.

2. Experimental section

2.1. Synthesis of titanate nanotubes

TiNTs were synthesized via the typical alkaline hydrothermal method. Typically, 4 and 12 g of TiO_2 particles (Degussa P25) were added to 200 and 600 mL of 10 M NaOH solution, respectively. Depending on the volume of the hydrothermal reaction, TiNT sam-

ples were denoted as TiNT-S or TiNT-L, representing 200 mL or 600 mL, respectively. Then, the mixtures were transferred to Teflon-lined autoclaves and hydrothermally reacted at 120 °C for 24 h. While no stirring was applied to the reaction using the 200-mL autoclave, the suspension in the 600-mL autoclave reactor was continuously stirred during the reaction. The obtained products were washed with distilled water until the washing solution reached a pH of 7, and the precipitates were subsequently freeze-dried.

2.2. Characterization

The morphology was examined using an analytical scanning electron microscope (SEM, Hitachi S-4800) with energy dispersive X-ray spectrometry (EDS) to provide the distribution of the elements, and a high-resolution transmission electron microscope (HR-TEM, Hitachi HD-2399) was also used. The phase identification of the samples was carried out by powder X-ray diffraction (XRD) using 60-kV Cu- $\text{K}\alpha_1$ radiation (PANalytical, Empyrean). The surface area and pore volume analyses were performed using the BET and BJH methods with ASAP 2020, Micromeritics. Zeta potentials were measured by an electrophoretic light scattering spectrophotometer (Zetasizer, Malvern). Raman spectra of the samples before and after Sr^{2+} adsorption were obtained with a Raman spectrometer (UniRAM, UniNanoTech, Korea) using a 532-nm laser. The laser power was approximately 2 mW, and the signal was accumulated for 30 s.

2.3. Adsorption experiments

TiNTs were dispersed in distilled water at 1 g/L (0.02 g/0.02 L) and sonicated for 30 s. A desired amount of Sr^{2+} and different metal cation stock solution was added to the suspension, and the solution pH was adjusted with an HCl or NaOH standard solution, which was subsequently stirred for 30 min to allow the equilibrium adsorption. The sample aliquots were intermittently withdrawn during the 30-min adsorption reaction and filtered through a 0.2- μm cellulose acetate membrane (ADVAN-TEC). The concentrations of Sr^{2+} and other metal cations were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin and Elmer). The performances of TiNT samples were evaluated in terms of the uptake of Sr^{2+} (see SI). To investigate the effects of coexisting ions, the solutions were varied with different electrolyte ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) for which the concentrations in seawater are much higher than that of Sr^{2+} . The initial concentration of Sr^{2+} was fixed to 10 mg/L, and those of coexisting ions ranged from 10 mg/L to their concentrations in seawater. Competitive adsorption studies between Sr^{2+} and Ca^{2+} were performed with different molar ratios of Sr^{2+} to Ca^{2+} and equivalently increasing concentrations of Sr^{2+} and Ca^{2+} . For the regeneration of the samples, TiNTs were immersed in a 0.1 M HCl solution for 30 min and washed with DI water to neutralize the samples. Regenerated TiNTs were repeatedly used for the consecutive adsorption experiments.

3. Results and discussion

3.1. Morphology of titanate nanotubes

Fig. 1 shows the SEM and TEM images of hydrothermally synthesized TiNT samples with different reaction volumes. The formation of nanostructures during the hydrothermal process follows a 3D \rightarrow 2D \rightarrow 1D mechanism [22,23]. The SEM images shown in Fig. 1a and b revealed that 10 M of NaOH was sufficient to induce the formation of the fibril-type nanostructure of titanates. Further observation from TEM images (Fig. 1c and d) confirmed that the

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