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Three-dimensional barium-sulfate-impregnated reduced graphene oxide aerogel for removal of strontium from aqueous solutions

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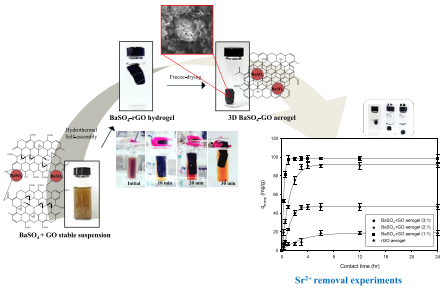
HIGHLIGHTS

- 3D barium-sulfate-impregnated reduced graphene oxide aerogels were synthesized.
- The mass ratio of $BaSO_4$ in the aerogels substantially affected strontium adsorption.
- The Langmuir isotherm gave the best fit to the experimental adsorption data.
- The strontium adsorption capacity was relatively high even with competing ions in simulated seawater.

GRAPHICAL ABSTRACT



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ABSTRACT

A three-dimensional barium-sulfate-impregnated reduced graphene oxide ($BaSO_4$-rGO) aerogel was successfully synthesized by a facile one-step hydrothermal method and was used as an adsorbent to remove strontium from aqueous solutions. The characterized elemental composition, crystal structure, and morphology of the prepared aerogel confirmed that barium sulfate particles were firmly anchored on the surface of the rGO sheets and exhibited a porous 3D structure with a high surface area of 129.37 m^2/g. The mass ratio of $BaSO_4$ in the $BaSO_4$-rGO aerogel substantially affected strontium adsorption, and the optimal $BaSO_4$/rGO ratio was found to be 1:1. The synthesized $BaSO_4$-rGO aerogel not only reached adsorption equilibrium within 1 h, but also showed much higher adsorption capacity than an rGO aerogel. The experimental data were well fitted to a pseudo-second-order kinetic model and the adsorption behavior followed the Langmuir isotherm. The adsorption capacity of strontium on $BaSO_4$-rGO aerogels remained relatively high even under ionic competition in simulated seawater. These results showed that the $BaSO_4$-rGO aerogel is an efficient and promising adsorbent for the treatment of strontium in aqueous solutions.

1. Introduction

Effectiveness and safety in waste management are primary requirements for the nuclear industry. Operational nuclear wastes are treated to ensure that they comply with stringent regulatory standards before final disposal. The need to dispose of wastes resulting from decommissioning of nuclear installations has gradually increased over the past two decades and will become the prime focus in the next two decades. Two radioactive strontium isotopes, ^{90}Sr and ^{89}Sr, are among the most hazardous and abundant contaminants in radioactive waste owing to their high specific radioactivity, high mobility, high water solubility, and long half-life. A high level of strontium (2.3–8.5 GBq/d) was accidentally discharged from the Fukushima Daiichi nuclear power plant into

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groundwater and seawater, which might cause destruction of aquatic ecosystems and human diseases such as anemia and leukemia [1–3]. At Fukushima various water treatment systems have been investigated for the decontamination of strontium as well as cesium. Some systems are even in application on an industrial scale and millions of liters of water have been processed. These systems have been in operation since the event and each uses different materials such as hexacyanoferrate, titanium oxide, and silicotitanate [4,5]. However, it is still essential to develop safe, simple, and highly efficient materials and methods for removing strontium from aqueous radioactive nuclear waste solutions.

Many physicochemical methods such as solvent extraction, evaporation, precipitation, adsorption, ion exchange, and membrane filtration have been developed for treating and conditioning radioactive wastes [6–10]. Among the available technologies, adsorption is known to be less costly and easier to operate than other methods for large volumes of liquid wastes, which can be easily transferred from a liquid phase to a solid phase and stored in shielded containers [11–13]. Many powder-type adsorbents including montmorillonite, carbon nanotubes, titanates, sodium nonatitanate, and antimony silicate have been developed to remove strontium from water [14–19]. However, large-scale application of these materials is still limited owing to their low strontium affinity and potential risk of secondary contamination [20,21].

Graphene oxide (GO), which can be easily prepared by chemical exfoliation of natural graphite power, has a high surface area, a flexible two-dimensional (2D) structure, and unique physical and chemical properties. In particular, GO possesses abundant oxygen-containing functional groups (hydroxyl, carbonyl, epoxide, carboxyl, etc.), which are available on the surface of GO sheets, making GO water soluble and improving the affinity of GO to adsorbates [22]. However, its practical application is still limited owing to its intrinsic property of forming a colloid in water, and it is also hard to separate it from an aqueous solution using centrifugation or filtration after sorption processes.

To overcome these obstacles, two strategies can be employed. The first is to assemble 2D GO into three-dimensional (3D) GO aerogels. These aerogels exhibit interconnected macro- and mesoporous structures, large surface areas, and low density, and can provide an excellent solution for designing advanced adsorbents for strontium. In particular, GO aerogels with a 3D porous framework can provide multidimensional adsorption sites and afford greatly improved adsorption efficiency [23]. Different types of GO aerogels have already exhibited improved performance in a variety of applications [24–29]. The second strategy is to impregnate the surface of GO sheets with barium sulfate ($BaSO_4$) for improved strontium removal. Barium sulfate, also known as barite, is commonly used to remove radioactive strontium in the nuclear industry [30,31]. Barium sulfate is precipitated to decontaminate liquid nuclear effluents containing radioactive strontium.

In the application investigated here, the structural properties of 3D reduced graphene oxide (rGO) and $BaSO_4$ co-precipitation were simultaneously employed to remove strontium ions from aqueous solution. First, functional groups on the basal planes and edges of rGO sheets were used to impregnate the sheets with barium sulfate particles. Then, 3D barium-sulfate-impregnated rGO ($BaSO_4$-rGO) aerogels were synthesized through a facile one-step hydrothermal process using hydroquinone as a crosslinking and reducing agent. The synthesized aerogels were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FT-IR) spectroscopy, Brunauer–Emmett–Teller (BET) analysis, and field emission-scanning electron microscopy (FE-SEM). The performance of the aerogels in adsorption experiments for strontium removal under different experimental conditions, such as various contact times, pH, and competing ions, was investigated, and the experimental results were analyzed using kinetic and isotherm models.

2. Experimental

2.1. Synthesis of GO and $BaSO_4$-rGO aerogels

GO sheets were synthesized by the modified Hummers' method from natural graphite powder [32,33]. Briefly, concentrated H_2SO_4 (23 mL) was added to a mixture including natural graphite (1 g, 1 wt equiv) and $NaNO_3$ (0.5 g, 0.5 wt equiv) in a glass flask under magnetic stirring. The mixture was cooled to 0 °C in an ice bath, and then $KMnO_4$ (3 g, 1 wt equiv) was slowly added to the reaction mixture. The mixture changed from dark green to light brown during the oxidation process. After the reaction was complete, the mixture was refluxed at 35 °C for 2 h. Subsequently, distilled water (50 mL) was gradually added, and the temperature was raised to 98 °C. The mixture was cooled to room temperature, and 30% H_2O_2 solution was added. The precipitated product was washed with distilled water several times until the pH of the solution was neutral. Finally, the precipitated GO was dried in a vacuum oven at 25 °C for 24 h.

The 3D $BaSO_4$-rGO aerogels were obtained via a hydrothermal self-assembly method, as illustrated schematically in Fig. 1. In detail, $BaSO_4$ in different mass ratios with respect to GO (1:1 to 3:1) was added under sonication to homogeneous aqueous GO dispersions (5 mg/mL, 10 mL) in a 13 mL glass vial. A certain amount of hydroquinone as a crosslinking and reducing agent was then dissolved in the mixture, which was again sonicated for 15 min to obtain a homogeneous suspension. The sealed glass vial was kept at 120 °C for 30 min in an oil bath. The obtained hydrogel was washed with distilled water several times and finally freeze-dried for characterization and further use in adsorption studies. Moreover, rGO aerogels were also obtained using the hydrothermal self-assembly method and their adsorption capacity in strontium removal was checked and compared with that of the $BaSO_4$-rGO aerogels.

2.2. Characterizations of GO and aerogels

The synthesized GO sheets were characterized by Raman spectroscopy (InVia Reflex, Renishaw, England) with a 532 nm laser. The surface chemical compositions of the GO sheets were analyzed using XPS (Quantera SXM, ULVAC-PHI, Japan). The surface chemical properties of the GO, rGO aerogels, and $BaSO_4$-rGO aerogels were measured using FT-IR spectroscopy (FT-IR/NIR Spectrum 100, PerkinElmer, USA) in a spectral range of 500–4000 cm^{-1}. The surface morphology of the rGO and $BaSO_4$-rGO aerogels was analyzed using FE-SEM images (SU8220, Hitachi, Japan). N_2 adsorption/desorption isotherms were obtained at 77.4 K using a surface area and pore size analyzer (Autosorb-iQ & Quadrasorb SI, Quantachrome, USA). Specific surface areas were evaluated using the BET equation, and the pore size distributions were calculated from the Barrett–Joyner–Halenda (BJH) equation for the isotherm.

2.3. Adsorption experiments

Inactive strontium nitrate [$Sr(NO_3)_2$] from Sigma-Aldrich (USA) was used for the adsorption experiments. Batch adsorption experiments were conducted using 100 mg of the as-prepared synthesized aerogels in 15 mL conical tubes of solution containing different initial strontium concentrations. The pH values were adjusted to 1–11 using 0.1 M HNO_3 and 0.1 M NaOH. The conical tubes were constantly shaken for 24 h in a shaking incubator at 150 rpm. Samples were taken at predetermined time intervals and