Analysis of rare earth elements in seawater by inductively coupled plasma mass spectrometry after pre-concentration using TSK[TM]-HD-MW-CNTs (highly dispersive multi-walled carbon nanotubes)

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ARTICLE INFO

ABSTRACT

This study aimed to identify easy-to-use multi-walled carbon nanotubes (MW-CNTs) having a high capacity to adsorb metals and thereby expand the usability of these materials as a solid-phase adsorbent for the analysis of trace metals in seawater. High-dispersion-type MW-CNTs had the highest metal binding capacity (70.8 ± 5.1 mg/g for La) after a strong acid oxidation procedure, possibly because the high dispersibility resulted in a more complete reaction than with highly crystalline types. Because the high-dispersion-type MW-CNTs leaked from a conventional column, they were attached to polymer beads (TSK[TM]) (pore diameter about 20 µm). Flow rate, pH, and volume of the seawater sample, as well as eluent type and volume, were optimized to obtain 0.01–0.16 pg/mL detection limits for rare earth elements (REEs). In addition, normalized patterns for samples collected from the East Sea showed characteristic features of REEs in seawater, i.e., a negative Ce anomaly, low atomic number REE (LREE) depletion, and high atomic number REE (HREE) enrichment.

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1. Introduction

Y and lanthanides, which are called "rare earth elements (REEs)", behave similarly in an aqueous environment because of their similar atomic properties such as ionic size and charge. With the exception of Ce and Eu, REEs have a trivalent oxidation state in seawater but have different particle reactivities and complexing abilities depending on their atomic number [1–3]. This results in the depletion of low atomic number REEs (LREEs) and enrichment in high atomic number REEs (HREEs) in seawater compared to continental rocks [1–3]. Ce and Eu have soluble divalent and insoluble tetravalent oxidation states. The fractionation of LREEs, mid-atomic number REEs (MREEs), and HREEs, and the anomaly with Ce and Eu, enables them to be used as tracers for ocean circulation [1–3] and the origin of terrestrial materials [4], as a probe for investigating the scavenging process of particles [1], and as a proxy for the redox state in ancient oceans [6]. Although REEs are useful tracers for chemical processes in the marine environment and several precise and reliable analytical techniques have

been developed [3–5,8–11], the development of more easy and rapid analytical method with high throughput and simple procedure is essential because of their low concentrations in seawater (sub-nanomolar to picomolar levels).

Inductively coupled plasma mass spectrometry (ICP-MS) is commonly used to quantify REEs [2–6] because of its multi-element detection over a wide concentration range with low detection limits, e.g., picomolar. Although REEs in seawater have sub-nanomolar to picomolar concentrations [7,8], pre-concentration and chemical separation of REEs is essential because of the high dissolved salt contents in seawater and for the acquisition of consistent data. Liquid–liquid extraction [9,10], co-precipitation [14], and solid-phase extraction (SPE) [6,11,12] have been used for pre-concentration of ultra-trace REEs and matrix separation in seawater. SPE using column chromatography has several advantages such as high throughput, automation, small sample and reagent quantities, simple procedure, low analyte levels in the blank, and low quantities of wastes.

Recently, carbon nanotubes have been evaluated as sorbents for trace metals, organic pollutants, and biomolecules [13–15]. Multi-walled carbon nanotubes (MW-CNTs), which have large surface area, high mechanical strength, and chemical stability, have been widely used as a solid sorbent for the analysis of Pb, Au, Rh, Mn, Fe, Cu, and REE in samples such as mineral water, serum, synthetic seawater, garlic, and rocks [13,16]. However, van der

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Waals attractions frequently cause CNTs to aggregate into bundles [17], which hinders their usefulness as sorbents in SPE applications. To overcome the aggregation problem and improve dispersibility, oxidation of CNTs by various concentrated acids [17–22], organic peroxide [23], and ozone [24] has been applied. In addition, oxidation enhances the capacity of CNTs to adsorb metals in solution, which is a critical factor for sorbents of metals because higher capacity permits a higher pre-concentration factor in the analysis of trace metals in seawater.

This study aimed to identify CNTs having a higher capacity for metal adsorption. Various types of CNTs were evaluated: highly dispersible, highly crystalline, oxidized, and non-oxidized. We present the analytical merits of REEs in seawater for CNTs having the highest capacity.

2. Materials and methods

2.1. CNTs

Two types of CNTs were purchased from Hanwha Nanotech (Inchon, Korea): CM95 and CM250, which are highly crystalline (HC) and highly dispersive (HD) MW-CNTs, respectively [25,26]. The HC-MW-CNTs are short and entangled, while the HD-MW-CNTs are long, aligned bundles. The absorbance of supernatants after centrifugation was used as the metric for dispersibility; HC types decreased to 40.7%, while HD types remained at 93.4% [25,26].

The CNTs were oxidized using the procedure of Datsyuk et al. (2008). CNTs (5 g) were washed sequentially with acetone and aqueous sodium hydroxide (100 mL for HC type and 150 mL for HD type), and purified water (18.2 MΩ). These pre-treated CNTs were refluxed at 160 °C for 60 min with concentrated HNO_3 and H_2SO_4 (1:3) and then rinsed with purified water until neutral pH. The capacities of the pre-treated non-oxidized and oxidized HD-MW-CNTs and HC-MW-CNTs were measured after oven-drying at 100 °C.

Scanning electron microscopy (SEM, S-4800, Hitachi High-Technologies Co., Tokyo, Japan) and surface area analyzer (ASAP 2020, Micromeritics, Georgia, USA) were used to study the surface morphology, surface area, pore volume, and diameter.

The capacity of each CNT type for the adsorption of La was determined batch-wise. About 30 mg of CNTs were added to 50 mL of a 50 μg/mL La standard solution (ANAPURE, Daejeon, Korea) adjusted to pH 4 using 20% ammonium acetate buffer. The mixed solution was shaken for 2 h and then filtered under vacuum through a 0.45-μm membrane filter. La attached to CNTs was eluted using 10 mL of 2 M HNO_3 solution to check for mass balance. The filtered solution was acidified to pH 1.5 using concentrated HNO_3, and the La content was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; Perkin Elmer Inc., Optima 4300DV, California, USA).

2.2. Preparation of resin and column

CNTs were usually packed into micro-columns with glass wool at the ends [16,25] and containing polyethylene frits having a nominal pore size of 10–30 μm [26]. Although the column could be used in the usual way with HC-MW-CNTs, HD-MW-CNTs leaked from the column even at low pressure because of their high degree of dispersion. Although a small-pore-size filter (e.g., 0.45-μm filter paper [27]) could be used instead of a column to prevent the leakage of CNTs, in practice it was difficult to filter volumes of seawater larger than 100 mL with a 27-mm-diameter membrane filter.

The attachment of CNTs to large beads (e.g., silica [28]) is another option. Because silica beads can give higher levels of metal in the blank, we chose a vinyl polymer gel, TSK[TM] (TOYOPEARL HW75F, SUPELCO). This material has been widely used as a support for 8-hydroxyquinoline [29]. CNTs (0.8 g) and TSK[TM] (5 g) were immersed in about 40 mL of purified water, and the solution was shaken for 24 h. After centrifugation, the supernatant was discarded. Purified water (40 mL) was added to the centrifuge vial; the sample was then shaken and centrifuged to remove unattached CNTs. This step was repeated until the supernatant was almost clear. The quantity of CNTs attached to the TSK[TM] was determined by gravimetric analysis after oven-drying the TSK[TM]-attached CNTs. However, it was difficult to obtain reliable data because the small CNT bundles could not be separated. Thus, the quantity of CNTs attached to TSK[TM] was estimated by measuring the adsorption capacity of TSK[TM], CNTs, and CNTs attached to TSK[TM] (TSK[TM]-HD-MW-CNT).

TSK[TM]-HD-MW-CNT resin (1.5 mL) was packed into a polypropylene column (8 mm diameter, 5 cm long) having 20-μm polyethylene frits as supports at both ends. Ten columns were run simultaneously using a 12-channel peristaltic pump capable of controlling the water flow rate at 0.1 mL/min.

2.3. Optimization of REE analysis in seawater

The separation of the matrix and the appropriate adsorption/elution of REE are the most important procedures for obtaining reliable REE data in seawater. The optimized conditions for sample pH, sample flow rate, sample volume, and eluent volume and type were determined. To identify the best sample pH for providing maximum REE recovery and the separation of major cations (Na^+, Ca^{2+}, Mg^{2+}), 10 ng/mL standard solutions containing mixed REEs, transition-metal cations, and major cations were prepared from stock solutions (SPEX Certi Prep Co.) and pH was adjusted from 1.6 to 9.5 with appropriate buffer solutions, i.e., phosphoric acid–potassium phosphate, acetic acid–ammonium acetate, ammonium acetate, and ammonia–ammonium acetate. The flow rate was 2 mL/min, and the eluent was 2 M HNO_3 solution. Eluent types (0.1, 0.5, 1, and 2 M HNO_3 or HCl) and volume (1, 2, 3, and 4 mL of 2 M HNO_3) were also evaluated for recovery at a sample pH of 4. The sample flow rate (2, 3, and 5 mL/min) and volume (50, 100, 300, and 400 mL) were tested at a sample pH of 4 and flow rate of 2 mL/min for 2 M HNO_3 eluent.

For the analysis of REEs in seawater, the procedure was as follows: 100 mL of filtered seawater was adjusted to pH 4 with 20% acetic acid–ammonium acetate buffer and passed through the TSK[TM]-HD-MW-CNT column at a flow rate of 2 mL/min using the peristaltic pump. Residual salts in the column were subsequently washed out with 10 mL of purified water. Metals adsorbed onto the resin were eluted using 3 mL of 2 M HNO_3. After mixing of the eluted sample with an internal standard solution having 5 ng/mL of In and Tl (SPEX Certi Prep Co.), the REEs, In, and Tl isotopes were measured using ICP/MS (Thermo Elemental Ltd., X7, Manchester, UK) at the Korean Basic Science Institute (KBSI). Signal drift and suppression by the matrix solution was corrected using the [105]In and [205]Tl intensities.

The performance of the analytical method for REEs in seawater was evaluated through the estimation of the detection limit, recovery, and precision. The detection limit was determined using seven laboratory procedural blanks each comprising 10 mL of acidified deionized water. Recovery was measured for metal-free seawater samples (seawater after the removal of transition metals and REEs) spiked with REEs in the range of 0.1–200 pg/mL. Precision estimates were established for five replicate measurements of purified seawater spiked with REEs (5 pg/mL). In addition, REEs in actual seawater samples were analyzed and compared to data obtained by another pre-concentration method, i.e., using NOBIAS chelate-PA1 [30].