

ORIGINAL RESEARCH PAPER

Determination of samarium (III) ions in environmental samples after magnetic solid phase extraction using 1, 10- phenanthroline-2, 9-dicarboxylic acid modified Fe₃O₄/GO nanosheets

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ABSTRACT

There is a growing interest in the development of new methods for extraction of REEs from nuclear wastes. In this study, we fabricated a novel material composed of 1,10-phenanthroline-2,9-dicarboxylic acid (PDA) functionalized magnetic graphene oxide (Fe₃O₄/GO) for extraction of Sm(III) from aqueous solutions. Our interest in selection of carboxyl-containing ligand was due to its good coordination characteristic with Sm (III) which can be used to design a new sorbent. Under the optimized extraction conditions, the calibration graph for Sm (III) was linear in a concentration range of 6.2-784.5 µg L⁻¹ with a correlation coefficient of 0.9900. A detection limit of 1.4 µg L⁻¹ with an enrichment factor of 125 was obtained. Precisions, expressed as relative standard deviation for single-sorbent repeatability and sorbent-to-sorbent reproducibility, were 5.9% and 8.7% (n =5), respectively. Finally, spiked sea and river waters were analyzed to evaluate the performance of the proposed method. The high recoveries (>97) indicate that the suggested protocol is acceptable for determination of Sm (III) ions in the water samples.

Keywords: ICP-OES; Magnetic Graphene Oxide; Samarium; Water Samples

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INTRODUCTION

Samarium (Sm) as a rare-earth element (REE) is of major interest for the development of several disciplines: coordination chemistry, organometallic compounds, luminescent compounds, catalysis and industrial applications. Rare-earth elements have found a variety of applications in nuclear and non-nuclear industries. These elements can enter the human body via therapeutic and diagnostic agents (diagnostic and therapeutic radionuclides) and also contaminated air, food and drinking water as a result of industrial activities. Long-time exposure to REEs may exert a harmful influence on human liver, kidney, lung, and bone quality and result in some negative effects of the immunologic system [1].

Each year, more than 10 thousand tons of

spending fuels are discharged from nuclear power plants in the world [2]. Therefore, the proper management of spending fuels is a key issue for the sustainable development of nuclear energy. The isotope samarium-151 (¹⁵¹Sm) is a significant radionuclide in spent nuclear fuels, high-level radioactive wastes resulting from the processing of spent nuclear fuels and radioactive wastes associated with the operation of nuclear reactors and fuel reprocessing plants. This hazardous radionuclide with a half-life of 90 years, decays by emitting a relatively low-energy beta particle. This element is widely used in the nuclear reactors as controlling materials of neutron fluxes. In addition, ¹⁵³Sm (1.9 days) has been suggested for treatment of painful metastatic bone disease [3]. So, an effective

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treatment method for determination of Sm (III) is strongly required. For this purpose, magnetic solid phase extraction (MSPE) is one of the most used methods for waste treatment due to simple operation, easy separation of the sorbent from matrix solution by the application of an external magnet, wide applicability and application in large scale [4]. Many kinds of sorbents such as activated carbons and biochars [5], seaweeds [6], ion imprinted polymers (IIP) [7], ion exchangers [8] and nanosorbents with the large surface area to volume ratio have been applied for treatment of Sm (III) contaminated waste-waters. Among these sorbents, carbon based nanomaterials especially graphene (G) and its derivatives have created noteworthy commercial interest their unique chemical and physical properties [9].

Graphene oxide (GO) is a new class of electron-rich carbon sorbents which shows promising applications in sample treatment. Fe₃O₄/GO nanocomposites combine the beneficial magnetic properties of the core and the possibility of binding to their surface [10, 11]. Some of the GO properties such as high surface area, ease of functionalization and good dispersibility due to the presence of the oxygen functionalities make it an ideal sorbent [4]. Despite the impressive properties of GO, direct application of GO as a selective and efficient adsorbent is still an insurmountable challenge [1]. In order to resolve the above problem, modification of inorganic or organic materials onto the GO sheets proves to be a feasible strategy. It is notable that the both sides of the planar sheets of graphene are available for modification with macromolecular ligands compared with fullerenes and carbon nanotubes (CNTs). In fact, a further incident that has attracted a great deal of interest towards GO is the advent of GO modification with various materials.

In recent years, the coordination chemistry of rare-earth cations with various carboxylic acids has attracted a lot of interest, due to the potential applications in many areas especially separation and extraction. According to the previous studies [12–14], it has been reported that carboxylic acids can act as excellent ligands for solvent extraction of lanthanides. The most important feature of the rare-earth carboxylate complexes is the large number of coordination types exhibited by these ligands, e.g. bidentate chelating, and bidentate bridging or tridentate chelating/bridging [15]. In our previous study [16], a magnetic

reduced GO decorated with thioglycolic acid (TGA) -capped CdTe quantum dots (QDs) was developed for SPE of cerium (Ce) ions from aqueous samples. The analytical potential of CdTe QDs in the extraction field was exploited through the manipulation of their surface chemistry by their capping with TGA, which improves their selective behavior towards Ce (III) ions in samples of complex matrices. In the current work, we reported a 1, 10-phenanthroline-2, 9-dicarboxylic acid (PDA) modified Fe₃O₄/GO nanocomposite for MSPE of Sm (III) ions from aqueous samples prior to determine by inductively coupled plasma-optical emission spectroscopy (ICP-OES). This measurement technique suffers from interferences from the coexisting ions, especially some other lanthanides, Fe (III) and phosphate ions. Moreover, the problem is further complicated when the normal analytical concentrations are in the ultra-trace levels. Thus, a preconcentration step of Sm ions is recommended prior to its evaluation.

EXPERIMENTAL

Chemicals and reagents

All chemicals were of analytical grade purity and used as received. Natural graphite powder, hydrochloric acid (HCl, 37%), nitric acid (HNO₃, 65%), acetic acid (CH₃COOH, 100%), sulfuric acid (H₂SO₄, 98%), ethanol (C₂H₅OH, ≥99.8%), potassium permanganate (KMnO₄, 99.9%), hydrogen peroxide (H₂O₂, 30%), ferric chloride hexahydrate (FeCl₃·6H₂O, 97%), ferrous chloride tetrahydrate (FeCl₂·4H₂O, 98%), ammonium hydroxide (NH₄OH, 30%) and element standard solutions (1000 mg L⁻¹) were purchased from Merck Company (Germany). 1, 10-phenanthroline-2, 9-dicarboxylic acid (PDA, C₁₄H₈N₂O₄) and ethylenediaminetetraacetic acid (EDTA, ≥98%) was supplied by Sigma Aldrich (USA).

Apparatus

Trace elements were determined by using a Perkin Elmer Optima 3100XL ICP-OES instrument (Shelton, CT, USA). Energy dispersive X-ray spectroscopy (EDX) analysis and FESEM studies was carried out by a Mira 3-XMU analytic microscope equipped with an energy dispersive X-ray analyzer. A 780 pH Meter was used for measuring pH at 25 °C (Metrohm, Switzerland). A sonoreactor UTR200 (Hielscher, Germany) with a maximum output power of 200 W, operating frequency of 24 kHz and ultrasonic intensity of

80 W cm⁻² was employed for ultrasound-assisted exfoliation of graphite oxide.

Synthesis of Fe₃O₄/GO

The GO nanosheets were synthesized by oxidation and exfoliation of graphite powder based on the modified Hummer's method [10]. In brief, 23 mL of concentrated sulphuric acid was added to the mixture of 1.0 g graphite flakes and 0.5 g sodium nitrate under constant stirring. After 1 h, 3.0 g KMnO₄ was added to the above mixture gradually under stirring in an ice bath for 2 h to prevent overheating and explosion. Then, the mixture was placed in ultrasonic bath and irradiated for 2 h at 25 °C, and the resulting suspension was diluted by adding 500 mL of water under vigorous stirring. The resulting mixture was filtered and was washed three times with ultrapure water and 0.1 % HCl, respectively, and then dried at 60 °C for 12 h in a vacuum oven.

The magnetic graphene was synthesized by a chemical coprecipitation of iron ions according to the reported procedure by our group with slight modification [10]. In a similar experiment, 0.5 g GO was dispersed in 20 ml of deionized water using an ultrasonic bath for 1 h. Subsequently, 0.43 g FeCl₃.6H₂O and 0.12 g FeCl₂.4H₂O were added to the GO suspension. The solution was heated up to 80 °C under nitrogen atmosphere with vigorous stirring (1000 rpm). Then, 1 mL of ammonia solution was quickly added to the mixture and the black precipitate was instantly formed. The mixture was allowed to stand for 5 min for complete precipitation. The precipitate was then collected using a magnet and the solution was decanted. The black precipitate was washed with double distilled water and was dried in vacuum at 65 °C.

Synthesis of PDA modified Fe₃O₄/GO

0.2 g of GO was ultrasonicated in 100 mL ethanol containing 0.1 g of 1, 10- phenanthroline-2, 9-dicarboxylic acid for 1 h and stirred at room temperature overnight. The resulting product was collected by filtration and washed several times with distilled water, then dried at 40 °C under a vacuum for 12 h.

Extraction procedure

To extraction of Sm, 60 mg of PDA modified Fe₃O₄/GO nanosheets was added in 50 ml of solution (pH 6), and shaken for 20 min at 35 °C. Then, the magnetic sorbent was collected at the bottom of the

beaker by applying an external magnetic field via a super magnet (10 × 5 × 4 cm with a 1.4 Tesla magnetic field). The supernatant was separated by decantation and the magnet was removed. To desorption of analyte, 800 μL of HNO₃-HCl-CH₃COOH (40: 30: 30 %v/v) was added and the suspension was stirred for 12 min. Finally, the eluent was separated by magnetic decantation and analyzed using by ICP-OES for determination of elemental Sm.

RESULTS AND DISCUSSION

Characterization of nanomaterials

Morphological studies

The morphologies of the (a) GO and (b) Fe₃O₄/GO nanocomposites were extensively characterized by FESEM (Fig. 1). The small Fe₃O₄ nanoparticles with an average size of about 30 nm (30 ± 10 nm) decorate the surface of GO sheets. In addition, these images clearly show transparent, regular and clear flakes of GO. But after modification with PDA (c), the surface of modified Fe₃O₄/GO nanocomposite becomes opaque, rough and irregular.

EDX analysis

The functionalization of GO with PDA was supported by the elemental analysis. Fig. 2 shows the EDX spectra of Fe₃O₄/GO sorbent before (a) and after (b) binding with carboxylated ligand. The related spectra confirm the presence of this ligand on the surface of Fe₃O₄/GO as the nitrogen was found in the corresponding EDX. GO nanosheets were noncovalently functionalized with PDA through π-π interactions.

Magnetic analysis

The magnetization hysteresis loop of GO/Fe₃O₄ and histidine functionalized GO/Fe₃O₄ nanocomposites was shown in Fig. 3. The saturation magnetization of the GO/Fe₃O₄ found to be 59.8 emu/g, while the respective value of functionalized GO/Fe₃O₄ was smaller (46.7 emu/g). This can be attributed to the smaller percentage of magnetite in PDA modified GO/Fe₃O₄, due to the formation of functional groups on the surface of GO.

Optimization of the extraction condition

In order to achieve the satisfactory extraction performance of the developed method, different parameters affecting the extraction conditions such as pH, sorbent dose, breakthrough volume, type and volume of eluent, adsorption and desorption times were optimized.

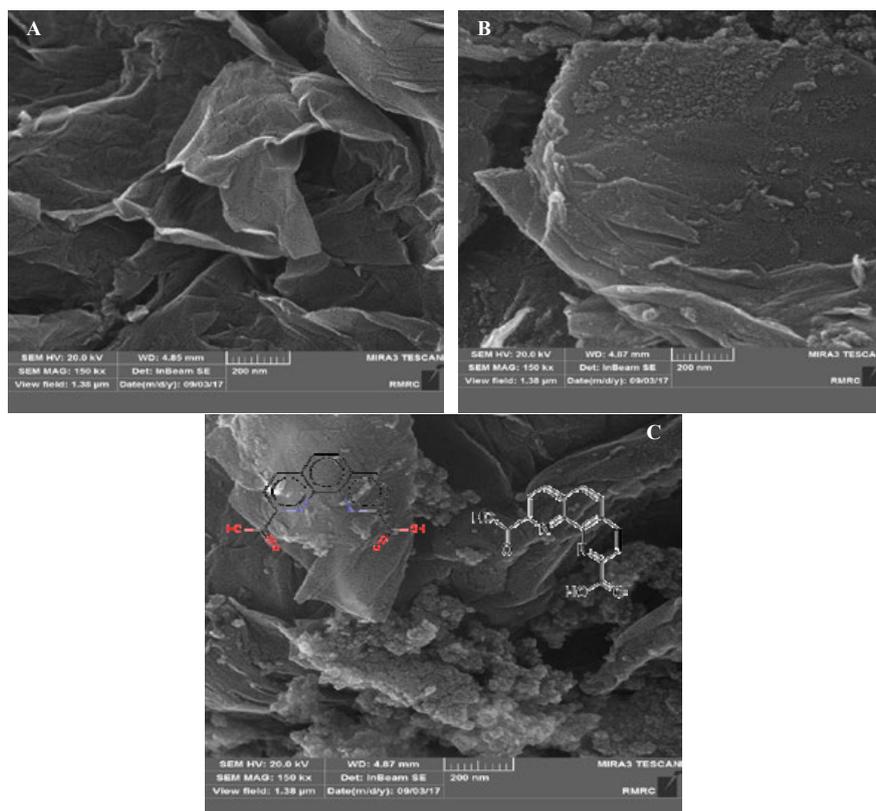


Fig. 1. The SEM of (A) GO, (B) Fe₃O₄/GO, (C) PDA modified Fe₃O₄/GO.

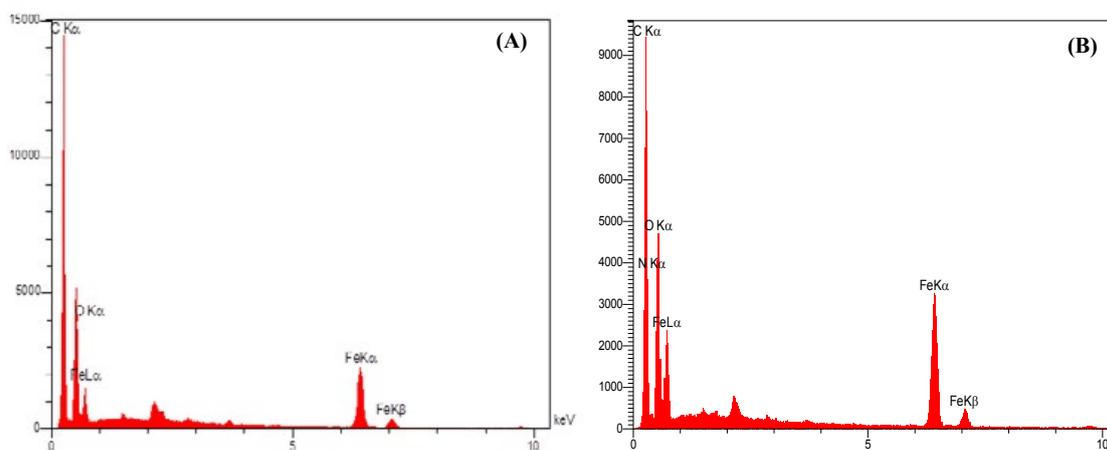


Fig. 2. The SEM of (A) Fe₃O₄/GO and (B) PDA modified Fe₃O₄/GO.

Effect of solution pH

The solution pH can be critical to obtain high yields of the Sm (III) adsorption on the surface of nanosorbent. The proton concentration is a key factor governing the hydrolysis of trivalent lanthanides [8]. So, the binding of the trivalent lanthanides by the carboxylated ligands is

strongly pH dependent. pH can influence the state of analyte and the accessibility of binding sites. Hence, the effect of pH on the extraction recovery of Sm (III) ions was evaluated within the range of 3–12. The predominant ionic species of Sm is Sm³⁺ at pH < 6, whereas the insoluble Sm(OH)₃ is formed at pH > 7.5 and become

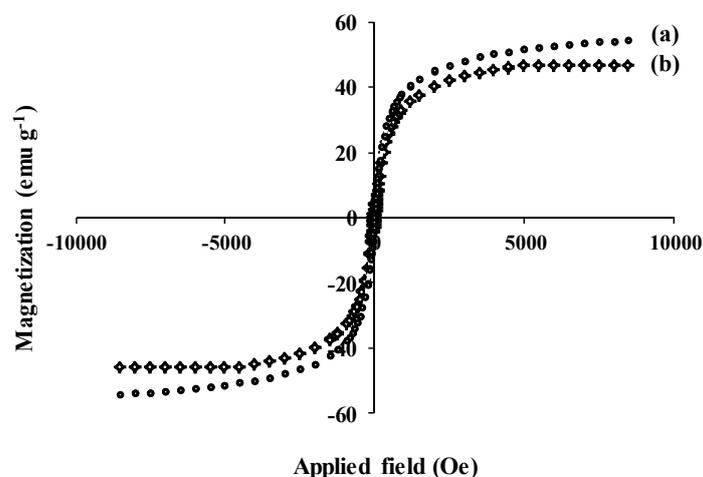


Fig. 3. VSM of (a) GO/Fe₃O₄ and (b) PDA modified GO/Fe₃O₄ nanocomposites.

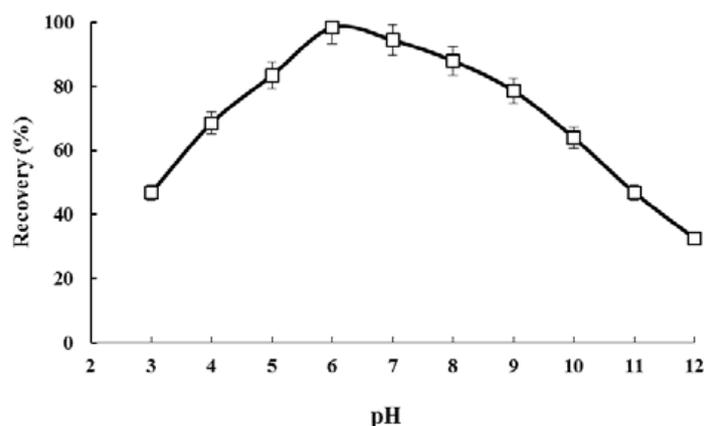


Fig. 4. Effect of pH on the recovery of 50 µg L⁻¹ of Sm(III).

predominant at pH > 11.5 [17]. Under very acidic conditions, a decrease in recovery was observed, probably due to the protonation of PDA and occupation of active sites by protons rather than analyte ions. Therefore, pH 6.0 was selected as the optimal value in subsequent experiments (Fig. 4).

Effect of sorbent dose

The amount of sorbent plays an important role in the SPE procedure and affects the extraction efficiency. To investigate the effect of this parameter on the recovery of Sm ions, the amount of PDA modified Fe₃O₄/GO was varied in the range of 10–80 mg. As shown in Fig. 5, the recovery of 50 µg L⁻¹ of analyte ions reaches a maximum value when using 60 mg of sorbent.

Breakthrough volume

To achieve a higher enrichment factor, the samples with large volume should be transferred into a smaller volume via the SPE. So, the maximum applicable sample volume was determined by increasing the dilution of solution in range of 25–150 mL, while the total amount of analyte was remained constant. The quantitative recovery for Sm was found to be stable until 100 mL and a decrease was observed with further increase in sample volume. Therefore, the enrichment factor of analyte can be extended by increasing the sample volume up to 100 mL.

Effect of elution conditions

The SPE procedure recovery significantly can be improved by efficient selection of a suitable

eluent. In fact, the solvent has a significant effect on the desorption process of the retained ions of the solid phase. Under strong acid conditions, the coordinated interaction of chelated Sm (III) ions can be easily disrupted and, subsequently, ions release into the eluent medium. For this purpose, different eluents such as EDTA, HNO₃, HCl, CH₃COOH and a mixture of HNO₃-HCl-CH₃COOH were used. As seen in Fig. 6, a recovery of 98.3% was obtained for Sm (III) when eluted with a highly pure acid mixture of HNO₃-HCl-CH₃COOH (40: 30: 30 % v/v).

Eluent volume in solid phase extraction is important to achieve high enrichment factor. The minimum volume of eluent for quantitative recoveries of adsorbed elements in this procedure was found 800 µL. Thus 800 µL of eluent was used in all further experiments.

Adsorption and desorption times

The extraction and back extraction experiments were carried out in time intervals of 5–25 and 5–15 min, respectively. At the beginning of the

adsorption process, the recoveries increased rapidly by increasing time from 5 to 20 min. After this time, no substantial increase was obtained with longer adsorption time. So, based on these results, 20 min was chosen as the optimal adsorption time. Meanwhile, the experimental results indicated that 12 min is sufficient for quantitative desorption of elements by 800 µL of highly pure acid mixture.

Effect of foreign ions

In order to assess the application of the recommended procedure, the effect of potentially interfering ions on the extraction recovery of Sm (III) was also examined. Foreign ions in different interference-to-analyte ratios were added individually to 100 mL of solutions containing 50 µg L⁻¹ of the analyte, followed by applying the method discussed earlier. As shown in Table 1, the interfering ions have no significant effects on the preconcentration of Sm (III) ions under the mentioned optimum conditions. The obtained results can be attributed to the high affinity of PDA ligand towards Sm ions.

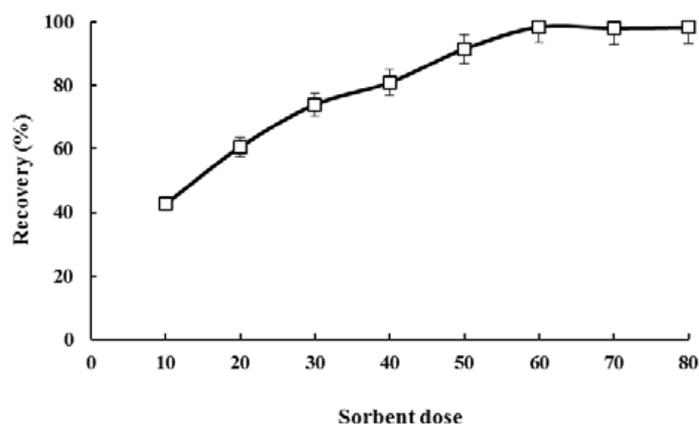


Fig. 5. Effect of sorbent dose on the recovery of 50 µg L⁻¹ of Sm(III).

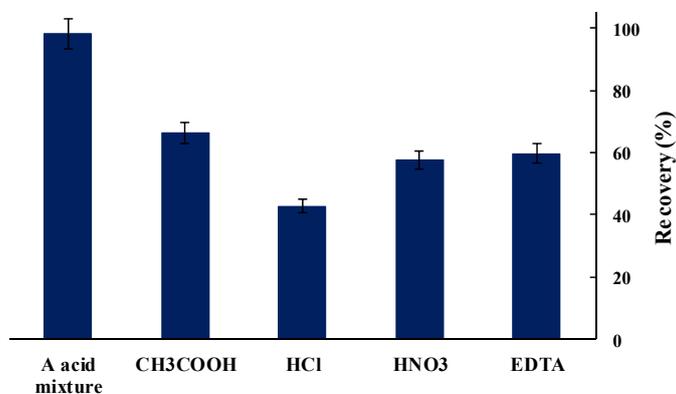


Fig. 6. Effect of eluent type on the recovery of 50 µg L⁻¹ of Sm(III).

Table 1. Effect of interfering ions on extraction and determination of 50 µg L⁻¹ of Sm (III).

Interference	Interference to Sm (III) ratio	Recovery (%)
La (III)	100	98.2
Eu (III)	125	96.5
Ce (III)	100	91.1
Ru (III)	170	90.7
Fe (III)	200	100.8
Cr (III)	150	108.9
Co (III)	240	91.5
Cd (II)	380	95.6
Hg (II)	310	103.6
Pd (II)	400	98.8
Fe (II)	330	89.7
Ni (II)	500	108.9
Mn (II)	320	99.0
Cu (II)	480	98.6
Zn (II)	375	90.2
Pb (II)	290	88.7
Na (I)	1000	109.0
K (I)	1000	97.7
Mg (II)	850	93.5
Ca (II)	900	94.3

Table 2. Results for the determination of Sm (III) in water samples.

Sample	Added standard (µg L ⁻¹)	^a Found by present method (µg L ⁻¹)	Recovery (%)
Sea water	0	NF	---
	10.0	10.93	109.3
	50.0	51.08	102.1
River water	0	NF	---
	5.0	5.35	102.4
	50.0	48.6	97.2

NF: No Founded.

Analytical figures of merit

The described extraction method was validated in terms of linearity, limit of detection (LOD), repeatability, reproducibility and enrichment factor. The calibration curve for Sm was linear in the concentration range 6.2-784.5 µg L⁻¹ with a correlation coefficient value greater than 0.9900. The LOD and LOQ for Sm based on 3S_b/m and 10S_b/m (where m is the slope of the calibration curve and S_b is the standard deviation of five blank measurements) were 1.4 and 4.6 µg L⁻¹, respectively. The relative standard deviations (RSDs) for single-sorbent repeatability and sorbent-to-sorbent reproducibility were 5.9% and 8.7% (n=5), respectively. The enrichment factor, calculated by dividing the initial volume of sample solution to the final volume of preconcentrated solution for all elements was 125.

Real sample analysis

To evaluate the applicability of the developed method, spiking water samples were carried out using the standard addition technique, and the results are shown in Table 2. The samples, including sea water and river water were tested before the

addition of Sm (III) standard with the optimized approach and also after its addition. In fact, the samples are analyzed with and without the spike to test recovery. The recovery of the added standards was calculated according to the described protocol. A good correlation was achieved between the added and measured amounts. Generally, the recoveries of Sm (III) ions obtained were in the range of between 97.2% and 109.3%. It should be noted that the evaluation of Sm (III) in sea water as a complex saline matrix at ultra-trace levels has always been a hard task, due to spectral interferences and matrix effects for powerful techniques such as ICP-OES. Thus, the design of a novel method for separation of the matrix components and preconcentration of the analyte procedures is of critical importance.

CONCLUSION

The current study presents a simple approach for synthesis of an effective nanosorbent, in which Fe₃O₄/GO nanocomposite was noncovalently functionalized with PDA through π-π interactions. Then, we assessed the potential of the PDA ligand for the extraction of Sm (III) from aqueous solutions by using a combination of ICP-OES and

recovery studies. It was found that PDA is highly preorganized for samarium complexation and tends to coordinate to Sm^{3+} . An important result from our studies is that the developed nanosorbent has several advantages over the traditional sorbents. By using of PDA ligand, we showed that the interference effects could be overcome. In addition, easy separation of the magnetic sorbent from matrix solution by the application of an external magnet, low consumption of sorbent (60 mg), high recovery (>97%) and low LOD ($1.4 \mu\text{g L}^{-1}$) are other obvious advantages compared to the alternative sorbents. In conclusion, the high extraction efficiency without interference effects shows that the proposed design improves performance throughout the doping of Fe_3O_4 nanoparticles into graphene oxide nanosheets as well as modification with a carboxyl-containing ligand.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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