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Determination of trace/ultratrace rare earth elements in environmental samples by ICP-MS after magnetic solid phase extraction with Fe_3O_4@SiO_2@polyaniline–graphene oxide composite

Shaowei Su, Beibei Chen, Man He, Bin Hu*, Zuowei Xiao

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, PR China

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ABSTRACT

A novel Fe_3O_4@SiO_2@polyaniline–graphene oxide composite (MPANI-GO) was prepared through a simple noncovalent method and applied to magnetic solid phase extraction (MSPE) of trace rare earth elements (REEs) in tea leaves and environmental water samples followed by inductively coupled plasma mass spectrometry (ICP-MS) detection. The prepared MPANI-GO was characterized by transmission electron microscopy and vibrating sample magnetometer. Various parameters affecting MPANI-GO MSPE of REEs have been investigated. Under the optimized conditions, the limits of detection (LODs, 3σ) for REEs were in the range of 0.04–1.49 ng L^{-1} and the relative standard deviations (RSDs, $c=20$ ng L^{-1}, $n=7$) were 1.7–6.5%. The accuracy of the proposed method was validated by analyzing a Certified Reference Material of GBW 07605 tea leaves. The method was also successfully applied for the determination of trace REEs in tea leaves and environmental water samples. The developed MPANI-GO MSPE-ICP-MS method has the advantages of simplicity, rapidity, high sensitivity, high enrichment factor and is suitable for the analysis of trace REEs in samples with complex matrix.

1. Introduction

Since discovered in 2004 [1], graphene, a new two-dimensional material comprising a single layer of sp^2-hybridized carbon atoms [2], has become one of the hottest research topics and gain great attention in material sciences due to its various unique properties [3–5]. It is reported that graphene possesses a high theoretical specific surface area (2630 $m^2\,g^{-1}$) [3], suggesting a high sorption capacity. In addition, due to its large delocalized π-electron system, graphene can form a strong π–π stacking interaction with the benzene ring [6]. These unique properties make graphene suitable for the adsorption of benzenoid compounds [7–11]. However, the research works involving graphene as an adsorbent for heavy metals are scarce [12,13], probably owing to the lack of functional groups on its surface to bind with metal ions.

Graphene oxide (GO), traditionally served as a precursor for graphene, consists of a hexagonal carbon network bearing hydroxyl and epoxide functional groups on its "basal" plane, whereas the edges are mostly decorated by carboxyl and carbonyl groups [14,15]. These oxygen-containing functional groups can bind with metal ions, especially the multivalent metal ions, through both electrostatic and coordinate approaches, which makes GO an ideal adsorbent for metal ions. Recently, the utilization of GO as a sorbent for the removal of heavy metal ions from water has been reported [16,17]. Yang et al. found that the adsorption capacity of Cu(II) on GO was 10 times higher than that of Cu(II) on activated carbon [16]. Wang et al. prepared a few-layered graphene oxide (FGO) and found that the maximum adsorption capacities of Pb(II) ions on FGO is higher than any currently reported materials [17]. In these works, centrifugation or filtration was employed to separate or retrieve the GO from dispersion [16,17]. However, it is hard to fully recover GO from aqueous solution even by high-speed centrifugation, due to its high hydrophilicity and good dispersibility [18], which make GO unsuitable to be applied directly as an adsorbent for the separation/preconcentration of metal ions.

To solve the above-mentioned problems, GO was anchored onto the surface of some substrates, such as silica [18,19], monolithic column [20] and Fe_3O_4 [21–24], to improve its stability. Among them, coating GO onto Fe_3O_4 to fabricate magnetic GO composite is a good choice. On one hand, due to the superparamagnetic properties, magnetic GO composite could be quickly and easily separated from the dispersion by an external magnetic field without centrifugation or filtration. On the other hand, extraction was processed with the aid of ultrasonication, which makes the magnetic GO composite be completely dispersed without

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* Corresponding author. Tel.: +86 27 68752162; fax: +86 27 68754067.
E-mail address: binhu@whu.edu.cn (B. Hu).

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aggregation. Up to now, various methods including electrostatic interactions [21,22], chemical precipitation [23] and covalent bonding [24] have been applied to prepare magnetic GO composite. However, GO will easily fall off from the magnetic substrate when magnetic GO composite was prepared via electrostatic interactions due to the weak interaction. By forming chemical bond or coordination bonding between oxygen-containing functional groups on GO and the magnetic substrate or Fe^{3+}/Fe^{2+}, GO could be stably coated on the surface of magnetic substrate. But plenty of oxygen-containing functional groups are consumed for chemical bonding, leading to insufficient sites for the adsorption of metal ions. Therefore, advanced methods to prepare magnetic GO composite to maintain active sites on the surface of GO for adsorption of metal ions are expected. Polyaniline (PANI), a well-known conducting polymer, has been applied to fabricate the GO/PANI composite for supercapacitors [25,26]. The composites are proposed to be combined through π–π stacking interaction, hydrogen bonding and electrostatic interaction between PANI and GO [25,26]. It gives us a hint that with PANI as the intermediate GO can be effectively anchored on magnetic substrate through these interactions, which will not only reserve the oxygen-containing functional groups of GO but also enhance the stability of the magnetic GO composite.

Rare earth elements (REEs), owing to their specific characteristics, have been widely used in industry, such as electronics, superconductors, catalysts, as well as ceramics, and agriculture as microelement fertilizer [27], resulting in a potential pollution to environment. It was reported that long-term intake of low dose REEs may lead to accumulation in the bone structure, changes in the bone tissue, and aberration of bone marrow cells and even bring about genetic toxicity in bone marrow cells [28]. Besides, REEs can invade the central nervous system because they are susceptible to cerebral cortex and cause subclinical damage [29]. So the determination of REEs in environmental samples is of great importance. Inductively coupled plasma mass spectrometry (ICP-MS) is considered to be one of the most powerful techniques for REEs analysis because of its high sensitivity, wide dynamic linear range, multi-element capability etc. However, the direct determination of REEs in real-samples is difficult, due to the low concentration of REEs in environmental samples (sub ng L^{-1} level) and the complex sample matrix. Therefore, a sample pretreatment step, which can separate the analytes from the matrix and preconcentrate them before their measurement, is often mandatory. Among various methods [27,30–33] for separation/preconcentration of REEs, solid phase extraction (SPE) based on adsorbent is an effective method. A number of studies have been demonstrated that materials functionalized with oxygen possess high binding affinity to REEs [27,33,34]. GO is featured with an ultrahigh specific surface area and plenty of oxygenous groups, which is expected to be a good alternative as an adsorbent for REEs.

Therefore, the purpose of this work was to prepare Fe_3O_4@SiO_2@PANI-GO composite (MPANI-GO) and develop a novel method of magnetic solid phase extraction (MSPE)-ICP-MS for the determination of REEs in tea leaves and environmental water samples. The adsorption capacity and stability of MPANI-GO were examined. Experimental parameters affecting MSPE were studied in detail and the optimal experimental conditions were established. The developed method has been successfully applied for the determination of trace REEs in tea leaves and environmental water samples.

2. Experimental

2.1. Instrumentations

An Agilent 7500a ICP-MS (Agilent, Tokyo, Japan) with a Babington nebulizer was applied and the optimal operation conditions are summarized in Table 1. The pH values were controlled with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. The transmission electron micrograph (TEM) image of the prepared materials was captured on a JEM-2010 electron microscope (Tokyo, Japan). Magnetic properties of the materials were characterized by a PPMS-9 vibrating sample magnetometer (QUANTOM, USA). A WX-4000 microwave-accelerated digestion system (Shanghai EU Microwave Chemistry Technology Co. Ltd., Shanghai, China) and SKML model temperature control heating panel (Beijing, China) were used for sample digestion. A KQ 5200DE model Ultrasonicator (Shumei Instrument Factory, Kunshan, China) was used to disperse the materials in solution. An Nd-Fe-B magnet (15.0 × 6.0 × 1.6 cm) was used for magnetic separation.

Table 1
Operating conditions of ICP-MS.
Spectrum

ICP-MS plasma	
Rf power	1250 W
Plasma gas (Ar) flow rate	14 L min^{-1}
Auxiliary gas (Ar) flow rate	0.88 L min^{-1}
Carrier gas (Ar) flow rate	1.08 L min^{-1}
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0/0.4 mm
Data acquisition	
Scanning mode	Full quant
Dwell time	100 ms
Points per spectral peak	3
Isotopes	^{89}Y, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{158}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu

2.2. Standard solutions and reagents

The stock standard solutions (1.000 g L^{-1}) of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu were prepared by dissolving appropriate amounts of their specpure oxides (Merck, Darmstadt, Germany) in dilute HNO_3. Working solutions were prepared daily by appropriate dilutions of their stock solutions. Graphite powder (325 mesh, 99.9995%) was obtained from Alfa Aesar (MA, USA). P_2O_5, $K_2S_2O_8$, H_2O_2, $KMnO_4$, HCl, H_2SO_4 and aniline were bought from Sinopharm Chemistry Reagent Co. Ltd (Shanghai, China). Tetraethoxysilane (TEOS) was purchased from Organic Silicon Material Company of Wuhan University (Wuhan, China). High purity water (18.2 MΩ cm) obtained from Milli-Q Element system (Millipore, Molsheim, France) was used throughout this work. All reagents were of analytical grade unless otherwise noted. Plastic and glass containers and all other laboratory materials that could come into contact with samples and standards were stored in 20% (v/v) nitric acid over 24 h and rinsed with high purity water prior to use.

2.3. Synthesis of graphene oxide

Graphene oxide was synthesized according to the modified Hummers method [35,36]. About 3 g of graphite powder was added into a 25 mL 3-necked round-bottom flask containing 12 mL of concentrated H_2SO_4, 2.5 g of $K_2S_2O_8$ and 2.5 g of P_2O_5. Then the mixture was kept at 80 °C for 4.5 h. After dilution with 1 L of high purity water and filtration, the products were washed with high purity water and dried at 40 °C. Then, the pretreated oxidized graphite was dispersed in 120 mL of concentrated H_2SO_4 in a 3-necked round-bottom flask under stirring, and the 3-necked round-bottom flask was placed in an ice bath. About 15 g of

$KMnO_4$ was added slowly into the 3-necked round-bottom flask with temperature strictly controlled below 10 °C. Afterwards, the mixture was allowed to react at 35 °C for 7 days. Then, 250 mL of high purity water was added, and the mixture was kept at 98 °C for 2 h. After the temperature was reduced to 60 °C, 15 mL of H_2O_2 (30%, v/v) was added and the mixture was further stirred for 2 h. The above mixture was centrifuged to collect the graphite oxide, and the graphite oxide was washed with 10% (v/v) HCl solution for 5 times, and then washed with high purity water until the pH of the supernatant was neutral. The as-synthesized graphite oxide was dispersed in water (0.5 mg mL^{-1}) and ultrasonicated for 1 h to obtain a clear dispersion of GO.

2.4. Preparation of MPANI-GO

The Fe_3O_4 nanoparticles were prepared by the conventional co-precipitation method with minor modifications [37]. The 11.68 g of ferric chloride and 4.30 g of ferrous chloride were dissolved in 200 mL of high purity water under nitrogen gas with vigorous stirring at 85 °C. Then 40 mL of 30% (v/v) $NH_3 \cdot H_2O$ was added with further increased nitrogen passing rate and stirring speeds, and the orange–red clear solution became a black suspension immediately. The reaction was stopped after half an hour, and the obtained suspension was cooled down to room temperature naturally. The nanoparticles were sequentially washed with high purity water, 0.02 mol L^{-1} sodium chloride and ethanol for several times. The cleaned nanoparticles were stored in ethanol at a concentration of 40 g L^{-1}.

A quantity of 4 mL of TEOS, 50 mL of glycerol and 150 mL of ethanol were mixed under ultrasonication in a 500 mL beaker, and adjusted to pH 4.5 by acetic acid–sodium acetate buffer solution, then transferred to a three neck flask. After 50 mL of above-prepared magnetite suspension was added, the suspension was stirred and heated to 90 °C, refluxed for 2 h under a nitrogen atmosphere. After cooling to room temperature, the suspension was washed sequentially with high purity water (3 × 500 mL) and ethanol (3 × 100 mL). The silica coated Fe_3O_4 composite (Fe_3O_4@SiO_2) was stored in high purity water at a concentration of 40 g L^{-1}.

The MPANI was synthesized according to the method of Ref. [38] with a minor modification. About 1 g of Fe_3O_4@SiO_2 was added into 200 mL of high purity water, followed by the addition of 0.6 mL of aniline. After adjusted the pH to 3 by 1 mol L^{-1} HCl aqueous solution, the mixture was vigorously stirred for 1 h. Then 50 mL of 1.2% (m/v) $(NH_4)_2S_2O_8$ was slowly added into the mixture to start the in-situ polymerization of aniline monomers. The polymerization was maintained under stirring for 10 h at room temperature. The obtained MPANI was washed sequentially with high purity water (3 × 500 mL) and ethanol (3 × 100 mL). Then the MPANI was dried in oven at 60 °C for 12 h.

To prepare MPANI-GO, 1 g of MPANI was dispersed in 100 mL of high purity water with the aid of ultrasonication. Then 250 mL of 0.5 mg mL^{-1} GO was added into the above suspension under ultrasonication. After ultrasonication for 30 min, MPANI-GO was formed. The obtained MPANI-GO was washed several times with high purity water. Then the composite was dried in oven at 60 °C for 12 h.

2.5. Magnetic solid phase extraction procedure

The specific steps of MSPE were similar to Ref. [39]. First, a portion of sample solution containing the REEs was transferred into a 25 mL beaker, and adjusted to about pH 4.0 with diluted HNO_3 and $NH_3 \cdot H_2O$. Second, 10 mg of MPANI-GO was added and dispersed by ultrasonication for 2 min at room temperature, and then isolated from the suspension with an Nd-Fe-B strong magnet. Third, the adsorbed analytes were desorbed from the isolated adsorbent with 0.5 mL of 0.5 mol L^{-1} HNO_3 by ultrasonication for 2 min. Finally, the eluate was separated by magnet again and introduced into ICP-MS for subsequent determination.

High purity water adjusted to about pH 4.0 with diluted HNO_3 and $NH_3 \cdot H_2O$ was employed as the blank solution and was subjected to the same procedure.

2.6. Sample preparation

A Certified Reference Material of GBW 07605 (tea leaves, the Institute of Geophysical and Geochemical Exploration, Langfang, China) was employed for verifying the accuracy of the proposed method. In addition, four kinds of tea leaves and environmental water samples were analyzed. Details of the sample preparation are as follows.

Four kinds of tea leaves were purchased from a local supermarket in Wuhan, China. About 2 g of each tea leaves was ground into powder before digestion. The digestion procedure was described as follows. A 50 mg sample was weighed and put into a PTFE digestion vessel. After adding 4 mL of 65% HNO_3 and 0.5 mL of 48% HF, the vessel was placed on a temperature control heating panel at 140 °C for 30 min. After cooling to room temperature, the vessel was then placed on a turntable and subjected to microwave digestion. The microwave system was operated as follows: 5 min at 18 atm and 150 °C, 5 min at 25 atm and 180 °C. After cooling, the vessels were opened and heated to near dryness on a hot plate at 200 °C. The residue was transferred into a 50 mL flask, adjusted to pH 4 with 0.1 mol L^{-1} $NH_3 \cdot H_2O$, and diluted to the mark with high purity water.

The Certified Reference Material of GBW 07605 tea leaves was subjected to the same microwave treatment.

East Lake water and Yangtze River water (Wuhan, China) were collected and filtered through the 0.45 μm membrane filter (Tianjing Jinteng Instrument Factory, Tianjin, China), then acidified to pH 3.5 with concentrated HNO_3 prior to storage. Before use, the pH value was adjusted to 4 with 0.1 mol L^{-1} HNO_3 and $NH_3 \cdot H_2O$.

The blank was prepared by using high purity water without addition of target REEs, subjecting to the same procedure described above.

3. Results and discussion

3.1. Characterization of MPANI and MPANI-GO

TEM was employed to characterize the structure and morphology of the prepared MPANI and MPANI-GO. Fig. 1a shows that the prepared MPANI has a uniform size of about 20 nm. From the Fig. 1b, it can be seen that the MPANI was anchored on the lamellar and wrinkled GO, indicating that the MPANI-GO was successfully prepared.

Meanwhile, the images of the GO dispersion solution and the GO dispersion solution with the addition of Fe_3O_4@SiO_2 and MPANI were also carried out. As can be seen in Fig. 2, in the absence of Fe_3O_4@SiO_2 or MPANI (Fig. 2a), the color of the GO dispersion solution is brown. With the addition of Fe_3O_4@SiO_2 (Fig. 2b), the color of the solution remained unchanged, while the added Fe_3O_4@SiO_2 was sedimented under external magnetic field, indicating that there is no obvious interaction between GO and Fe_3O_4@SiO_2. With the addition of MPANI (Fig. 2c), it can be seen that the color of the GO dispersion solution changed from brown to colorless under external magnetic field, indicating that GO was complexed with MPANI completely, and the formed MPANI-GO can be separated well from the matrix under external magnetic

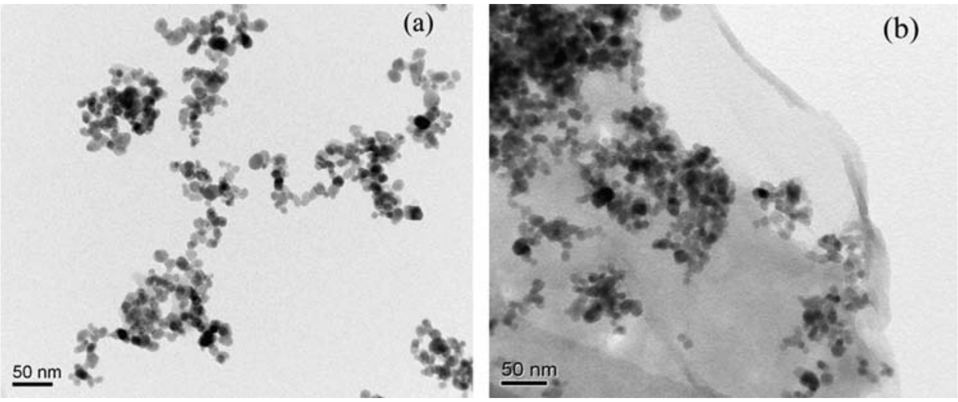

Fig. 1. TEM images of MPANI (a) and MPANI-GO (b).

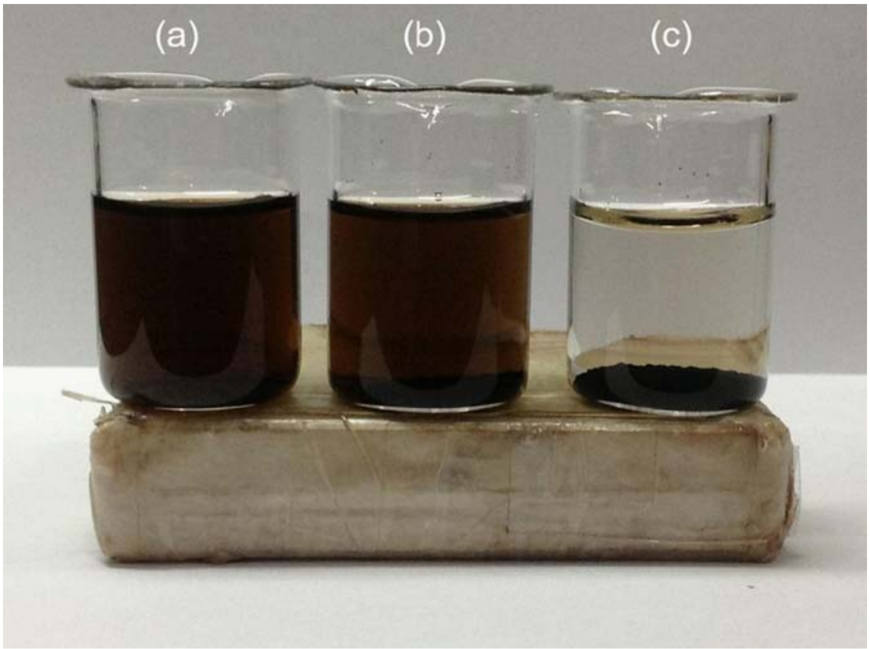

Fig. 2. The images of the GO dispersion solution (a) and the GO dispersion solution with the addition of $Fe_3O_4@SiO_2$ (b) and MPANI (c) under external magnetic field.

field. The above results demonstrated that GO could be effectively anchored on magnetic nanoparticles with PANI as the intermediate.

The hysteresis loops of the MPANI and MPANI-GO measured at 300 K are shown in Fig. 3. The saturation magnetization values for MPANI and MPANI-GO were 61.2 and 52.4 emu g^{-1}, respectively. The relatively high saturation magnetization value indicates good superparamagnetism of MPANI-GO. As shown in the insets of Fig. 3, MPANI-GO (10 mg) was well dispersed in aqueous solution (25 mL) without external magnetic field, and rapidly separated from aqueous solution under an external magnetic field.

Besides, the studies on the effect of pH (seen in Section 3.2.1) showed different adsorption behaviors of MPANI and MPANI-GO to REEs, which also demonstrated a successful preparation of MPANI-GO.

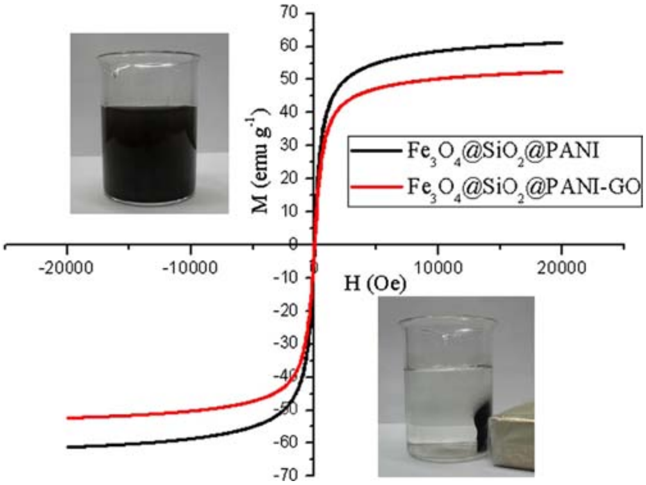

Fig. 3. Magnetic hysteresis loops of MPANI and MPANI-GO; The insets show the digital images of MPANI-GO dispersions before (left inset) and after (right inset) exposing to an external magnetic field for 5 min.

3.2. *The optimization of magnetic solid phase extraction procedure*

3.2.1. *Effect of pH*

pH value plays an important role with respect to the adsorption of different ions on MPANI-GO. When the sample solution is alkaline at pH > 8, REEs would majorly be precipitated. An appropriate pH can not only improve the adsorption efficiency, but also depress the interference of the coexisting ions. So, the adsorption behavior of REEs on MPANI-GO was examined, and the results are given in Fig. 4a. As can be seen, the adsorption percentage of REEs increased rapidly with the increase of sample pH from 2 to 2.5 and quantitative adsorption was achieved in the pH range of 2.5–9. To ascertain the function of GO in MPANI-GO, the adsorption behavior of REEs on MPANI was also studied according to the same procedure. The results (Fig. 4b) show that adsorption percentage of REEs increased with the increase of sample pH from 2 to 9, but quantitative adsorption for most of the REEs was not achieved in the whole investigated pH range. At high pH values (> 8), the relative high adsorption percentage is attributed to the precipitation of M (OH)n formed between REEs and OH^-. These results demonstrated that the GO plays a key role in the adsorption of REEs on MPANI-GO and the function of MPANI was mainly to anchor and magnetically functionalize GO. The adsorption mechanism of the REEs on the MPANI-GO could be attributed to the chelation of the functional groups of GO containing hydroxyl, epoxide, carboxyl and carbonyl groups with REEs. Finally, a sample pH of 4.0 was selected to guarantee quantitative adsorption of all REEs for further experiments.

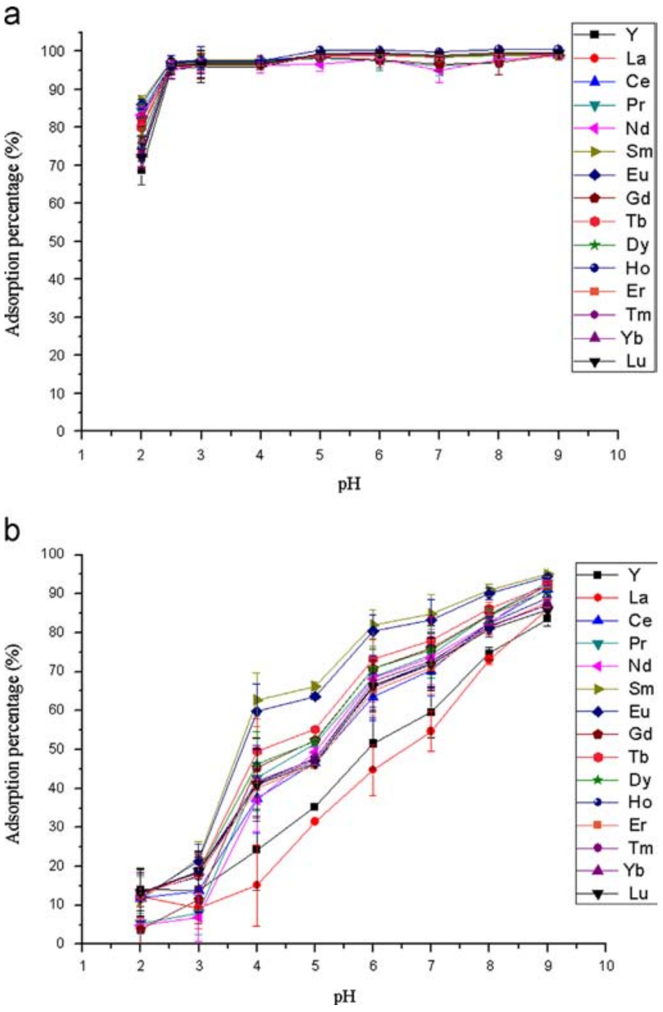

Fig. 4. Effect of pH on the adsorption percentage of the REEs (10 ng mL^{-1}) on the MPANI-GO (a) and MPANI (b); Sample volume: 5 mL; adsorption time: 20 min.

3.2.2. *Effect of HNO_3 concentration*

It is clear in Fig. 4a that lower adsorption percentage of REEs on MPANI-GO was obtained at a lower pH value, indicating that H^+ ions can easily compete with the REEs retained on the sorbent at lower pH values (< 2.5). Additionally, considering that HNO_3 is the mostly recommended solvent in ICP-MS measurement, HNO_3 was selected as the eluent and various concentrations of HNO_3 were studied for elution of the retained REEs from the MPANI-GO. It was found that all REEs could be eluted quantitatively within the whole tested range of 0.1–1.5 mol L^{-1} HNO_3. In the following experiments, 0.5 mol L^{-1} HNO_3 was employed.

3.2.3. *Effect of elution volume and time*

The elution volume and time could affect the efficiency of the elution significantly. It should be pointed out that 0.5 mL is the minimal volume for one determination run in the pneumatic nebulizer (PN)-ICP-MS measurement. Thus, to study the effect of elution volume, 0.5, 1, 1.5 and 2 mL of 0.5 mol L^{-1} HNO_3 were used to elute the REEs retained on the MPANI-GO, respectively, and the experimental results show that 0.5 mL of 0.5 mol L^{-1} HNO_3 was sufficient to quantitatively elute all the REEs. The influence of elution time varying from 1 to 15 min on the recovery of the REEs was also investigated. It was found that the REEs could be quantitatively recovered when the elution time was above 1 min, which indicates that the prepared MPANI-GO has fast elution kinetics for REEs. Finally, 0.5 mL of 0.5 mol L^{-1} HNO_3 with elution time of 2 min was employed as the optimum elution conditions.

3.2.4. *Effect of sample volume*

In order to obtain a higher enrichment factor, a larger sample volume is required. To investigate the effect of the sample volume on the recoveries of the REEs, the sample solutions of 5, 25, 50, 100 and 200 mL containing 50 ng of each REE were prepared and subjected to the general procedure, respectively. From Fig. 5, it is found that the recovery of REEs was quantitative when the sample volume was in the range of 5–100 mL, and then slightly decreased with further increase of sample volume to 200 mL. In subsequent experiment, 25 mL sample volume was used, and an enrichment factor of 50 was obtained by applying 0.5 mL of 0.5 mol L^{-1} HNO_3 as the elution solution.

3.2.5. *Effect of adsorption time*

The adsorption time should be optimized to ensure quantitative retention along with a minimal time required for sample

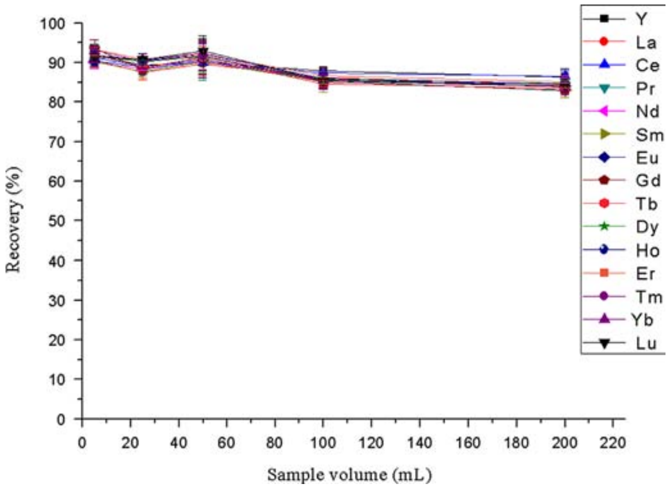

Fig. 5. Effect of the sample volume on the recovery of the REEs; adsorption time: 20 min; eluent: 0.5 mol L^{-1} HNO_3; elution volume: 0.5 mL.

processing. To study the effect of adsorption time, 25 mL of sample solution containing 2 ng mL^{-1} REEs was ultrasonicated for 1, 2, 5, 10 and 15 min and the recovery was studied, respectively. The experimental results show that quantitative recoveries could be obtained for the REEs in 1 min, which indicates the prepared

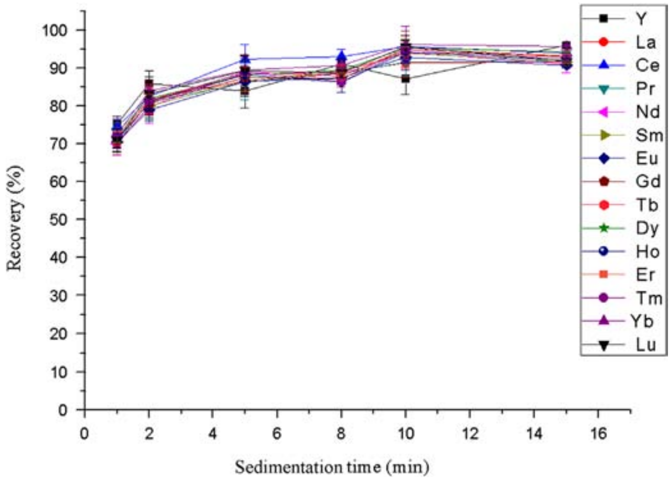

Fig. 6. Effect of the sedimentation time on the recovery of the REEs; Sample volume: 25 mL; concentration of each REEs: 2 ng mL^{-1}; adsorption time: 2 min; eluent: 0.5 mol L^{-1} HNO_3; elution volume: 0.5 mL.

Table 2
Tolerance limit of coexisting ions.

Coexisting ions	Tolerance limit of ions (mg L^{-1})
K^+	5000
Na^+	5000
Ca^{2+}	2000
Mg^{2+}	2000
Zn^{2+}	100
Fe^{3+}	100
Al^{3+}	5
Cu^{2+}	10
Cl^-	8000
NO_3^-	8000
SO_4^{2-}	5000
SiO_3^{2-}	5000

Table 3
Comparison of adsorption capacities (mg g^{-1}).

REEs	MPANI-GO	MWCNT [33]	MAF-8HQ [41]	Nano-sized TiO_2 [42]	Alkyl phosphinic acid resin [43]	Mesoporous TiO_2 [44]
Y	8.1	–	–	6.1	1.4	–
La	15.5	8.3	8.3	7.0	2.0	21.3
Ce	8.6	–	–	–	2.0	13.8
Pr	11.1	–	–	––	2.0	–
Nd	8.5	–	–	–	2.0	–
Sm	7.7	9.7	5.4	–	2.1	–
Eu	11.0	9.4	–	8.3	2.1	19.5
Gd	16.3	9.9	–	–	2.2	–
Tb	11.8	8	–	–	2.2	–
Dy	16	–	–	8.8	2.2	16.7
Ho	8.1	7.2	–	–	2.2	–
Er	15.2	–	–	–	2.2	–
Tm	10.4	–	–	–	2.3	–
Yb	10.3	8.7	10.4	9.8	2.3	16.5
Lu	14.9	–	–	–	2.4	–

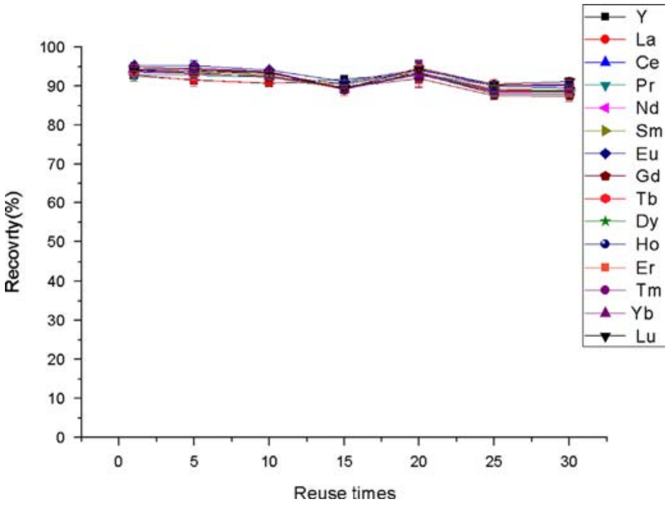

Fig. 7. Effect of the reuse times on the recovery of the REEs; Sample volume: 25 mL; concentration of each REEs: 2 ng mL^{-1}; adsorption time: 2 min; eluent: 0.5 mol L^{-1} HNO_3; elution volume: 0.5 mL.

Table 4
The analytical performance data of the MSPE-ICP-MS system.

Target ions	Linear equation	Linear range (ng L^{-1})	LOD (ng L^{-1})	RSD%[a] ($n=7$)	r
Y	$y=1148{,}900x-10{,}752$	0.5–10,000	0.15	2.8	0.9998
La	$y=973{,}957x-2038$	0.5–10,000	0.16	2.4	0.9999
Ce	$y=1084{,}430x-534$	1–10,000	0.21	1.7	0.9999
Pr	$y=1175{,}800x+1140$	2–10,000	0.69	5.9	0.9999
Nd	$y=210{,}151x+1454$	5–10,000	1.49	6.5	0.9999
Sm	$y=161{,}021x-687$	1–10,000	0.18	2.2	0.9999
Eu	$y=595{,}237x+1323$	0.5–10,000	0.07	2.5	0.9999
Gd	$y=170{,}415x+809$	2–10,000	0.54	3.9	0.9999
Tb	$y=1072{,}580x+5768$	0.3–10,000	0.04	2.3	0.9999
Dy	$y=276{,}000x+1495$	1–10,000	0.21	2.8	0.9999
Ho	$y=1154{,}420x+9628$	0.3–10,000	0.05	1.8	0.9999
Er	$y=323{,}650x+2588$	0.5–10,000	0.07	2.3	0.9999
Tm	$y=1080{,}210x+11{,}021$	0.3–10,000	0.04	2.4	0.9999
Yb	$y=225{,}759x+2087$	1–10,000	0.20	3.4	0.9999
Lu	$y=1066{,}330x+13{,}806$	0.3–10,000	0.04	3.1	0.9998

[a] $c=20$ ng L^{-1}.

Table 5
Comparison of limits of detection (ng L^{-1}) for REEs obtained by the proposed method with other analytical methods.

REEs	This work	SPE-ICP-MS [41]	DLLME-ICP-MS [31]	SPE-ICP-MS [45]	SPE-ICP-MS [27]
Y	0.15	0.13		0.6	0.04
La	0.16	0.10	0.55	1	0.17
Ce	0.21	0.12	0.34	1.2	0.16
Pr	0.69	0.06	0.16		0.03
Nd	1.49	0.04	0.52		0.13
Sm	0.18	0.12	0.25	0.4	0.09
Eu	0.07	0.08	0.21	0.6	0.04
Gd	0.54	0.18	0.19		0.08
Tb	0.04	0.06	0.05		0.02
Dy	0.21	0.16	0.20	0.2	0.04
Ho	0.05	0.07	0.08		0.01
Er	0.07	0.09	0.18		0.02
Tm	0.04	0.08	0.16		0.01
Yb	0.20	0.30	0.24		0.07
Lu	0.04	0.05	0.16		0.04

MPANI-GO has fast adsorption kinetics for REEs. In this work, 2 min was selected for quantitative adsorption.

3.2.6. *Effect of sedimentation time*

In this study, the adsorbent could be separated rapidly from the sample solution using an external magnetic field instead of filtration or centrifugation, due to the superparamagnetism of MPANI-GO. Therefore, the effect of sedimentation time on the recovery of REEs was investigated and the experimental results are shown in Fig. 6. It can be seen that the MPANI-GO could be completely sedimented with quantitative recoveries of target REEs when the sedimentation time was greater than 5 min. In subsequent experiments, a sedimentation time of 5 min was employed.

Table 6
Analytical results of REEs in Certified Reference Material of GBW 07605 tea leaves (mean ± s.d., $n=3$).

REEs	Determined (μg g^{-1})	Certified (μg g^{-1})
Y	0.36 ± 0.02	0.36 ± 0.03
La	0.65 ± 0.03	0.60 ± 0.03
Ce	0.90 ± 0.04	1 ± 0.1
Pr	0.110 ± 0.005	0.12
Nd	0.49 ± 0.02	0.44
Sm	0.086 ± 0.003	0.085 ± 0.017
Eu	0.016 ± 0.001	0.018 ± 0.002
Gd	0.099 ± 0.004	0.093
Tb	0.012 ± 0.002	0.011
Dy	0.070 ± 0.002	0.074
Ho	0.016 ± 0.002	0.019
Er	0.042 ± 0.002	–
Tm	0.0050 ± 0.0003	–
Yb	0.042 ± 0.002	0.044 ± 0.004
Lu	0.0060 ± 0.0005	0.007

3.3. *Effect of coexisting ions*

To study the effect of coexisting ions such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Zn^{2+}, Al^{3+} and Cu^{2+} on the extraction and determination of REEs, solutions of 25 mL containing 2 ng mL^{-1} of REEs and a certain amount of interfering ions were subjected to the proposed procedure. The tolerance limit was defined as the largest amount of coexisting ions, in the presence of which the recovery of the REEs could be maintained in the range of 85–115%. The results in Table 2 showed that 5000 mg L^{-1} K^+ and Na^+, 2000 mg L^{-1} Ca^{2+} and Mg^{2+}, 100 mg L^{-1} Zn^{2+} and Fe^{3+}, 5 mg L^{-1} Al^{3+}, 10 mg L^{-1} Cu^{2+}, 8000 mg L^{-1} Cl^- and NO_3^- or 5000 mg L^{-1} SO_4^{2-} and SiO_3^{2-} had negligible effect on the extraction and determination of REEs. From the experimental results obtained, it can be concluded that the developed method has an excellent selectivity for the adsorption of REEs and is suitable for the analysis of samples with complicated matrix.

3.4. *Adsorption capacity*

Adsorption capacity is an important factor to evaluate the performance of sorbent. In this work, the method used in adsorption capacity study was adapted from that recommended by Angel Maquelera and Puchades [40]. To evaluate the adsorption capacity

Table 7
Analytical results of REEs in tea leaves (mean ± s.d., $n=3$).

REEs	Added (ng g^{-1})	Tieguanyin green tea[a]		Lvdun black tea[b]		Puer black tea[c]		Hanzhong green tea[d]	
		Found (ng g^{-1})	Recovery (%)	Found (ng g^{-1})	Recovery (%)	Found (ng g^{-1})	Recovery (%)	Found (ng g^{-1})	Recovery (%)
Y	0	228 ± 9	–	243 ± 17	–	89 ± 3	–	64 ± 2	–
	100	330 ± 9	102	342 ± 6	99	183 ± 4	94	148 ± 5	84
La	0	80 ± 8	–	309 ± 26	–	45 ± 5	–	84 ± 6	–
	100	192 ± 6	113	415 ± 13	109	136 ± 12	91	168 ± 10	84
Ce	0	667 ± 36	–	430 ± 16	–	315 ± 9	–	160 ± 7	–
	100	781 ± 12	114	543 ± 4	113	404 ± 15	90	248 ± 8	87
Pr	0	37 ± 4	–	64 ± 7	–	30 ± 2	–	24 ± 2	–
	100	143 ± 6	106	172 ± 6	108	132 ± 8	101	119 ± 8	95
Nd	0	147 ± 13	–	228 ± 24	–	112 ± 5	–	88 ± 5	–
	100	258 ± 17	111	349 ± 16	118	215 ± 14	103	178 ± 12	90
Sm	0	33 ± 2	–	44 ± 4	–	18.4 ± 0.4	–	15 ± 1	–
	100	140 ± 4	107	145 ± 3	101	120 ± 6	101	106 ± 4	91
Eu	0	4.7 ± 0.1	–	4.7 ± 0.6	–	1.6 ± 0.2	–	2.4 ± 0.2	–
	10	15.8 ± 0.6	111	15.9 ± 0.5	112	12.2 ± 0.3	105	11.4 ± 0.3	89
Gd	0	50 ± 3	–	70 ± 2	–	28 ± 2	–	26 ± 2	–
	100	158 ± 5	108	170 ± 4	100	129 ± 8	101	118 ± 6	92
Tb	0	3.3 ± 0.3	–	4.6 ± 0.5	–	0.36 ± 0.04	–	1.1 ± 0.1	–
	10	14.3 ± 0.7	110	15.8 ± 0.6	111	10.9 ± 0.4	105	10.5 ± 0.2	94
Dy	0	23 ± 1	–	30 ± 2	–	2.0 ± 0.2	–	3.2 ± 0.4	–
	10	35 ± 2	118	41 ± 1	116	13 ± 1	112	12 ± 1	92
Ho	0	5.9 ± 0.3	–	6.3 ± 0.5	–	1.3 ± 0.1	–	1.2 ± 0.2	–
	10	17 ± 1	111	17.6 ± 0.4	113	11.7 ± 0.3	105	10.4 ± 0.4	91
Er	0	29 ± 1	–	29 ± 2	–	9.3 ± 0.3	–	5.7 ± 0.4	–
	10	40 ± 2	119	40 ± 2	115	20 ± 1	109	15.0 ± 0.6	94
Tm	0	2.3 ± 0.2	–	1.7 ± 0.3	–	N.D.[e]	–	N.D.	–
	10	13.4 ± 0.6	111	12.7 ± 0.4	110	9.8 ± 0.3	98	8.8 ± 0.5	88
Yb	0	38 ± 2	–	31 ± 2	–	12 ± 2	–	5.8 ± 0.5	–
	10	49 ± 3	110	43 ± 1	118	21.6 ± 0.7	94	14 ± 1	86
Lu	0	2.4 ± 0.1	–	1.6 ± 0.3	–	N.D.	–	N.D.	–
	10	13.5 ± 0.6	111	12.3 ± 0.3	107	9.1 ± 0.4	91	8.1 ± 0.5	81

[a] Produced in Fujian province, China.
[b] Produced in Anhui province, China.
[c] Produced in Yunnan province, China.
[d] Produced in Shanxi province, China.
[e] N.D.: Not detected.

of the prepared MPANI-GO, 5 mg of MPANI-GO was added and dispersed by ultrasonication for 2 min in 10 mL sample solution containing target analytes with a series of concentration and then the analytes in the effluent were determined by ICP-MS. The maximal adsorption capacities of the prepared composite evaluated from the breakthrough curve are listed in Table 3. For comparison, the adsorption capacities of the other sorbents reported in the literatures are also listed in Table 3. As can be seen, the adsorption capacities of MPANI-GO is higher than that of other reported adsorbents including multiwalled carbon nanotubes (MWCNT) [31], 8-quinolinole-immobilized fluorinated metal alkoxide glass (MAF-8-HQ) [41], nanometer-sized TiO_2 [42] and alkyl phosphinic acid resin [43]. The possible reason is that the abundant oxygen-containing functional groups of GO, which are the active sites for binding with REEs, were reserved in the preparation of MPANI-GO by noncovalent method. Although the adsorption capacity of the target REEs is lower than that of the mesoporous TiO_2 [44], the prepared material possesses superparamagnetic properties and fast adsorption/desorption kinetics.

Table 8
Analytical results of REEs in environmental water samples (mean ± s.d., $n=3$).

REEs	East Lake water			Yangtze River water		
	Added ($ng\ L^{-1}$)	Found ($ng\ L^{-1}$)	Recovery (%)	Added ($ng\ L^{-1}$)	Found ($ng\ L^{-1}$)	Recovery (%)
Y	0	16 ± 1	–	0	49 ± 3	–
	5	20 ± 1	91	50	91 ± 2	86
	50	58 ± 2	85	100	142 ± 1	94
La	0	29 ± 2	–	0	86 ± 5	–
	5	35 ± 2	119	50	125 ± 3	80
	50	72 ± 1	88	100	185 ± 5	100
Ce	0	34 ± 1	–	0	131 ± 1	–
	5	38 ± 2	94	50	178 ± 5	100
	50	78 ± 1	91	100	243 ± 1	115
Pr	0	15 ± 3	–	0	20 ± 2	–
	5	20 ± 1	108	5	25.5 ± 0.5	119
	50	71 ± 2	113	50	66 ± 4	93
Nd	0	42 ± 2	–	0	64 ± 4	–
	5	47 ± 4	121	50	114 ± 13	102
	50	99 ± 12	115	100	179 ± 8	116
Sm	0	3.5 ± 0.1	–	0	15.6 ± 0.3	–
	5	7.5 ± 0.5	82	5	20 ± 1	102
	50	48 ± 2	88	50	60 ± 3	90
Eu	0	1.5 ± 0.1	–	0	3.5 ± 0.2	–
	5	5.7 ± 0.2	85	5	8.3 ± 0.5	98
	50	46 ± 1	89	50	49 ± 2	91
Gd	0	9.8 ± 0.5	–	0	25.9 ± 0.1	–
	5	14.7 ± 0.3	102	5	31.0 ± 0.4	113
	50	57 ± 3	95	50	70 ± 5	89
Tb	0	0.54 ± 0.04	–	0	2.0 ± 0.1	–
	5	4.8 ± 0.2	85	5	6.8 ± 0.5	98
	50	44 ± 1	87	50	46 ± 2	88
Dy	0	3.8 ± 0.6	–	0	10.5 ± 0.7	–
	5	8.0 ± 0.3	86	5	15.2 ± 0.7	98
	50	48 ± 1	90	50	54 ± 2	88
Ho	0	0.33 ± 0.05	–	0	1.6 ± 0.2	–
	5	4.8 ± 0.1	90	5	6.8 ± 0.5	105
	50	44 ± 1	88	50	46 ± 2	89
Er	0	0.70 ± 0.04	–	0	5.4 ± 0.4	–
	5	6.1 ± 0.2	108	5	10.5 ± 0.6	105
	50	46 ± 2	91	50	50 ± 2	89
Tm	0	N.Q.[a]	–	0	0.50 ± 0.04	–
	5	4.4 ± 0.2	86	5	5.5 ± 0.5	100
	50	44 ± 2	87	50	45 ± 2	88
Yb	0	1.0 ± 0.1	–	0	4.5 ± 0.3	–
	5	6.1 ± 0.1	103	5	9.5 ± 0.7	101
	50	45 ± 2	87	50	49 ± 2	88
Lu	0	N.Q.	–	0	0.40 ± 0.03	–
	5	4.2 ± 0.1	81	5	5.2 ± 0.4	100
	50	42 ± 2	85	50	44 ± 2	87

[a] N.Q.: Not quantified.

3.5. *Regeneration of the prepared MPANI-GO*

Regeneration is one of the key factors for evaluating the performance of the adsorbent. Fig. 7 is the dependence of recovery of the target REEs on the reused times of the prepared MPANI-GO. As can be seen, when the 0.5 mol L^{-1} HNO_3 was used as the eluting agent, the MPANI-GO can be reused for more than 30 times without obvious decrease of the recoveries of REEs, which indicates that the composite prepared through the noncovalent method exhibit excellent stability even in the acidic solution.

3.6. *Analytical performance*

Under the optimum conditions, the analytical performance of the proposed method was evaluated, and the results are summarized in Table 4. According to the IUPAC definition, the limits of detection (LODs, 3σ) of the method, defined as three times the standard deviation of blank signal intensity in 11 runs, were 0.15, 0.16, 0.21, 0.69, 1.49, 0.18, 0.07, 0.54, 0.04, 0.21, 0.05, 0.07, 0.04, 0.20 and 0.04 ng L^{-1} for Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, respectively. The relative standard deviations (RSDs) for seven replicate determinations of 20 ng L^{-1} of the target REEs were in the range of 1.7–6.5%. The enrichment factor was 50-fold, and the linear range covered over four orders of magnitude with correlation coefficient (r) higher than 0.9998. Table 5 is the comparison of the analytical performance data obtained by the developed method with that obtained by some other methods reported in the literatures. As can be seen, the LODs obtained by this work were lower than that reported in Refs. [31,45] and comparable with that reported in Ref. [27], but a little higher than that reported in Ref. [25]. Besides, compared with all these reported methods, the present MSPE method is fast, easy to operate, and has high adsorption capacity.

3.7. *Sample analysis*

To verify the accuracy of the proposed method, a Certified Reference Material of GBW 07605 tea leaves was analyzed, and the analytical results are shown in Table 6. As can be seen, the determined values were in good agreement with the certified values.

The proposed method was also applied to the determination of REEs in four kinds of tea leaves and environmental water samples (lake and river). The analytical results and the recoveries for the spiked samples are given in Tables 7 and 8. It can be seen that the recovery for the spiked samples was between 80 and 121%.

4. Conclusions

In this work, a novel MPANI-GO has been prepared through a simple noncovalent method and applied to MSPE of trace REEs in tea leaves and environmental water samples followed by ICP-MS detection. The prepared MPANI-GO possesses high saturation magnetization values, high adsorption capacity, fast adsorption and elution kinetics for REEs and good stability under acidic conditions. Compared with the other established methods, the developed method provided high enrichment factor, low LODs, wide linear range, high throughput, good anti-interference ability and is suitable for the determination of ultra trace REEs in real-samples with complex matrix.

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