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Graphene oxide based dispersive micro solid phase extraction for selective preconcentration of erbium from water samples and its determination by high-resolution continuum source electrothermal atomic absorption spectrometry

Sajjad Aghabalazadeh[a,b], Mohammad Reza Ganjali[a,c,*], Parviz Norouzi[a,c]

[a]*Center of Excellence in Electrochemistry, School of Chemistry, College of Science, University of Tehran, Tehran, Iran, Tel. +98-21-88001318, email: s.aghabalazadeh@ut.ac.ir (S. Aghabalazadeh), ganjali@khayam.ut.ac.ir (M.R. Ganjali), norouzi@khayam.ut.ac.ir (P. Norouzi)*
[b]*CinnaGen Medical Biotechnology Research Center, Alborz University of Medical Sciences, Karaj, Iran*
[c]*Biosensor Research Center, Endocrinology and Metabolism Molecular-Cellular Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran*

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ABSTRACT

In this paper, graphene oxide nanosheets noncovalently functionalized with 3-hydroxy-N′-[(1Z)-pyridin-2-ylmethylidene]naphthalene-2-carbohydrazide Schiff base were used as a dispersive solid phase adsorbent for the preconcentration of erbium from water samples followed by high-resolution continuum source electrothermal atomic absorption spectrometry determination. Fe_3O_4 microparticles were applied for magnetic separation of the adsorbent from water samples. The effect of various parameters including the Fe_3O_4/graphene oxide ratio, pH of the sample, the amount of the sorbent, and the salt effect on the extraction efficiency of erbium was investigated. In the optimized conditions, the limit of detection and the limit of quantification were 6 ng L^{-1} and 20 ng L^{-1} respectively. The enrichment factor was 194, the relative standard deviation under optimal conditions was 3.3% for 500 ng L^{-1} (n=6) of Er. The calibration curve was linear up to 1.8 μg L^{-1}. The accuracy of the method was confirmed by analysis of certified reference solution of erbium.The proposed method was applied for the determination of ultratrace amounts of erbium in various water samples.

Keywords: Erbium; Dispersive micro solid phase extraction; Graphene oxide; Noncovalent functionalization; High-resolution continuum source electrothermal atomic absorption spectrometry

1. Introduction

Erbium (Er) was discovered by Mosander in 1843. This element has a wide range of applications from photographic filters to metallurgical additives. Due to its pink color, it has been used in manufacturing of glass, cubic zirconium, and porcelain coloring, and the glass colored with Er is finally used in manufacturing of sunglasses and fake jewelry. Er also has a large variety of medical applications which utilize erbium ion's 2940 nm emission, which is highly absorbed in water, and can be interestingly applied for laser surgery [1]. The element has not been proven as a biologically effective agent but, some extent of metabolic influences has been reported [1]. The concentrations of Er and other rare-earth elements (REEs) are very low in most of the environmentally important samples like biological, soils and sediments, and water samples. The concentration of REEs is in the range of ng to pg g^{-1} for natural waters and fg g^{-1} for saline waters. Due to the low concentration of REEs and interferences from major elements, usually, a preconcentration and separation step is required for determination of these elements in water samples [2].

Solid phase extraction (SPE) is a popular separation and preconcentration technique for REEs and other metal ions. SPE has been used combined with ICP-MS [3–7], and ICP-AES [8–11] techniques for the determination of

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*Corresponding author.

REEs. Different materials have been used as a sorbent in SPE techniques for the determination of REEs. Application of SPE technique with different kinds of solid sorbents for determination of REEs in environmental samples has been reviewed elsewhere [12]. In recent years, a large number of carbon-based materials like, carbon nanotubes, fullerenes, nanodiamonds, nanofibers, graphene, graphene oxide, and their derivatives have been used as a sorbent in SPE techniques [13–15].

Graphene oxide which is an oxidized derivative of graphene has great features which makes it an excellent sorbent for solid phase extraction of metal ions. The main advantage of graphene oxide is its large surface area which makes it a sorbent with high adsorption capacity. Unlike carbon nanotubes and fullerenes, both sides of graphene sheets are available for adsorption of metal ions and molecular species. Graphene oxide sheets also have some hydrophilic groups such as hydroxyl and carboxyl, which makes GO water dispersible unlike graphene and carbon nanotubes [14].

GO has relatively low adsorption capacity and is not selective, different methods have been used for functionalization of graphene oxide and its use as a sorbent for the separation and preconcentration of different organic and inorganic species in different matrices [16–18], in this work 3-hydroxy-N′-[(1Z)-pyridin-2-ylmethylidene]naphthalene-2-carbohydrazide Schiff base which has been used previously as a selective ligand for potentiometric determination of erbium [19], has been utilized for noncovalent functionalization of graphene oxide and it is used as a sorbent for separation and preconcentration of ultratrace amounts of erbium from different water samples.

As reviewed in literature, conventional SPE techniques have some limitations. The main limitation is the long sample loading time due to the slow diffusion rate and mass transfer of the analytes into the bulk phase of the sorbent in the cartridge. Dispersive solid phase extraction (DSPE) is a suitable alternative for conventional SPE. In this technique, the sorbent is dispersed in the sample matrix providing a larger surface area for sorbent/analyte contact. Some main advantages of DSPE are simplicity, rapidity, and high extraction recovery and enrichment factors [13,20].

Magnetic graphene oxide/Fe_3O_4 composites have been used as adsorbents for separation and preconcentration of organic and inorganic analytes [21–26]. The main advantage of the magnetic adsorbents is that, after analyte adsorption, the adsorbent can be separated from the solution using a magnet, and does not need a high-speed centrifugation for separation of graphene oxide and its functionalized form from the solution. The main drawback for the use of graphene oxide/Fe_3O_4 composite in DSPE is the low dispersibility of this composite in water samples due to the aggregation of the magnetic particles. Hence, to overcome this problem, in this study, noncovalently functionalized graphene oxide which has high dispersibility in water, injected to the samples solutions, after the adsorption of the analyte by the sorbent, the suspension of Fe_3O_4 particles was injected into the solution, because of the opposite surface charge between the sorbent and Fe_3O_4 particles, and coloumbic attraction between them, by using a strong magnet, Fe_3O_4 along with functionalized graphene oxide nanosheets was separated from the solution and washed with 1 M HNO_3 to release the adsorbed Er ions. The eluted solution was next transferred to the autosampler cup for absorbance measurement.

2. Experimental

2.1. Apparatus

A ContrAA 700 High Resolution Continuum Source Atomic Absorption Spectrophotometer (Analytic Jena, Jena, Germany), which was optimized for erbium determination [27], was used for all absorbance measurements. FT-IR spectra were obtained as KBr discs using a Perkin Elmer Spectrum Two spectrometer. The zeta potential of the sorbent and Fe_3O_4 particles was measured using a StabiSizer PMX 200 C apparatus (Particle Metrix, Germany). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT-500 MHz NMR spectrometer. Elemental analysis was performed on Costech elemental analyzer (model ECS 4010, COSTECH analytical instruments, Valencia, CA, USA). Transmission electron microscopy (TEM) of the samples was performed using a Philips CM-120 instrument (Philips, Eindhoven, Netherlands). Magnetic stirrer with heater (Heidolph MR-Hei-Standard, Germany), Sigma 3K30 centrifuge (Laborzentrifugen GmbH, Germany), Ultrasonic bath (DSA100-SK2-4.0L, Fuzhou Desen Precision Instrument Co., China) were used through experiments.

2.2.Reagents and materials

Graphite (Cat. No. 332461), phosphoric acid (Cat. No. 438081), erbium oxide (Cat. No. 203238), lanthanum oxide (Cat. No. 199923), pyridine-2-carbaldehyde (Cat. No. P62003), p-Toluenesulfonic acid (Cat. No. 402885), 3-hydroxynaphthalene-2-carboxylic acid (Cat. No. UPL0014), dichloromethane (Cat. No. 270997), hydrazine (Cat. No. 207942) were purchased from Sigma-Aldrich Co. Sulfuric acid (Cat. No. 10071), potassium permanganate (Cat. No. 105082), hydrochloric acid (Cat. No. 137007), hydrogen peroxide (Cat. No. 108597), iron (III) chloride hexahydrate (Cat. No. 103814), iron (II) sulfate heptahydrate (Cat. No. 103963), ethanol (Cat. No. 100986), methanol (Cat. No. 106008), sodium hydroxide (Cat. No. 106498), sodium chloride (Cat. No. 106404), and erbium standard (Cat. No. 170316) were all purchased from Merck Chemical Company. Nitric acid (Cat. No. CL00.1905) was purchased from Chem-Lab (Zedelgem, Belgium).

2.3. Preparation of GO

Graphene oxide (GO) was prepared by oxidation of graphite via the Tour's method [28]. The preparation procedure was as follows: 3 g of graphite powder was added to 400 mL of a concentrated H_2SO_4/H_3PO_4 (9:1) mixture, subsequently while maintaining stirring, 18 g of $KMnO_4$ was slowly added to the mixture. Next, the mixture was placed on a hotplate and stirred at 50°C for 12 h. Then, the mixture was cooled to room temperature and poured into a beaker containing 400 g of ice and 5 mL of 30% H_2O_2 solution, the color of the reaction mixture turned to bright yellow after this step. In the next step, the reaction mixture was centrifuged, and the supernatant was poured away, the remaining solid was washed three times with 5% HCl solution and then, repeatedly washed with distilled water until the pH of the dispersion reached to about 4. The prepared graphite oxide was dispersed in deionized water and stored in refrigerator for further use. Parts of this suspension were dried for characterization.

2.4. Synthesis and characterization of Schiff-base ligand

For the synthesis of the 3-hydroxy-N′-[(1Z)-pyridin-2-ylmethylidene]naphthalene-2-carbohydrazide (Fig. 1), 1 mmol of 3-hydroxynaphthalene-2-carbohydrazide and 1 mmol pyridine-2-carbaldehydeand a catalytic amount of p-toluenesulfonic acid was refluxed in ethanol for 1 h. After ensuring the completion of the reaction, the mixture was poured into ice water. The resulting precipitate was collected by filtration and recrystallized in methanol. The yield of the reaction was 75%.

3-hydroxynaphthalene-2-carbohydrazide was synthesized as follows: 10 mmol of 3-hydroxynaphthalene-2-carboxylic acid and a catalytic amount of sulfuric acid was refluxed in methanol for 24 h. After removing the solvent, the mixture was extracted with water and dichloromethane. Then 10 mmol of hydrazine was added to the mixture of dichloromethane, and the mixture was refluxed for 10 h resulting in a white precipitate. The ^{1}H-NMR and ^{13}C-NMR shifts of the Schiff's base are shown below.

^{1}H-NMR (500 MHz, DMSO-d$_6$): δ = 7.33–7.38 (m, 2H, 2CH), 7.44 (t, J = 6.0 Hz, 1H, CH), 7.52 (t, J = 7.0 Hz, 1H, CH), 7.77 (d, J = 8.5 Hz, 1H, CH), 7.90–7.93 (m, 2H, 2CH), 8.03 (d, J = 8.0 Hz, 1H, CH), 8.43 (s, 1H, CH), 8.48 (s, 1H, CH), 8.64 (d, J = 4.5 Hz, 1H, CH), 11.15 (bs, 1H, OH), 12.15 (s, 1H, NH). ^{13}C-NMR (125.7 MHz, DMSO-d$_6$): δ = 110.6, 120.0, 120.7, 123.8, 124.3, 125.8, 126.7, 128.3, 128.6, 130.2, 135.8, 136.8, 148.5, 149.4, 153.1, 153.8, 164.0 (C=O).

2.5. Noncovalent functionalization of graphene oxide using the Schiff-base ligand

20 mg of the Schiffbase was added to 50 mL of ethanol and ultrasonicated for 5 min to obtain a clear solution, then 100 mg of GO (6.66 mL of 15 mg/ml stock suspension) was added to the solution and sonicated for 45 min, to this mixture 200 mL of deionized water was added and sonication was continued for 2 h more. The resulting suspension was centrifuged at 12,000 rpm for 20 min; the supernatant was discarded, then 50 mL of deionized water was added to the precipitate and sonicated for 3 min, this process was repeated two more times to remove unbounded Schiff-base and ethanol. 50 mL of water was added to the resulting precipitate and sonicated for 45 min to obtain a clear suspension of noncovalently functionalized GO for further use. An aliquot of this suspension was dried for characterization.

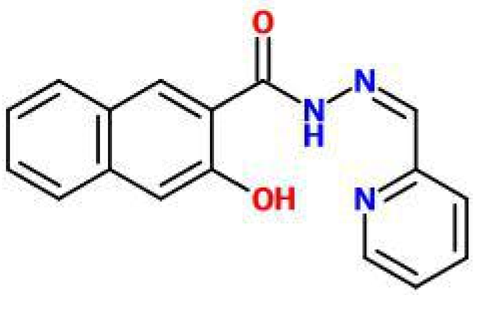

Fig. 1. Chemical structure of the Schiff base.

2.6. Synthesis of magnetic Fe_3O_4 particles

Magnetic Fe_3O_4 particles were synthesized through the chemical coprecipitation of Fe(III) and Fe(II) ions. Briefly, 0.1 M solution of $FeCl_3 \cdot 6H_2O$, 0.05 M solution of $FeSO_4 \cdot 7H_2O$ and 0.4 M solution of NaOH was prepared. After complete dissolving of the salts, the solutions were heated to 80°C, then 100 mL of $FeCl_3 \cdot 6H_2O$ was mixed with 100 mL of $FeSO_4 \cdot 7H_2O$ solution in a 500 mL beaker and 100 mL of NaOH solution was added to this solution gradually while stirring. The mixture was stirred at 80°C for 1 h. The obtained precipitate separated with magnet and was washed several times with deionized water until it reached to neutral pH. The Fe_3O_4 could be dried or stored as suspension in water for several weeks in the refrigerator.

2.7. Recommended procedure

Dispersive micro solid phase extraction (DMSPE) was performed as follows: firstly, 1 mL of a stock suspension of the sorbent (0.5 mg mL^{-1}) was injected to 50 mL of 0.5 µg L^{-1} of Er solution using 1 mL syringe, which the pH of the solution was adjusted to 5.0, after shaking the solution, 1 mL of Fe_3O_4 suspension (1 mg mL^{-1}) was injected into the solution for magnetic separation of the sorbent from the solution, after separation with strong neodymium magnet the adsorbent washed with 250 µL of 1 M HNO_3 and transferred to the autosampler cup for absorbance measurement, Fig. 2 shows the addition of the sorbent to the solution containing erbium followed by adding magnetic Fe_3O_4 particles for separation of the sorbent using strong magnet.

3. Results and discussion

3.1. Characterization of the Graphene oxide and the sorbent

For characterization of the graphene oxide and the sorbent, different techniques including FT-IR, TEM, and, elemental analysis were used, zeta potential analysis was also used to measure the surface charge of the sorbent and Fe_3O_4 particles, details of these techniques are described.

3.2. FT-IR

The FT-IR spectra were recorded for GO and the sorbent. As shown in Fig. 3, As for GO, the strong absorption band at 3434 cm^{-1} is characteristic of the stretching vibration of hydroxyl groups. The characteristic absorption band at 1753 cm^{-1} is corresponding to C=O stretching of the carboxylgroup, and the absorption band at 1639 cm^{-1} is corresponding to aromatic C=C stretching on the unoxidized domain. As for the Schiff base absorption band at 1693 cm^{-1}, C=O is corresponding to the amide group of the Schiff base. As for the sorbent, the shift of the stretching band cor-

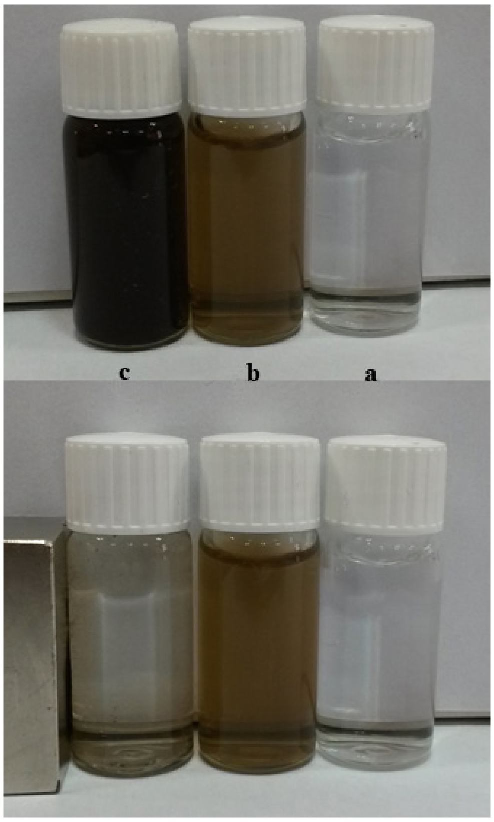

Fig. 2. The addition of the sorbent and magnetic Fe_3O_4 particles to the solution containing erbium followed by magnetic separation, a: a solution containing erbium, b: the solution A after adding the sorbent, c: the solution B after adding magnetic Fe_3O_4 particles. The lower part shows the same solution in the presence of the magnetic field.

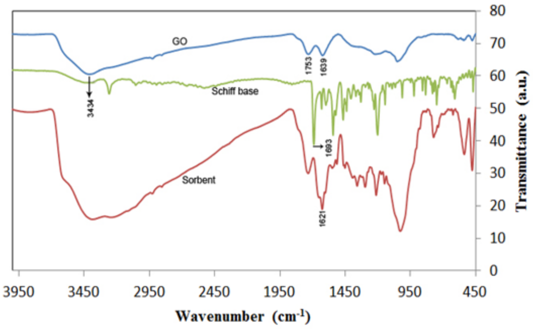

Fig. 3. FT-IR spectrum of GO, Schiff base, and the sorbent.

responding to the amide group of the Schiff base to 1621 cm^{-1} C=O can be attributed to hydrogen bonding between the amide group of the Schiff base and the surface of the graphene oxide sheets.

3.3. TEM

The morphological structure of GO and the sorbent was observed using TEM. TEM image of the graphene oxide and the sorbent are shown in Fig. 4. A flake-like structure of GO and the sorbent can be seen in the TEM image. The surface morphology of both the GO and the sorbent shows a few layers flake–like structure, rather than an aggregated structure.

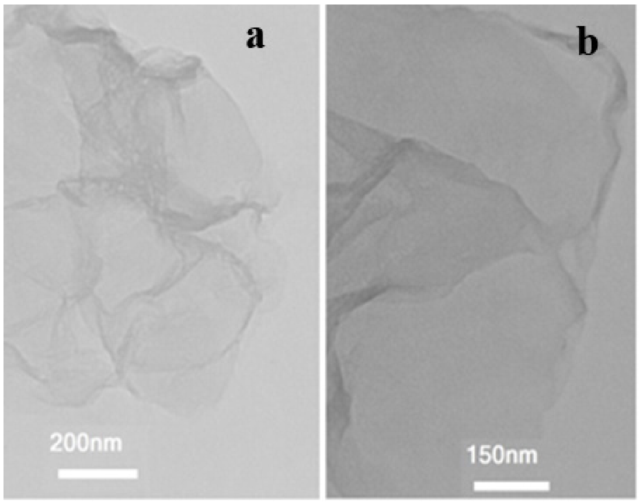

Fig. 4. TEM image of the graphene oxide and the sorbent, a: GO, b: the sorbent.

3.4. Elemental analysis

Elemental analysis of the graphene oxide and the sorbent are shown in Table 1, Due to the presence of nitrogen atom in the structure of the Schiff base that was used for functionalization of the graphene oxide, these data can be used for the calculation of the amount of the Schiff base that is adsorbed on graphene oxide. The results show that the 17.8 % (w/w) of the sorbent composed of the Schiff base.

3.5. Zeta potential study

Zeta potential analysis in the pH range of about 2–10 was used to measure the surface charge of the sorbent and Fe_3O_4 particles; the results are shown in Fig. 5. As can be seen in the figure, the sorbent has negative surface charge in the entire studied pH range, the surface charge of Fe_3O_4 particles are negative at pH values higher than 8, but at pH values lower than 8, the surface charge of Fe_3O_4 particles are positive, so at pH values below 8, there is a coulombic attraction between Fe_3O_4 particles and Sorbent sheets, and the sorbent sheets can be separated from the solution using Fe_3O_4 particles followed by applying a strong magnet.

3.6. Optimization of the extraction conditions

To optimize extraction conditions, effect of various factors influencing the extraction efficiency including pH, the sorbent amount, the ionic strength, and the effect of coexisting ions, were investigated, the effect of these factors are described below.

Table 1
Elemental analysis of the graphene oxide and the sorbent

Sample	Carbon (% W)	Nitrogen (% W)	Hydrogen % W)
Graphen oxide	40.38	0	2.46
Sorbent	44.87	2.57	2.44

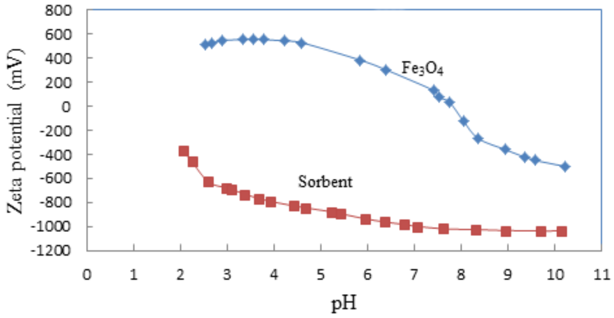

Fig. 5. pH-dependent zeta potentials of the sorbent and Fe_3O_4.

3.7. Effect of pH

The pH of the solution has an essential role in the adsorption of metal ions; lower pH values can reduce the complexation capability of the sorbent by protonation of its heteroatoms. The surface charge of sorbent and Fe_3O_4 particles are also highly pH dependent, so it is important to adjust the pH of the solution to the optimum value for maximum adsorption of the erbium ions on the sorbent and also an effective coulombic attraction between the sorbent and Fe_3O_4 particles in the solution. The effect of pH on the extraction efficiency of erbium was in investigated over the pH range of 2–9. As shown in Fig. 6 the maximum extraction efficiency of erbium is at pH = 5.0, the low extraction recovery of erbium at pH values lower than 3 is due to the protonation of the heteroatoms on the sorbent, and the low extraction efficiency at pH values higher than 8 is due to the coulombic repulsion between the Fe_3O_4 particles and the sorbent as a result of surface charge reversal of Fe_3O_4 particles at pH ≈ 8.

3.8. Effect of the sorbent amount

The amount of sorbent is another important parameter that can affect the extraction recovery. To find the optimum amount of the adsorbent, different amounts of adsorbent in the range of 0.05 to 1 mg were injected into solutions containing 0.5 µg L^{-1} of erbium at pH = 5.0, and Fe_3O_4 to the sorbent ratio of 2. As shown in Fig. 7, the maximum extraction recovery was obtained in 0.5 mg, and at values above this amount, the extraction recovery was almost invariable. So this amount was chosen for further studies.

3.9. Effect of Fe_3O_4 to the sorbent ratio

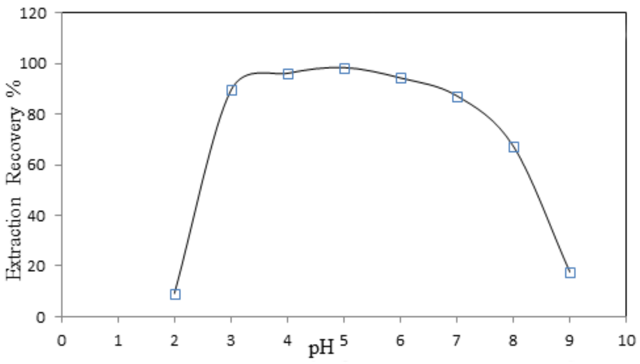

Fig. 6. The effect of pH on the extraction efficiency of erbium.

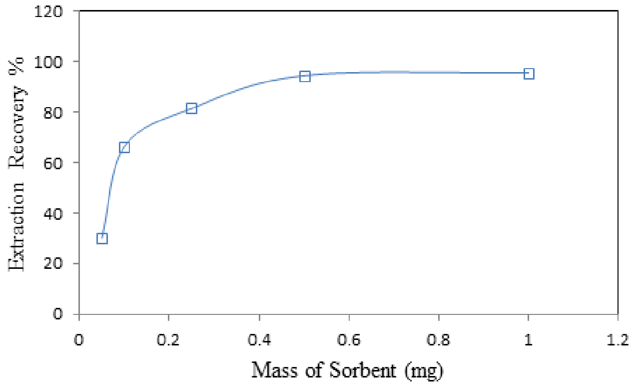

Fig. 7. Effect of the sorbent amount.

Other important parameter that also affect the extraction recovery, is the Fe_3O_4 to the sorbent ratio. To find the optimum ratio, the different ratios of Fe_3O_4 to the adsorbent in the range of 1–4 were examined. For this purpose, 1 ml of the sorbent (0.5 mg mL^{-1}) was injected into solutions containing 0.5 µg L^{-1} of erbium at pH = 5.0, after shaking the solution, different amounts of Fe_3O_4 (Fe_3O_4 to the sorbent ratio of 1–4) were injected into the solution. As shown in Fig. 8, the maximum extraction recovery was obtained in the Fe_3O_4 to the sorbent ratio of 2, so this ratio was chosen for further studies.

3.10. Effect of ionic strength

The effect of the various amount of NaCl on the extraction recovery of Er was examined in the range of 0.1–5%; it was observed that at up to 1% of salt concentration extraction can be performed with the recovery of more than 85%, whereas at higher salt concentrations, lower extraction recovery was observed for erbium. At higher salt concentrations the electronic repulsion between the graphene oxide sheets decreases and the probability of the aggregation of these sheets increases, this condition can reduce the dispersion ability of the sorbent in the solution resulting in adecrease extraction recovery of erbium.

3.11. Sorbent capacity

The sorbent capacity is defined as the maximum amount of the erbium which can be adsorbed by the sorbent. The sor-

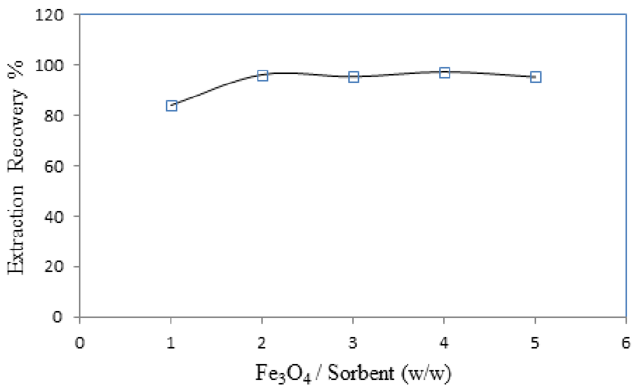

Fig. 8. Effect of Fe_3O_4 to the sorbent ratio.

bent capacity was determined under the optimum condition by injecting 0.5 mg of the sorbent into 50 mL of 10 mg L^{-1} solution of erbium, and separation of the sorbent after adding Fe_3O_4 and applying external magnetic field. The sorbent capacity was calculated through the difference in the initial and final concentration of erbium in the solution. The sorption capacity of the sorbent was calculated to be 220 mg g^{-1} of the sorbent.

3.12. Effects of coexisting ions

The effect of various coexisting ions on the extraction recovery of erbium was investigated under the optimum condition. The results are shown in Table 2. The results indicate that the presence of different cations in high concentration does not have any significant effect on the determination of erbium. These results show that erbium can be determined successfully in different water samples in the presence of interfering ions.

3.13. Analytical performance

Under optimized condition, the calibration curve was linear up to 1.8 µg L^{-1} with a correlation coefficient of $R^2 = 0.9967$, and the calibration equation of $A = 0.4952\,C + 0.0213$ where C is the concentration of Er in µg L^{-1} and C is the integrated absorbance value. The limit of detection (LOD) and limit of quantification (LOQ) calculated based on the three and ten times of standard deviation of the blank solution to the slope of the calibration curve were 6 and 20 ng L^{-1}. The enrichment factor was 194, which was calculated by dividing the concentration of the analyte in the eluent (1 M HNO_3) by the concentration of the analyte in the original sample. The relative standard deviation under optimal conditions was 3.3% for 500 ng L^{-1} ($n = 6$) of Er. The accuracy of the method was confirmed by analysis of certified reference solutions of erbium, the results are shown in Table 3.

3.14. Analytical application

The developed method was applied to the determination of erbium content in various water samples, due to the low concentration of erbium in analyzed samples, 500 ng L^{-1} of erbium was spiked to the samples, and the recovery of the erbium was calculated, the results are shown in Table 4. As can be seen in the table, the recoveries from 93.6 to 94.8 were obtained. The result shows the capability of the method for determination erbium in real water samples with different matrices.

Table 2
The effects of coexisting ions on extraction recovery of erbium

Interfering ion	Interfering ion/Er	Recovery % (% RSD)
Na^+	10000	96.8 (3.5)
K^+	10000	97.5 (2.8)
Mg^{2+}	10000	98.9 (1.2)
Ca^{2+}	10000	96.8 (3.4)
Cr^{3+}	1000	98.7 (2.7)
Ni^{2+}	1000	101.4 (3.1)
Cu^{2+}	1000	98.4 (3.9)
Al^{3+}	1000	96.7 (3.7)
Fe^{3+}	1000	102.5 (2.9)
Co^{2+}	1000	98.1 (2.6)
Zn^{2+}	1000	100.6 (1.8)
Yb^{3+}	500	96.0 (2.8)
Eu^{3+}	500	93.8 (2.4)
Sm^{3+}	500	94.7 (2.5)
La^{3+}	500	96.2 (3.4)
Ce^{3+}	500	96.9 (3.1)

*Results are the average for three replicate measurements.

Table 3
Determination of erbium in two samples of diluted erbium certified reference solution

Sample	Certified value (ng L^{-1})	Proposed method (ng L^{-1})	Recovery (%)* (RSD %)
1	500	529	105.8 (2.2)
2	1000	1032	103.2 (4.3)

*Results are the average for three replicate measurements.

Table 4
Determination of erbium in various water samples employing the proposed method

Sample	Concentration (ng L^{-1})	Spiked (ng L^{-1})	Found (ng L^{-1})	Recovery (%)* (RSD %)
Mineral water	N.D.	500	482	96.4 (2.9)
Tap water	N.D.	500	474	94.8 (3.4)
River water	N.D.	500	468	93.6 (3.1)

*Results are the average for three replicate measurements.

4. Conclusions

In this work, graphene oxide nanosheets were noncovalently functionalized with a selective Schiff-base and were used as a dispersive solid phase adsorbent for the separation and preconcentration of erbium from water samples followed by high-resolution continuum source electrothermal atomic absorption spectrometry determination. Utilizing noncovalent approach for functionalization of graphene oxide has several advantages over the covalent approach including simple and quick process, and preserving the structural and electronic properties of the selective Schiff's base which is used for functionalization. Using dispersive micro solid phase extraction instead of traditional solid phase extraction increase the contact between sorbent and analyte and substantially increase the extraction efficiency. Magnetic separation of the sorbent from water samples utilizing the coulombic attraction between the sorbent and Fe_3O_4 particles eliminates the need for high-speed centrifugation.

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