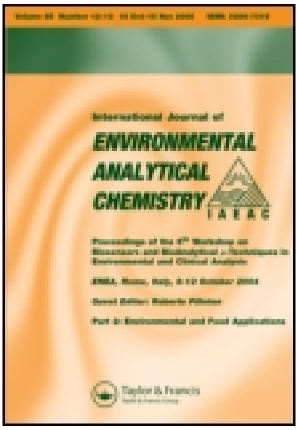

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A selective modified nanoporous silica as sorbent for separation and preconcentration of dysprosium in water samples prior to ICP-OES determination

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A selective modified nanoporous silica as sorbent for separation and preconcentration of dysprosium in water samples prior to ICP-OES determination

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In this research a new physically functionalized nanoporous silica (SBA-15) using N′-[(2-hydroxy phenyl) methylene] benzohydrazide (BBH) was utilized as a selective sorbent for the separation, preconcentration and determination of dysprosium (Dy) in natural water by inductively coupled plasma optical emission spectrometry (ICP-OES). The selectivity of BBH to Dy (III) ion was previously tested by conductometric and spectroscopic methods. Conditions for effective adsorption of Dy were optimized with respect to experimental parameters in batch process. The extraction recovery was 96.5, analytical curve was linear in the range 0.2–1000 $\mu g L^{-1}$, and the detection limit was 0.05 $ng\,mL^{-1}$. The relative standard deviation (RSD) under optimal conditions was 3.2% ($n = 10$). The sorbent exhibited high adsorption capacity and fast rate of equilibrium for sorption of Dy ions. The method was applied for recovery and determination of dysprosium in different environmental water samples.

Keywords: dysprosium; nanoporous silica; solid phase extraction; environmental water samples

1. Introduction

Dysprosium is a rare earth element that has a metallic, bright silver luster, relatively stable in air at room temperature, but dissolves readily in dilute or concentrated mineral acids with the release of hydrogen [1]. It is soft enough to be cut with a knife, and can be machined without sparking if overheating is avoided. Dysprosium's physical characteristics can be greatly affected even by small amounts of impurities [2,3]. Dy (III) is disposed to the environment in many different places, mainly by petrol-producing industries and will gradually accumulate in soils and water which will eventually leads to increase concentrations in humans, animals, and soil particles [4,5]. It can react with water to produce flammable hydrogen gas. Soluble dysprosium salts, such as dysprosium chloride and dysprosium nitrate, are mildly toxic when ingested. The insoluble salts, however, are non-toxic. Based on the toxicity of dysprosium chloride to mice, it is estimated that the ingestion of 500 grams or more could be fatal to a human [6]. Therefore, determination and measurement of dysprosium in different mediums is important.

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Different analytical methods such as inductively coupled plasma mass spectroscopy (ICP-MS) [7–9], isotope dilution mass spectrometry [10,11], resonance light scattering (RLS) [12], voltammetry [13], inductively coupled plasma optical emission spectroscopy (ICP-OES) [14–17], capillary electrophoresis [18], X-ray fluorescence (XRF) [19,20], fluorimetry [21], ion-microprobe [22] and other methodology [23–26], has been reported for determination of Dy (III) ions in various sample matrices. Different sensors have been presented for determination of Dy (III) ions in different media [27–29]. Inductively coupled plasma optical emission spectrometry (ICP-OES) has become the most appropriate technique for their determination but the capability of this method is not sufficient when the concentrations of cations are too low. Also, the ICP–OES method sometimes suffers from problems, such as signal suppression and clogging of the sample introduction system when the sample contains dissolved salts at concentrations higher than 0.2% (w/v) [30,31]. On the other hand, ICP–MS has the detection power to determine trace elements at sub-$\mu g\ L^{-1}$ levels but it suffers from the problem of isobaric polyatomic interferences and also it is very expensive and its maintenance is very difficult [32]. So, in order to monitor low content of analytes and overcome the problems mentioned above, preconcentration techniques are performed before instrumental determination. Solid phase extraction (SPE) has been used as an effective method prior to spectrometric determination. Methods utilizing solid sorbents are simpler and faster, reduce organic solvent consumption and yield higher enrichment factors [33]. The choice of adsorbent is a key factor in SPE because it can control the analytical parameters such as selectivity, affinity and adsorption capacity [34,35]. Different sorbents such as inorganic chemically active beads [36], aminocarboxylic sorbents [37], nanometer-sized titanium dioxide [38], octadecyl silica [39], activated alumina [40,41], activated carbon [42] were used for preconcentration of rare earth elements. The discovery of new nanoporous molecular sieves such as MCM-41, MCM-48 [43], SBA-15 [44], nanoporous silica gels [45] have attracted much attention in the field of catalysis, separation and host materials for inclusion compounds. They can be a promising adsorbent owing to its novel structure that comprises uniform ordered structure, large and defined pore sizes, high surface area (up to 1000 m^2g^{-1}), and excellent mechanical and thermal stability. These materials can be functionalized with different organic groups for fast extraction process and higher selectivity for the removal of metals in different environmental waters [46–49]. Among these compounds MCM-41 and MCM-48 silica materials can hardly be used as adsorbents or catalysts under hydrothermal conditions because of their low structural stability ascribed to their extremely thin pore walls [50]. SBA-15 is characterized by having mesopores of larger size and lower surface area. Moreover, the mesopores in SBA-15 are interconnected by the presence of micropores across the silica walls. SBA-15 presents also a higher stability than MCM-41 materials owing to the larger thickness of the silica walls [51] and the ligand can be immobilized into the pores.

In the present study, nanoporous silica, SBA-15, is modified by N′-[(2-hydroxy phenyl) methylene] benzohydrazide (BBH), as a new sorbent for preconcentration and separation of dysprosium in water samples prior to determination by ICP-OES. The selectivity of BBH to Dy(III) ion was previously tested by conductometric and spectroscopic methods [31,52].

Table 1. ICP-OES operating conditions.

Parameters	Values
RF generator power	1.55 kW
Plasma gas (Ar) flow rate	15 L min^{-1}
Auxiliary gas (Ar) flow rate	1.5 L min^{-1}
Nebulizer pressure	150 kPa
Sample uptake flow rate	1 mL min^{-1}
Observation position	6 mm
Integration time	8 s
Wavelength	353.71 nm

2. Experimental

2.1 *Apparatus*

A Varian (model: VISTA-MPX) inductively coupled plasma optical emission spectrometer (ICP-OES) was used for determination of dysprosium. The operation conditions are summarized in Table 1. The pH values were measured with a Metrohm pH-meter (model:713, Herisau, Switzerland) supplied with a glass-combined electrode.

2.2 *Reagents and solutions*

All chemicals used in this work were of analytical grade purchased from Merk company (Darmstadt, Germany). All solutions were prepared in double-distilled deionized water. A stock solution (1000 mg L^{-1}) of Dy (III) was prepared by dissolving the appropriate amounts of Dy $(NO_3)_3$ in 0.2 mol L^{-1} nitric acid. A stock standard buffer solution, 0.1 mol L^{-1} was prepared by dissolving appropriate amounts of sodium acetate and hydrochloric acid in double distilled water. The pipettes and vessels used were kept in 10% nitric acid for at least 24 h and subsequently washed four times with deionized water before use.

2.3 *Synthesis of BBH*

N′-[(2-hydroxyphenyl) methylene] benzohydrazide (BBH) (Figure 1) was synthesized by refluxing a mixture of 2-hydroxybenzaldehyde (0.01 mol, 1.22 g), benzohydrazide (0.01 mol, 1.36 g), and a catalytic amount of acetic acid for 5 h in absolute ethanol (20 mL). Then, the reaction mixture was cooled to room temperature and the colourless crystals were filtered, washed with ethanol, and dried under the reduced pressure, m.p.: 172–173°C, 2.1 g, yield 90%; IR (KBr) (νmax/cm^{-1}): 3267 and 3153 (OH and NH), 1672 (C = O), 1612, 1537, 1407, 1352, 1271, 1138, 868, 752, 708, 681. MS, m/z (%): 240 (M, 38), 219 (5), 193 (10), 164 (12), 122 (28), 105 (29), 97 (9), 82 (25), 38 (9), 28 (100). Anal. Calcd. for $C_{14}H_{12}N_2O_2$ (240.26): C, 69.99; H, 5.03; N, 11.66. Found: C, 70.1; H, 5.1; N, 11.7%. ^{1}HNMR (250.1 MHz, DMSO-d$_6$ solution): δ 6.25 (1 H, d, J = 7.5 Hz, CH), 6.79 (1 H, d, J = 7.9 Hz, CH), 7.05 (1 H, d, J = 5.9 Hz, CH), 7.10–7.40 (4 H, m, 4 CH), 8.25 (2 H, br., NH_2), 8.55 (1 H, s, N = CH), 11.02 (1 H, fairly br., OH).^{13}C NMR (62.5 MHz, DMSO-d$_6$ solution): δ 108.24, 113.55, 117.94, and 120.63 (4 CH), 129.21 (C), 133.71, 135.43, and

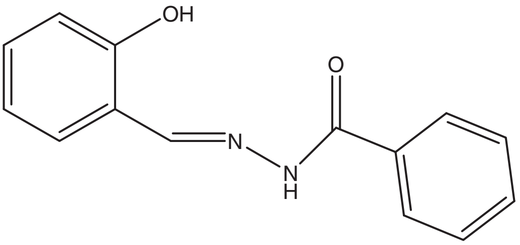

Figure 1. Chemical structure of N′-[(2-hydroxy phenyl) methylene] benzohydrazide (BBH).

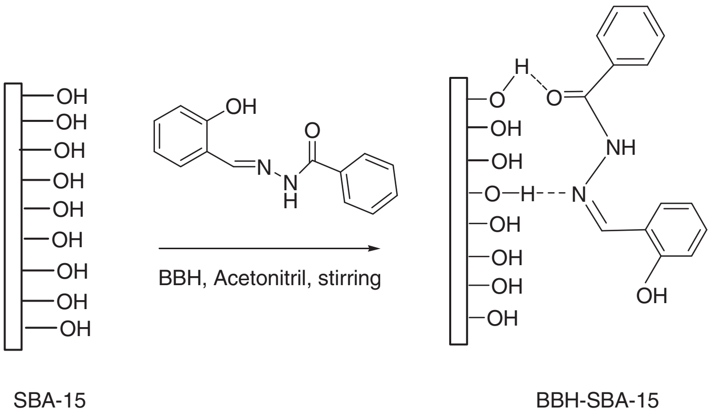

Figure 2. Preparation of BBH-SBA-15 as modified selective sorbent.

139.21 (3 CH), 154.25, 159.09, and 160.25 (3 C), 160.32 (CH). BBH has been applied for construction of an optical sensor for determination of dysprosium ions [31].

2.4 *Preparation of modified SBA-15*

The nanoporous silica SBA-15 was prepared according to the literature [42]. In a typical synthesis, 2 g of triblock copolymer P123 (EO20PO70EO20) was dissolved in 60 g of 2 M HCl aqueous solution with stirring at 40°C. Then, 4.25 g of tetraethylorthosilicate (TEOS) was added to the homogeneous solution and stirred at this temperature for 24 h. Finally, it was heated to 100°C and held at this temperature for 24 h under static conditions. The prepared sample was recovered by filtration, washed with water, and air-dried at room temperature. The removal of the template was carried out at 550°C in air for 5 h. Modification of the prepared SBA-15 was performed as shown in Figure 2, 50 mg of BBH was dissolved in adequate amount of acetonitril and 50 mg of SBA-15 was added and mixed for 15 min, after filtration the functionalized product was exposed to atmosphere and was used as a sorbent for this research.

2.5 *Procedure*

A batch system was employed for extraction and preconcentration of dysprosium. Extraction was performed in a beaker containing Dy (III) ions in 10 mL acetate buffered solution ($pH = 5$). About 50 mg functionalized SBA-15 (BBH-SBA-15) was added to the solution. Then, the mixture was stirred for 5 min to extract dysprosium from the solution. Finally, filtration was performed and back extraction was done using 1.0 mL of $1.0\,\mathrm{mol\,L^{-1}}$ nitric acid solution, and dysprosium concentration was determined by ICP-OES.

3. Results and discussion

The major problem in selective solid phase extraction of lanthanoid ions is finding a suitable and selective ligand. This series of elements has 15 members which are all rather similar. Lanthanoid ions have different radii (from Ce^{3+} to Lu^{3+} their radii vary from 1.02 to 0.80 A, respectively) which cause their different properties, such as different charge densities and hydration energy (from Ce^{3+} to Lu^{3+} their hydration energy ranges from 3370 to 3760 kJ/mol). Thus, ligands possessing rigid and specific cavity size in their structures are not able to vary among the series and show a selective manner. Hence, the only way to design a selective ligand for the lanthanide ions is using ionophores having semi-cavity, heteroatoms (N, O and S as donor atoms), and high flexibility. Such ligands can easily wrap around a cation and form a template complex with reference to the size of the lanthanoid cation. Furthermore, these kinds of ionophores are able to form a stronger complex with one of the lanthanide cations than the other ones with the optimum free energies. The selectivity manner can be attributed to the type, the number and the site of its donor atoms, its flexibility as well as the size and the charge density of the cation.

Our previous studies [31,57] showed that BBH has selective interaction with Dy(III) ion. Thus, it was used in modification of SBA-15 for selective extraction of Dy(III) ions. The preliminary experiments showed that the extraction of dysprosium by non-functionalized SBA-15 and functionalized SBA-15 is obviously different and non-functionalized SBA-15 cannot extract Dy (III) quantitatively.

The extraction recovery is defined as the percentage of the total amount of analyte (*m*), which was extracted into the eluent (Equation (1)):

$$R\,\% = \left(\frac{m_e}{m_s}\right) \times 100 = \left(\frac{C_e V_e}{C_s V_s}\right) \times 100 \qquad (1)$$

where V_e, V_s, C_e and C_s are volume of eluent, volume of sample solution, initial concentration of analyte in aqueous sample and concentration of analyte in eluent, respectively.

3.1 *Effect of pH*

Adjustment of pH in solid phase extraction is critical in order to obtain efficient recoveries. The effect of pH on the extraction of Dy^{3+} was studied in the range of 2.0 to 8.0. The higher pH values were not studied because modified nonporous silica may be hydrolyzed in alkali solutions due to the breaking of the Si-O-Si bonds by hydroxide ions attack. As shown in Figure 3, extraction was nearly constant and quantitative in the range of 3 to 8. At lower pH, the nitrogen atom in modified nanoporous are protonated which may reduce the stability of sorbent. Therefore, pH of sample solutions was adjusted at 5 on the subsequent experiments.

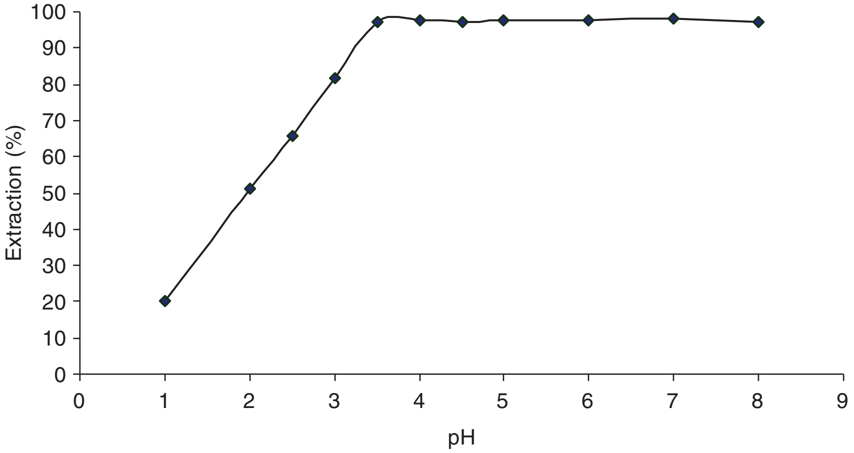

Figure 3. Effect of pH on the extraction of Dy(III). Experiment conditions: sample volume, 10 mL, concentration of Dy, 100 ngmL^{-1}, amount of sorbent, 50 mg, eluent (HNO_3) concentration, 1.0 mol L^{-1}, eluent volume, 1.0 mL.

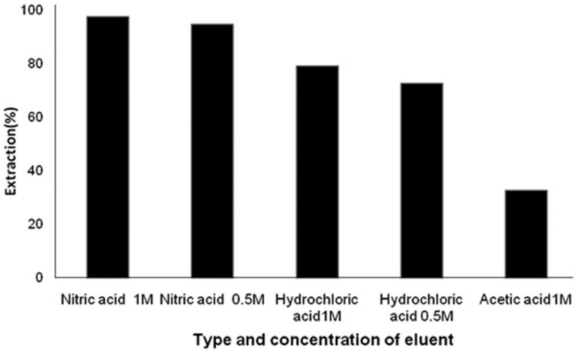

Figure 4. Effect of eluent type and concentration on the desorption efficiency of Dy(III). Experiment conditions: sample volume, 10 mL; concentration of Dy, 100 ng mL^{-1}; amount of sorbent, 50 mg; pH = 5.

3.2 *Nature, concentration and volume of eluent*

Desorption of dysprosium ions from the sorbent surface is performed by testing different acids. The hydrogen in acid structure protonates the nitrogen atoms of sorbent, so the adsorbed ions releasees from modified nanoporous. Selection of the proper eluent for desorption is an important factor for this extraction system. Some experiments were carried out in order to select an effective eluent for the adsorbed Dy (III) ions after extraction. As can be seen in Figure 4, 1.0 mol L^{-1} nitric acid could accomplish the quantitative elution of Dy (III) from the functionalized SBA-15. The nitric acid volume should adopt the lowest value so that a large preconcentration factor could be assessed. So 1.0 mL of 1.0 mol L^{-1} nitric acid was selected as eluent in order to achieve higher preconcentration factor.

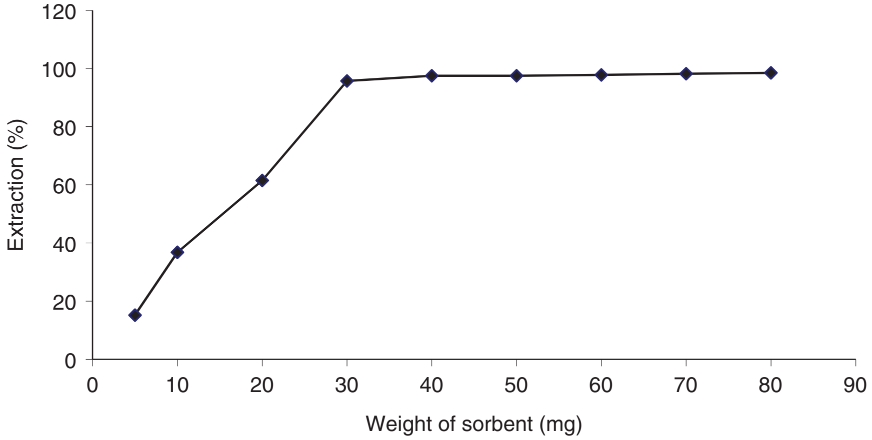

Figure 5. Effect of amount of sorbent on the extraction of dy(III). Experiment conditions: sample volume, 10 mL; concentration of Dy(III), 100 ng mL^{-1}; eluent (HNO_3) concentration, 1.0 mol L^{-1}; eluent volume, 1.0 mL; pH = 5.

3.3 *Effect of the amount of sorbent*

The effect of the amount of the modified SBA-15 on the quantitative extraction of Dy (III) was investigated by testing different amount of sorbent (5–80 mg) for extraction of Dy (III) from water. The results shown in Figure 5 describe that the extraction of Dy (III) was quantitative by using 30 mg of modified SBA-15. Subsequent experiments were performed with 50.0 mg of modified sorbent to achieve higher capacity without any interferences.

3.4 *Adsorption capacity of sorbent*

The capacity of the sorbent is a factor that shows how much sorbent is required to remove a specific amount of metal ions from the solution quantitatively. The adsorption capacity was calculated as:

$$a_E = (C_0 - C_E)Vm^{-1} \tag{2}$$

where C_0 is the initial concentration and C_E is equilibrium concentration (μg mL^{-1}) of analyte ions in the solution. The equilibrium concentration was determined directly by ICP-OES. m is the weight of the sorbent and V is the volume of the aqueous solution. The mg of adsorbed dysprosium per gram of sorbent, a_E, was found to be 47 mg g^{-1}. Owing to the existence of two nitrogen atom in BBH, using HNO_3 as eluent, protonation of nitrogens of BBH is done and its property will change from insoluble to soluble in solvent of eluent, and therefore the functionalizing of SBA-15 reduced drastically (from 96.5% to 45% after first use).

3.5 *Effect of equilibrium time*

The effect of stirring time on the extraction recovery was investigated by performing a series of extraction experiments of solution (pH = 5) containing 10 ng mL^{-1} Dy (III).

The results showed that the stirring time (5–15 min) has no special effect on the extraction efficiency of dysprosium. Thus, the mixtures were stirred for 5 min to reach equilibrium in the experiments.

3.6 *Effect of ionic strength*

The effect of ionic strength on the extraction of dysprosium was studied in the presence of electrolytes like potassium nitrate and sodium chloride with different concentrations from 0.5% to 5% (w/w). The observations have shown that there is no interference in the presence of these electrolytes up to 5% (w/w) and the modified sorbent has specific tendency of BBH-SBA-15 for Dy (III) so using this method for separation of Dy from highly saline solutions like sea water is possible.

3.7 *Interference studies*

The effect of some common coexisting ions in natural water samples were investigated on the recovery of dysprosium. For this purpose 10 mL of solutions containing 100 ng mL^{-1} of target ions and foreign ions were treated according to the recommended procedure. The results showed that, in excess of 10,000-fold Li^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, Sn^{2+}, Al^{3+} and 1000-fold Gd^{+3}, Cr^{3+}, Er^{+3}, Lu^{+3}, Tb^{+3}, La^{3+}, Ce^{3+}, HO^{3+}, Sm^{+3}, and Er^{3+} ions did not show significant interferences in the extraction and determination of dysprosium. As can be seen, the used sorbent (BBH-SBA-15), has shown high tolerance limit for coexisting ions. This property is noticeable for analysis of water samples which contains earth metal ions.

3.8 *Real sample analysis*

The capability of the presented method was examined by different real water samples. Separation, preconcentration and determination of dysprosium from 100 mL of different environmental waters were carried out by this system. All experiments were replicated three times, and the results are reported in Table 2. The suitability of this procedure was tested by spiking standard stock solutions of dysprosium (4 and 6 µg L^{-1}) to real water samples. The achieved recoveries (97.5–102%) indicate that the proposed procedure is suitable for quantitative extraction of dysprosium in different matrices.

3.9 *Analysis of certified reference material*

CGDY10 (10,000 µg/mL Dysprosium, Dysprosium in Dilute Nitric Acid) from Inorganic Ventures Company was used as certified reference material. The proposed extraction procedure was carried out on certified reference material. The accuracy of the method is calculated to be 3.62%.

3.10 *Analytical performance of this method*

The break-through volume of the sample solution was studied by using different volume (250, 500, 1000, 1500 and 2000 mL) of sample. The recommended procedure was followed

Table 2. Determination of dysprosium in environmental water samples by applying proposed extraction procedure.

Sample	Concentration	Dy^{3+} spiked ($ng\,mL^{-1}$)	Dy^{3+} found ($ng\,mL^{-1}$)	Recovery (%)
Tap water1[a]	nd[e]	4	4.1 (1.2)[f]	102
		6	6.1 (1.8)	101
Tap water2[b]	nd	4	3.9 (1.8)	97.5
		6	5.9 (1.2)	98
Sea water[c]	nd	4	3.9 (1.8)	97.5
		6	6.1 (1.7)	101
River water[d]	nd	4	4.1 (1.8)	102
		6	5.9 (2.1)	98

[a] Drinking water system of Tehran, Iran.
[b] Drinking water system of Babol, Iran.
[c] Caspian sea water, Iran.
[d] Babolsar river water, Iran.
[e] not detected.
[f] R.S.D. of three replicate experiments.

Table 3. Comparison of the present method with other SPE reported methods.

Sorbent	Method of detection	LOD ($\mu g L^{-1}$)	Adsorption capacity ($mg g^{-1}$)	Ref.
Acetyl acetone-modified Silica Gel	ICP-AES	0.2	24.86	[17]
Ion imprinted polymer	ICP-AES	0.2	42.6	[14]
Ion imprinted polymer	Spectro photometer	8	39.17	[25]
BBH-SBA-15	ICP-OES	0.05	47	Present work

and in all cases the extraction by modified SBA-15 was accomplished quantitatively. The elution is performed by 5 mL nitric acid and the preconcentration factor is 400. Under the optimum condition, the limit of detection (LOD), calculated as three times the standard deviation of the measurement of blank divided by the slope of the calibration curve which was found to be $0.05\,\mu g\,L^{-1}$. The relative standard deviation (RSD) obtained for the determination of $100\,\mu g\,L^{-1}$ of Dy (III) was 3.2% ($n = 10$). The linearity of calibration curve under the optimum conditions was in the range of $0.2–1000\,\mu g\,L^{-1}$ with the regression equation as $I = 985.47\,C\ (\mu g\,L^{-1}) + 71.72$ and the correlation coefficient of 0.9979. The comparison of this method with other SPE methods is reported in Table 3.

4. Conclusion

In the present study, a new, simple and selective solid phase extraction method in batch mode was performed by functionalized nanoporous (SBA-15) as a sorbent for preconcentration and separation of dysprosium in water. The adsorption/desorption kinetics and high adsorption capacity was the properties of this synthesized sorbent. The low detection limits, wide range of linearity of calibration curve and good RSD values obtained by this procedure show the potential of this method which could be applied to determination of dysprosium in various environmental water samples.

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