Solid Phase Extraction of Some Lanthanide Ions by Functionalized SBA-15 from Environmental Samples

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ABSTRACT: In this research, nanoporous silica (SBA-15) was physically functionalized using 2-(2-nitrobenzylideneamino) guanidine compound. This functionalized SBA-15 was utilized as a new sorbent for separation and preconcentration of some lanthanide ions. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used as a detection technique. The preconcentration factor of the method is 100 and detection limit of this technique is obtained 2.9 ng/mL for Dy^{3+}, 1.6 ng/mL for Eu^{3+}, 8.4 ng/mL for Nd^{3+}, 3.8 ng/mL for Sm^{3+} and 2.5 ng/mL for Yb^{3+} ions. The time and optimum amount of the sorbent, pH effect, presence of other ions on extraction condition were also tested. The maximum capacity of 5 mg functionalized SBA-15 was found to be about 155.2 µg for Sm^{3+}, 131.2 µg for Yb^{3+}, 128.1 µg for Nd^{3+}, 143.3 µg for Eu^{3+}, 140.6 µg for Dy^{3+} ions. The method was successfully applied for preconcentration and determination of these lanthanides in some natural water samples.

Key words: Lanthanides, Solid phase extraction, Functionalized nanoporous silica, SBA-15, Inductively coupled plasma emission spectrometry

INTRODUCTION

The lanthanides along with Scandium and Yttrium are known as rare earth elements (REEs). They are called "rare" because it is not common to find them in commercially viable concentration. Lanthanides due to their unique chemical and physical properties find various applications in industries such as electronic publishers, superconductors, alloys, catalytic converters, permanent magnets and rechargeable batteries. Some lanthanides are used in optoelectronic applications like optical fibers (Kuriki & Koike, 2002) to increase the transmission rates and lasers such as Nd-YAG laser. Lanthanides have been also used as anticancer agents (Kostova, 2005) and luminescent useful probes (Bunzil & Claude, 2005; Reifernberg, *et al*. 2005). Biological properties of the lanthanides due to their similarity to calcium cause therapeutic and/or toxicological properties of lanthanides since the early part of the twentieth century. The lanthanides have similar ionic radii to calcium, but by virtue of possessing a higher charge, they have a high affinity for Ca^{2+} sites on biological molecules, and a stronger binding to water molecules (Zhang, *et al*. 2003; Fricker, 2006). The lanthanides can substitute for calcium in proteins, though it should be noted that the Ln^{3+} can also substitute for other metal ions such as Mg^{2+}, Fe^{3+}, and Mn^{2+}. Calcium dependent enzymes can either be inhibited by lanthanides, or in some cases be activated to a similar or greater extent than by calcium. However, lanthanides toxicity is dependent on the chemical form and the administration mode.

According to numerous applications of lanthanides and from a nutritional and a toxicological point of view, the detection and the evaluation of the lanthanide elements in some biological materials r environmental samples have recently received an increasing attention. The several analytical techniques were applied to determine lanthanides in samples such as ion chromatography (Dybczynski, *et al*. 2010), neutron activation analysis (NAA) (Wang, *et al*. 1999), inductively coupled plasma mass spectrometry (ICP-MS) (Kajiya, *et al*. 2004), inductively coupled plasma optical emission spectroscopy (ICP-OES) (Zhang *et al*. 2007) and X-ray fluorescence (XRF) (Orescanin, *et al*. 2006). These techniques are very precise and accurate but they are expensive methods and are not available in some laboratories. For example, ICP-MS can be used for determination of trace elements at low

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concentration levels but it suffers some limitation included high price, difficult maintenance and isobaric polyatomic interferences (Berijani, *et al.* 2012). Or because of simultaneous analysis and high sensitivity of ICP-OES, this instrument can be used for determination of lanthanide ions, but in some samples such as environmental samples when the concentration of the lanthanide ions are too low detection ability of this instrument is not sufficient. Therefore, to improve the limit of detections of simpler techniques, preconcentration methods are usually applied. Separation and preconcentration of lanthanides in environmental samples seems essential. There are some techniques for separation and preconcentration include liquid-liquid extraction, solid phase extraction, flotation and etc. Recently solid phase extraction (SPE) because of high recovery, rapid phase separation, high enrichment factor, low use of organic solvent and low cost is most usual (Simpson 2000). Solid phase extraction has been used for preconcentration of lanthanides by using various sorbents such as activated alumina (Manoochehri & Khalesi, 2012), multiwall carbon nanotubes (Liang, *et al.* 2005), muromac A-1 (Hirata, *et al.* 2002), octadecyl silica (Karimi, *et al.* 2004), activated carbon (Murty & Chakarpani 1996) and carbon-based magnetic nanocomposites (Tajabadi, *et al.* 2013). The nanoporous materials such as MCM-41, MCM-48 (Kresge, *et al.* 1992) and SBA-15 (Kresge, *et al.* 1992; Hajiaghababaei, *et al.* 2011), due to their high surface area (up to 1000 m²/g), defined and large pore size and good mechanical and thermal stability have been applied more than other sorbents . SBA-15 is a mesopores material which is interconnected by the presence of micropores across the silica walls. SBA-15 presents also a higher stability than MCM-41 materials

due to the larger thickness of the silica walls and ligand can be immobilized into the pores (Hajiaghababaei, *et al.* 2012a,b; 2013).

In this study an organic ligand 2-(2-nitrobenzylideneamino) guanidine (Scheme 1) has been used to physically modify SBA-15 to apply this new sorbent to separate and preconcentration of some lanthanides in environmental samples prior to determination by ICP-OES.

MATERIALS & METHODS

Analytical grade nitrate and chloride salts of used cations (all from Merck, Darmstadt, Germany) were of highest purity available. Tetraethyl orthosilicate (TEOS) as silica source, poly(ethylene glycol)-block poly(propylene glycol)-block-poly(ethylene glycol) (p123, Sigma-Aldrich, Mo, USA) as structure directing agent, 3-[2-(2-Aminoethylamino) ethylamino]propyl-trimethoxy-silane (AEAPTES) (Sigma-Aldrich, Mo, USA) as amine compound were used as received from suppliers. Organic solvents and all acids were from Merck Company (Darmstadt, Germany). A Shimadzu UV-Visible spectrophotometer (model: UV-3100S) was used for UV spectrum. The pH values are measured with a Metrohm pH-meter (model: E603-Herisua, Switzerland) supplied with a glass-combined electrode. A scanning electron microscope (Zeiss "igma/UV) used for SEM images. A Varian (model: 735-OES) inductively coupled plasma optical emission spectrometer (ICP-OES) was used for determination of lanthanides. The conditions of analyzing are summarized in Table 1. The SBA-15 was prepared according to the literature (Zhao, *et al.* 1998). The image of the structure of prepared SBA-15 is shown in Fig. 1. An organic ligand 2-(2-nitrobenzylidenamino)guanidine is a kind of Schiff Base was synthesized according to the general procedure

Table 1. Condition operating of ICP-OES

Parameters	Values
Plasma gas (Ar)	15 (L/min)
Auxiliary gas (Ar)	1.5 (L/min)
RF power	1.2 KW
Pump speed	7RPM
Integration time	3 Sec
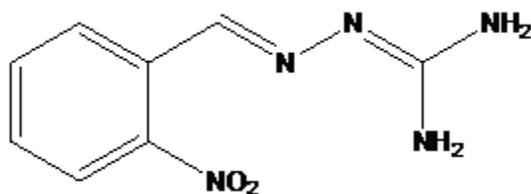
Scheme 1. Chemical structure of 2-(2-nitrobenzy lideneamino) guanidine
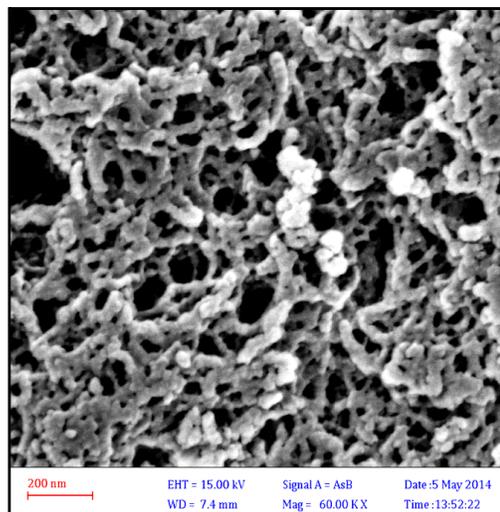
Fig. 1. Scanning electron microscopy of SBA-15
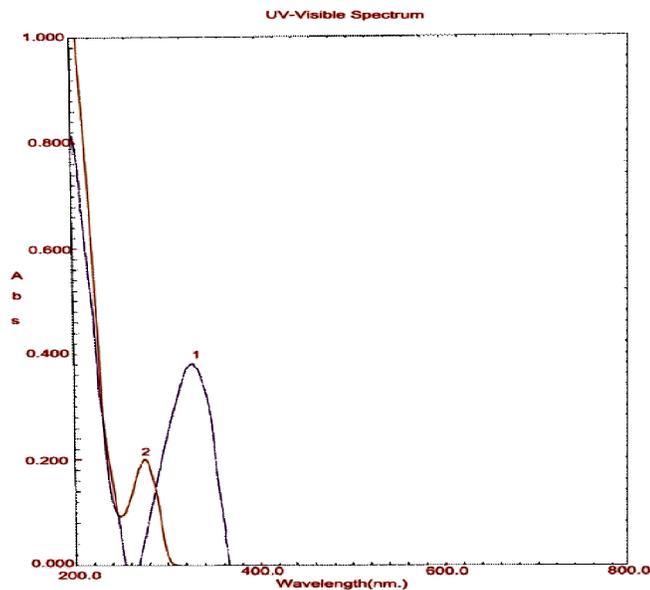
Fig. 2. UV-Vis. spectra, spectrum 1 is related to the ligand, and number 2 is the same solution after mixing ligand with SBA-15

Table 2. Recovery percent with functionalized SBA-15

Ions	Dy^{3+}	Eu^{3+}	Nd^{3+}	Sm^{3+}	Yb^{3+}
Recovery%	97.4 ±(2.2)*	98.9±(1.9)	96±(2.9)	97.2±(2.4)	97.7±(2.1)

Initial solution contained 1.5 µg of mono element in 10 mL solution.*RSD for three replicate experiments.

Table 3. Recovery percent for mixed standard solution with functionalized SBA-15

Ions	Dy^{3+}	Eu^{3+}	Nd^{3+}	Sm^{3+}	Yb^{3+}
Recovery%	94.1 ±(1.2)*	95.3±(0.9)	93.9±(1.9)	95.6±(1.4)	94.9±(2.1)

Initial solution contained 1.5µg of above lanthanide ions in 10 mL solution.*RSD three replicate experiments.

Table 4. Recovery percent with SBA-15 non-functionalized

Ions	Dy^{3+}	Eu^{3+}	Nd^{3+}	Sm^{3+}	Yb^{3+}
Recovery%	59.9 ±(1.2)*	66.6±(1.5)	56.6±(1.9)	60.5±(2.1)	60.1±(1.7)

Initial mixture contained 1.5 µg of $Dy^{3?}$, $Eu^{3?}$, $Nd^{3?}$, $Sm^{3?}$, $Yb^{3?}$ ions in 10 mL solution.*RSD for three replicate experiments

(Zamani, et. al 2011; 2012; Hosseini et. al 2011) and used to physically modify the SBA-15. 50 mg of modifying ligand was dissolved in 10 mL of acetonitrile 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 new sorbent for this research.

To confirm the adsorption of the ligand on SBA-15, a $3×10^{É5}$ mol/L solution of the ligand in acetonitrile was prepared. UV-Vis spectrum of this solution was taken (spectrum 1 in Fig. 2), then 30 mg of ligand was added to this solution and mixed for 15 min, and the solution was filtered and again UV-Vis spectrum of the

remain solution was taken in (spectrum 2 in Fig. 2). Comparison of two UV spectrums confirms the adsorption of ligand on SBA-15 surface.

Cations stock solutions (1000 mg /L) were prepared by dissolving the appropriate amounts of nitrate or chloride salts in double-distilled water. Working standard solutions were prepared by appropriate dilution of the stock standard solutions with double-distilled water. General procedure for the method is as follow: At initial experiment, a mixed standard solution of the cations with concentration of 150 ng/mL was prepared. To 10 mL of this solution containing 1.5 µg of each cations 30 mg of SBA-15 was
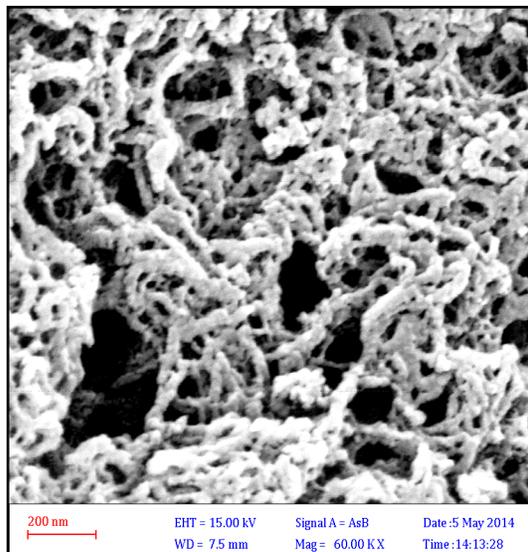
Fig. 3. SEM image of functionalized SBA-15 after extraction of Eu³⁺

added and mixture was stirred for at least 15 min. Then the resulting mixture was filtrated on filter paper. Then the extracted ions were stripped using 10 mL of 1.0 mol/L nitric acid. Finally cations in stripping solution were determined by ICP-OES.

RESULTS & DISCUSSION

In initial studies, adsorption of different cations in various mixed solutions on SBA-15 and functionalized SBA-15 were investigated according to the general procedure stated above. The results show that the functionalized SBA-15 has an ability to selective adsorb of Dy^{+3}, Eu^{+3}, Nd^{+3}, Sm^{+3}, Yb^{+3} ions.

In next experiment, to 10 mL of a mono element solution containing 1.5 µg of Dy^{3+} 30 mg of functionalized SBA-15 was added and mixture was stirred for 15 min. Then the resulting mixture was filtrated on filter paper. Then the extracted ions were stripped using 10 mL of 1.0 mol/L nitric acid. Finally Dy^{3+} concentration in stripping solution was determined by ICP-OES. For Eu^{3+}, Nd^{3+}, Sm^{3+}, Yb^{3+} ions mono element process were also performed and recovery of each ions was calculated. Table 2 shows the obtained results.

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

$$R\% = (m_e/m_s) \times 100 = (C_e V_e / C_s V_s) \times 100 \qquad (1)$$

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

In another experiment, to a 10 mL of a mixed solution containing 1.5 µg of Dy^{+3}, Eu^{+3}, Nd^{+3}, Sm^{+3}, Yb^{+3}, 30 mg of functionalized SBA-15 was added and mixture was stirred well for at least 15 min and the same procedure was repeated. The recovery was calculated and is shown in Table 3.

As a blank experiment, a mixture of these lanthanide ions was in contact with non-functionalized SBA-15. The recovery results were calculated and have been shown in Table 4.

To confirm the adsorption of these five lanthanide ions on functionalized SBA-15, to 25 mL solution containing one of the lanthanide ion, 30 mg of functionalized SBA-15 was added and stirred for 15 min after that, solution was filtered. Then, SEM image of functionalized SBA-15 after extraction is taken. Fig. 3 shows the SEM image of functionalized SBA-15 after extraction of Eu³⁺ ion as an example. The result of energy dispersive X-ray spectroscopy (EDS) analysis and EDS map of functionalized SBA-15 after extraction are shown in Fig. 4 and Fig. 5, respectively. These results confirm the adsorption of Eu³⁺ on the surface of functionalized SBA-15.

The optimum amount of the sorbent for maximum extraction was determined by using different amount of functionalized SBA-15 in 10 mL of 150 ng/mL of mixed Eu^{3+}, Dy^{3+}, Sm^{3+}, Nd^{3+}, Yb^{3+}. Recovery percent is shown in Fig. 6. According to the obtained results, subsequent extractions were carried out with 30 mg of functionalized SBA-15.

The effect of extraction time on the efficiency of the extraction for a series of solution containing 1.5 µg of Dy^{3+}, Eu^{3+}, Sm^{3+}, Nd^{3+}, Yb^{3+} in 10 ml of solution was investigated and the results are depicted in Fig. 7. As it can be seen, all ions can be extracted completely in the stirring time of 15 minutes or upper by functionalized SBA-15. The effect of the pH of the standard solution on the extraction of 1.5 µg of Dy^{3+}, Eu^{3+}, Nd^{3+}, Sm^{3+}, Yb^{3+} in 10 ml of solution was investigated in pH range 2-10. The result are shown in Fig. 8. According to the obtained results, at higher pH, the different hydroxyl species of lanthanide ions forms $(Ln(OH)^{2+}, Ln(OH)_2^{+}, Ln(OH)_3 Ln(OH)_4^{-})$. At lower pH the functional group in the structure of the sorbent are protonated and the sorbent cannot interact with lanthanide ions.

The effect of ionic strength on the extraction of ions 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 to lanthanide ions.
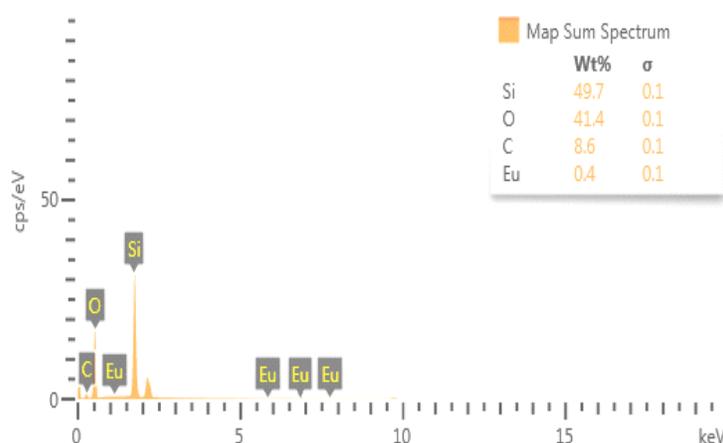
Fig. 4. EDS analysis of functionalized SBA-15 after extraction of Eu³⁺

Table 5. Recovery percent of lanthanide ions in presence of other ions

Ions	Dy^{3+}	Eu^{3+}	Nd^{3+}	Sm^{3+}	Yb^{3+}
Recovery%	88.3 ±(2.2)	89.3±(2.9)	87±(1.6)	89.5±(1.9)	88.5±(2.1)

Initial mixture contained 1.5µg of lanthanides, Ba^{+2}, Hg^{+2}, Zn^{+2}, Ag+ cations,15 µg of Al^{+3}, Fe^{+3}, Na^+,K^+,Ca^{+2},Mg^{+2},Pb^{+2},Cu^{+2},Ni^{+2} cations in 10 mL solution.

Table 6. Capacity of sorbent for Dy^{3+}, Eu^{3+}, Nd^{3+}, Sm^{3+},Yb^{3+}

Lanthanide ion	Dy^{3+}	Eu^{3+}	Nd^{3+}	Sm^{3+}	Yb^{3+}
Capacity of 5 mg of sorbent	140.6µg	143.3µg	128.1µg	155.2 µg	131.2µg

Table 7. Analysis of real samples by spiking standard

Water Samples	Lanthanides spiked (ng/mL)	Yb^{3+} ion Recovery%	Sm^{3+} ion Recovery%	Nd^{3+} ion Recovery%	Eu^{3+} ion Recovery%	Dy^{3+} ion Recovery%
A well in Qazvin	3	94.5	93.2	95.5	92.3	91.3
A spring in Qazvin	3	93.6	93.1	95.2	91.5	93.5
A spring in Sanandaj	3	94.2	94.3	93.3	92.4	92.6

Initial samples contain 1.5 µg of lanthanides in 500ml of solution

Hence, this method can be used for separation in highly saline solutions.

In order to investigate the effect of other ions in extraction yield of lanthanides, an aqueous solution (10 mL) containing 1.5 µg of Eu^{+3}, Dy^{+3}, Nd^{+3}, Sm^{+3},Yb^{+3} and various amount of other cations were added and the recommended procedure was followed and the results are shown in Table 5. The results showed that, in excess of 10,000-fold Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Ag^+, Al^{3+} and 1000-fold other lanthanide ions did not show significant interferences in the extraction and determination.

Selection of the proper eluent for desorption of the ions is an important factor for this extraction system. Some acidic solutions (1.0 mol/L) were selected as an effective eluent for the adsorbed ions after extraction. Among the nitric acid, hydrochloric acid and acetic acid, HNO_3 select as an effective eluent for desorption.

Eu Lα1

250nm
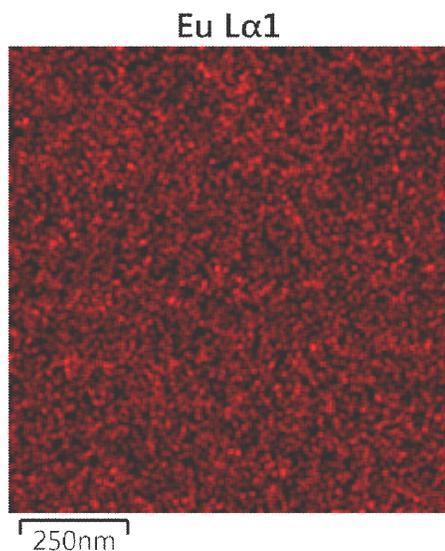
Fig. 5. EDS map of functionalized SBA-15 after extraction of Eu³⁺ (the red points shows the Eu)

Some experiments were one to choose a proper volume of nitric acid for the recovery of Eu^{+3}, Dy^{+3}, Nd^{+3}, Sm^{+3}, Yb^{+3} ions after extraction by the functionalized SBA-15. The ions were stripped with varying volumes of acid. Results showed that 10 mL of 1.0 mol/L nitric acid can accomplish the quantitative elution of these ions from the functionalized SBA-15. It should be noted that, if the experiment used in real samples contains more ionic species maybe more volume of acid is needed for stripping. The capacity of sorbent shows the weight of the sorbent which is required to remove a specific amount of analyte from the solution. The adsorption efficiency of the ions was calculated by the following equations:

$$\%R = (C_0 - C_t/C_0) \times 100 \tag{2}$$

$$q_e = V(C_0 - C_e)/m \tag{3}$$

Where, R is the adsorption efficiency of the metal ions, C_0 is the initial concentration (mg/L) and Ce is the
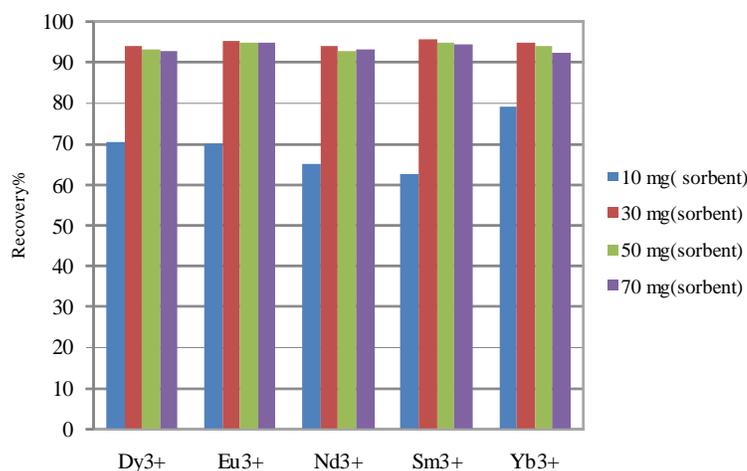
Fig 6. Effect of amount of adsorbent on extraction yield
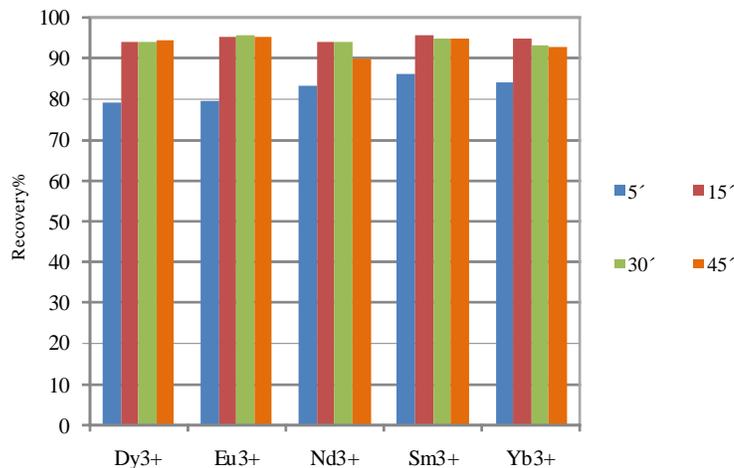
Fig. 7. The effect of extraction time on extraction yield
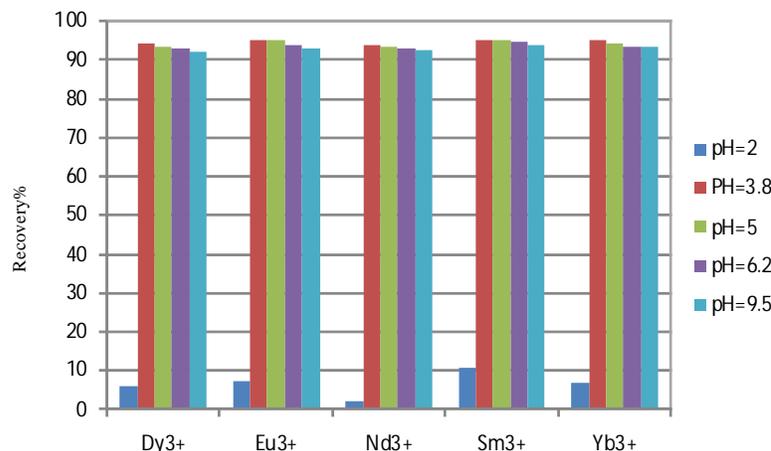
Fig. 8. The pH effect of solution on extraction yield

final concentration of the metal after absorption ions at time t, q_e is quantity of ion adsorbed on the adsorbent at the time of equilibrium (mg/g), Vis the volume of the solution (mL), and m= content of adsorbent (g).

In order to determination of adsorption capacity a 500 µg/mL of mono standard solution was prepared. 30 mg of functionalized SBA-15 was added to a 10 mL of this solution and stirred for 15 minutes. After filtration the remain solution was determined directly by ICP-OES. The maximum capacity of 5 mg of functionalized SBA-15 was determined for each lanthanide ions [15]. The results are shown in Table 6.

Finally, experiments carried out in order to study the regeneration capacity of the functionalized SBA-15. The adsorbent was used in some cycles of the adsorption/desorption process. The results revealed that the adsorbent capacity was remained constant only in 2 cycles and decreased slowly in next cycles of the adsorption/desorption process.

The limits of detection of the proposed method for the determination of these lanthanide ions were investigated under the optimal experimental conditions. The LODs obtained from $C_{LOD} = K_b S_b /m$ for a numerical factor $K_b = 3$, are 2.9 ng/ml for Dy^{3+}, 1.6 ng/mL for Eu^{3+}, 8.4 ng/mL for Nd^{3+}, 3.8 ng/mL for $Sm^{3+}$and 2.5 ng/mL for Yb^{3+} ions. "S_b" is standard deviation of blank solution and "m" is the slope of calibration curve.

The applicability of this method to preconcentration and determination of lanthanides in real water samples was investigated by spiking of 10 mL of 150 ng/mL of standard stock solutions of lanthanides in 500 mL of the three different water samples. The back extraction was done using 5.0 ml of HNO_3 (1mol/L) preconcentration factor was 100. The results are shown in Table 7.

CONCLUSION

In the present research, a solid phase extraction (SPE) method was developed using physically functionalized nanoporous (SBA-15) as a new sorbent for preconcentration of Dy^{3+}, Eu^{3+}, Nd^{3+}, Sm^{3+},Yb^{3+} in environmental samples. The adsorption/desorption kinetics, easy preparing and high adsorption capacity are the advantages of this sorbent compared with the commonly used sorbent. Low limit of detection, good enrichment factor, wide range of linearity of calibration curve and good RSD value can be used for rapid extraction and preconcentration of some lanthanide ions in environmental samples.

ACKNOWLEDGEMENTS

REFERENCES

Berijani, S., Ganjali, M.R., Sereshti, H. and Norouzi, P. (2012) A selective modified nanoporous silica as sorbent for separation and preconcentration of dysprosium in water samples prior to ICP-OES determination. Intern. J. Envoron. Anal. Chem., **92**, 355-365.

Bunzil, J. and Claude P. (2005). Taking advantage of luminescent lanthanide ions. Chemical Society Reviews, **34 (12)**, 1048–77.

Dybczynski, S.R., Czerska, E., Danko, B., Kulisa, K. and Samczynski, Z. (2010). Comparison of performance of INAA, RNAA and ion chromatography for the determination of individual lanthanides, Appl. Radit Isot., **68**, 23-27.

Fricker, S.P. (2006). Therapeutic application of lanthanides, Chem. Soc. Rev., **35**, 524–533.

Kajiya, T., Aihara, M. and Hirata, S. (2004). Determination of rare earth elements in seawater by inductively coupled

plasma mass spectrometry with on-line column pre-concentration using 8-quinolinole-immobilized fluorinated metal alkoxide glass. Spectrochim. Acta B, **59**, 543-550.

Karami, H., Mousavi, M.R., Yamini, Y. and Shamsipur, M. (2004). On-line preconcentration and simultaneous determination of heavy metal ions by inductively coupled plasma atomic emission spectrometry, Anal. Chim. Acta, **509**, 89-94.

Kostova, I. (2005). Lanthanides as anticancer agents.Curr. Med. Chem. Anticancer Agents., **5 (6)**, 591-602.

Kuriki, K. and Koike, Y. (2002). Plastic Optical Fiber Lasers and Amplifiers Containing Lanthanide Complexes, Chem. Rev., **102**, 2347-2356.

Hajiaghababaei, L., Badiei. A., Ganjali, M.R., Heydari, S., Khanian, Y. and Ziarani. M.G. (2011). Highly effective removal and preconcentration of lead and cadmium cations from water and wastewater samples using ethylenediamine functionalized SBA-15. Desalination, **266**, 182-187.

Hajiaghababaei, L., Badiei, A., Shojaan, M., Ganjali, M.R., Ziarani, G.M. and Zarabadi-Poor, P. (2012a). A novel method for the simple and simultaneous preconcentration of Pb^{2+}, Cu^{2+} and Zn^{2+} ions with aid of diethylenetriamine functionalized SBA-15 nanoporous silica compound. Int. J. Environ. Anal. Chem., **92 (12)**, 1352-1364.

Hajiaghababaei, L., Ghasemi, B., Badiei, A., Goldooz, H., Ganjali, M.R. and Ziarani, G.M. (2012b). Aminobenzenesulfonamide functionalized SBA-15 nanoporous molecular sieve: A new and promising adsorbent for preconcentration of lead and copper ions. J. Environ. Sci., **24 (7)**, 1347-1354.

Hajiaghababaei, L., Tajmiri, T., Badiei, A., Ganjali, M.R., Khaniani, Y. and Ziarani, G.M. (2013). Heavy metals determination in water and food samples after preconcentration by a new nanoporous adsorbent. Food Chemistry, **141(3)**, 1916-1922.

Hirata, S., Kajia, T., Aihara, M., Honda, K. and Shikino, D. (2002). Determination of rare earth elements in seawater by on-line column preconcentration inductively coupled plasma mass spectrometry. Talanta, **58**, 1185-1194.

Hosseini, M., Abkenar, S.D., Ganjali, M.R. and Faridbod, F. (2011). Determination of zinc(II) ions in waste water samples by a novel zinc sensor based on a new synthesized Schiff's base. Mater. Sci. Eng. C, **31 (2),** 428-33.

Liang, P., Liu, Y. and Guo, L. (2005). Determination of trace rare earth elements by inductively coupled plasma atomic emission spectrometry with multiwalled carbon nanotubes. Spectrochim. Acta B, **60**, 125-129.

Manoochehri, M. and Khalesi, P. (2012). Synthesis and Evaluation of Ion Imprinted Mercapto-Functionalized Nano Alumina as a Selective Sorbent for Nd(III) Removal from Water Samples, World Applied Science, **19**, 215-222.

Murty, D.S.R. and Chakarpani, G. (1996). Preconcentration of rare earth elements on activated carbon and its application to groundwater and sea-water analysis, J. Anal. At. Spectrom., **11**, 815-820.

Orescanin, V., Mikelic, L., Roje, V. and Lulic, S. (2006). Determination of lanthanides by source excited energy dispersive X-ray fluorescence (EDXRF) method after preconcentration with ammonium pyrrolidine dithiocarbamate (APDC). Anal. Chim. Acta, **570**, 277-282.

Reifernberg, J.G., Ge, P. and Selvin P.R. (2005). Progress in Lanthanides as Luminescent Probes, Review in fluorescence, **2005**, 391-433.

Simpson, N.J.K. (2000). Solid Phase Extraction, principles, Strategies and Application, Marcel Dekker, New York.

Tajabadi, F., Yamini, Y. and Sovizi, M. R. (2013). Carbon – based magnetic nanocomposites in solid phase dispersion for the preconcentration some lanthanides, Followed by their quantitation via ICP-OES, Microchim. Acta, **180**, 65-73.

Wang, Y.Q., Sun, J.X., Chen, H.M. and Guo, F.Q. (1999). Determination of the contents and distribution characteristics of REE in natural plants by NAA, J. Radioanal. Nucl. Chem., **219**, 99-103.

Zhang, N., Hu, B. and Huang. C. (2007). A new ion-imprinted silica gel sorbent for on-line selective solid-phase extraction of dysprosium(III) with detection by inductively coupled plasma-atomic emission spectrometry, Anal. Chim. Acta, **597**, 12-18.

Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C. and Beck, J.S. (1992). Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. Nature, **359**, 710–712.

Zamani, H.A., Zabihi, M.S., Rohani, M., Zangeneh-Asadabadi, A., Ganjali, M.R., Faridbod, F. and Meghdadi, S. (2011). Quantitative monitoring of terbium ion by a Tb^{3+} selective electrode based on a new Schiff's base. Mater. Sci. Eng. C, **31(2)**, 409-13.

Zamani, H.A., Ganjali, M.R., Faridbod, F. and Salavati-Niasari M. (2012). Heptadentate Schiff-base based PVC membrane sensor for Fe(III) ion determination in water samples. Mater. Sci. Eng. C, **32(3)**, 564-8.

Zhang, J.C., Xu, S.J., Wang, K. and Yu, S.F. (2003). Effects of the rare earth ions on bone resorbing function of rabbit mature osteoclasts in vitro. Chinese Sci. Bull., **48**, 2170–2175.

Zhao, D, Huo, Q., Feng. J., Chemelka, B.F. and Stucky, G.D. (1998). Noninic triblock and star diblock copolymer and olygometric surfactant syntheses of highly orderd, hydrothermally stable, mesoporous silica structures. Am. Chem. Soc., **120**, 6024-6036.