

Preconcentration and atomic spectrometric determination of rare earth elements (REEs) in natural water samples by inductively coupled plasma atomic emission spectrometry

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Abstract

The usage of a variety of sorbents has been shown as promising matrix removal/preconcentration strategies for the determination of rare earth elements (REEs) in various natural water samples by inductively coupled plasma atomic emission spectrometry (ICP-AES). The sorption efficiency of various zeolites (clinoptilolite, mordenite, zeolite Y, zeolite Beta), ion-exchangers (Amberlite CG-120, Amberlite IR-120, Rexyn 101, Dowex 50W X18) and chelating resins (Muromac, Chelex 100, Amberlite IRC-718) towards REEs was investigated in terms of solution pH, shaking time and sorbent amount. The results have shown that most of the materials can take up REEs at a wide pH range. The experiments were continued with clinoptilolite, zeolite Y and Chelex 100 and it was demonstrated that all three materials displayed very fast kinetics for REE sorption (higher than 96% in 1 min). Desorption from the sorbents was realized with 2.0 M HNO₃ for clinoptilolite and 0.1 M HNO₃ for zeolite Y and Chelex 100. Only the lower concentration range (0.01–2.0 mg l⁻¹) of matrix-matched standards were used in quantitation although the calibration graphs were linear at least up to 10.0 mg l⁻¹ for all REEs studied. The limit of detection (3 s) without preconcentration was 0.1, 1.0, and 0.2 μg l⁻¹ for Eu, La, and Yb, respectively. The validity of the method with the selected sorbents was checked through spike recovery experiments.

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1. Introduction

Rare earth elements (REEs) are used in industrial applications due to their metallurgical, optical and electronic properties. The rising use of the REEs in industry, and thus increasing the possibility of their release into the environment, has necessitated the development of new sensitive, precise and accurate analytical methods for their determination in various environmental matrices including water.

There have been many analytical techniques used for the determination of REEs in solid and solution samples; neutron activation analysis [1,2], isotope dilution mass spectrometry [3,4], inductively coupled plasma atomic emission spectrometry

(ICP-AES) [5–9], and inductively coupled plasma mass spectrometry (ICP-MS) [10–16] are the most popular ones. These techniques are usually applied after a separation and/or a preconcentration step due to low concentrations of REEs in environmental samples. Also, major constituents in several samples, such as organic compounds and inorganic salts, may result in interference effects. Various methods have been used for matrix removal/preconcentration purposes, such as coprecipitation [4], liquid–liquid extraction [17,18], ion-exchange [7–9,13], and a variety of sorbents including chelating resins [5,6,10–12,15,19,20].

A high number of the materials recommended in REE studies can be suitable candidates for the substrates in solid phase extraction (SPE) methods. The simplicity, ease of availability and compatibility of SPE methods with different measurement techniques make them proper alternatives for

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expensive and time-consuming separation/preconcentration procedures. For example, Liang et al. [6] used a microcolumn of TiO_2 for the on-line preconcentration of La, Y, Yb, Eu, Dy. Rucandio [7] applied Dowex 50W X18, a strong cation-exchange resin, to separate REEs from Ba. The same resin was used by Djingova and Ivanova [8] for the separation of REEs from the matrix elements in the soil and sediment extracts. Resins with iminodiacetate functional groups have also been used in REE studies. In one of these studies, Hirata et al. [11] utilized a microcolumn of Muromac A-1 resin for the preconcentration and determination of REEs in sea water. Inagaki and Haraguchi [12] employed a preconcentration step with Chelex 100 (another very popular chelating resin with iminodiacetate functionality) to human blood serum for the determination of REEs whereas Möller et al. [20] used Chelex 100 for onboard preconcentration of REEs from sea water. Willie and Sturgeon [21] determined the REEs in sea water by utilizing a microcolumn of Toyopearl AF Chelate 650 M, a chelating resin with iminodiacetate functional groups, prior to inductively coupled plasma time of flight mass spectrometric determination. Amberlite XAD resins are also among the well-known adsorbents applied in the preconcentration of REEs, either with direct use or employed after a suitable functionalization step. For example, Dev et al. [22] investigated the sorption behavior of La(III), Nd(III), Tb(III), Th(IV) and U(VI) on Amberlite XAD-4 resin functionalized with bicine ligands. De Vito et al. [23] functionalized XAD-7 with thorin and used the resin for REE preconcentration prior to X-ray fluorescence determination. Vicente et al. [10] followed a different strategy and preconcentrated the oxine complexes of some REEs on Amberlite XAD-7 resin. More information on the determination of REEs and other metals can be found in reviews [24,25].

The aim of the present study was to investigate the sorption behavior of various zeolites (clinoptilolite, mordenite, zeolite Y, zeolite Beta), ion-exchangers (Amberlite CG-120, Amberlite IR-120, Rexyn 101, Dowex 50W X18) and chelating resins (Muromac, Chelex 100, Amberlite IRC-718) towards REEs in terms of solution pH, shaking time, and sorbent amount; and to make some conclusions about their applicability to matrix removal/preconcentration purposes in natural water samples.

2. Experimental

2.1. Instrumentation and apparatus

A Varian Liberty Series II Axial view ICP-AES was used in all measurements. The instrument was operated applying an incident power of 1.2 kW, a plasma gas (Ar) flow rate of 15 l min^{-1} , a sampling gas flow rate of 0.9 l min^{-1} and an auxiliary gas (Ar) flow rate of 1.5 l min^{-1} . Continuous nebulization at a sampling flow rate of 1.4 ml min^{-1} was applied during the measurements by means of a concentric glass nebulizer equipped with cyclonic spray chamber.

Quantitative measurements were based on the evaluation of peak height measurements. Background correction was realized by utilizing the polynomial plot method. The REEs investigated and their emission wavelengths were as follows: Ce (413.380 nm), Dy (353.170 nm), Er (337.276 nm), Eu (420.505 nm), Gd (342.247 nm), Ho (345.600 nm), La (379.478 nm), Nd (460.109 nm), Pr (390.844 nm), Tb (350.917 nm, and Yb (369.419 nm). In batch sorption studies, Yellowline RS 10 (Staufen, Germany) lateral shaker was used to provide efficient mixing. pH measurements were performed using a Corning 450 pH/ion meter with a pH combination electrode.

2.2. Reagents and materials

All reagents were of analytical grade. Ultra pure water ($18 \text{ M}\Omega$) was used throughout the study. All reagents were stored in polyethylene/polypropylene containers. Plastic ware was soaked in 10% (v/v) nitric acid for cleaning and rinsed with ultra pure water prior to use. Standard multielement REEs stock solution (1000 mg l^{-1}) were prepared by dissolving the appropriate amount of oxide or nitrate forms of the REEs in 100 ml of ultra pure water. pH buffers, ranging from 2 to 10, were prepared using various concentration of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$), potassium phthalate ($\text{K}_2\text{C}_8\text{H}_4\text{O}_4$), NaOH, HCl, and $\text{Na}_2\text{B}_4\text{O}_7$. Clinoptilolite-rich natural zeolite mineral used in this study was obtained from Enli Mining Co. (from deposits in Gördes, Turkey). Other adsorbents studied are listed in Table 1.

2.3. Sorption studies

Sorption characteristics of the potential sorbents for REEs were examined by a batch process in a way that, 20.0 ml of REE solution in the prescribed concentration was prepared and 0.1 g of the selected sorbent was added into this solution. The mixture was shaken for 1–2 min manually and then placed on a lateral shaker for 30 min at room temperature. After the shaking period, the solid and the liquid phases were separated by filtration and the liquid part was analyzed for REEs by ICP-AES. The solid portion was put into 2.0 M HNO_3 in the case of clinoptilolite or 0.1 M HNO_3 in the cases of zeolite Y and Chelex 100 and shaken as before for further 30 min for the desorption of REEs. After filtration, the filtrate was analyzed as described.

For the examination of the effect of solution pH on the sorption of REEs by the selected sorbents, 1.0 mg l^{-1} multielement REE standard was prepared in pH buffer solutions ($\text{pH} = 2.0\text{--}10.0$) at a constant ionic strength, and the usual sorption procedure was employed. For the adjustment of pH, NH_3 (0.1–1.0 M) and HCl (0.1–1.0 M) were used. Similar experiments were also performed in different HNO_3 concentrations (0.5–4.0 M). Percent sorption values as a function of pH and HNO_3 concentration were calculated from the concentration of REEs in the filtrate. Similar experiments were

Table 1
Sorbents investigated in this study and proper pH ranges for efficient uptake

Type	Sorbent	Functional groups	pH range ^a
Strong cation exchanger	Dowex 50W X18	Sulfonic acid groups	~0.4–6
	Rexyn 101	Sulfonic acid groups	~0.4–5
	Amberlite CG-120	Na ⁺ form, sulfonic acid groups	~0.4–10
	Amberlite IR-120	H ⁺ form, sulfonic acid groups	~0.4–5
Chelating resin	Amberlite IRC-718	Na ⁺ form, iminodiacetate groups	2–5
	Chelex 100	Na ⁺ form, iminodiacetate groups	3–10
	Muromac	Iminodiacetate groups	1–5
Zeolite	Clinoptilolite (natural)	^b	4–10
	Zeolite Y (synthetic)	Ammonium form	4–10
	Zeolite Beta (synthetic)	Ammonium form	4–10
	Mordenite (synthetic)	Ammonium form	5–10

^a Useful pH range for the uptake of REEs.

^b Approximate chemical composition: (K,Na,1/2Ca)₂O·Al₂O₃·10SiO₂·8H₂O.

carried out to determine the optimum shaking time and the amount of sorbent for a quantitative sorption.

Since the present study describes the possibility of using clinoptilolite, in addition to the other sorbents, for matrix removal/preconcentration purposes prior to ICP-AES determination of REEs, equilibrium sorption isotherm studies were also conducted over a wide range of concentrations in order to investigate the sorption behavior of REEs on clinoptilolite. These studies were also carried out by a batch process in a way that 0.100 g clinoptilolite was added into 20.0 ml of solutions containing the specified concentrations of REEs (ranging from 1.0 to 100.0 mg l⁻¹) and the mixtures were shaken at room temperature for 30 min. At the end of the shaking period, the solid and the liquid phases were separated by filtration and the liquid part was analyzed by ICP-AES for REEs, as explained before. The amount of REEs sorbed per unit mass of clinoptilolite was determined from the mass balance.

3. Results and discussion

The results of the experiments carried out in the present study under the specified conditions have shown very strong similarities among REEs. Therefore, the results for only La are given in the subsequent sections except Section 3.6 in which a comparison is made based on the affinity of clinoptilolite towards La (a light REE), Eu (a medium REE), and Yb (a heavy REE).

3.1. Calibration

In the initial stages of the study, the effect of solution matrix after the sorption/desorption step employed on the ICP-AES signal of the REEs was examined. For this purpose, two types of calibration graphs were prepared, i.e., either with aqueous, or with matrix-matched standard solutions. The matrix-matched calibration graph was ob-

tained by applying the proposed sorption/desorption steps with each adsorbent. For example, for clinoptilolite, 20.0 ml standard solutions from 0.01 to 2.0 mg l⁻¹ were mixed with clinoptilolite and the usual sorption/desorption step was applied; 20.0 ml of HNO₃ was the desorbing solution. In this way, any possible suppression effect from the treated sorbent was expected to be eliminated. For La, calibration line equations (and correlation coefficients) for aqueous and matrix-matched standards were: $y = 5.1 \times 10^4 x + 550$ ($R^2 = 0.9999$) and $y = 4.0 \times 10^4 x + 135$ ($R^2 = 0.9996$), respectively. As can be seen, the calibration sensitivity (the slope of the calibration plot) is affected from sorption/desorption step and the matrix-matched standards always gave sensitivity approximately 20% lower than those of aqueous standards. This result was expectable when the “percentage sorption versus pH and acidity” graph is examined in the following section.

3.2. Effect of pH on sorption

The effect of solution pH on the sorption of REEs on the sorbents was investigated as explained in Section 2.3. As can be seen in Fig. 1, a pH range is generally available for any sorbent, over which it demonstrates an efficient sorption capability. The most appropriate pH ranges for the investigated sorbents under the experimental conditions employed in this study are given in Table 1. This table (together with Fig. 1) can be considered as a rough guide in deciding the working pH for various samples having different pH values. Keeping in mind the other parameters affecting the sorption, it can be said that the zeolites (clinoptilolite, mordenite, zeolite Y and zeolite Beta) can be used for matrix removal/preconcentration during the determination of REEs in neutral solutions. The choice should be based on the expected concentration of REEs in the sample, the background REE levels in the sorbent, and also the availability of the sorbent. The lower the background REE level of the sorbent (the purer the material), the higher the possibility of its use in the trace/ultra

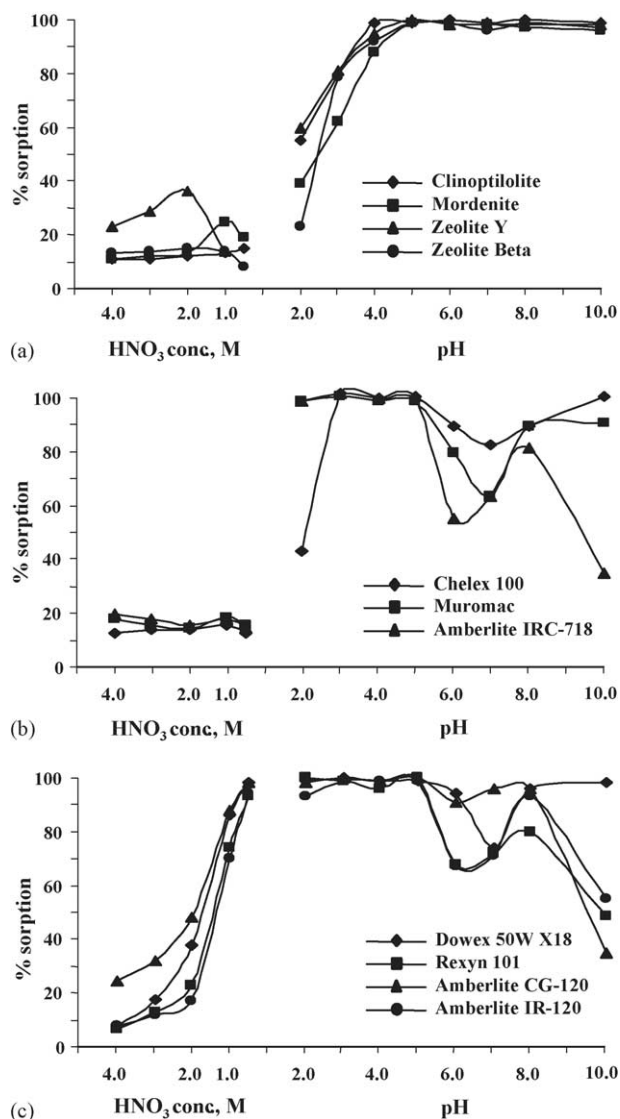


Fig. 1. La(III) sorption as a function of pH and HNO₃ concentration on different sorbents: (a) zeolites, (b) chelating resins, and (c) ion-exchangers.

trace preconcentration applications. Clinoptilolite, in this respect, can be a good matrix removal/preconcentration material only for REE concentrations higher than 0.02 mg l⁻¹. Due to the possibility of desorbing some REEs which are naturally present in clinoptilolite, it cannot be applied for lower concentrations; or the analyst can find an efficient purification method. Another observation in Fig. 1 is that the strong cation exchangers (Amberlite CG-120, Amberlite IR-120, Rexyn 101, Dowex 50W X18) can be employed even at a HNO₃ concentration of 0.5 M. These resins can be used in the preconcentration of REEs especially from the dissolved solutions of precipitated solids, fusion fluxes, or acid digests.

Since natural waters are considered in this study, any sorbent which has been shown to be working effectively for the uptake of REEs at the pH of natural waters could be appropriate for the matrix removal/preconcentration step prior to

ICP-AES measurements. Therefore, clinoptilolite, zeolite Y and Chelex 100 were selected and employed in the subsequent studies.

3.3. Effect of shaking time

One of the criteria that must be given a high priority in choosing a suitable material for sorption of the analytes in natural water is the fast kinetics of the sorption process. The selected sorbents were examined in this respect and the shaking time was varied between 1 and 120 min. The percentage sorption was higher than 96 for all the three sorbents even after 1 min manual shaking. The results demonstrated the suitability of the selected sorbents for the matrix removal/preconcentration step. These values are also indicative of the applicability of the sorbents in SPE cartridges, and mini- or micropacked columns. To ensure attainment of equilibrium, a shaking time of 30 min was applied in the subsequent studies with batch method.

3.4. Effect of sorbent amount

Similar sorption experiments were carried out to determine the optimum amount of the sorbent for 20.0 ml of 1.0 mg l⁻¹ REEs standard solution. The amounts of the sorbents used were: 0.01, 0.05, 0.10, 0.20, and 0.50 g. Clinoptilolite exhibited very similar sorption behavior for all the amounts investigated (97(±1)%). Zeolite Y was not able to show a sufficient sorption with 0.01 g (47%) whereas 0.05 g gave 93% sorption. It worked quantitatively (>99%) beyond 0.10 g. For Chelex 100, percent sorption was 83% with 0.01 g and >99% with 0.05–0.50 g. The sorption value for 0.01 g Chelex 100 does not reflect its capacity when used in its original particle size in bead form, possibly because of insufficient solid-to-liquid ratio for a quantitative sorption for a shaking time of 30 min. When the amount of sorbents used in this study is considered (0.1 g), it can be said that all three sorbents can be good candidates for environmental samples. In terms of economy of the process, the use of clinoptilolite exhibits the best condition.

3.5. Desorption

The first candidate for desorbing REEs from the sorbents was HNO₃ since the percent sorption values in HNO₃ concentrations of 0.5–4.0 M were between 10 and 20%. Very close recoveries were obtained with the HNO₃ concentrations applied and 2.0 M was decided to be used for desorption from clinoptilolite and 0.1 M from Chelex 100 and zeolite Y. It must be noted here that the matrix stability of clinoptilolite at such a high acidic concentration was examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results of both examinations confirmed the structural and morphological stability of the mineral following its exposure to 2.0 M HNO₃.

Table 2
Spike recovery results for ultra pure water^a

La(III) spike (mg l ⁻¹)	Initial volume (ml)	Final volume (ml)	Enrichment factor	La(III) found (mg l ⁻¹)		
				Clinoptilolite	Zeolite Y	Chelex 100
1.00	20	20	1.0	>0.99	>0.99	>0.99
0.40	50	20	2.5	0.85 (±0.02)	0.75 (±0.03)	0.75 (±0.01)
0.08	250	20	12.5	0.84 (±0.03)	0.56 (±0.05)	0.70 (±0.02)
0.04	500	20	25	0.83 (±0.01)	0.35 (±0.02)	0.63 (±0.05)
0.02	1000	20	50	0.77 (±0.01)	0.17 (±0.01)	–
Eu(III) spike (mg l ⁻¹)	Initial volume (ml)	Final volume (ml)	Enrichment factor	Eu(III) found (mg l ⁻¹)		
				Clinoptilolite	Zeolite Y	Chelex 100
1.00	20	20	1.0	>0.99	>0.99	>0.99
0.40	50	20	2.5	0.87 (±0.01)	0.77 (±0.03)	0.74 (±0.01)
0.08	250	20	12.5	0.82 (±0.04)	0.53 (±0.04)	0.69 (±0.02)
0.04	500	20	25	0.82 (±0.02)	0.33 (±0.02)	0.61 (±0.05)
0.02	1000	20	50	0.77 (±0.77)	0.16 (±0.01)	–
Yb(III) spike (mg l ⁻¹)	Initial volume (ml)	Final volume (ml)	Enrichment factor	Yb(III) found (mg l ⁻¹)		
				Clinoptilolite	Zeolite Y	Chelex 100
1.00	20	20	1.0	>0.99	>0.99	>0.99
0.40	50	20	2.5	0.92 (±0.01)	0.75 (±0.03)	0.80 (±0.01)
0.08	250	20	12.5	0.87 (±0.03)	0.62 (±0.02)	0.75 (±0.02)
0.04	500	20	25	0.87 (±0.02)	0.44 (±0.03)	0.70 (±0.04)
0.02	1000	20	50	0.79 (±0.02)	0.26 (±0.01)	–

^a Recovery results are the average of three separate determinations (±standard deviation).

Table 3
Spike recovery results for bottled drinking water^a

La(III) spike (mg l ⁻¹)	Initial volume (ml)	Final volume (ml)	Enrichment factor	La(III) found (mg l ⁻¹)		
				Clinoptilolite	Zeolite Y	Chelex 100
1.00	20	20	1.0	>0.99	>0.99	>0.99
0.40	50	20	2.5	0.83 (±0.03)	0.78 (±0.04)	0.78 (±0.01)
0.08	250	20	12.5	0.83 (±0.04)	0.60 (±0.02)	0.62 (±0.05)
0.04	500	20	25	0.82 (±0.02)	0.38 (±0.01)	0.46 (±0.02)
0.02	1000	20	50	0.79 (±0.02)	0.17 (±0.01)	–
Eu(III) spike (mg l ⁻¹)	Initial volume (ml)	Final volume (ml)	Enrichment factor	Eu(III) found (mg l ⁻¹)		
				Clinoptilolite	Zeolite Y	Chelex 100
1.00	20	20	1.0	>0.99	>0.99	>0.99
0.40	50	20	2.5	0.83 (±0.03)	0.80 (±0.04)	0.77 (±0.01)
0.08	250	20	12.5	0.81 (±0.03)	0.60 (±0.02)	0.60 (±0.05)
0.04	500	20	25	0.81 (±0.03)	0.35 (±0.01)	0.41 (±0.03)
0.02	1000	20	50	0.71 (±0.02)	0.15 (±0.01)	–
Yb(III) spike (mg l ⁻¹)	Initial volume (ml)	Final volume (ml)	Enrichment factor	Yb(III) found (mg l ⁻¹)		
				Clinoptilolite	Zeolite Y	Chelex 100
1.00	20	20	1.0	>0.99	>0.99	>0.99
0.40	50	20	2.5	0.87 (±0.04)	0.78 (±0.02)	0.83 (±0.01)
0.08	250	20	12.5	0.84 (±0.04)	0.64 (±0.02)	0.71 (±0.05)
0.04	500	20	25	0.86 (±0.02)	0.49 (±0.01)	0.61 (±0.03)
0.02	1000	20	50	0.83 (±0.00)	0.26 (±0.01)	–

^a Recovery results are the average of three separate determinations (±standard deviation).

Table 4
Spike recovery results for sea water^a

La(III) spike (mg l ⁻¹)	Initial volume (ml)	Final volume (ml)	Enrichment factor	La(III) found (mg l ⁻¹)		
				Clinoptilolite	Zeolite Y	Chelex 100
1.00	20	20	1.0	>0.99	>0.99	>0.99
0.40	50	20	2.5	0.83 (±0.03)	0.38 (±0.03)	0.83 (±0.03)
0.08	250	20	12.5	0.61 (±0.01)	0.47 (±0.03)	0.76 (±0.02)
0.04	500	20	25	0.53 (±0.01)	0.33 (±0.03)	–
0.02	1000	20	50	0.48 (±0.01)	–	–
Eu(III) spike (mg l ⁻¹)	Initial volume (ml)	Final volume (ml)	Enrichment factor	Eu(III) found (mg l ⁻¹)		
				Clinoptilolite	Zeolite Y	Chelex 100
1.00	20	20	1.0	>0.99	>0.99	>0.99
0.40	50	20	2.5	0.84 (±0.02)	0.49 (±0.03)	0.84 (±0.03)
0.08	250	20	12.5	0.61 (±0.02)	0.51 (±0.02)	0.81 (±0.02)
0.04	500	20	25	0.53 (±0.02)	0.34 (±0.02)	–
0.02	1000	20	50	0.42 (±0.01)	–	–
Yb(III) spike (mg l ⁻¹)	Initial volume (ml)	Final volume (ml)	Enrichment factor	Yb(III) found (mg l ⁻¹)		
				Clinoptilolite	Zeolite Y	Chelex 100
1.00	20	20	1.0	>0.99	>0.99	>0.99
0.40	50	20	2.5	0.85 (±0.03)	0.74 (±0.01)	0.87 (±0.02)
0.08	250	20	12.5	0.67 (±0.02)	0.62 (±0.02)	0.75 (±0.03)
0.04	500	20	25	0.56 (±0.03)	0.48 (±0.02)	–
0.02	1000	20	50	0.52 (±0.03)	–	–

^a Recovery results are the average of three separate determinations (±standard deviation).

An approximate total recovery of 80–90% could be expected under the experimental conditions employed; 20.0 ml sample at pH 7, 0.1 g sorbent, 30 min shaking, 20.0 ml HNO₃ for desorption. This observation also explains the reason of obtaining approximately 20% lower sensitivity for the matrix-matched standard calibrations compared to the aqueous calibration. It should be mentioned here that any increase in the sample volume may lead to even lower calibration sensitivities to be obtained.

3.6. Determination of sorption isotherms

The sorption data of La(III), Eu(III), and Yb(III) on clinoptilolite were fitted to Langmuir and Freundlich isotherm models in order to reveal which of them described better the partitioning of the sorbate ions between the liquid and solid phases.

Langmuir isotherm is among the most widely applied isotherm models in sorption studies. This isotherm model assumes that the surface of the sorbent can accommodate only a monolayer of the sorbate ions on energetically equivalent sorption sites. This model assumes also no interaction between the sorbed species, i.e., that the ability of an ion to occupy a certain site is independent of the occupancy on the neighbouring sites [26]. Langmuir isotherm model is given by the equation:

$$[C]_s = \frac{C_m K [C]_l}{1 + K [C]_l} \quad (1)$$

This equation can be rearranged to get the linear form:

$$[C]_s = C_m - \frac{[C]_s}{K [C]_l} \quad (2)$$

where $[C]_s$ is the equilibrium concentration of sorbate on the solid (mmol g⁻¹), $[C]_l$ is the equilibrium concentration of sorbate in the liquid (mmol l⁻¹), $[C]_m$ is the monolayer sorption capacity, and K is a constant related to the energy of sorption.

Freundlich isotherm model, on the other hand, does not have any restriction on the sorption capacity of the sorbent, and is more appropriate in situations where the sorption sites possess a heterogeneous nature [26]. This model is given by the equation:

$$[C]_s = k [C]_l^n \quad (3)$$

The linear form of this equation is:

$$\log [C]_s = \log k + n \log [C]_l \quad (4)$$

Here $[C]_s$ and $[C]_l$ are as defined above, 'n' and 'k' are Freundlich constants which provide information on the sorption linearity and affinity and are obtained from the slope and intercept of Freundlich plots, respectively.

Plotting the sorption data of La(III), Eu(III), and Yb(III) on clinoptilolite (Fig. 2a) and using Freundlich model (Fig. 2b) showed that these data obeyed Freundlich isotherm model, as demonstrated by the linear behavior presented in Fig. 2(b) for the three REE cations. Langmuir isotherm equation, on the other hand, did not yield linear behavior for any of these

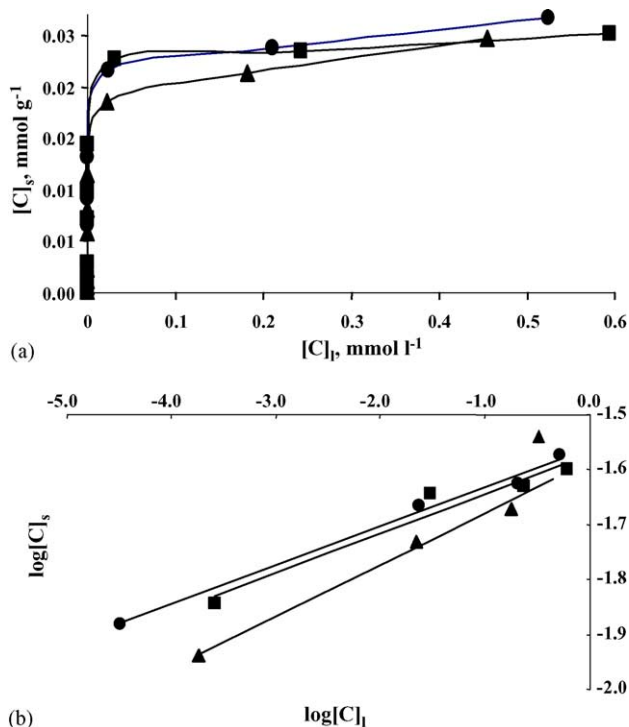


Fig. 2. (a) General, (b) Freundlich sorption isotherm for (■) La(III), (●) Eu(III), and (▲) Yb(III) on clinoptilolite. Line equations (and correlation coefficients) for Freundlich isotherm model were $y = 0.0723x - 1.5717$ ($R^2 = 0.9500$) for La, $y = 0.0708x - 1.5607$ ($R^2 = 0.9916$) for Eu, and $y = 0.0938x - 1.5856$ ($R^2 = 0.9921$) for Yb.

cations. In general, Langmuir isotherm model is not obeyed when the sorption sites are inequivalent in terms of sorption energy, and when there is a possibility for the interaction between the sorbate species on their fixation sites, the things accounted to by Freundlich isotherms. Multilayer sorption can also cause deviation from Langmuir isotherm equation, but this type of sorption is not plausible in the case of cation-solid interaction where the cations are attracted by the negative charge (either permanent or pH-dependent) on the solid surface.

The values of Freundlich constants, n and k , obtained for sorption La(III), Eu(III), and Yb(III) were: 0.071, 0.072, 0.094 and 0.027, 0.028, 0.026 (mmol g⁻¹), respectively. The n values, being far away from unity, indicate that sorption is highly non-linear, which means that the energetic barrier against sorption is fastly increasing as loading is increased. The values of k reveal no significant difference in the affinity of clinoptilolite towards the three ions on a mole basis.

Surveying literature revealed a scarcity in the number of studies devoted to tackle the issue of sorption isotherms of REEs on natural sorbents with specifically no data available on the isotherms describing uptake of those elements by clinoptilolite. Thus, a meaningful comparison is difficult, as the type of fitting isotherm depends closely on the set of experimental conditions and structural details of the solid sorbent.

3.7. Spike recoveries and preconcentration

In order to investigate the efficiency of clinoptilolite, zeolite Y and Chelex 100 in the enrichment of REEs from different water types, at different volumes and different concentrations, a set of solutions was prepared and subjected to the usual sorption/desorption process. In these studies, the absolute amount of REEs was fixed at 20.0 mg by spiking the solutions with 0.02–1.0 mg l⁻¹ corresponding to sample volumes of 1000–20 ml, respectively. Depending on the volume, appropriate amounts of clinoptilolite, zeolite Y and Chelex 100 (0.1–1.0 g) were added into the solutions. The results are given in Tables 2–4. It should be remembered here that in all calculations, the matrix-matched standard calibration plots were used. Both the initial and final volumes employed during matrix-matching were 20.0 ml. As can be seen from the tables, clinoptilolite and Chelex 100 give satisfactory results for all three water types with an enrichment factor of 2.5. In contrast to zeolite Y, these two sorbents also show acceptable performances for ultra pure and bottled drinking water samples even at high initial sample volumes (≥ 250 ml). It is interesting to note that clinoptilolite displays a better performance than the other two sorbents for so-called ‘clean’ water types, such as ultra pure water and bottled drinking water whereas Chelex 100 is superior for sea water samples being referred to as ‘heavy-matrix’.

Another point to consider, is the effect of volume of the standard solutions applied in matrix-matching. All results for higher sample volumes were calculated based on the matrix-matching of 20.0 ml sample. Therefore, these matrix-matching standard calibration graphs are most appropriate for sample volumes of 20.0 ml (first row in the data section of Tables 2–4). The decrease in spike recovery values for higher volumes could have been caused by this fact.

4. Conclusion

Possibility of utilizing several sorbents has been demonstrated as alternative matrix removal/preconcentration routes for various environmental water samples prior to the determination of REEs by ICP-AES. It was found that 0.1 g of the sorbent was adequate for 20.0 ml sample solution containing 0.02–1.0 mg l⁻¹ REEs. The kinetic studies have shown that the sorbents can take up more than 95% of REEs in 1 min. This fast kinetic is promising in terms of the applicability of the sorbents in SPE cartridges, and mini- or micro-packed columns. To investigate the sorption mechanism of REEs on clinoptilolite, Langmuir and Freundlich isotherm models were applied. It was found that the sorption data much better obey the Freundlich isotherm model.

It has been also demonstrated that there can be found a suitable sorbent for different applications, and for different pH values. In addition, the proposed sample treatment method has the potential of being used with more sensitive techniques, such as ICP-MS. With its very fast and superior

detection capability (lower detection limits), ICP-MS may offer higher preconcentration factors with even smaller volumes.

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