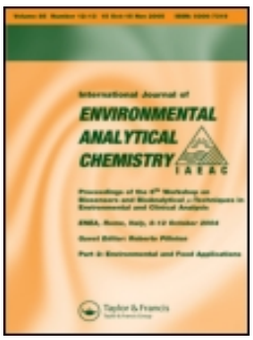

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Selective preconcentration of Lanthanum(III) by *Coriolus versicolor* immobilised on Amberlite XAD-4 and its determination by ICP-OES

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Coriolus versicolor, a wood fungus, was immobilised on Amberlite XAD-4 and used as solid-phase biosorbent for preconcentrations of rare earth elements. La(III), Th(IV), U(IV) and Ce(III) were subjected to solid-phase extraction procedure. We observed that La(III) was selectively preconcentrated, while other ions remained in solution at pH 6.0. 5.0 mL of 1.0 mol L^{-1} HCl was used to elaute La(III) from column. 250 mg of *C. versicolor* loaded on 1000 mg of XAD-4 was optimised as solid-phase matrix. Concentrations of ions in solutions were determined by inductively coupled plasma– optical emission spectrometry (ICP-OES). The calibration plot after preconcentration was linear in the range from 1.0 to 50.0 ng mL^{-1} for La(III). Limit of detection was found as 0.27 ng mL^{-1} for La(III) by SPE method. Relative standard deviation was found lower than 6.7% for 1.0 ng mL^{-1} of La(III) solution (n = 10). The sensitivity of ICP-OES was improved by a factor of 46.8. The applicability of the method was validated through the analysis of certified reference samples of tea (NCS ZC-73014) and spinach (NCS ZC-73013).

Keywords: Lanthanum; rare earth elements; selective preconcentration; *Coriolus versicolor*; solid-phase extraction

1. Introduction

Among the rare earth elements (REEs), lanthanum (La) has currently obtained special attention due to the increasing demands in the field of advanced functional materials [1,2]. Owing to its interesting physical and chemical properties, La has been widely used in the pharmacological and electronics industries. It is also known that La compounds are excellent stimulants of agricultural products and hence are extensively used as an important trace fertiliser [3]. Furthermore, La is generally applied in the making of advanced new materials such as super alloys, catalysts, special ceramics and synthetic materials [4].

However, it has been reported that La can cause cancer in humans, and it affects especially the liver. Considering the risk of accumulation of La(III) and its relative toxicity to living organisms, there is a need to find a suitable and economical treatment method for La-bearing solutions [5].

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Conventional methods for removal of metals from industrial wastewaters include chemical precipitation, oxidation-reduction, filtration, electrochemical techniques and membrane processes [6–8]. However, these methods are expensive if relatively high concentrations of metals, such as 1–100 mg L^{-1}, are to be removed [7,9,10]. Furthermore, a major disadvantage of conventional treatment methods is the production of toxic sludge. In recent times, the method of removal of metallic ions from liquid effluents with the help of microorganisms has received greater attention over the conventional physical/chemical methods [11].

Biosorption and bioaccumulation are attractive alternative strategies over existing technologies for the removal and preconcentrations of metal ions [7,8,12]. Biosorption is considered in cases of living and nonliving biomass; however, bioaccumulation is mediated only by living biomass [13–15]. Biosorption, a passive, non-metabolically active process of metal ion binding by living or dead biomass, appears to be a cost-effective technique. The cell walls of microbial biomass, mainly composed of polysaccharides, proteins and lipids, contain abundant metal-binding functional groups, such as carboxylate, hydroxyl, sulphate, phosphate and amino groups. Biosorption enables passive metal uptake by microbial biomass through processes such as complexation, ion-exchange, physical adsorption and inorganic microprecipitation [9,12,13,15]. Several algae, bacteria, fungi and yeasts have been found to be effective metal sorbents [9,12].

Owing to insufficient sensitivity of the atomic absorption spectrometry (AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES), a preconcentration step is required before low level measurement of La concentration in a variety of samples. Solid-phase extraction (SPE) technique is generally applied for this purpose [16–20]. SPE is the most common technique for preconcentration of metal ions, and its role in modern analytical science is evident [21]. This extraction method offers several advantages, including higher preconcentration factor, less waste generation, short extraction time, low cost, reduced interference of the matrix and low consumption of organic solvents, environment-friendly and high recovery [21–24].

Amberlite series resins were generally employed as solid-phase sorbent with and without functionalisation to preconcentrate in a variety of metals include Cu, Co, Ag [25], U(VI), Th (IV) [26], Cu, Mn, Zn [27], Cr, Mn, Fe, Co, Ni, Cu [28], Co [29], Bi [30], Cu, Ni, Pb [31] Fe, Ni, Cu, Zn, Cd, Co [32] and speciations of Cr(III) and Cr(VI) [33,34]. Complexes of some transition elements include La(III) were retained on octadecyl silica before their measurements by ICP-OES [35]. Off-line column using 2,6-diacetylpyridine functionalised Amberlite XAD-4 was also used for preconcentration of La (III) before inductively coupled plasma mass spectrometry (ICP-MS) [36]. The sorption efficiencies 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 include La(III) were investigated by considering the important experimental parameters such as pH of the solutions, shaking time and sorbent amount [37]. Cloud point extraction (CPE) was also used for preconcentration of La(III) [38,39].

The present work examined the use of XAD-4 as an immobilisation matrix for the preconcentration of La(III) by *Coriolus versicolor*, a wood fungus. The effects of several parameters on SPE procedure and elution efficiency of La(III) were studied by column modes. Finally, this method was validated by analysis of certified reference samples of tea (NCS ZC-73014) and spinach (NCS ZC-73013) and of natural water samples with satisfactory results.

2. Experimental

2.1 *Instrumentation and reagents*

The concentrations of REEs were determined by ICP-OES using Perkin Elmer Optima 7000 DV. The operating conditions for ICP-OES are available in literature [40]. La(III), U(IV), Th

(IV) and Ce(III) were measured at 408.672, 385.958, 283.730 and 413.764 nm, respectively. A digital pH meter (Mettler Toledo MPC 227; Polaris Parkway, Columbus) was used to measure the pH of the solutions. The required amounts of 0.1 mol L^{-1} of HCl and NaOH were added to solutions to adjust the desired pH value. Solid-phase experiments were performed on filtration columns (1.0 × 10.0 cm) equipped with polypropylene frits. A peristaltic pump (Watson Marlow 323; Milford, MA) was used in SPE experiments.

About 1000 mg L^{-1} of La(III) and U(VI) in 2% HNO_3 (high purity standard; Charleston, SC), 1000 mg L^{-1} of Th(IV) and Ce(III) (Sigma, St. Loius, MO), NaOH (Merck, Darmstad-Germany), NH_3 (Merck), HCl (Merck), Amberlite XAD-4 (Sigma) were used in experiments. Certified reference tea and spinach samples were obtained from National Analysis Center for Iron and Steel (China). All laboratory glasswares were cleaned with 1.0 mol L^{-1} nitric acid for at least 24 h. They were further rinsed with double distilled water prior to use.

2.2 *Preparation of SPE column for La(III) preconcentration*

Coriolus versicolor was obtained from an area in south-eastern Turkey. It was washed twice with distilled water to remove contaminants and then dried at room temperature. Dry cells were ground in a porcelain mortar to obtain a fine powder. To ensure whole death of dried cells, the biomass was oven-dried at 80°C for 24 h. Finally, the cells were inoculated in malt agar at 25°C for 240 h, and the absence of mycelia of *C. versicolor* indicated whole death of the fungus. Dry biomass powder (250 mg) was mixed with 1.0 g of Amberlite XAD-4 (prepared by a procedure from our previous studies) and 15 mL of doubly distilled water and then thoroughly mixed [41]. Amberlite XAD-4 has been used as important adsorbent for the preconcentrations of organic and inorganic compounds [42] due to its high surface area, high affinity to complexation and/or coordination to related analytes, low particle size, chemical stability, reusability and easily functionability [43]. From these points of view, Amberlite XAD-4 was selected as sorbent for immobilisation of *C. versicolor*. The amount of biomass taken up by the resin was determined by measuring the increase in the weight of resin after mixing the paste and then heating in an oven at 105°C for 1 h to dry the mixture. These steps (wetting and drying) were repeated to maximise the contact between biomass and resin, thereby improving the immobilisation efficiency. It was found from experiments that 98.2 ± 1.3% of *C. versicolor* was immobilised to Amberlite XAD-4 and this value was evaluated as immobilisation efficiency and used to calculate the biosorption capacity also. Finally, the product obtained was sieved to get original size (20–60 mesh) and packed in solid-phase column (1.0 × 10.0 cm). Stability of the column was controlled by passing through the distilled water and 20 mL of 1.0 mol L^{-1} of HCl to SPE column at 1.0 mL min^{-1} flow rate. FT-IR spectra of solutions received from column were evaluated to decide the stability of the *C. versicolor* immobilised on Amberlite XAD-4. No individual peak arised from *C. versicolor* was observed. This showed the immobilisation with stable conditions.

A model solution containing 50.0 μg L^{-1} of La(III), Th(IV), U(IV) and Ce(III) was prepared. The pH of 50.0 mL portions of it was adjusted to a desired value and then it was passed through the column using peristaltic pump. After passing this solution entirely, 10.0 mL distilled water was passed through the column followed by 5.0 mL of 1.0 mol L^{-1} HCl as eluent.

2.3 *Preparation of samples*

Certified reference samples of tea and spinach were digested in a temperature- and pressure-controlled analytical microwave oven following the procedure given in our earlier study [44]. A final sample volume of 50.0 mL was subjected to SPE procedure.

This method was also applied to different water samples. Tap and river water samples were collected in polyethylene bottles and filtered using a cellulose membrane filter (Millipore) of pore size 0.45 μm before SPE procedure.

3. Results and discussion

3.1 *Effect of pH on the recoveries of REE*

Previous studies on REE biosorption indicated that pH dependence of metal uptake could be related to the functional groups of biosorbent and solution chemistry [45,46]. The pH of mixture of La(III), Th(IV), U(IV) and Ce(III) was adjusted to 2.0–8.0 (Figure 1). After SPE procedure was applied, concentrations of ions were determined. The highest recovery was obtained at pH 6.0 for La(III). Recovery percentages of Th(IV), U(IV) and Ce(III) were 8.6, 1.9 and 6.5%, respectively, at pH 6.0. Further experiments were conducted on Amberlite XAD-4 without *C. versicolor* to investigate the effect of sorption property of its. In the other hand, recovery values were determined as 4.3, 3.3, 0.6 and 2.9 respectively for La(III), Th(IV), U(IV) and Ce(III) in case of Amberlite XAD-4 without *C. versicolor*. It should be highlighted that no selectivity was found for different pHs. Thus, we presumed that proposed method was selective for La(III) versus Th(IV), U(IV) and Ce(III). From the results presented in Figure 1, the biosorption efficiency of La(III) ions was 36% at pH 2.0, and it increased significantly when pH was increased to 6.0. At pH 6.0, the removal rate was nearly quantitative. At low pH (<4.0), the surface area of fungal cells is surrounded by hydronium ions (H_3O^+), which competes with positively charged metal ions for binding, and this could result in a decrease in the biosorption capacity of fungal cells for metal ions [44,47]. However, metals precipitate at high pH values (>7.0), inhibiting the contact of metals with most fungal biomass [48]. Subsequent experiments were carried out at an initial pH of 6.0.

3.2 *Effect of sample flow rate on biosorption of La(III)*

We noted that *C. versicolor* immobilised on Amberlite XAD-4 SPE column showed selectivity to La(III). Therefore, the effect of flow rate of La(III) solutions through the packed bed column

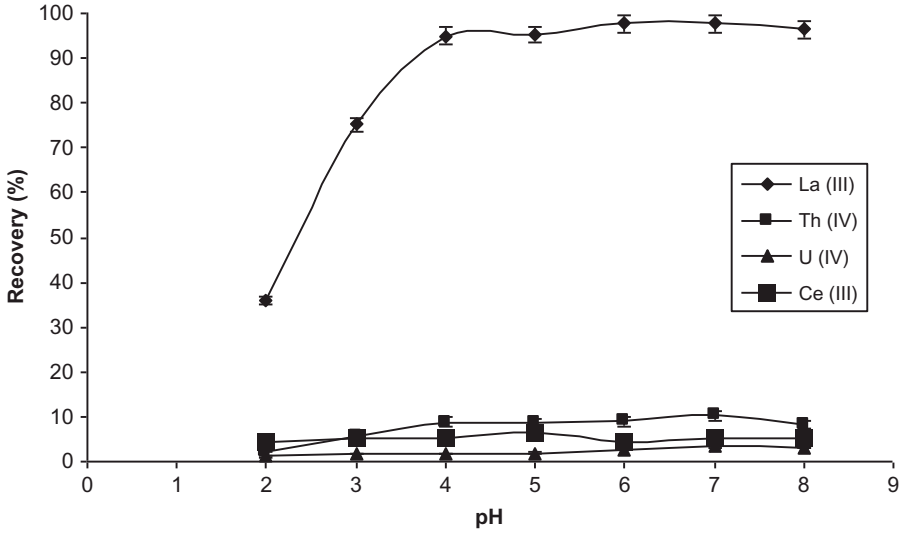

Figure 1. Effect of pH on recovery of 50.0 μg L^{-1} La (III), Th (IV), U (IV) and Ce (III).

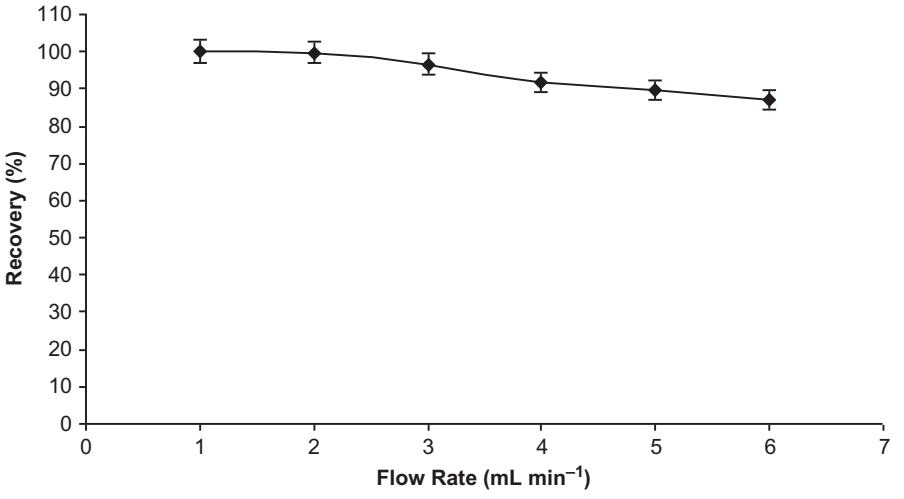

Figure 2. Effect of flow rate of solution on recovery of 50.0 μg L^{-1} La (III).

was also investigated, because the flow rate of solutions affects the recovery of the analyte and controls the time of analysis [49]. The effect of sample flow rate on the preconcentration of La (III) ions was investigated by adjusting the flow rate between 1.0 and 6.0 mL min^{-1}. The experimental results were presented in Figure 2. The recovery of La(III) was higher than 95% for a flow rate of 2.0 mL min^{-1}, and we chosen a flow rate of 2.0 mL min^{-1} for subsequent experiments.

3.3 *Effects of amounts of biosorbent and resin*

The effects of varying amounts of XAD-4 on the retention of 50 mL of 50.0 μg L^{-1} of La(III) solutions while amount of fungus was constant as 250 mg were examined at optimum pH and flow rate of 2.0 mL min^{-1}. After passing this solution through the column, 10.0 mL distilled water was passed followed by 5.0 mL of 1.0 mol L^{-1} HCl. Quantitative recovery values were obtained in 250–2000 mg range of XAD-4. From the results presented in Figure 3, the biosorption efficiency increased from 81.5% to 100.0% for La(III) as XAD-4 was increased from 250 to 1000 mg. It was decided to use 1000 mg of XAD-4 for further experiments.

The effect of varying amounts of *C. versicolor* on the biosorption of La(III) was investigated at a flow rate of 2.0 mL min^{-1} and pH 6.0. It was observed that biosorption of La(III) gradually increased up to 1000 mg of biosorbent and reached a plateau thereafter (Figure 4). In further experiments, 250 mg of *C. versicolor* was loaded on 1000 mg of XAD-4.

3.4 *Effect of sample volume on preconcentration of La(III)*

As most samples, especially water, contain very low concentrations of metal ions, the maximum applicable sample volume should be determined [50]. The effect of sample volume on the preconcentration of La(III) onto *C. versicolor* immobilised on Amberlite XAD-4 was examined for 50, 100, 250, 500 and 1000 mL of solution containing 50.0, 25.0, 10.0, 5.0 and 2.5 ng mL^{-1}, respectively, at optimum pH and flow rate. As seen in Table 1, the quantitative biosorption of La (III) onto *C. versicolor* immobilised on Amberlite XAD-4 was 97% for a sample volume up to 250 mL. Above 250 mL of the sample solution, the quantitative biosorption decreased

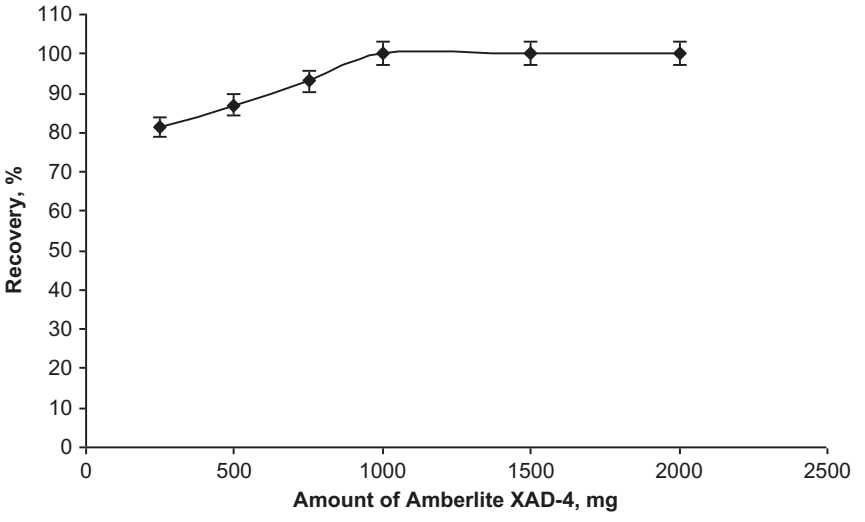

Figure 3. Effect of amount of Amberlite XAD-4 on recovery of 50 μg L^{-1} La (III).

gradually. As sample volume increased, the concentration of analyte decreased. It is generally observed that dilute solutions of different metal ions at μg L^{-1} levels could not be identical at higher concentrations. Therefore, as sample volume increases, adsorption decreases [51]. In the present study, initial volume of the solution was chosen as 250 mL. When a final volume of 5 mL was considered, a 50-fold preconcentration factor was obtained for La(III).

3.5 *Effects of eluent parameters*

From the above, we understand that concentration and volume of the solution are important to obtain a high preconcentration factor. Additionally, the effects of eluent parameters on the recovery of analyte ions were investigated. For this, 0.5 and 1.0 mol L^{-1} HCl and HNO_3 were

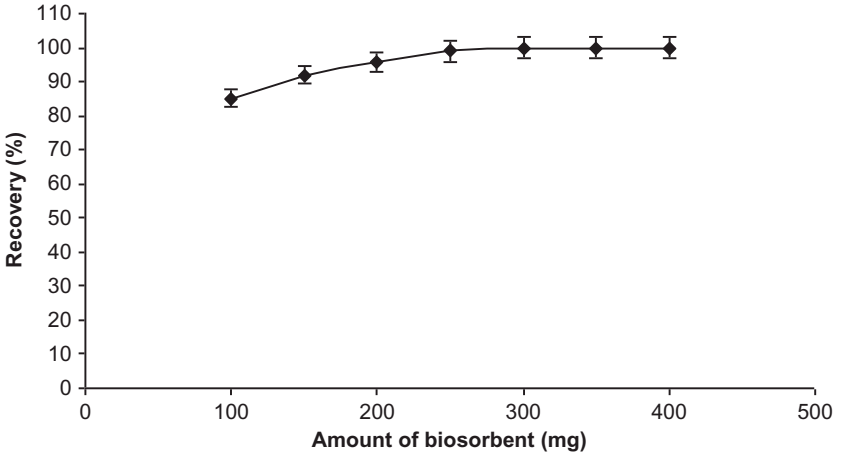

Figure 4. Effect of amount of biosorbent on recovery of 50 μg L^{-1} La (III).

Table 1. Effect of volume of initial solution on the recovery of La(III) (n = 3).

Volume	Concentration of La (ng mL^{-1})	Recovery (%)
50	50	97.6 ± 0.8
100	25	96.5 ± 0.4
250	10	96.5 ± 0.3
500	5.0	91.0 ± 0.5
1000	2.5	85.6 ± 0.9

Table 2. Effect of the type and volume of elution solutions on the recovery of La (n = 3).

Type of elution solution	Volume (mL)	Concentration (mol L^{-1})	Recovery (%)
HCI	1.0	0.5	84.5 ± 0.3
	3.0	0.5	92.1 ± 0.5
	5.0	0.5	97.2 ± 0.4
	1.0	1.0	90.6 ± 0.2
	3.0	1.0	96.5 ± 0.5
	5.0	1.0	99.9 ± 0.2
HNO_3	1.0	0.5	82.6 ± 0.6
	3.0	0.5	89.9 ± 0.4
	5.0	0.5	93.1 ± 0.5
	1.0	1.0	87.4 ± 0.6
	3.0	1.0	93.3 ± 0.5
	5.0	1.0	98.1 ± 0.2

passed through the column at a flow rate of 2.0 mL min^{-1}. For the elution of retained analyte, 50.0 mL standard solution containing 50.0 μg L^{-1} of La(III) was passed through the column. The results were presented in Table 2. From the results, quantitative recoveries of 97.2 ± 0.4% and 99.9 ± 0.2% were obtained when HCl concentration was increased from 0.5 to 1.0 mol L^{-1} in an elution volume of 5.0 mL. Elution recoveries for HNO_3 were lower than for HCl. For further studies, eluent concentration was 1.0 mol L^{-1} HCl and elution volume was 5.0 mL.

3.6 *Interference studies*

The effects of cations and anions on the recovery of La(III) in SPE system were also studied. They were selected by considering their availability in waters and plants and could possible interfere the SPE procedure by considering the interference studies in literatures. The results were presented in Table 3. The concentration ratios of interferent to analyte were selected as 1.0, 10.0, 100.0 and 1000. Tolerance limit was defined as the ion concentration causing a relative error smaller than 5% related to the preconcentration and determination of analytes. It was observed that recovery values of La(III) were not affected even at interferent concentration of 1000, except for Fe(III). The recovery of La(III) here was 92.9%. Further experiments were performed to investigate the possible interferic effect of Fe to La on different ratios with a column that not used previously. Ratios of Fe to La were changed as 250, 500, 750 and 1000. Results showed that recovery values were 96.5 ± 0.4, 95.5 ± 0.7, 97.6 ± 0.3, 94.4 ± 0.7, respectively. From the results it could be concluded that Fe had no significant interference on La even if we reported a recovery value as 92.9 for Fe/La ratio was 100. We have a reported value

Table 3. Effects of the major components on the recovery of 50 ng mL^{-1} of La (n = 3).

Ion	$c_{interferent}/c_{La}$	Recovery (%)
Na	1	98.6 ± 0.4
	10	99.5 ± 0.1
	100	98.8 ± 0.5
	1000	98.4 ± 0.6
K	1	99.7 ± 0.3
	10	99.8 ± 0.1
	100	96.4 ± 0.3
	1000	95.6 ± 0.8
Ca	1	100.2 ± 0.4
	10	99.1 ± 0.4
	100	98.9 ± 0.3
	1000	98.0 ± 0.7
Mg	1	100.2 ± 0.3
	10	96.8 ± 0.3
	100	98.2 ± 0.4
	1000	97.6 ± 0.6
Fe	1	95.3 ± 0.1
	10	99.7 ± 0.5
	100	92.9 ± 0.3
	1000	94.4 ± 0.7
SO_4^{-2}	1	96.1 ± 0.9
	10	96.0 ± 0.6
	100	96.1 ± 0.6
	1000	93.5 ± 0.7
NO_3^-	1	97.6 ± 1.1
	10	98.1 ± 0.8
	100	96.7 ± 0.8
	1000	92.1 ± 0.7
Cl^-	1	96.7 ± 0.7
	10	98.7 ± 0.6
	100	97.6 ± 0.8
	1000	91.9 ± 0.8
PO_4^{-3}	1	99.1 ± 0.4
	10	98.7 ± 0.5
	100	98.7 ± 0.6
	1000	96.5 ± 0.8

from our experiments and controlled by further experiments. Finally, it could be discussed that it could be attributed to poorer retention of used column in previous experiments.

Interferic effects of common anions, SO_4^{-2}, NO_3^-, Cl^- and PO_4^{-3} which could be found in samples were also investigated. Results showed that there were no interference even if their concentrations were 100 times higher than La(III). Decreasing in recovery was observed at the ratio of 1000. However, they were higher than 90%. It is assumed that ions normally present in natural water do not interfere under experimental conditions [52].

3.7 *FT-IR studies*

FT-IR spectra of *C. versicolor*, Amberlite XAD-4, LaIII) on *C. versicolor* immobilised Amberlite XAD-4 were comparetively presented in Figure 5. Peaks from Amberlite XAD-4 (Figure 5a) were agreed with our previous works and commented there [41]. Peaks at approximately 3500 cm^{-1}, 1650 cm^{-1}, 1500 cm^{-1} and 1000 cm^{-1} were recorded from spectra of *C. versicolor* (Figure 5b)

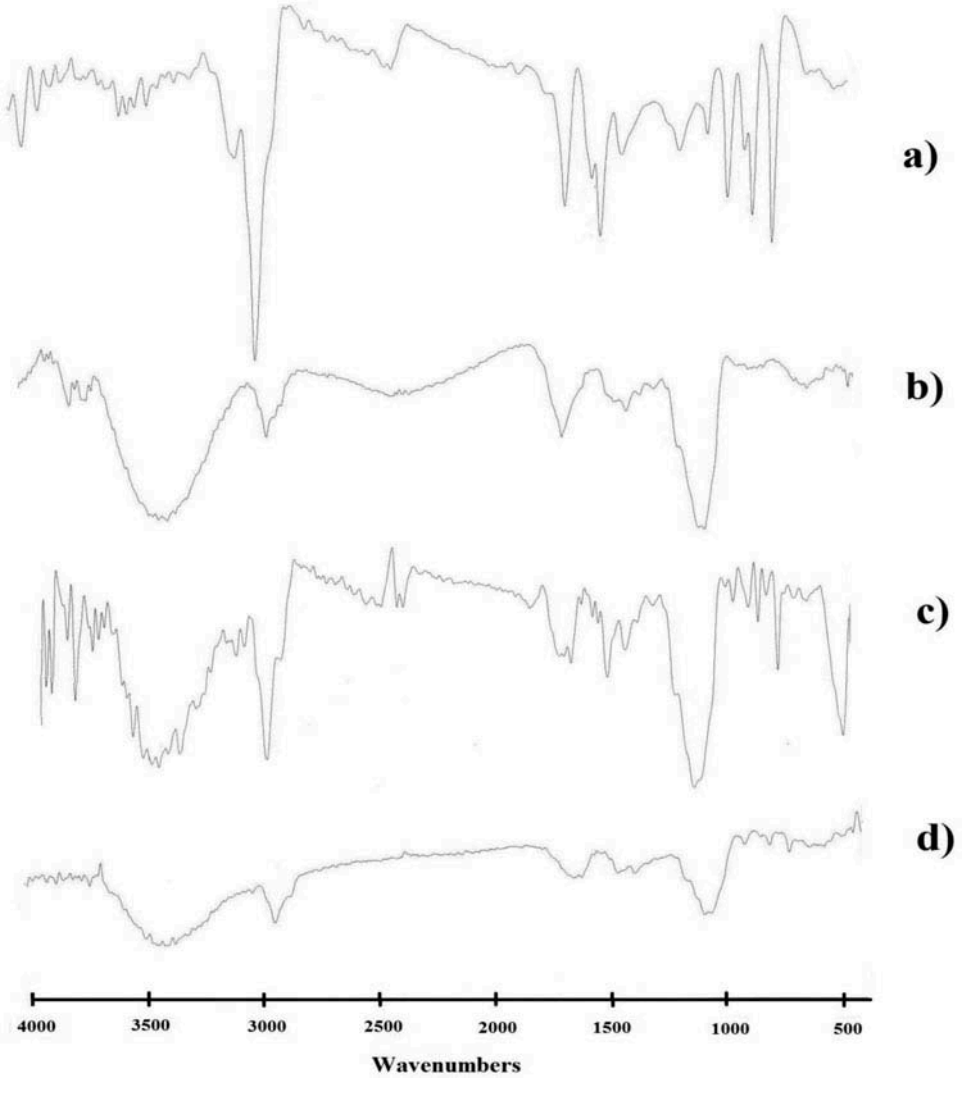

Figure 5. FT-IR studies on (a) Amberlite XAD-4 (b) *C. versicolor* (c) *C. versicolor* immobilised on Amberlite XAD-4 (d) La(III) on *C. versicolor* immobilised Amberlite XAD-4.

and could be due to amine and/or hydroxyl, carboxyl, -C = C- vibrations and aromatic bonds, respectively. From Figure 5c. it could be concluded that *C. versicolor* was immobilised on Amberlite XAD-4 by considering the individual peaks of them. Variations in spectra could be attributed to complexation with La(III). They were observed at 500–1000 cm^{-1} region. Important decreasing in peak intensity and shifting at peak positions at 500^{-1} and 800 cm^{-1} could be due to complexation with La(III).

3.8 *Analytical characteristics of the method*

It is well known that stability and potential regeneration of the biosorbent are economically important parameters [45,46]. To investigate the reusability of the column, 100 mL solution of

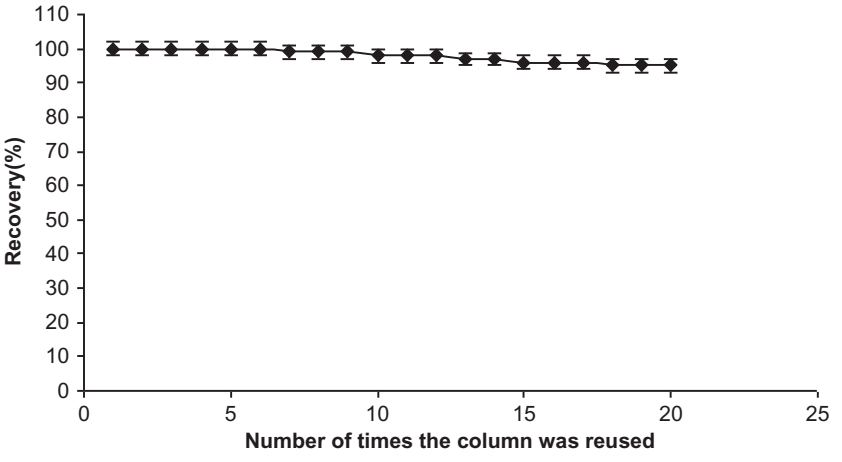

Figure 6. Number of times the column was reused (III).

La(III) at concentration of 25.0 μg L^{-1} were sorbed and desorbed several times under optimum experimental conditions. It was observed that the column could be reused with good precision and quantitative recovery (>96%) for 20 cycles (Figure 6). Therefore, it could be concluded that reusing of the column was possible because each experiment was performed as three times.

It is important to determine how much biosorbent is required to quantitatively remove a specific amount of metal ions from a solution [53]. To investigate this, 0.25 g *C. versicolor* immobilised on 1.0 g of Amberlite XAD-4 was packed in a column. Then 100 mL of solution containing 250 mg L^{-1} of La(III) was passed through the column at 2.0 mL min^{-1} and pH 6.0. The maximum capacity of biosorbent for La(III) was calculated from equation given in literature [40] as 16.5 mg of metal for a gram of resin.

The linear range of ICP-OES for La(III) was found as 50.0–2500.0 ng mL^{-1} with linear equation of $y = 63.472x + 34.032$ ($r^2 = 0.9977$) in case of developed preconcentration method was not employed. The limit of detection (LOD) and limit of quantitation (LOQ) were calculated from equation given in our other study [54] as 4.9 and 16.3 ng mL^{-1}, respectively. The correlation coefficient was found as 0.9966. The analytical performance of SPE column was improved by *C. versicolor* immobilised Amberlite XAD-4. A 50-fold preconcentration factor was found for 250.0 mL of initial volume and 5.0 mL of final volume. The calibration plot was found as $y = 2968.6x - 114.2$ ($r^2 = 0.9958$) in a linear range of 1.0–50.0 ng mL^{-1}. Linear calibration graphs were given in Figure 7. LOD and LOQ were calculated as 0.27 and 0.90 ng mL^{-1}, respectively. Ratio of three times of standard deviation to slope ratio was employed to calculate LOD, ten times to ratio was accepted as LOQ. 1.0 ng mL^{-1} of La(III) solution was subjected to SPE procedure 10 times. The relative standard deviation (RSD) was found as 6.7%. 46.8 fold sensitivity improvements were found from slope ratio of linear calibration plot of preconcentration method to direct ICP-OES measurement.

The accuracy of our method was validated through the analysis of certified reference materials of tea and spinach. La(III) concentrations were found as 0.23 ± 0.03 and 0.33 ± 0.01 μg g^{-1}, while certified values were 0.25 ± 0.02 and 0.35 ± 0.04 μg g^{-1}, both of which were comparable. It could be concluded that results were agreed with certified values by considering the standard deviations. By considering the total analysis time per sample, the developed method was also applied at 3.0 mL min^{-1} of sample flow rate. For this purpose certified reference materials were digested and subjected to SPE procedure at 3.0 mL min^{-1} of

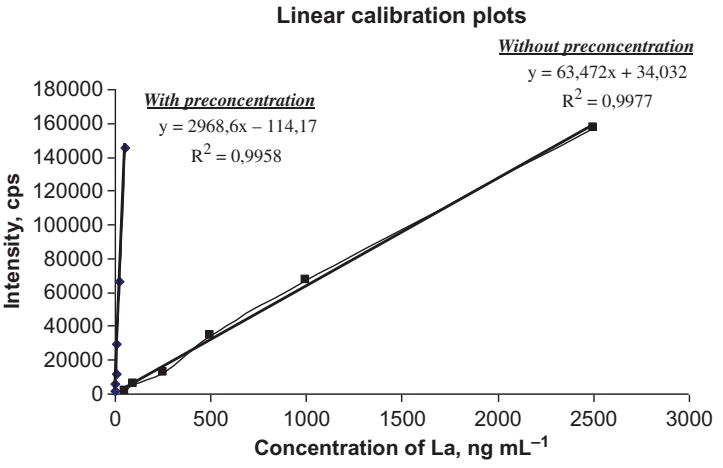

Figure 7. Linear calibration plots for La in cases of with and without preconcentration.

sample flow rate. La(III) concentrations were found as 0.23 ± 0.04 and 0.33 ± 0.05 μg g^{-1}, respectively for tea and spinach samples. It could be concluded that the method also successfully applied to samples in shorter times without loss in accuracy.

Our method was applied to determine La(III) concentration in water samples. For this purpose, tap water samples from Siirt city and water from Tigris River were applied to solid-phase extraction procedure. The concentration of La(III) in these samples were found lower than LOD. Subsequently, a known concentration of La(III) was spiked to the samples. The spiked amounts of La(III) were recovered quantitatively. The results are presented in Table 4. It should be noted that highly salt matrix of samples as well as organic compounds could affect the recovery values. However, results were in the analytical ranges. Variations in recovery values were not poorer than 5% for all spiking experiments. The higher results for CRMs were attributed to decomposition of organic matrix components and reduce and interaction with C. versicolor immobilised on Amberlite XAD-4 surface in SPE.

LOD was found as 0.31 ng mL^{-1} for La(III) by SPE method coupled with ICP-OES [35]. Calix [4]arene-o-vanillinsemicarbazone immobilised on a polymeric matrix was used as solid-phase sorbent. La(III) concentration in solution was determined by ICP-OES. LOD was found

Table 4. The results for the addition-recovery tests for the La in real water samples.

	Tap water			River water		
Spiked (ng mL^{-1})	Found (ng mL^{-1})	RSD (%)	Recovery (%)	Found (ng mL^{-1})	RSD (%)	Recovery (%)
–	<LOD[1]	–	–	<LOD	–	–
1.0	0.94 ± 0.04	4.3	94	0.95 ± 0.05	5.3	95
5.0	4.7 ± 0.2	4.3	94	4.8 ± 0.3	6.3	96
10.0	9.8 ± 0.3	3.1	98	9.7 ± 0.5	5.2	97
15.0	14.4 ± 0.3	2.1	96	14.6 ± 0.5	3.4	97
20.0	19.8 ± 0.5	2.5	99	19.4 ± 0.8	4.1	97
25.0	24.3 ± 0.7	2.9	97	24.1 ± 1.4	5.8	96

Note: <LOD: under detection limit.

as 3.05 ng mL^{-1} [18]. 1-Phenyl-3-methyl-4-benzoylpyrazol-5-one was prepared and used for the preconcentration of REE, including La(III), in water samples prior to its determination by ICP-OES. LOD was found as 0.1 ng mL^{-1} [19]. La(III) was determined in geological samples by ICP-OES with on line iron separation using flow injection (FI) with an ultrasonic nebulisation system. The anion exchange separation method of a hydrochloric system was applied to the separation of REEs from iron. The system was found to have a detection limit of 0.30 μg L^{-1} for La(III) [55]. N-phenyl-(1,2-methanofullerene C60)61-formohydroxamic acid was used for the complexation with La and Ce and their liquid–liquid extraction. LOD was reported as 0.5 ng mL^{-1} for La(III) [16].

Thus, it is evident that our method gave sufficient LOD when compared with literature. In addition, the use of chemical ligands for complexation was avoided by using *C. versicolor* as biosorbent. It could be concluded that developed method had satisfactory analytical characteristics to literatures as well as its cheaper nature. Another advantage of the method was selectivity to La(III) while it showed lower affinity to other REEs; Th(IV), U(IV) and Ce(III could be together found with La(III). Repeatable use of same column showed the applicability of its with economically and environmental friendly. By considering the three times application of all experiments ($n = 3$), it could be concluded that same column could be used up to 60 times.

4. Conclusion

Amberlite XAD-4 was modified with *C. versicolor* and used as biosorbent for the preconcentration of REEs. A mixture of La(III), Th(IV), U(IV) and Ce(III) was subjected to SPE procedure. The results suggested that the SPE column was selective for La(III). Parameters such as flow rate of solution, amount of resin and biosorbent and volume of sample solution were investigated. The effects of possible interferences by some ions were also evaluated. The accuracy of the SPE method was validated through the analysis of certified reference samples of tea (NCS ZC-73014) and spinach (NCS ZC-73013). The results of both were in agreement. Lastly, our method was applied to natural water samples with satisfactory results.

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