Magnetic solid-phase extraction based on *Coriolus versicolor*-immobilized γ-Fe$_2$O$_3$ nanoparticles for preconcentration and determination of Al(III) in water and food samples

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Abstract: A method for preconcentration of Al(III) prior to its determination by inductively coupled plasma-optical emission spectrometry (ICP-OES) was developed because the sensitivity of ICP-OES is insufficient for trace-level measurement of Al(III). The method is based on the use of *Coriolus versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles as a solid phase sorbent. The best experimental conditions were found as pH 6.0, 2.0 mL/min flow rate, 100 mg amount of *C. versicolor* on 150 mg of γ-Fe$_2$O$_3$ nanoparticles, and 500 mL of sample volume. The Al(III) absorbed on biosorbent was eluted with 5.0 mL of 1.0 mol/L HCl. Limit of detection, limit of quantitation, linear range, correlation coefficient, relative standard deviation, and preconcentration factor were achieved as 0.03 ng/mL, 0.11 ng/mL, 0.2 to 20 ng/mL, 0.9994, 3%, and 100, respectively. Al(III) was preconcentrated in different water and food samples after successful results were achieved in the case of certified reference samples.

Key words: Aluminum, food, preconcentration, biosorbent, magnetic solid phase extraction, ICP-OES

1. Introduction

As a nonessential element, aluminum (Al) is the third most abundant element in the earth's crust and is present in air, water, and soil [1]. It has been used in automotive and aerospace industries, the food industry, cooking utensils, etc. [2,3]. It was highlighted that a great abundance of this element can increase the risk of exposure and related health issues in humans [4]. Al-containing medicines, drinking waters, and foods are known as major sources for Al exposure [5]. The World Health Organization (WHO) regulated the maximum allowable content of Al in drinking water as 0.2 mg/L [6]. This element may accumulate in the brain, bone, liver, and kidneys. It has a link with renal osteodystrophy, Alzheimer and Parkinson diseases [5–7], Gulf War syndrome [8], and amyotrophic lateral sclerosis [9]. These are probably the result of a combination of some mechanisms, including induction of apoptosis, neuronal damage, neuroglia inflammatory reaction, and oxidative brain injury [10].

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Considering its high abundance and ubiquitous distribution, Al can be accepted as an environmental and industrial pollutant. From this perspective, routine monitoring of Al concentration in environmental and food samples is a major concern in analytical and environmental chemistry. The complexation before spectrofluorimetric determination [2], deep eutectic solvent-based microextraction method before electrothermal atomic absorption spectrometry (ET-AAS) [3], vortex-assisted ionic liquid-based dispersive liquid-liquid microextraction prior to atomic absorption spectrometry (AAS) [11], multivariate optimization of dual-bed solid phase extraction (SPE) prior to ICP-OES [12], use of 3,5,7,2′-4′ pentahydroxy flavones as a complexing reagent, cloud point extraction before spectrofluorimetric determination [7], SPE before flame atomic absorption spectrometry (FAAS) [5], SPE before ICP-OES [13], and solidified floating organic drop microextraction before orthogonal signal correction-partial least squares calibration method by spectrophotometry [14] have been used for the preconcentration of Al for routine monitoring.

Researchers have developed different promising and effective sorbents such as activated carbon, nanocomposites, mesoporous carbon, metal-organic frameworks, biopolymers, and biomaterials based on microorganisms because of their economic advantages and environmentally sensitive properties [15–19]. *Coriolus versicolor* is one of the most commonly applied wood-rotting fungi due to its different biologically active components and cell wall structures. *C. versicolor* also can be widely found in the natural environment. For these reasons, *C. versicolor* was selected as a sorbent.

The aim of this paper is to develop a new, simple method for the sensitive monitoring of Al(III) in real samples after preconcentration on *C. versicolor*-immobilized γ-Fe_2O_3 magnetic nanoparticles prior to its determination using ICP-OES. Experimental parameters were investigated in details. The recommended method was verified by analyzing certified reference materials.

2. Materials and methods

2.1. Chemicals and instrumentation

Stock solutions of 1000 μg/mL Al(III) in 5% HCl were ordered from High-Purity Standards (Charleston, SC, USA). HNO_3 (65%) and H_2O_2 (35%) (Merck, Darmstadt, Germany), NIST 1643e simulated fresh water (Gaithersburg, MD, USA), NIST 1568B rice flour (Gaithersburg, MD, USA), EU-L-2 wastewater (SCP Science, Quebec, Canada), and NWTM-15 spiked/fortified water (Techlab, France) were available in the laboratory. They were used to check the accuracy of the recommended method. Double-distilled water was used throughout the experiments. A temperature- and pressure-controlled analytical microwave oven was used to digest the samples (Berghof MWS3, Germany). pH was measured by using a SevenExcellence pH meter (Mettler Toledo, USA).

Concentrations of Al(III) was measured by ICP-OES (PerkinElmer, Shelton, CT, USA) at 396.153 nm. A polyethylene filtration column (1.0 cm × 10.0 cm) was used for SPE experiments.

A 50-mL solution containing 1000 μg/mL Al(III) was mixed with *C. versicolor*-immobilized γ-Fe_2O_3 nanoparticles for 2 h at 25 °C at 120 rpm using a shaker. Then Al(III)-loaded biosorbent was separated using a magnet and dried at 60 °C for 24 h before Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) investigations. Surface functionalities was investigated using FT-IR (Spectrum 400, PerkinElmer), SEM, and EDX (Zeiss LEO 440).

A 50-mL solution containing 20.0 ng/mL Al(III) was prepared and pH was adjusted to the desired value. This was passed through a *C. versicolor*-immobilized γ-Fe_2O_3 magnetic nanoparticle-loaded column using a

peristaltic pump. Then 10.0 mL of pure water was passed through the SPE column to control the performance of the extraction process. Biosorbed Al(III) ions were then eluted by 5.0 mL of 1.0 mol/L HCl. The concentration of Al(III) in eluate was analyzed by ICP-OES.

2.2. Preparation of column

C. versicolor was collected from Sulun village, Afyonkarahisar, Turkey. It was used as the biosorbent in this study. Procedures for preparation of biological materials were detailed in our previous study [15].

The γ-Fe_2O_3 nanoparticles (< 10 nm) were synthesized according to the method proposed by Kılınç [20]. Dried *C. versicolor* (100 mg) was added to the suspension containing γ-Fe_2O_3 nanoparticles. The suspension was refluxed at 65 °C for 30 min. After that, the suspension was filtrated and black particles were washed with double-pure water until the pH of the washing solution was 7.0. They were dried at 90 °C for 24 h. Loaded *C. versicolor*-immobilized γ-Fe_2O_3 magnetic nanoparticles (100 mg) were weighed using a precision scale. *C. versicolor*-immobilized γ-Fe_2O_3 magnetic nanoparticles as described above were added to 5.0 mL of distilled water and mixed until homogeneous. Before use, the polyethylene filtration column was washed with 1.0 mol/L HCl and pure water, respectively. After that, magnetized biosorbent was slowly added to the column.

The recommended method was applied to real samples for the preconcentration of Al(III). Detailed information on sample preparation was given in our recent study [21]. Samples of 5.0 g of black tea (powdered), baby biscuit (powdered), mushroom (dried and powdered), tomato (dried and powdered), rice (dried and powdered), pepper (dried and powdered), and yogurt were digested by a microwave oven. Then 5.0 mL of HNO_3:HCl (1:1, v/v) was added to samples, and the mixture was heated on a hot plate. The mixture was evaporated until dryness, and 6.0 mL of HNO_3:HCl:H_2O_2 (1:1:0.2, v/v/v) was added before transfer to a microwave vessel. The mixture was heated to 170 °C by microwave and was left for 5.0 min. When the temperature reached 200 °C, the sample was kept at this temperature for another 1 min. The temperature was reduced to 100 ° C and the mixture was left for 20 min. After digestion, the final volume was made up to 50.0 mL. Before the SPE procedure, the pH of the sample was adjusted to the desired value. The SPE procedure was directly applied to a 100-mL portion of NWTM-15 spiked/fortified water and NIST 1643e simulated fresh water after pH adjustment. A 5.0-g portion of certified reference NIST 1568B rice flour was digested according to the same method explained above.

3. Results and discussion

3.1. Surface characterization

SEM images, EDX analyses, and FT-IR spectra are comparatively presented in Figures 1, 2, and 3, respectively. From the SEM images in Figures 1a and 1b, it can be concluded that *C. versicolor*-immobilized γ-Fe_2O_3 magnetic nanoparticles presented nearly homogeneous surfaces. This may be attributed to the reusability of the same functional structure towards the targeted metal ion. In Figure 2a, an Al(III) peak is not observed, whereas in Figure 2b, an Al(III) peak is detected after immobilization of Al(III). This is evidence that Al(III) can bind the prepared nanomaterial. FT-IR presents details on surface functionalities. From Figure 3a, the broad peak at 3263 cm^{-1} can arise from the –OH group (stretch), 1653 cm^{-1} from conjugated ketone, 1358 cm^{-1} from aromatic secondary amine (CN stretch), and 1034 cm^{-1} from primary amine (CN stretch). After biosorption of Al(III), no significant differences (except shifting on peaks and a peak at 3263 cm^{-1}) were observed for *C. versicolor*-immobilized γ-Fe_2O_3 magnetic nanoparticles (Figure 3b). Al(III) could interact

with the surface hydroxyl group of *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles and the peak at 3263 cm^{-1} disappeared.
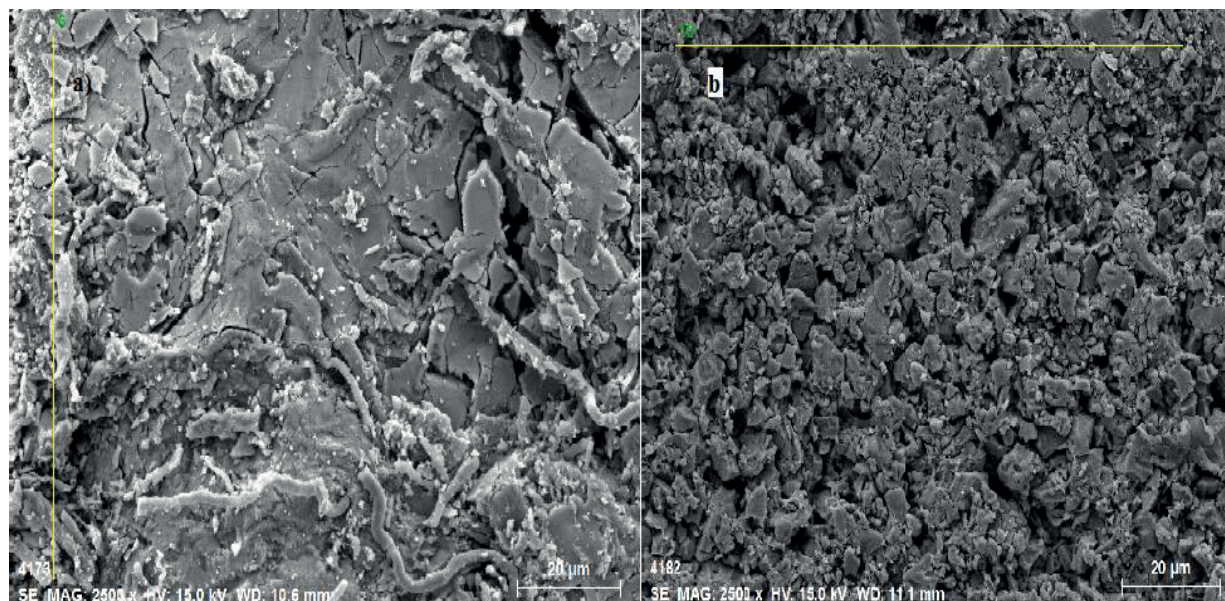

Figure 1. Comparison of SEM images of a) *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles and b) Al(III) on *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles.

3.2. Effect of initial pH

The biosorption capacity of biomass in the SPE process is greatly affected by the pH value of the aqueous solution because of differences in the biomass cell wall compositions [22]. In order to find the effect of pH of the aqueous solution on biosorption capacity, biomass-loaded γ-Fe$_2$O$_3$ magnetic nanoparticles in the pH range of 2.0–9.0 were investigated. As seen in Figure 4a, the quantitative retention values for Al(III) were observed at pH 5.0–6.0. According to the literature, it seems that the optimal pH for such studies is 3.0–6.0 [23,24]. Our results are consistent with this literature. However, to achieve high biosorption capacity, pH 6.0 was used for subsequent studies. pH 5.0 gave high recovery as quantitatively as pH 6.0 in the experimental procedure. By considering the hard-soft acid-base theory, the surface should be negative with a lower pH. By considering the conversion from Al^{3+} to AlO$_2$-, we decided to select pH 6.0 as the best acidity for the stability of the analyte and surface.

3.3. Effect of sample flow rate

The retention of a metal ion on a biomass-loaded γ-Fe$_2$O$_3$ magnetic nanoparticle in a column relies on the flow rate of the sample solution. It is a significant step that controls the time of analysis [25]. Hence, the influence of the flow rate of the sample solution on the recovery of the Al(III) was tested at flow rates from 1.0 mL/min to 6.0 mL/min. It can be seen from Figure 4b that the quantitative recovery of Al(III) ions was acquired at sample flow rate of 2.0 mL/min. At higher flow rates the recoveries were decreased due to the inadequate contact of analyte ions and biosorbent. Similar results for different biomasses and metal ions were reported [26,27]. For this reason, all subsequent experiments were implemented at 2.0 mL/min flow rate for the sample solution.
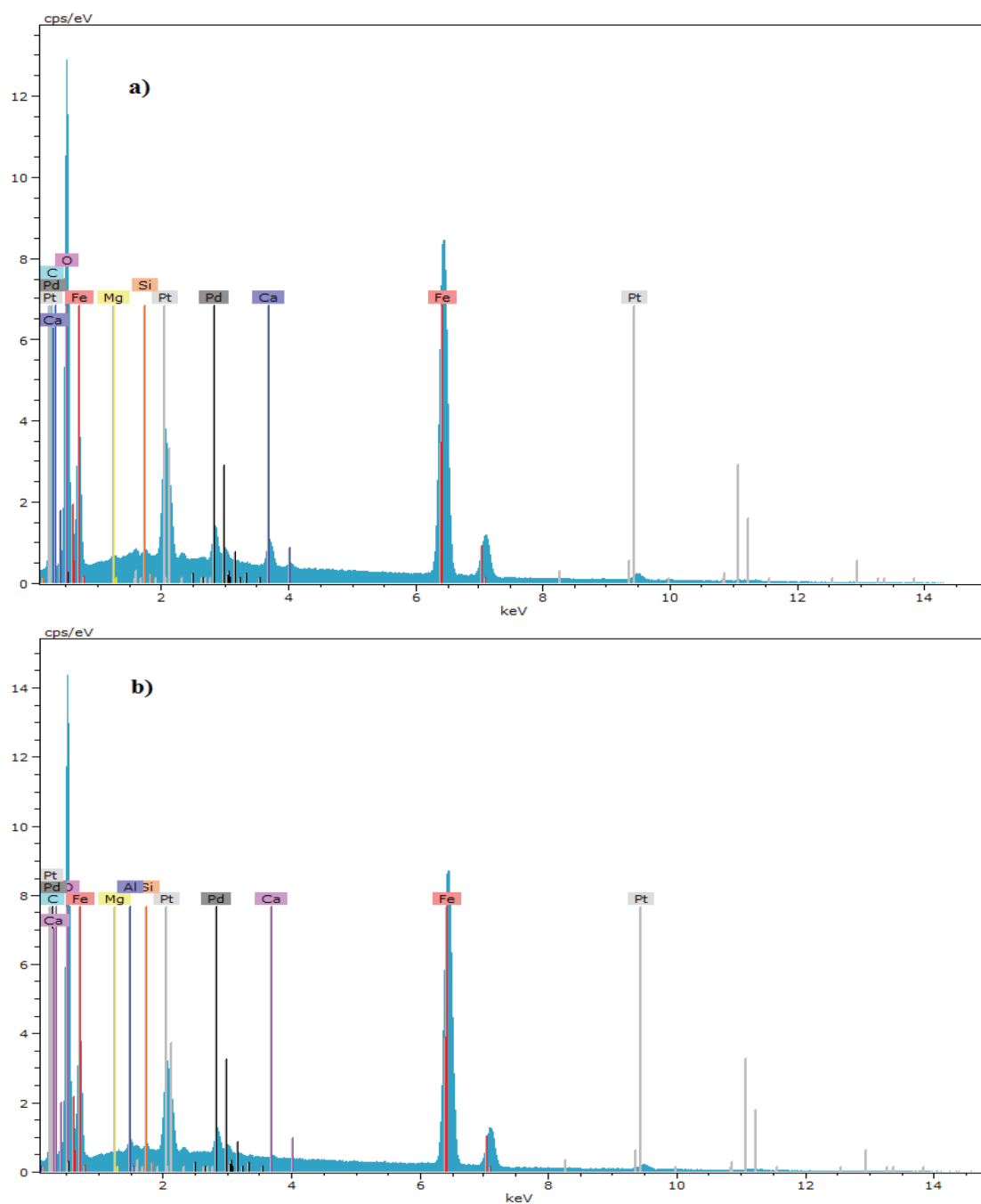
Figure 2. Comparison of EDX results of a) *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles and b) Al(III) on *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles.

3.4. Effect of amount of biomass

The effect of the amount of biomass for the biosorption studies of metal ions should be delimitated and optimized. An increase in the biomass ratio brings about more surface area and binding sites; therefore, the uptake of the metal ions increases, too [28]. The influence of the amount of *C. versicolor* as a biosorbent was tested at different amounts from 50 to 250 mg. Figure 4c represents the effect of biosorbent amount on the recovery of Al(III).
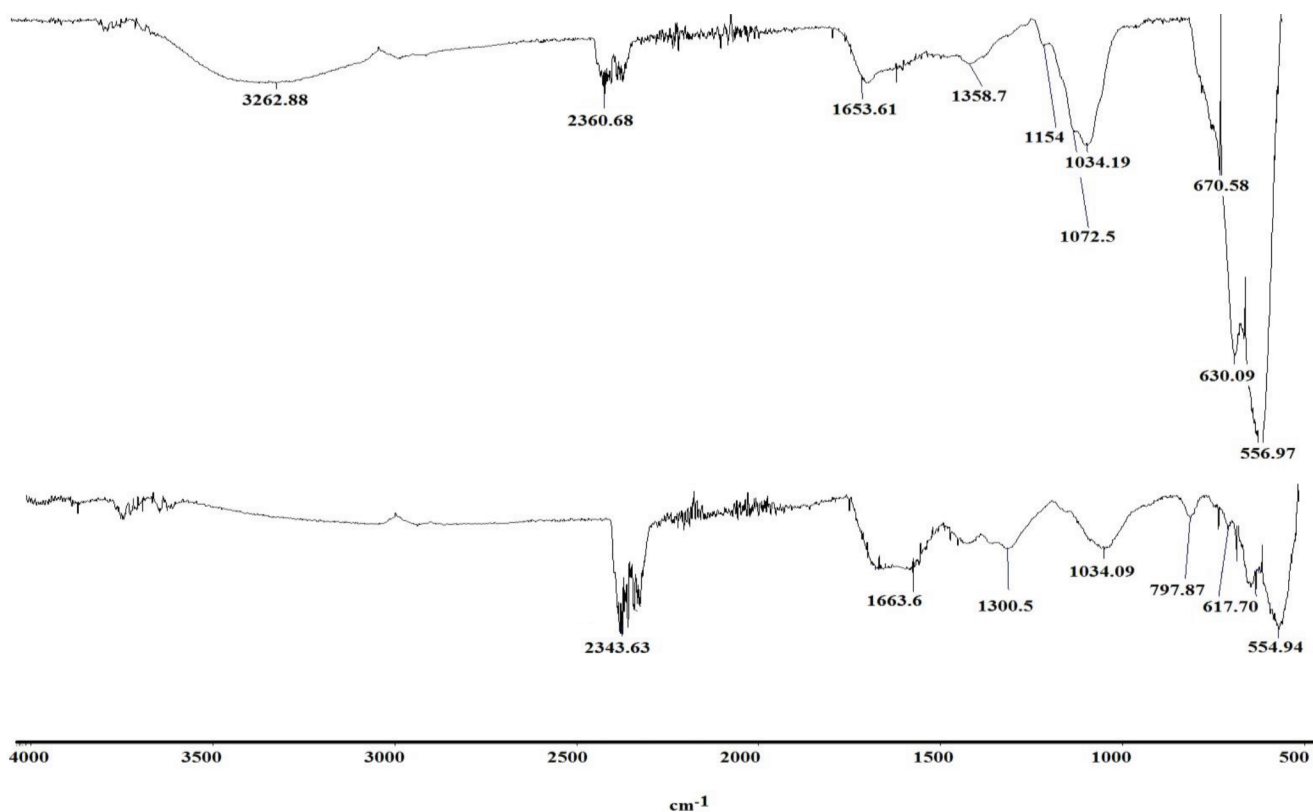
Figure 3. Comparison of FT-IR spectra of a) *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles and b) Al(III) on *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles.

The recovery of the analyte ion increased from 72.3% to 100.0% when the amount of biosorbent was increased from 50.0 mg to 100.0 mg. Therefore, further studies were conducted at 100 mg amount of *C. versicolor* as a biosorbent.

3.5. Effect of amount of γ-Fe$_2$O$_3$ magnetic nanoparticles

The support materials need to have some physical properties like low particle size, sufficient pore size, and high surface area [20]. Under optimum conditions, the effect of the amount of γ-Fe$_2$O$_3$ nanoparticles on the recovery of Al(III) was examined by changing the γ-Fe$_2$O$_3$ magnetic nanoparticle amounts from 50.0 to 300.0 mg. The result is given in Figure 4d. Obviously, the quantitative recovery of Al(III) ions was reached at 150 mg. Thus, 150 mg amount of γ-Fe$_2$O$_3$ magnetic nanoparticles was used for further studies.

3.6. Effect of the eluent

The choice of eluent is an important factor for preventing the degradation of the biosorbent in the SPE process [29]. In order to determine the most suitable eluent type, volume, and concentration to desorb Al(III) ions from the biosorbent surface, various concentrations and volumes of HCl and HNO$_3$ were used. As can be seen from Table 1, when the volume (from 3.0 to 5.0 mL) and concentration (from 0.5 to 1.0 mol/L) of HCl and HNO$_3$ increased, the elution degrees increased, too. This distinctly showed that 5.0 mL of 1.0 mol/L HCl desorbed the Al(III) ions from the biosorbent surface by 99.4%. Similar results were previously reported by Mendil et al. and Türker et al. [29,30]. For further experiments, 5.0 mL of 1.0 mol/L HCl was used as the eluent.
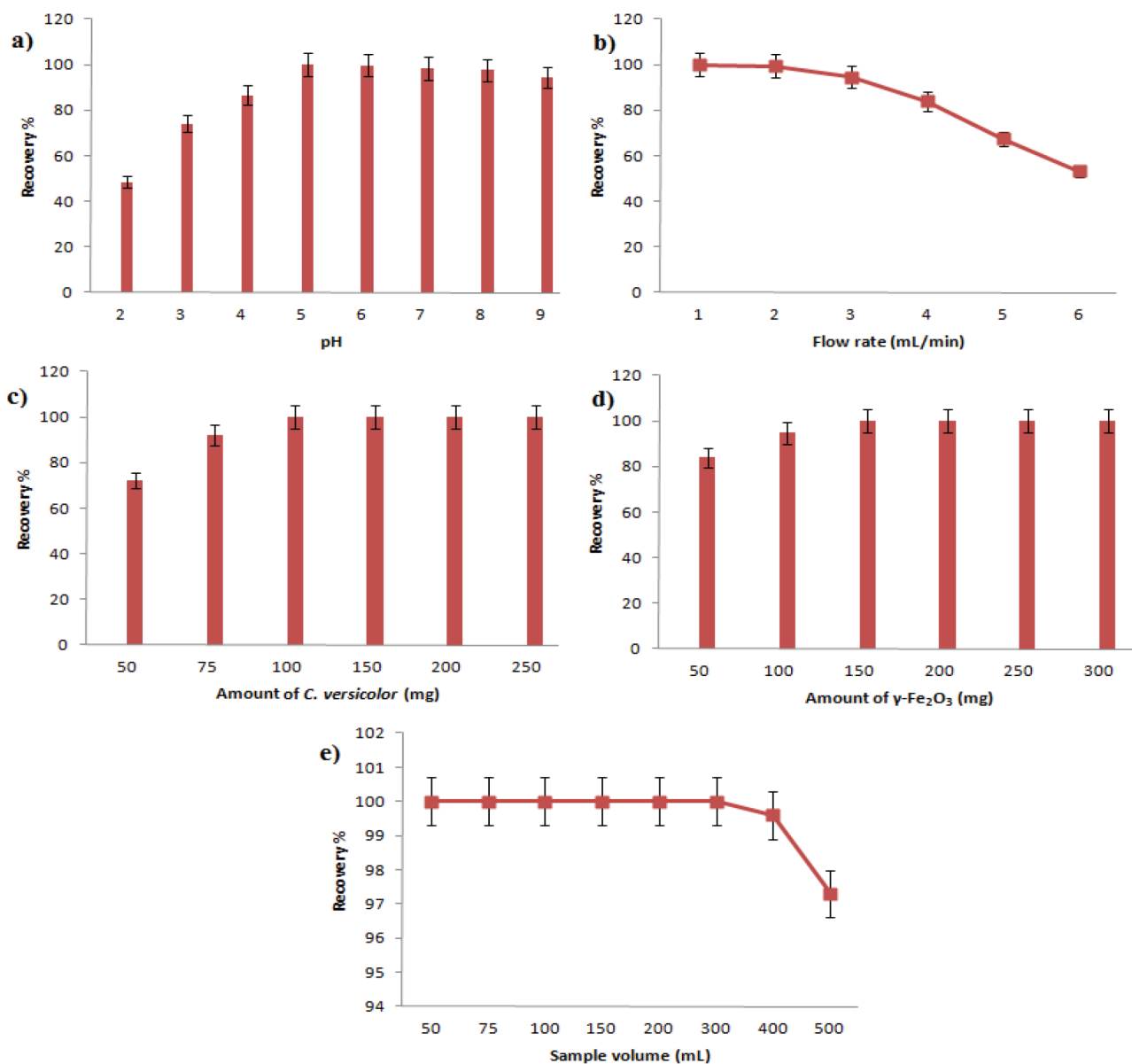
Figure 4. Influence of the a) pH, b) sample flow rate of initial solution, c) amount of biomass, d) amount of γ -Fe$_2$O$_3$ nanoparticles, and e) sample volume on the recovery of Al(III).

3.7. Effect of the sample volume

Generally, the concentrations of metal ions are at trace and ultratrace levels in real samples such as foods, water, biological materials, and environmental samples [31]. In order to optimize the sample volume for the recovery of Al(III) ions in the range of 50–500 mL, sample solutions were passed through the SPE column. The results in Figure 4e indicate that Al(III) ions could be recovered quantitatively when up to 500 mL of the sample solution was used. Accordingly, a PF of 100 was reached when a volume of 500 mL of the sample was eluted from the magnetic solid phase extraction (MSPE) column with 5.0 mL of 1.0 mol/L HCl. The same PF was reported by Ozdemir et al. [32].

Table 1. Effect of eluent type, volume, and concentration on recoveries of Al(III) by using *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles.

Type of elution solution	Volume (mL)	Concentration (mol/L)	Recovery %
HCl	3	0.5	84.1 ± 0.6
	5	0.5	90.6 ± 1.2
	3	1	92.8 ± 0.9
	5	1	99.4 ± 0.5
HNO$_3$	3	0.5	81.6 ± 1.4
	5	0.5	88.7 ± 1.1
	3	1	90.6 ± 0.9
	5	1	95.1 ± 0.4

3.8. Interference studies

One of the main problems during the determination of metal ion concentrations by atomic spectrometric techniques could be the interference from the matrix [33]. The influence of some interfering ions on the recovery of Al(III) was examined under the best conditions. These ions and their results are given in Table 2. The results showed that the studied ions did not interfere with the determination of analyte ions.

Table 2. Influence of interference studies on recoveries of Al(III) by using *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles.

Ion	Interference to metal ion ratio	Recovery[a] %
Na(I)	2000	98.5 ± 0.7
K(I)	2000	99.4 ± 1.2
Ca(II)	100	98.3 ± 1.3
Pb(II)	50	95.5 ± 1.6
Cr(III)	25	94.9 ± 3.5
Fe(III)	25	96.0 ± 2.5
As(III)	25	95.5 ± 1.7
Mg(II)	25	98.7 ± 1.1
Fe(II)	25	95.8 ± 1.0
Cd(II)	5	96.3 ± 1.5
Co(II)	5	95.9 ± 1.4
Ni(II)	5	97.1 ± 1.4
Zn(II)	5	98.6±0.9

[a] Concentrations of the ions are 100 μg/L.

3.9. Effect of column recyclability

The recyclability of the column is an economically important factor in the SPE process. In order to assess the recyclability of the column containing *C. versicolor*-immobilized γ-Fe$_2$O$_3$ magnetic nanoparticles, it was investigated by monitoring until the recovery values for the analyte ions were lower than 95%. After the use of the MSPE column for 40 cycles, the recovery of Al(III) was found as 96.2%.

3.10. Analytical application

Analytical figures of merit of the developed method were investigated under the best experimental conditions. Limit of detection (LOD), limit of quantitation (LOQ), correlation coefficient, linear range, RSD, and PF (determined as the ratio of initial sample volume to final volume) were determined as 0.03 ng/mL, 0.11 ng/mL, 0.9994, 0.2–20 ng/mL, 3%, and 100 (initial volume was 500 mL, final volume was 5.0 mL), respectively. The biosorption capacity of *C. versicolor*-immobilized γ-Fe_2O_3 magnetic nanoparticles for Al(III) was investigated under the best experimental conditions and it was found as 36.9 mg/g. Analytical characteristics of the methods for preconcentration of Al(III) are compared in Table 3 in detail. It can be said that the developed method has advantages such as low LOD, wider linear range, and reusability of the same column.

Table 3. Comparison of analytical characteristics of different methods for the preconcentration of Al(III).

Method	LOD, ng/mL	Linear range, ng/mL	PF	Ref.
Chelation of Al(III) and measurement by fluorimetry	3.02	-	-	[2]
Deep eutectic solvent-based ultrasound-assisted Liquid-phase microextraction before ET-AAS measurement	0.032	0.1 to 20	50	[3]
Vortex-assisted ionic liquid-based dispersive liquid-liquid microextraction before FAAS measurement	0.02	0.07 to 100	95	[11]
Dual-bed resin SPE before ICP-OES measurement	0.16	-	-	[12]
Solidified floating organic drop microextraction before spectrophotometric measurement	0.17	1 to 32	96	[14]
SPE on *C. versicolor*-immobilized γ-Fe_2O_3 magnetic nanoparticles	0.03	0.2 to 20	100	This study

Al(III) concentrations were determined in NWTM-15 spiked/fortified water as 21.4 $\pm$ 1.1 ng/mL while it was certified as 21.7 ng/mL, in EU-L-2 52 waste water as 51.3 $\pm$ 3.7 ng/mL while it was certified as 52 ng/mL, in NIST 1643e simulated fresh water as 139.4 $\pm$ 7.7 ng/mL while it was certified as 141.8 $\pm$ 8.6 ng/mL, and in NIST 1568B rice flour as 4.20 $\pm$ 0.32 μg/g while it was certified as 4.21 μg/g. Results were evaluated with the Student t-test to check whether there was a significant difference or not. The t-values for the above-mentioned results were found to be lower than the t_{critic} value at 99% confidence interval (t_{critic} = 31.82). Therefore, it could be concluded that there were no significant differences between the certified and found values. Satisfactory results were obtained from the analysis of the certified materials and then concentrations of Al(III) in real samples were determined by ICP-OES. Applications of the presented method were performed for some food samples. The results are presented in Table 4.

3.11. Conclusions

This paper proposes a novel MSPE method for the preconcentration of Al(III) before its determination by ICP-OES by using *C. versicolor*-immobilized γ-Fe_2O_3 magnetic nanoparticles as a magnetized biosorbent. The main advantages of the recommended method were summarized as no need for a toxic organic solvent, low cost, rapidity, simplicity, reliability, low LOD, and reusability of the same column for up to 40 cycles. In addition, the method had good tolerance towards many potentially interfering ions. As a result, the recommended method

Table 4. Al(III) concentrations in water and food samples measured by ICP-OES after the developed method was applied (mean $\pm$ standard deviation, n = 3).

Sample	μg/g
Black tea	2.0 ± 0.1
Baby biscuit	0.8 ± 0.05
Yogurt	4.7 ± 0.5
Tap water	0.4 ± 0.02
Mushroom	3.3 ± 0.5
Tomato	0.18 ± 0.01
Rice	0.63 ± 0.04
Pepper	0.8 ± 0.05

can be an alternative method for preconcentration of Al(III) and it can also be applied to real samples. The major contribution of our study is a 100-fold improvement of the sensitivity of ICP-OES for ultratrace level measurements of Al(III).

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