

REMIEDIATION TREATMENT

Solid phase extraction of trace level Ag(I) using *Coriolus versicolor* immobilized magnetic nanoparticles and its determination by ICP-OES

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Abstract

In the recent past, biosorbents of biological origin such as bacteria, algae, and fungus have found a specific application in the solid phase extraction as an alternative column packing material. It is feasible to use them in the column after their immobilization onto a convenient support material. In the present work, alternative biosorbent *Coriolus versicolor* immobilized γ -Fe₂O₃ nanoparticles (NPs) were prepared for the preconcentration of trace amounts of Ag(I) in environmental samples. The surface structure of *C. versicolor* immobilized γ -Fe₂O₃ NPs were identified via the Fourier transform infrared spectroscopy, the scanning electron microscope, and the energy dispersive X-ray. Experimental parameters were investigated. The following elution with 1 mol/L HCl, Ag(I) was measured by an inductively coupled plasma optical emission spectrometer. The limit of detection, limit of quantitation, and preconcentration factor were achieved as 0.0018, 0.0062 ng/ml, and 100, respectively. The biosorption capacity of the biosorbent was found as 31.7 mg/g. In addition, γ -Fe₂O₃ NPs without *C. versicolor* were tested and the results showed that the recovery value of Ag(I) was lower than 25%. The efficiency of the method was tested through recovery measurements of certificated reference materials and high recoveries ($\geq 95\%$) with low-relative standard deviation were obtained. Additionally, it was successfully used for the quantification recovery of Ag(I) in spiked environmental samples.

KEYWORDS

biosorbent, *Coriolus versicolor*, magnetic solid phase extraction, preconcentration, silver

1 | INTRODUCTION

It is known that toxic metal ions have harmful effects on the living world because of being even toxic at trace concentrations.¹ Their biodegradability in the environment is impossible and they can accumulate in tissues if taken in by the human body. In this way, they lead to fatal complications like mental or central nerve malfunctions and give damages to other vital organs.² Trace amounts of some metals (as Fe, Cu, Mn, and Zn) are essential elements and have a diversity of metabolic functions in living organisms. Although being essential, they exhibit toxic effects if they are consumed in excessive quantities.

Likewise, some other metals (As, Pb, and Cd) are not crucial for the human, and their existence, generally being a result of pollution related or occupational exposure, is harmful to human health.^{3,4}

Silver (Ag), for example, is mainly used to make silverware, dental fillings, electronic equipment, and jewelry. Silver nanoparticles (AgNPs), on the other hand, exhibit excellent antibacterial properties, therefore they are often used in antibacterial and sterile fields such as medicine, cosmetics, and clothing.^{5,6} Due to the raising interest in AgNPs and noteworthy uses of it, considering the safety of such materials and the possible damage they give to the environment has become very necessary.^{7,8} Without doubt, it can be said that the toxicity of nanoparticles

(NPs) to various organisms emphasizes a number of research issues in the field of environmental science.⁹ In vitro studies have revealed that AgNPs cause damage to the liver, brain, and reproductive cells in mammals. Consequently, determining silver ions in different matrices accurately and precisely is very essential for analytical chemistry and the monitoring of environmental pollution. The trace amount detection of metal ions in different matrices can be done by several useful spectroscopic techniques such as atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma optical emission spectrometer (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS).¹⁰ The sensitivity of ICP-OES for some metal ions is not sufficient if the concentration is at trace and ultra-trace levels. In addition, the amount of samples limits the measurement due to interference of sample matrix components. To overcome these problems, preconcentration procedures such as solid phase extraction (SPE), ion exchange, flotation, electrochemical deposition, co-precipitation, liquid-liquid extraction, and chelating matrices are required.¹¹⁻¹³ Therefore, the sensitivity of the ICP-OES could be enhanced together with reducing the effect of matrix. By considering the low cost of ICP-OES with respect to GFAAS and ICP-MS, preconcentration of sample could be accepted as the best solution to overcome the analytical limits.

SPE, is a method currently used for the preconcentration and separation of toxic metals, providing advantages like simplicity, flexible selection of sorbents, low consumption of organic solvents, higher preconcentration factors (PFs), and the removal of potentially interfering matrices.^{14,15}

Extensive studies on magnetic iron oxide NPs have been made because of their wide variety of application in targeting and drug delivery, separation of biochemicals, ferrofluids, biological cell labeling and sorting, high-density information storage, and magnetic resonance imaging.^{16,17} Additionally, magnetic NPs were applied in analytical chemistry as a new efficient adsorbent in the SPE process for separation, preconcentration, determination, and the removal of chemical species.¹⁸ Magnetic NPs are declared as quite interesting for their ability to be easily separated from the reaction environment via an external magnetic field.¹⁹

Researchers have developed SPE procedures using promising and effective biosorbents because of their economic advantages and environmentally sensitive properties. For this purpose, biomaterial, based on microorganisms (fungi, bacteria, algae, yeast, etc.) and biopolymers (cellulose, chitin, chitosan, etc.), provide benefits in the fields of extraction, removal, sequestration, and speciation.²⁰ *Coriolus versicolor*, is one of the most popular wood-rotting fungi due to its different biologically active components and cell wall structures. *Coriolus versicolor* also can be widely found in the natural environment. In heavy metal SPE studies, there are not enough investigations using immobilized *C. versicolor*. For that reason, *C. versicolor* was selected as a biosorbent.

In this present work, preconcentrations of Ag(I) ions were examined using an alternative magnetic solid phase bio-extractor, based on the use of *C. versicolor* immobilized γ -Fe₂O₃ NPs from environmental samples. After detailed analyzes of the effects of remarkable experimental factors was done, the recommended method was validated and applied to environmental samples such as river water, tap water, wastewater, sediment, and soil samples.

2 | MATERIALS AND METHODS

2.1 | Instrumentation

The concentrations of Ag(I) were measured by ICP-OES (Optima™ 2100 DV, Perkin Elmer, Inc., Shelton, CT) at 328.068 nm under the producer's recommended instrumental operating conditions. SPE experiments were performed in a filtration column (1.0 cm × 10.0 cm), equipped with polypropylene frits. The solutions were passed through the column by the Marlow 323 peristaltic pump (Watson-Marlow, Wilmington, MA). A total of 50 ml of 1 mg/L Ag(I) solution was mixed with *C. versicolor* immobilized γ -Fe₂O₃ magnetic NPs, at 120 rpm for 120 min at 25°C using a shaker. Later, Ag(I)-loaded *C. versicolor* immobilized γ -Fe₂O₃ sorbent was separated via a magnet and dried in an oven at 60°C during 1 day before Fourier transform infrared (FT-IR), scanning electron microscope (SEM), and energy dispersive X-ray (EDX) investigations. FT-IR analyzes were applied by the Perkin-Elmer Spectrum 400 spectrometer to examine the surface characterization. The samples were coated with Au/Pd to provide conductivity (Quorum, Q150R, UK) before SEM images. SEM and EDX analysis were done under convenient magnification and increasing voltage using a Zeiss Supra55 SEM.

2.2 | Reagents and solutions

Stock solutions of Ag(I) 1,000 µg/ml were provided according to High Purity Standards, (Charleston, SC) HNO₃, H₂O₂ (Merck, Germany). Spiked/fortified water-trace elements NWTM-15, trace elements in water NIST 1643e and bush branches and leaves NCS DC 73349 were available in the laboratory and applied to control the method efficiency.

2.3 | Preparation of column

Coriolus versicolor, a mushroom of the *Basidiomycetes* class, was collected in Sülün, Afyonkarahisar, Turkey and utilized as the biomaterial. To remove contaminants, it was first cleaned with distilled water, before being dried at room temperature for 1 week. The dried *C. versicolor* was then grinded and powdered. After that, it was kept in an oven at 80°C for 24 hr until all cells were killed. In the end, *C. versicolor* was vaccinated with malt agar at 25°C for 1 day, resulting in the total absence of *C. versicolor* micelles, which meant that all these cells had completely died.

γ -Fe₂O₃ magnetic NPs were synthesized by the method explained in literature.²¹ To achieve immobilization, 100 mg of the dried *C. versicolor* was added to the aqueous suspension, which contained γ -Fe₂O₃ NPs and flowed back at 65°C for 60 min. Following the filtration, the black precipitate was washed with pure water to be neutralized before being dried at 90°C for 24 hr. Hundred milligram of *C. versicolor* immobilized γ -Fe₂O₃ NPs were weighed with a precision scale before they were added to 5 ml of purified water and mixed for 120 min, until becoming homogeneous in the magnetic stirrer. The column was completely washed with 1 mol/L HCl and purified water, commonly before usage. Afterward, the mixture was slowly added to a 1.0 cm x 10.0 cm size of polyethylene column.

2.4 | Sampling

The recommended method applied to tap water, Tigris river water and sediment, waste water, and soil samples (soil 1 from Hevsel Gardens, Diyarbakır-Turkey; soil 2 from Siirt University campus Siirt-Turkey) for the preconcentration of Ag(I) in accordance with the detailed description in the literature.²² The soil samples were collected from the sample locations using clean stainless steel material. They were collected at 15 cm depth around the sample area; it was thoroughly mixed and transferred into clean and labeled polythene bags for onward analysis in the laboratory. Tap water samples were obtained from Diyarbakır city, Turkey after 10 min flushing and sampled in polyethylene containers. For water sampling, the polyethylene bottles were rinsed at least three times before sampling. River water samples from 10 cm depth (about 0.25 L for each one) were taken at each sampling site and placed into a 500 ml polyethylene bottle, well closed to avoid contamination. A counterparts of sediment samples were collected from 0 to 10 cm using grab sampler, and immediately transferred to the laboratory for analysis to avoid changes of the redox potential, pH, and pore water. In the laboratory, subsediment samples were air-dried ($23 \pm 1^\circ\text{C}$) and passed through a 2 mm sieve to obtain the fine fraction.

3 | RESULTS AND DISCUSSION

3.1 | Surface characterization

FT-IR spectroscopy, SEM, and EDX were used for the characterization of the sorbent surface. The obtained results from characterization studies are comparatively presented in Figure 1. The SEM images indicated that *C. versicolor* immobilized $\gamma\text{-Fe}_2\text{O}_3$ NPs surface is nearly homogenous. This may contribute to the reusability of the same functional structure toward Ag(I) ions. To confirm the uptake of Ag(I) by *C. versicolor* immobilized $\gamma\text{-Fe}_2\text{O}_3$ NPs, EDX analysis was done. Figure 1a,b shows the typical EDX pattern for *C. versicolor* immobilized $\gamma\text{-Fe}_2\text{O}_3$ NPs, before and after the biosorption of Ag(I). The EDX pattern (Figure 1a) for the unloaded *C. versicolor* immobilized $\gamma\text{-Fe}_2\text{O}_3$ NPs, did not show the characteristic signal of Ag(I), whereas for Ag(I)-loaded *C. versicolor* immobilized $\gamma\text{-Fe}_2\text{O}_3$ NPs (Figure 1b) a clear signal of the presence of Ag(I) was observed. This is evidence that Ag(I) bounded the prepared sorbent. The pattern of sorption of Ag(I) onto *C. versicolor* immobilized $\gamma\text{-Fe}_2\text{O}_3$ NPs were attributable to the active groups and bonds present on them. For details on surface functionalities, FT-IR spectroscopy was applied. As can be shown in Figure 1a, broad peak at $3,262\text{ cm}^{-1}$ was assigned to the stretching of O—H group. The peak at $1,653\text{ cm}^{-1}$ can arise from conjugated ketone. The peaks observed at $1,358$ and $1,034\text{ cm}^{-1}$ were stretching vibrations of C—N bonds of aromatic secondary amine and primary amine, respectively. Before and after the sorption of Ag(I) onto *C. versicolor* immobilized $\gamma\text{-Fe}_2\text{O}_3$ NPs, there were no major differences observed (except shifting on peaks $1,653\text{--}1,640\text{ cm}^{-1}$, $1,358\text{--}1,339\text{ cm}^{-1}$, $1,072\text{--}1,030\text{ cm}^{-1}$). Considering the electrostatic interactions between metal cation and surface functionality, shifting

could be attributed to complexation. Shifting is clearly attributed to binding of Ag(I) onto *C. versicolor* immobilized $\gamma\text{-Fe}_2\text{O}_3$ NPs. Because the properties of bond change after the interaction with metal cations and this leads to shifting on the peak in the FT-IR spectrum.

Additionally, the soft acidic behavior of Ag(I) confirms the possibility of CN^- groups that act as a soft base from the hard and soft acid and base theory.²³ It is possible to discuss that the following reaction could be effective during complexation with $K_{\text{formation}} = 5.3 \times 10^{18}$.



3.2 | Effect of initial pH

The pH value of the aqueous solution is recognized as the most critical experimental parameter affecting the adsorption and preconcentration process in the SPE studies.²³ Therefore, the role of hydrogen ion concentration was investigated and optimized on the recovery value of Ag(I). In accordance with this purpose, the pH value effect was examined in the range from 2.0 to 9.0. The recovery values of the Ag(I) are presented in Figure 2. According to these results, it was observed that the quantitative recovery of Ag(I) was achieved at pH:6.0. These results were in good consistent with findings of Baytak and Turker²⁴ and Karimi et al.²⁵ Hence, all subsequent works were performed at pH: 6.0. In addition, $\gamma\text{-Fe}_2\text{O}_3$ NPs without *C. versicolor* were tested and the results showed that the recovery value of Ag(I) was lower than 25%. So, we confirmed the usability of the *C. versicolor* as biological material that improves the adsorption ability.

3.3 | Effect of sample flow rate

In the SPE studies, the flow rate of the aqueous sample solution directly influences the retention of the analytes on an adsorbent, being directly related to the duration of the analysis. It is preferred to elute the analytes from the column with quantitative recovery within short time. In this study, the influence of the sample solutions flow rate on the biosorption of Ag(I) was analyzed in the range of 1.0–6.0 ml/min. Figure 3 shows clearly that the quantitative recoveries of Ag(I) were attained within a sample flow rate of 1.0 ml/min (100%) and 2.0 ml/min (98.1%). Short-term processes are a very important criterion in biotechnology studies. In this study, the recovery efficiency at a flow rate of 2.0 ml/min was analytically quantitative. Considering the shortness of the processing time, I decided to use the sample flow rate of 2.0 ml/min, which is compatible with the results obtained by Vellaichamy and Palanivelu.²⁶ Thus, in all following studies flow rates for sample solutions were maintained at 2.0 ml/min.

3.4 | Effect of the biomass amount

The amount of biosorbents in biosorption studies is one of the important factors in attaining quantitative recovery of the toxic metal. It is clear that the increase in the quantity of biomass raises the surface

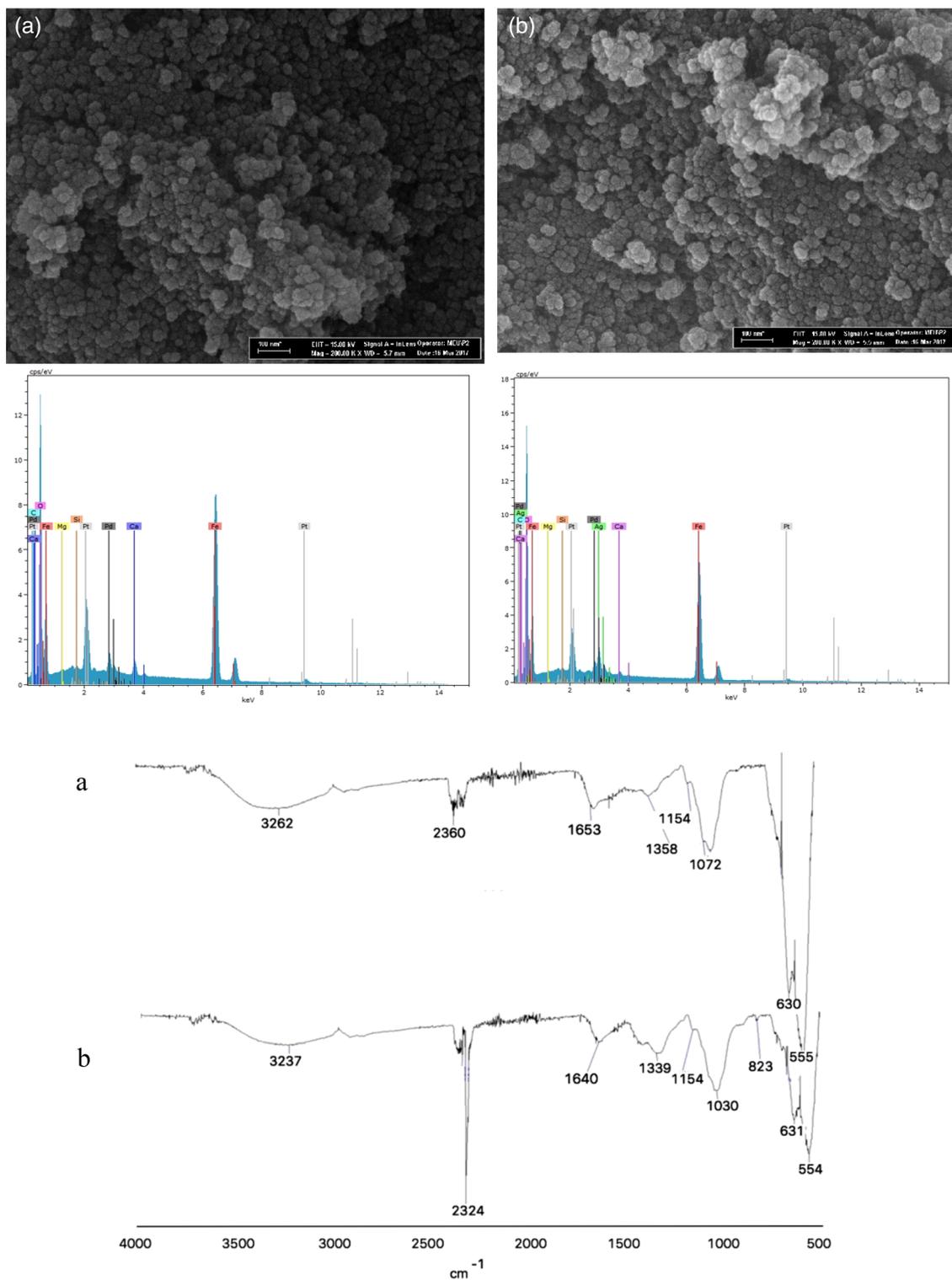


FIGURE 1 SEM, EDX, and FT-IR comparisons of (a) *C. versicolor* immobilized γ -Fe₂O₃ nanoparticles, (b) Ag(I) on *C. versicolor* immobilized γ -Fe₂O₃ nanoparticles. FT-IR, Fourier transform infrared; EDX, energy dispersive X-ray; SEM, scanning electron microscope [Color figure can be viewed at wileyonlinelibrary.com]

area as well as the amount of binding sites, leading to the uptake of the metal ions. From this point of view, various amounts of *C. versicolor* ranging from 50 to 250 mg were studied, under the best conditions. It can be seen from Figure 4, that Ag(I) recoveries gradually increased and reached the plateau point over 100 mg amount of

C. versicolor. This phenomenon can be explained as follows. The increase in the amount of biomass may cause an increase in the electrostatic interactions between the cells to result in an agglomerate, which contributes to the reduction of the present binding sites.²⁷ Thus, 100 mg of *C. versicolor* was utilized in all following studies.

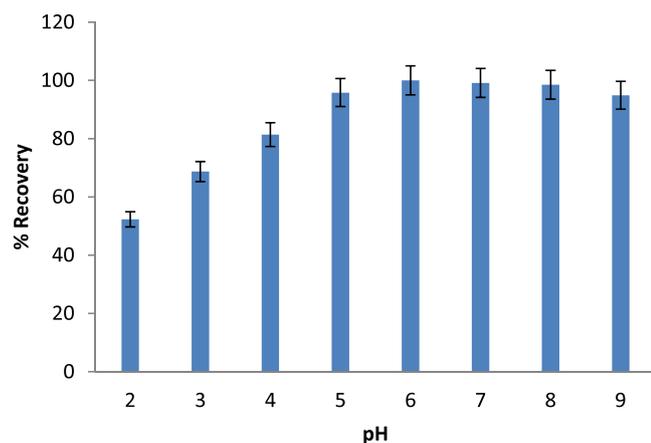


FIGURE 2 Effect of the pH on the recovery of Ag(I) [Color figure can be viewed at wileyonlinelibrary.com]

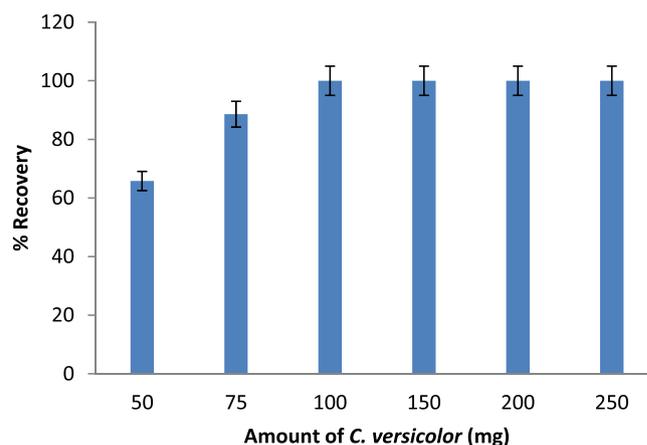


FIGURE 4 Effect of amount of biomass on the recovery of Ag(I) [Color figure can be viewed at wileyonlinelibrary.com]

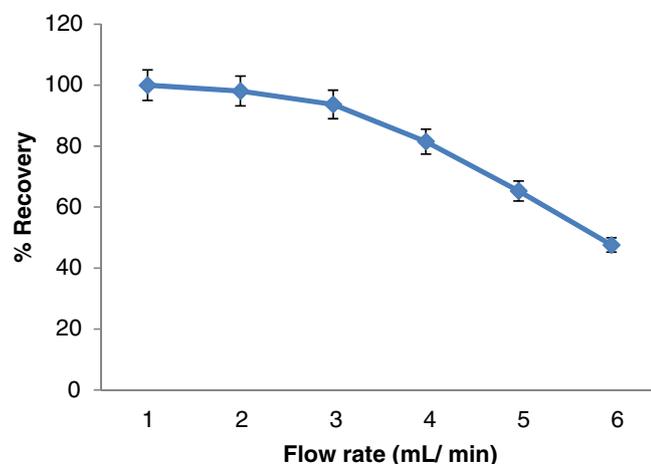


FIGURE 3 Effect of sample flow rate of initial solution on the recovery of Ag(I) [Color figure can be viewed at wileyonlinelibrary.com]

3.5 | Effect of amount γ -Fe₂O₃ nanoparticles

The amount of the support material influenced the metal ion preconcentration in the SPE process. Therefore, this preconcentration should be studied to detect the best value. The best amount of γ -Fe₂O₃ NPs on the recovery of Ag(I) was analyzed via changing the amounts from 50 to 300 mg. The quantitative recoveries of Ag(I) were reached at 150 mg, as the results in Figure S1 show obviously. Thus, a 150 mg amount of γ -Fe₂O₃ NPs was preferred for all following studies.

3.6 | Effect of volume and concentration of eluent

The concentration of the eluent has to be in the possible lowest level to prevent the degradation of the biomass cell wall structure.²⁷ To determine the most suitable eluent to desorb Ag(I) from the *C. versicolor* immobilized γ -Fe₂O₃ NPs column, different concentrations (from 0.5 to 1.0 mol/L) and volumes (from 3.0 to 5.0 ml) of HCl

TABLE 1 Eluent type, volume, and concentration on recoveries of Ag(I) using *C. versicolor* immobilized γ -Fe₂O₃ nanoparticles

Type of elution solution	Volume (ml)	Concentration (mol/L)	% Recovery
Ag(I)			
HCl	3	0.5	89.6 ± 0.7
	5	0.5	93.5 ± 0.9
	3	1	92.8 ± 1.1
	5	1	100 ± 1.0
HNO ₃	3	0.5	83.7 ± 1.2
	5	0.5	91.0 ± 0.9
	3	1	92.6 ± 1.2
	5	1	97.1 ± 0.9

and HNO₃ were evaluated. As can be shown in Table 1, the desorption efficiency for Ag(I) increased with the increase of the HCl and HNO₃ concentrations. Finally, a 5.0 ml amount of 1.0 mol/L HCl was discovered to be the best eluent for subsequent experiments.

3.7 | Effect of the sample volume

Real samples contain a very low metal ion concentration, which makes it very difficult to determine the metals at these levels. Therefore, a preconcentration step is needed inevitably. To detect the best sample volume on the recovery of Ag(I), sample solutions in the range of 50–500 ml were passed through the column. As to be shown in Figure S2, the recoveries of Ag(I) were found as 95.1% when 500 ml volume of the sample solution was used. At volumes higher than 500 ml, the recoveries for analytes were not quantitative, which was related to the excess analytes, loaded over the column capacity with increasing sample volumes. Consequently, a 500 ml volume of the sample was determined as the best and the column with 5 ml of 1.0 mol/L HCl was eluted, so that a PF of 100 could be reached. The same PF was reported by Ozdemir et al.²⁸

TABLE 2 Effect of interference studies on recoveries of Ag(I) using *C. versicolor* immobilized γ -Fe₂O₃ nanoparticles

Ion	Interference to metal ion ratio	% Recovery ^a Ag(I)
Na(I)	2,000	99.2 ± 0.9
K(I)	2,000	99.6 ± 0.7
Ca(II)	100	98.9 ± 1.9
Mg(II)	25	99.1 ± 1.6
Fe(II)	25	97.3 ± 1.4
Cd(II)	5	97.5 ± 1.3
Co(II)	5	96.8 ± 1.0
Ni(II)	5	98.3 ± 0.7
Zn(II)	5	99.2 ± 1.6

^aThe concentration of the heavy metal ion is 100 µg/L.

3.8 | Effect of interference studies on the recoveries of Ag(I)

The presence of some foreign ions in real samples causes matrix effects throughout the detection of the analyte concentration by analytical applications. The influence of different foreign ions such as K(I), Na(I), Mg(II), Ca(II), Fe(II), Cd(II), Co(II), Ni(II), and Zn(II) on the recoveries of Ag(I) was investigated under the best conditions. There

TABLE 3 Comparison of analytical characteristics of different methods for the preconcentration of Ag(I)

Method	Instrument	Linear range ng/ml	LOD ng/ml	PF	RSD %	Matrix	References
Dual-bed resin solid phase extraction	ICP-OES	–	0.17	100	1.2	Gasoline	29
A hollow fiber-liquid phase microextraction (HF-LPME)	ICP-OES	0.040–50	0.08	150	4.5	Diesel and gasoline	30
A newly synthesized chelating resin in an online preconcentration system	FAAS ^a	2–20	0.3	65	1.5	Water	31
Solid phase extraction using chloromethylated polystyrene polymer (CMSP) modified with 2-mercaptobenzothiazole (MBT)	AAS ^b	–	8	250	<3	Waste and medicinal	32
One-step displacement cloud point extraction (D-CPE)	FAAS	5–450	1	24	2.7	Soils, artificial seawater, high-purity salts	33
Solid phase extraction using magnetically activated carbon nanocomposite	ETAAS ^c	0.01–28	0.0023	125	3.5	Water	34
Solid phase extraction using magnetic nanoparticles coated by 3-(trimethoxysilyl)-1-propanol and modified with 2-amino-5-mercapto-1,3,4-thiadiazole	ICP-OES	–	0.12	194	5.31	Water	35
Displacement-dispersive liquid–liquid microextraction	GFAAS ^d	0.1–5.0	0.02	72	2.7	Environmental and geological	36
Magnetic solid phase extraction on <i>C. versicolor</i> immobilized γ -Fe ₂ O ₃ nanoparticles	ICP-OES	0.2–10	0.00184	100	2.34	Water, soil and sediment	This study

Abbreviations: ICP-OES, inductively coupled plasma optical emission spectrometer; LOD, limit of detections; PF, preconcentration factor; RSD, relative standard deviation.

^aFlame atomic absorption spectrometry.

^bAtomic absorption spectrometry.

^cElectrothermal atomic absorption spectrometry.

^dGraphite furnace atomic absorption spectrometry.

are no significant effects of tested ions on the recoveries of Ag(I), as Table 2 shows clearly.

3.9 | Effect of column reusability

In view of economic terms, the reusability and stability of the column are significant factors for the SPE method. For this purpose, the potential reusability of the SPE column loaded with *C. versicolor* immobilized γ -Fe₂O₃ NPs was determined by supervising the change in the recoveries of Ag(I), which were lower than 95%. The recovery of Ag(I) was 95.3% even after the use of the column for 40 times (Figure S3).

3.10 | Analytical performance and application

The analytical characteristics of the recommended method were investigated under optimized conditions. In the concentration range of 0.2–10 ng/ml, a linear analytical curve was achieved. The limit of detections (LOD) was calculated as 0.0018 ng/ml, according to the regulation by IUPAC (3Sb/b where Sb is the standard deviation of blank and b is the slope of calibration graph), and the limit of quantitation (LOQ) was calculated as 0.0062 ng/ml from 10Sb/b. The correlation coefficient was calculated as 0.9998. The relative standard deviation (RSD) of the recommended method for the determination of Ag(I) was

TABLE 4 Applicability of the developed method to real samples

Sample	Ag(I), ng/ml (ng/g for solids)
Tap water	<LOD
Tap water ^a	9.9 ± 0.5
Tap water ^b	19.7 ± 1.2
Dicle river water	<LOD
Dicle river water ^a	10.0 ± 0.8
Waste water	<LOD
Waste water ^a	9.9 ± 0.9
Soil 1	<LOD
Soil 1 ^a	9.8 ± 0.4
Soil 2	<LOD
Soil 2 ^a	9.8 ± 0.7
Sediment 1	<LOD
Sediment 1 ^a	9.9 ± 0.5
Sediment 2	<LOD
Sediment 2 ^a	9.9 ± 0.6

^aSpiked with 10 ng/ml of Ag (10 ng/g for solid samples).

^bSpiked with 20 ng/ml of Ag (20 ng/g for solid samples).

less than 2.3%. PF was achieved as 100 by taking 500 ml as the initial and 5.0 ml as the final volume. The biosorption capacity of *C. versicolor* immobilized γ -Fe₂O₃ NPs for Ag(I) was investigated under the best conditions and the result was found as 31.7 mg/g (mg of metal/g of dry cell). In Table 3, analytical characteristics of some methods, which are presented in literature related to the preconcentration of Ag(I), were compared. Obviously, the recommended method offers advantages such as low LOD, wide linear range, and further usability.

To verify the accuracy of this method, certified reference materials were employed. The Ag(I) concentration was determined in NWTM-15 spiked/fortified water as 12.0 ± 0.9 ng/ml, while it was certified as 12.1 ng/ml. In NIST 1643e water, it was assessed as 1.062 ± 0.075 ng/ml, while it was certified as 1.054 ± 0.083 ng/ml, and in NCS DC 73349 bush branches and leaves it was detected as 49 ± 7 ng/g, while it was certified as 49 ± 5 ng/g. It is obvious that satisfactory agreement was accomplished between the obtained results and accepted values of the certified materials. The applications of the recommended method were performed to some real samples. The method was successfully performed for the determination of Ag(I) trace amount in water, soil, and sediment samples. The outcomes are demonstrated in Table 4, and satisfactory recoveries for spiked Ag(I) were obtained.

4 | CONCLUSIONS

In this study, *C. versicolor* immobilized γ -Fe₂O₃ NPs were successfully applied to environmental samples as an alternative biosorbent for SPE of Ag(I). This new magnetized biosorbent has some advantages such as easy preparation, low cost, and being harmless to the environment. Besides its easy separation due to magnetization contributes to

shortened analysis times and low-energy consumption. Under the best process conditions, suitable figures of merit were attained with low RSD. The recommended method was confirmed with satisfying results due to the analysis of certified reference materials. After that, it was used to real samples. The results demonstrated that the suggested process was very adequate for the rapid preconcentration of Ag(I) from environmental patterns. In addition, the sensitivity of the ICP-OES was improved up to 100 times by applying the developed preconcentration method. Thus, it could be concluded that ICP-OES could be used at ultratrace level measurement of Ag(I) after developed method was applied. Therefore, the use of more expensive instruments could be eliminated.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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