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Determination of trace silver by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) after separation/preconcentration on *Rhodococcus ruber* bacterial biomass

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In the present study, a preconcentration method was developed by using *Rhodococcus ruber* bacterial biomass (RrBB) for the determination of silver in various water samples by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS). *R. ruber* is important in many biotransformations and some transformations result in useful commercial processes. RrBB was used for the first time as a sorbent, for bioadsorption of silver in various water samples. The optimum experimental and analytical parameters such as pH of the sample solution, sample volume, flow rate of sample solution and eluent, volume and concentration of the eluent, effect of common matrix ions and capacity of the adsorbent were investigated and optimized. A sample volume of 1000 mL resulted in a preconcentration factor (PF) of 200. Under the optimized conditions, the detection limit and relative standard deviation (RSD) for silver were found to be 1.24 μg L^{-1} and 3.9% ($n = 7$), respectively. The sorbent exhibited excellent stability and its sorption capacity has been found to be 28.4 mg g^{-1} for silver. The accuracy of the procedure was confirmed by analyzing certified reference materials (NIST SRM 1640a, trace elements in natural water). The developed method was applied successfully for the determination of silver in different water samples.

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1. Introduction

Silver is an industrially and commercially important element widely used in everyday life. Widespread use of silver compounds and silver-containing procedures in medicine, healthcare, domiciliary applications, and jewellery is generally found in hard surface materials and textiles.[1–3] In many countries, silver impregnated filters are used for drinking water preparation.[4] Because of its bacteriostatic properties, silver compounds are often used in dental and pharmaceutical preparations, medical products, implanted prostheses, electronic devices, photographic materials, mirrors, filters as well as in the processing of foods, drugs and beverages. Such an extensive use raises questions about its safety, environmental toxicity and the risks associated with microbial resistance and cross-resistance.[3,5]

Silver is considered to be toxic to humans and the recommendations of the World Health Organization (WHO) permit a maximum concentration of 0.1 mg L^{-1} of silver in drinking water disinfection, but the United States Environmental Protection Agency (USEPA) recommends 0.05 mg L^{-1} as the maximum. Thus, the determination of low concentrations of silver is of increasing interest.[4] The determination of trace silver in water samples by atomic spectroscopic techniques is notably difficult due to the low levels of this metal in the samples and the high complexity of the sample matrices. It is usually necessary to carry out a separation and preconcentration step prior to the analysis.[6,7] Solid-phase extraction (SPE) is the most common technique for the removal and separation of metal ions from environmental samples. The basic principle of SPE for trace elemental ions is the transfer of the analyte from the aqueous phase to the active site of the adsorbent. It has advantages such as high recovery, fast extraction, high enrichment factor, less waste generation, milder matrix effect, low cost and low consumption of organic solvents.[8] Conventionally, several adsorbents including polymeric materials, some species of activated carbon, metal oxide and carbon-based nanomaterials, modified silica and biomass were used as solid phase

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supported materials for trace metal removal and preconcentration.[9,10]

In recent years, biosorption has become one of the alternative treatment technologies to remove heavy metals from aqueous solutions.[11] Biomass of bacteria, algae, fungi and yeasts has been used successfully as the biosorbent due to its low cost, high efficiency, larger surface area, regeneration of biosorbent stability against acidic media and selectivity for some analytes.[12,13] Cell walls of microorganisms have negatively charged groups and various functional groups to capture selectively the metal ions.[14]

In the present work, a new solid-phase extraction method was developed for separation, removal and preconcentration of trace silver in different water samples using RrBB. RrBB was used for the first time as a biosorbent, for separation and enrichment of Ag^+ from various water samples. *R. ruber* is a species of the genus *Rhodococcus*, which is a part of the phylogenetic group nocardioform actinomycetes. The genus *Rhodococcus* has cell walls of chemotype IV, which means that the only diamino acid in the peptidoglycan is meso-diaminopimelic acid and that the major sugars are arabinose and galactose.[15,16] The rhodococci exhibit an unusual diversity of novel enzymatic capabilities for the transformation and degradation of many classes of substrates. These organisms are important in many biotransformations and some transformations result in useful commercial processes.[17,18] For this reason, these microorganisms have a vital importance in environmental, commercial and economical aspects. We investigated bioadsorption and separation parameters of silver in various water samples as a new study. Various experimental and analytical parameters such as pH of the sample solution, sample volume, flow rate of sample solution and eluent, volume and concentration of the eluent, amount of adsorbent, effect of other ions and capacity of the adsorbent were investigated. The proposed method was applied for the determination of trace amounts of Ag^+ in various water samples and the method was verified using standard reference materials.

2. Experimental

2.1. Apparatus

The analysis was performed by a ContrAA 300, a HR-CS FAAS (Analytik Jena AG, Jena, Germany), equipped with a 50 mm burner head. An acetylene flame (C_2H_2) was used for atomization of Ag^+. All absorption lines of elements in the spectral range of 185–900 nm can be analytically evaluated by using a Xe short-arc lamp as a continuum lamp source. The spectral background of the sample in the HR-CS FAAS is always corrected directly on the analysis line simultaneously and independently. All pH measurements were made with an Orion Star (Thermo Fisher, USA) model pH meter. The operating conditions for Ag^+ by HR-CS FAAS are given in Table 1.

A FT-IR spectrometer (Model Nicolet 6700, Thermo Scientific) was used for recording FT-IR spectra of RrBB. Elemental analysis was performed by FLASH 200 CHNS/O Analyzers (Thermo Scientific). Scanning electron microscopes (JSM-7600F model (Jeol, USA)) were used for scanning electron micrographs (SEM) of RrBB.

Table 1 The operating conditions for HR-CS AAS for silver determination

Parameters	Ag^+
Wavelength, nm	328.068
Flow rate of C_2H_2-air, L h^{-1}	50
Burner height, mm	5
Evaluation pixels, pm	3
Background correction	Simultaneous

2.2. Reagents

All solutions were prepared using ultrapure water (specific resistance: 18 MΩ cm) from a Milli-Q purification system (Millipore Corporation, Massachusetts, USA). Standard solutions of the analyte were prepared from their 1000 mg L^{-1} stock solutions (Merck). In this study, buffer solutions (Merck) of sodium acetate–acetic acid (for pH 3–5), sodium monohydrogen phosphate–potassium dihydrogen phosphate (for pH 6–8), and ammonium chloride–ammonia (for pH 9) were used. Calibration standards of Ag^+ were obtained from suitable dilutions of the stock solutions. The required pH adjustments were made by using 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCI solutions. The glassware used was washed with potassium dichromate sulfuric acid, NaOH, ethanol and finally soaked in dilute nitric acid overnight and thoroughly washed with distilled water.

2.3. Growth of *Rhodococcus ruber*

Single colony isolates of *Rhodococcus ruber* JCM 0205 (JCM, Japanese Collection of Microorganisms) were grown on GYEA streak plates at 30 °C for 72 hours. These cultures were then used to inoculate sterile mineral salt media (500 mL) in 2 L flasks, which were subsequently incubated at 30 °C with shaking at 160 rpm in an orbital shaker. *R. ruber* cells were harvested at logarithmic phases by centrifugation at 9000 rpm for 20 minutes. The cells were stored by freezing them at −70 °C, followed by freeze drying.

2.4. Column preparation

An adsorption column was prepared according to the literature.[19] The glass column was 10 cm in length and 0.8 cm in internal diameter. A small amount of glass wool was placed at the bottom of the column in order to hold the adsorbent, 0.3 g RrBB was placed and another small glasswool plug was inserted into the tap of the biomass. The adsorbent bed height in the column was approximately 2.0 cm. It was washed successively with water, 2 mol L^{-1} HCl and HNO_3 solutions, respectively. Before each cycle, the column was preconditioned by passing the blank solutions at working pH. The sample solution was passed with a peristaltic pump.

2.5. Preconcentration procedure

The proposed method was tested by using standard test solutions before its application to the various water samples. The standard test solutions were prepared as follows: 1 mL of 5 mg L^{-1} of Ag^{+} standard solution was added to 2 mL buffer solutions in a volumetric flask. The pH was adjusted by adding 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH to the medium. Afterwards, the final volume of the sample was diluted to 50 mL with distilled water. The column was preconditioned by passing the aqueous solutions at working pH through the column and then the model solution was passed through the column at a flow rate of 6 mL min^{-1}. The adsorbed silver on the column was eluted with 5 mL of 2 mol L^{-1} HCl solution that had a flow rate of 1 mL min^{-1}. Silver was analyzed using the method of a direct calibration curve by HR-CS FAAS. The device setting is controlled after every five readings. A blank solution was also run under the same conditions without adding any silver. In this study, each measurement was repeated three times by HR-CS FAAS.

2.6. Analysis of water samples

Tap water was taken from the Kırşehir water supply network while river water was collected from the Kızılırmak River. Commercial natural drinking water and mineral water were bought directly from a local supermarket in Kırşehir, Turkey. A wastewater sample was collected from the Organized Industrial Site in Kırşehir. These samples were analyzed regarding their Ag^{+} contents. Analyses of samples were performed in compliance with the recommended preconcentration procedure. In order to confirm the validity of the developed procedure, this method was applied for the determination of Ag^{+} in a Standard Reference Material: SRM 1640a, for trace elements in natural water.

3. Results and discussion

In order to obtain quantitative recoveries of silver on RrBB, various analytical parameters such as pH of the sample solution, type and concentration of the eluent, volume of the sample solution, flow rate of the sample solution, eluent solution, interfering ions and amount of RrBB were investigated and optimized. The analytical parameters such as limit of detection (LOD), precision, accuracy and dynamic range were determined under the optimum conditions. Additionally, the chemical structure of RrBB was investigated.

3.1. The characterization of RrBB

The characterization of RrBB was performed by using various instrumental techniques such as FT-IR, element analyzer and SEM. Fig. 1 shows FT-IR spectra of RrBB. The broad band at 3283 cm^{-1} indicates the presence of hydroxyl groups. The peaks observed at 2920 cm^{-1} and 1634 cm^{-1} must be attributed to the C–H group and C=C stretching, respectively. The region between 1610 and 1500 cm^{-1} was seen to be associated with C–C stretching in aromatic rings found on the lignin structure.

Elemental analysis of RrBB is shown in Table 2. Carbon, nitrogen, hydrogen and sulphur levels (%, m/m) were found to be 49.72, 3.55, 7.64 and 0.14, respectively.

Scanning electron micrographs of RrBB are shown in Fig. 2. The surface of RrBB is irregular, porous and it has honeycomb holes which are about ten microns. The porous structure of RrBB has a relatively large specific surface area and this surface characteristic would substantiate high adsorption through mass transport inside the sorbent.

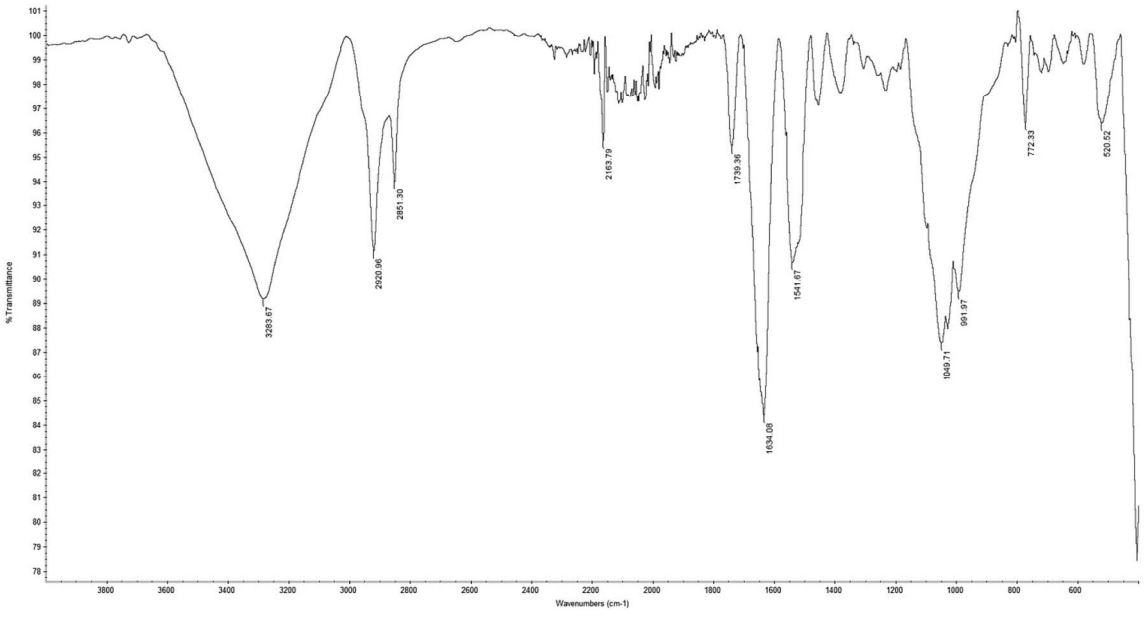

Fig. 1 IR spectrum of RrBB.

Table 2 Elemental analysis of RrBB

Material	% C	% N	% H	% S
RrBB	49.72	3.55	7.64	0.14

3.2. Effect of pH on the recovery of Ag^+

In the SPE, pH of the working solution is the main factor for the quantitative adsorption of analytes.[20] Its influence strongly depends on the nature of the adsorbent used. The recoveries of the analytes were determined by applying the preconcentration procedure and by changing the pH of the model solution in the range of 2.0–8.0. The depicted pH profile revealed that the extraction was quantitative (recovery > 95%) Ag^+ in the pH range of 6.0–7.5. The recoveries of Ag^+ was decreased when the sample solution pH was over 7.5 and less than 6.0 (Fig. 3). Hence, pH 7.0 was selected as an optimum pH for adsorption and recovery of the analyte ions for further experiments.

The cell walls of most organisms are negatively charged, which provides them with the ability to adsorb the positively charged metal ions. Biosorption of metal species is a result of the interaction between the cell walls and these metal species. Therefore, some parameters such as pH, temperature, time, flow rate of solution, ionic strength and metal concentration are very important for adsorption. In addition, the proteins on the cell wall prefer functional groups and peptide bonds in order to bind the metal ions.

3.3. Effects of eluent type and concentration on the recovery of Ag^+

The nature and concentration of the eluent agent were found to have significant effects on the elution process of the retained ions from the solid phase. The type and concentration of the eluent are also important for the performance of the solid-phase preconcentration system.[21] In order to choose the most effective eluent for desorbing, different concentrations and different volumes of eluent agents such as HCl and HNO_3 were studied. They rapidly decrease the pH of the medium and assist the proton exchange to replace the bound metal ions in the solid phase. Among the solvents studied, especially the hydrochloric acid solution provided higher recovery efficiency compared to the other solutions. A quantitative recovery (>95%) was obtained using 2 mol L^{-1} of HCI solutions. Finally, 2 mol L^{-1} HCI was taken as the eluent for desorption of Ag^+ from RrBB and was used for the optimization of the other parameters. The effects of 2 mol L^{-1} HCI solutions at volumes ranging between 2 and 10 mL were investigated and quantitative recoveries were obtained for 5 mL or more of the eluent (Table 3).

3.4. Effect of sample volume on the recoveries of Ag^+

For the preconcentration purposes, to achieve the higher preconcentration factor (PF), the eluent volume should be as small as possible and the volume of the sample solution should be as high as possible.[22] In order to obtain the maximum applicable sample solution (or analyte concentration), model solutions including the same amount of analyte with different volumes were used. The influence of the sample volume on recovery values was examined on the RrBB column at a 6 mL min^{-1} flow rate. For this purpose, 50, 100, 250, 500, 750, 1000 and 1250 mL of the sample solutions (corresponding silver concentrations are: 0.1, 0.05, 0.02, 0.01, 0.0066, 0.005 and 0.004 μg mL^{-1}), each of which contained 5 μg of silver passed through the column under optimum conditions. As can be seen from Fig. 4, at a sample volume lower than 1000 mL, Ag^+ present in the adsorption medium could interact with the binding sites. The recovery of the samples having volumes higher than 1000 mL decreased (<95%) probably because of the saturation of the adsorption sites and exceeding column capacity. The maximum PF for Ag^+ was found to be 200.

3.5. Effect of the sample flow rate on the recovery of Ag^+

The sample flow rate has an effect on the extraction efficiency because the lower the flow rate is, the higher is the residence and retention time of the analytes in the column due to the

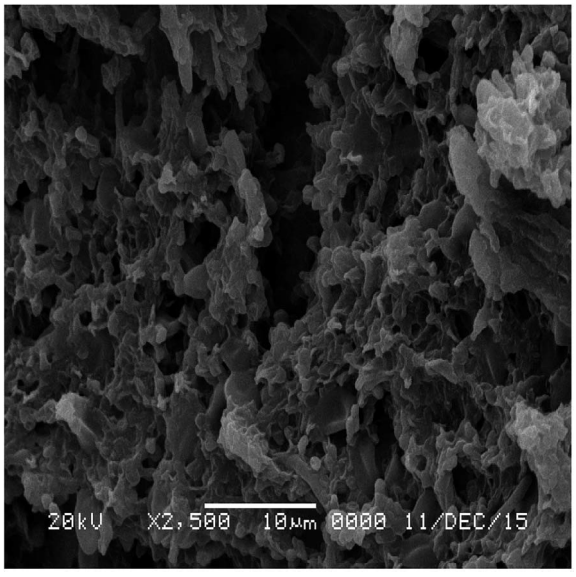

Fig. 2 Scanning Electron Microscopy (SEM) image of RrBB.

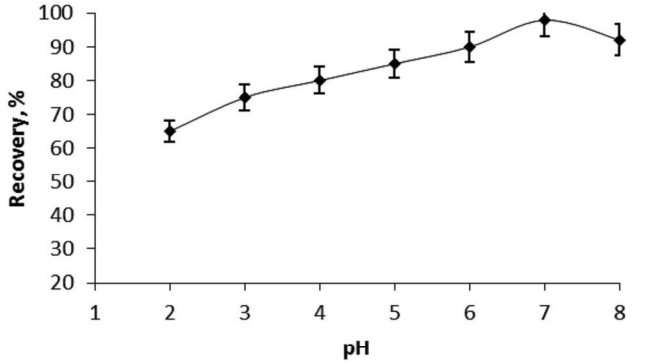

Fig. 3 The effect of pH of the sample solution on the recovery of silver.

Table 3 The effect of eluent type/concentration/volume of eluent on the recovery of silver

Eluent	Recovery[a] (%)
1 mol L^{-1} HCl, 5 mL	92 ± 1
1 mol L^{-1} HCl, 10 mL	93 ± 2
2 mol L^{-1} HCl, 5 mL	96 ± 3
2 mol L^{-1} HCl, 10 mL	95 ± 1
1 mol L^{-1} HNO_3, 5 mL	85 ± 2
2 mol L^{-1} HNO_3, 5 mL	88 ± 3
2 mol L^{-1} HNO_3, 10 mL	90 ± 2

[a] Results are mean ± standard deviation of three replicate analyses.

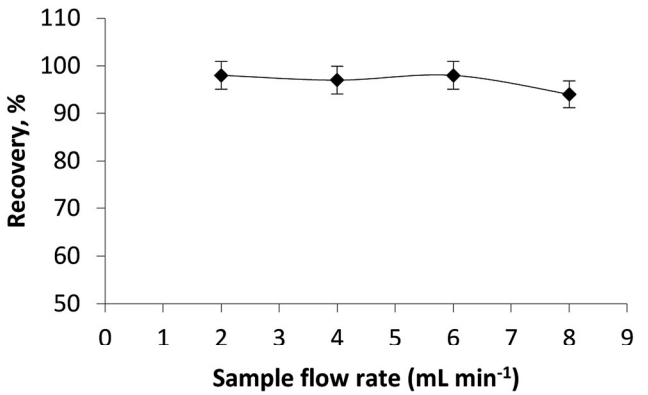

Fig. 5 Effect of the flow rate of the sample solution on the recovery of silver.

increasing interaction (complexation) between ions and sorbents. The effect of the flow rate of sample solutions on the recovery of the analyte was examined in the range of 1–8 mL min^{-1}. The effect of the flow rate was also investigated under the optimum conditions (pH 7.0, eluent: 5 mL of 2 mol L^{-1} HCl). As shown in Fig. 5, the optimum value for the flow rate of the sample solution was found to be up to 6 mL min^{-1}. Above this value, the recovery decreased gradually. Therefore, to decrease the duration of analysis without decreasing recovery values, a flow rate of 6 mL min^{-1} was chosen as the optimum flow rate for subsequent experiments.

3.6. Effect of the eluent flow rate on the recovery of Ag^+

The flow rate effect of the eluent solution (5 mL of 2 mol L^{-1} HCl) on the recovery of Ag^+ was examined in the range of 1.0–5.0 mL min^{-1} under optimum conditions. The recovery of analyte ions ranged between 95 and 100% at the eluent flow rates varying up to 4.0 mL min^{-1}. To decrease the analysis time, the eluent flow rate was selected as 4.0 mL min^{-1}.

3.7. Effect of adsorbent amount on the recovery of Ag^+

The influence of the amount of RrBB on recoveries of silver was studied at different amounts of the sorbent. For this purpose, different amounts of the sorbent (20–50 mg) were tested in adsorption columns. The test solution, which had a volume of 50 mL and contained 5.0 μg of silver, was passed through the column under optimum conditions (pH: 7.0, flow rate: 6 mL min^{-1}, eluent: 5 mL of 2 mol L^{-1} HCl). The results showed that the recovery of the analytes increased up to 300 mg RrBB value and remained almost constant above this value (Fig. 6). Therefore, 300 mg minimum sorbent amount providing the maximum recovery of analytes was selected for further studies.

3.8. Matrix effect on the recoveries of Ag^+

Matrix effects are important problems in the determination of heavy metals by atomic spectroscopic techniques in real samples. Other ions present in the sample solution also affect the retention and the recovery of the analytes on the sorbent.[6] Therefore, the effects of common coexisting ions on the determination of Ag^+ were investigated. For this purpose, the influence of some cationic species was investigated. In these experiments, 50 mL of solutions, each of which contains 5.0 μg of silver and various amounts of possible interfering ions, were treated according to the preconcentration procedure. The recovery values given in Table 4 show no significant interferences up to 1000 mg L^{-1} of K^+, 2000 mg L^{-1} of Na^+, 500 mg L^{-1} of Ca^{2+}, 200 mg L^{-1} of Mg^{2+}, and 10 mg L^{-1} of Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Cr^{3+} and Fe^{3+} ions in the extraction and determination of silver in the sample solutions.

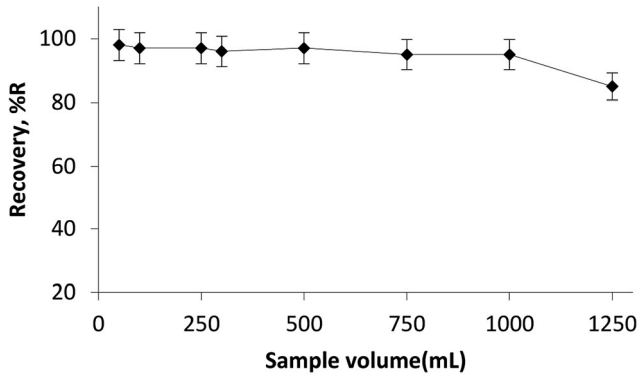

Fig. 4 Effect of sample volume on the recovery of silver.

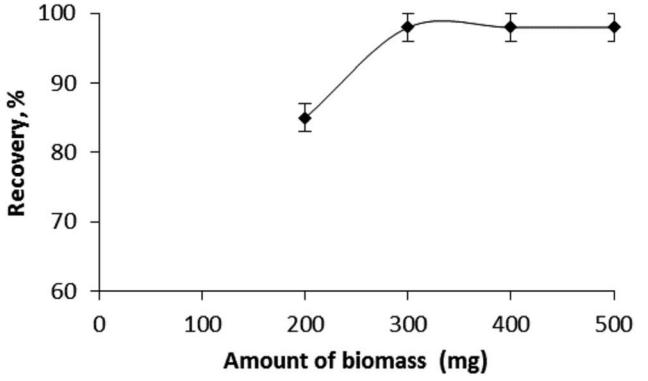

Fig. 6 Effect of sorbent amount on the recovery of silver.

Table 4 Effects of some foreign ions on the recovery of silver

Foreign ions	Concentration (mg L^{-1})	Recovery[a] (%) Ag^+
K^+	1000	96 ± 2
Na^+	2000	98 ± 1
Ca^{2+}	500	101 ± 2
Mg^{2+}	200	97 ± 2
Zn^{2+}	10	95 ± 1
Cu^{2+}	10	97 ± 2
Co^{2+}	10	98 ± 1
Ni^{2+}	10	98 ± 2
Cd^{2+}	10	96 ± 1
Cr^{3+}	10	102 ± 2
Fe^{3+}	10	97 ± 1

[a] Results are mean ± standard deviation of three replicate analyses.

3.9. Reusability of the sorbent

The stability and reusability of the sorbent were evaluated by determining the recoveries of the analytes and by applying adsorption–elution cycles. One adsorption–elution cycle was considered as follows: 50 mL of model solution, 5 mL of eluent solution and 50 mL of ultrapure water were passed through the column loaded with 300 mg of sorbent, respectively. The adsorbent was always stored in water when it was not in use. It was observed that the sorbent was stable up to 80 cycles without any major loss in its quantities and metal recovery properties. The sufficiently good recoveries and low relative standard deviations reflect the high accuracy and precision of the proposed solid phase extraction.

3.10. Capacity of RrBB

The adsorption capacity of the sorbent is an important factor in the evaluation of the properties of a sorbent as it determines how much sorbent is required for the analyte ion concentrations quantitatively from a given solution.[23]

Adsorption capacity of RrBB was obtained by batch experiments. For this purpose, 100 mg of RrBB was added into a 250 mL flask containing 100 mL of model solution which had various concentrations of analyte ions under the optimum experimental conditions. The prepared solutions containing different amounts of analytes were shaken for 2 h at 150 rpm at room temperature. Then, 10 mL of supernatant was taken from each solution and the amount of residual Ag^+ in the solution was determined by using HR-CS FAAS.

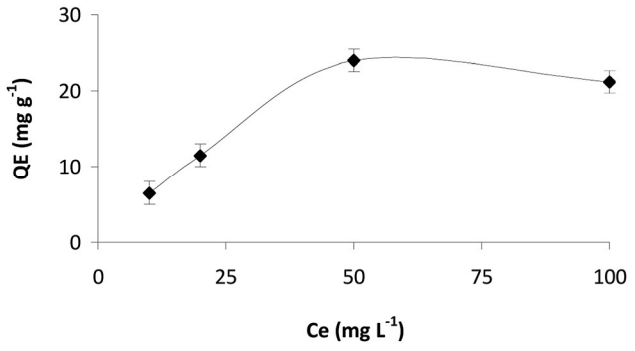

Fig. 7 Adsorption isotherm of Ag^+ on RrBB.

Table 5 Analytical performance and optimum conditions of the proposed method for determination of silver

pH	7
Amount of biomass (mg)	300
Adsorption capacity of biomass (mg g^{-1})	28.4
Eluent volume (2 mol L^{-1} HCl) (mL)	5
Eluent flow rate (mL min^{-1})	4
Sample flow rate (mL min^{-1})	6
Maximum sample volume (mL)	1000
Maximum preconcentration factor	200
Linear range (mg L^{-1})	0.1–20
Linear range (μg L^{-1})[a]	4.1–50
Regression equation (mg L^{-1})	$A = 0.0939 \times C + 0.00029$
Correlation coefficient (R^2)	0.999
Detection limit (μg L^{-1})	1.24
Quantification limit (μg L^{-1})	4.10
Precision (RSD, $n = 7$) (%)	3.9

[a] With a preconcentration step.

In order to indicate the adsorption type, the Langmuir adsorption model was applied to describe the equilibrium isotherm. The linearized equation form of the Langmuir model used to evaluate maximum metal uptake is expressed by the following equation:

$$C_e/q_e = C_e/q_{max} + 1/K_L q_{max}$$

in this equation, C_e is the final metal concentration in the solution at equilibrium (mg L^{-1}), q_e is the amount of sorbed metal ions per gram of sorbent at equilibrium (mg g^{-1}); K_L is a constant related to the energy of adsorption/desorption (L g^{-1}) and q_{max} is the maximum adsorption capacity of the sorbent (mg g^{-1}).

The Langmuir model was seen to fit the experimental data well, with the correlation coefficient (R^2) of 0.9217 for Ag^+. The Langmuir monolayer adsorption capacity (q_{max}) was estimated as 28.4 mg g^{-1} for Ag^+. The constant of the energy (K_L) for Ag^+ was calculated as 0.0376 L g^{-1} (Fig. 7). High correlation coefficients indicate that the adsorption of Ag^+ on the sorbent complies with the Langmuir adsorption isotherm. This means that the solid surface presents a finite number of identical sites that are genetically uniform. There are no interactions between adsorbed species. A monolayer adsorption occurs when the solid surface reaches saturation.[24]

Table 6 Results for a certified reference material (NIST SRM 1640a, trace elements in water, 50 mL)

Element	Certified (μg L^{-1})	Found[a] (μg L^{-1})	Relative error (%)
Ag^+	8.08 ± 0.04	7.81 ± 0.02	−3.34

[a] Results are mean ± standard deviation of three replicate analyses.

Table 7 Levels of Ag^+ in various water samples (sample volume, 200 mL)[a]

Sample	Added ($\mu g\ L^{-1}$)	Found[b] ($\mu g\ L^{-1}$)	Recovery (%)
Commercial drinking water	0	n.d	98
	10	9.8 ± 0.5	
Tap water	0	n.d	103
	10	10.3 ± 0.7	
Mineral water	0	n.d	94
	5	4.7 ± 0.3	
River water	0	6.5 ± 0.5	97.4
	5	11.2 ± 0.4	
Wastewater	0	16.4 ± 0.3	102.6
	10	27.1 ± 0.4	

[a] n.d: not detected. [b] Mean and standard deviation from three determinations.

3.11. Analytical features

For the present study, the optimized experimental parameters and analytical performance of methods are given in Table 5. Under the optimum experimental conditions, linear dynamic range, correlation coefficient, LOD, precision and accuracy were examined. The calibration graphs were obtained without applying the preconcentration step and with the preconcentration step (200 mL of standard solutions with various concentrations) separately. The linear ranges for silver determination were found to be 0.1 to 20.0 mg L^{-1} ($R^2 = 0.999$) without applying the preconcentration step and 4.1 to 50.0 μg L^{-1} ($R^2 = 0.998$) on applying the preconcentration step. RSDs of concentration levels are less than 5%. In order to determine the detection limit for Ag^+, 50 mL of blank solution was passed through the column under the optimum experimental conditions. Blank solutions were prepared by adding a minimum amount of the analyte to water in order to obtain readable analyte signals. The sorbed analyte was eluted by 50 mL of 2.0 mol L^{-1} HCl solution (there is no preconcentration) and the signal of this blank solution was measured about 20 times. The detection limit (LOD) was calculated as 1.24 μg L^{-1} for Ag^+, which is three times the standard deviation of the blank (LOD = $3\sigma/m$, where m is the slope of the calibration curve). The precision of this procedure was examined by seven replicate measurements of 50 mL of sample solutions including 100 μg L^{-1} Ag^+. The precision from seven repeated measurements of 50 mL of 5 μg L^{-1} of silver solutions is excellent with a RSD value of 3.9%. The mean recoveries for Ag^+ was obtained as 96.8%. The accuracy of the procedure was confirmed by analyzing certified materials (NIST SRM 1640a, trace elements in natural water). The results were in good agreement with the certified value (Table 6).

3.12. Analytical applications

The validity of the proposed method was tested for the determination of Ag^+ in CRM under optimum experimental conditions. The accuracy of the method was also checked by determining the percent relative error of spiked real samples. The results obtained are given in Table 7. A good agreement was obtained between added and found values of the analytes. The relative standard deviations were less than 10%.

3.13. Comparison of the method with others

The data from the present method were compared with those of recently reported methods on preconcentration of silver (Table 8). Some parameters obtained are comparable to those presented by other methods. The present work has relatively low LOD and RSD when compared to other methods. PF, which was found to be 200, is relatively high enough when compared to those of some of the other methods.

4. Conclusion

A SPE procedure was developed for the determination of Ag^+ in various water samples on RrBB by high-resolution continuum source flame atomic absorption spectrometry. The proposed method has distinct advantages such as simplicity, low cost, and rapid and precise procedure for rapid adsorption of Ag^+ from large volumes of the sample solutions.

The results show that the proposed method is suitable for the preconcentration of silver at the μg L^{-1} level in real water samples. Furthermore, the sorbent material was stable for a period greater than 80 cycles.

Table 8 Comparison of the proposed method for preconcentration of Ag^+ in an aqueous solution with other methods described in the literature

Procedure/material	Procedure	Maximum PF	LOD ($\mu g\ L^{-1}$)	Adsorption capacity ($mg\ g^{-1}$)	References
SPE/benzothiazole calix[4]arene-silica gel	FI-FAAS	40	0.44	12.2	5
SPE/naphthalene MBT	FAAS	160	0.02	1.18	25
SPE/2-mercaptobenzothiazole MWCNTs	FAAS	160	0.21	5.4	26
SPE/2-mercaptobenzothiazole (MBT)	AAS	300	—	0.343	27
MSPE/alumina-coated magnetite nanoparticles	FAAS	250	0.56	11.6	28
M. oleifera seeds	—	—	—	23.13	29
Bacillus cereus	—	—	—	91.75	30
Macrofungus *Pleurotus platypus*	—	—	—	46.7	31
Magnetospirillum gryphiswaldense	—	—	—	13.5	32
SPE/RrBB	HR CS-FAAS	200	1.24	28.4	Current paper

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