Separation, preconcentration and determination of silver ion from water samples using silica gel modified with 2,4,6-trimorpholino-1,3,5-triazin

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Abstract

A new modified silica gel using 2,4,6-trimorpholino-1,3,5-triazin was used for separation, preconcentration and determination of silver ion in natural water by atomic absorption spectrometry (AAS). This new bonded silica gel was used as an effective sorbent for the solid-phase extraction (SPE) of silver ion from aqueous solutions. Experimental conditions for effective adsorption of trace levels of silver ion were optimized with respect to different experimental parameters in column process. Common coexisting ions did not interfere with the separation and determination of silver at pH 3.5 so that silver ion completely adsorbed on the column. The preconcentration factor is 130 (1 mL elution volume for a 130 mL sample volume). The relative standard deviation (R.S.D.) under optimum conditions is 3.03% ($n = 5$). The accuracy of the method was estimated by using spring and tap water samples that were spiked with different amounts of silver ion. The adsorption isotherm of silver ion was obtained. The capacity of the sorbent at optimum conditions has been found to be 384 μg of silver per gram of sorbent.

1. Introduction

The increasing use of silver compounds and silver-containing products in industry and medicine has resulted in an increased silver content of environmental samples [1,2]. Silver also enters the environment through industrial waters because it often occurs as an impurity in copper, zinc, arsenic and antimony ores [3]. Low-level exposure to silver compounds is widespread due to the use of soluble silver compounds to disinfect drinking water [4]. On the other hand, recent information about the interaction of silver with essential nutrients, especially selenium, copper, Vitamins E and B$_{12}$, has focused attention on its potential toxicity [4,5].

Due to the very low concentration of most elements, including silver, in environmental samples, their separation and sensitive determination necessitate the use of a preconcentration or trace enrichment method [6–8]. The classical liquid–liquid extraction and separation methods are usually time consuming and labor extensive and require relatively large volumes of high purity solvents. Of additional concern is disposal of the organic solvent used, which creates a severe environmental problem.

Solid-phase extraction (SPE) has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes [9–13]. The basic principle of SPE is the transfer of the analyte from the aqueous phase to bind to active sites of the adjacent solid phase. It has several advantages over other techniques, including stability and reusability of the solid phase, reach of high preconcenrtation factors, easiness of separation and enrichment under dynamic conditions, no need for organic solvents which may be toxic and minimal costs due to low consumption of reagents. Accordingly, several selective solid-phase extractors have been prepared by either physical loading or chemical binding of selected chelating reagents to different solid supports such as silica gel [14–21], activated carbon [22,23], cellulosic derivatives [24],

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polyurethane foam [25] and chelating ion exchange resins [26–29].

The typical sorbents used for silver separation contain organic agents with sulfhydryl groups that form stable complexes with silver. Gomez et al. [30] described an on-line preconcentration method for the determination of silver by flow injection FAAS using sulfhydryl cotton. Pei and Fang [31] determined silver in geological materials using FAAS coupled with on-line flow injection preconcentration by coprecipitation with diethyl dithiocarbamate. The sorption of silver was investigated by 2-mercaptobenzothiazole (MBT) fixed on modified silica gel and surfactant-coated alumina [32,33]. Also the sorption of silver, gold and palladium by thiourea immobilized on the silica gel was studied [34]. In those methods based on using modified silica gel [33,34], the use of aminopropylsilica gel as an expensive reagent is inevitable. To bond analytical reagents such as 2-mercaptobenzothiazole to aminopropylsilica gel, the Mannich type condensation with formaldehyde is required, which is a tedious procedure. Using this methodology, the formation of side products makes a serious problem. Recently, an easy and efficient method was reported for the preparation of silica-based reagents [35–37]. This method was used for the preparation of morpholinated and 8-hydroxyquinolinated silica gels [38]. On development of this simple method for the preparation of inexpensive and very stable solid-based analytical reagents, the synthesis of 2-mercaptobenzothiazole bonded silica gel and its application as a sorbent for preconcentration and determination of silver by atomic absorption spectrometry (AAS) was reported [39]. In this study we report the synthesis of a new 2,4,6-trimorpholino-1,3,5-triazin bonded on silica gel and its application as a selective sorbent for preconcentration and determination of silver by atomic absorption spectrometry.

2. Experimental

2.1. Apparatus

A Shimadzu model 670 atomic absorption spectrometer was used for determination of concentration of metal ion. The following conditions were used: absorption line: Ag: 328.1 nm; slit widths: 0.6 nm; and lamp currents: 4 mA. The flow rates of air and acetylene were set as recommended by the manufacturer. The mid-infrared spectra were recorded by KBr pellets using Perkin-Elmer FT-IR spectrometer Model spectrum GX. A Metrohm model 713 pH-meter with a combined glass electrode was used for pH measurements. An ISMATEC peristaltic pump type ISM404B was used for adjustment of the flow rate.

2.2. Reagents

Triply distilled water was used and analytical reagent grade chemicals were purchased from Merck and Aldrich chemical companies. 2,4,6-Trimorpholino-1,3,5-triazin
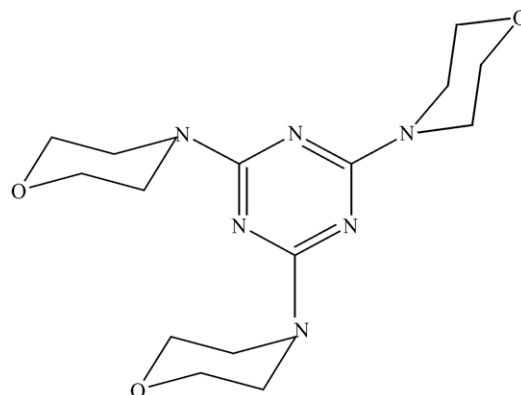
Scheme 1.

(Scheme 1) was prepared and purified according to [40].

2.3. Synthesis of the sorbent

Silica gel was activated with concentrated hydrochloric acid for 4 h under reflux conditions, then filtered off, washed thoroughly with doubly distilled water till it was acid-free and finally at 150 °C for 6 h [41].

For the synthesis of the sorbent, 1.50 g of activated silica gel was refluxed with 1.00 g 2,4,6-trimorpholino-1,3,5-triazin in 100 mL chloroform for 2 h. The residue was then washed several times with triply distilled water and filtered. The resulting residue was washed with chloroform, filtered and dried at 70 °C for 2 h.

In IR spectrum of the modified silica gel, the absorption band is observed at 2920 cm^{-1} which is due to the C−H stretching of triazine. The other two bands of interest are observed at 1542 and 1444 cm^{-1}, that can be assigned to the C=N triazine. The IR spectrum also shows the presence of unreacted OH groups of silica gel (3400 cm^{-1}) and Si−O as a strong broad band at 1100 cm^{-1}.

2.4. Analytical procedure

A 0.10 g of synthetic sorbent was transferred into a glass column of 15 cm length and 1.0 cm diameter. The height of the solid sorbent in the column was 8 mm. The packed column was washed with triply distilled water. The pH of silver ion solution was adjusted at 3.5 by the dropwise addition of diluted HNO$_3$ and diluted NH$_3$. Sample solution was passed through the column at a flow rate of 5 mL min^{-1}. Silver ion adsorbed on the column was then eluted with 1 mL of 0.05 mol L^{-1} thiosulfate solution at an elution rate of 1 mL min^{-1}. The silver concentration in the eluent solution was determined by AAS at 328.1 nm.

3. Results and discussion

To obtain the most suitable data from this method, different parameters were optimized. The pH of sample solution, the type and concentration of eluent, the pH of the eluent, the effect of sample and eluent flow rates on the extraction efficiency, interfering effect, foreign species and capacity factor of the sorbent for silver ion recovery have been studied. The optimization procedure was carried out by varying a parameter while the others were kept constant.

3.1. Optimization of pH

Aliquots of 5.0 mL of 5.0 μg mL^{-1} silver ion solution were passed through a series of columns containing 0.10 g sorbent in the pH range of 2.0–8.0. The results are shown in Fig. 1. The results showed that silver ion was completely adsorbed on the sorbent over the pH range of 3.0–6.0. Therefore pH 3.5 was chosen as the optimum pH for further studies. Diluted HNO$_3$ and diluted NH$_3$ were used for adjusting of the pH of solutions.

3.2. Effect of sample flow rate

The percent sorption of 5.0 mL of 5.0 μg mL^{-1} silver ion on the sorbent surface as a function of sample solution flow rate was examined in the range of 0.5–8.0 mL min^{-1}. The results indicated that at flow rates lower than 6 mL min^{-1}, complete sorption of silver ion was achieved on sorbent. However at flow rates greater than 6 mL min^{-1}, there was a decrease in the percentage of sorption. This may be due to the insufficient contact time of the sample solution with the sorbent. Thus a flow rate of 5 mL min^{-1} was chosen for further studies.

3.3. Choice of eluent

In order to choose a proper eluent for desorbing silver ion from the sorbent surface, a series of selected eluent solution such as sodium acetate, potassium thiosulfate, thiourea, potassium thiocyanate and sodium cyanide were
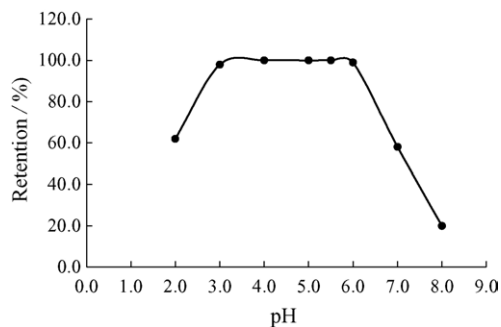
Table 1
Effect of nature of eluent on percent recovery of silver ion

Eluent	Recovery ($n = 5$) (%)
Sodium acetate	7 ± 1.0
Thiourea	97 ± 0.5
Potassium thiosulfate	100 ± 0.8
Sodium cyanide	100 ± 1.5
Potassium thiocyanide	57 ± 1.3

used. Because when HNO$_3$, HCl and H$_2$SO$_4$ pass through the column and cause decomposition of the modified silica gel and/or the formation of AgCl or Ag$_2$SO$_4$, these mineral acids were not used as eluents. Aliquots of 5.0 mL of 5.0 μg mL^{-1} silver ion solution were passed through a series of columns containing 0.10 g of adsorbent. A total of 5 mL of 0.05 mol L^{-1} of the above mentioned eluents were used for desorbing of adsorbed silver ions. The amount of silver ion back-extracted into the liquid phase by each eluent was measured using FAAS. Percent recoveries of silver ion were calculated for each sample. The results are given in Table 1. As Table 1 shows, the recovery is the best when potassium thiosulfate or sodium cyanide solution was used as the eluent. Using sodium cyanide as eluent caused decomposition of the sorbent and the elution of the ligand. Therefore, potassium thiosulfate was selected as eluent.

For desorbing silver ion, already adsorbed on adsorbent, different concentrations of the eluent, in the range 0.002–0.100 mol L^{-1} of thiosulfate have been used. As it is shown in Fig. 2, at concentrations more than 0.025 mol L^{-1}, thiosulfate completely desorbed silver ion from sorbent surface. Therefore a concentration of 0.05 mol L^{-1} of thiosulfate was selected for further studies.

To find the optimum pH value of the eluent solution for adsorbing of 25 μg silver ion, already adsorbed on 0.10 g of sorbent surfaces, a series of thiosulfate solution with different pH values have been used. The results are given in Fig. 3. At pH values less than 5.0, the eluent solution was not stable, and recovery is about 100% in pH 5.0. In higher pH values,
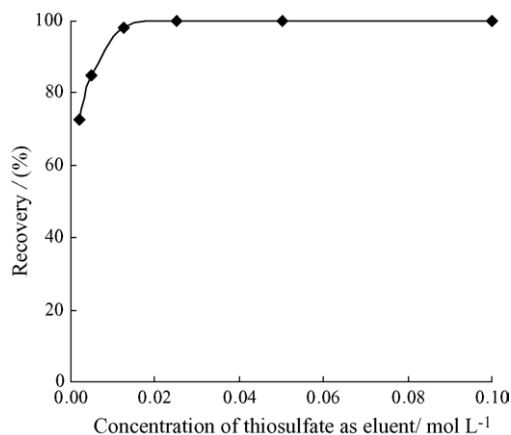

Fig. 1. Effect of pH of the silver ion solution on the percent of retention on sorbent. Experimental conditions: 5 mL 5.0 μg mL^{-1} silver ion solution at different pH, 0.10 g sorbent, 1 mL 0.05 mol L^{-1} thiosulfate solution.

Fig. 2. Effect of eluent concentration on percent recovery of silver ion. Experimental conditions: 5 mL 5.0 μg mL^{-1} silver ion solution at pH 3.5, 0.10 g sorbent, 1 mL thiosulfate at different concentration at pH 3.5.
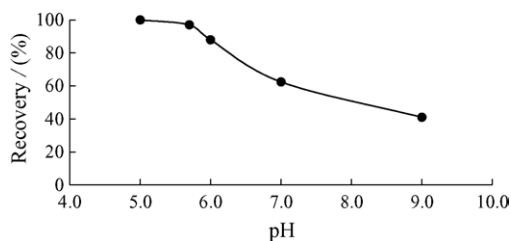
Fig. 3. Effect of pH of the eluent solution on percent recovery of silver ion. Experimental conditions: 5 mL 5.0 µg mL^{-1} silver ion solution at pH 3.5, 0.10 g sorbent, 1 mL 0.05 mol L^{-1} thiosulfate solution at different pH.

the recovery decreased. So, pH 5.0 was considered as the optimum pH value for the eluent solution. The pH of eluent was adjusted by diluted HNO$_3$ and diluted NH$_3$ using a pH meter.

The effect of the volume of eluent solution was also studied. The results are shown in Fig. 4. The percent of recovery of silver ion increased by increasing the volume of thiosulfate up to 0.9 mL and remained constant afterward. Therefore, optimum volume of the eluent was chosen as 1.0 mL. The flow rate of eluent was 1 mL min^{-1}.

3.4. Effect of foreign ions

The effect of different cations and anions was investigated on percent recovery of 5.0 µg mL^{-1} of silver ion in 5 mL of solution by the proposed method. The results are given in Table 2. The results indicated that high concentrations of all the ions tested did not interfere with separation and determination of silver.

3.5. Capacity of the sorbent

The capacity of the sorbent is an important factor that determines how much sorbent is required to quantitatively remove a specific amount of metal ion from the solution [42].

For investigation of adsorption isotherm of silver ion in solution, the same volumes of silver ion solution with different concentrations of silver ion was passed from column that packed with 0.10 g of sorbent. The adsorption isotherm is shown in Fig. 5. The number of microgram adsorbed per gram of adsorbent (N_f) versus the equilibrium concentration
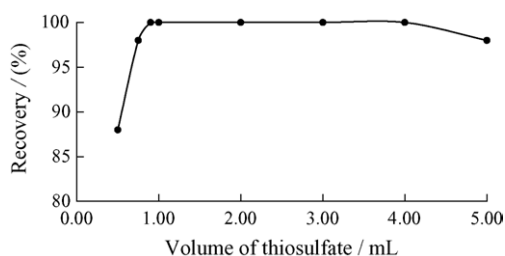
Table 2
Effect of foreign ions (in binary mixtures) on percent recovery of silver ion

Coexisting ions	Coexisting ions (µg mL^{-1})	Recovery of silver ion (%)
Na$^+$	1000	100
K$^+$	1000	100
Ca^{2+}	1000	100
Mg^{2+}	1000	98
Co^{2+}	1000	101
Ni^{2+}	1000	94
Pb^{2+}	1000	101
Cd^{2+}	1000	99
Zn^{2+}	1000	100
Fe^{3+}	1000	100
Mn^{2+}	1000	100
Cu^{2+}	1000	97
PO$_4{}^{3-}$	200	96
SO$_4{}^{2-}$	200	98

Experimental conditions: 5.0 mL of 5.0 µg mL^{-1} silver ion solution containing foreign ion at pH 5.0; sorbent, 0.10 g eluent, 1 mL of 0.05 mol L^{-1} thiosulfate solution at pH 5.0.

of cation is illustrated. Fig. 5 shows the process that conforms to the Langmuir model. Such isotherms are generally associated with monolayer adsorption.

The Langmuir equation was used to calculate the maximum retention capacity (N_s) [43,44]. The general form of Langmuir isotherm is:

$$Y = \frac{KC_s}{1 + KC_s} \qquad (1)$$

where Y is the fraction of adsorbent surface covered by adsorbed species, K a constant and C_s the equilibrium concentration of the cation solution. In our case, $Y = N_f/N_s$, where N_f represents the number of µg cation adsorbed per gram of adsorbent (µg g^{-1}) at equilibrium concentration, C_s and N_s is the maximum amount of solute adsorbed per gram of surface (µg g^{-1}) which depends on the number of adsorption sites. After linearization of the Langmuir isotherm, Eq. (1), we obtain:

$$\frac{C_s}{N_f} = \left(\frac{C_s}{N_s}\right) + \left(\frac{1}{KN_s}\right) \qquad (2)$$

All these adsorption studies were based on the linearization form of the Lanmgmuir isotherm derived from C_s/N_f

Fig. 4. Effect of the volume of thiosulfate on percent recovery of silver ion. Experimental conditions: 5 mL 5.0 µg mL^{-1} silver ion solution at pH 3.5, 0.10 g sorbent, 0.05 mol L^{-1} thiosulfate solution at pH 3.5 with different volumes.
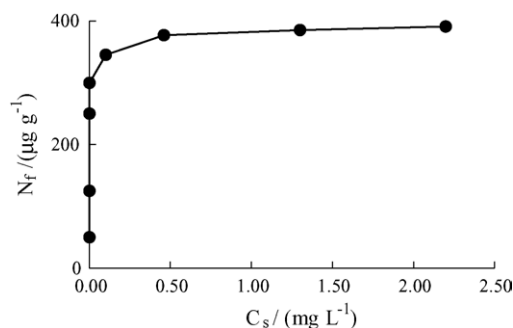

Fig. 5. Adsorption isotherm of silver ion on sorbent.
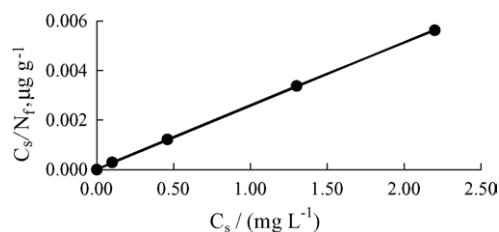
Fig. 6. Linearization of the adsorption isotherm of silver ion on sorbent.

Table 3
Recovery of Ag(I) spiked into samples of water after preconcentration with a factor 130

Sample	Ag(I) spiked (ng mL^{-1})	Ag(I) detected[a] (ng mL^{-1})	Recovery ($n = 5$) (%)
Spring water	0.0	n.d.	–
	10.0	9.9 (± 0.3)	99.2
	20.0	19.8 (± 0.9)	98.3
	50.0	49.2 (± 0.7)	98.5
Tap water	0.0	n.d.	–
	10.0	10.1 (± 0.4)	101.0
	20.0	19.8 (± 0.8)	99.1
	50.0	49.1 (± 0.7)	98.2

n.d.: not detected.
[a] Mean $\pm$ S.D. of five determinations.

as a function of C_s. The plot is shown in Fig. 6. This plot gives a straight line with slope equal to $1/N_s$, and intercept equal to $1/KN_s$. Therefore the Langmuir isotherm is an adequate description of the adsorption of silver ion on sorbent. The maximum retention capacity (N_s) for cation-surface interaction was determined from the slope, and a value of $384\,\mu g\,g^{-1}$ was obtained.

3.6. Effect of sample volume

The effect of the sample volume on the adsorption of silver ion on 0.10 g of sorbent was studied by passing sample volumes of 5–200 mL containing the same amount of silver ion (25 μg) through the column. The sample volume did not affect the adsorption of silver up to 130 mL. At higher volumes percent of recovery decreased. As the amount of silver in 130 mL was measured after elution of adsorbed silver by 1 mL thiosulfate solution, the solution was concentrated by a factor of 130. Preconcentration factor of 130 makes the method very promising for use at sub ng mL^{-1} level in combination with a more sensitive technique such as inductively coupled plasma (ICP).

3.7. Reproducibility and reusability

In order to find the reproducibility in the determination of silver ion, the recommended procedure was repeated five times under optimum conditions. The relative standard deviation (R.S.D.) was found to be 3.03%.

The prepared sorbent was subjected to several loading with the sample solution and subsequent elution with eluent. The capacity of the adsorbent did not change after six cycles of sorption and desorption.

3.8. Analytical application

The suitability of the proposed method for the analysis of natural water samples was checked by spiking samples of the spring water and tap water with 10, 20, and 50 ng mL^{-1} of silver. The results are given in Table 3. As the results show, the proposed method is suitable for the preconcentration of silver ion at the ng mL^{-1} level in real samples of water.

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