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Determination of silver(I) by flame atomic absorption spectrometry after separation/preconcentration using modified magnetite nanoparticles

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Abstract A new, simple, fast and reliable method has been developed for the separation/preconcentration of trace amounts of silver ions using 2-mercaptobenzothiazole/sodium dodecyl sulfate immobilized on alumina-coated magnetite nanoparticles (MBT/SDS-ACMNPs) and their determination by flame atomic absorption spectrometry (FAAS). Optimal experimental conditions, including pH, sample volume, eluent concentration and volume, and co-existing ions, have been studied and established. Under optimal experimental conditions, the enrichment factor, detection limit, linear range and relative standard deviation (RSD) of Ag(I) ions were 250 (for 500 mL of sample solution), 0.56 ng mL^{-1}, 2.0–100.0 ng mL^{-1} and 3.1% (for 5.0 μg mL^{-1}, $n = 10$), respectively. The presented procedure was successfully applied for determination of silver content in the different samples of water.

1. Introduction

Silver is an important element that is widely used for human life. Because of its bacteriostatic properties, silver compounds are often used in filters and other equipment to purify swimming pool and drinking water, and is used in the processing of foods, drugs and beverages [1]. Silver is usually found at extremely low concentrations in natural waters because of its low crustal abundance and low mobility in water. It is obvious that in order to monitor silver concentration in natural waters and to study silver toxicity effects on bio organisms in oceanographic research and survey work, highly sensitive and selective methods for silver determination are required.

A variety of methods, including spectrometric and electrochemical techniques, have been proposed for the determination of silver in different environmental samples [2–5]. However, aforementioned methods, except for Flame Atomic Absorption Spectrometry (FAAS), involve a greater cost and increased instrumentation complexity, limiting its widespread application to routine analytical work. Direct determination of trace amounts of metal ions in some samples by FAAS is difficult because of low sensitivity. Thus, preconcentration procedures are often required. Different techniques, such as cloud point extraction [6], liquid–liquid extraction [7], dispersive liquid–liquid microextraction [8–10] and solid-phase extraction [11–20], have been used to enrich the silver (I) ion and separate it from interferences.

Nanomaterials can offer several advantages over traditional SPE sorbents, such as having very high surface areas and a short diffusion route, which results in high extraction capacity and efficiency [21–23]. However, the use

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of nanomaterials has some inherent limitations, especially when applied to the adsorption and separation of species from large volumes of samples. Magnetic solid phase extraction (MSPE) or magnetically assisted chemical separation (MACS) is a new separation/preconcentration method for trace amounts of species, prior to their determination by spectroscopy techniques [24–27]. Magnetite nanoparticles (MNPs) can readily be isolated from sample solutions by the application of an external magnetic field [28,29]. These NPs are superparamagnetic, which means that they can readily be attracted by a magnet but do not retain magnetism after the field is removed. Therefore, suspended superparamagnetic particles tagged with organic and/or inorganic species can be removed from the matrix by applying a magnetic field, but they do not agglomerate after removal of the field. Hence, the NPs may be reused or recycled. In this paper, we will explore the possibility of 2-mercaptobenzothiazol/sodium dodecyl sulfate immobilized on alumina-coated magnetite nanoparticles (MBT/SDS-ACMNPs) to act as SPE sorbents for the separation and preconcentration of trace level silver ions from environmental samples.

2. Experimental

2.1. Reagents and apparatus

All chemicals were of analytical grade and prepared with double distilled water. 2-Mercaptobenzothiazole (MBT), sodium dodecylsulfate (SDS), ferrous chloride ($FeCl_2.4H_2O$), ferric chloride ($FeCl_3.6H_2O$), aluminum isopropoxide, ethanol, sodium thiosulfate, ammonia, hydrochloric acid and sodium hydroxide were used without further purification processes. All chemicals were obtained from Merck. A stock solution of silver at a concentration of $1000\ \mu g\ mL^{-1}$ was prepared by dissolving appropriate amounts of $AgNO_3$ in deionized water containing 1 mL concentrated nitric acid and stored in the dark. The pH's of the solutions were adjusted with a phosphate buffer.

A flame atomic absorption spectro-photometer (PG Instruments, England) was used with a silver hollow-cathode-lamp, an operating current of 2 mA, and a wavelength and spectral bandwidth of 328.1 and 0.2 nm, respectively. pH measurements were made with a Metrohm Model 780 pH meter with a combination glass electrode. Other instruments used were: an ultrasonic bath (S60H Elmasonic, Germany), a mechanical stirrer (Heidolph, RZR2020) and an orbital shaker (Ika, KS130 Basic). An electronic analytical balance (Adam, AA220LA) was used for weighing the solid materials. In addition, for magnetic separations, a strong neodymium–iron–boron ($Nd_2Fe_{12}B$) magnet (1.2T, 2.5 cm $\times$ 5 cm $\times$ 10 cm) was used.

The surface morphology of the powders was observed by the scanning electron microscope (LEO 1455VP SEM). A Fourier transform infrared spectrometer (IR Prestige-21, Shimadzu) was used to determine the identity of the as-prepared nanoparticles and to characterize the coated Fe_3O_4 nanoparticles. The magnetic properties of the particles were determined by a vibrating sample magnetometer (VSM 7400 Model Lake–Shore).

2.2. Preparation of alumina-coated Fe_3O_4 NPs (ACMNPs)

To date, many approaches have been developed for the preparation of iron oxide nanoparticles [28–30]. The alumina-coated Fe_3O_4 NPs (ACMNPs) were prepared according to Li et al., with minor modifications [31]. As a first step,

the Fe_3O_4 NPs (MNPs) were prepared by a chemical co-precipitation procedure [32]. Ferrous chloride (2.0 g), ferric chloride (5.2 g), and hydrochloric acid (12 mol L^{-1}, 0.85 mL) were dissolved in 25 mL of pure deionized water. The mixture was added dropwise into 250 mL of NaOH solution (1.5 mol L^{-1}) under vigorous stirring with nitrogen gas passing continuously through the solution during the reaction. After the reaction, the obtained MNPs precipitate was separated from the reaction medium under the magnetic field, and rinsed with 200 mL pure deionized water, four times. Then, the product was oven dried at 80 °C.

For preparation of ACMNPs, aluminum isopropoxide (1.0 g) was dissolved in ethanol (60 mL) to form a clear solution. MNPs (0.1 g) were then dispersed in the freshly prepared solution for 5 min with the aid of ultrasonic waves. A mixture of water and ethanol (1:5, v/v) was added dropwise to the suspension of MNPs with vigorous stirring. The mixture was stirred for half an hour after addition. Subsequently, the suspension stood for one hour before separating and washing with ethanol. After five cycles of separation/washing/redispersion with ethanol, the powder obtained was oven dried and calcined at 500 °C for three hours.

2.3. Preparation of MBT/SDS-ACMNPs

A MBT/SDS solution was prepared by dissolving 140.0 mg 2-mercapto-benzothiazole and 200.0 mg SDS in 50 mL of 0.1 mol L^{-1} aqueous ammonia diluted to 100 mL with deionized water. Ten milliliters of MBT/SDS solution was added to 10 mL of water containing 0.1 g of ACMNPs. The pH of this suspension was adjusted to 2 by the drop-wise addition of HNO_3 (0.1 mol L^{-1}) solution. The mixed solution was shaken for 15 min and then separated from the reaction medium under the magnetic field, and rinsed with 10 mL of pure water. This product was used as sorbent for the silver ion.

2.4. General procedure

The procedure for the magnetic extraction is presented in Figure 1 and details are as follows: 10 mL of silver (I) ion solution (5.0 $\mu g\ mL^{-1}$) was added to 0.1 g of MBT/SDS-ACMNPs; subsequently, the solution was shaken for 15 min to facilitate adsorption of the metal ions onto the NPs. Then, the magnetic adsorbent was separated easily and quickly using an adscititious magnet. Subsequently, the pH of 5 mL of sodium thiosulfate (0.5 mol L^{-1}) solution was adjusted to 6.0 with a phosphate buffer and added as eluent. Finally, after mixing, magnetite nano-adsorbents were separated magnetically from the solution using the magnet, and were reverted to the cycle according to Figure 1. The eluate solution was also pipetted into a test tube for FAAS analysis.

2.5. Sample preparation

Water and wastewater samples were collected in acid leached polyethylene bottles. The samples were filtered before analysis through a 0.45-μm membrane filter (Millipore) and stored in a polyethylene container for subsequent usage, after they were acidified to pH 2.0 with concentrated HNO_3 in order to prevent adsorption of the metal ions on the flask walls.

3. Results and discussion

3.1. Characteristics of modified magnetite nanoparticles

Figure 2 displays the SEM images of MNPs and ACM-NPs, which illustrate the uniform size distribution of the
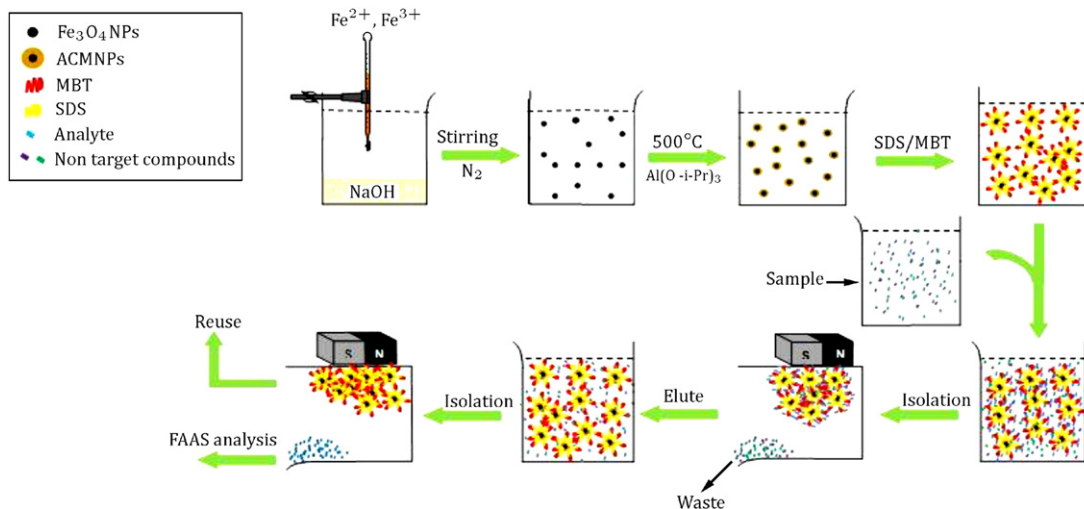
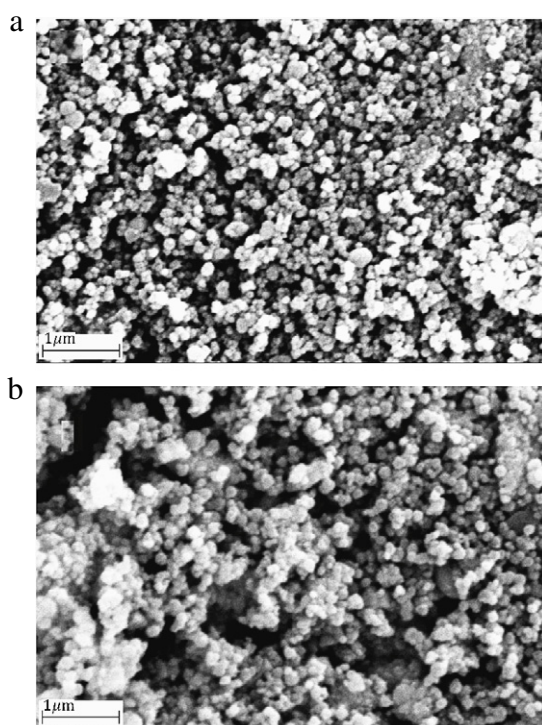Figure 1:   Procedure for magnetic solid-phase extraction.

Figure 2:   SEM images of MNPs (a) and ACMNPs (b).

Figure 3:   The magnetic behavior of MNPs (■) and ACMNPs (●).
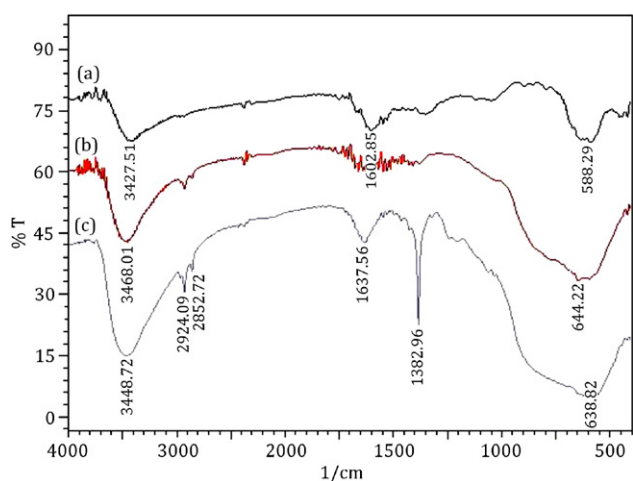
Figure 4:   FTIR spectra of the MNPs (a), ACMNPs (b), and MBT/SDS-ACMNPs (c).

nanospheres. The magnetic properties were also characterized by measuring the hysteresis and remanence curves by means of a vibrating sample magnetometer (VSM). The magnetization curves show that both MNPs and ACMNPs exhibit typical superparamagnetic behavior due to no hysteresis (Figure 3). Values of the large saturation magnetization of MNPs and ACMNPs were 56.72 and 9.34 emu g^{-1}, respectively. The large saturation magnetization decreases for ACMNPs, compared to the MNPs, due to Al$_2$O$_3$ coating on the Fe$_3$O$_4$ NPs. However, these ACMNPs are sufficient for magnetic separation with a conventional magnet.

The modified ACMNPs were confirmed by FT–IR analysis, as shown in Figure 4. As can be seen in Figure 4 (curve (a)), a broad band exists around 588.29 cm$^{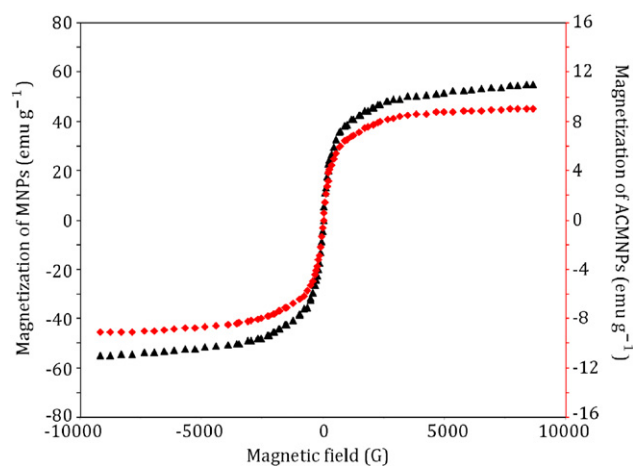-1}$, assignable to the Fe–O–Fe of the MNPs. The peak at about 1602.85 cm^{-1} can be assigned to the stretching vibration of N$_2$ adsorbed on the surfaces of the nanoparticles. The flexing vibration peak of hydroxyl, resulting from the adsorbed water, can be observed at 3427.51 cm^{-1} [33].
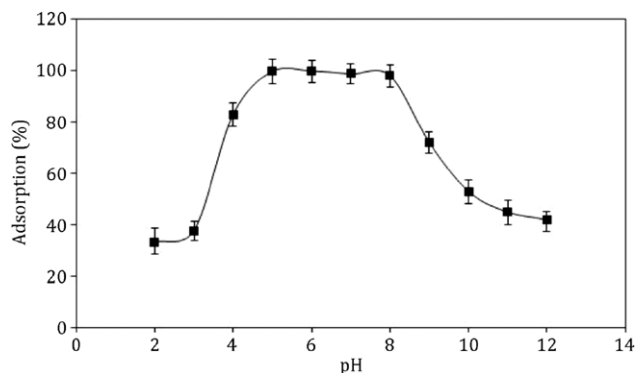
Figure 5: Effect of pH on adsorption of silver. Conditions: ACMNPs (0.1 g), MBT/SDS solution (10 mL, 4×10^{-7} mol $L^{-1}/2 \times 10^{-3}$ mol L^{-1}, pH2.0) and Ag (I) solution (10 mL, 5.0 μg mL^{-1}).

The spectrum of ACMNPs (Figure 4, curve (b)), is comparable with the spectrum of MNPs, after binding alumina and the broadening of the peak at 644.22 cm^{-1} can be assigned to Al–O, which overlapped with the Fe–O characteristic peak. Comparison of the FT–IR spectra of ACMNPs and MBT/SDS-ACMNPs (Figure 4, curve (c)) also shows that a new sharp peak at 1382.96 cm^{-1} appeared, which was due to the C–N stretching peak of MBT stabilized on ACMNPs. Consequently, the FT–IR data suggest that MBT are successfully immobilized on the ACMNPs surface.

3.2. Amounts of SDS and MBT

Negatively charged surfactants, such as SDS, can strongly adsorb on positively charged surfaces of ACMNPs in highly acidic solutions. A concentration of SDS, below its critical micellar concentration (CMC, 8×10^{-3} mol L^{-1}), was used. Above this concentration, the excess of SDS would form micelles in the aqueous solution, which were not adsorbed on alumina surfaces. The influence of amounts of SDS/MBT on the adsorption of silver ions on ACMNPs was investigated. The results showed that with an increase in SDS concentration, the adsorption increases, and a maximum is obtained after the SDS concentration approaches 2×10^{-3} mol L^{-1} and remains constant up to CMC and then decreases, because above this point, micelles were formed strongly. Thus, a concentration of 2×10^{-3} mol L^{-1} was selected as the optimum SDS concentration for further studies.

In order to study the effect of MBT concentration on the adsorption of Ag(I) on the ACMNPs, ammoniacal solutions of SDS/MBT with constant concentrations of SDS and different concentrations of MBT were used to study the percent of Ag(I) ions adsorbed on ACMNPs. At MBT concentrations less than 4×10^{-5} mol L^{-1}, the amount of MBT molecules immobilized into SDS cores is low, so Ag(I) adsorption less than 100 was observed. Therefore, 4×10^{-5} mol L^{-1} of MBT was selected as the optimum concentration for further studies.

3.3. Effect of pH variation

The effect of pH on the adsorption of 10 mL of silver ion (5.0 μg mL^{-1}) by 0.1 g MBT/SDS-ACMNPs at 25 °C showed that the adsorption of silver is quantitative (100%) in the pH range 5.0–8.0 (Figure 5). At acidic media, the nitrogen atom could be protonated and at basic media, the thiol proton dissociates. This reveals that the mechanism of the sorption of the silver ion is pH dependent and pH could affect the stability of the complex.
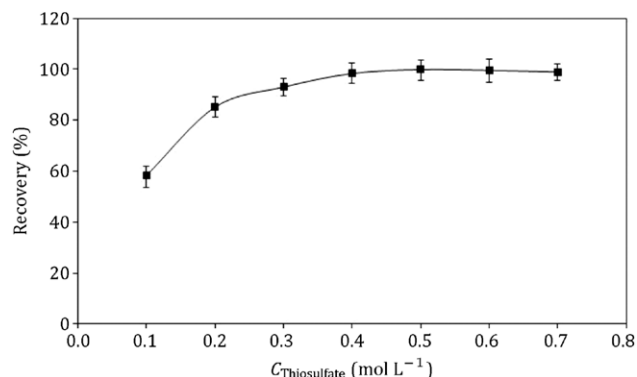

Figure 6: Effect of sodium thiosulfate concentration on recovery of silver. Conditions: ACMNPs (0.1 g), MBT/SDS solution (10 mL, 4×10^{-7} mol $L^{-1}/2 \times 10^{-3}$ mol L^{-1}, pH 2) and Ag(I) solution (10 mL, 5μg mL^{-1}, pH 6.5), sodium thiosulfate (5 mL, pH 5.0).

Thus, the mean pH value (6.5) was used as the optimum pH for further work.

3.4. Standing and magnetic separation time

We found that the standing time had an obvious effect on the target analyte extraction. When the MNPs were isolated immediately, without a standing process, the recovery of Ag(I) ions was only 45%. But, when the standing time was adjusted to 5, 10, 15, 20, 25 and 30 min, recovery was improved to 67, 72, 78, 85, 93 and 99.8% respectively. A standing time of 30 min was sufficient to achieve satisfactory adsorption and a better recovery of silver ion. Meanwhile, in the experiment, MBT/SDS-ACMNPs possessed super-paramagnetism properties and large saturation magnetization, which enabled them to be completely isolated in the least time (less than 1 min) by a strong magnet.

3.5. Effect of the type, concentration, volume and pH of the desorbing solution

Various desorbing reagents of sodium acetate, ammonia, sodium thiocyanate, sodium thiosulfate and thiourea were used to find the best desorbing solution for the adsorbed silver ion. For 50.0 μg of silver ion, adsorbed on 0.1 g of sorbent (MBT/SDS-ACMNPs), different concentrations of eluent were investigated. Among the different solutions used, a sodium thiosulfate solution provided the higher recovery. The concentration of the sodium thiosulfate solution was optimized. The recovery of desorbed silver ions as a function of thiosulphate concentration is represented in Figure 6. As shown, at concentrations larger than 0.5 mol L^{-1} sodium thiosulfate, silver ions were completely desorbed from sorbent surfaces. Therefore, a concentration of 0.5 mol L^{-1} sodium thiosulfate was selected as the most suitable eluent for further studies.

To find the optimum pH of the sodium thiosulfate solution for desorbing silver ions from sorbent surfaces, a series of sodium thiosulfate solutions with different pH values was used. The results show that the recovery of silver ions at pH < 6.0 is maximum. By this observation, it was proposed, as an idea, that at acidic pH, i.e. at a pH range of 2.0–6.0, the hydronium ion could compete with the silver ion for being adsorbed on sorbent surfaces. In acidic media, 2-mercaptobenzothiazole produces a complex form as ML$_2$, but in basic pH values, a secondary complex of the form M$_2$L is produced [34]. Recoveries less than 100%, at basic solutions, could be explained due to the

Table 1: Analytical characteristics of proposed method at the optimum conditions.

Regression equation	$A = 0.1654\,C + 0.007$
Correlation coefficient (r)	0.9987
Linear range	2.0–100.0 ng mL^{-1}
LOD ($n = 5$) (ng mL^{-1})	0.56
RSD (%) ($n = 5$)	3.1 (for 5 µg mL^{-1})
Enrichment factor	250

formation of silver hydroxide. Furthermore, MBT and/or SDS could be washed out at these pH values, which consequently decrease the capacity of the adsorbent. Therefore, pH 5 was selected as the optimum pH value for the eluent solution.

3.6. Effect of sample volume

The effect of a sample volume on the adsorption of silver ions on MBT/SDS-ACMNPs was investigated using different feed volumes of water samples, ranging between 50–1000 mL. The maximum sample volume with a high recovery percentage for the process was determined. The recovery of silver ions was quantitative, up to 500 mL of sample volume. By applying 500 mL sample volume under optimum conditions and, as stated previously, desorbing silver ions with 2 mL of sodium thiosulfate solution, a preconcentration factor of 250 was obtained.

3.7. Adsorption capacity study and sorbent regeneration

The adsorption capacity study used here was adapted from the method recommended by Maquieira et al. [35]. In order to study the adsorption capacity of a sorbent, 100 mg MBT/SDS-ACMNPs was added to 50 mL of standard solution, with different concentrations of Ag(I), at pH 6.5. After shaking for 2 h, the magnetic adsorbent was separated using a magnet and the supernatants were decanted directly. The magnet was removed, and a 5 mL solution containing 0.5 mol L^{-1} sodium thiosulfate was added as eluent and shaken for 5 min. Then, the magnet was used again to settle the ACMNPs and the eluate was separated for FAAS. The sorption capacity (Q, mg g^{-1}) was calculated as:

$$Q = [(C_i - C_e)\,V]\,/M,$$

where C_i and C_e are concentrations of analyte ions in the initial and equilibrium solutions after adsorption, respectively (mg L^{-1}); V is the volume of the solution (L); and M is the amount of sorbent (g). The results showed that the maximum amount of Ag ions that can be sorbed by MBT/SDS-ACMNPs was found to be 11.6 mg g^{-1}.

Regeneration is one of the key factors for evaluating the performance of the adsorption material. In this work, it was found that ACMNPs can be reused up to four times without loss of analytical performance. Considering that 5.0 g of ACMNPs could be prepared in one batch, and only 100 mg of ACMNPs were used for one extraction operation, this reusable time is acceptable.

3.8. Effect of co-existing ions

The recovery of 5.0 µg mL^{-1} of Ag$^+$ ions was investigated in binary mixtures containing silver ions and one foreign ion. The following excess of ions did not interfere with the reaction (i.e. caused a relative error of less than 5%): more than a 1000-fold amount of Na$^+$, Ca^{2+} and Mg^{2+}; a 200-fold amount of Mn^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Co^{2+}, Cd^{2+}, K$^+$, Cr^{3+}, Fe^{3+}, Bi^{3+} and Pd^{2+}; a 100-fold amount of NH$_4^+$, NO$_3^-$, CH$_3$COO$^-$, SO$_4^{2-}$, PO$_4^{3-}$, C$_2$O$_4^{2-}$, Hg^{2+} and a 50-fold amount of I$^-$, F$^-$, Cl$^-$ and Br$^-$. The results showed that most of the investigated ions do not interfere in the adsorption–desorption, and in determination of traces of silver ions in water samples.

3.9. Analytical performance

Table 1 shows the analytical characteristics of the method under optimal experimental conditions. The analytical features of the method, such as limit of detection (LOD), linear range of calibration curve and precision, were examined. The LOD of the proposed method based on three times the standard deviation of the blank ($3S_b$) was 0.56 ng mL^{-1} for the silver ion ($n = 10$). The linear range of the calibration curve for Ag(I) was 2.0–100.0 ng mL^{-1}, with a correlation coefficient of 0.9987. The regression equation for the line was $A = 0.1654\,C_{Ag} + (7 \times 10^{-3})$ ($n = 5$) where C_{Ag} is the concentration of Ag(I) in ng mL^{-1} and A is the absorbance. The relative standard deviation (RSD) for 10 replicate measurements of 5.0 µg mL^{-1} of silver ion was 3.1%

3.10. Analytical applications

In order to assess the applicability of the method to real samples, it was applied to the separation, preconcentration and determination of Ag(I) in different water samples. The reliability was checked by spiking experiments. The results are shown in Table 2. As the results show, the proposed method is suitable

Table 2: Recoveries results of real water samples spiked with silver ion and wastewater samples.

Sample	Ag(I) (ng mL^{-1})[a]		Recovery (%)
	Added	Founded	
Waste water (copper factory, Sarchashmeh, Rafsanjan)	0	12.4 ($\pm$0.5)	–
	5	17.2 ($\pm$0.6)	97
	10	21.1 ($\pm$0.3)	96
Tap water (Sirjan)	0	BLR[b]	–
	5	4.7 ($\pm$0.1)	99
	10	10.2 ($\pm$0.2)	102
River water (Hajiabad, Bandar Abbas)	0	BLR	–
	5	5.3 ($\pm$0.3)	101
	10	10.2 ($\pm$0.4)	99
Spring water (Koran, Sirjan)	0	BLR	–
	5	4.7 ($\pm$0.4)	98
	10	9.8 ($\pm$0.3)	96

[a] Mean $\pm$standard deviation ($n = 5$);.
[b] Below linear range.

Table 3: Comparison of the proposed method with other reported methods for separation/preconcentration of silver ion.

System	Analysis method	Sorbent	Sorbent capacity (mg g^{-1})	Enrichment factor	RSD (%)	Linear range (ng mL^{-1})	LOD (ng mL^{-1})	Reference
SPE	FAAS	Alumina	–	100	1.59	–	–	[13]
SPE	FAAS	Silica gel	0.384	130	3.03	–	–	[14]
SPE	FAAS	Naphthalene	0.029	10	4.4	10–100	3.9	[15]
SPE	FAAS	Amberlite XAD-16	12.4	200	3.1	–	110	[16]
SPE	FAAS	Octadecyl silica membrane disks	1.07	360	–	–	6	[17]
SPE	FAAS	Alumina	16.18	100	0.01–0.50	–	–	[19]
SPE	FAAS	Octadecyl silica membrane disks	0.91	200	1.6	–	100	[36]
SPE	FAAS	Dithizone	–	100	3.21	–	–	[37]
SPE	FAAS	2-Mercaptobenzo thiazole-silica gel	0.343	300	2.04	–	–	[38]
MSPE	FAAS	Alumina-coated Magnetite nanoparticles	11.6	250	3.1	2–100	0.56	This work

for the preconcentration of silver ions at the ng mL^{-1} level in real samples.

4. Conclusions

In this study, a new sorbent of MBT immobilized on SDS-ACMNPs has been prepared by the precipitation method. The modified nanoparticles are highly monodisperse and magnetically separable, and have been successfully employed for the magnetic solid-phase extraction of Ag(I) from environmental water. The developed method is simple, rapid and sensitive, and very suitable for rapid adsorption of Ag(I) from large volumes of the sample solution. In this work, regeneration found that the ACMNPs can be re-used up to four times without loss of analytical performance. Table 3 shows a comparison of the proposed method with other reported methods. It can be seen that some obtained values for the proposed method, such as LOD, linear range and enrichment factor, are as good as, or better than, some previously reported methods. Furthermore, it avoids the time-consuming column passing (about 1 h in the conventional SPE method) and filtration operation, and no clean-up steps were required.

Acknowledgments

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