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A Nano-Composite Based on Fe₃O₄@Styrene-Maleic Anhydride Copolymer as a Magnetic Sorbent for Preconcentration of Silver(I) Ion

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A magnetic nano-composite based on the modified styren-maleic anhydride copolymer and Fe₃O₄ nano-particles was introduced as a new sorbent for solid-phase extraction and preconcentration of trace levels of silver ion from aqueous solutions. The size and morphology of the nano-sorbent were characterized *via* X-ray diffraction analysis, scanning electron microscopy and Fourier transform infrared spectroscopy. Following its desorption with hydrochloric acid, silver was detected by flame atomic absorption spectrometry. Different variables separation/pre-concentration of the silver ion were optimized. Under the optimized conditions, the calibration graph was linear in the 1-200 µg l⁻¹ concentration range, with a correlation coefficient of 0.9991. The limit of detection and relative standard deviation for six replicate determinations at a silver ion level of 100 µg l⁻¹ were 0.3 µg l⁻¹ and 1.1%, respectively. The preconcentration factor and adsorption capacity of the sorbent for silver ion were 100 and 78.2 mg g⁻¹, respectively. The accuracy of the method was confirmed by analyzing the certified reference material NIST SRM 1566b. The method was successfully applied to determine silver ion in water samples and in radiology films, and satisfactory recoveries were obtained in the range of 96.8-99.6% for the spiked samples.

Keywords: Silver, Nano-composite, Styren-maleic anhydride copolymer, Magnetic solid-phase extraction, Flame atomic absorption spectrometry

INTRODUCTION

Silver is an important element, and in respect to electrical and thermal conductivity and ductility, it has been widely used in different fields such as aerospace, communications, chemical industry, medical equipment, electroplating, photographic materials and electronic industries. Silver has many antimicrobial properties since ancient Romans that used silver coins for pretreatment of drinking water. Antimicrobial coatings of colloidal silver have various applications such as deodorizing shoe inserts, washing machines, and wound dressings [1,2]. Although silver has many applications and advantages, its high levels can be toxic to human cells. For instance, exposure to relatively high levels of silver compounds may cause

breathing problems, lung and throat irritation, stomach pain and pigmentary disorders. Skin contact with silver compounds has been found to cause allergic reactions in some people [3]. Therefore, various instrumental techniques such as atomic absorption spectrometry [4,5], inductively coupled plasma-mass spectrometry [6] and inductively coupled plasma-optical emission spectrometry [7] have been employed for the determination of silver in different real samples. However, these techniques are so expensive that are not applicable for *in situ* analysis. Moreover, due to its very low concentration in real samples and high complexity of sample matrices, analysis of trace levels of silver is difficult. Accordingly, preliminary pre-concentration and matrix removal steps are highly needed to ensure the accuracy and precision of the analytical results [8,9].

Solid-phase extraction (SPE) is an efficient separation/

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pre-concentration technique for heavy metals because it has many important advantages, including simplicity, flexibility, high enrichment factors, absence of emulsion, low cost, and more importantly it is environment friendly. So far, various SPE materials have been successfully used for selective extraction and pre-concentration of trace levels of silver ions. Among a variety of solid phases used for extraction of silver ions such as activated carbon [10], calix[4]arene [11,12], magnetic nanoparticles (MNPs) [13], modified silica [14], and polymer gels [15], MNPs have gained much attention due to their high surface areas, chemical and mechanical stability, simplicity of synthesis, and the top possibility of easy separation. Thus, magnetic solid-phase extraction (MSPE) has several advantages over other techniques, including reusability of the solid phase, high pre-concentration factors, enrichment under dynamic conditions, no need for consumption of organic solvents which may be toxic and hazardous, minimum costs because of low consumption of reagents and finally, MNPs are easily assembled with a magnet [16].

Magnetic Fe₃O₄ NPs are good candidates for connecting chelating materials to their surfaces because of their inertness to surrounding environment, ease of surface modification with specific functional groups, and high surface area-to-volume ratio leading to enhancement of adsorption capacity [17]. The interactions between hydroxyl groups on the iron oxide surface and functional groups of organosilane coupling agents not only support terminal functional groups available for connecting to other targeting polymers but also decrease aggregation and enhance dispersion stability [16]. On the other hand, a polymeric ligand is applied to selectively bind with a specific metal ion in a mixture to isolate the target metal ion from aqueous media [18-21]. Styrene-maleic anhydride (SMA) copolymer is a commercial industrial polymer which is cheaper than any other polymers possessing reactive group in the main chain or side chain for further functionalization [22]. In recent years, various studies have been undertaken about metal ions adsorption with the SMA copolymer derivatives [23-25]. To the best of our knowledge, no attempt has been made to apply a magnetic nanocomposite (MNC) based on the modified styrene-maleic anhydride copolymer and Fe₃O₄ NPs in solid-phase extraction of metal ions. Consequently, in this work, Fe₃O₄ MNPs were firstly

synthesized and their surfaces were modified with an amino-terminated silane coupling agent. Then, styrene-maleic anhydride copolymer was synthesized by free radical polymerization of styrene and maleic anhydride, and after grafting with 3-aminobenzoic acid, the modified copolymer was reacted with amine terminated Fe₃O₄ NPs to prepare magnetic metal ions chelating nano-composite. Finally, after characterization of the synthesized MNC by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis, the obtained material was applied as a nano-sorbent for selective extraction of silver ions from aqueous solutions.

EXPERIMENTAL

Apparatus and Instruments

A SpectrAA 220 (Varian, Australia) flame atomic absorption spectrometer was used for the determination of silver. It was equipped with a silver hollow cathode lamp and an air/acetylene burner. The instrumental parameters were as follows: wavelength, 328.1 nm; lamp current, 4 mA; band pass, 0.5 nm. The flame composition was controlled at an acetylene flow rate of 1.5 l min⁻¹ and air flow rate of 3.5 l min⁻¹. To identify the crystal structure of the nano-sorbent, powder X-ray diffraction (XRD) measurements were performed at room temperature by employing a D8 Advance (Bruker, Germany) instrument with Cu-K_α radiation (1.54 Å), an acceleration voltage of 40 kV, and a current of 35 mA. In addition, a Vector 22 (Bruker, Germany) Fourier transform infrared spectrometer was employed to elucidate the functional groups present in the sorbent. FT-IR spectra were recorded in the range of 4000-400 cm⁻¹ at 4 cm⁻¹ resolution using the conventional KBr pellet technique with a ratio sample/KBr of 1:100 by mass. A MIRA3 (TESCAN, Czech Republic) field emission scanning electron microscope (FESEM) was additionally used to study the morphological characteristics of the nano-sorbent. An ultrasonic bath (SONICA, Italy) was used to disperse the nanosorbent in sample solution vials. A shaker (Pars Azma Co., Iran) was used for controlled stirring the sample solution vials in adsorption and desorption steps. The pH values were measured with a digital pH-meter model 827 (Metrohm Ltd., Switzerland) supplied with a glass-combined electrode. An electronic analytical balance

model PB303 (Mettler Toledo, Switzerland) was used to weight the solid materials.

Standard Solutions and Reagents

All chemicals were used of analytical-reagent grade and all solutions were prepared with high-purity deionized water (Shahid Ghazi Co., Iran). A stock solution of silver (1000 mg l⁻¹) was prepared in a 100 ml volumetric flask by dissolving 0.1575 g of silver nitrate (Merck, Germany) in diluted nitric acid (Merck, Germany) and stored in a dark place. The working solutions were prepared daily by stepwise diluting the stock solution with deionized water. A phosphate buffer solution (0.3 M) was prepared by dissolving appropriate amounts of sodium phosphate (Merck, Germany) in deionized water and adjusting to pH 7 by adding diluted NaOH (Merck, Germany) solution. All reagents and solvents including methanol, ethanol, sulfuric acid, acetic acid, hydrochloric acid, H₂O₂, THF, SOCl₂, 3-aminopropyltriethoxysilane (APTES), 1,3-diaminopropane (DAP), triethylamine (TEA), styrene, maleic anhydride (MA), 3-aminobenzoic acid (ABA), benzoyl peroxide (BPO), ferric chloride (FeCl₃·6H₂O), ferrous chloride (FeCl₂·7H₂O), ammonia, and all salts used for the interference study were purchased from Merck. All the plastic and glassware used for the trace analysis were kept in 15% (v/v) nitric acid at least overnight and rinsed three times with deionized water prior to use. A standard reference material (SRM 1566b) obtained from national institute of standards and technology (Gaithersburg, USA) was used for validation of the presented method.

Synthesis of the Modified Fe₃O₄ Magnetic Nano-Particles

Magnetic Fe₃O₄ NPs were prepared by chemical co-precipitation method [16]. FeCl₃·6H₂O (10 mmol, 2.730 g) and FeCl₂·7H₂O (5 mmol, 0.994 g) were dissolved in deionized water (20 ml) and stirred at 80 °C. Then, 80 ml of NH₄OH solution (1.5 M) was added into the mixture under N₂ atmosphere until the pH reached 10 and the reaction mixture was stirred for 1h. After the formation of a black precipitate, the Fe₃O₄ NPs were collected by a magnet and washed three times using deionized water until the pH reached 7 and then dried in vacuum oven for 24 h.

The synthesized Fe₃O₄ NPs (1 g) were dispersed in 200

ml of ethanol by sonication for 1 h. Then, the mixture was remained under the argon atmosphere for 30 min. Subsequently, 8 ml of APTES was added into the mixture under vigorous stirring and followed by sonication for 24 h at 50 °C. Finally, the modified APTES-Fe₃O₄ NPs were collected by applying a magnet, washed three times with ethanol, and dried in vacuum at 80 °C.

Synthesis of the Modified Styrene-Maleic Anhydride (SMA) Copolymer

The SMA copolymer was prepared by free radical polymerization of maleic anhydride and styrene at 70 °C in the presence of benzoyl peroxide as initiator [26]. Briefly, styrene and maleic anhydride were dissolved in 50 ml of THF at 1:1 molar ratio in a 250 ml three neck flask equipped with a magnetic stirrer, a condenser, and an inlet for inert gas. Then, BPO (0.05 mmol) was added and after stirring under argon atmosphere for 20 min, the mixture was heated at 70 °C and refluxed under these conditions for 7 h. After cooling down to room temperature, the SMA copolymer precipitation was completed by adding methanol into the mixture. Finally, the resultant white precipitate was separated by filtering and dried in vacuum at 80 °C.

For synthesis of the modified SMA copolymer, 1.25 g of the obtained SMA copolymer and 0.67 g ABA in ratio of 100:80 were poured in a three neck flask equipped with condenser, magnetic stirring bar, inlet and outlet of argon gas, and ultrasonic irradiation probe. Then, 0.5 ml of TEA as catalyst and 50 ml of THF as solvent were added and the reaction mixture was refluxed for 1 h at 70 °C [27]. Next, after adding 2 ml of SOCl₂, the reaction was continued at 65 °C for 24 h under argon atmosphere. Finally, the precipitation [poly(ABA-SMA)] was separated by filtration and dried in vacuum at 60 °C.

Synthesis of Magnetic Nano-Composite

For synthesis of MNC, the modified APTES-Fe₃O₄ NPs were firstly sonicated in 30 ml of THF for 20 min. Then, the modified ABA-SMA copolymer in weight ratio of 0.5:1 (APTES-Fe₃O₄:ABA-SMA) was added into the mixture, and the reaction mixture was sonicated for 24 h at 65 °C. After that, for further cross linking, DAP in weight ratio of 1:1 (DAP: ABA-SMA) was added dropwise into the mixture under sonication for 1 h. Finally, the synthesized

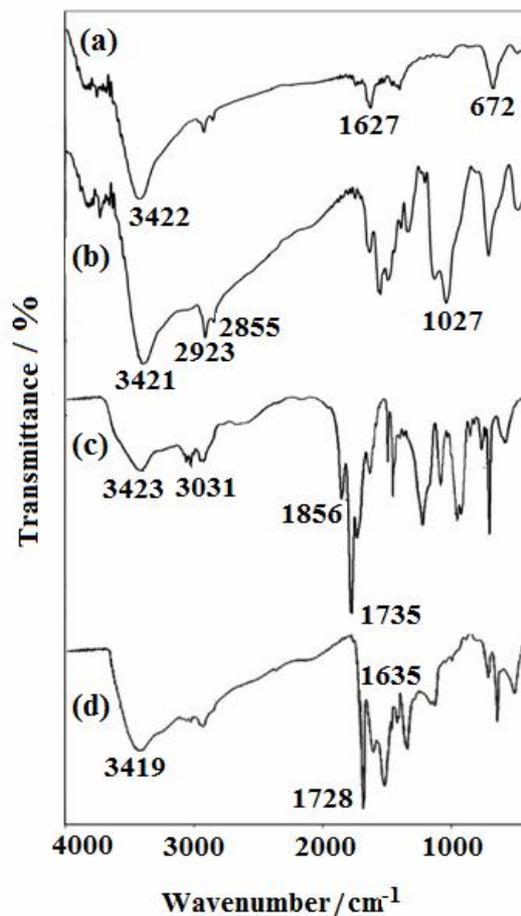


Fig. 1. FT-IR spectra of (a) Fe_3O_4 NPs, (b) APTES- Fe_3O_4 NPs, (c) poly(ABA-SMA), and (d) poly(ABA-SMA)@APTES- Fe_3O_4 MNC, respectively.

poly(ABA-SMA)@APTES- Fe_3O_4 MNC was collected by using a magnetic field, washed with THF to remove unreacted copolymers, washed several times with ethanol and dried in vacuum at 80 °C.

Sample Preparation

Water samples including tap water, distilled water, lake water, river water, wastewater and underground water were chosen for the analysis. Underground water, river water, sea water, wastewater and tap water were collected from local sources. On arrival to laboratory, water samples were filtered through a round filter paper (blue band, no. 300210) to remove suspended particulate matter, transferred to the PTFE container and stored in a refrigerator at 4 °C. Aliquots

of 100 ml of each sample solution were analyzed within 24 h of collection by following the procedure described in "General Procedure" section.

Radiology film samples were dissolved according to the following procedure [28]. 10 ml of concentrated nitric acid was added to 25 mg of radiology film sample in a beaker and boiled for 20 min. The resulting solution was then transferred into a 100 ml volumetric flask and diluted to the mark with deionized water. Finally, the solution was taken for analysis according to the procedure described in "General Procedure" section.

An accurately measured amount (50 mg) of the standard reference material (NIST SRM 1566b, Oyster Tissue) was heated on a hot plate at 120 °C for 45 min in the glass

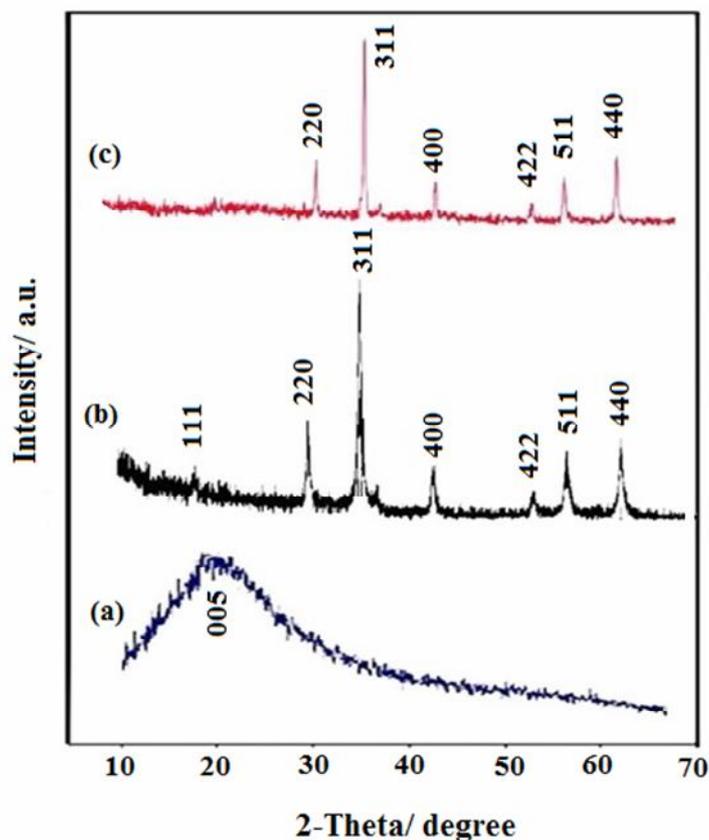


Fig. 2. XRD patterns of (a) poly(ABA-SMA), (b) Fe₃O₄ NPs and (c) poly(ABA-SMA)@APTES-Fe₃O₄ MNC, respectively.

beaker containing mixture of concentrated nitric acid 65% (10 ml) and hydrogen peroxide 35% (5 ml) after covering with a clock glass [29]. Afterward, the sample was heated at 150 °C for 45 min and the heating process was continued to dryness of the sample at 200 °C. Then, the sample was cooled down to room temperature and the residue was dissolved in a 1.0 ml of HNO₃ 0.1 M. After dilution with deionized water, the pH was adjusted to nearly 6 by adding diluted NaOH solution. Finally, the solution was transferred into a 100.0 ml volumetric flask and after dilution to the mark with the deionized water, the concentration of Ag(I) was determined as described in "General Procedure" section.

General Procedure

Aliquots of 100 ml sample or standard solution

containing silver ions in the range of 1-200 µg l⁻¹ (pH 7, adjusted by 2 ml of 0.3 M phosphate buffer solution) was transferred into a 250 ml glassware beaker. Then, 100 mg of the synthesized magnetic nano-sorbent was added to the solution and the mixture was shaken for 10 min at room temperature. After that, the magnetic nano-sorbent was gathered at one side of the beaker under a strong external magnetic field (Nd-Fe-B, 10,000 gauss) and the clear supernatant was directly decanted. To desorb the extracted analyte, 1 ml of 2 M HCl solution was added on the isolated nano-sorbent. After shaking for 10 min, the nano-sorbent particles were gathered again, with the aid of a magnet, and the supernatant containing the concentrated silver ions was transferred into a small vial. Finally, the absorbance of silver atoms as an analytical signal was measured by atomic absorption spectrometer at $\lambda = 328.1$ nm. A reagent blank

was prepared using a similar procedure but without silver ion.

RESULTS AND DISCUSSION

Characterization of Poly(ABA-SMA)@APTES-Fe₃O₄ Magnetic Nano-Composite

The structure and the surface nature of the poly(ABA-SMA)@APTES-Fe₃O₄ MNC were characterized by FT-IR spectroscopy. Figure 1 shows the FT-IR spectra of (a) Fe₃O₄ NPs, (b) APTAS-Fe₃O₄ NPs, (c) poly(ABA-SMA), and (d) poly(ABA-SMA)@APTES-Fe₃O₄ MNC. In Fig. 1a and 1b, the absorption bands at around 672 cm⁻¹ can be ascribed to the Fe-O stretching vibration of Fe₃O₄. In addition, O-H stretching vibration around 3422 cm⁻¹ and O-H deformed vibration at 1627 cm⁻¹ are observed in these spectra, suggesting that -OH groups coat the surface of Fe₃O₄ NPs as reported [16]. The presence of APTMS on the surface of Fe₃O₄ NPs is also certified by the bands at 1120 and 1027 cm⁻¹ which are due to Si-O stretching vibrations (Fig. 1b). This reveals that the covalent bonds of Fe-O-Si are formed after modification of Fe₃O₄ NPs through silanization reaction with APTMS. The broad band at 3421 cm⁻¹ is referred to the N-H stretching vibration which can be overlapped by the O-H stretching vibration band. Moreover, the characteristic peaks of C-H stretching vibrations at 2855 and 2923 cm⁻¹ confirm the presence of an anchored propyl group. Comparison of the FT-IR spectra of poly(ABA-SMA) (Fig. 1c) and poly(ABA-SMA)@APTES-Fe₃O₄ MNC (Fig. 1d) indicates that characteristic absorption bands of the anhydride linkage of poly(ABA-SMA) at 1735, 1784, and 1856 cm⁻¹ disappear after reaction with the APTMS-Fe₃O₄ NPs. As shown in Fig. 1d, in the case of poly(ABA-SMA)@APTES-Fe₃O₄ MNC, the absorption band at 1728 cm⁻¹ is related to the amide groups and the peaks at 1635 and 3419 cm⁻¹ confirm the presence of the carboxylic groups.

The powder X-ray diffraction (XRD) is a very powerful technique for characterizing the structure of materials. To study the crystal structure of poly(ABA-SMA)@APTES-Fe₃O₄ MNC, the XRD patterns of the as-prepared poly(ABA-SMA), Fe₃O₄ NPs and poly(ABA-SMA)@APTES-Fe₃O₄ MNC are shown in Figs. 2a-c, respectively. As shown in Fig. 2a, there is only a broad

diffraction peak at about $2\theta = 20^\circ$, which is assigned to the (0 0 5) reflection of poly(ABA-SMA), indicating the amorphous nature of the copolymer. The XRD pattern of Fe₃O₄ NPs indicates their cubic spinel structures, and the presence of sharp and intense peaks confirms the formation of highly crystalline Fe₃O₄ NPs (Fig. 2b). The XRD pattern of the synthesized poly(ABA-SMA)@APTES-Fe₃O₄ MNC shows diffraction peaks at the Bragg angles of about 30.21, 35.51, 43.21, 53.61, 57.11 and 62.91, which are respectively ascribed to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) facets of the cubic spinel crystal planes of Fe₃O₄ (JCPDS No.19-0629) (Fig. 2c). So, the existence of Fe₃O₄ NPs in poly(ABA-SMA)@APTES-Fe₃O₄ is confirmed, while the (0 0 5) reflection peak of poly(ABA-SMA) is almost disappeared. It may be due to the fact that after covering with Fe₃O₄ NPs, the poly(ABA-SMA) particles cannot stack with each other anymore to form crystalline structures [30,31].

Additionally, SEM was employed to explore the morphology of the synthesized materials. Figures 3a-c show the SEM images of APTES-Fe₃O₄ NPs, poly(ABA-SMA), and poly(ABA-SMA)@APTES-Fe₃O₄ MNC, respectively. The morphology of poly(ABA-SMA) reveals that the copolymer has amorphous nature and average diameter of the observed particles in SEM image can be estimated under 100 nm with reasonable monotony and grainy shape (Fig. 3b). FESEM image of poly(ABA-SMA)@APTES-Fe₃O₄ MNC demonstrates an aggregate that consists of MNC crystallites that are collected as small pseudo-spherical particles with approximate sizes in the range of 10-50 nm and are stacked with each other, which makes plate-like morphology (Fig. 3c). The successful synthesis of the MNC was further confirmed by the chemical composition analyzed by electron dispersive X-ray (EDX). Fig. 3d, shows the distribution of C, O, Si, Fe and N elements.

Choice of Adsorbent

To find the best adsorbent for extraction of Ag(I) ion as a target analyte from aqueous solutions, the synthesized adsorbents including Fe₃O₄ NPs, modified SMA, and modified SMA@Fe₃O₄ MNC were individually tested. As can be seen from Fig. 4, the analyte recovery is negligible in the case of unmodified Fe₃O₄ nanoparticles. However, the recovery of the analyte on the modified SMA@Fe₃O₄ MNC

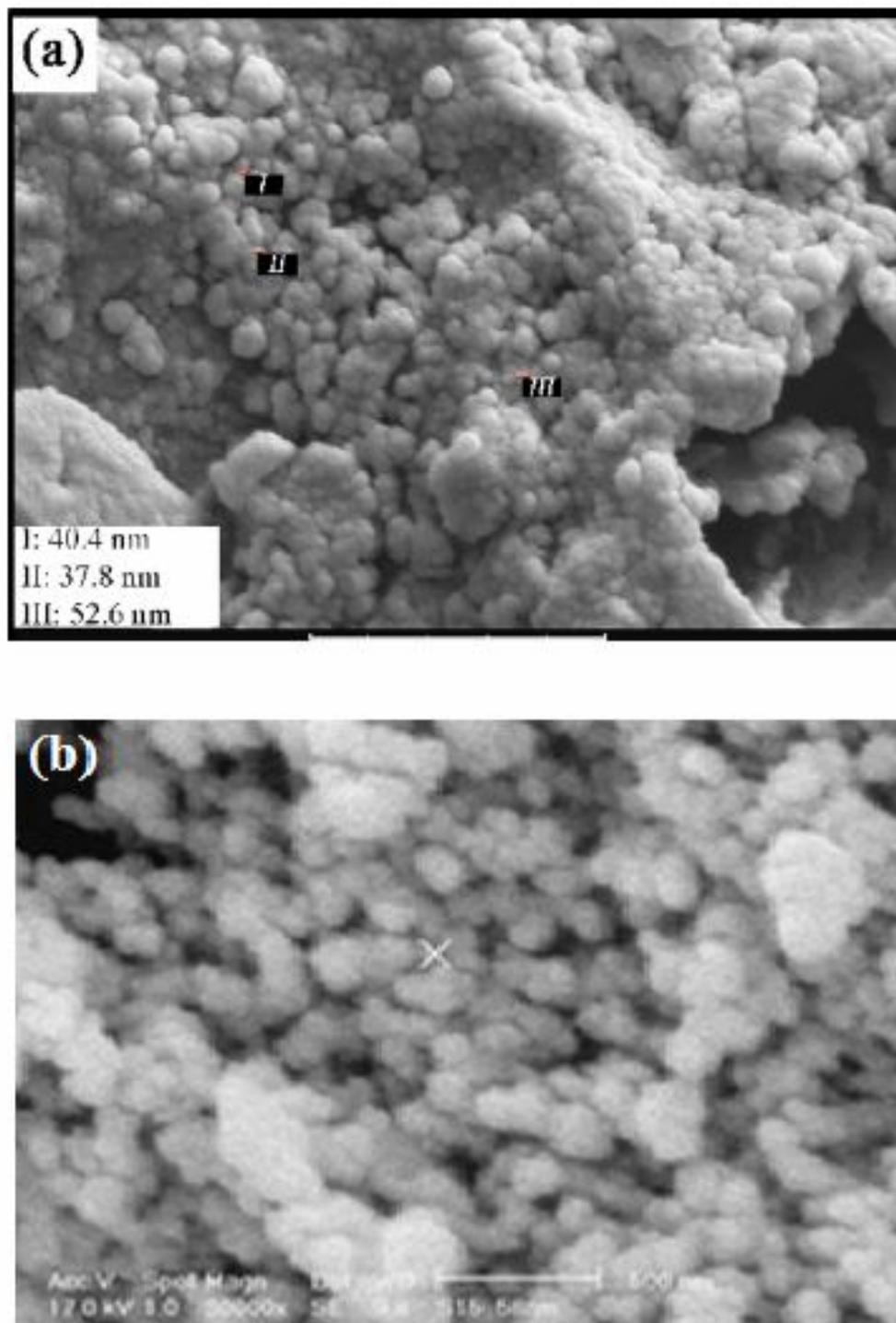


Fig. 3. SEM images of (a) APTES- Fe_3O_4 NPs, (b) poly(ABA-SMA), and (c) poly(ABA-SMA)@APTES- Fe_3O_4 MNC, respectively and (d) EDX spectrum of poly(ABA-SMA)@APTES- Fe_3O_4 MNC.

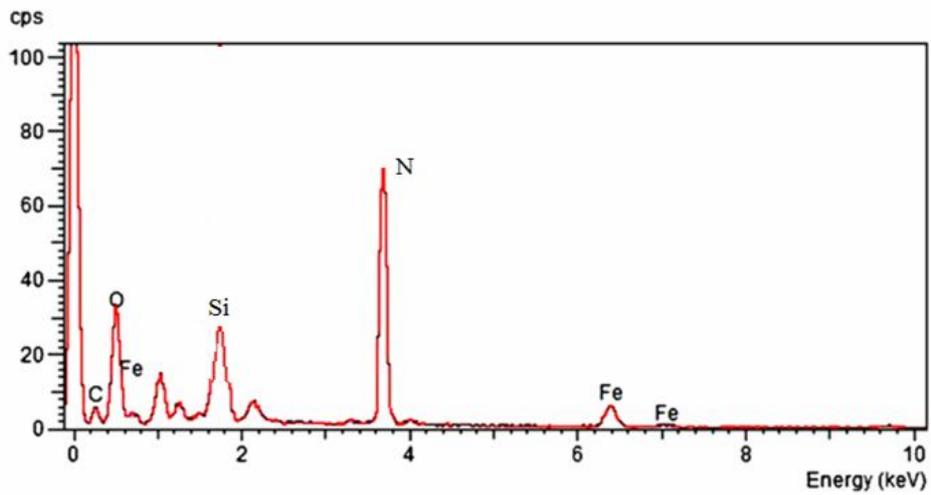
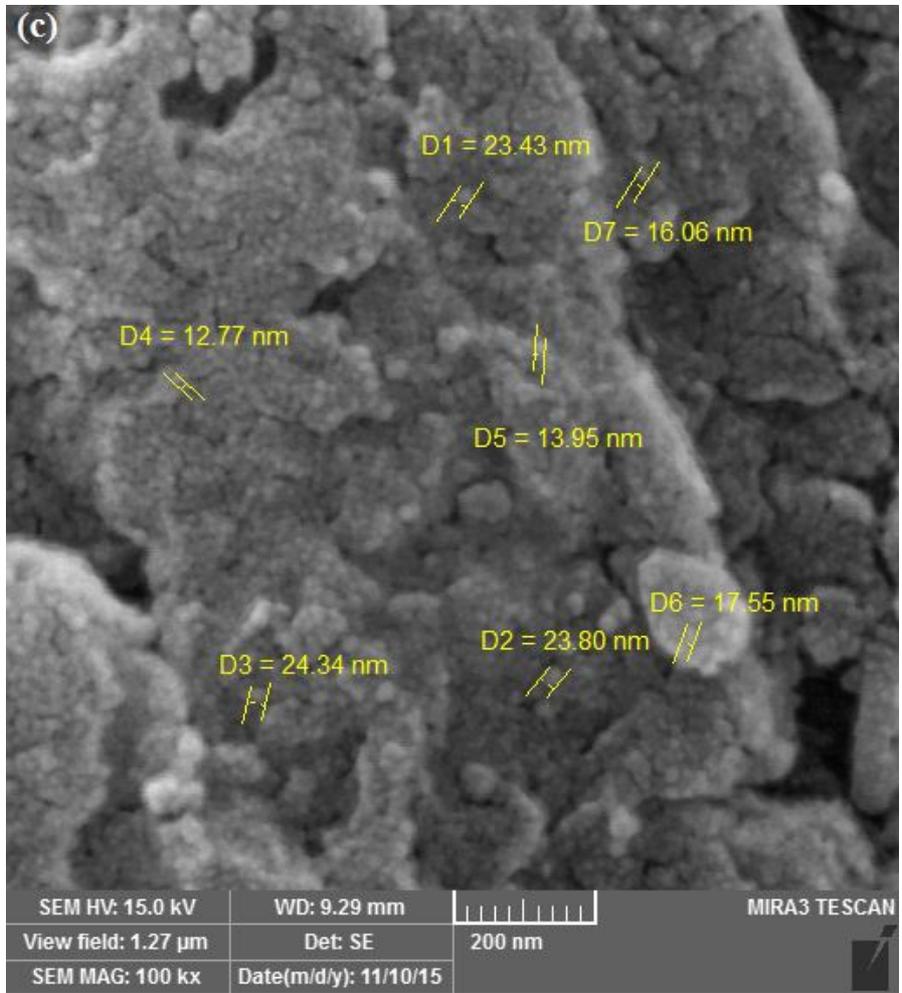


Fig. 3. Continued.

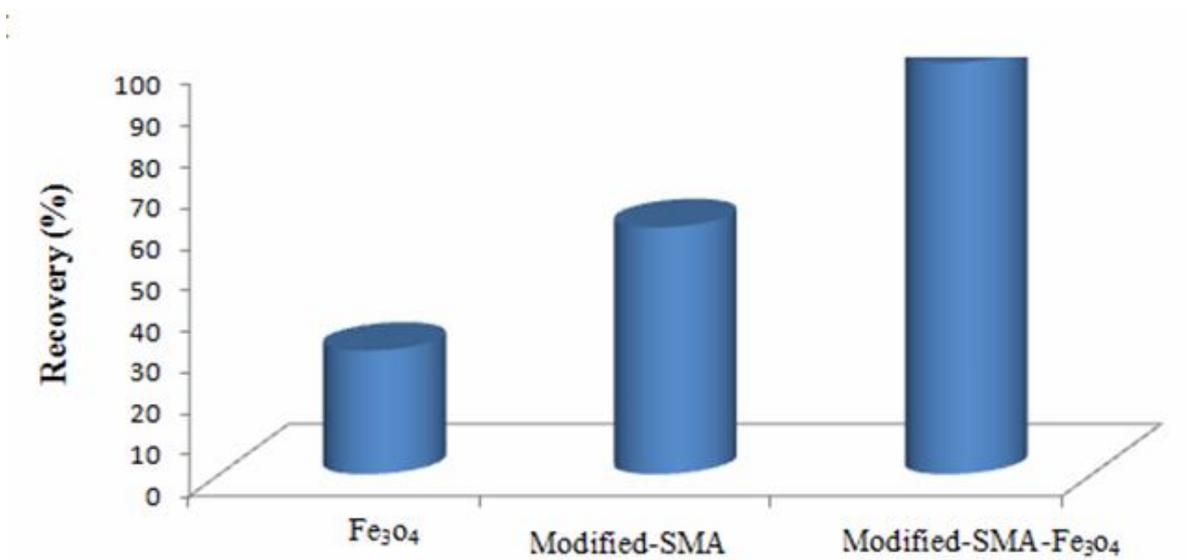


Fig. 4. Effect of adsorbent type on the extraction efficiency of Ag(I) ions.

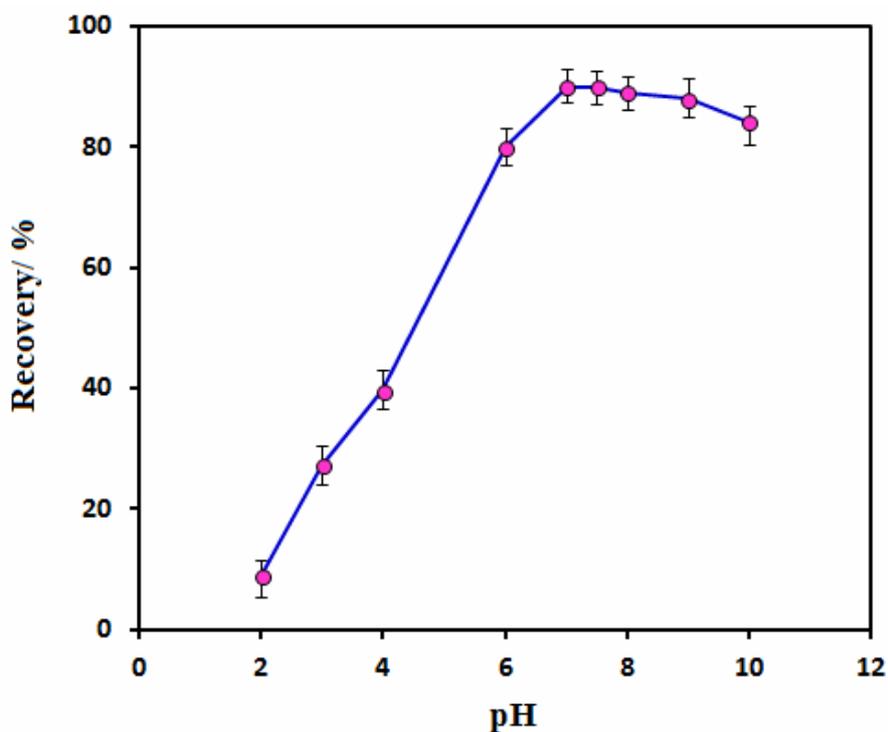


Fig. 5. Effect of the sample solution pH on the recovery of 100 µg l⁻¹ Ag(I) ion by poly(ABA-SMA)@APTES-Fe₃O₄ MNC nano-sorbent. Experimental conditions: amount of sorbent; 200 mg, sample volume; 50 ml, eluent conditions; 2 ml of 1 M HCl.

is the highest. As a result, the modified SMA@Fe₃O₄ MNC was employed as an adsorbent for the further experiments.

Optimization of Magnetic Solid Phase Extraction Conditions

To evaluate the capability of the presented method for separation and pre-concentration of silver ions, the effect of several variables on the extraction efficiency including pH, amount of the sorbent, extraction and desorption times, sample volume and elution conditions were studied and optimized. In all cases, the recovery percentage used as the analytical signal was calculated from the amount of silver ions in the starting sample and the amount of silver ions eluted from the sorbent. Method optimization was carried out using the one variable at a time method with a concentration of 100 µg l⁻¹ of the silver ions. In the impact parameters optimization procedure, the limits marked on the figures were obtained from three experiments that repeated under the same conditions.

Effect of pH

The influence of pH on the recovery of Ag(I) ion was investigated by adjusting the pH values of sample solution in the range of 2.0-10.0 using diluted HNO₃ or NaOH solution, or both. As can be seen from Fig. 5, the recovery increases with increasing the pH from 2 to 7 and remains constant between pH 7 and 9 before decreasing at pH values higher than 10. By increasing the pH, coordination ability of amine groups in the nano-sorbent structure may increase, leading to high recovery of the analyte. However, an increase in the concentration of OH⁻ anions, leading to silver hydroxide formation at pH > 10, might be ascribed to the observed decrease in the recovery. Accordingly, pH 7 was selected as the optimum pH for further experiments, and phosphate buffer solution (0.3 M) was used for adjusting the pH.

Effect of the Amount of Poly(ABA-SMA)@APTES-Fe₃O₄ Nano-Sorbent

The effect of the amount of poly(ABA-SMA)@APTES-Fe₃O₄ nano-sorbent on the sorption of Ag(I) ion at pH 7 was examined in the range of 25-200 mg. The results demonstrated that quantitative recoveries (>95%) of the working analyte are obtained by using at least 100 mg of the

nano-sorbent. Therefore, in the presented procedure, 100 mg of poly(ABA-SMA)@APTES-Fe₃O₄ is recommended.

Optimization of Elution Conditions

The nature of the eluent is of prime importance and should optimally meet three criteria: efficiency, selectivity and compatibility. In addition, it may be desirable to recover the analytes in a small volume of solvent to ensure a significant enrichment factor. In this work, elution of the extracted silver ions from the nano-sorbent surface was examined using various reagent solutions such as H₂SO₄, HCl, HNO₃ and CH₃COOH with different concentrations. Based on the obtained results, shown in Fig. 6, the best recovery was achieved when 2 M HCl solution was used as an eluent. The effect of elution volume (0.5-5.0 ml) on the recovery was also investigated. The recovery of the analyte increased by increasing the volume of the eluent up to 1 ml and remained constant afterward. So, to achieve the highest pre-concentration factor, 1 ml of the eluent was chosen as the optimum value.

Effect of the Adsorption/Desorption Time

Due to the super paramagnetic property of the nano-sorbent, the sorbent could be rapidly separated from the sample solution in about 2 min using an external magnetic field instead of filtration or centrifugation. However, to achieve satisfactory recovery and short analysis time during the separation and determination of the analyte, the effect of adsorption/desorption time on the recovery of Ag(I) ions was investigated. Both the adsorption and desorption times were varied in the range of 1-20 min. It was observed that 10 min is sufficient for each stage to achieve satisfactory recoveries during determination of silver (results are not shown).

Effect of Sample Volume

In the analysis of real samples, the sample volume is one of the most important parameters influencing the pre-concentration factor. Therefore, the effect of sample volume on the quantitative adsorption of Ag(I) ions was investigated. For this purpose, the volumes of sample solutions containing 10 µg Ag were varied from 10 to 250 mL, and the analyte in each sample solution was pre-concentrated and determined by applying the presented

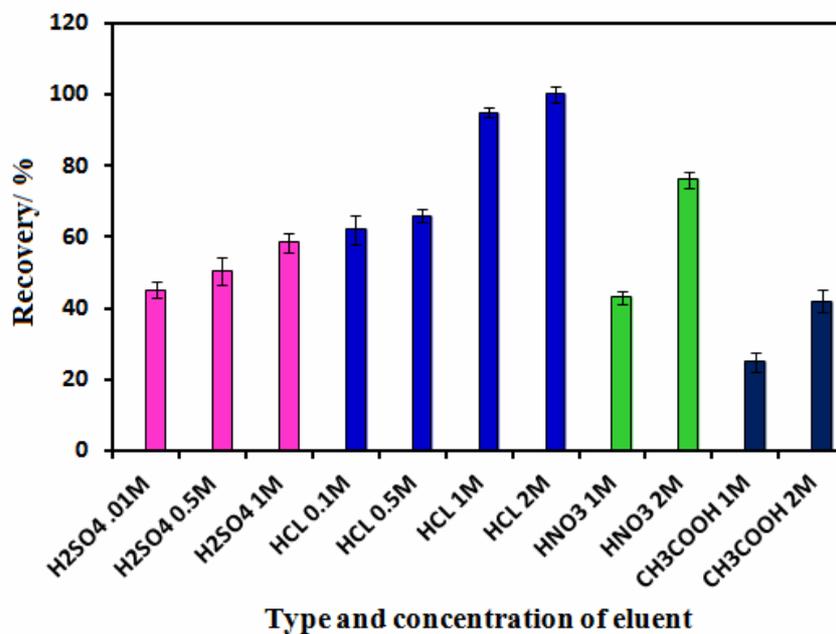


Fig. 6. Effect of eluent type and concentration on the recovery of 100 µg l⁻¹ Ag(I) ion. Experimental conditions: pH; 7, amount of sorbent; 100 mg, sample volume; 50 ml.

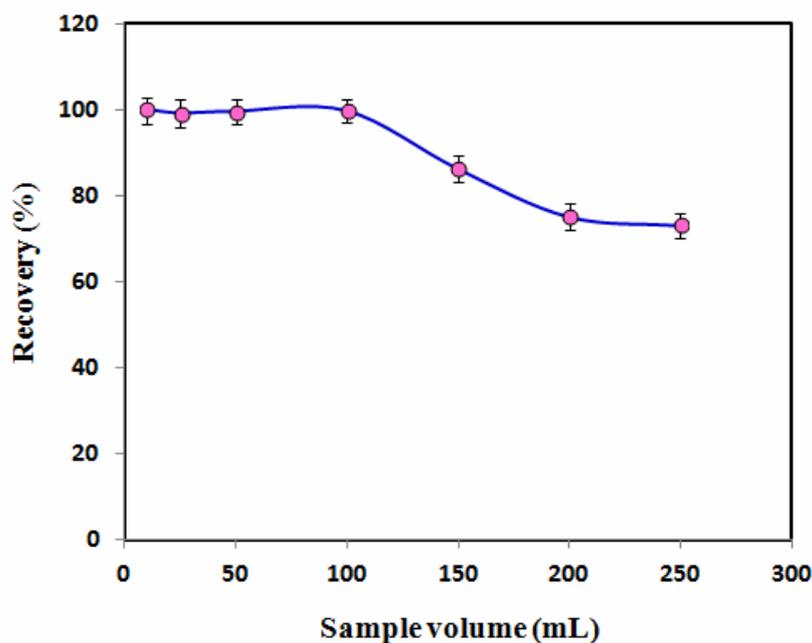


Fig. 7. Effect of sample volume on the recovery of 100 µg l⁻¹ Ag(I) ion. Other experimental conditions are given in Table 2.

MSPE-FAAS method. As shown in Fig. 7, the quantitative recovery values obtained were up to 100 ml of sample solution. Above 100 ml, the recovery decreased for the analyte. So, by analyzing 1 ml of the final solution, after the pre-concentration of 100 ml of sample solution, an enrichment factor was found to be 100.

Adsorption Capacity

The adsorption capacity (q_e , mg g⁻¹) of the nano-sorbent for Ag(I) ion was calculated using the following equation:

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

where, C_0 (mg l⁻¹) and C_e (mg l⁻¹) are the initial and equilibrium concentrations of the analyte in aqueous solution, respectively, V (L) is the volume of sample solution, and W (g) is mass of the used poly(ABA-SMA)@APTES-Fe₃O₄ magnetic nano-composite. To determine the maximum sorption capacity, 100 mg of the nano-sorbent was added to 250 ml of solution containing 100 mg l⁻¹ of the analyte and sonicated for 5 min. To reach equilibrium, the extraction process was continued for 60 min by stirring the solution on a mechanical stirrer at room temperature. Afterward, the nano-sorbent was separated from the solution under magnetic field. Then, the extracted Ag(I) ions were eluted from the nano-sorbent with 1 ml of 2.0 M HCl solution. Finally, the concentration of the analyte was determined by FAAS after an appropriate dilution. As a result, maximum capacity of the nano-sorbent for Ag(I) ion was found to be 78.2 mg g⁻¹.

Regeneration and Reusability of the Nano-Sorbent

The potential reusability and stability of the nano-sorbent were studied by monitoring the change in recovery of the analyte through several adsorption/desorption cycles. The nano-sorbent could be reused after regenerating with 2 ml of 2 M HCl and 10 ml deionized water, respectively. Moreover, based on the obtained results, 100 mg of the prepared magnetic nano-composite could be reused up to 100 times without an obvious loss in recovery of the analyte or magnetic properties of the nano-sorbent. Average recovery and coefficient variation values after 100 times adsorption/desorption cycles ($n = 5$, and Ag(I)

concentration; 100 µg l⁻¹) were >95% and <5%, respectively, suggesting the good reusability of the sorbent.

Study of Interferences

In order to demonstrate the selectivity of the developed extraction method for pre-concentration and determination of Ag(I) ion, the effect of alkali and alkaline earth metal ions and several potentially interfering ions in water samples on the recovery of the Ag(I) ion was investigated. In these experiments, different amounts of ions were added to the test solutions containing 100 µg l⁻¹ of Ag(I) ion and then followed according to the general procedure. The tolerance limit was considered as the highest ion concentration causing ±5% deviation in recovery of the analyte. As can be seen from Table 1, the tested potential interfering ions have no significant effect on the recovery of Ag(I) ions. Therefore, the developed method is fairly free from the interference resulting from the coexisting ions commonly found in water samples.

Analytical Figures of Merit

The optimized experimental parameters and analytical characteristics of the method are given in Table 2. Under the optimized experimental conditions, the analytical features of the presented method, such as the linear range of the calibration graph, the limit of detection (LOD) and limit of quantification (LOQ), the accuracy and the precision were examined. The calibration graph was linear in the range between 1 and 200 µg l⁻¹ with the correlation coefficient of 0.9991. The calibration equation was $A = 0.0161 C_{Ag} + 0.0022$, where A is the absorbance and C_{Ag} is silver ion concentration in µg l⁻¹. The LOD and LOQ, defined as $3S_b/m$, and $10 S_b/m$ (where S_b is the standard deviation of the blank and m is the slope of the calibration curve), were 0.3 µg l⁻¹ and 1 µg l⁻¹, respectively. To study the precision of the method, a series of six solutions were measured at the same day. The relative standard deviation resulting from the analysis of six replicates of 100 ml solution containing 100 µg l⁻¹ of Ag(I) ion under the optimized experimental conditions was 1.1%, showing the good precision of the developed method. The absolute recovery of the method is measured as the response of a processed spiked matrix standard expressed as a percentage of the response of a pure standard, which has not been subjected to sample pre-treatment. In the present work, absolute recoveries were

Table 1. Tolerance Limits of Interfering Ions in the Determination of 100 ng ml⁻¹ of Ag(I)

Interfering ions	Interferent to analyte ratio
Li ⁺ , Na ⁺ , K ⁺ , Cs ⁺ , Ca ²⁺ , Mg ²⁺ , Ba ²⁺ , Sr ²⁺ , Sn ²⁺ , Mn ²⁺ , CH ₃ COO ⁻ , NO ₃ ⁻ , H ₂ PO ₄ ⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , HPO ₄ ²⁻	>1000:1
F ⁻ , Cl ⁻ , Br ⁻	800:1
Ni ²⁺ , Co ²⁺ , Cr ³⁺ , Al ³⁺ , Fe ³⁺	400:1
Cu ²⁺ , Zn ²⁺ , Pb ²⁺ , Cd ²⁺	100:1

Table 2. Optimized Experimental Parameters and Analytical Characteristics of the Presented Method for Ag(I) Ion Extraction and Determination

Experimental conditions	Unit	
Amount of sorbent	mg	100
Sample volume	ml	100
Eluent concentration	M	2
Eluent volume	ml	1
Final volume	ml	1
pH	-	7.0
Buffer concentration	M	0.3
Analytical parameters	Unit	
Linear range	(µg l ⁻¹)	1-200
Intercept	-	0.0022
Slope	-	0.0161
Limit of detection ^a	(µg l ⁻¹)	0.3
Correlation coefficient	-	0.9991
RSD (%) (n = 6)	-	1.1 (100) ^b
Enrichment factor	-	100

Calculated as three times the standard deviation of the blank signal divided by the calibration curve slope. ^bValue in parentheses is the Ag concentration (µg l⁻¹) for which the RSD was obtained.

Table 3. Determination of Silver in Real Samples (Result of Recoveries of Spiked Samples and a Certified Reference Material Analysis)

Sample	Added Ag ($\mu\text{g l}^{-1}$)	Found Ag ^a ($\mu\text{g l}^{-1}$)	Recovery (%)
Tap water ^b	-	ND ^c	-
	5.0	4.93 \pm 0.05	98.6
	10.0	9.94 \pm 0.15	99.4
River water ^d	-	ND ^c	-
	5.0	4.94 \pm 0.02	98.8
	10.0	9.94 \pm 0.14	99.4
Underground water ^e	-	8.20 \pm 0.05	-
	5.0	13.04 \pm 0.14	96.8
	10.0	17.92 \pm 0.02	97.2
Lake water ^f	-	13.81 \pm 0.10	-
	5.0	18.68 \pm 0.14	97.4
	10.0	23.65 \pm 0.12	98.4
Distilled water ^g	-	ND ^c	-
	5.0	4.91 \pm 0.02	98.2
	10.0	9.96 \pm 0.12	99.6
Waste water ^h	-	126.06 \pm 1.25	-
	50.0	175.06 \pm 1.92	98.0
	100.0	225.36 \pm 2.32	99.3
Radiology film	-	416.38 \pm 4.16 ⁱ	-
	50.0	465.68 \pm 3.83 ⁱ	98.6
	100.0	515.88 \pm 5.23 ⁱ	99.5
NIST SRM 1566b	Certified values ($\mu\text{g g}^{-1}$)	Assayed values ($\mu\text{g g}^{-1}$)	Relative error (%)
	0.666 \pm 0.009	0.646 \pm 0.021	-3.0

^aMean of three experiments \pm standard deviation. ^bFrom drinking water system of Azarshahr, Iran. ^cND: Not detected. ^dCollected from Shaharchay river, Uremia, Iran. ^eObtained from local source, Azarshahr, Iran. ^fObtained from Uremia lake, Iran. ^gFrom distilled water of our laboratory, Azarbaijan Shahid Madani University, Tabriz, Iran. ^hObtained from wastewater of Shahrouz plating factory, Uremia, Iran. ⁱConcentration unit is $\mu\text{g g}^{-1}$.

Table 4. Comparison of the Presented Method with other Reported Solid-phase Extraction Methods

Detection technique	Sorbent	Linear range ($\mu\text{g l}^{-1}$)	LOD ($\mu\text{g l}^{-1}$)	EF	RSD (%)	Ref.
FAAS	CMPS-MBT	10-100	8	250	<3	[33]
FAAS	PTP-TiO ₂	3-120	1.2	100	2.2	[34]
FAAS	DBBT-XAD-16	n.r.	0.1	200	3.1	[35]
FAAS	MWNTs	Up to 800	0.60	50	3.8	[36]
ETAAS	TREN-Fe ₃ O ₄	1.5-1000	0.8	142	n.r.	[37]
ICP-OES	AMT-TMSPT-MNPs	n.r.	0.12	194	5.31	[38]
FAAS	SMA-modified Fe ₃ O ₄ MNPs	1-200	0.3	100	1.1	This work

LOD: Limit of detection; EF: Enrichment factor; RSD: Relative standard deviation; CMPS-MBT: Chloromethylated polystyrene modified with 2-mercaptopbenzothiazole; TiO₂-PTP: Poly-thiophene coated TiO₂ nanoparticles; DBBT-XAD-16: *N,N*-dibutyl-*N*¹-benzoylthiourea impregnated onto Amberlite XAD-16 polymeric matrix; n.r.: Not reported; MWNTs: Multiwalled carbon nanotubes; TREN-Fe₃O₄: Tris(2-aminoethyl)amine-functionalized Fe₃O₄ nano-particles; AMT-TMSPT-MNPs: Magnetic nanoparticles coated by 3-(trimethoxysilyl)-1-propanol and modified with 2-amino-5-mercapto-1,3,4-thiadiazole; MPSMA-modified Fe₃O₄ MNPs: Modified Fe₃O₄ nanoparticles coated with modified styren-maleic anhydride copolymer.

obtained between 95% and 98% regarding the known amounts of the target analyte in the different matrices.

Analysis of the Real Samples and Method Validation

To test the applicability of the method, it was used to determine Ag(I) in radiology film and water samples including tap water, distilled water, lake water, river water, wastewater and underground water. The obtained results are

summarized in Table 3. In order to evaluate the accuracy of the presented method, known quantities of Ag(I) ions were added into the real samples, and then the samples were prepared and analyzed according the procedure described in "General Procedure" section. As can be seen from Table 3, relative recoveries between 96.8 and 99.6% were obtained, confirming the accuracy of the developed method. Furthermore, the accuracy of the method was also verified by determining the content of Ag(I) ions in a certified

reference material, SRM 1566b, with a certified silver content of $0.666 \pm 0.009 \mu\text{g g}^{-1}$. The obtained value for silver by using the presented procedure was $0.646 \pm 0.021 \mu\text{g g}^{-1}$ (mean of three determinations \pm standard deviation). It was found that there is no significant difference at 95% confidence level between the result found by the developed method and the certified value according to Student *t*-test [32]. It can be concluded that the synthesized nano-sorbent could be used as a promising solid-phase extractor for extraction and determination of silver ions in water samples, radiology film and biological samples. Moreover, the results indicate that the presented method for Ag(I) ion determination is not affected by the matrix elements of the analyzed samples.

Comparison of the Presented Method With Other Solid-Phase Extraction Procedures

Table 4 compares the analytical characteristic data of the presented method with other solid-phase extraction techniques reported in the literature for the pre-concentration and determination of silver ion. This methodology gives excellent precision, relatively low detection limit, good enrichment factor and good accuracy showing its potential ability in trace analysis of various samples with complicated matrix such as environmental samples. The coupling of poly(ABA-SMA)@APTES-Fe₃O₄ MNC nano-sorbent for SPE procedure with FAAS detection exhibits a simple, inexpensive, sensitive, reproducible, and environment-friendly technique that can be used for the pre-concentration and determination of Ag(I) ion in routine analytical laboratories.

CONCLUSIONS

The introduced poly(ABA-SMA)@APTES-Fe₃O₄ MNC was found suitable and efficient nano-sorbent for the trace enrichment of Ag(I) ion. The presented procedure is simple and fast for sorption and pre-concentration of the metal ion without using any chelating agent and organic solvents. High selectivity and accuracy of the presented method have made it a suitable and selective method for the extraction and pre-concentration of silver ions from aqueous solutions. The simplicity of Fe₃O₄ modification with an amino-terminated silane coupling agent, easy separation by a

magnet, good reusability (more than 100 times) and high capacity factor improves the application of the synthesized magnetic nano-composite as a special nano-sorbent for magnetic solid-phase extraction of silver ion. The presented method possesses some advantages such as: simplicity, low matrix effect, a short extraction time (10 min), high preconcentration factor (100), low detection limit ($0.3 \mu\text{g l}^{-1}$), good precision (RSD = 1.1%), excellent accuracy and high sorption capacity (78.2 mg g^{-1}).

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REFERENCES

- [1] L.C. Giannossa, D. Longano, N. Ditaranto, M.A. Nitti, F. Paladini, M. Pollini, M. Rai, A. Sannino, A. Valentini, N. Cioffi, *Nanotechnol. Rev.* 2 (2013) 307.
- [2] V.E. Jones, *Lett. Appl. Microbiol.* 49 (2009) 147.
- [3] Agency for Toxic Substances Disease Registry (ATSDR), *Toxicological Profile for Silver*, US Department of Health and Human Services, Atlanta, GA, 1990.
- [4] A.M. Donia, A.A. Atia, K.Z. Elwakeel, *Hydrometallurgy* 87 (2007) 197.
- [5] S. Dadfarnia, A.M. Haji Shabani, M. Gohari, *Talanta* 64 (2004) 682.
- [6] M. Krachler, C. Mohl, H. Emons, W. Shotyk, *Spectrochim. Acta B* 57 (2002) 1277.
- [7] M. Faraji, Y. Yamini, A. Saleh, M. Rezaee, M. Ghambarian, R. Hassani, *Anal. Chim. Acta* 659 (2010) 172.
- [8] X. Wang, L. Zhang, C. Ma, R. Song, H. Hou, D. Li, *Hydrometallurgy* 100 (2009) 82.
- [9] G. Yang, W. Fen, C. Lei, W. Xiao, H. Sun, *J. Hazard. Mater.* 162 (2009) 44.
- [10] G. Chakrapani, P.L. Mahanta, D.S.R. Murty, B. Gomathy, *Talanta* 53 (2001) 1139.
- [11] K. Ohto, H. Yamaga, E. Murakami, K. Inoue, *Talanta* 44 (1997) 1123.
- [12] J. Waluvanaruk, W. Aeungmaitrepirom, T. Tuntulani,

- P. Ngamukot, *Anal. Sci.* 30 (2014) 389.
- [13] M.A. Karimiab, A.H. Mehrjadiab, S.Z. Mohammadiac, A. Mohadesiac, M.M. Ardakanid, A.A. Kabirb, M. Kazemipoure, N. Afsahi, *Intern. J. Environ. Anal. Chem.* 92 (2012) 1325.
- [14] L. Hajiagha-Babaei, Z. Ghasemi, F. Darviche, M. Shamsipur, F. Raoud, M.R. Ganjali, *Anal. Sci.* 17 (2001) 1305.
- [15] G. Yang, W. Fena, C. Lei, W. Xiao, H. Sun, *J. Hazard. Mater.* 162 (2009) 44.
- [16] A. Masoumi, M. Ghaemy, A. NikBakht, *Ind. Eng. Chem. Res.* 53 (2014) 8188.
- [17] A.R. Turker, *Clean* 35 (2007) 548.
- [18] P.A. Kavaklı, O. Güven, *J. Appl. Polym. Sci.* 93 (2004) 1705.
- [19] S. Thamizharasi, A.V.R. Reddy, S. Balasubramanian, *React. Funct. Polym.* 40 (1999) 143.
- [20] T. Shiraishi, M. Tamada, K. Saito, T. Sugo, *Radiat. Phys. Chem.* 66 (2003) 43.
- [21] L.C.S. Maria, M.C.V. Amorim, M.R.M.P. Aguiar, P.I.C. Guimaraes, M.A.S. Costa, A.P. Aguiar, P.R. Rezende, M.S. Carvalho, F.G. Barbosa, J.M. Andrade, R.C.C. Ribeiro, *React. Funct. Polym.* 49 (2001) 133.
- [22] Y. Rong, H. Chen, D. Wei, J. Sun, M. Wang, *Colloids Surf. A: Physicochem. Eng. Asp.* 242 (2004) 17.
- [23] M.K. Rofouei, M. Payehghadr, M. Shamsipur, A. Ahmadalinezhad, *J. Hazard. Mater.* 168 (2009) 1184.
- [24] P.N. Moghadam, R. Hasanzadeh, J. Khalafy, *Iran. Polym. J.* 22 (2013) 133.
- [25] P.N. Moghadam, R. Hasanzadeh, F. Fathi, A. Nasr, *J. Macromol. Sci. Pure Appl. Chem.* 50 (2013) 1167.
- [26] M. Świtła-Żeliazkow, *Polym. Deg. Stab.* 91 (2006) 1233.
- [27] R. Hasanzadeh, P. N. Moghadam, N. Samadi, *Polym. Adv. Technol.* 24 (2013) 34.
- [28] M.R. Fathi, N. Pourreza, S. Purweis, *J. Chinese Chem. Soc.* 56 (2009) 725.
- [29] E.G.P. Silva, V. Hatje, W.N.L. Santos, L.M. Costa, A.R.A. Nogueira, S.L.C. Ferreira, *J. Food Comp. Anal.* 21 (2008) 259.
- [30] R. Liang, C. Liu, X. Meng, J. Wang, J. Qiu, *J. Chromatogr. A* 1266 (2012) 95.
- [31] X. Liu, L. Yan, W. Yin, L. Zhou, G. Tian, J. Shi, Z. Yang, D. Xiao, Z. Gu, Y. Zhao, *J. Mater. Chem. A* 2 (2014) 12296.
- [32] J.C. Miller, J.N. Miller (Eds.), *Statistics for Analytical Chemistry*, 2th ed, Ellis Horwood, Chichester pp 55, 1988.
- [33] A.M. El-Menshawy, I.M. Kenawy, A.A. El-Asmy, *J. Hazard. Mater.* 173 (2010) 523.
- [34] M. Behbahani, M. Babapour, M.M. Amini, O. Sadeghi, A. Bagheri, M. Salarian, B. Rafiee, *Am. J. Anal. Chem.* 4 (2013) 90.
- [35] S. Ayata, I. Kaynak, M. Merdivan, *Environ. Monit. Assess.* 153 (2009) 333.
- [36] Q. Ding, P. Liang, F. Song, A. Xiang, *Sep. Sci. Tech.* 41 (2006) 2723.
- [37] H.R. Lotfizadeh Zhad, F. Aboufazeli, O. Sadeghi, V. Amani, E. Najafi, N. Tavassoli, *J. Chem.* (2013) Article ID 482793, <http://dx.doi.org/10.1155/2013/482793>.
- [38] M.H. Mashhadizadeh, Z. Karami, *J. Hazard. Mater.* 190 (2011) 1023.