Scientia Iranica F (2014) 21(3), 1151–1162

Sharif University of Technology
Scientia Iranica
Transactions F: Nanotechnology
www.scientiairanica.com

Separation/preconcentration and speciation of very low amounts of selenium using modified magnetite nanoparticles before electrothermal atomic absorption spectrometric determination in water

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Received 20 April 2013; received in revised form 8 February 2014; accepted 15 April 2014

KEYWORDS
Speciation analysis;
Solid phase extraction;
Selenium;
Ammonium pyrrolidine dithiocarbamate;
Modified magnetite nanoparticles.

Abstract. A new, simple, fast and reliable procedure for the speciation of selenium(IV) and selenium(VI) using Solid-Phase Extraction (SPE) with ammonium pyrrolidine dithiocarbamate/sodium dodecyl sulfate immobilized on alumina-coated magnetite nanoparticles (APDC/SDS-ACMNPs), followed by electrothermal atomic absorption measurement, is proposed. The method is based on the adsorption of Se(IV) on modified ACMNPs. Total selenium concentration in different samples was determined as Se(IV), after reduction of Se(IV) to Se(VI), by heating the samples in a microwave oven with 4.0 mol L^{-1} HCl. Se(VI) concentration was calculated as the difference between the total selenium content and Se(IV) content. The effect of parameters such as pH, amount of adsorbent, contact time, sample volume, eluent type, and HCl and APDC/SDS concentration ratios as modifiers, on the quantitative recovery of Se(IV), was investigated. Under optimal experimental conditions, the preconcentration factor, detection limit, linear range and Relative Standard Deviation (RSD) of Se(IV) were 125 (for 250 mL of sample solution), 0.05 ng mL^{-1}, 0.1-8.0 ng mL^{-1} and 4.1% (for 5.0 ng $mL^{-1}, n = 7$), respectively. This method avoided the time-consuming column-passing process of loading large volume samples in traditional SPE through the rapid isolation of APDC/SDS-ACMNPs with an adscititious magnet. The proposed method was successfully applied to the determination and speciation of selenium in different water samples and suitable recoveries were obtained.

1. Introduction

Speciation refers to the chemical and/or physical forms of an element, namely, its oxidation state, stoichiometry, or the possible presence of various ligands. Thus, speciation analysis is the process of identification and determination of different physical and/or chemical species in a sample. Despite the advances made in the field of speciation analysis of selenium over the last decades, there is still a relatively limited number of studies dealing with the determination of Se(IV) and Se(VI) species in real samples such as food, organisms, biological tissue and even environmental water [1]. The toxicity of selenium highly depends on its chemical forms. The organoselenium compounds are less toxic than the inorganic forms of Se(IV) and Se(VI), because these oxidation states are the most environmentally mobile in this element [2]. Except

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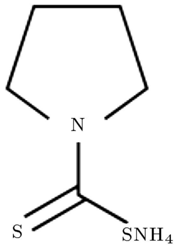
for some methods, like electroanalysis [3], simultaneous and direct determination of Se(IV) and Se(VI) species is difficult using other instrumental techniques such as Atomic Absorption Spectrometry (AAS). The use of prior separation/preconcentration of the samples can aid in improving the determination of Se(IV) and Se(VI) by AAS. In recent years, several separation/preconcentration methods such as liquid-liquid extraction [4], ion exchange [5], cloud point extraction [6], coprecipitation [7] and Solid Phase Extraction (SPE) [2,8-16] have been developed. Among them, SPE, due to faster operation, easier manipulation, reduction of the use of organic solvents, less stringent requirements for separation, higher preconcentration factors and easier compatibility with analytical instruments such as AAS, has been widely studied by many researchers. At present, nano-sized materials such as Al_2O_3, SiO_2, TiO_2 and carbon nanotubes have more importance in SPE due to their special capacity for high adsorption [17-20]. In relation to the use of these nanoparticles, Li and Deng reported the separation/preconcentration of Se(IV) and Se(VI) species by adsorption onto nanometer-sized TiO_2 and determination by a graphite furnace, AAS [21]. But, separation of these particles from aqueous medium is difficult because of their small dimension and high dispersion. Magnetite nanoparticles (MNPs), as a new kind of NP, are widely used in many separation fields, such as cell labeling and separation [22], and SPE methods [23-35]. A distinct advantage of these NPs is that MNPs can be readily isolated from sample solutions by the application of an external magnetic field. The surface modification of MNPs is an important challenging key to the application of SPE. SPE, with a magnetic core consisting of Fe_3O_4 with a nonreactive shell made of alumina, has been synthesized and, as sorbent, applied recently [24,25,30,31,34]. The main advantage of the preparation of alumina-coated magnetite nanoparticles (ACMNPs), compared to MNPs, is their higher stability in acidic and basic solutions. Recently, we also reported the methods for separation and preconcentration of Ag(I), Pb(II) and Hg(II) using ACMNPs [30,31,34]. These methods were based on the SPE of trace amounts of silver and lead ions, using dithizone and mercaptobenzothiazole/sodium dodecyl sulfate-immobilized on ACMNPs. To our knowledge, this is the first report to use ACMNPs-based SPE for the speciation analysis of species from large-volume real samples, such as environmental water.

Ammonium pyrrolidine dithiocarbamate (APDC) is a well known complexing agent (Scheme 1), which has been used in the past for solvent extraction of metal ions. The reagent is readily soluble in water and is stable in a wide pH range [36]. It forms a neutral complex with Se(IV) without inducing a change in its oxidation state [36,37]. The selectivity of APDC for this oxidation state is presumably due to the higher stability of the oxyanion of Se(VI), which prevents it from forming a complex, leaving only the lower oxidation state for complexation [38,39]. In this study, ACMNPs were successfully synthesized and modified by APDC with the aid of sodium dodecylsulfate (SDS) in acidic media to form mixed hemimicelles for the extraction of Se(IV) from real samples. After reduction of Se(VI), by heating the samples in a microwave oven with HCl, APDC/SDS-ACMNPs were applied to the adsorption of total selenium. Then, the adsorbed Se(IV) ions were eluted with HNO_3 solution, and quantified using Graphite Furnace Atomic Absorption Spectrometry (GFAAS).

2. Experimental

2.1. Apparatus and reagents

A scanning electron microscope (LEO 1455VP SEM), Fourier transform infrared spectrometer (IR Perresttige-21, Shimadzu) and vibrating sample magnetometer (VSM 7400 Model Lake-Shore) were used to characterize the structure of the prepared ACMNPs. A graphite furnace atomic absorption spectrometer (PG Instrument, England) was used, with the operating optimized parameters for the working element set as given in Table 1. For graphite furnace measurements, argon was used as inert gas, and samples of 20 μL plus 10 μL of a mixture of 0.015 mg Pd +0.01 mg $Mg(NO_3)_2$, as a matrix



Scheme 1. Structure of APDC.

Table 1. Instrumental settings and analytical conditions.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)
Drying 1	100	5	20
Drying 2	130	15	20
Ashing	1100	10	25
Atomization	2200	0	4
Cleaning	2600	1	3

The wavelength, slit width, lamp current, argon flow and reading time were 196 nm, 2 nm, 10 mA, 250 mL min^{-1} and 4 s, respectively.

modifier during the research, were injected into the furnace.

Other instruments such as ultrasonic bath (S60H Elmasonic, Germany), mechanical stirrer (Heidolph, RZR2020), and orbital shaker (Ika, KS130 Basic) were used, and an electronic analytical balance (Adam, AA220LA) was used for weighting the solid materials. In addition, for magnetic separations, a strong neodymium-iron-boron ($Nd_2Fe_{12}B$) magnet (1.2 T, 2.5 cm× 5 cm× 10 cm) was used. The milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300° C) was used.

All chemicals used were of analytical grade and all solutions were prepared using triple distilled and deionized water. Stock solutions (1000 μg mL^{-1}) of Se(IV) and Se(VI) were prepared by dissolution of Na_2SeO_3 and Na_2SeO_4 in 1.0 mol L^{-1} HC1 and 1.0 mol L^{-1} HNO_3, respectively. The working solutions of the metals were obtained by appropriate dilution of the stock solutions. Ammonium pyrrolidine dithiocarbamate (APDC), sodium dodecylsulfate (SDS), ferrous chloride ($FeCl_2.4H_2O$), ferric chloride ($FeCl_3.6H_2O$), aluminum isopropoxide, ethanol, nitric acid, hydrochloric acid and sodium hydroxide were used without further purification processes. The pHs of the solutions were adjusted with phosphate buffer. All chemicals were obtained from Merck. The pH adjustments were made with HCl/KCl buffer solution to pH 1-2, CH_3COONa/CH_3COOH buffer solution to pH 3-5, CH_3COONH_4/CH_3COOH buffer solution to pH 5-7 and NH_3/NH_4Cl buffer solution to pH 8-9.

2.2. *Preparation of ammonium pyrrolidine dithiocarbamate/alumina-coated magnetite nanoparticles (APDC/SDS-ACMNPs)*

The alumina-coated magnetite nanoparticles (ACMNPs) were prepared according to Karimi et al. [30,31]. APDC/SDS solution was prepared by dissolving 160.0 mg APDC and 200.0 mg SDS in 100 mL deionized water. Ten milliliters of APDC/SDS solution were added to 10 mL water containing 0.05 g of ACMNPs. The pH of this suspension was adjusted to 5.0 by dropwise addition of 0.1 mol L^{-1} CH_3COONa/CH_3COOH buffer 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 pure water. This product was used as sorbent for Se(IV).

2.3. *General procedure*

The procedure for magnetic extraction is presented in Figure 1, and details are as follows: For GFAAS analysis, 10 mL of 5 ng mL^{-1} Se(IV) solution were transferred into an Erlenmeyer flask and the pH value was adjusted to∽5.0 with CH_3COONa/CH_3COOH buffer solution. Then, 0.1 g of APDC/SDS-ACMNPs was added, and the solution was shaken for 10 min to facilitate adsorption of the metal ions onto the nanoparticles. The magnetic adsorbent was separated easily and quickly using a magnet and the supernatant was decanted directly. The magnet was removed, and 2 mL solution containing 4.0 mol L^{-1} HNO_3 was added as eluent. Finally, the magnet was used again to settle

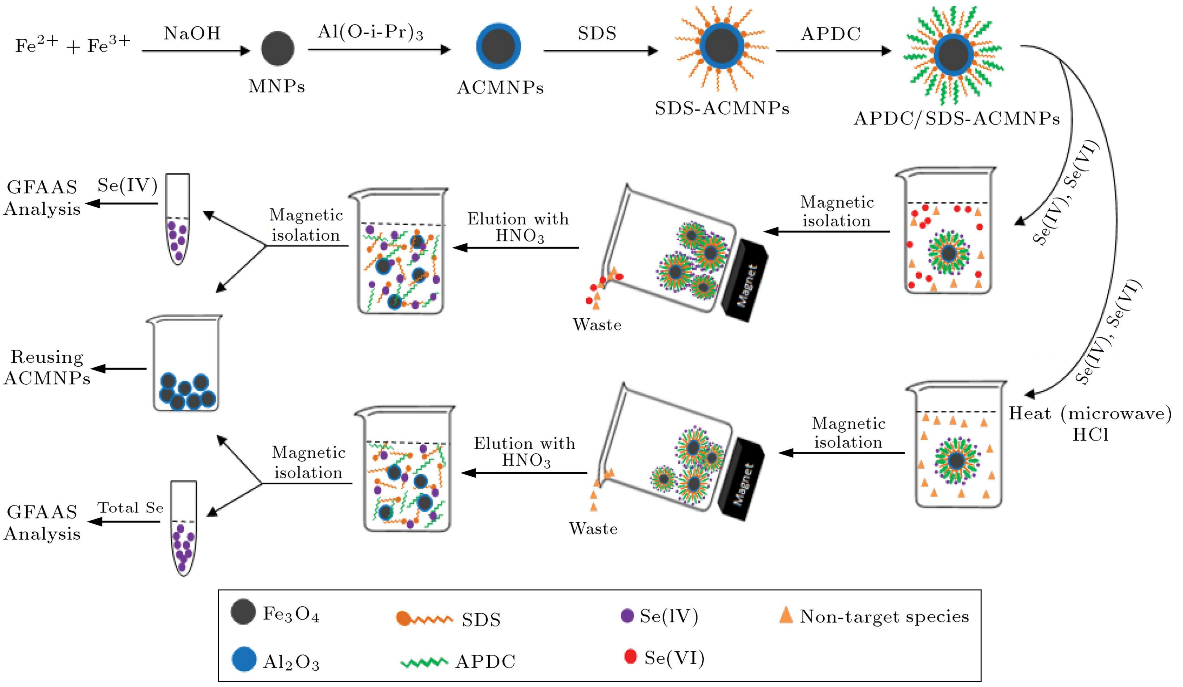


Figure 1. Procedure for preparation of APDC/SDS ACMNPs and their application for preconcentration and speciation of the Se based on magnetic SPE.

the ACMNPs, and the eluate was separated for GFAAS analysis.

2.4. Reduction of Se(VI) to Se(IV) and determination of total selenium

Reduction of Se(VI) to Se(IV) has been performed using a procedure given by Ferri et al. [40]. After adjustment of the pH of the solution (pH 5.0), the method given in Section 2.4 was applied to determine the total selenium. The level of Se(VI) is calculated using the difference of total selenium and Se(IV) concentrations.

2.5. Sample preparation procedure for different water samples

Water samples (i.e., tap water, spring water, river water, sea water and waste water) were filtered after collection through filter paper (Whatman, no. 4) to remove suspended particulate matter, and acidified by 5.0 mL of concentrated HNO_3 prior to storage in polyethylene containers for use. The pH of the samples was adjusted to 5.0 with buffer solution. Then, the procedures given in Sections 2.4 and 2.5 were applied to the determination of Se(VI), Se(IV) and total selenium in the samples. The levels of Se(VI), Se(IV) and total selenium in the samples were determined by GFAAS.

3. Results and discussion

3.1. Characterization of ACMNPs

The MNPs, ACMNPs and APDC/SDS-ACMNPs were characterized by Scanning Electron Microscopy (SEM), Fourier transform infrared spectrometry (FT-IR) and Vibrating Sample Magnetometery (VSM). SEM images of NPs and ACMNPs also show the uniform size distributions of the NPs (Figure 2). The modified ACMNPs were also confirmed by FT-IR analysis, as shown in Figure 3. As can be seen in Figure 3(a), a broad band exists around 588.18 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 3433.64 cm^{-1} [41]. In Figure 3(b), the spectrum of ACMNPs, compared with the spectrum of MNPs after binding alumina, and the broadening of the peak at 620.00 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 APDC/SDS ACMNPs (Figure 3(c)) also shows a new sharp peak at 1443.46 cm^{-1}. This was due to the C-S stretching peak of APDC stabilized on ACMNPs. Consequently, the FT-IR data suggest that APDC are successfully immobilized on the ACMNPs surface. The magnetization curves show that both MNPs and ACMNPs exhibit typical superparamagnetic behavior due to no hysteresis (Figure 4). Values of large saturation magnetization of MNPs and ACMNPs were 56.27 and 9.14 emu g^{-1}, respectively. The large

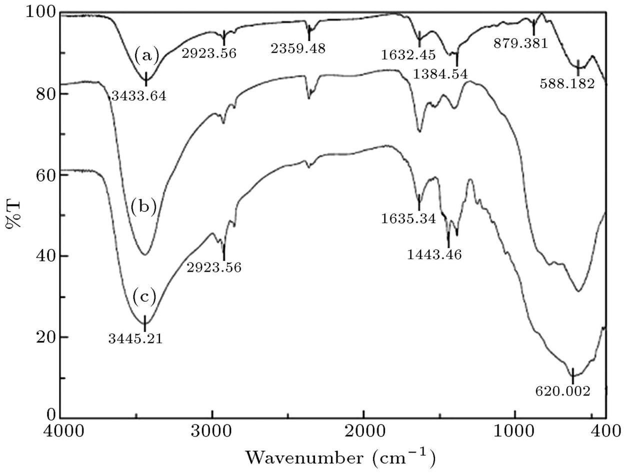
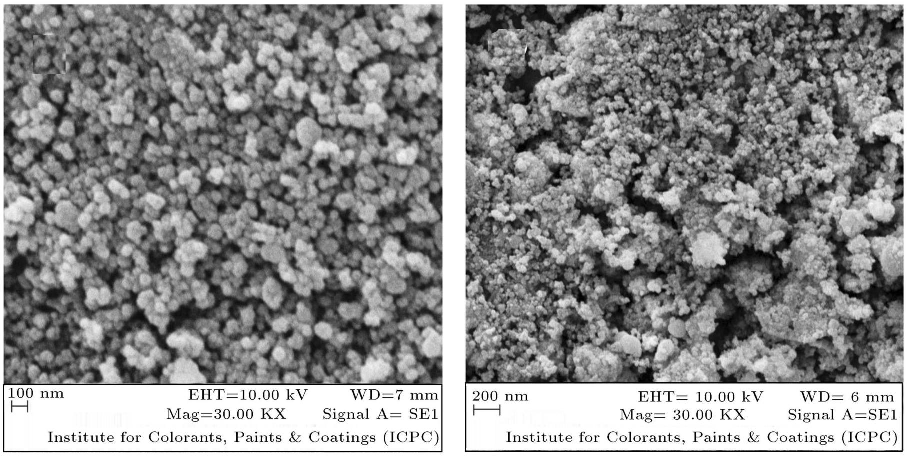


Figure 3. FTIR spectra of the MNPs (a), ACMNPs (b) and APDC/SDS ACMNPs (c).



(a) (b)

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

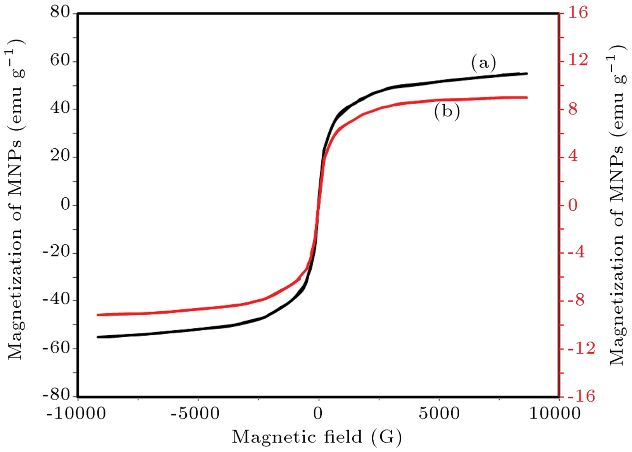


Figure 4. The magnetic behavior of MNPs (a) and ACMNPs (b).

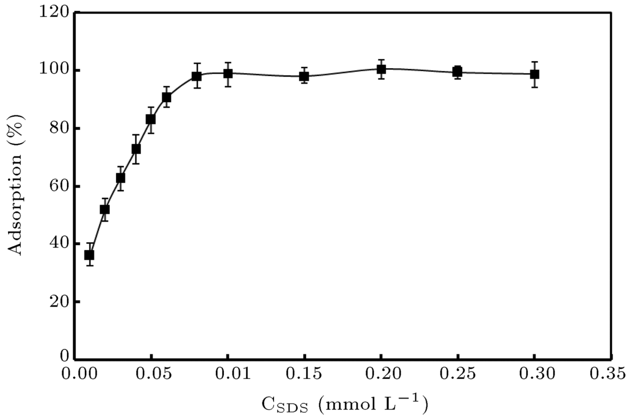


Figure 5. Effect of SDS concentration on adsorption of Se(VI). Conditions: ACMNPs (0.05 g), APDC (10 mL, 5.0×10^{-1} mmol L^{-1}) and Se(VI) solution (10 mL, 5.0 μg mL^{-1}, pH 5.0).

saturation magnetization decreases for ACMNPs, in comparison to the MNPs, due to the alumina coating on the MNPs. However, these ACMNPs are sufficient for magnetic separation with a conventional magnet.

3.2. Amounts of SDS and APDC

The molecules of Sodium Dodecyl Sulfate (SDS) can effectively be sorbed on the positively charged surface of ACMNPs in highly acidic solutions [30,31,34]. A concentration of SDS, below its critical micellar concentration (CMC, 8 mmol L^{-1}), was used (Figure 5). Above this concentration, the excess of SDS would form micelles in the aqueous solution, which were not adsorbed on alumina surfaces. Results show that with the increase of SDS concentration, the absorbance increases. A maximum is obtained after the SDS concentration approaches 8.0×10^{-2} mmol L^{-1} and remains constant up to CMC. It then decreases, because, above this point, micelles are strongly formed. Therefore, 1.0×10^{-1} mmol L^{-1} SDS concentration was employed for further experiments.

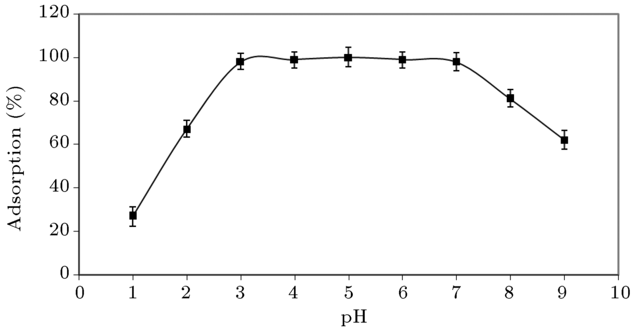


Figure 6. Effect of pH on the adsorption of Se(IV). Conditions: ACMNPs (0.05 g), APDC (10 mL, 5.0×10^{-1} mmol L^{-1}), Se(VI) solution (10 mL, 5.0 μg mL^{-1}) and SDS (10 mL, 1.0 mmol L^{-1}).

In order to study the effect of APDC concentration on adsorption of Se(IV) ions on the ACMNPs, ammoniacal solutions of APDC/SDS with constant concentration of SDS and different concentrations of APDC were used. At APDC concentrations less than 5.0×10^{-2} mmol L^{-1}, the amount of APDC molecules immobilized into SDS cores is too low to completely complex all Se(IV) ions, so, recoveries less than 100 were observed. At concentrations more than 5.0×10^{-2} mmol L^{-1} of APDC, the sorbent sites are too rich, with respect to APDC molecules, to allow Se(IV) ions to be adsorbed by formation of its APDC complex. Therefore, 5.0×10^{-2} mmol L^{-1} of APDC was selected as the optimum concentration for further studies.

3.3. Effect of pH

In order to establish the effect of pH on the adsorption of Se(IV), batch equilibrium studies at different pH values were carried out in the range of 1.0-9.0. The acidity of the preconcentration solution has an influence over the adsorption efficiency of Se(IV) on APDC/SDS ACMNPs. This effect is shown in Figure 6. As can be seen from this figure, high adsorption efficiency was achieved at a pH range of 3.0-7.0, and the adsorption of Se(IV) is quantitative ($> 97\%$). At pH values below 3.0 and pH > 7.0, the recovery decreased, due to the adsorption competition of H$^+$ ions with Se(IV) and the formation of negative charge (reduction of SDS adsorption) on the APDC/SDS ACMNPs surface, respectively. Therefore, a pH of 5.0, in the middle of the pH range, was selected as the optimum pH for further studies.

3.4. Desorption conditions

Different eluents of HNO$_3$, H$_2$SO$_4$, HCl, HBr, thiosulphate and thiourea at various concentrations were tested in order to elute the adsorbed Se(IV) from the sorbent. It was found that 2.0 mL of nitric acid with a concentration of 4.0 mol L^{-1} was sufficient for quantitative recovery ($> 95\%$) of adsorbed Se(IV).

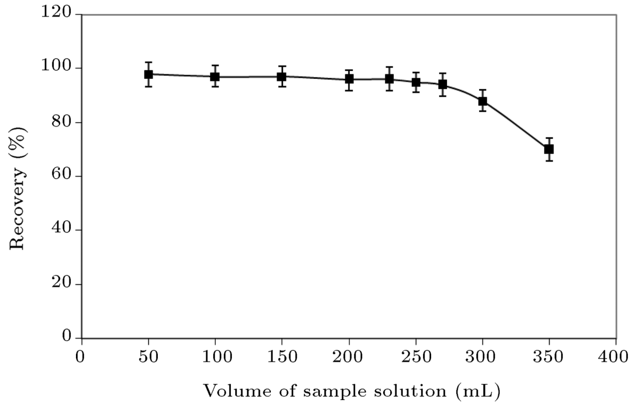


Figure 7. Effect of sample volume on Se recovery; Conditions: ACMNPs (0.05 g), APDC/SDS (10 mL, 5.0×10^{-1} mmol L^{-1}/1.0 mmol L^{-1}), Se(VI) solution (5.0 μg, pH 5.0).

3.5. *Effect of sample volume*

In order to obtain a preconcentration factor, a larger volume of sample solution is required. For study the effect of sample volume on the recovery of selenium ions, sample solutions in the range of 50-400 mL, containing 5.0 μg of Se(IV) ions, were studied. For this purpose, 50, 100, 150, 200, 230, 250, 270, 300 and 350 mL of sample solutions containing 5.0 μg of Se were operated, according to the general procedure, and eluted using 2.0 mL of HNO_3 (4.0 mol L^{-1}). As shown in Figure 7, in sample volumes higher than 250 ml, recovery decreased. Consequently, a preconcentration factor of 125 could be attained for quantitative recovery of 95±2% of Se(IV) when the sample volume is 250 mL.

3.6. *Effect of ACMNPs amounts and sorbent regeneration study*

The effect of nanoparticle amounts on the quantitative extraction of Se(IV) was studied by applying various amounts of APDC/SDS ACMNPs (from 10 to 200 mg). The extraction was found to be quantitative when 50 mg or more were applied. Experiments were carried out with 50 mg modified nanoparticles. It was found that the ACMNPs can be reused up to three times without loss of analytical performance. This reusable number is suitable because 4.0 g of ACMNPs could be prepared in one batch and only 0.05 g of ACMNPs was used for one extraction operation.

3.7. *Standing and magnetic separation time*

The effect of time of adsorption of Se(IV) on APDC/SDS ACMNPs was investigated. In the experiment, APDC/SDS ACMNPs possessed large saturation magnetization and superparamagnetism properties, which enabled them to be completely isolated in less than 1 minute by a strong magnet. When the APDC/SDS ACMNPs were isolated immediately without a standing process, the recovery of Se(IV) ions was only 57%. But, when the standing time was adjusted to 2, 5, 8, 10 and 15 min, recovery was improved to 92, 95, 97, 98 and 98%, respectively. Standing time of 10 min was sufficient to achieve satisfactory adsorption and better recovery of Se(IV).

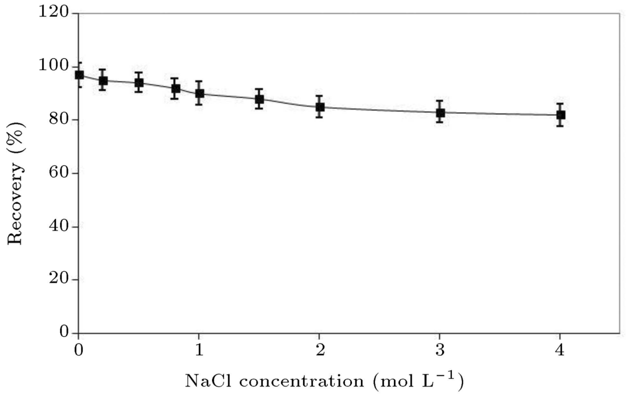


Figure 8. Effect of salt concentration on the extraction efficiency. Conditions as in Figure 7.

3.8. *Interference study*

The study of interference ions was performed by binary mixtures containing 5.0 ng mL^{-1} of Se(IV) and a certain amount of one of the foreign ions. The following excesses of ions do not interfere (i.e., cause a relative error of less than 5%): less than a 10000-fold (largest amount tested) amount of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-; a 1000-fold amount of F^-, I^-, Br^-; a 500-fold amount of NH_4^+, Ba^{2+}, Co^{2+}, Zn^{2+}, Co^{2+}, NO^{3-}; a 100-fold amount of Ni^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}, Al^{3+}, and a 20-fold amount of Pb^{2+}, Hg^{2+}, Ag^+, PO_4^{3-} and $C_2O_4^{2-}$. The results showed that most of the investigated ions do not interfere in the adsorption-desorption and determination of traces of Se(IV) in real samples.

The extraction efficiency of Se(IV) as a function of NaCl concentration was also investigated and the results are shown in Figure 8. The extraction efficiency gradually decreases as the salt concentration increases in the range of 0-4 mol L^{-1}.

3.9. *Sorption capacity and sorbent regeneration*

The sorption capacity study used here was adapted from the method recommended by Maquieira et al. [42]. The static adsorption capacity of APDC/SDS-ACMNPs was found to be 8.72 mg g^{-1} for Se(IV). Regeneration is one of the key factors for evaluating the performance of the adsorption material. In this work, it was found that the sorbent can be re-used up to three times without loss of analytical performance (Figure 9). Considering that 4.0 g of ACMNPs could be prepared in one batch and only 50 mg of ACMNPs was used for one extraction operation, this reusability time is acceptable.

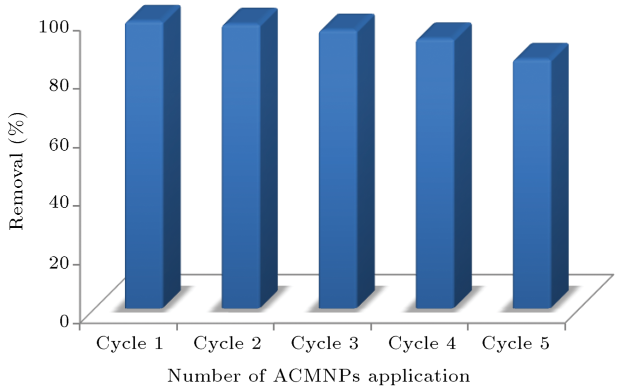


Figure 9. The removal efficiency during five repetition usage of ACMNPs. Conditions as in Figure 7.

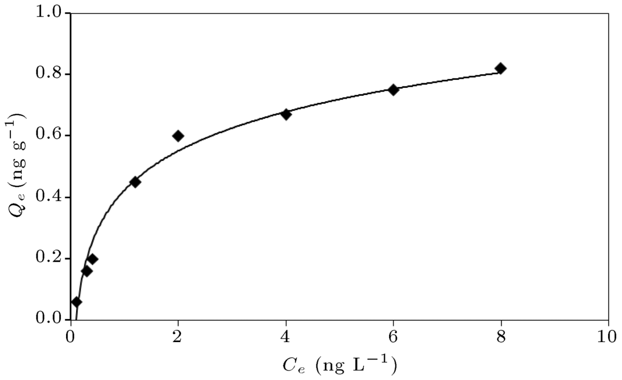


Figure 10. Equilibrium adsorption isotherm of Se(VI) on APDC/SDS ACMNPs. Conditions: ACMNPs (50 mg), APDC/SDS (10 mL, 5.0×10^{-1} mmol L^{-1}/1.0 mmol L^{-1}, pH 5.0), Se(VI) solution (10 mL, 0.1-10 mg L^{-1}, pH 5.0), equilibrium time: 10 h, temperature: 25°C.

3.10. Adsorption isotherms

The equilibrium adsorption isotherm is principle in depicting the reciprocal behavior between adsorbates and adsorbent, and is important for understanding the model of adsorption systems. Analysis of the isotherm data, by fitting them to different isotherm models, is an important step towards finding a suitable model that can be used for design purposes [43]. The adsorption studies were investigated at a fixed adsorbent portion (50 mg) of ACMNPs, temperature 25°C and varying Se(IV) concentrations (0.1-10 ng mL^{-1}). The concentration of Se(IV) in the liquid phase (C_e) was determined by GFAAS. Figure 10 shows the adsorption isotherms, which were fitted to the Langmuir model using the nonlinear regression method. The adsorption behavior could be described by the Langmuir adsorption Eq. (1) [44]:

$$C_e/Q_e = 1/KQ + Ce/Q, \tag{1}$$

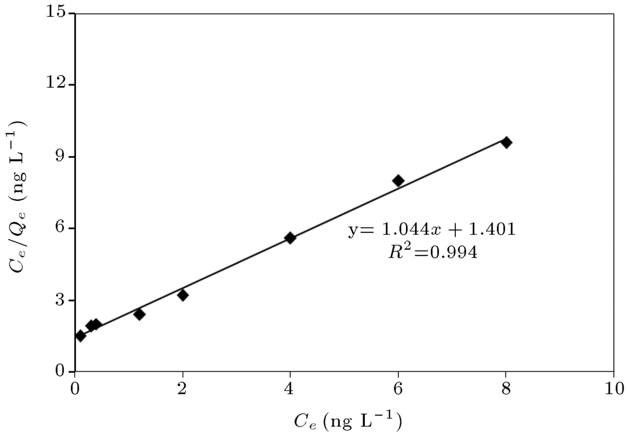


Figure 11. Plot of C_e/Q_e against C_e for the adsorption of Se(VI) on APDC/SDS ACMNPs. Conditions as in Figure 10.

where Q_e is the equilibrium adsorption amount of Se(IV) (mg g^{-1}), C is the equilibrium Se(IV) ion concentration in the solution (mg mL^{-1}), Q is the maximum adsorption amount of Se(IV) per gram of adsorbent (mg g^{-1}) and K is the Langmuir adsorption equilibrium constant (L mg^{-1}). Plotting of C_e/Q_e against C_e will result in a straight line with slope $1/Q$ and intercept $1/KQ$ (Figure 11). Also, the separation factor values (R_L) that describe whether a sorption system is favorable or unfavorable can be expressed as Eq. (2):

$$R_L = 1/1 + KC_e. \tag{2}$$

The R_L value implies the adsorption to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The value of R_L was found and it was approved that prepared APDC/SDS ACMNPs is favorable for adsorption of Se(IV).

3.11. Analytical performance and method validation

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 ($3S_b$) with a preconcentration factor of 125, was 0.05 ng mL^{-1}. The linear range of calibration curve for Se(IV) was 0.1-8.0 ng mL^{-1} with a correlation coefficient of 0.9916. The regression equation was $A = 0.0947\ C_{\text{Se(IV)}} + 0.0076$ ($n = 8$), where $C_{\text{Se(IV)}}$ is the concentration of Se(IV) in ng mL^{-1} and A is the absorbance. The Relative Standard Deviation (RSD) for 7 replicate measurements of 5.0 ng mL^{-1} of Se(IV) was 4.1%.

3.12. Real sample analysis

In order to determine total selenium, a synthetic set of model solutions, including different concentrations of Se(IV) and Se(VI), was prepared. Then, the reduction of Se(VI) to Se(VI) in the test solutions was performed

Table 2. Determinations of Se(IV), Se(VI) and total selenium in spiked test solutions (volume: 50 mL, $N = 3$).

Added (ng mL^{-1})		**Found (ng mL^{-1})**			**Recovery (%)**		
Se(IV)	**Se(VI)**	**Se(IV)**	**Se(VI)**	**Total Se**	**Se(IV)**	**Se(VI)**	**Total Se**
0.0	10.0	—	9.92 ± 0.24	9.92 ± 0.24	—	99.2 ± 2.4	99.2 ± 2.4
0.5	8.0	0.48 ± 0.08	7.80 ± 0.18	8.28 ± 0.15	96.0 ± 8.0	97.5 ± 2.2	97.4 ± 1.7
0.8	5.0	0.76 ± 0.07	4.90 ± 0.24	5.66 ± 0.20	95.0 ± 8.7	98.0 ± 4.8	97.6 ± 3.4
2.0	7.0	1.92 ± 0.18	7.04 ± 0.28	8.96 ± 0.27	96.0 ± 9.0	100.5 ± 2.4	99.5 ± 3.0
6.0	0.8	5.95 ± 0.20	0.75 ± 0.06	6.67 ± 0.22	99.1 ± 3.3	93.7 ± 7.5	98.1 ± 3.2
10.0	0.0	9.85 ± 0.32	—	9.85 ± 0.32	98.5 ± 3.2	—	98.5 ± 3.2

Table 3. Application of the proposed method to the speciation of Se in different water samples (sample volume: 50 mL, $N = 3$). The results are the mean of three measurements ± standard deviation.

Sample	**Added, Se(IV) (ng mL^{-1})**	**Added, Se(VI) (ng mL^{-1})**	**Found, Se(IV) (ng mL^{-1})**	**Found, Se(VI) (ng mL^{-1})**	**Found, total Se (ng mL^{-1})**	**Recovery (%)**		
						Se(IV)	**Se(VI)**	**Total Se**
Tap water from Sirjan city	-	-	0.18 ± 0.02	0.15 ± 0.02	0.33 ± 0.03	-	-	-
	5.0	-	5.10 ± 0.14	0.17 ± 0.03	5.27 ± 0.18	98.4	-	99
	-	5.0	0.20 ± 0.03	5.15 ± 0.15	5.35 ± 0.2	-	100.0	100.4
	5.0	5.0	5.12 ± 0.10	5.12 ± 0.22	10.24 ± 0.20	98.8	99.4	99.1
River water from Hajiabad river	-	-	0.25 ± 0.03	0.32 ± 0.02	0.57 ± 0.03	-	-	-
	5.0	-	5.30 ± 0.08	0.30 ± 0.03	5.60 ± 0.06	101.0	-	100.6
	-	5.0	0.27 ± 0.02	5.28 ± 0.12	5.55 ± 0.10	-	99.2	99.6
	5.0	5.0	5.26 ± 0.11	5.35 ± 0.27	10.61 ± 0.24	100.2	100.6	100.4
Sea water from Caspian sea	-	-	0.50 ± 0.03	0.42 ± 0.05	0.92 ± 0.04	-	-	-
	5.0	-	5.44 ± 0.14	0.38 ± 0.03	5.82 ± 0.10	98.8	-	98.4
	-	5.0	0.52 ± 0.03	5.32 ± 0.20	5.84 ± 0.18	-	98.0	98.4
	5.0	5.0	5.45 ± 0.16	5.55 ± 0.28	11.00 ± 0.30	99.0	102.6	100.8
Spring water from Koran of Sirjan city	-	-	0.26 ± 0.04	0.20 ± 0.03	0.46 ± 0.04	-	-	-
	5.0	-	5.26 ± 0.24	0.18 ± 0.02	5.44 ± 0.21	100.0	-	99.6
	-	5.0	0.23 ± 0.03	5.32 ± 0.20	5.55 ± 0.24	-	102.4	101.8
	5.0	5.0	5.32 ± 0.18	5.40 ± 0.28	10.72 ± 0.28	101.2	104.0	102.6
Waste water from copper factory Sarchashmeh of Sirjan	-	-	0.75 ± 0.06	0.054 ± 0.04	1.29 ± 0.06	-	-	-
	5.0	-	5.52 ± 0.34	0.45 ± 0.03	5.97 ± 0.32	95.4	-	93.6
	-	5.0	0.68 ± 0.08	5.42 ± 0.30	6.10 ± 0.30	-	97.6	96.2
	5.0	5.0	5.50 ± 0.28	5.39 ± 0.20	10.89 ± 0.26	95.0	97.0	96.0

by the reduction procedure given by the procedure explained in Section 2.5. Then, the procedure given in Section 2.4 was applied to these solutions. The results are given in Table 2. The performance and reliability of the method for the analysis of real samples was checked by determination of Se(IV), Se(VI) and total selenium content in different water samples. The results show that the proposed method could be successfully applied to the determination and speciation of selenium (Table 3).

4. Conclusions

It has been demonstrated that modified NP provides a new and fast route for separation/preconcentration and speciation analysis of Se(IV) and Se(VI). This

Table 4. Comparative data from some recent studies on SPE and speciation simultaneously of selenium.

Sorbent	Species	Enrichment factor	Sorbent capacity ($mg\ g^{-1}$)	RSD (%)	Detection limit ($ng\ mL^{-1}$)	Detection method	Reference
APDC/Diaion HP-2MG	Se(IV), Se(VI) converted to Se(IV)	100	5.2	2.8-8.3	10	GFAAS	[1]
TiO_2	Se(IV), Se(VI) converted to Se(IV)	NR[a]	NR	2.4-6.8	0.06	GFAAS	[45]
APDC/C-18	Se(IV), Se(VI) converted to Se(IV)	50	NR	NR	0.37	ICP-MS[b]	[46]
CuO	Se(IV), Se(VI)	NR	NR	NR	7	HGAAS[c]	[47]
Mercapto-silica-MNPs	Se(IV), Se(VI) converted to Se(IV)	300	12.3	8.1	0.094	ICP-MS	[16]
APDC/C-18	Se(IV)	NR	NR	5-13	7	ICP-MS	[48]
PU/HMDC[d]	Se(IV)	150	NR	NR	30.08	ICP-AES[e] ETAAS[f]	[49]
APDC/SDS -ACMNPs	Se(IV), Se(VI) converted to Se(IV)	125	8.72	4.1	0.05	GFAAS	This work

[a] Not reported;

[b] Iductively coupled plasma-mass spectrometry;

[c] Hydride generation atomic absorption spectrometry;

[d] Polyurethane foam (PU) immobilized with ammonium hexamethylenedithiocarbamate (HMDC);

[e] Inductively coupled plasma-atomic emission spectrometry;

[f] Electrothermal atomic absorption spectrometry.

method is certainly faster and more convenient than other methods proposed for the simultaneous SPE and speciation of selenium. This sorbent was successfully applied for efficient enrichment of trace amounts of selenium ions from real samples. The main benefits of this methodology are: simplicity and high capacity of sorbent, preconcentration factor, fast adsorption and low cost. Magnetic separation greatly shortened the analysis time of the method. Table 4 shows a comparison of the proposed method with other reported methods of the SPE and speciation, simultaneously, of selenium. It could be seen that some obtained values for the proposed method are as good as, or better than, some of the previously reported methods.

Acknowledgments

The authors would like to express their appreciation to Professor Afsaneh Safavi for her valuable discussions and useful suggestions. This research was supported by the Nanoscience and Nanotechnology Research Laboratory (NNRL) of Payame Noor University of Sirjan, Iran.

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