



# Synthesis of silver nanoparticles by pistachio skin extract and its application for solid phase extraction of Bi(III) followed by electrothermal atomic absorption spectrometry

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## Abstract

The aim of this paper is to synthesize of Ag-nanoparticles (Ag-NPs) by the pistachio skin extract followed by its application for preconcentration and measurement of ultra-trace levels of Bi(III) by electrothermal atomic absorption spectrometry. Pistachios skin extract was used as a green reducing agent to produce Ag-NPs from silver ion solution. The results of the FT-IR spectroscopy, UV–Vis spectrophotometry, Scanning electron microscopy, Transmission electron microscopy (TEM) and X-ray diffraction spectroscopy show that Ag-NPs with uniform size of 25–40 nm in diameter were synthesized successfully. In order to optimize different parameters affecting the extraction efficiency, Response surface methodology-Box Behnken optimization technique was used. Under the optimum conditions, the calibration curve was linear in the range of 0.5–8  $\mu\text{g L}^{-1}$  of Bi(III) with a correlation coefficient of 0.9993. The relative standard deviation (%) was 3.5% for five replicate analysis of 1  $\mu\text{g L}^{-1}$  Bi(III). Also, the limit of detection was 0.09  $\mu\text{g L}^{-1}$  Bi(III), and the preconcentration factor calculated from the ratio of the volume of sample solution to the desorbent solvent volume after preconcentration step was 100. The accuracy of the method was evaluated by the analysis of certified reference material and spike methods. Finally, this technique was successfully applied for determination of ultra-trace levels of Bi(III) in water, food, human serum and hair samples.

**Keywords** Ag-nanoparticles · Pistachios skin extract · Bismuth(III) · Electrothermal atomic absorption spectrometry (ETAAS)

## Introduction

Bismuth (Bi) is a lustrous, silvery-white heavy metal with a tendency to crystallize in coarse grains. It has many applications for the synthesis of alloys, medicine, pharmaceutical products, cosmetic and pigments and superconductor materials (Maile et al. 2005; Ojebuoboh 1992). Due to its wide applications in different industries; its leakage to the

environment is also increasing. Although Bi is slightly toxic; however in long times, it can damage the kidney and liver. Therefore, measurement of Bi in real samples has great significance (Pamphlett et al. 2000). Different analytical tools including atomic absorption spectrometry (Vakilzadeh et al. 2015; Shemirani et al. 2005), electrochemical methods (Koper and Grabarczyk 2011; Liu and Wang 2006), ultraviolet–visible spectrophotometry (Afkhami et al. 2006; Madrakian et al. 2003) and inductively coupled plasma-mass spectrometry (Sun and Wu 2011) were used for detection of Bi. Electrothermal atomic absorption spectrometry (ETAAS) is a prevalent instrument for determination of heavy metals with high sensitivity. However, accurate results especially at trace levels of the analyte need a more additional step to reduce or remove interfering ions (Eftekhari et al. 2015). Solid phase extraction (SPE) as a sample preparation technique has advantages including simplicity, the wide range of adsorbents and also high enrichment factor (Tuzen et al. 2008, 2005; Faraji et al. 2010; Sun et al. 2015; Ziaei et al. 2014). Today, metal nanoparticles have considered much

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attention due to their applications in electronic instruments, sensors, catalytic, etc (Abou El-Nour et al. 2010). Chemically reduction of metal ions by using different reducing agents is one of the synthesise routes for the production of metal nanoparticles (Mulfinger et al. 2007); however, many of them such as sodium borohydride ( $\text{NaBH}_4$ ) or hydrazine ( $\text{N}_2\text{H}_4$ ) are toxic and expensive. To overcome these problems, green methods using natural reducing agents have gained much attention.

Pistachio is one of the main export of Iran, so that Iran and USA provide more than 60% of total pistachio in the world. One of the main byproducts of the pistachio industry is its skins which considered as a waste material. However, different researches show that pistachio skin contains lots of phenolic compounds that serve as natural anti-oxidant agents (Tomaino et al. 2010).

In this work, we have used a green method for the synthesis of Ag nanoparticles (Ag-NPs) followed by its application for efficient preconcentration of Bi(III). Pistachios skin extract as a green reducing agent was used to produce Ag-NPs from silver ion solution. X-ray diffraction spectroscopy (XRD) and transmission electron microscopy (TEM) were employed for characterization of the synthesized Ag-NPs. Also, FT-IR spectrophotometry was used to characterize of the functional groups on the surface of Ag-NPs. The results show that Ag-NPs with the size of 25–40 nm in diameter were synthesized successfully and used as an adsorbent for preconcentration of Bi(III). Response surface methodology-Box Benhken experimental design was used and optimum conditions were determined. Finally, the proposed SPE technique was applied for determination of Bi(III) in water, milk powder, black tea, human serum and hair samples.

## Experimental

### Reagents

A solution of  $1000 \text{ mg L}^{-1}$  Bi(III) was made from Bismuth(III) nitrate pentahydrate ( $\geq 98\%$ , Sigma Aldrich, USA) in deionized water.  $\text{AgNO}_3$  (99–100.5%, Merck, Darmstadt, Germany) was used as a precursor of Ag-NPs. Various concentrations (1, 3 and  $5 \text{ mol L}^{-1}$ ) of  $\text{HNO}_3$  (65%, Merck, Darmstadt, Germany), HCl (37%, Merck, Darmstadt, Germany),  $\text{CH}_3\text{COOH}$  (99.5%, Mojallali, Tehran, Iran) and  $\text{HCOOH}$  (98–100%, Merck, Darmstadt, Germany) were prepared and used for desorption of Bi(III) from Ag NPs. Concentrated  $\text{H}_2\text{O}_2$  (30%, Merck, Darmstadt, Germany) and  $\text{HNO}_3$  were used for sample digestion.

### Instrumentation

Analytic Jena 400P Atomic Absorption Spectrometry was used as a detection system for Bi. A Bismuth HCL lamp (wavelength of 223.1 nm) as a radiation source, argon (Ar) gas as an inert gas with 99.99% purity were used in ETAAS. The electrothermal conditions of the instrument are shown in Table 1. A Metrohm 827 (Switzerland) was used for pH adjustment and Centurion Centrifuge (Hettich D72, Germany) was used for separation of adsorbent from the sample solution. A UV–Vis spectrophotometry (Agilent 8453) with 1 cm quartz cell was used for recording of UV–Vis spectrum. A Leo 912AB Transmission Electron Microscopy (TEM) was used to determine the size of the synthesized Ag NPs and X-Plorer instrument (Italy) was used for recording of the XRD spectrum. The morphology of the synthesise Ag NPs was studied by the Philips S360 SEM (Oxford, UK).

### Sample preparation

#### Water samples

Tap water (Mashhad, Iran), Dijlah (Kadhimiya, Iraq) and Al-Furat River (Karbala, Iraq) were collected and after filtering by filter paper (Whatman No. 42); an aliquot of each sample was diluted to 10 mL and analyzed for determination of Bi(III) based on the preconcentration procedure.

#### Milk Powder and Black tea

Approximately 1 g of milk powder and powdered black tea samples were transferred into the crucibles. Each sample was heated at  $400 \text{ }^\circ\text{C}$  for 2 h followed by addition of 2 mL concentrated  $\text{HNO}_3$  to it and heating at  $70 \text{ }^\circ\text{C}$  for 15 min. Then, the crucible content was diluted to 25 mL with deionized water. Finally, 2 mL of each sample was diluted to 10 mL with deionized water and analyzed for its Bi content based on the preconcentration procedure.

**Table 1** The program of ETTAS for detection of Bi

Step	Temp ( $^\circ\text{C}$ )	Ramp time (s)	Hold time (s)	Argon flow ( $\text{mL min}^{-1}$ )
Drying 1	90	3	15	300
Drying 2	130	10	20	300
Ashing	600	20	15	300
Atomization	2000	0	3	0
Cleaning	2200	2	3	300

### Human serum samples

The human serums were prepared from volunteer and kept at 4 °C before analysis. To the 1 mL of each serum sample, 1 mL of concentrated HNO<sub>3</sub> and 100 µL concentrated H<sub>2</sub>O<sub>2</sub> were added and heated at 60–70 °C for 10 min. After filtering with No. 40 Whatman paper, it was diluted to 10 mL with deionized water and an aliquot of 2 mL of each sample was diluted to 10 mL and analyzed for its Bi(III) content based on the preconcentration procedure.

### Human hair sample

The human hair sample was washed with deionized water and dried at 50 °C for 3 h. Then, approximately, 1 g of sample was transferred into the crucible and heated at 400 °C for 2 h. Other sample preconcentration steps are similar to the method explained for milk powder and black tea samples.

### Preparation of pistachio skin

Pistachio skins were collected from Feyzabad, Torbat Heydariyeh and dried at 35–40 °C for 2 days. The dried pistachio skins were grounded and used for the green synthesis of Ag-NPs.

### Synthesis of Ag-NPs

150 mL of deionized water containing 10 g of powdered pistachio skin was heated at 60–65 °C for 20 min. By filtering of the mixture using No. 40 Whatman filter paper; 50 mL of the filtered solution was added to the 150 mL deionized water containing 0.005 mol L<sup>-1</sup> Ag<sup>+</sup>. The solution was incubated in a dark place for 6 h. Finally, it was centrifuged at 12,000 rpm, washed with deionized water and dried at 50 °C for 9 h.

### Preconcentration procedure

10 mL of 1 µg L<sup>-1</sup> Bi(III) sample solution was adjusted at the pH 10 and transferred into the test beaker followed by adding of 10 mg Ag-NPs to it. The mixture was stirred for 5.8 min at 400 rpm. By its centrifugation at 3500 rpm for 10 min, the supernatant was discarded by a syringe and then 100 µL of 3 mol L<sup>-1</sup> HCOOH was added to it. The whole mixture was vortexed for 4.7 min at 2800 rpm. Finally, after

centrifugation for another 5 min, 20 µL of the solution was injected into the ETAAS for quantification of Bi.

## Results and discussions

### Optimization of ETAAS

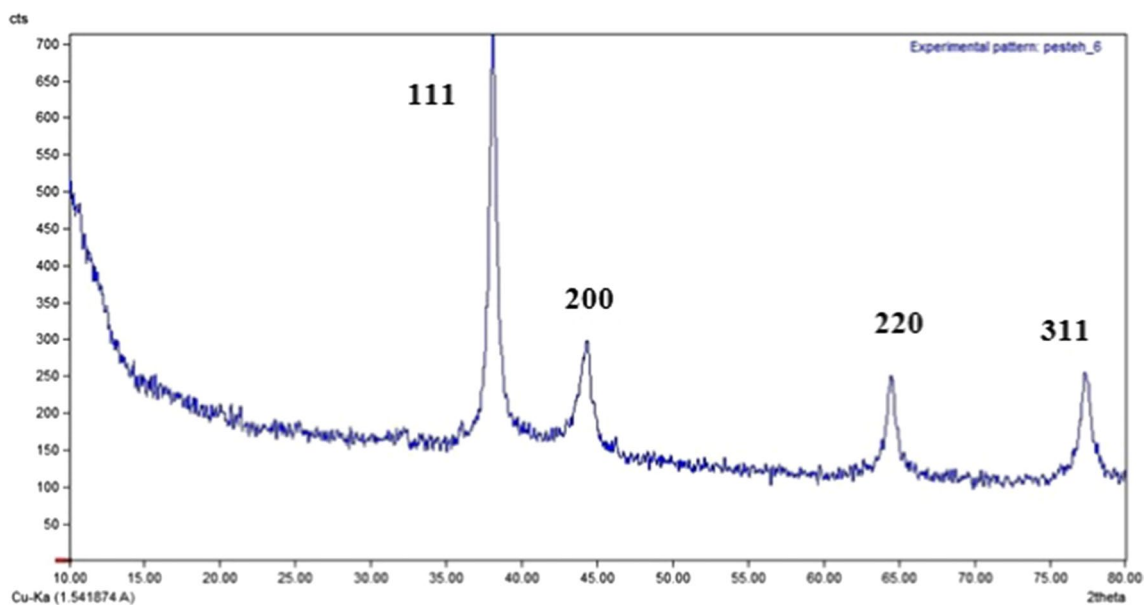
Drying, ashing and atomization temperatures are three main steps in ETAAS. In order to successfully removal of the extraction solvent; two drying steps (90 and 130 °C) were used. Ashing temperature was studied in the range of 400–900 °C and based on the results, 600 °C was considered as the optimum. Finally, atomization temperature was tested in the range of 1700–2200 °C and the results show that the temperature of 2000 °C obtained maximum absorbance for determination of Bi. The detailed ETAAS program was presented in Table 1.

### Characterization of adsorbent

Different analytical techniques including FT-IR spectrophotometry, TEM images, XRD spectroscopy and UV–Vis spectrophotometry were used for characterization of the synthesized Ag NPs. Figure 1, shows the XRD pattern of the synthesized Ag-NPs. As it shows, the characteristic peaks of Ag-NPs were corresponding to 111, 200, 220 and 311 planes are located at  $2\theta = 38, 44, 64.5$  and  $77$ , respectively. The results from the XRD spectrum clearly show that the Ag-NPs with crystalline phase has been synthesized successfully (Bar et al. 2009).

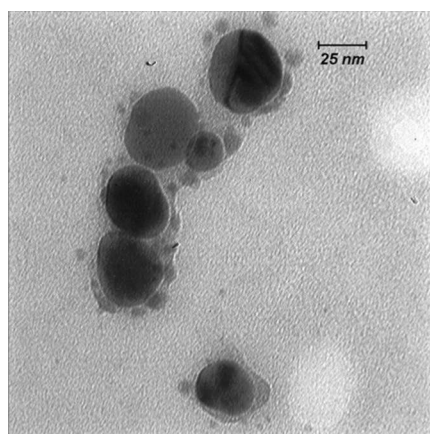
TEM and SEM images of the synthesized Ag-NPs are shown in Fig. 2a, b, c and d, respectively. As it could be seen, Ag-NPs have an average size of 25–40 nm and spherical in shape. Also, Fig. 3 shows the UV–Vis spectrum of the sample solution containing Ag-NPs. The broad peak at 420–450 nm is due to the surface plasmon of Ag-NPs and shows that the Ag-NPs were successfully synthesized.

FT-IR spectroscopy (Fig. 4) was used for the characterization and identification of the biomolecules adsorbed on the synthesized Ag-NPs. Based on the results, the peaks at 1505 cm<sup>-1</sup>, 1600 cm<sup>-1</sup> and 1650 cm<sup>-1</sup> are related to the carboxylate groups, N–H functional groups and aromatic C=C groups, respectively. Also, the alcoholic C–O and aromatic OH– groups are appeared at the wavelength of 1016 and 1196 cm<sup>-1</sup>, respectively. Finally, the broad peak at 3100–3500 cm<sup>-1</sup> is related to the OH– and N–H groups. The obtained results show that the surface of the synthesized Ag-NPs is covered by different functional groups which can interact with Bi(III) to physically adsorb it from sample solution (Bar et al. 2009; Rafiee et al. 2017).

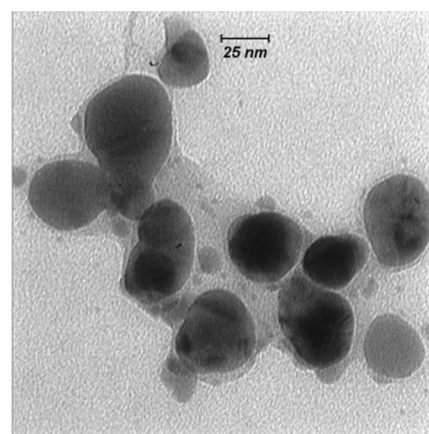


**Fig. 1** XRD pattern of the synthesized Ag-NPs by green aspect

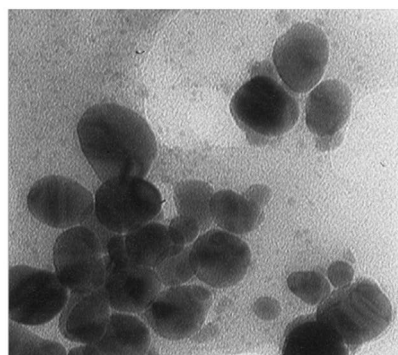
**Fig. 2** TEM (a, b, c) and SEM (d) images of the Ag-NPs synthesized by green aspect



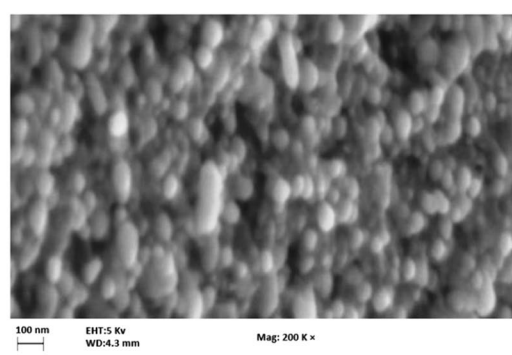
(a)



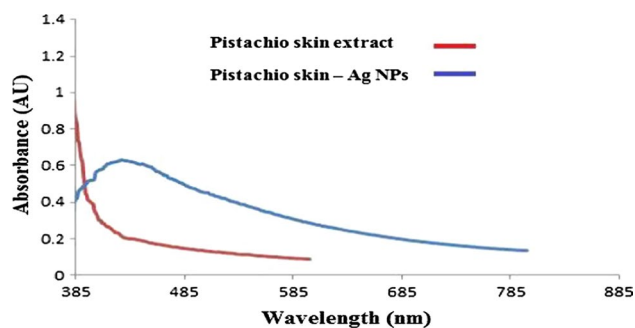
(b)



(c)



(d)



**Fig. 3** UV-Vis spectrum of the pistachio skin extract and pistachio skin-Ag NPs mixture. (diluted 1:10 with deionized water)

### Response surface methodology—BOX Behnken optimization

The critical parameters including sample pH (A), amounts of adsorbent (B), extraction time (C) and desorption time (D) were optimized simultaneously with Response Surface Methodology (RSM)-Box Behnken optimization technique. The centrifuge rate, centrifuge time and stirrer rate were kept constant at 3500 rpm, 10 min and 400 rpm, respectively. These variables and their levels are presented in Table 2.

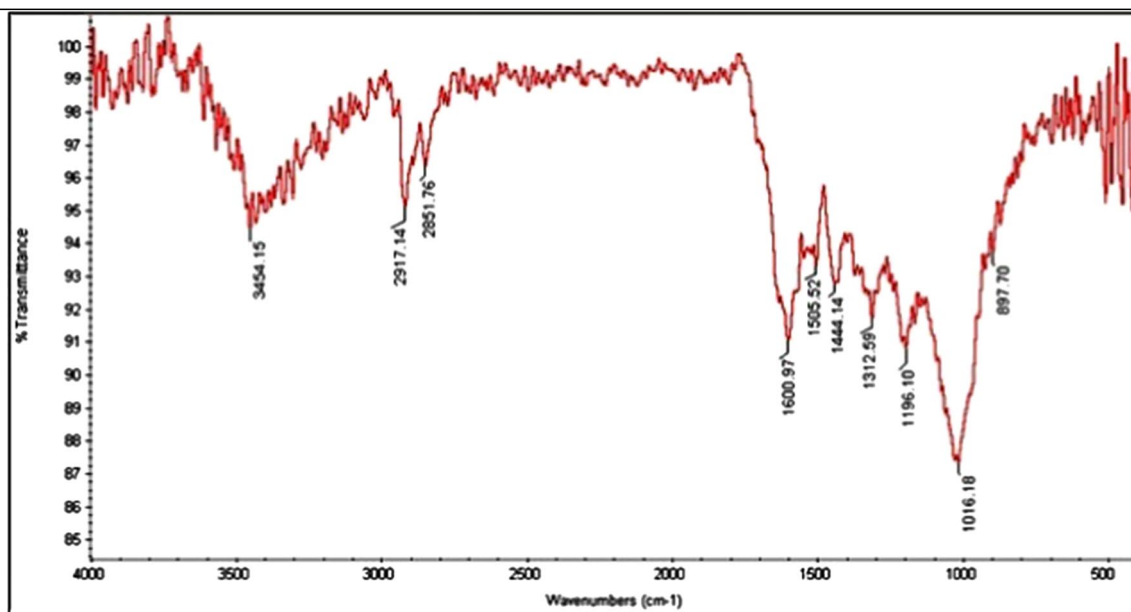
$$\begin{aligned}
 \text{RP}(\%) = & +96.92884 - 36.20396 \times A - 1300.12500 \times B \\
 & + 0.11153 \times C + 0.39975 \times D + 572.91667 \times A \times B \\
 & + 0.045000 \times A \times C - 0.054167 \times A \times D + 27.50000 \times B \times C \\
 & + 78.12500 \times B \times D - 0.030000 \times C \times D + 3.26020 \times A^2 \\
 & - 1.73167E + 005 \times B^2 - 3.32667E - 003 \times C^2 + 0.019833 \times D^2
 \end{aligned} \quad (1)$$

**Table 2** The Box-Behnken experimental design variables and their considered levels

Variable	Symbol	Coded factor levels		
		- 1	0	+ 1
pH	A	4	7	10
Amounts of adsorbent (g)	B	0.002	0.006	0.01
Extraction time (min)	C	5	10	15
Desorption time (min)	D	1	3	5

By the analysis of four models including Linear, 2FI, Quadratic and Cubic; Quadratic experimental model was selected as the optimum. The experimental design for the preparation of quadratic curves is shown in Table 3 and designed by Design Expert 7.0.0 software. The relationship between variables and recovery percentage (RP) was expressed by Eq. 1.

Also, the analysis of variance (ANOVA) for four variables is shown in Table 4. Based on the results, the parameters A, B and  $A^2$  had low P values ( $< 0.0001$ ) which show that these parameters had highly significant effects on the recovery percentage. However, the parameters C, AB and  $B^2$  had significant effects ( $P < 0.05$ ).



**Fig. 4** FT-IR spectrum of the synthesized Ag-NPs by green aspect

**Table 3** The model optimization responses for the Box-Behnken experimental design

Run	pH	Amounts of adsorbent (g)	Ext. time	Des. Time	Recovery (%)
1	10	0.002	10	3	68.7
2	7	0.01	5	3	17.5
3	10	0.006	15	3	92.7
4	7	0.002	10	5	12.5
5	4	0.002	10	3	8.7
6	10	0.01	10	3	95
7	7	0.006	10	3	17.75
8	7	0.006	10	3	21.34
9	10	0.006	5	3	87.5
10	10	0.006	10	1	90
11	7	0.006	5	5	16.2
12	7	0.006	10	3	20.75
13	4	0.006	10	5	10
14	7	0.006	15	1	21.2
15	7	0.002	5	3	13.7
16	7	0.006	5	1	15
17	7	0.01	10	1	21.2
18	7	0.006	15	5	21.2
19	7	0.002	15	3	16.2
20	4	0.006	10	1	7.5
21	7	0.002	10	1	12.5
22	4	0.006	15	3	10
23	4	0.006	5	3	7.5
24	7	0.006	10	3	19.5
25	7	0.01	10	5	23.7
26	4	0.01	10	3	7.5
27	10	0.006	10	5	91.2
28	7	0.006	10	3	18.7
29	7	0.01	15	3	22.2

The result of lack of fit P-value, 0.0867, shows that it is not significant and the model *F* value is 253.2 showing that this model is significant. A normal probability plot of the residuals is illustrated in Fig. 5 provided by the Design Expert software. As the results shown, the points are close to the linear line which confirms that it obeys a normal distribution.

Also, the variables and their values were processed by the full quadratic multiple linear regression model and presented in Fig. 6a–e. Based on the Fig. 6a, pH and amounts of adsorbent (g) have highly significant influence on the RP of Bi(III). As the results shown, by increasing of the pH values, the RP increases. It should be noted that at pH < 7, Bi(III) has Bi(OH)<sub>3</sub> and Bi(OH)<sub>2</sub><sup>+</sup> structures which electrostatically repulse from the Ag-NPs surface (Zeta Potentials analysis show that at pH < 7 the surface of

Ag-NPs has positive charge), however, Bi(III) has Bi(OH)<sub>3</sub> structure at pH 7–10 which could be adsorbed on the Ag NPs by hydrogen bonding interaction between Bi(OH)<sub>3</sub> and phenolic groups of the Ag-NPs. Figure 6b, c show the effects of extraction and desorption time on the RP of Bi(III). As it was predicted by the ANOVA test, extraction time is a significant parameter while desorption time (in the time interval of 1–5 min) is not a significant factor. Also, Fig. 6d shows that the amounts of adsorbent has a high significant effect on RP; and again the extraction time could be considered as a significant factor. Finally, based on the Fig. 6e, f, desorption time was considered as an insignificant factor which means that desorption of analyte from the Ag NPs occurred immediately.

The optimum conditions were determined by RSM-Box Behnken and equal to: pH 10, amounts of adsorbent: 10 mg, extraction time: 5.8 min and desorption time of 4.7 min.

Different desorption solvents such as HCl, HNO<sub>3</sub>, CH<sub>3</sub>COOH and HCOOH were tested to find the optimum desorption solvent for the determination of Bi. The results in Fig. 7 show that the solutions of 3 and 5 mol L<sup>-1</sup> HCOOH have maximum efficiency for desorption of Bi(III) from Ag NPs. Therefore, 3 mol L<sup>-1</sup> HCOOH was selected as the optimum desorption solvent.

### Effect of diverse ions

The effect of different ions on the RP of Bi(III) were investigated and presented in Table 5. Interfering ion defined as an ion causes the changes in the recovery of analyte more than ± 5% (Iranzad et al. 2018; Alikhani et al. 2018). Based on the results, the proposed method has an acceptable tolerance limit for determination of Bi(III).

### Effect of ionic strength

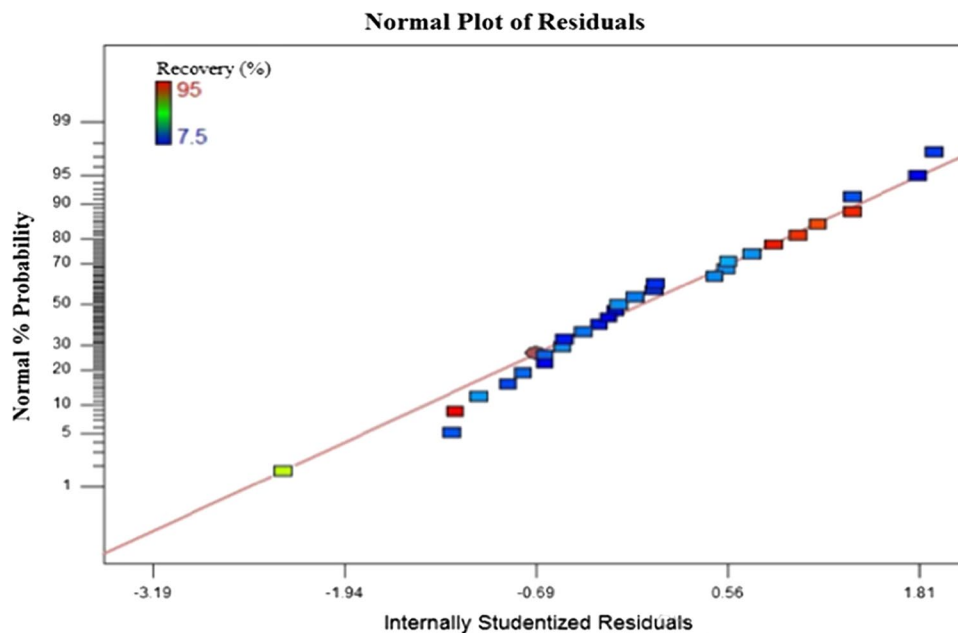
To study the influence of ionic strength on the RP of Bi(III), different sample solutions containing KNO<sub>3</sub> and NaCl (in the range of 0–1% g mL<sup>-1</sup>) were examined. Based on the results, no significant changes in the RP were observed up to 0.6% (g mL<sup>-1</sup>) and 0.2% (g mL<sup>-1</sup>) for KNO<sub>3</sub> and NaCl, respectively.

### Analytical figures of merit

The calibration curve of Bi(III) was determined in the range of 0.5–8 µg L<sup>-1</sup> with the *R*<sup>2</sup> value of 0.9993. Its equation was Absorbance = 0.0655 *C*<sub>Bi(III)}</sub> + 0.0019; where *C* is the concentration of Bi(III) in µg L<sup>-1</sup>. The RSD value for the analysis of 1 µg L<sup>-1</sup> Bi(III) was 3.5% (*n* = 5) and LOD was 0.09 µg L<sup>-1</sup> Bi(III) (*n* = 6). The preconcentration factor was 100 which calculated from the ratio of the volume of sample solution (10 mL) to the volume of desorbent solvent

**Table 4** The obtained results for the Analysis of Variance (ANOVA)

Source	Sum of squares	df	Mean Square	F value	P value, Prob > F	
Model	25,488.70443	14	1820.621745	253.245725	<0.0001	Significant
A	18,715.10083	1	18,715.10083	2603.242157	<0.0001	
B	250.2533333	1	250.2533333	34.80985933	<0.0001	
C	56.7675	1	56.7675	7.896273201	0.0139	
D	4.563333333	1	4.563333333	0.634752749	0.4389	
AB	189.0625	1	189.0625	26.29830716	0.0002	
AC	1.8225	1	1.8225	0.253506987	0.6224	
AD	0.4225	1	0.4225	0.05876911	0.812	
BC	1.21	1	1.21	0.168309166	0.6878	
BD	1.5625	1	1.5625	0.217341382	0.6482	
CD	0.36	1	0.36	0.050075454	0.8262	
A <sup>2</sup>	5584.496325	1	5584.496325	776.7949736	<0.0001	
B <sup>2</sup>	49.7941218	1	49.7941218	6.926286864	0.0197	
C <sup>2</sup>	0.044865045	1	0.044865045	0.00624066	0.9382	
D <sup>2</sup>	0.040824505	1	0.040824505	0.005678627	0.941	
Residual	100.6481133	14	7.189150952			
Lack of fit	92.05583333	10	9.205583333	4.285513663	0.0867	Not significant
Pure error	8.59228	4	2.14807			
Cor total	25,589.35254	28				

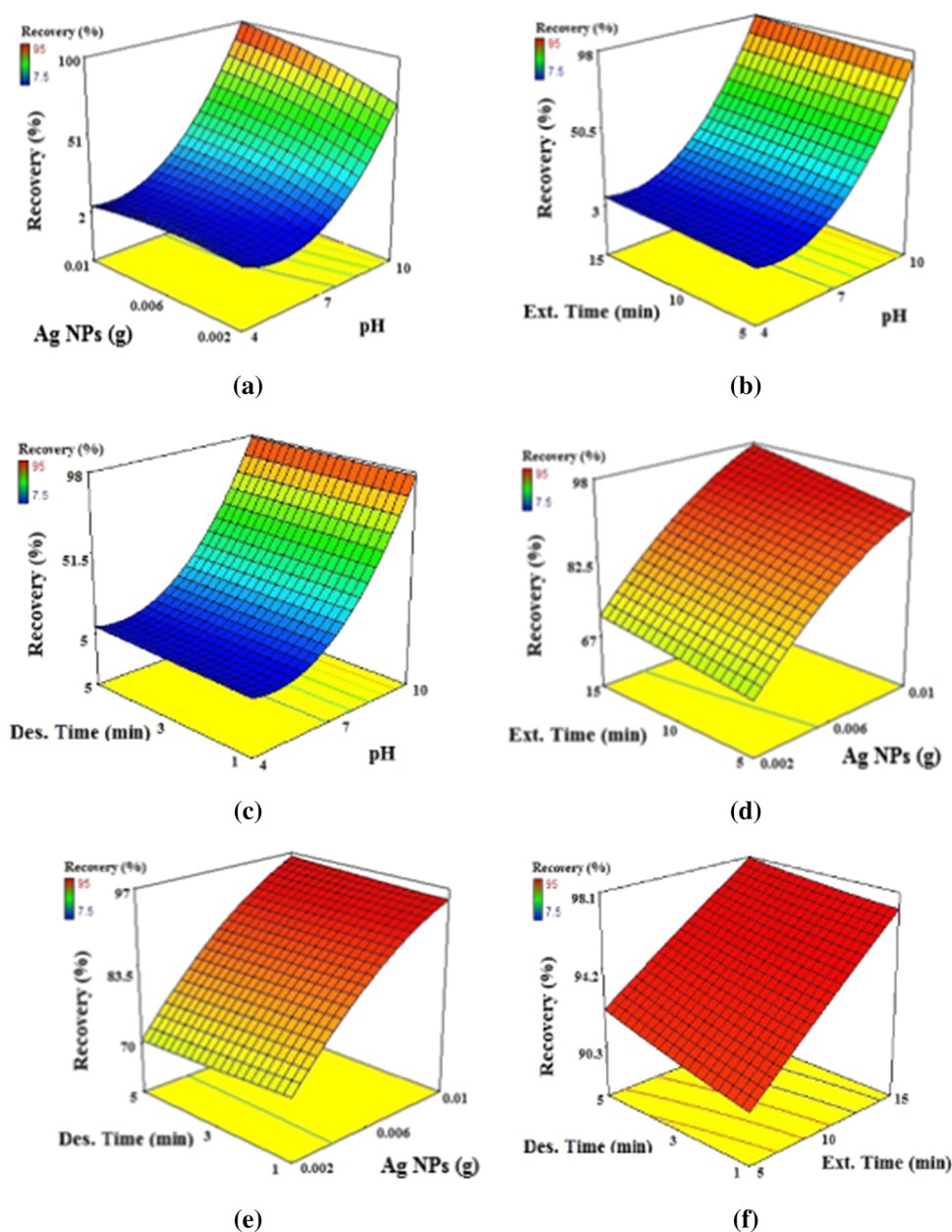
**Fig. 5** The normal plot of probability (%) versus studentized residuals

(100  $\mu$ L). Also, the enrichment factor (EF) defined as the ratio of the slope of calibration curve after preconcentration to the direct analysis of analyte ( $A = 0.0007 C_{\text{Bi(III)}} - 0.002$ ) was 94 (Eftekhari et al. 2018; Al-Kinani et al. 2018; Khodarahmi et al. 2018).

### Real samples analysis

Water (tap, river), milk powder, black tea and human serum and hair samples were tested for determination of their Bi content. The results are presented in Tables 6 and 7. Spike analysis was also examined on the samples to

**Fig. 6** The response surface model of the proposed method versus the affecting parameters



certify the validity of the results. The results show very good recoveries for determination of Bi. Also, a certified reference material, trace metal in drinking water (CRM-TMDW) which containing  $10 \mu\text{g L}^{-1}$  Bi(III) was analyzed. By the analysis of CRM sample,  $9.9 \pm 0.33 \mu\text{g L}^{-1}$  Bi(III) was obtained and shows that the obtained value is in the good agreement with the certified value (student t-test, 95% confidence limit,  $n = 5$ ).

### Comparison with other methods

The SPE technique was compared by the other methods for the measurement of Bi(III) and the results are presented in Table 8. As it shows, the proposed Ag NPs SPE

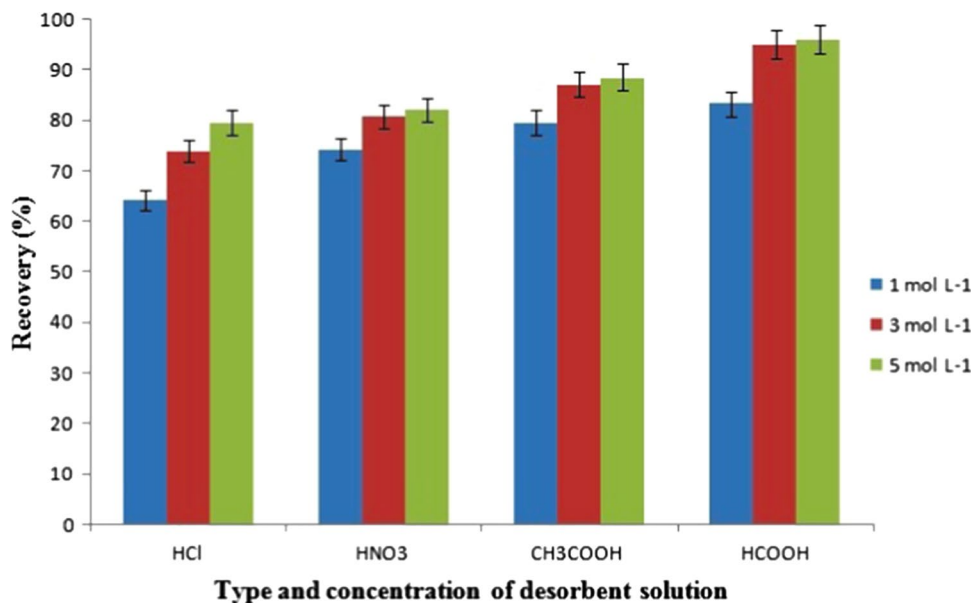
method has acceptable LOD and RSD. Also, this method is green, very rapid and very efficient for preconcentration of Bi(III).

### Conclusion

In this research, we have used the plant extract for the green synthesize of Ag-NPs followed by its application for preconcentration and measurement of Bi(III). As Pistachios skin extract contains lots of polyphenol compounds, it could be considered as a natural reducing agent for synthesizing of the Ag-NPs. The results of the XRD spectrum, TEM and SEM images and UV-Vis spectrophotometry



**Fig. 7** Effect of type and concentration of desorbent solution on the recovery percentage of Bi(III). Conditions: 1 µg L<sup>-1</sup> Bi(III), pH 10, Extraction time 5.8 min and desorption time 4.7 min



**Table 5** Effect of different cations and anions on the recovery percentage of 1 µg L<sup>-1</sup> Bi(III)

Interfering Ions	Concentration (µg L <sup>-1</sup> )	Recovery (%)
Ca <sup>2+</sup>	50,000	97.7
Zn <sup>2+</sup>	100	95.2
Cu <sup>2+</sup>	100	98.6
Mn <sup>2+</sup>	50	97.0
Ni <sup>2+</sup>	50	96.0
Pb <sup>2+</sup>	50	98.0
Cr <sup>3+</sup>	50	96.9
Cd <sup>2+</sup>	50	96.5
Sn <sup>4+</sup>	50	97.0
Al <sup>3+</sup>	50	98.1
Co <sup>2+</sup>	50	98.8
SO <sub>4</sub> <sup>2-</sup>	50,000	96.0
Cl <sup>-</sup>	50,000	98.2

**Table 6** The results of the analysis of Bi(III) in water samples

Sample	Added (µg L <sup>-1</sup> )	Found (µg L <sup>-1</sup> )	Recovery (%)
Tap Water	-	ND	-
	2	2.3 ± 0.1	115.0
	5	5.2 ± 0.2	104.0
Dijlah (Kadhimiya, Iraq)	-	ND	-
	2	1.9 ± 0.1	95.0
	5	4.8 ± 0.2	96.0
Al-Furat (Karbala, Iraq)	-	0.6 ± 0.02	-
	2	2.5 ± 0.1	96.1
	5	5.8 ± 0.3	103.6

Results (mean ± standard deviation based on three replicate analysis)

show that the uniform Ag-NPs with the average size of 25–40 nm were synthesized successfully and then used for preconcentration of Bi(III) followed by its determination with ETAAS. The critical parameters on the RP of Bi(III) including pH of sample solution, amounts of Ag NPs, extraction time and desorption time were optimized by RSM-Box Behnken experimental design. The main advantages of the proposed SPE technique are the green approach for the synthesizing of Ag NPs, high rapidity (approximately 6 min extraction time), easy to use and high efficiency for determination of ultra-trace levels of Bi(III). Also, the results of the analysis of real samples show that this method could be used for determination of Bi(III) in different real samples.

**Table 7** Results of the analysis of Bi(III) in different food and real samples

Sample	Added (µg g <sup>-1</sup> )	Found (µg g <sup>-1</sup> )	Recovery (%)
Black tea	-	0.15 ± 0.01	-
	0.1	0.27 ± 0.01	108.0
Milk powder	-	0.08 ± 0.01	-
	0.1	0.19 ± 0.01	105.5
Human serum no.1 (µg L <sup>-1</sup> )	-	ND	-
	20	21.5 ± 0.6	107.5
Human serum no.2 (µg L <sup>-1</sup> )	-	ND	-
	20	22.6 ± 0.6	113.0
Human serum no.3 (µg L <sup>-1</sup> )	-	35.5 ± 1.1	-
	10	43.6 ± 1.6	95.8
Human serum no.4 (µg L <sup>-1</sup> )	-	60.7 ± 2.7	-
	10	68.9 ± 2.5	97.4
Human Hair (µg g <sup>-1</sup> )	-	0.13 ± 0.01	-
	0.1	0.22 ± 0.01	95.6

Results (mean ± standard deviation based on three replicate analysis)

**Table 8** Comparison of the proposed solid phase extraction with other reported preconcentration techniques

Method	LOD <sup>b</sup> ( $\mu\text{g L}^{-1}$ )	RSD <sup>c</sup> (%)	PF <sup>d</sup>	Linear range ( $\mu\text{g L}^{-1}$ )	References
DLLME <sup>a</sup> -UV-Vis detection	1.6	1.14–2.66	62.5	5–400	Rastegarzadeh et al. (2014)
CPE-FAAS <sup>e</sup>	4	4.2	–	–	Wen et al. (2012)
DLLME-GFAAS <sup>f</sup>	0.2	4.7	–	2–30	Wen et al. (2014)
DLLME-ICP-MS <sup>g</sup>	0.0047	2.6–6.7	–	0.01–1	Jia et al. (2010)
DLLME-FAAS	3	1.5	28.6	30–1700	Fayazi et al. (2011)
IP <sup>h</sup> -DLLME-GFAAS	0.07	4.8	125	0.3–8	Vakilzadeh et al. (2015)
SPE-GFAAS	0.09	3.5	100	0.5–8	Proposed method

<sup>a</sup>Dispersive liquid liquid microextraction<sup>b</sup>Limit of detection<sup>c</sup>Relative standard deviation<sup>d</sup>Preconcentration factor<sup>e</sup>Cloud point extraction-flame atomic absorption spectrometry<sup>f</sup>Graphite furnace atomic absorption spectrometry<sup>g</sup>Inductively coupled plasma-mass spectrometry<sup>h</sup>Ion paired

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## Compliance with ethical standards

**Conflict of interest** The authors declared that they have no conflict of interest.

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