J Nanostruct 9(2): 238-248, Spring 2019

RESEARCH PAPER

Thiol Modified Au Nanoparticles Grafted Manganese Doped Magnetic Iron Oxide Nanoparticles for Spectrometric Determination of Short-term Release of Mercury and Copper from Dental Amalgam in Saliva

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ARTICLE INFO

Article History:
Received 13 October 2018
Accepted 09 January 2019
Published 01 April 2019

Keywords:
Cold vapor atomic absorption spectrometry
Dental amalgam
ICP-OES
Mn doped Fe_3O_4 nanoparticles
Magnetic solid phase extraction Saliva

ABSTRACT

A new adsorbent, ethylene glycol bisthioglycolate modified gold nanoparticles grafted Mn doped Fe_3O_4 nanoparticles (EGBTG-Au@Mn-Fe_3O_4 NPs) were synthesized through chemical precipitation followed by an oxidative Mn doping process to use for extraction and preconcentration of trace amounts of Hg, and Cu ions in artificial and natural saliva. The prepared adsorbent was characterized by TEM, BET, XRD and VSM techniques. Fusayama artificial saliva was prepared and used as blank sample and natural saliva was collected from nine volunteers ranged from 15-29 years old who exposed to posterior decayed teeth amalgam filling and short-term release of heavy metal ions was assessed in 24, 72 and 96 h after filling. Various factors affecting extraction/desorption efficiency of target ions have been investigated and analytical characteristics of the recommended method were determined. Detection limits of 0.12 and 0.09 ng mL^{-1} were obtained for Cu and Hg ions respectively with preconcentration factor of 96. The results revealed that the adsorbent has high adsorbent capacity and good reusability for extraction/preconcentration of target ions in relatively high saline solution like biological fluids.

How to cite this article
Amoli Diva M, Pourghazi K and Amoli Diva M. Thiol Modified Au Nanoparticles Grafted Manganese Doped Magnetic Iron Oxide Nanoparticles for Spectrometric Determination of Short-term Release of Mercury and Copper from Dental Amalgam in Saliva. J Nanostruct, 2019; 9(2): 238-248. DOI: 10.22052/JNS.2019.02.006

INTRODUCTION

Amalgam is the most frequently used restorative material for dental treatment and many concern has been raised about this filling material because it contains mercury (Hg) and silver (Ag) and very small amounts of copper (Cu), zinc (Zn) and lead (Pb) [1]. Several studies demonstrated that amalgam filling is able to release metal ions into the oral cavity [2, 3] and this may cause destructive effects on human body. For example, amalgam fillings are known to release significant amounts of Hg in saliva which can represent a continuous source of oxidative damage to oral tissues [4]. It also induces production of free radicals and modifies the redox potential of the cells [1]. The release behavior of metal ions in the oral cavity is complex and involves several parameters, such as composition and treatment of applied amalgam, pH and oxygen variations in the oral cavity, presence of proteins, and etc. and a

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straightforward comparison of in-vitro and in-vivo results is consequently rendered difficult.

However, certain trends might be outlined based on in vitro determination. Thus, release measurements during laboratory tests may simulate the clinical situations. Successful measurement of clinical release through saliva sampling is difficult because of the fast flow of saliva in the oral cavity. In establishing of in-vitro testing, synthetic environments are used more frequently than natural body fluids due to easy access to artificial saliva solutions. Saliva contains organic and inorganic substances suspended in an aqueous medium. The pH of saliva may vary between 2 and 11 and it is dependent on the age, eating habits, and oral hygiene [5]. Thus, metal release from materials used for dental applications has usually been studied in artificial saliva.

Different artificial saliva solutions have been formulated, often aimed to satisfying different requirements. In all of these solutions, strong electrolytes usually NaCl and/or KCl, are present as the principal and most concentrated component. In addition, a buffer system such as HCO_3^-/CO_3^{2-} or $H_2PO_4^-/HPO_4^{2-}$ is also existed. In some cases, a complexing anion like SCN^- is also present which is an anion that actually present at quite high concentration in human saliva [6].

Recently, modified magnetic nanoparticles (MNPs) had wide application in magnetic solid phase extraction (MSPE) and preconcentration of heavy metal ions in different matrices [7-10]. For example, MNPs modified with mercaptopropionic acid have been used for extraction of hard metals in plasma, urine and water matrices [11]. Dithizone modified Si/Fe_3O_4 nanoparticles have been used for extraction and determination of Cu, Cr, Pb, and Zn in water and human hair samples [12]. Cd, Cu, Hg, and Pb were extracted from environmental and biological samples using 7-mercaptopropyl trimethoxysilane modified silica coated MNPs [13] and modified MNPs were used for extraction of different metal ions from food samples [14]. To the best of our knowledge, this is the first time that MNPs were used for preconcentration of metal ions in such a complicated sample like saliva for dental applications. In addition, this adsorbent was synthesized for the first time and not used for preconcentration of analytes.

In this study, ethylene glycol bisthioglycolate modified gold nanoparticles grated Mn doped Fe_3O_4 nanoparticles (EGBTG-Au@Mn-Fe_3O_4 NPs) were used as a magnetic adsorbent for extraction and preconcentration of metal ions in artificial and natural saliva. The levels of Cu, ions were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) and Hg ions were determined using cold vapor atomic absorption spectrometry (CV-AAS). The factors affecting extraction efficiency of the analytes were investigated and optimized. Finally, the proposed method was successfully applied to the extraction and preconcentration of these ions from natural saliva samples.

MATERIALS AND METHODS

TEM images of the adsorbent were obtained using a Philips CM200 transmission electron microscope (Amsterdam, Netherlands). The X-ray diffraction (XRD) analysis of modified nanoparticles was performed by an Ital Structures APD 2000 X-ray diffractometer (Riva Del Garda, Italy) using Cu K_α radiation source λ 1.540598 Aº with reflection scan mode. A Metrohm 827 pH/mV meter (Herisau, Switzerland) with a combined glass electrode was used for pH measurements. Determination of Cu ions was carried out by a Varian Vista-Pro ICP-OES (Springvale, Australia). The instrument was operated at applied power of 1.2 kW and plasma and argon flow rates were 13.5 and 0.75 L min^{-1} respectively. A Varian SPECTRAA 20 plus (Palo Alto, CA, USA) cold vapor atomic absorption spectrometry was used for determination of Hg ions.

All chemicals and reagents were of analytical grade and used as supplied. Ethylene glycol bisthioglycolate (EGBTG) was purchased from Sigma chemical (St Louis, MO, USA). Ferrous chloride tetrahydrate ($FeCl_2.4H_2O$), ferric chloride hexahydrate ($FeCl_3.6H_2O$), manganese sulphate ($MnSO_4$), hydrogen tetrachloroaurate ($HAuCl_4$), mercury nitrate, cupper nitrate, sodium chloride, potassium chloride, calcium chloride ($CaCl_2.2H_2O$), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4.2H_2O$), sodium sulfide nine hydrate ($Na_2S.9H_2O$), urea ($CO(NH_2)_2$), lactic acid, sodium hydroxide, ammonia solution (25% w/w), hydrochloric acid, glycerol, and methanol were purchased from Merck Company (Darmstadt, Germany). Deionized water was used through the experiments.

Preparation of artificial saliva

The artificial saliva solution which used in this study was prepared as described by Fusayama et al. [15, 16] and its composition was: NaCl (0.40 mg mL^{-1}), $CaCl_2.2H_2O$ (0.79 mg mL^{-1}), KCl (0.40 mg mL^{-1}), $NaH_2PO_4.2H_2O$ (0.78 mg mL^{-1}), $Na_2S.9H_2O$ (0.005 mg mL^{-1}), CO $(NH_2)_2$. (1.00 mg mL^{-1}). The final volume with deionized water was 1000 mL. The prepared artificial saliva has pH 5.5. For recommended procedure, 5 mL of the solution was diluted 200 mL and lactic acid and ammonia solutions were used to adjusting saliva pH.

Preparation of magnetic adsorbent

Magnetite nanoparticles were prepared according to the previously reported method [17]. Briefly, 2.15 g ferrous chloride tetrahydrate and 5.84 g ferric chloride hexahydrate salts were dissolved in 100 mL deionized water under nitrogen atmosphere with vigorous stirring at 90 ºC. Then, 30 mL NH_3 solution (25% w/w) was added and the mixture was stirred for 15 min at the same condition. In these conditions, magnetite nanoparticles (Fe_3O_4 NPs) were produced which was cooled down to the room temperature. Then, the precipitate was isolated from the solution by applying an external magnet and the supernatant was removed. After that, the precipitate was washed three times with deionized water (250 mL) and twice with 0.02 mol L^{-1} sodium chloride solution (100 mL). Sodium chloride can accelerate magnetic separation particularly in alkaline solutions [18, 19]. Then, the suspension was transferred to a 250 mL round bottom flask and allowed to settle. The supernatant was removed and an aqueous solution of $MnSO_4$ (10 mL, 0.1 M) was added to the mixture and stirred for 30 min, followed by the addition of $KMnO_4$ (10 mL, 0.1 M) as oxidant. The mixture then stirred for another 1 h at room temperature and the precipitate was washed with deionized water by decantation using supermagnet until the supernatant was free of potassium permanganate. After preparing Mn doped Fe_3O_4 NPs, chloroauric acid (5 mL, 5 mM) was added to the mixture and allowed to boil with constant stirring under reflux. The reaction was followed by addition of 10 mL trisodium citrate (25 mM) under continuous stirring. The mixture was remained at the same condition for 15 min and then rapidly cooled to the room temperature using an ice bath.

In the next step, the supernatant was removed and an aqueous solution of EGBTB (1.0% v/v, 150 mL) was added followed by glycerol (60 mL). The mixture was stirred at 90 ºC for 2 h. After cooling down slowly to the room temperature, the precipitate (EGBTG Au@Mn-Fe_3O_4 NPs) was easily isolated from the supernatant using a supermagnet

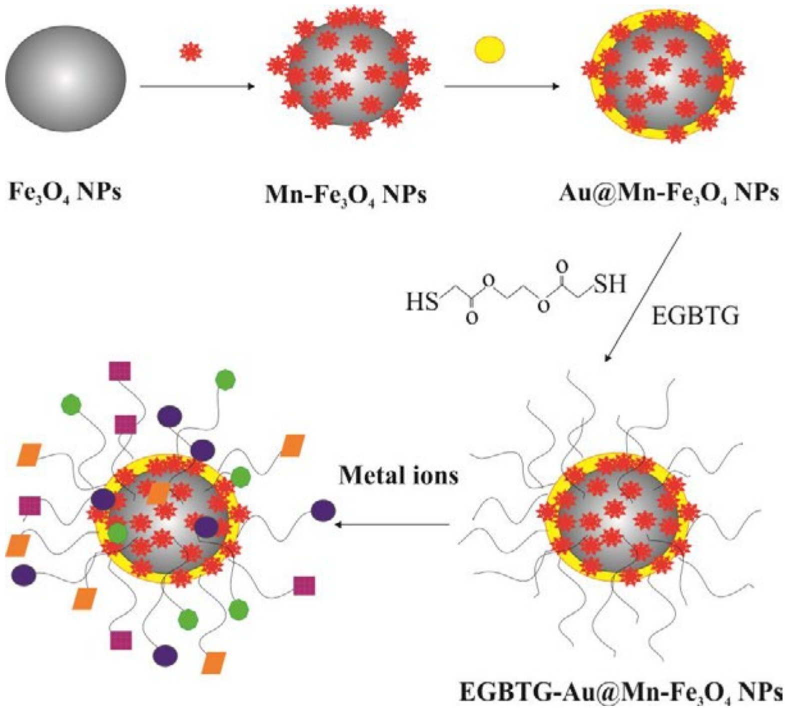


Fig. 1. Schematic procedure of adsorbent synthesis.

and the suspension was washed sequentially with deionized water (250 mL, three times), methanol (200 mL, twice), and deionized water (250 mL, once) before it was dried in vacuum oven at 50 ºC for 24 h. Schematic procedure of the adsorbent synthesis was shown in Fig. 1.

Recommended MSPE procedure

The MSPE procedure was performed using batch experiment. The following steps were applied to extraction, pre-concentration, and determination of the metal ions:

A portion of artificial saliva solution containing 5 µg of target metal ion was transferred to a 250 mL beaker. The pH was adjusted by lactic acid or/and ammonia solution and diluted to the final volume of 200 mL. Then, 100 mg of EGBTG-Au@Mn-Fe_3O_4 NPs adsorbent was added and the solution was stirred for 5 min. The mixture was placed on a supermagnet and the supernatant was completely decanted. The magnet was removed; a solution of HCl (2 mL, 0.1 M) was added and the mixture was stirred for 2 min. The solution was placed on a supermagnet again to hold the adsorbent whist and the supernatant was transferred to a test tube for subsequent ICP-OES or CV-AAS analysis.

Method validation

Linearity of the proposed method was evaluated by analyzing different concentrations of metal ions in the range 5-500 ng mL^{-1} and a seven-point calibration curve was constructed which each point is the mean value of three replicates analyses. The slope, intercept and correlation coefficient were calculated using the least square regression method. The limit of detection (LOD) and limit of quantitation (LOQ) were calculated based on the standard deviation of blank (S_b) and slope of calibration curve (m) determined according to the following equations:

$$LOD = 3.3S_b/m \tag{1}$$

$$LOQ = 10S_b/m \tag{2}$$

Precision of the proposed method was determined by five replicates analyses of artificial saliva spiked with each analyte at 50 ng mL^{-1}. The recovery was calculated by using the following equation:

$$\text{Recovery (\%)} = (\text{Measured concentration}/\text{Nominal concentration}) \times 100$$

Preconcentration factor (PF) of the method was calculated using the following equation:

$$PF = V_s/V_e \times R\% \tag{4}$$

Where V_s is the sample volume, V_e is elution volume, and R% is percent recovery of each analyte.

RESULTS AND DISCUSSION

High affinity to the analyte and reusability of a nano-adsorbent provide significant cost reduction for any MSPE procedure. Furthermore, ability to remove adsorbed analytes from the adsorbent is a critical parameter when recovery of metal ions (and not removal) is desired for applications which need recycling and resource recovery. These desired features inspire searching a method which has capability of tuning analyte-affinity through direct adsorbent modification and to obtain an efficient adsorbent, particularly for applications in harsher matrices such as highly saline and biological fluids or processes where repetitive utilization is desired.

As mentioned before, the known properties of Fe_3O_4 NPs and MnO_2 suggested a hybrid nanomaterial of manganese (Mn) and Fe_3O_4 NPs which yields a magnetically active adsorbent on par with or better than each precursor [20-23]. On the other hand, soft coordination sites like SH groups are known to have a great tendency to soft metal ions, such as Cu^{2+} and Hg^{2+}. This work shows that combination of high adsorbent capacity of Mn doped Fe_3O_4 nanoparticles and modification with an S donor ligand using known Au nanoparticles-SH end group chemistry will significantly increase the quantitative retention of these ions along with lowering their detection limits.

Characterization of adsorbent

The morphology of Fe_3O_4 NPs, Mn-Fe_3O_4 NPs, Au@Mn-Fe_3O_4 and EGBTG-Au@Mn-Fe_3O_4 NPs were characterized by SEM images. As can be seen from Fig. 2, Fe_3O_4 NPs and Mn-Fe_3O_4 NPs have very good magnetization that affect SEM instrument. All the prepared adsorbents have uniform size distribution and most of the particles are quasi spherical in shape..

In addition, the size distribution of Fe_3O_4 NPs, Mn-Fe_3O_4 NPs, Au@Mn-Fe_3O_4 and EGBTG-Au@Mn-Fe_3O_4 NPs were characterized by TEM images. As can be seen from Fig. 3, due to the magnetization property of Fe_3O_4 NPs, Mn-Fe_3O_4 NPs, all particles attend to adsorb each other

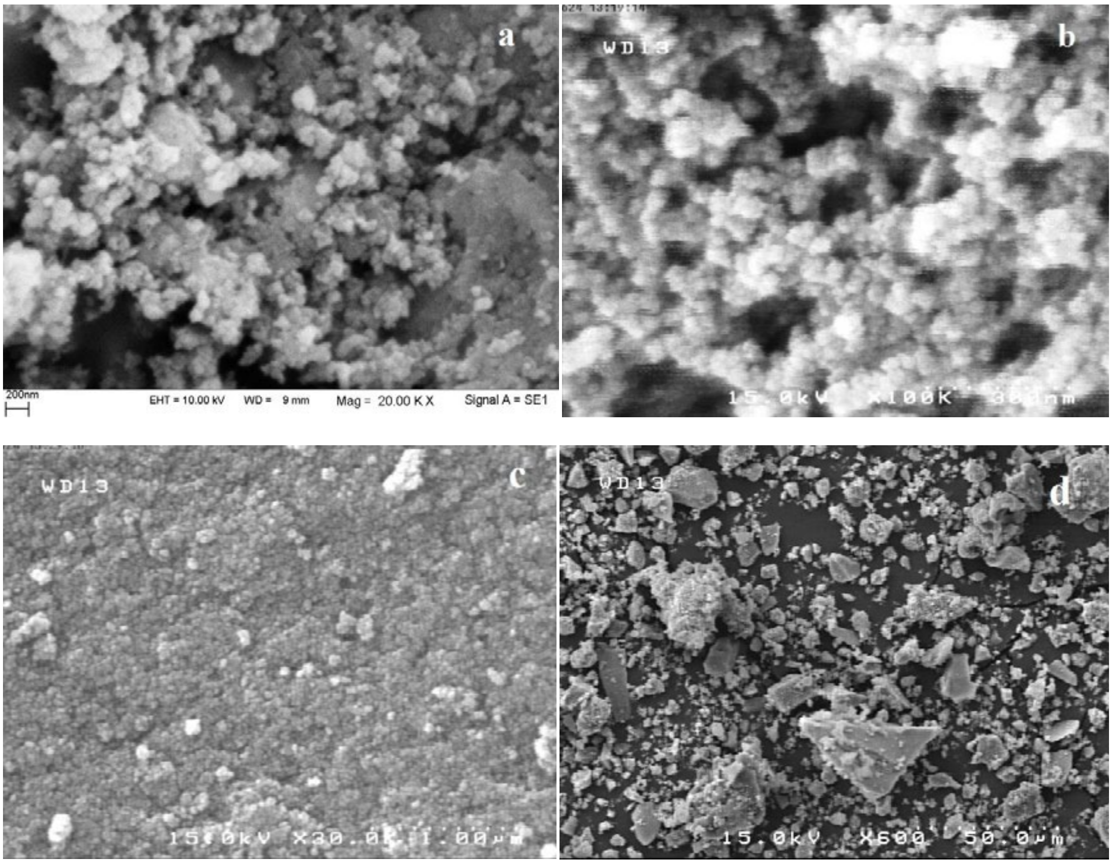


Fig. 2. SEM images of the (a) Fe_3O_4 NPs, (b) Mn-Fe_3O_4 NPs, (c) Au@Mn-Fe_3O_4 and (d) EGBTG-Au@Mn-Fe_3O_4 NPs adsorbent.

and aggregate together. Coating with Au NPs and then EGBTG were decreased their magnetization a little. The final adsorbent has average diameter of 40±5 nm.

BET analysis of Fe_3O_4 NPs before and after doping with Mn shows increasing surface area from 47 $m^2 g^{-1}$ to 73 $m^2 g^{-1}$ respectively, which cause increasing in analyte affinity of the adsorbent.

XRD analysis of the adsorbent before and after doping with Mn was presented in Fig. 4 and shows Bragg reflections indexed to the inverse cubic spinel phase of iron oxide for both samples and matches well with those obtained by JCPDS for magnetite [11, 24]. There was no indication of additional phases and each sample contains identical peaks regardless of Mn content. There is no evidence of peaks corresponding to MnO_2 or Mn_3O_4, confirming that the Mn is incorporated into the ferrite structure rather than precipitating as oxides on the surface of Fe_3O_4 NPs. Further, peak positions of Mn doped Fe_3O_4 NPs were shifted to lower peak position which also suggesting that the Fe^{3+} ions are effectively substituted by larger radius Mn^{2+} ions [25].

The saturation magnetization curves of Fe_3O_4 NPs, Mn doped Fe_3O_4 NPs and EGBTG-Au@Mn-Fe_3O_4 NPs were shown in Fig. 5. As can be seen, Fe_3O_4 NPs has a saturation magnetization about 43 emu/g. The saturation magnetization of EGBTG-Au@Mn-Fe_3O_4 NPs adsorbents was decreased due to the thickening of the shells, but its magnetization still shows 24 emu g^{-1}, which is more than 56% of Fe_3O_4 NPs magnetization. This appears to be due to the oxidative doping process removing Fe^{3+} ions from the lattice and incomplete replacement with the larger radius Mn ions, resulting in a more disordered structure and subsequent decrease in magnetic strength which confirms the results obtained by XRD analysis. However, the prepared adsorbent has enough magnetic responsiveness for applications which need magnetic manipulation. It was clear because its suspension was quickly cleared from solution with the use of a strong supermagnet.

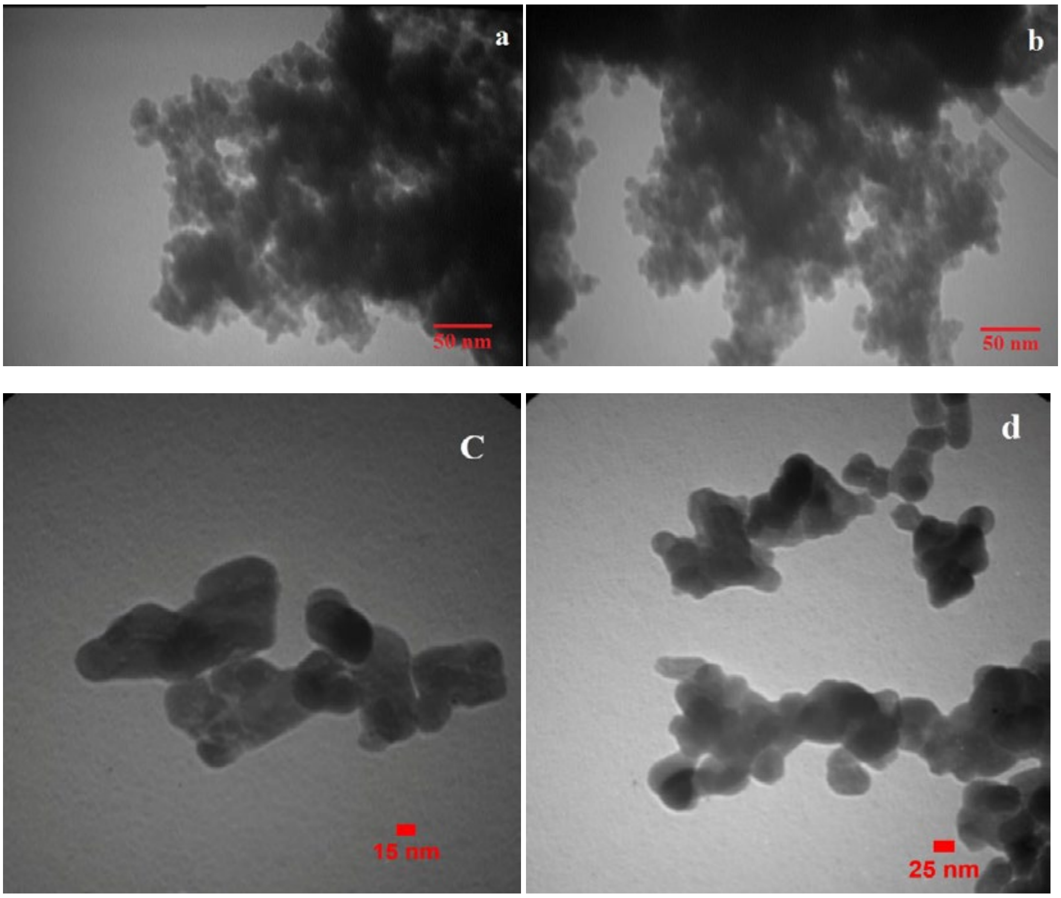


Fig. 3. TEM images of the (a) Fe_3O_4 NPs, (b) Mn-Fe_3O_4NPs, (c) Au@Mn-Fe_3O_4 and (d) EGBTG-Au@Mn-Fe_3O_4 NPs adsorbent.

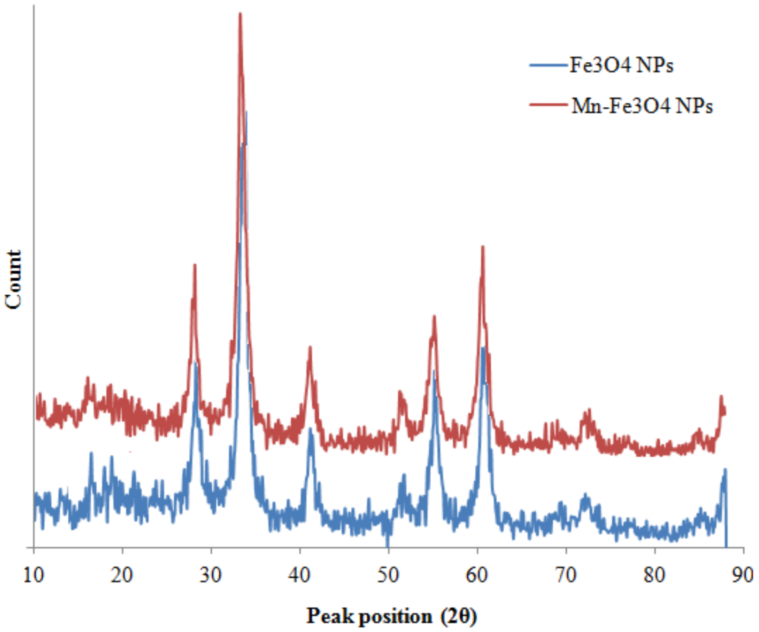


Fig. 4. XRD pattern of the (a) Fe_3O_4 NPs and (b) Mn-Fe_3O_4NPs

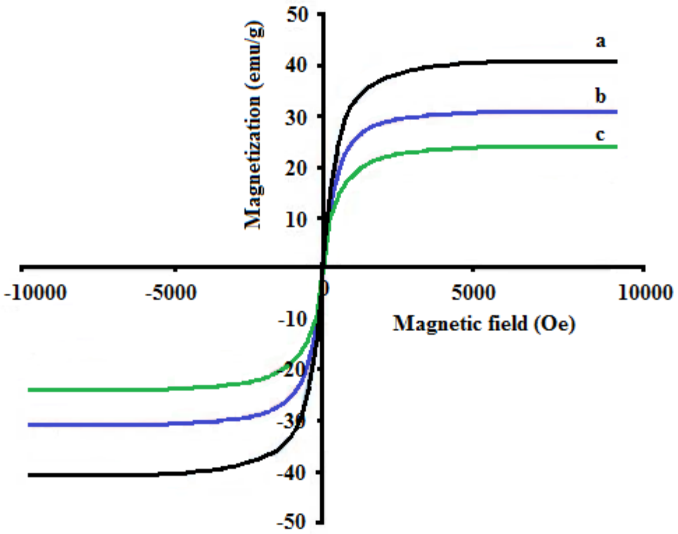


Fig. 5. VSM analysis of Fe_3O_4 NPs, Mn doped Fe_3O_4 NPs and EGBTG-Au@ Mn-Fe_3O_4 adsorbent.

Extraction/preconcentration optimizations

Effect of pH

To determine the optimal pH required for quantitative extraction of the target ions, effect of solution pH on the adsorption of metal ions was studied over the range of 2.0-7.0 with 5 µg mL^{-1} of each metal ion in artificial saliva solution. Higher pH was not considered due to probability of hydroxide precipitation. As can be seen from Fig. 6, quantitative absorption (>90%) was obtained in different pH value for each metal ion. Quantitative recovery of Cu^{2+} was increased in pH 2.0-4.0 and it remained constant as pH increased in higher than this value. Maximum adsorption of Hg ions was occurred over the pH rang of 4.5-7.0. Thus, optimum pH for simultaneous extraction of Hg and Cu ions from artificial saliva ranged from 4.5 to 7.0. Considering the fact that normal pH of artificial saliva is 5.5 and -SH end groups of EGBTG can be oxidized in low pH, the value of 5.5 was selected for all our subsequent experiments including natural saliva samples.

Effect of Eluent

From the pH studies, it reveals that the adsorbent shows low tendency to target metal ions in high acidic media. Thus, the effect of desorbing solvent on the recovery of target ions was investigated by choosing some strong acids such as HNO_3, HCl, and H_2SO_4 (0.1 M of each) and organic solvent such as ethanol and acetonitrile. The experimental results demonstrated that a solution of 0.1 M HCl has higher elution efficiency with respect to the other eluent. Therefore, it was selected for all subsequent experiments.

On the other hand, eluent volume is a critical parameter affecting on the preconcentration factor and extraction kinetics. Thus, the effect of eluent volume for quantitative elution of target ions was investigated by changing it in the range of 0.5-10 mL. Based on the results, minimum volume for quantitative elution of the retained analytes was 2.0 mL. Thus, the eluent volume of 2.0 mL was selected for the next experiments.

Effect of sample volume

Achieving higher preconcentration factor needs large sample volume along with lower eluent volume. The effect of sample volume on the extraction efficiency of targeted metal ions was studied by applying recommended MSPE procedure to different sample volumes of artificial saliva (25-500 mL) containing fixed amount of each metal ion (5.0 µg). The results indicate that quantitative recovery of Hg and Cu was obtained when sample volumes were less than 200 mL. Decreasing in the extraction recoveries can be explained by considering mass-balance equation. Theoretical recovery (R) can be calculated using the following equation [12]:

$$R = 1/1+(\beta/K_{s,w}) \qquad (5)$$

Where, β is phase ratio (sample to adsorbent volume ratio) and $K_{s,w}$ is partition coefficient.

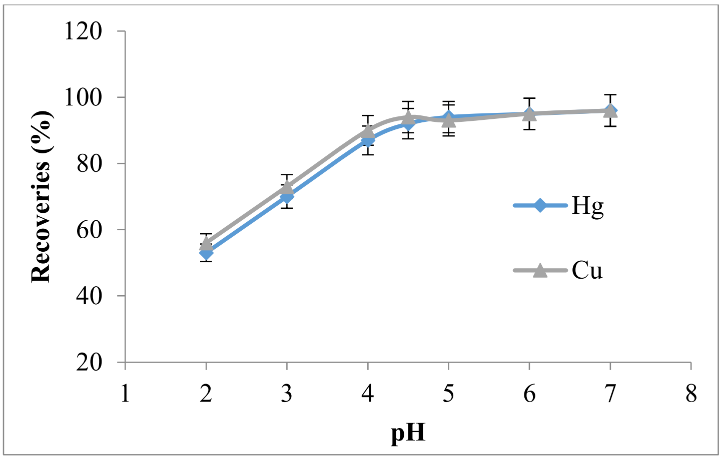


Fig. 6. Effect of pH on the recovery of targeted metal ions. Sample volume; 200 mL, adsorbent amount; 100 mg, extraction time; 5 min, desorption time; 2 min, and eluent solvent; 0.1 M HCl.

From the equation, when the sample volume is too large (here > 200 mL), the β raises and causes decreasing in recovery. Therefore, a value of 200 mL was selected for sample volume in subsequent experiments.

Adsorbent amount and adsorbent capacity

It was proved that nanoparticles have significantly higher surface area and short diffusion route compared to the ordinary adsorbents. This can result high extraction efficiency and fast extraction dynamics and satisfactory results can obtain with lower adsorbent amount. In order to investigate the minimum adsorbent amount requiring for quantitative extraction of target analytes, the amount of EGBTG-Au@Mn-Fe_3O_4 NPs was varied from 10 to 200 mg in the procedure. The results revealed that quantitative recoveries were obtained by using 100 mg of the adsorbent. Thus, this value was selected for the next experiments.

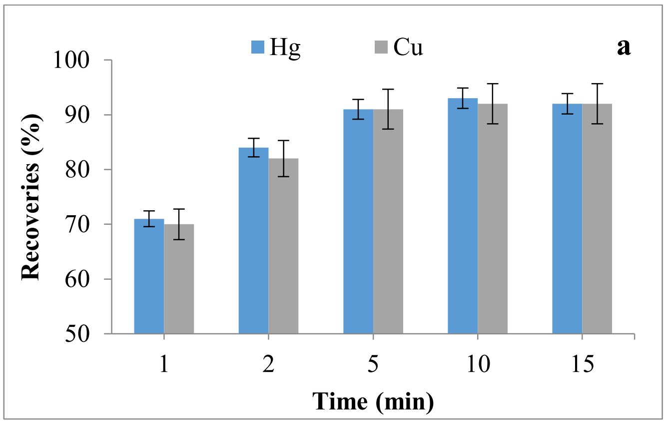
On the other hand, one of the most advantages of using modified MNPs in any MSPE procedure is their higher adsorption capacity due to their very high surface area. The capacity of an adsorbent determines how much adsorbent is requiring for quantitative extraction of certain amount of metal ions from the solution. In order to determine the adsorption capacity, 100 mg of EGBTG-Au@Mn-Fe_3O_4 NPs and 200 mL of various concentrations of metal ions were examined and the concentrations were increased until saturation occurred at equilibration time of 15 min. The maximum adsorption capacity has found to be 23.1 and 17.3 mg g^{-1} for Hg and Cu ions, respectively. The results indicate that adsorption capacity of the prepared adsorbent was much higher than the requiring amount for determination of these ions in biological samples such as saliva.

Effect of extraction and desorption times

Efficient dispersion of the adsorbent can considerably increase its contact surface with the analyte leading to a higher adsorption efficiency and faster extraction time. Nanomaterials have higher surface area with respect to the traditional adsorbents and can rapidly collect from sample solution by using a magnetically assisted separation procedure. Hence, fast extraction and desorption times can be achieved with these materials. Fig. 7 show recovery values of metal ions as a function of extraction and desorption times. Based on the results, 5 min is sufficient for achieving appropriate adsorption and 2 min was enough for quantitative desorption which are much lower needed time with compare to the traditional column-passing SPE.

Adsorbent reusability

Reusability is one of the key parameters for evaluation of an adsorbent’s performance. In order to determine regeneration capability of EGBTG-Au@Mn-Fe_3O_4 NPs, the adsorbent which previously used in the general MSPE procedure were washed with desorbing solvent (10 mL, twice) and deionized water (10 mL, five times), then dried in oven at 50 ºC and reused. Experimental results revealed that the adsorbent can be reused at least



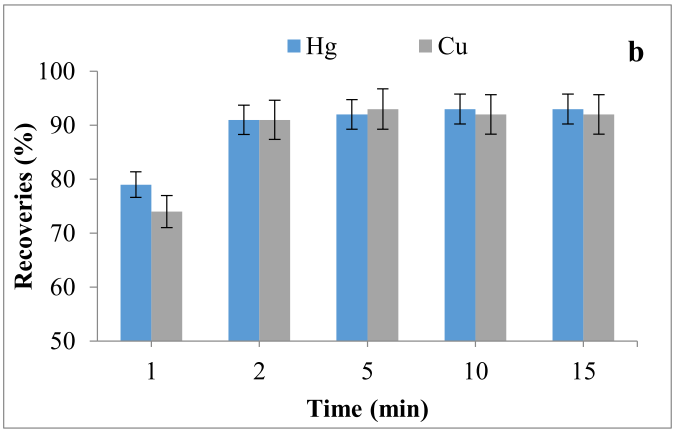


Fig. 7. Effect of extraction and desorption times on the recovery of targeted metal ions. Sample volume; 200 mL, adsorbent amount; 100 mg, eluent solvent; 0.1 M HCl and pH; 5.5.

Table 1. Analytical parameters of proposed method for determination of Cu and Hg ions using the recommended MSPE procedure.

Analyte	Calibration equation	R^2	LOD	LOQ	RSD (%)	Recovery (%)
Cu	Y=2644x-922	0.992	0.12	0.37	3.9	96.0
Hg	Y=0.042x-0.02	0.994	0.08	0.25	4.1	96.1

up to ten times (RSD <4.1%) without sacrifice the analytical performance which makes it a suitable alternative to conventional SPE adsorbent.

Analytical performance

Under the optimum conditions, the target ions were quantitatively extracted from spiked artificial saliva by applying the recommended MSPE procedure and the resulted analytical characteristics are summarized in Table 1. Linearity of the proposed method was obtained in the range 5-500 ng mL^{-1} with correlation coefficients (R^2) better than 0.992. As can be seen from the table, LOD was obtained 0.08 and 0.12 ng mL^{-1} and LOQ was obtained 0.25 and 0.37 ng mL^{-1} for Hg and Cu ions respectively. Relative standard deviation (RSD%) of the method for determination of the analytes was calculated in the range of 4.1 and 3.9 % respectively. The enrichment factor for each metal ion was found to be 96.

Application of the method

To investigate the accuracy and applicability of the optimized method to real biological samples, the concentration of Hg and Cu ions was determined in saliva samples obtained from 9 volunteers (3 male and 6 female) with average of 19 years old and in the range of 15-29 years old that had no amalgam fillings. The informed consent was obtained from all volunteers at the beginning

Table 2. Results for the determination of targeted of Cu and Hg ions in saliva samples (n=3).

Sample	Found (ng mL^{-1}), RSD%		sRecovery (%)	
	Cu	Hg	Cu	Hg
Saliva I	96.1,3.8	87.3, 4.5	-	-
Saliva II	95.5, 3.7	93.4, 4.1	95	96
Saliva III	192.2, 3.2	183.5, 3.5	98	98

to the study and before fillings. Then, in 24, 72 and 96 hours after that one of their posterior decayed teeth was filled with amalgam, 2 mL of their saliva were collected by spitting in a special tube and kept at -18 ºC in a freezer immediately. Once all the samples were collected, they were transferred to the laboratory for analysis. Before testing, the samples were transferred into a three 200 mL flask, put in three groups and labeled to saliva I, II and III. If needed, pH was adjusted and then diluted to the volume. Samples labeled saliva I were analyzed without any treatment and samples labeled saliva II and III were spiked with 10 and 100 ng mL^{-1} of each metal ion respectively for recovery tests and then, were analyzed with the recommended MSPE procedure. The short-term release of the targeted metal ions was summarized in Table 2. As can be seen, the recoveries of target metal ions were in the range of 95 to 98% and the method has good merit to determination of these metal ions in biological high saline saliva.

CONCLUSION

A new thiol modified Au NPs grafted Mn doped Fe_3O_4 NPs was synthesized as an efficient adsorbent and successfully used for extraction/preconcentration of heavy metal ions released to saliva samples which were exposed to posterior decayed teeth amalgam filling. Cu ions were determined by ICP-OES and Hg ions were determined by CV-AAS. The method combines high surface area of the nanoparticles and magnetic separation, providing a fast, convenient, effective, and sensitive method for preconcentration/separation of metal ions in high saline samples. In addition, reusability studies demonstrated the potential of prepared adsorbent for recyclable usage in compare to the conventional column-based SPE. The method is simple and inexpensive, and eliminates the need to use any auxiliary facilities to immobilize the adsorbent. What is more, usage is not limited to the applications demonstrated here; other detection systems can be used depending on the actual requirements.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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