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استخراج و پیش‌تغلیظ یون جیوه با استفاده از نانوذرات مغناطیسی عامل‌دارشده قبل از تعیین با دستگاه اسپکتروفتومتر مرئی- ماورائ بنفش

هما شفیعی خانی[۱و*]، علی معدلی[۲]، فیروزه امینی پور[۳]
۱. بخش شیمی، دانشگاه پیام نور، صندوق پستی ۳۶۹۷-۱۹۳۹۵، تهران، ایران
۲. سازمان پزشکی قانونی، تهران، ایران
۳. دانشگاه آزاد اسلامی، واحد لامرد، صندوق پستی ۵۵۳۸۸۱-۷۴۳۴۱، فارس، ایران

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Extraction and Preconcentration of Trace Amounts of Mercury Using Functionalized Magnetic-Nanoparticles Prior to Their Determination by UV-Vis Spectrophotometry

Homa Shafiekhani[1,*], Ali Moaddeli[2], Firoozeh Aminipour[3]
1. Chemistry Department, Payame Noor University, P.O. BOX 19395-4697, Tehran, Iran
2. Legal medicine organization, Tehran, Iran
3. Islamic Azad University, Lamerd Branch, P.O.Box: 74341-553881, Fars, Iran

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چکیده

در این مقاله، نانوذرات مغناطیسی عامل‌دارشده با لیگاند تری آزن برای استخراج و پیش‌تغلیظ یون جیوه در نمونه‌های آبی با دستگاه اسپکتروفتومتر مرئی- ماورائ بنفش اندازه‌گیری شده است. ویژگی‌های نانو ذرات اصلاح‌شده با تکنیک‌های مختلف از جمله میکروسکوپ روبش الکترونی، میکروسکوپ الکترونی عبوری و دیفراکسیون اشعه ایکس مورد ارزیابی قرار گرفت. در فرایند جداسازی، محلول آبی یون جیوه با نانوذرات مغناطیسی اکسید آهن اصلاح‌شده با لیگاند تری آزن مخلوط شد و سپس یک میدان مغناطیسی خارجی برای جداسازی نانو ذرات شامل یون جیوه مورد استفاده قرار گرفت. شرایط آزمایشگاهی برای جذب موثر شامل مقدار اصلاح گر، مقدار نانو ذره و نوع شوینده بررسی گردید. تحت شرایط بهینه استخراج و پیش تغلیظ، دامنه خطی منحنی کالیبراسیون از۸۰-۴ میکرو گرم بر لیتر با ضریب رگراسیون۰/۹۹۲ برای ۲۰ بار اندازه‌گیری، حد تشخیص ۱/۰۵ میکروگرم بر لیتر و فاکتور پیش‌تغلیظ ۳۸ بدست آمد. این تکنیک برای نمونه‌های آبی یون جیوه موفقیت‌آمیز بوده است.

واژه‌های کلیدی

ای-۱- (۲- اتوکسی فنیل)-۳-(۴- نیتروفنیل) تری آز ۱- ان؛ یون جیوه؛ ذرات نانومغناطیسی، پیش‌تغلیظ؛ اسپکترو فتومتری ماورابنفش –مرئی.

Abstract

In this paper, magnetic nanoparticles functionalized by triazene ligand were prepared for extraction/preconcentration of trace amounts of mercury ions in water samples former on its determination with UV-Vis spectrophotometry. The modified magnetic nanoparticles were characterized by the various techniques such as Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM) and X –Ray Diffractometry (XRD). In the separation process, aqueous solution of Hg^{2+} ion was mixed with Fe_3O_4 magnetite nanoparticles modified with (E)-1-(2-Ethoxyphenyl)-3-(4-nitrophenyl)triaze-1-ene (ENT), ($MNPs@SiO_2$-ENT) and then external magnetic field was applied for isolation of magnetite nanoparticles containing mercury ions. Experimental conditions for effective adsorption including pH, ENT amount, Fe_3O_4 NPs amounts, and eluent type have been studied and established. Under the optimal extraction and preconcentration conditions, calibration curve was linear in the range of 4–80 µgL^{-1} with $r^2 = 0.9992$ (n=20), the limit of detection (LOD) 1.05µg L^{-1} and enrichment factor was 38, respectively. This technique was successfully used for the determination of Hg (II) in aqueous samples.

Keywords

(E)-1-(2-Ethoxyphenyl)-3-(4-nitrophenyl) triaze-1-ene; Hg^{2+} ions; Magnetic Nanoparticles; Preconcentration; UV-Vis Spectrophotometry.

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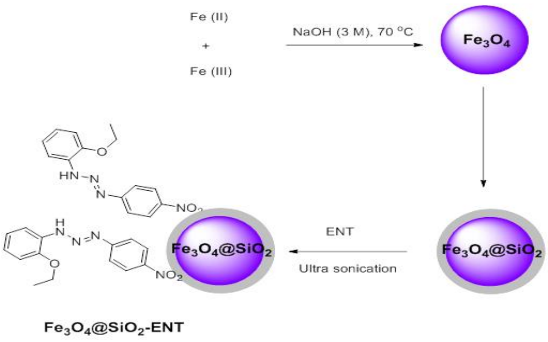
*Corresponding Author: shafieekhani20@gmail.com

1. INTRODUCTION

Determination of traces of mercury in the environmental samples is of great importance due to its high toxicity, high reactivity, accumulative character, wide usage and relative solubility in water and living tissues [1-5]. Toxic effects include damage to the brain, kidney, and lungs. Mercury pollution constitutes serious worldwide environmental problem [6-9].

Mercury can solve in natural water and change over to methyl mercury, neurotoxic compound that interferes in protein synthesis by blockages of the enzyme binding sites, by the action of aerobic microorganisms [10]. Recent reports evaluate a total mercury concentration in non-polluted water ranging from 0.006 to 5 ng mL^{-1} [11-16]. Hg (II) can diffuse and accumulate into the aquatic ecosystem as contaminant in the environment. Therefore, determination of Hg (II) levels in water samples is very important. Total mercury concentration in marine species and natural water is about 0.1-200 ng mL^{-1} and the allowed mercury level set by World Health Organization (WHO) for drinking water is 1 ng mL^{-1} [17, 18]. Therefore, a great variety of techniques have been applied for the determination of Hg (II) ions in trace levels, such as cold vapor atomic absorption spectrometry(CV-AAS) [19], inductively coupled plasma atomic emission /or mass spectrometry [20,21], spectrofluorimetry [22, 23], atomic florescence spectrometry [24-26] gas chromatography[27] X-ray spectrometry[28,29]. However, these high-performance techniques require expensive instruments and technical expertise in sample preparation steps. Nowadays, the colorimetric method acting is a common technique used for analysis without prerequisite of complex instrumental design and carrying out. The method is based on monitoring of the color change of solutions, e.g. by UV–visible absorption spectrophotometry, which is related to concentration of analytes.

This work concentrates on advancement a simple and sensitive spectrophotometric method to determination of the Hg^{2+} ion. In this work, ($MNPs@SiO_2$) were prepared and functionalized by (E)-3-(2-ethoxyphenyl)-1-(4-nitrophenyl) triaz-1-ene (ENT), (Scheme 1) to create ($MNPs@SiO_2$-ENT). Among magnetic nanoparticles, Fe_3O_4 nanoparticles are highly dispersible in solutions. with particle sizes of less than 40 nm. They offer a large surface area and super paramagnetic properties; they are attracted to a magnetic field but do not retain magnetic properties when the field is removed, making them highly useful in novel separation processes [19, 20].The prepared ($MNPs@SiO_2$-ENT) was utilized as a novel dispersible solid phase extraction sorbent that can be magnetically collected and has a high capacity and selectivity toward mercury ion. This method is very simple and fast separation that needs a little amount of adsorbent for extraction.



Scheme 1. Preparation steps for fabrication of ENTfunctionalized magnetic Fe_3O_4 nanoparticle

2. EXPERIMENTAL

2.1. Reagents and solutions

All used reagents were of analytical grade. Ferric chloride($FeCl_3$•$6H_2O$),ferrous chloride ($FeCl_2$•$4H_2O$), sodium hydroxide, mercury chloride ($HgCl_2$), sodium acetate, tetraethyl orthosilicate (TEOS), methanol, acetone, acetonitrile, nitric acid and hydrochloric acid were all purchased from Merck Darmstadt, Germany). The stock solution of Hg (II) (1000 mgL^{-1}) was prepared by dissolving the 0.0135g of $HgCl_2$ in doubly distilled water and 1 mL H_2SO_4 (0.1 mol L^{-1}) and diluted to 10 mL in a volumetric flask. Working solutions were prepared from the stock solution by serial dilutions with doubly distilled water. A solution of (1×10^{-4} mol L^{-1}) triazene ligand was prepared by dissolving the appropriate amount of ENT in 1, 4-Dioxane and was then kept away from the light. A buffer solution (pH 4) was prepared by mixing a sodium acetate solution (0.1mol L^{-1}) with a concentrated hydrochloric acid (12 mol L^{-1}) solution.

2.2. Instrument

Perkin- Elmer (Lambda) PC UV-Vis spectrophotometer with 1 cm cell quartz was used for recording all spectra and absorbance measurements. The pH measurements were conducted by a pH-meter (Metrohm-827) calibrated against two standard buffer solutions. Scanning electron microscopy (SEM) was taken with KYKY, EM-3200, TEM images of the nanoparticle were obtained by using a Zeiss EM 900 transmission electron microscope (Carl Zeiss, Germany). The powder XRD pattern was collected with a Philips-PW 12C diffractometer (Philips PW, Amsterdam, The Netherlands) using Cu Kα radiation.

2.3. Synthesis of Fe_3O_4 nanoparticles (MNPs)

The chemical co-precipitation method was used to preparation of the Fe_3O_4 nanoparticles (MNPs) [21]. First, for preparation of a stock solution, $FeCl_3 \cdot 6H_2O$ (0.037 mol, 9.94 gr) with (0.0081 mol, 1.62 g) of $FeCl_2 \cdot 4H_2O$ and in 10.0 mL of HCl (2 mol L^{-1}) were mixed in a beaker which was then degassed using nitrogen gas for 20 min before use. Simultaneously, 100 mL of (3 mol L^{-1}) NaOH solutions was degassed (for 15 min) and heated to 70°C in a reactor. The stock solution was then added drop wise using a dropping funnel for 30 min under nitrogen gas protection and vigorously stirring (1000 rpm) using a glassware stirrer. During the whole process, the solution temperature was maintained at 65-70°C and nitrogen gas was used to prevent the intrusion of oxygen. The color of the solution changed immediately from orange to dark after addition of NaOH solutions. The pH of the suspension was adjusted to pH=7.0 using HCl (2 mol L^{-1}). The magnetic nanoparticles were separated from the resulting solution with a magnet and the supernatant was discarded. The obtained MNPs were rinsed twice with deionized water and ethanol. Finally, MNPs were dried in oven at 50°C for 4 hours. The obtained MNPs were stable under these conditions for up to about one month.

2.4. Preparation of silica coated (MNPs@SiO_2)

The Fe_3O_4@SiO_2 Nanospheres were prepared by a modified Stöber method [30]. Briefly, MNPs (0.50 g) was dispersed in a mixture of ethanol (50 mL), deionized water (5 mL) and TEOS (0.20 mL), followed by the addition of 5.0 mL of NaOH (10 wt.%). This solution was stirred mechanically for 30 min at room temperature. Then the product, MNPs@SiO_2, was separated by an external magnet and was washed with deionized water and ethanol three times and dried at 80°C for 10 h.

2.5. Preparation of ENT functionalized MNPs (MNPs@SiO_2-ENT)

For the preparation of ENT modified magnetic nanoparticles, triazene ligand (solution in acetonitrile, 1 mL, and 1.3×10^{-3} mol L^{-1}) was added to 1 gr of MNPs@SiO_2 and stirred for 1h in ultrasonic bath. Subsequently, the suspension was stood for half one hour before separating and washing with ethanol. After five cycles of separation/washing/re-dispersion with ethanol, the powder obtained was oven dried at 50 °C for 10 hours.

2.6. Characterization of MNPs@SiO_2-ENT

In order to investigate the morphology and particle size of the prepared MNPs@SiO_2-ENT scanning electron microscopy (SEM) was performed and results were depicted in Fig. 1. The SEM image of MNPs@SiO_2-ENT shows spherical and uniform nanoparticles with size range of <100 nm. As shown in Fig. 3, during the modification of MNPs@SiO_2, a considerable change was not taken place on shape and size of nanoparticles but partial agglomeration of nanoparticles was observed.

XRD pattern of magnetite nanoparticles is shown in Fig. 2. Both Fe_3O_4 and MNPs@SiO_2-ENT show diffraction peaks at 2θ= 30.3, 35.6, 43.3, 53.8, 57.4 and 62.9 that are indexed to the crystalline cubic inverse spinel structure of Fe_3O_4 nanoparticles.

Fig. 4. Shows the magnetization versus applied field of MNPs@SiO_2-ENT that was obtained by VSM. The saturation magnetization value was measured to be ~60 emu g^{-1} for Fe_3O_4 and ~40 emu g^{-1} for MNPs@SiO_2-ENT. The results show that surface modification of MNPs has insignificance effect on the magnetic properties of MNPs.

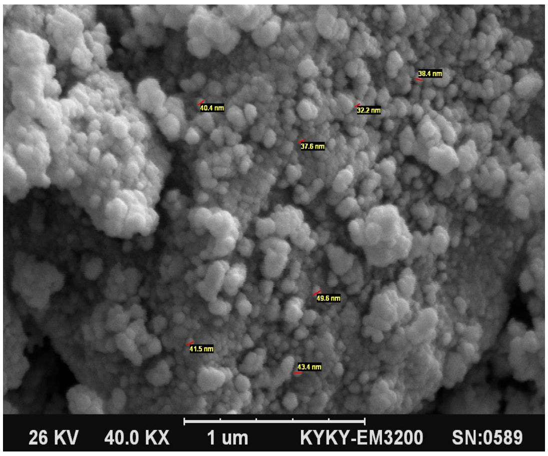


Fig. 1. SEM image of MNPs@SiO_2-ENT.

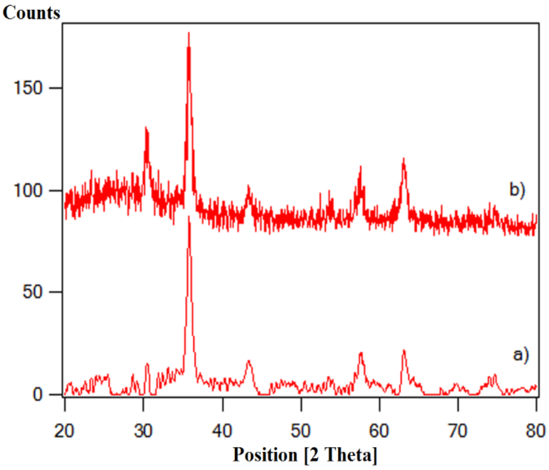


Fig. 2. X-ray diffraction patterns of a) MNPs and b) MNPs@SiO_2-ENT.

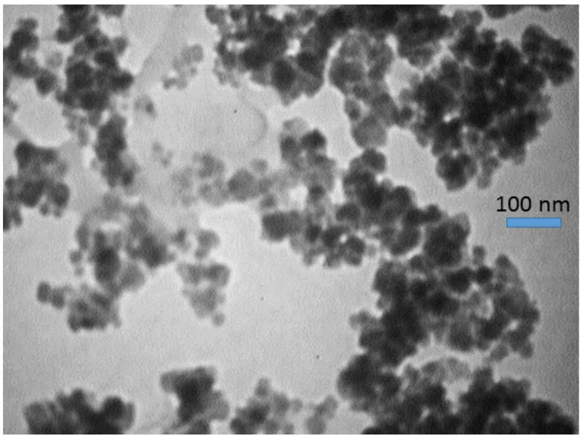


Fig. 3. TEM image of MNPs@SiO_2-ENT.

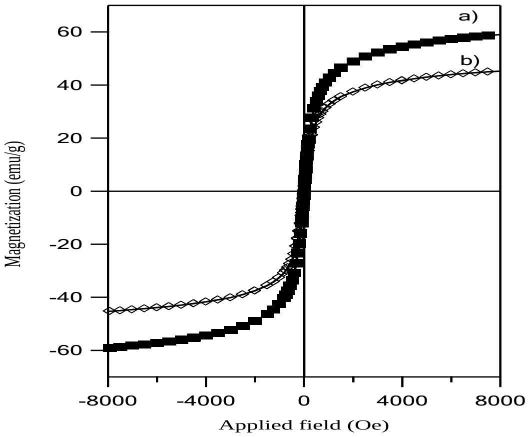


Fig. 4. Vibrational of sample MNPs@SiO_2-ENT vs. magnetization curve.

2.7. Absorption of Hg^{2+}

The procedure for the magnetic solid-phase extraction of Hg^{2+} ion in a batch experiment is as follows: A solid adsorbent (1 gr) was added to a 50 mL of Hg^{2+} ion solution (1oo µg L^{-1}), then the pH value was adjusted to 4.0 with acetate/ acetic buffer and the solution was shaken in ultrasonic batch for 10 min to facilitate adsorption of the metal ions onto the nanoparticles. Then the magnetic adsorbents was separated easily and quickly using an external magnet and decanted directly. Subsequently, 2 mL of 1 mol L^{-1} HNO_3 solution was added as eluent. Finally, the magnet was used again to settle the magnetic nanoparticles and elute was separated for spectrophotometric analysis. In this section, we used change color dithizone for determination of Hg^{2+} ion. The amount of Hg^{2+} adsorbed onto the absorbent was calculated using the concentration of before and after absorption as follows $X = (C_0 - C)\ V/M$ where X is amounts of Hg^{2+} adsorbed, Hg^{2+} (mg/g), C_0 is the initial concentration before adsorption (mg L^{-1}), C is the concentration after absorption (mgL^{-1}), V is the solution volume (L), and M is the mass of adsorbent.

3. RESULT AND DISCUSSION

3.1. Effect of pH

The pH of the sample solution plays a key role in the solid phase extraction procedure. A proper pH value can improve the adsorption efficiency, and diminish interference from the medium. The effect of pH on the extraction mercury was studied between the pH ranges of 2–7, the results are shown in Fig. 6. Based on the obtained results, the extraction of Hg (II), increased as the pH in the aqueous solution was increased from 2 to 4, and then it decreased when the pH increased from 4 to 6. Therefore, the optimum pH was 4 for extraction of Hg (II) from the aqueous solution. At strong acidic media, pH (<2) the nitrogen atoms of ligand could be protonated, so the stability of complex formation between the sorbent and Hg (II) ions were reduced. It is worthy to note that no precipitation of the mercury hydroxide is expected in the pH range of 4–7 [31]. The higher pH values (>9) were not studied because functionalized Fe_3O_4 magnetic nanoparticles were not stable in alkali solutions due to the breaking of the Si-O-Si bonds by hydroxide ion attack.

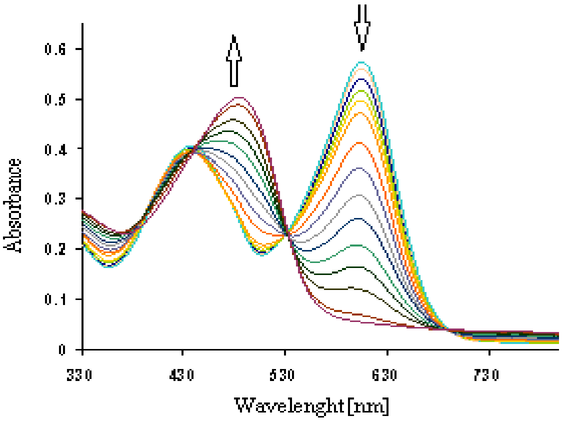


Fig. 5. Absorbance spectra of Dithizone solution (5.0×10^{-5} mol L^{-1}) in 1, 4-Dioxane and increasing concentration of Hg(II) ion solution (1.30×10^{-3} mol L^{-1}). The arrows show the direction of absorbance by increasing the ion concentration.

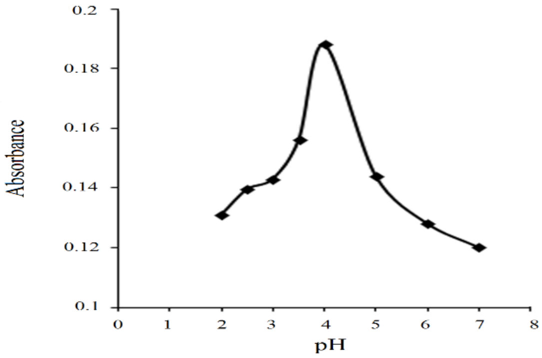


Fig. 6. Effect of pH on the extraction of Hg(II) ions.

3.2. Effect of ligand amount

Chemical structure of ENT ligand is shown in Fig. 7. ENT can form Hg–ENT complexes with stoichiometry's of 1:2 (Hg: ENT) [32]. The advantages of using ENT can be summarized as follows: (a) ENT forms selective complex with Hg (II). In addition, Hg (II) gives a color complex with ENT, it is especially suitable when the detection system used is a spectrophotometer; (b) reaction between Hg (II) and ENT is extremely fast. In order to investigate the effect of the amount of ENT on the quantitative extraction of Hg (II), the extraction was conducted by varying the amounts of ENT from 143 to 715 mg and the results are shown in Fig. 8. As can be seen, the obtained results showed that the extraction of Hg (II) ion was quantitative by using only 429 mg of ENT. Subsequent extraction experiments were carried out with 429 mg of ENT in order to achieve high capacity and to account for other extractable species.

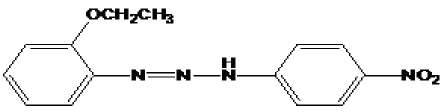


Fig. 7. Chemical structure of the Triazene ligand.

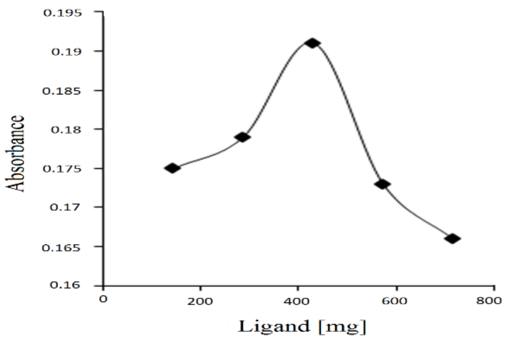


Fig. 8. Effect of ligand amount on the extraction of Hg(II) ions.

3.3. Effect of $MNPs@SiO_2$-ENT dosage

In order to investigate the effect of $MNPs@SiO_2$-ENT amount on the quantitative extraction of Hg (II) ions, the extraction was conducted by varying amount of the modified $MNPs@SiO_2$-ENT from 100 to 800 mg. The obtained results showed that the extraction of Hg (II) was quantitative by using only 400 mg of $MNPs@SiO_2$-ENT. Subsequent extraction experiments were carried out with 400 mg of $MNPs@SiO_2$-ENT in order to achieve higher capacity and to account for other extractable species.

3.4. Choice of eluent

Some experiments were carried out in order to choose the proper eluent for the adsorbed Hg (II) ions after the extraction of 100 µg L^{-1} of Hg (II) in a 50 mL solution by 400 mg $MNPs@SiO_2$-ENT. The Hg (II) ions were stripped with different volumes of various acids including HNO_3, HCl, $HClO_4$ and CH_3COOH, which could accomplish the quantitative elution of Hg (II) from the modified MNPs. It is obvious from the data given in Fig. 10, 11 that 2.0 mL of 1 mol L^{-1} HNO_3 gave the best results for preconcentration factor.

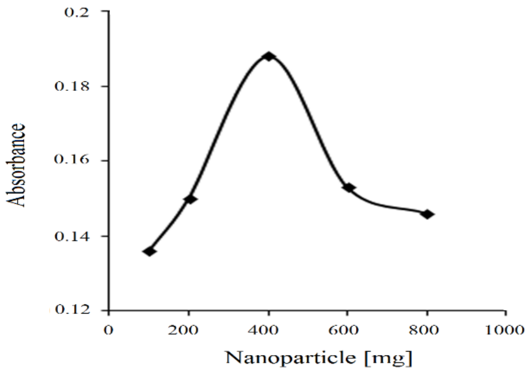


Fig. 9. Effect of the adsorbent amount on the extraction of Hg(II) ions.

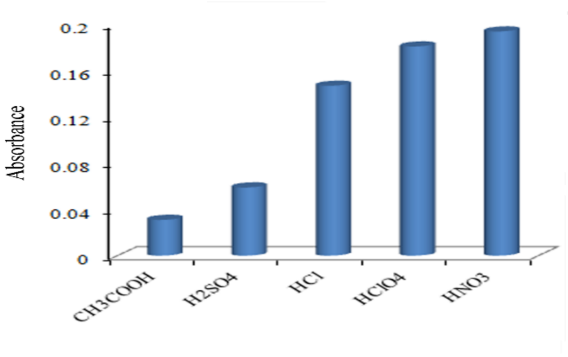


Fig. 10. Choice of eluent: The Hg(II) ions were stripped with different of eluent.

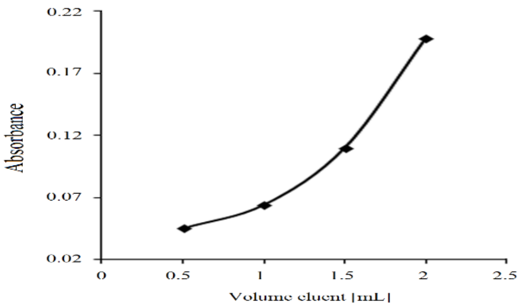


Fig. 11. Volume of eluent: The Hg(II) ions were stripped with different of volume.

3.5. Analytical performance

The method showed a good linearity over the calibration range (4–80 µg L^{-1}) and the correlation of determination (r^2) was higher than 0.9992. The limit of detection (LOD = 1.05 µg L^{-1}) was calculated as $3S_b/m$ (S_b, standard deviation of the blank signals and m, slope of calibration curve after preconcentration). An enhancement factor of 38 was calculated as the ratio between the slopes of the calibration curve submitted by the SPE procedure (for V = 50 mL) and the direct calibration curve (without preconcentration).

4. CONCLUSION

A novel magnetic adsorbent of silica coated Fe_3O_4 magnetic nanoparticle that modified with triazene ligand (MNPs@SiO2-ENT) was prepared and applied for preconcentration and determination of Hg (II) ions from water samples by using dithizone as a reagent and UV-Vis spectrophotometry. The proposed method offers a simple, sensitive, and inexpensive method for extraction and determination of Hg(II). Furthermore, Hg(II) was quantitatively extracted and an enhancement factor of 38-fold was obtained. The results demonstrated that the method is very suitable for the rapid extraction of Hg(II) ions from large volumes of water samples at ppb levels besides having both good accuracy and precision. In addition, sensitivity of the method is enough for the determination of Hg (II) in variety of environmental samples. The proposed method can be a guideline for the extraction of other metal ions from large volumes of sample.

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