

Immobilization of the Thenoyltrifluoroacetone on Sodium Dodecyl Sulfate Modified Magnetite Nanoparticles for Magnetic Solid Phase Extraction of Pb (II) from Water Samples

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Abstract – Magnetite nanoparticles (Fe_3O_4 NPs) were synthesized by co-precipitating method under optimized condition. The Fe_3O_4 NPs coated with sodium dodecyl sulfate-thenoyltrifluoroacetone (Fe_3O_4 NPs-SDS-TTFA) were then exerted as the magnetic solid phase extraction (MSPE) adsorbent for the extraction process prior to introducing to a flame atomic adsorption spectrometry (FAAS). The synthesized Fe_3O_4 NPs-SDS-TTFA were applied for the extraction of Pb(II) ions from different water samples. The characterization studies of nanoparticles were performed via scanning electron microscopy-energy dispersive micro-analysis (SEM-EDAX), X-ray diffraction (XRD) and vibrating sample magnetometer (VSM) techniques. The substantial parameters affecting the extraction efficiency were surveyed and optimized. A dynamic linear range (DLR) of 10–400 $\mu\text{g L}^{-1}$ was obtained and the limit of detection (LOD, $n=7$) and relative standard deviation (RSD%, $n=6$, $C=20 \mu\text{g L}^{-1}$) were found to be 2.3 $\mu\text{g L}^{-1}$ and 1.9%, respectively. According to the results, the proposed method successfully applied for the extraction of Pb(II) ions from different environmental water samples and satisfactory results achieved.

Key words: Magnetite (Fe_3O_4) NPs, Sodium dodecyl sulfate (SDS), Thenoyltrifluoroacetone (TTFA), Extraction, Pb(II), Water sample

1. INTRODUCTION

For decades it has been a great challenge to protect the environment against hazardous elements, especially heavy metals such as Cr, Hg, Pb, Ni and Cd. Water resources are known as one of the most common path ways of heavy metals into the environment and subsequently the human body, which makes it a great concern for environmental protection agencies and also researchers to monitor the natural resources and prevent those mentioned heavy metals entrance into the environment. The presence of above-mentioned pollutants and their relatives in the district of living creatures, most considering human being, can be a cause of many serious risks and various malfunctions, mostly cancers [1,2]. Lead is one of the most jeopardous elements that is toxic even at rare concentrations and can occur in the environment and living organs. The usual sources that can be mentioned for its existence are entirely related to human beings' artificial activities, such as smelting, mining, metal plating, tanneries, batteries, alloy, paper and fertilizer industries, pesticides, coating, lead paints, electroplating, petrochemical units and photographic materials production [3,4]. The waste water resulting from those mentioned industries includes different levels of varied elements and heavy metals especially lead as noted before. Therefore, lead ions can be absorbed

and accumulate in the plants, dairy cattle and other animals' tissues and enter the human food chain as result [5,6]. This metallic ion revokes biosynthesis and has very disastrous effects on the kidneys, brain cells and liver-membrane permeability, disorganizing these organ's functions. Plus, its accumulation in the body can lead to disturbances such as vomiting, nausea, sweating, diarrhea, and in some cases, convulsions, coma and death. Thus, continuous exposure to even very low amounts of Pb can be adverse, especially to infants and children. Hence it is very urgent to monitor the trace levels of mentioned element in the environment [7,8-13]. The lower limit of Pb(II) concentration in natural water systems according to the World Health Organization (WHO) is enunciated as 10 mg L^{-1} . The drinking water and wastewater standard set and declared by the Environmental Protection Agency (EPA) for lead is 0.05 and 0.5 mg L^{-1} , respectively [14,15]. Because of the low concentrations of lead ions in samples gathered from the industrial or environmental zones, commonly below the detection limit of conventional techniques, a pre-concentration/enrichment step is required for overcoming this difficulty. Some of these common pre-concentration separation methods for enrichment include dispersive liquid-liquid microextraction (DLLME) [16], membrane filtration [17], liquid-liquid extraction (LLE) [18], cloud point extraction (CPE) [19], liquid phase micro extraction (LPME) [20] and solid-phase extraction (SPE) [21-27]. Those above-mentioned systems enhance the sensitivity and also selectivity of the determination techniques. Also, in the past two decades, nanosized materials have been synthesized and used for a wide scope of scientific studies and elicited great interest

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because of their unique physical and chemical characteristics [28]. The surface atoms are unsaturated and have high chemical activity and adsorption capacity to different substances [29]. Nanoscale materials divided into two major inorganic and organic groups have specific adsorptive, electronic, optical, magnetic and catalytic properties that make them suitable for various sorts of scientific researches and goals [30-32].

One of the most significant approaches that has been considered in recent years is using magnetic solid phase extraction (MSPE) as a high-yield and applicable method for pre-concentration process, which uses magnetic adsorbents such as iron oxide nanoparticles, cobalt ferrite (Fe_2CoO_4) and chromium dioxide (CrO_2) [33,34] and also outward magnetic field for separation of indicated analyte. Magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) with characteristics of black color, spherical shape, large surface area, biocompatibility with different complex matrices and overcoming the difficulties of conventional classic solid phase extraction (SPE) like column packing and time consuming issues, is recognized as one of the most significant magnetic materials [35,36]. The magnetite NPs in exposure of open air at room temperature gradually turn to other forms of iron oxides and lose their magnetic properties, dispersion capability and finally undergo biodegradation [37]. Therefore, the optimization of MNPs surface area is an important factor which can ensure the purity and stability of Fe_3O_4 NPs and prevent their aggregation pertaining to surface high energies reduction [38-40]. Thus, in order to protect MNPs from possible damages during and after synthesis process and make them more selective to certain considered analyte, they must be coated with appropriate modifying agents to fulfill complexation with analyte and high yield extraction. Recently, various studies have represented the utilization of coating agents such as tetraethyl orthosilicate-(3-aminopropyl)trimethoxysilane (TEOS-APTMS) [41], dithizone-sodium dodecyl sulfate (DTZ/SDS) [42], 3-(trimethoxysilyl)-1-propanethiol-ethylene glycol bis-mercaptoacetate (TMSPT-EGBMA) [43], cetyltrimethylammonium bromide (CTAB) [44], polydopamine [45] and amino group (NH_2) [46] to imprint functional groups of thiol, carboxylic and amino on the surface of MNPs for the pre-concentration process of trace metal ions.

In this study, a Fe_3O_4 NPs-assisted MSPE procedure was applied and optimized based on the co-precipitation of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ as precursors and also SDS-TTFA external functionalization for the extraction and subsequent determination of Pb(II) ions in several water samples. To gain the most effective extraction process, different parameters including pH, adsorbent and coating agents amount, and contact time were investigated and optimized. Moreover, for the recovery process of Pb(II), desorption parameters such as type, concentration and least amount of eluent were surveyed and optimized. In the present research, for the first time the application of sodium dodecyl sulfate-thenoyltrifluoroacetone (SDS-TTFA) coated on magnetite nanoparticles (Fe_3O_4 NPs-SDS-TTFA) for the extraction of

trace amounts of Pb(II) from different water samples has been investigated and reported.

2. Experimental

2-1. Chemicals

Ferrous chloride tetrahydrate ($\text{FeCl}_2\cdot 4\text{H}_2\text{O}$), ferric chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$), Lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$), sodium dodecyl sulfate (SDS, $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$), sodium hydroxide (NaOH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), methanol (CH_3OH), acetic acid ($\text{CH}_3\text{CO}_2\text{H}$), phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3) were all purchased from Merck (Merck, Darmstadt, Germany). The thenoyltrifluoroacetone (TTFA, $\text{C}_8\text{H}_5\text{F}_3\text{O}_2\text{S}$) was purchased from Sigma-Aldrich (Germany). A stock solution of lead (1000 mg L^{-1}) was prepared by dissolving 1.6 g of $\text{Pb}(\text{NO}_3)_2$ in 1000 mL of deionized water containing 0.5 mL of concentrated HNO_3 and was diluted daily to prepare required standard and working solutions. All of the solutions were stored in appropriate and cleaned polypropylene containers. Also, the stock solutions of different coexistent ions (1000 mg L^{-1} -acidified) were prepared from their nitrate or chloride. All of the chemicals and reagents used in the present research were of analytical grade without any further purification. Also, the chelating solution was prepared by dissolving of 0.0865 g of the thenoyltrifluoroacetone (TTFA) solution in 50 mL of methanol as the solvent. The pHs of the solutions were adjusted by addition of suitable volumes of HCl or NaOH.

2-2. Apparatus

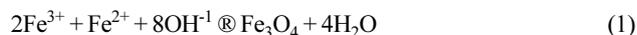
The ultrasonic related experiments were accomplished by a Eurosonic 4D model (Euronada, Italy) for complete dissolving of coating agents and synthesis process of magnetic adsorbent. Various techniques and methods applied for clear characterization of pre-synthesized magnetic nanoparticles. The properties like morphology and size of nanoparticles were determined via SEM micrographs utilizing scanning electron microscopy-energy dispersive micro-analysis (SEM-EDAX, VEGA/TESCAN-LMU). The determination of chemical structure and average size of the magnetic nanoparticles were recorded by powder X-ray diffraction (XRD) patterns at room temperature using a Philips-X'Pert Pro diffractometer-MPD (Netherlands) equipped with a high-power Cu-K α radionuclide source ($\lambda=1.54060 \text{ nm}$) at 40 kV and 30 mA. Data were collected over the range 4–90° in 2 θ with a scattering speed of 2° min $^{-1}$. A LDJ9600 model vibrating sample magnetometer (VSM, Electronics Inc Troy, MI, USA) was used for determination of magnetic properties of Fe_3O_4 NPs. A strong neodymium-iron-boron ($\text{Nd}_2\text{Fe}_{12}\text{B}$) magnet (10 \times 5 \times 4 cm, 1.4 Tesla) provided a desirable magnetic field for subsequent separations steps. The pH measurements were performed with a Metrohm Model 774 pH meter.

2-3. Synthesis of Fe_3O_4 NPs

In a typical procedure, 8.59 g of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ and 3.17 g of

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ with a molar ratio of 2:1 were added to a beaker and dissolved in 200 mL of deionized water comprising 1 mL of HCl 10 mol L^{-1} collectively. Then, the solution was heated to 80 °C under vigorous stirring using a hand-crafted mechanical stirrer along with the injection of nitrogen gas for protection against oxidation and maintained at mentioned temperature for 30 min. Next, 100 mL of NaOH 2 mol L^{-1} was added into the solution gradually through a titration column under nitrogen atmosphere during time scope of 30 min. After 1 h, a black precipitate magnetite was formed. During the ongoing synthesis procedure, in order to prevent Fe_3O_4 NPs transforming to the other sorts of iron oxides, nitrogen gas injected through the solution continuously to degas the solution and maintain the Fe_3O_4 NPs safe against air exposure. The Fe_3O_4 precipitates were then separated from the solution via a magnetic field provided by a 1.4 T magnet and

washed three times with deionized water and ethanol. Consequently, the black precipitates of Fe_3O_4 NPs were dried in a vacuum oven at 80 °C [47]. The synthesis of magnetite nanoparticles is represented by the overall reaction equation given below (1):



2-4. Modification of Fe_3O_4 NPs

To approach high yield and selective extraction and subsequent recovery, the pre-synthesized magnetic nanoparticles surfaces had to be modified with substantial functional groups originating from chemicals and coating materials. To gain this goal, at first 1 g of synthesized Fe_3O_4 NPs was added to a 250 mL beaker containing 100 mL of HNO_3 5 mol L^{-1} and stirred in ultrasonic bath container for 10 min to charge the Fe_3O_4 NPs surface before starting the coating pro-

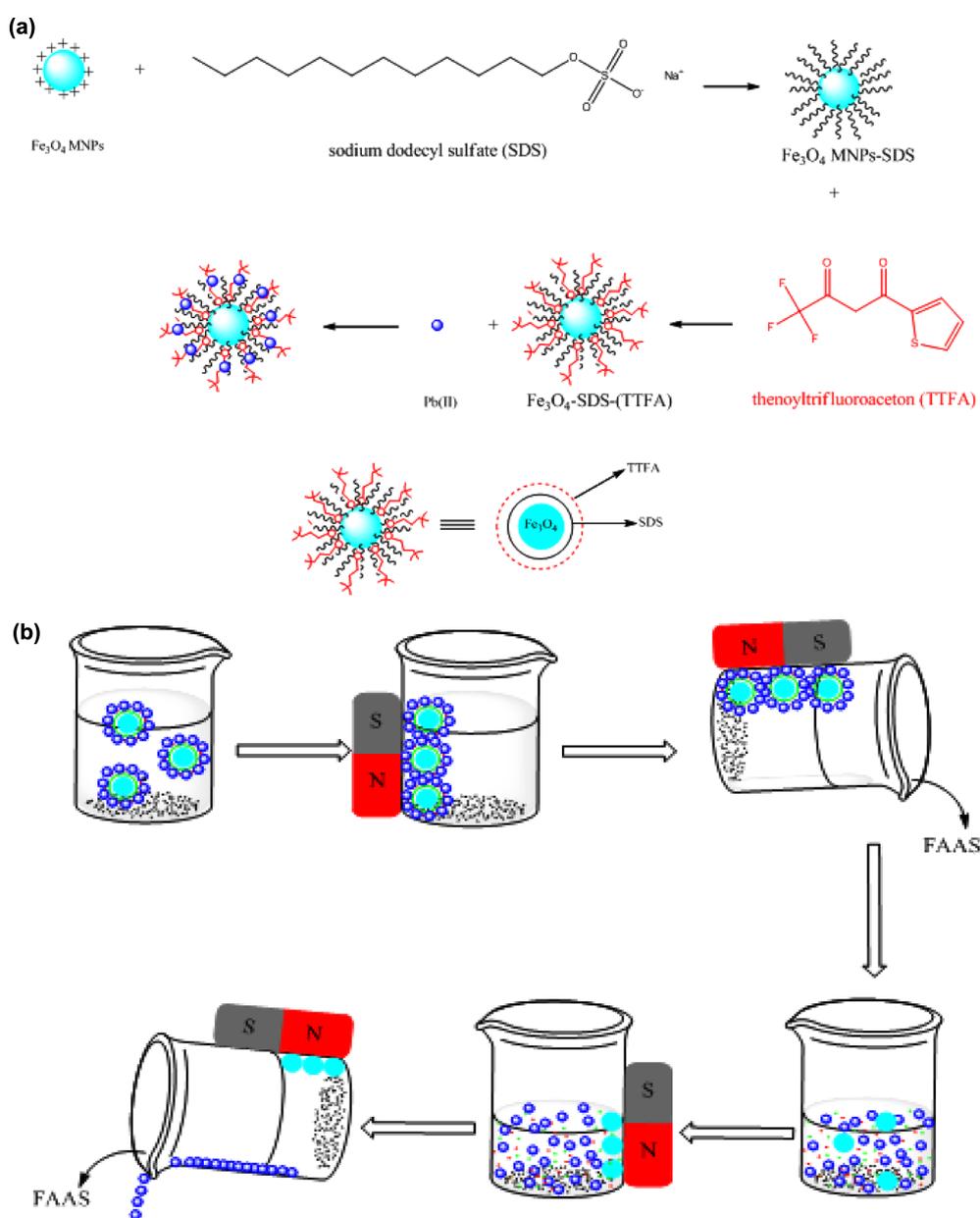


Fig. 1. (a) A schematic illustration of the Fe_3O_4 NPs modification with SDS and TTFA groups, and adsorption of $\text{Pb}(\text{II})$ ions, (b) application of Fe_3O_4 NPs-SDS-TTFA for separation and preconcentration of $\text{Pb}(\text{II})$ ions in water samples based on MSPE.

cess. The charged magnetite NPs was separated from solution by magnet and washed three times with distilled water. Then, 0.09 g of sodium dodecyl sulfate (SDS) in addition of 100 mL distilled water was introduced to 1g above-mentioned charged Fe_3O_4 NPs. The suspension remained at optimized pH:5 by adding HNO_3 (1 mol L^{-1}) and stirred for 15 min in ultrasonic bath. In the next step, 400 μL of thenoyltrifluoroacetone (TTFA) 0.01 mol L^{-1} was added to the above suspension and pH value remained at 8 utilizing NaOH 1 mol L^{-1} with stirring for 15 min. Finally, the coated Fe_3O_4 NPs-SDS-TTFA was isolated by a strong magnet and the supernatant was poured away. The precipitate was washed with high purity deionized water then dried at 70°C in an autoclave for 2 h and saved in a desiccator.

2-5. MSPE procedure

The adsorption procedure was accomplished in a 250 mL beaker containing $400 \mu\text{g L}^{-1}$ of Pb(II) ions. The pH of solution was adjusted to 6 via addition of 1 mol L^{-1} of NaOH and 1 mol L^{-1} of HNO_3 . 0.1 g of Fe_3O_4 NPs-SDS-TTFA was added to the container containing $400 \mu\text{g L}^{-1}$ of analyte solution and the mixture was shaken for 5 min to facilitate the adsorption of Pb(II) ions on the Fe_3O_4 NPs. Then, the Fe_3O_4 NPs-SDS-TTFA was separated from supernatant solution via Nd-Fe-B strong magnet. 1 mL of HNO_3 1 mol L^{-1} used as eluent to recover Pb(II) ions from the precipitate. The mixture of nano adsorbents and eluent acid was shaken for 5 min and the Fe_3O_4 NPs of Fe_3O_4 NPs-SDS-TTFA were again separated by Nd-Fe-B strong magnet and the eluent was injected to the FAAS to measure the concentration of desorbed Pb(II). Afterwards, the variations related to Pb(II) ions concentration in the solution and the value of adsorbed Pb(II) ions were measured and determined via FAAS analysis and monitored with certain standard solutions of Pb. Also, a blank (not containing the targeted Pb^{2+} ion) sample was applied and treated by synthesized Fe_3O_4 NPs-SDS-TTFA for each stage of experiments with similar conditions used for the other test solutions. The following equation was also utilized to calculate the extraction percentage of extracted Pb(II) ions (2):

$$\text{Extraction Percentage (E\%)} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (2)$$

where C_i and C_f refer to the Pb(II) ions concentration before and after extraction process, respectively. Schematic illustration of the modification procedure of Fe_3O_4 NPs with sodium dodecyl sulfate (SDS) and thenoyltrifluoroacetone (TTFA) groups and subsequent adsorption of Pb(II) ions is shown in Fig. 1.

2-6. Preparation of real world water samples

Different water samples, including drinking water, seawater, river water, spring water, well water, mineral water, steam water, and waste water, all gathered from various regions of Iran (indicated in Table 3) were prepared by filtration and pH adjusted to 6 to perform the extraction process. Plus, 1 mL of Pb(II) solution $100 \mu\text{g mL}^{-1}$ was diluted up to 250 mL by the addition of those above noted water samples in 500 mL volumetric flasks for each case separately. The changes in the concentration of Pb(II) ions in the solution and also the adsorption amounts of Pb(II) ions on the Fe_3O_4 NPs-SDS-TTFA were measured by FAAS analysis and checked with known Pb(II) standard solutions.

3. Results and Discussion

3-1. SEM-EDAX

The size and morphology identification of the synthesized Fe_3O_4 NPs were investigated through magnification via scanning electron microscopy (SEM) as presented in Fig. 2. The SEM study shows the Fe_3O_4 NPs with homogeneous morphology, porous structure, approximately quasi-spherical shape and also unveils that the coating process with SDS-TTFA has no destructive effect on the morphology and crystallinity characteristics of synthesized Fe_3O_4 NPs. The SEM images of (a) and (b) in Fig. 2 depicts the Fe_3O_4 NPs and Fe_3O_4 NPs-SDS-TTFA, respectively. Moreover, the average crystalline sizes of synthesized Fe_3O_4 NPs indicated their nanometric dimensions (less than 100 nm). Fig. 3 gives the composition elements present in the synthesized Fe_3O_4 NPs samples that were investigated by Energy dispersive micro-analysis (EDAX) analysis. In the EDAX spectra, the appeared peaks of oxygen (O) and iron (Fe) are corresponded to the Fe_3O_4 NPs. On the other hand, in the spectrum (Fig. 3b), the appearing four peaks are related to the binding energies of

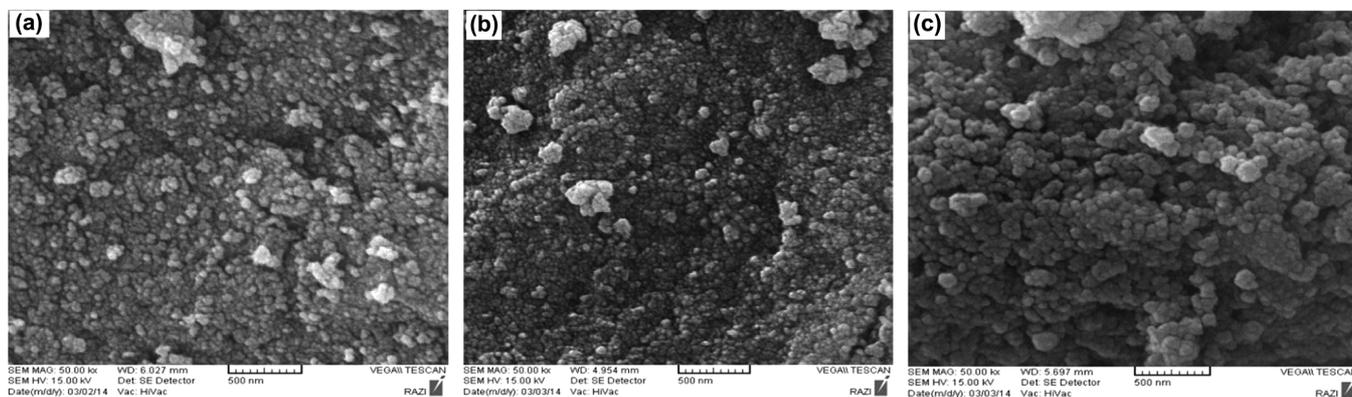


Fig. 2. SEM images of (a) Fe_3O_4 NPs, (b) Fe_3O_4 NPs-SDS and (c) Fe_3O_4 NPs-SDS-TTFA.

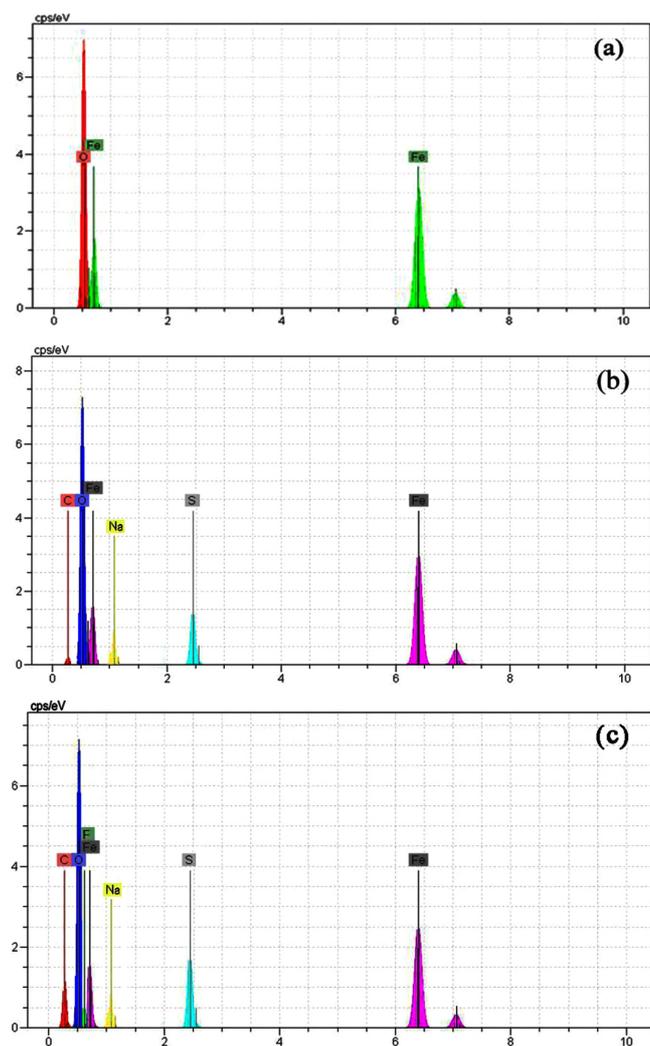


Fig. 3. EDAX spectra of (a) Fe_3O_4 NPs, (b) Fe_3O_4 NPs-SDS and (c) Fe_3O_4 NPs-SDS-TTFA.

sulfur (S), sodium (Na), Fluor (F) and carbon (C) which reveal the presence of SDS and TTFA in the synthesized adsorbent.

3-2. XRD

To elucidate the crystalline structure and phase purity of synthesized Fe_3O_4 NPs samples, the X-ray diffraction (XRD) was exerted as described in Fig. 4. Besides, the peaks related to Fe_3O_4 NPs observed at scattering angles (2θ) of 30.440° , 35.852° , 42.995° , 54.369° , 63.225° , 71.350° and 79.210° corresponding to diffraction planes of (220), (311), (222), (400), (422), (622) and (444), respectively, with reference code (ICSD card#86-2267). No characteristic peaks referring to the existence of impurities occurred in the pattern during synthesis process. There is a certain line broadening of the scattering patterns in Figs. 4(a) and 4(b), which is a sensible proof for the synthesized Fe_3O_4 NPs and Fe_3O_4 NPs-SDS-TTFA particles to be in nano range. Furthermore, the size of the prepared Fe_3O_4 NPs and Fe_3O_4 NPs-SDS-TTFA were surveyed via XRD measurement and line broadening of the peak at $2\theta=4^\circ\text{--}90^\circ$ by Debye-Scherrer equation (3) [16]:

$$d = \frac{0.94\lambda}{\beta \cos\theta} \quad (3)$$

where d represents the crystalline size, λ is the wavelength of X-ray source, β is the full width at half maximum (FWHM) and θ is Bragg diffraction angle. According to this equation, the average crystalline size in diffraction plane of (311) for the Fe_3O_4 NPs and Fe_3O_4 NPs-SDS-TTFA were calculated about 21.2 nm and 35.3 nm, respectively and obtained data are given in Table 1. The crystalline sizes obtained from XRD measurement are consistent with those of the SEM study.

3-3. VSM

The magnetic specifications of bare Fe_3O_4 NPs, Fe_3O_4 NPs-SDS and Fe_3O_4 NPs-SDS-TTFA were illustrated and compared via vibrating sample magnetometer (VSM) magnetization curves at room temperature and represented in Fig. 5. The characteristic feature of super paramagnetism or ferromagnetism can be clearly explained and distinguished via VSM curves. Besides, the maximum magnetic strength under the term-saturation magnetization could be derived that its magnitude determines the power of the utilized magnet. The three curves show a similar shape and symmetry about the origin. Two naked and functionalized Fe_3O_4 NPs exhibit typical superparamagnetic behavior since no hysteresis or remanence is observed. The saturation magnetization of naked Fe_3O_4 NPs was 50 emu g^{-1} (Fig. 5a), while as predicted Fe_3O_4 NPs-SDS (Fig. 5b) and Fe_3O_4 NPs-SDS-TTFA (Fig. 5c) groups over nanoparticles declined the quantity to 45 and 40 emu g^{-1} , respectively. However, the noted variation was not significant and the superparamagnetic characteristic of the synthesized nano adsorbent was sufficient for MSPE with a conventional magnet.

3-4. The optimization of extraction process parameters

The extraction procedure is highly dependent on different factors which affect the process and should be optimized to reach the best level for a high yield extraction/recovery. In the present research, the affected parameters included pH for various steps, amount of sorbent, amount of surfactant, volume/concentration of ligand, characteristics of eluent and contact time were surveyed and discussed. Note that a concentration of $400 \mu\text{g L}^{-1}$ of Pb(II) was considered for all optimization steps.

3-5. Effect of pH

The optimization of pH in the sample solution was one of the most noticeable parameters which directly affect the extraction efficiency and adsorption capacity of Fe_3O_4 NPs-SDS-TTFA. The acidity of sample solution has two notable effects on metal sorption. First, protons in acid solution can protonate binding sites of the chelating molecules. Second, hydroxide in basic solution may complex and precipitate many metals. Therefore, pH of a solution is the first parameter to be optimized [48]. In this work, the optimization of pH was investigated upon three steps: (a) SDS addition, (b) TTFA addition and eventually

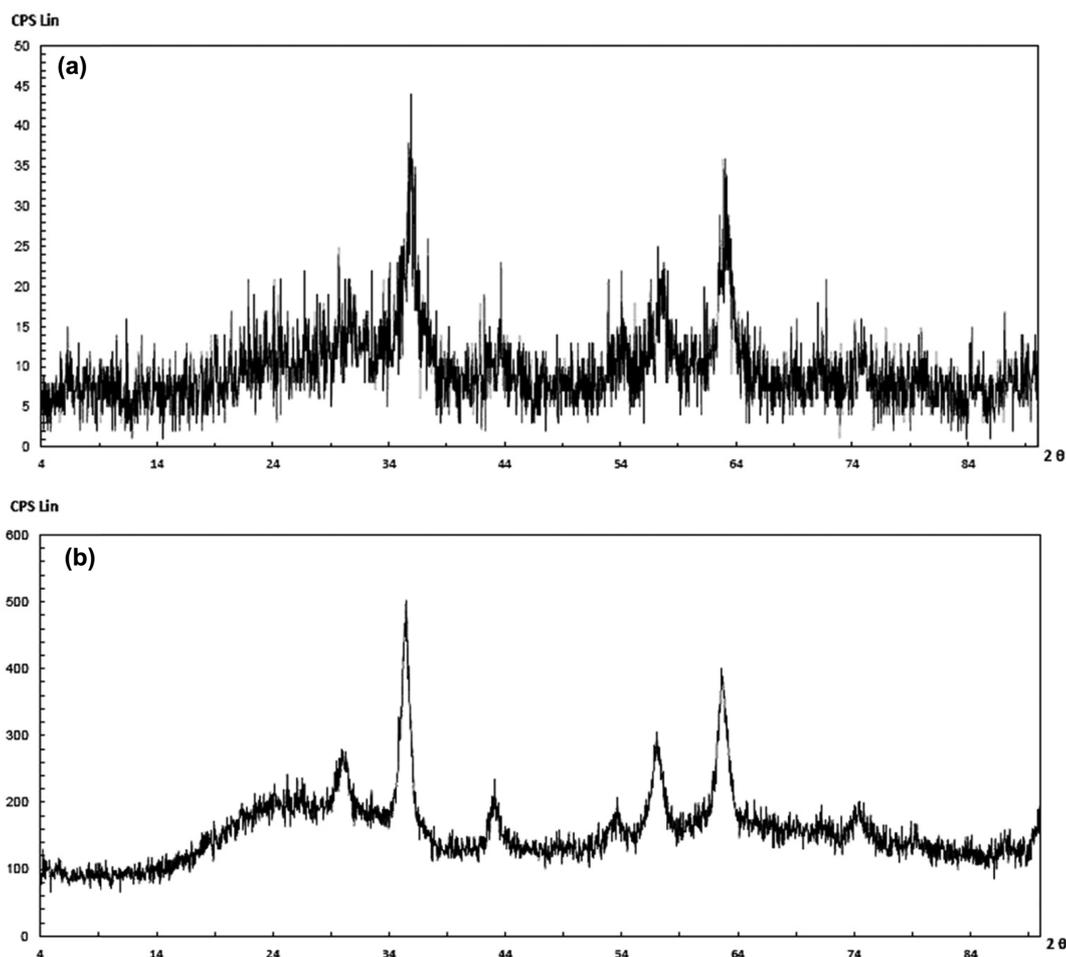


Fig. 4. XRD spectra of (a) Fe_3O_4 NPs, (b) Fe_3O_4 NPs-SDS-TTFA.

Table 1. The obtained results for X-ray diffraction (XRD)

Diffraction plane	Intensity (%)	FWHM	Height	2 Theta (2θ)
311	100	0.3936	17.95	35.852°
222	16.97	0.7872	3.95	42.995°
400	53.35	0.6298	9.57	54.369°
422	84.10	0.5760	15.09	63.225°

(c) MSPE process. As illustrated in Fig. 6, the adsorption/extraction of Pb(II) ions was surveyed at pH ranges of 2~9 for steps a and b and 3~7 for step c. As referred to before, the metal chemistry in the solution and ionization state of coating agents, which results in the availability of adsorption active sites, thoroughly depend on pH. The Pb(II) retention that progressively decreased at low pH ranges pertains to the intense interaction of H^+ ions with the adsorptive active sites of Fe_3O_4 NPs-SDS-TTFA than that of Pb(II) ions. The protonation of SDS and TTFA in highly acidic solutions decreases the available ionized groups and has reverse feedback on the adsorption procedure. Furthermore, at high pH ranges, the concentration of negative charge density on the adsorbent surface leads to a decrease in the SDS adsorption, which along with the emerging of lead hydroxide (due to excess of OH ions in basic media) causes a reduction in Pb(II) adsorption procedure. Therefore, to achieve the best selectivity and high yield extraction, pHs of 3, 6 were considered for surface

modification of adsorbent by the SDS and TTFA, respectively, and also the pH of 6 was selected for extraction process of Pb(II) via Fe_3O_4 NPs-SDS-TTFA.

3-6. Effect of SDS and adsorbent amounts

The selection of appropriate amounts of modifying agents has an influential effect on the entire extraction and recovery process and must not be overlooked. Fe_3O_4 NPs tolerate particular values of modification agents. The over-loading by modifying agents might be cause of their disruption from the surface of the nano adsorbent into the media and eventually formation of lead complexes within sample solution instead of Fe_3O_4 NPs surfaces. On the other hand, due the amphiphilic characteristics induced by both head and tail parts of the organosulfate, SDS represents a micellar behavior in aqueous media depending on its critical micelle concentration (CMC, 8×10^{-3} mol L^{-1}). Above CMC the surface tension remains relatively con-

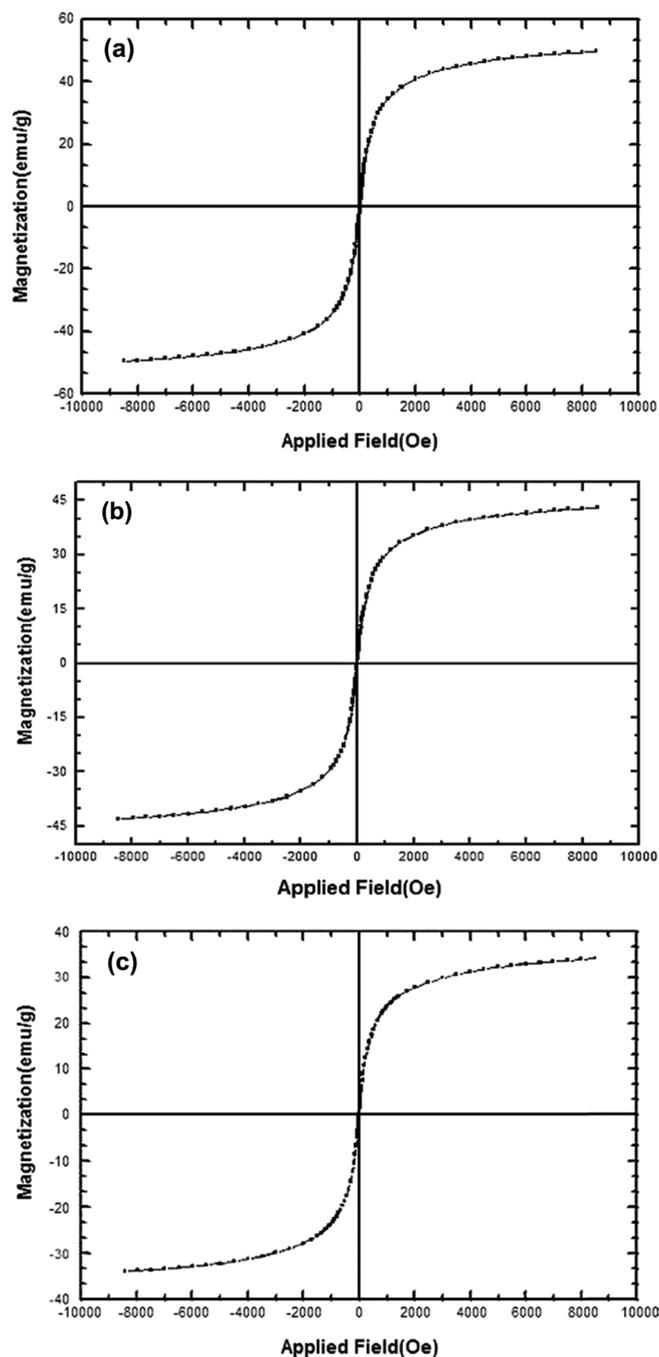


Fig. 5. VSM magnetization curves of (a) Fe_3O_4 NPs, (b) Fe_3O_4 NPs-SDS and (c) Fe_3O_4 NPs-SDS-TTFA.

stant. Thus, SDS forms micelles and would not adsorbed on the surface of Fe_3O_4 NPs as expected. As depicted in Fig. 7, with increasing the amount of SDS, extraction percentage of Pb(II) was enhanced and nailed to a maximum. When the SDS amount approached 0.09 g in 100 mL ($0.0031 \text{ mol L}^{-1}$) of deionized water, a decreasing trend occurred. Thereupon, 0.09 g of SDS was selected for further experiments.

Also, the amount of adsorbent was studied as depicted in Fig. 8, where it can be obviously observed that the extraction recoveries gradually decreased as the Fe_3O_4 NPs mass increased. This could be

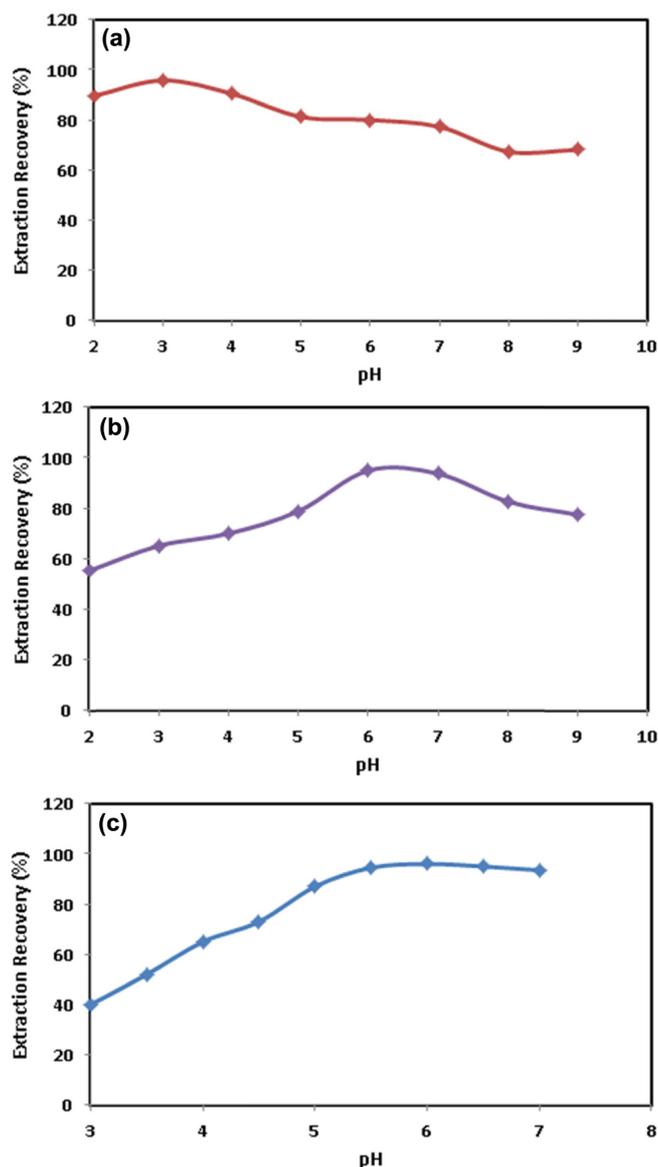


Fig. 6. Effect of pH of (a) SDS, (b) TTFA and (c) Fe_3O_4 NPs-SDS-TTFA on the extraction efficiency Pb(II) ions using the proposed MSPE procedure.

explained by the fact that with sufficiently high surface area and low diffusional resistance of nanoparticles, less amount of adsorbent would provide satisfactory results in extraction efficiency. On the other hand, the higher the amount of nanoparticles, the weaker the capability of eluent to recover all Pb(II) ions from adsorptive sites. Hence, the mass range of 10~300 mg of adsorbent was investigated to select the most significant amount. Thus, 100 mg was selected as the suitable mass for Fe_3O_4 NPs-SDS-TTFA to perform the pre-mentioned high yield extraction.

3-7. Effect of ligand and eluent various characteristics (volume, concentration and type) on the extraction process

The effects of the volume and concentration of TTFA on the extraction/recovery of Pb(II) from samples solutions are of great

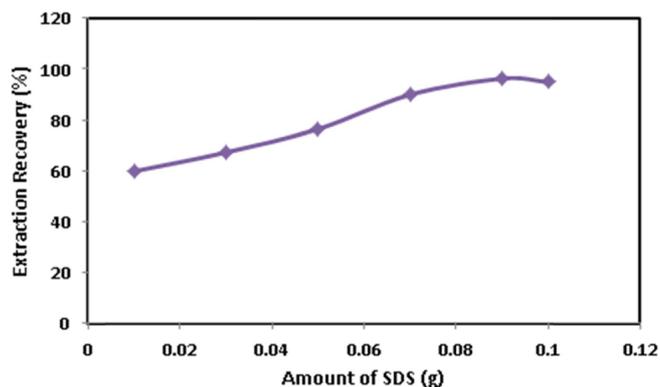


Fig. 7. Effect of amount of SDS on the extraction efficiency of Pb(II) ions using the proposed MSPE procedure.

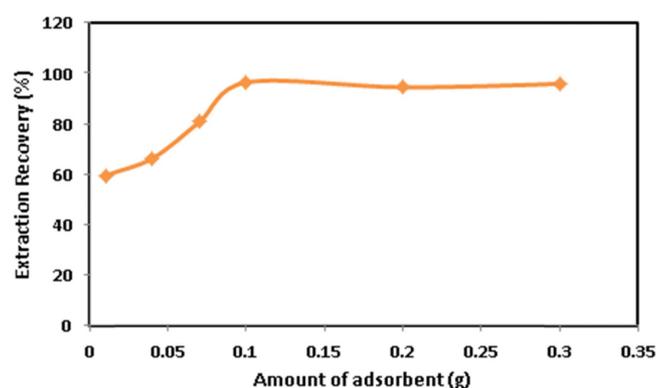


Fig. 8. Effect of amount of Fe_3O_4 NPs-SDS-TTFA on the extraction efficiency of Pb(II) ions using the proposed MSPE procedure.

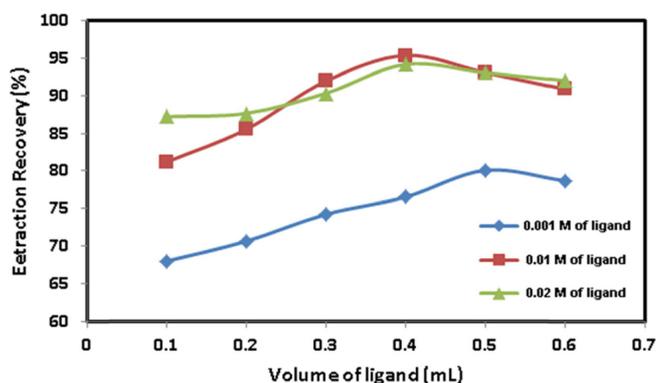


Fig. 9. Effect of volume and concentration of ligand on the extraction efficiency of Pb(II) ions using the proposed MSPE procedure.

importance and were evaluated in the scope of 0.1–0.6 mL and 0.001–0.02 mol L^{-1} respectively. The extraction recovery increases up to 0.4 mL of TTFA 0.01 mol L^{-1} and remains constant for subsequent values. Therefore, 0.4 mL of TTFA 0.01 mol L^{-1} was considered as an optimized value as depicted in Fig. 9. As, the optimization of adsorption process has a key role in extraction experiments, desorption study and selection of the most appropriate eluent is also a substantial factor and can increase the recovery percentage of desired analyte. The type, concentration and least-amount of the eluent was surveyed to establish conditions for significant desorption of

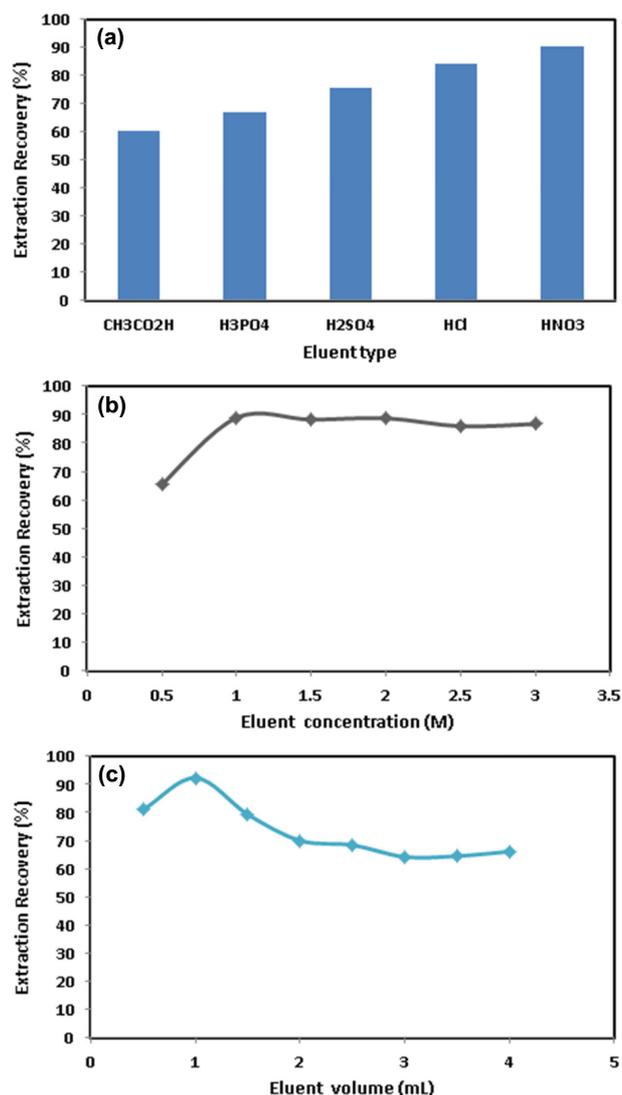


Fig. 10. Effect of (a) type, (b) concentration and (c) volume of eluent (HNO_3) on the desorption characteristics of Pb(II) ions from Fe_3O_4 NPs-SDS-TTFA using the proposed MSPE procedure.

Pb(II) ions from Fe_3O_4 NPs-SDS-TTFA. Various eluents such as HCl, HNO_3 , H_2SO_4 , H_3PO_4 , and $\text{CH}_3\text{CO}_2\text{H}$ at different concentrations and volumes were examined and the results have been represented in Fig. 10. It should be seriously noted that desorption acid must not decompose the Fe_3O_4 NPs. From this aspect, concentrations and volumes higher than 3 mol L^{-1} and 3.5 mL were observed to have reverse effects on Fe_3O_4 NPs. On the other hand, the less volume of eluent acid for desorption will lead to higher enrichment factor. Thus, 1 mL of HNO_3 1 mol L^{-1} was recognized as optimized volume of eluent which is highly effective for quantitative recovery of adsorbed Pb(II) ions and excrete them from Fe_3O_4 NPs-SDS-TTFA.

3-8. Effect of contact time and co-existing ions

Many researches tend to develop less time consuming analytical procedures which lead them to the results in shorter period of time, and this point is interpreted as an advantage for a proposed method. Applying Fe_3O_4 NPs as sorbent for analytical experiments such as

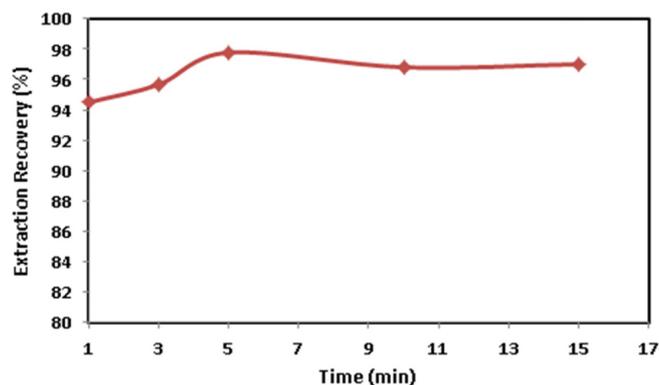


Fig. 11. Effect of contact time on the extraction efficiency of Pb(II) ions using the proposed MSPE procedure.

extraction methods has beneficial advantages, for instance, lack of internal resistance, high surface to volume ratio, shorter diffusion route and the ease of separation procedure via MSPE proposed for less time even for larger volumes of samples. The extraction time was investigated in the time range of 1–15 min, and according to FAAS analysis, the extraction recovery first increased up to 5 min and then maintained constant (Fig. 11). Thereupon, to attain a shorter analysis time, 5 min was considered as optimum value.

Matrix-like environmental water samples are likely to contain a wide range of anions and cations as constituents that may react with modifying chemical agents and induce interference via reduction of the adsorption efficiency of the target analyte. To survey this effect, solutions (250 mL) containing 1 mg L⁻¹ of Pb(II) ions with different amounts of coexisting ions were prepared and extracted according to the procedure described in the experimental section. Interference

Table 2. Effect of different co-existent on Pb(II) extraction

Coexistent ions	Permissive limit (ppm)	ER ^a %
NO ₃ ⁻	100	95.07
Cl ⁻	500	97.72
SO ₄ ²⁻	500	96
PO ₄ ³⁻	50	97.43
Ca ²⁺	100	100
Ni ²⁺	500	99.38
Zn ²⁺	200	98.26
Hg ²⁺	200	102.19
NH ₄ ⁺	100	100.27
Co ²⁺	100	95.12
Mn ²⁺	100	95.38
Cu ²⁺	50	101.23
Cd ²⁺	50	97.18
Fe ³⁺	25	100.12
Fe ²⁺	20	95.65

^aExtraction recovery

Table 3. Figures of merit of the presented method for the extraction procedure of Pb(II) ions

DLR ^a (μg L ⁻¹)	R ²	LOD (μg L ⁻¹)	RSD% (n = 6, C = 20 μg L ⁻¹)	EF ^b	Calibration equation
10–400	0.9981	2.3	1.9	250	y = 0.5805x + 0.0224

^aDynamic linear range

^bEnrichment factor

was interpreted as the deviation of ±5% from the recovery of the standard solution. The results depicted in the Table 2 refer to good selectivity of the presented procedure toward Pb(II) ions.

3-9. Effect of sample solutions volume

To investigate the volume of sample solutions on the adsorption and recovery processes, different volumes of high purified water samples in the range of 50–1000 mL, containing 400 μg L⁻¹ of Pb(II) prepared and the adsorption procedure performed using 0.1 g of pre-synthesized Fe₃O₄ NPs-SDS-TTFA under optimized conditions for each sample. After the desorption of adsorbed Pb(II) ions from mentioned nano adsorbent via 1 mL of HNO₃ 1 mol L⁻¹, the sample was subjected to FAAS instrument. Based on experimental observations, it can be inferred that in the volumes less than 250 mL no sensible changes on adsorption/recovery value occurred. Furthermore, increasing the volume above the 250 mL shows a clear decrease in extraction recovery. Thereupon, the sample volume of 250 mL was selected as optimized amount.

3-10. Analytical Figure of merit and analytical application-validation

The linear calibration range for the extraction of Pb(II) ions under optimized experimental conditions was gained between 10 to 400 μg L⁻¹ (R²=0.9981) for 250 mL of solution. The limit of detection (LOD) of the extraction procedure for subsequent lead analysis was determined as 2.3 μg L⁻¹ using LOD=3(σ) blank/m, where σ is the standard deviation of seven replicate measurements of blank solution and m is the slope of the calibration curve. The precision and repeatability of the proposed method was assigned via six adsorption/elution cycles within 250 mL sample solution containing 20 μg of Pb(II). The recovery percentage of lead as a function of sample volume was quantitative and calculated at >95%. A relative standard deviation (RSD) of 1.9% was achieved for a concentration of 20 μg L⁻¹. Further, an enrichment factor of 250 was attained using 250 mL sample volume and 1 mL eluent. The characteristics corresponding to the analytical results are summarized in Table 3.

The validity and applicability of the present proposed MSPE procedure were distinguished through real-world sample analysis. Table 4 represents the mean values (n=3) of founded amounts of Pb(II) ions and mean recoveries of certain values of spiked Pb (II) ions from various water samples previously adjusted pH and subjected to recommended optimizations with external calibration method. Eventually, the proposed method has been compared with the other similar methods applied for Pb (II) extraction and the results that are exhibited in Table 5 clarify the applicability of the present method for extraction of Pb (II) ions from different aqueous media.

Table 4. Data for the determination of Pb(II) ions in different water samples

Relative recovery (%)	Found ($\mu\text{g L}^{-1}$) ^a	Added ($\mu\text{g L}^{-1}$)	Sample
98.55	nd ^b	0.0	Drinking water ¹
	394.2±2.1	400	
95.07	nd	0.0	Drinking water ²
	380.3±2.0	400	
100.4	182±2.5	0.0	Waste water ³
	583.6±3.1	400	
96.8	64.6±2.0	0.0	River water ⁴
	451.8±2.8	400	
98.1	nd	0.0	Mineral water ⁵
	392.4±2.1	400	
102.2	nd	0.0	Sea water ⁶
	408.8 ± 2.9	400	
97.5	nd	0.0	Stream water ⁷
	390±2.3	400	
100.2	nd	0.0	Well water ⁸
	400.8±2.5	400	
99	nd	0.0	Spring water ⁹
	396±2.2	400	

^aRSD% of three replicate experiments (n=3), ^bNot detected, ¹Tehran city, ^{2,7,8,9}Andimeshk city, ^{3,4}Dezful city, ⁵kouhrang mineral water, ⁶Caspian sea

Table 5. Comparison of the proposed method with some methods reported in the literature for extraction and determination of Pb(II) ions

Adsorbent	Method	EF	LOD ($\mu\text{g L}^{-1}$)	RSD%	References
Teewn 80	FAAS	10	7.2	-	[49]
2-pyridyliminosalicylcellulose	FAAS	-	0.0038	2.52-3.50	[50]
Triketone/ethyle2-(4-methoxybenzoyl)-3-(4-methoxyphenyl)-3-oxo-propanoylcarbamate (EMPC)	FAAS	40	0.3-0.7	≤4	[51]
Nano polyacrylonitril modified ethylendiamins	FAAS	200	0.167	0.81	[52]
1-(2-pyridylazo)-2-naphthole	FAAS	50	1.3	5	[53]
Z-furan-2-carbaldehyde thiosemicarbazone/alumina	FAAS	100	0.0055	-	[54]
Cellulose nitrate	FAAS	60	0.02~7.8	<10	[55]
Solid sulfur	FAAS	250	3.2	5.1	[35]
Methylthiosalicylate-silica gel	ICP-AES	41.0	15.3	0.9	[56]
poly(aminophosphonic acid)	FAAS	14.0	6.3	2.1	[57]
Multiwall carbon nanotubes	FAAS	44.2	2.6	1.4	[3]
3-(trimethoxysilyl)-1-propanethiol-ethylene glycol bis-mercaptoacetate-Fe ₃ O ₄ NPs	ICP-OES	236	0.08	4.0	[58]
Fe ₃ O ₄ NPs-SDS-TTFA	FAAS	250	2.3	1.9	This work

Conclusions

MSPE method based on magnetite nanoparticles (Fe₃O₄ NPs) was successfully employed for sufficient and fast lead adsorption through complexation of Pb(II) ions by SDS-TTFA coating/modifying groups under pre-optimized conditions. Different techniques, including SEM-EDAX, XRD and VSM, were applied for the identification and characterization of synthesized nano adsorbent, and the extraction process followed by FAAS analysis. The high surface area of nanoparticles and rapid magnetic separation led to high extraction capacity and enrichment factor. The recoveries of Pb(II) ions were almost quantitative (>95%). Also, the represented method is simple and proposes for sensitivity and time saving adsorption for large volumes of sample solutions. The synthesized adsorbent was utilized for effective removal of Pb(II) ions from different natural and industrial water media. According to obtained results, Fe₃O₄ NPs-SDS-TTFA is suf-

ficiently suitable for extraction processes of Pb(II) ions from various aqueous media.

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