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Nano Magnetic Solid Phase Extraction for Preconcentration of Lead Ions in Environmental Samples by a Newly Synthesized Reagent

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Abstract

In this study, magnetite nanoparticles with particle size lower than 47 nm were synthesized and were applied for preconcentration of Pb^{2+} ions from aqueous solutions. To preconcentrate the Pb^{2+} ions, the surface of the synthesized nano particles was modified with sodium dodecyl sulfate (SDS) as an anionic surfactant. A new chelating agent (2-((E)-2-amino-4,5-dinitrophenylimino)methyl)phenol) was synthesized and used to form a very stable complex with Pb^{2+} ions. The lead ions formed complexes and were quantitatively extracted with SDS-coated magnetite nanoparticles. After magnetic separation of adsorbent, the adsorbent was eluted with 0.5% (v/v) HCl in dimethyl sulfoxide (DMSO) prior to analysis by flame atomic absorption spectrometry (FAAS). Orthogonal array design (OAD) was used to study and optimize the different experimental parameters. Under the optimum conditions, enhancement factor up to 63.5 was achieved for extraction from only 10 mL of sample solution and the relative standard deviation (RSD %) of the method was lower than 2.8%. The obtained calibration curve was linear in the range of 1–300 μg L^{-1} with reasonable linearity ($r^2 > 0.998$). The limit of detection (LOD) based on S/N = 3 was 0.04 μg L^{-1} for 10 mL sample volumes. Finally, applicability of the proposed method was successfully confirmed by preconcentration and determination of trace amounts of lead ions in environmental samples and satisfactory results were obtained.

Keywords: Magnetite nanoparticles, lead ions, aqueous samples, magnetic solid phase extraction.

1. Introduction

Water and wastewaters contamination by heavy metals is a serious problem that has an adverse impact on public health and economy. Exposure to heavy metals even at trace levels is believed to be a risk for humans.[1,2] Strict environmental regulations on the discharge of heavy metals and rising demands for clean water with extremely low levels of heavy metals make it very important to develop various efficient methods for determination of trace amounts of heavy metals in environmental water samples.[3]

Lead is recognized as a heavy metal poison that forms complexes with oxo-groups in enzymes and obstructs heme synthesis and porphyrin metabolism. It also inhibits acetylcholinesterase, acid phosphatase, ATPase and inhibits protein synthesis, probably by modifying t-RNA. Typically, symptoms of lead poisoning are headaches, convulsions, chronic nephritis, and central nervous system disorders.[4,5]

Magnetic separation has been applied recently in various fields such as analytical biochemistry,[6] medical science[7] and biotechnology.[8] From an environmental point of view, magnetic separation offers advantages due to the easy recovery of the adsorbent without filtration or centrifugation. Several studies have reported magnetic separation using modified magnetite (Fe_3O_4) as an environmentally friendly approach to remove heavy metal ions[9,10] and organic pollutants.[11,12]

The aim of the present study was to develop a magnetic solid phase extraction (MSPE) for the preconcentration and determination of trace amounts of lead ions. The proposed method is based on the complexation of lead ions with a new synthetic reagent, and further extraction

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of hydrophobic complex on SDS-coated Fe_3O_4 MNPs. After extraction, the amount of lead in the extracted phase was determined by FAAS. To the best of our knowledge, this new reagent has not been employed previously in the extraction and determination of trace amounts of lead from aqueous samples.

2. Experimental

2. 1. Reagents and Materials

Lead nitrate, ferric chloride ($FeCl_3.6H_2O$), ferrous chloride ($FeCl_2.4H_2O$), sodium hydroxide, sodium dodecyl sulfate (SDS), 4,5-dinitro-*o*-phenylenediamine, 2-hydroxybenzaldehyde and hydrochloric acid were purchased with high purity from Merck (Darmstadt, Germany). All solutions were prepared in doubly distilled water. A stock standard solution of lead ions at a concentration of 1000 mg L^{-1} was prepared by dissolving the pure $Pb(NO_3)_2$ in ultra pure water. This standard solution was diluted with distilled water to prepare stock solutions with the concentration of 5, 10 and 50 mg L^{-1} of lead ions. The chelating agent (2-((E-2-amino 4,5-dinitrophenylimino)methyl)phenol) was synthesized and its solution was prepared daily by dissolving appropriate amount of reagent in DMSO. Hydrochloric acid (1 mol L^{-1}) and ammonia (1 mol L^{-1}) were used to adjust the pH of solutions.

2. 2. Apparatus

Atomic absorption spectrophotometer from Shimadzu (Japan, model AA- 680) was used for determination of lead ions. Atomic absorption measurements were conducted in air/acetylene flame. Absorbance measurements were carried out at 217.0 nm using lead hollow cathode lamps operated at 4.0 mA with deuterium background correction, and at 10 mA, respectively. All measurements were based on peak height. A digital Jenway pH meter equipped with a combined glass-calomel electrode was used for the pH adjustments. SEM images were obtained with a XI-300 scanning electron microscope (Philips, Japan). For separation of magnetic solid phase from solution a Nd-Fe-B strong magnet (10 × 5 × 4 cm, 1.4 Tesla) was used and magnetic properties were analyzed using a vibrating sample magnetometer (VSM, LDJ 9600).

2. 3. Synthesis of Fe_3O_4 MNPs

Fe_3O_4 MNPs were chemically synthesized with a slight modification in the methodology already described in the literature.[13] In order to prepare the stock solution of ferrous and ferric chloride, 6.3 g $FeCl_3.6H_2O$, 4.0 g $FeCl_2.4H_2O$ and 1.7 mL HCl (12 mol L^{-1}) were dissolved in 50 mL of deionized water. After that, the solution was de-

gassed with argon gas and heated to 80 °C in a reactor. Simultaneously, 250 mL of a 1.5 mol L^{-1} ammonia solution was slowly added to the solution under argon gas protection and vigorous stirring (1000 rpm). During the whole process, the solution temperature was maintained at 80 °C and argon gas was purged to prevent the access of oxygen. After completion of the reaction, the obtained precipitate of Fe_3O_4 MNPs was separated from the reaction medium by the magnetic field, and then washed four times with 500 mL doubly distilled water. Finally, the obtained Fe_3O_4 MNPs were resuspended in 500 mL of degassed deionized water. The obtained concentration of Fe_3O_4 MNPs was 6.2 mg mL^{-1} and the MNPs were stable in this condition up to one month.

2. 4. Synthesis of 2-((E-2-amino-4,5-dinitrophenylimino)methyl)phenol

The chelating agent was synthesized according to the methodology already described in the literature.[14] Briefly, 0.4 g of 4,5-dinitro-*o*-phenylenediamine (2 mmol) was dissolved in 40 mL of absolute ethanol and was added into a round- bottom two necked flask that was connected to a reflux condenser. After 10 min, 20 mL ethanolic solution of 2-hydroxybenzaldehyde (2 mmol) was drop-wise added to the solution via the dropping funnel during approximately 20 min. The resulting yellow solution was stirred and refluxed for a further 60 min. The product as a dark orange solid was filtered and recrystallized with ethanol. The crystalline target material was collected by suction filtration, washed successively with cold ethanol and diethyl ether and then air dried. The melting point of product was determined as 222 °C and the yield of reaction was 71 %. Fig. 1 shows the structure of synthesized chelating agent. The FT-IR and ^{1}H-NMR spectra of the synthesized compound confirm the structure of chelating agent. Selected FT-IR data (v/cm^{-1} KBr) were obtained as: 3392, 3500 (mN–H); 1629 (m C–N). ^{1}H NMR (500 MHz, DMSO) data were as: 11.40 (1H, OH); 8.97 (1H, s, CHN); 7.94 (1H, s, HAr); 7.87 (1H, d, HAr), 7.44 (1H, m, HAr); 7.13 (3H, HAr and NH_2); 6.99 (2H, m, HAr).
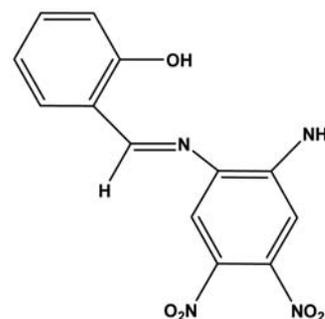

Figure 1. Structure of 2-((E-2-amino-4,5-dinitrophenylimino)methyl) phenol

2. 5. Extraction Procedure

For the preconcentration of Pb^{2+}, aliquots of the solution containing lead ions (10 mL with 100 μg L^{-1} concentration) were adjusted to the appropriate pH (pH 5.0) to form a very stable complex with 2-((E-2-amino-4,5-dinitrophenylimino)methyl) phenol. For preconcentration of complex, 0.2 mL of the suspension of Fe_3O_4 MNPs (6.2 mg mL^{-1}) and 0.5 mL of the SDS solution (1 mg mL^{-1}) were sequentially added to the sample solution and then mixed at room temperature for 2 min. Subsequently, using a Nd-Fe-B strong magnet, the SDS-coated Fe_3O_4 MNPs were isolated from the solution. After 1 min, the solution became clear and supernatant solutions were decanted. Finally, the preconcentrated complex was eluted from the MNPs with 1.0 mL of 0.5 % HCl in DMSO and this solution was introduced into FAAS for determination of lead concentration.

The synthesis procedure of SDS-coated MNPs and application of it as a magnetic solid phase for preconcentration of lead ions is shown brifely in Fig. 2.
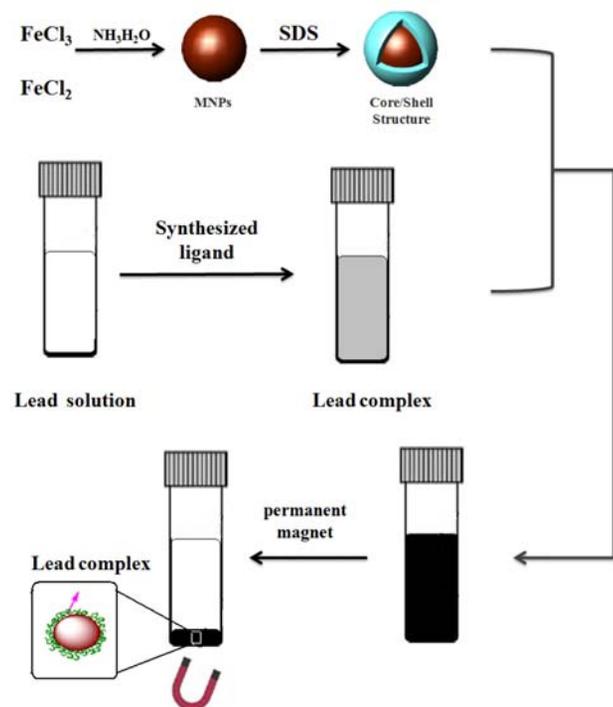
Figure 2. Synthesis procedure of SDS-coated MNPs for extraction process.

3. Results and Discussion

3. 1. Method Development

In the proposed procedure, to achieve maximum extraction efficiency, various parameters affecting the extraction of lead ions were studied using the Taguchi orthogonal array design (OAD). Taguchi method is a type of fractional factorial design in which orthogonal array is used to assign the selected factors to a serial of experimental combinations.[15] The results of the OAD experiments can be treated by the analysis of variance (ANOVA). In ANOVA, the effects of different factors on the response function can be evaluated by computing F-ratio (variances ratio) and percent contribution (PC) values for each factor.[16,17] All optimizing experiments were done at 100 μg L^{-1} of lead ions and glass Falcon tubes with 15 mL volumes were used for optimization.

3. 2. Experimental Design and Data Analysis

The effect of five experimental parameters including pH, ligand to metal (L/M) molar ratio, amount of MNPs, surfactant concentration and contact time on the extraction of Pb^{2+} ions was studied at four levels using Taguchi OA_{16} design.

The used levels and the OA_{16} (4^5) matrix employed to assign the considered factors are shown in Tables 1 and 2, respectively.

The designing of table was done via experimental design 7.0 software. To increase the precision of the optimization process, each trial was repeated twice ($n = 32$). The sequence, in which the experiments were carried out, was randomized to avoid any personal or subjective bias. Analysis of variance was used to assess the OA design results. For ANOVA calculations, absorbance of lead in the AAS peak was used and the results of the sum of squares (SS) for different variables were calculated.

The mean values of the four levels of each parameter revealed how the extraction efficiency changes with variation of the level of each factor. Fig. 3 shows the mean extraction efficiency as a function of the studied levels of each parameter.
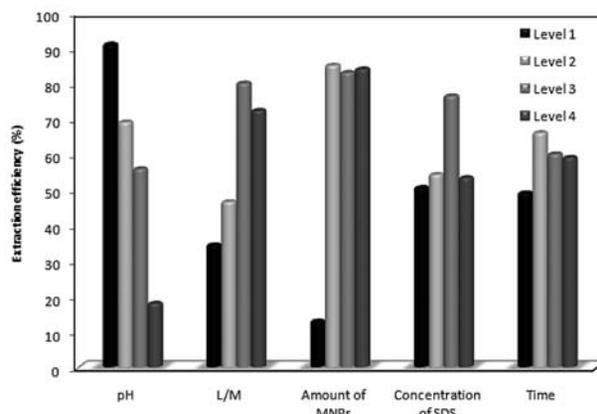
Figure 3. The response graph illustrating the variation of the mean absorbance values plotted against various extraction parameters.

The ANOVA results (Table 3) showed that the amount of MNPs (62.56 %) was the most important parameter, contributing to the extraction efficiency. The results also showed that contact time does not have any significant effect on the extraction efficiency.

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Table 1. Factors and parameters for Taguchi orthogonal array design (A-E are the respective codes for each parameter).

Levels	Factors				
	A	**B**	**C**	**D**	**E**
	pH	**L/M**	**Amount of MNPs (mg mL^{-1})**	**SDS (mg mL^{-1})**	**Contact time (min)**
1	5	0.1	0.01	0.0	0.5
2	6	1.0	0.2	0.02	1
3	7	10	0.5	0.05	2
4	8	30	1.0	0.1	5

Table 2. OA$_{16}$ (4^5) experimental design for the extraction of lead.

Trial no.	pH	L/M	Amount of MNPs (mg mL^{-1})	SDS (mg mL^{-1})	Contact time (min)
1	8.0	10	0.5	0.0	1
2	7.0	10	0.2	0.1	0.5
3	6.0	10	0.01	0.02	5
4	8.0	30	0.5	0.1	5
5	8.0	1.0	0.2	0.02	1
6	7.0	0.1	0.5	0.02	2
7	8.0	10	1.0	0.05	2
8	7.0	30	0.01	0.05	1
9	6.0	0.1	1.0	0.1	1
10	7.0	1.0	1.0	0.0	5
11	5.0	0.1	0.2	0.05	5
12	5.0	0.1	0.01	0.0	0.5
13	6.0	1.0	0.5	0.05	0.5
14	5.0	1.0	0.01	0.1	2
15	5.0	30	1.0	0.02	0.5
16	6.0	30	0.2	0.0	2

Table 3. ANOVA results for experimental responses in the OA$_{16}$ (4^5) matrix.

Factor	DOF[a]	Sum of squares	Variance	F-ratio[b]	Pure sum of squares	PC[c] (%)
pH(A)	3	0.335	0.115	5.52	0.332	13.1
L/M(B)	3	0.330	0.108	5.19	0.326	12.2
Amount of MNPs (C)	3	1.835	0.611	29.3	1.812	62.56
Concentration of SDS (D)	3	0.109	0.033	0.64	0.105	8.57
Time (E)	3	0.044	0.012	0.16	0.08	2.42
Error	32	0.032	0.002			1.15
Total	31	2.68				100.00

[a] Degrees of freedom [b] F, critical value is 3.24 (p < 0.05) [c] Percent of contribution

3. 3. Characterization of the MNPs

Magnetite nanoparticles (Fe$_3$O$_4$) of 47 nm average diameter were prepared by the chemical coprecipitation technique. The SDS-coated MNPs were synthesized via two different chemical precipitation methods: (i) preparation of colloidal iron oxide magnetic nanoparticles and (ii) development of a SDS layer within the MNPs surface. The synthesized nanoparticles were characterized via FT-IR, XRD, DRS and SEM techniques.

Fig. 4 shows the FT-IR spectra of the synthesized MNPs and SDS-coated MNPs respectively. For the bare MNPs (Fig. 4a), the peak at ~ 575 cm^{-1} is attributed to the Fe ¦ O band vibration of Fe$_3$O$_4$. In the case of SDS-coated MNPs (Fig. 4b), the FT-IR spectra showed high intensity peaks for the CH$_2$ stretching modes located at ~ 2850 cm^{-1} and 2920 cm^{-1} (symmetric and asymmetric), as well as for the CH$_2$ bending mode at ~ 1370 cm^{-1}.

X-ray diffraction (XRD) pattern of Fe$_3$O$_4$ is shown in Fig. 5 for the bare MNPs. The MNPs showed peaks with 2θ at 29.72, 35.57, 43.17, 57.15 and 62.77 which are quite identical to pure magnetite and matched well with the XRD pattern of the standard Fe$_3$O$_4$ from Joint Committee on Powder Diffraction Standards (JCPDS No. 19–692).[18] The iron oxide nanoparticle diameter was 47.3 nm as obtained by an integral breadth analysis of the XRD peaks.
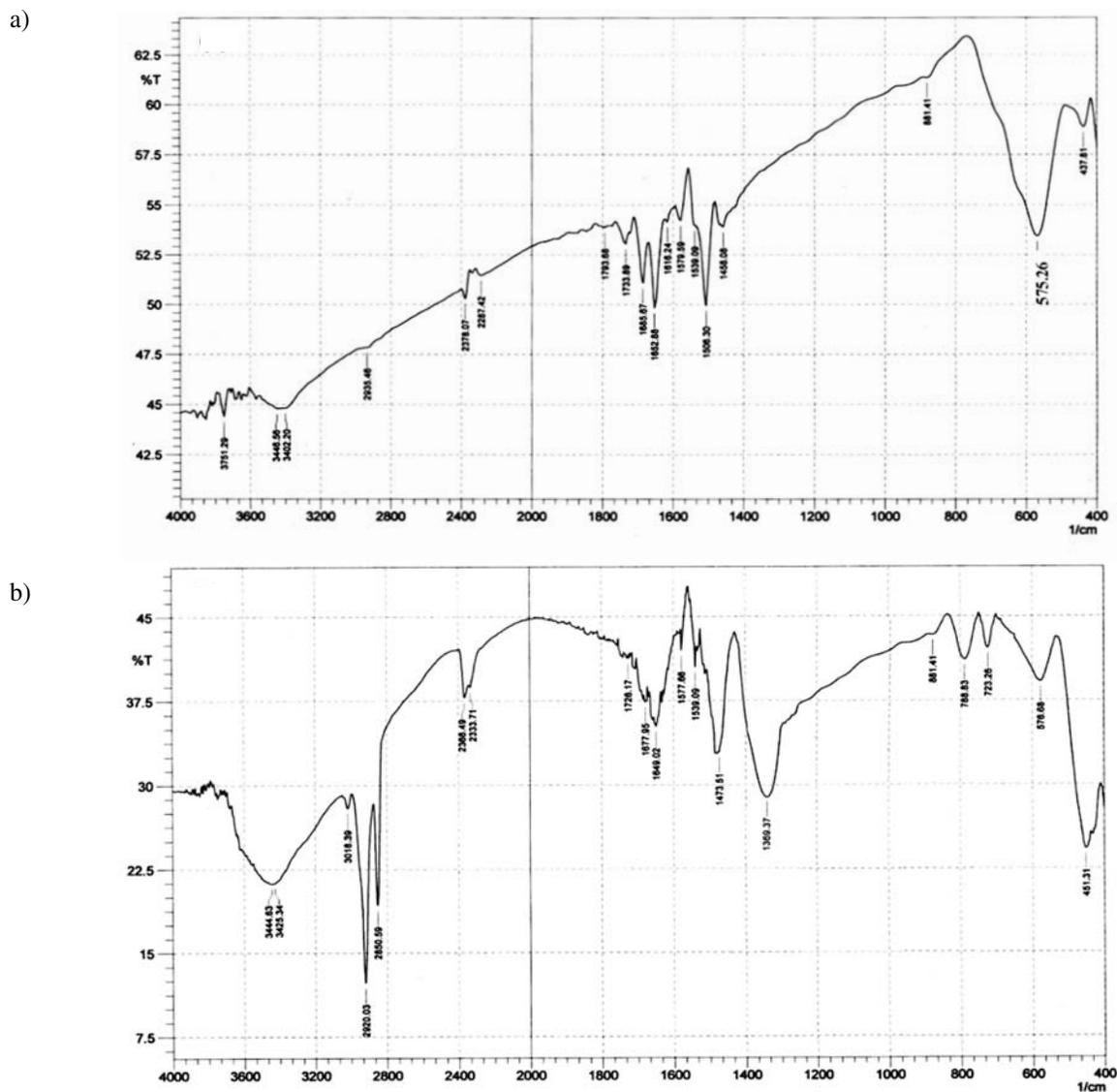
a)

b)

Figure 4. FT-IR spectra of Fe_3O_4 (a) and SDS-coated MNPs (b)

The SEM images of the prepared MNPs are shown in Fig. 6. Based on the SEM images, analysis of Fe_3O_4 and SDS-coated MNPs surface morphology demonstrated the agglomeration of many ultrafine particles with a diameter of about 47 nm.

Fig. 7 shows the diffuse reflectance spectroscopy (UV-DRS) of the synthesized bare MNPs and SDS-coated MNPs, respectively. The MNPs indicated peaks at 220 nm, which indicating the purity of the synthesized Fe_3O_4. The same peaks were observed in SDS-coated nano particles. The UV-DRS patterns indicate existence of the magnetic core during the both synthesized MNPs.

3. 4. Effect of pH

The charge density of mineral oxide surface is a main factor affecting the adsorption of analytes. Thus, pH is a very important parameter for the adsorption of target compounds. On the other hand, pH plays an important role in the complexation of lead with chelating agent. To examine the effect of pH on extraction efficiency of lead ions, pH of the samples was adjusted in the range of 5.0–8.0 using ammonia (1.0 M) or HCl (1.0 M) solutions, according to the experimental design (Table 2). As can be seen from Fig. 3, there is no obvious adsorption of lead complex to Fe_3O_4 MNPs at pH values lower than 5.0. When pH value was around its isoelectric point (about 7.0), the charge density of Fe_3O_4 MNPs surface was very low. At pHs lower than isoelectric point, the surface of particles became positively charged which gave rise to the strong electrostatic attraction between the anionic surfactant molecules (such as SDS) and the surface of charged Fe_3O_4 MNPs. Under this circumstances, hydrophobic complexes of lead can interact with SDS-coated Fe_3O_4
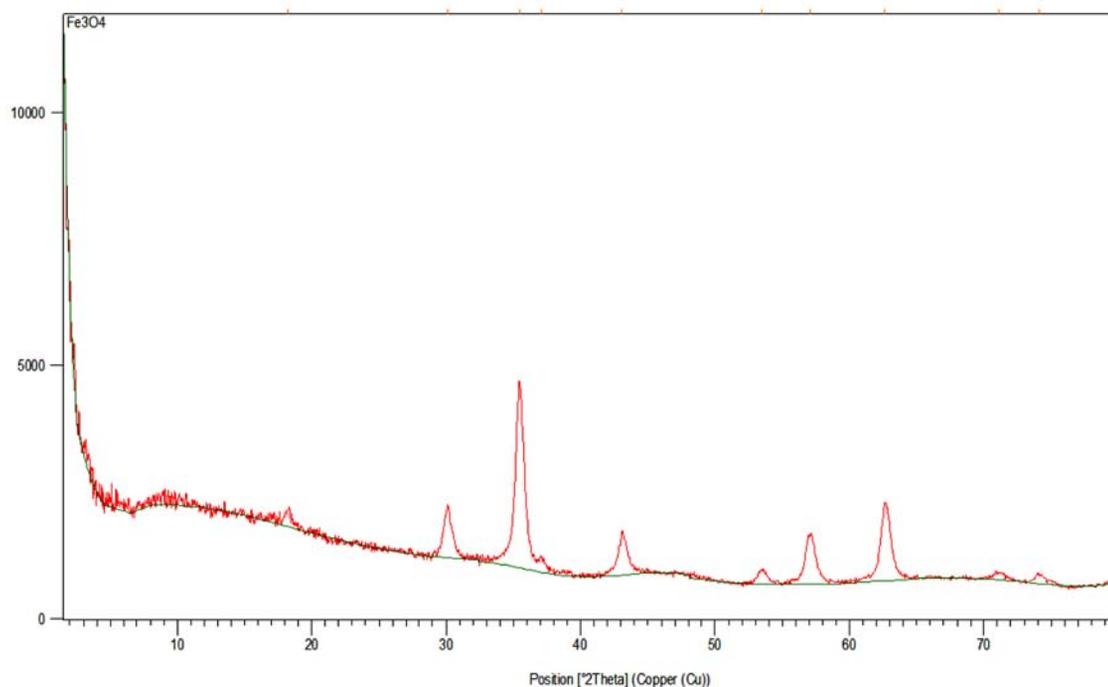
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Figure 5. XRD pattern of Fe_3O_4

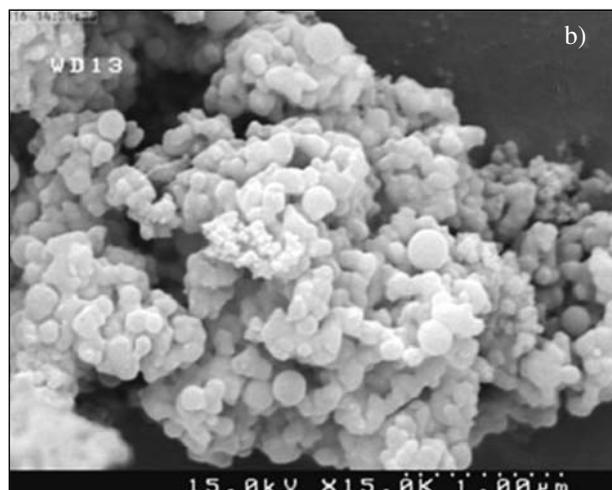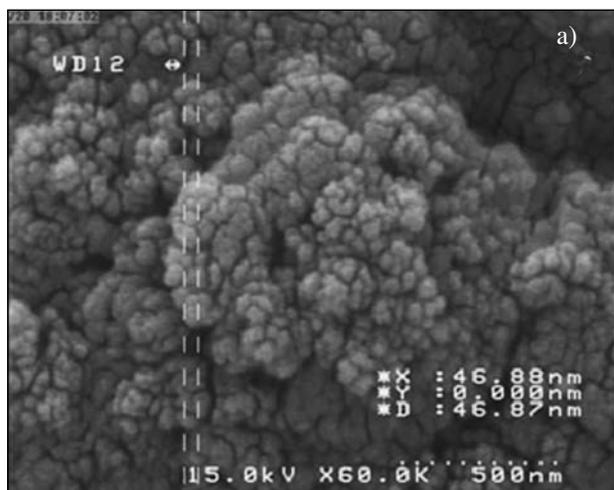**Figure 6.** SEM images of Fe_3O_4 (a) and SDS-coated MNPs (b)

MNPs surface. According to the obtained results, pH 5.0 was chosen as an optimum pH.

3. 5. Influence of Chelating Agent Concentration

The reagent 2-((E-2-amino-4,5-dinitrophenylimi-no)methyl) phenol acts as a tridentate ligand and can form very stable complexes with lead ions through oxygen and nitrogen atoms of hydroxyl and amine groups. The complex of lead can be easily interacted with SDS-coated Fe_3O_4 MNPs. At 10 mg L^{-1} of lead, the effect of chelating agent concentration on the extraction efficiency was studied by changing the molar ratio of ligand to lead in the range of 0.1–30 (Fig. 3). According to the results, increasing the ligand to lead molar ratio up to 10, resulted an increase in the extraction recovery; after that, it remained constant. Therefore, ligand to lead molar ratio of 10 was used for the subsequent studies.

3. 6. Effect of Magnetic Nanoparticles Amount

The effect of the MNPs amount on the extraction efficiency was studied in the range of 0.01–1.0 mg mL^{-1}. According to the Fig 3, the extraction efficiency was increased slowly due to the increase in the accessible sites, and then remained constant. So, 0.2 mg mL^{-1} of the

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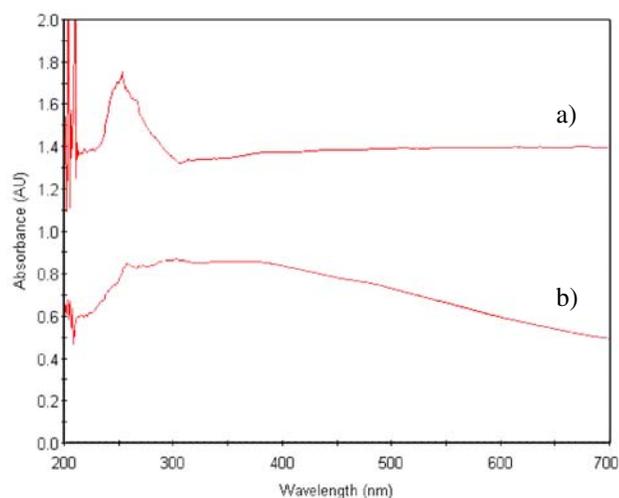
Figure 7. UV-DRS spectra of Fe_3O_4. The synthesized bare MNPs (a) and SDS-coated MNPs (b)

Fe_3O_4 MNPs was selected for all subsequent experiments.

3. 7. Effect of The Amount of Surfactant

In the present work, for modifying the surface of Fe_3O_4 MNPs, the SDS surfactant was added to the solution. The hemimicelles, mixed hemimicelles and admicelles are three forms for adsorption of surfactant on the surface of mineral oxides. In the first part, the zeta potential of mineral oxides changed from negative to zero due to the fact that hemimicelles were gradually formed on the mineral oxide surfaces. Upon increasing the anionic surfactant concentration, admicelles were formed predominantly on the surface [11]. Therefore, the outer surface of hemimicelles is hydrophobic, whereas that of admicelles is

ionic, which provides different mechanisms for retention of compounds and are both suitable for the MSPE method. In mixed hemimicelles phase, both hemimicelles and admicelles are formed on the surface of mineral oxides and the adsorption is driven by both hydrophobic interactions and electrostatic attraction. The effect of the surfactant concentration on the extraction efficiency was examined ranging from 0.0 to 0.1 mg mL^{-1} and the results are shown in Fig. 3. At 0.05 mg mL^{-1} of SDS, nearly a complete extraction of the analyte occurred.

3. 8. Effects of Ccontact Time

The study of adsorption capacity of the lead complex by the SDS coated Fe_3O_4 showed that the adsorption capacity of the lead complex increased with contact time up to 1.0 min and after that a maximum removal is attained. For this reason, the optimum contact time was selected as 1.0 min.

3. 9. Desorption Conditions

For separation of lead complex from the nanoparticles after preconcentration process, organic solvents were used in order to disrupt surfactant aggregates. So, acetonitrile, DMSO, methanol and acetone were selected as eluents. Among these eluents, DMSO showed better desorption ability. Subsequently, effect of DMSO pH on desorption efficiency was considered. According to the experimental results, desorption improved using 0.5 % (v/v) HCl in DMSO.

3. 10. Interferences

The effects of potential interfering species on complexation and extraction of lead ions (100 μg L^{-1}) were

Table 4. Effect of interferences on preconcentration and determination of lead ions (100 μg L^{-1}).

Interference	Added as	Interference to metal ion ratio(W/W)	Recovery (%)
Na^+	$NaNO_3$	10000	103
Li^+	$LiNO_3$	10000	102
K^+	KNO_3	10000	99
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	100	96
Mg^{2+}	$Mg NO_3 4H_2O$	7500	101
Ca^{2+}	$Ca(NO_3)_2.4H_2O$	7500	104
Co^{2+}	$Co(NO_3)_2.6H_2O$	100	97
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	7500	102
Pb^{2+}	$Pb(NO_3)_2$	7500	99
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	1000	101
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	5000	102
As^{3+}	$As(NO_3)_3.6H_2O$	1000	98
Cu^{2+}	$Cu(NO_3)_2.6H_2O$	5000	100
Ba^{2+}	$Ba(NO_3)_2.6H_2O$	5000	98

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studied by addition of higher amounts of foreign ions to the aqueous phase (Table 4). The results showed that Na^+, Li^+ and K^+ (up to the concentration level of 1000 mg L^{-1}), Zn^{2+}, Mg^{2+} and Ca^{2+} (up to 750 mg L^{-1}), Cu^{2+}, Fe^{3+}, Ba^{2+} (up to 500 mg L^{-1}), As^{3+} and Cd^{2+} (up to 100 mg L^{-1}), Co^{2+} and Ni^{2+} (up to 10 mg L^{-1}) did not cause any significant interference on the preconcentration of lead ions. These concentrations are higher than actual concentration of these ions in the environment. It can be seen that a very good selectivity was achieved.

3. 11. Figures of Merit of the Proposed Method

The analytical features of the proposed method such as precision, linear range of calibration curve and limit of detection were also examined. The calibration curve was obtained under the optimized conditions with linear dynamic range of 1.0–300 μg L^{-1} and correlation coefficient (r^2) of 0.998. The limit of detection (LOD) of the proposed method was calculated from $C_{LOD} = 3S_b/m$,

where m is the slope of the calibration curve and S_b is the standard deviation of ten extractions of the blank measurement. The calculated LOD was 0.04 μg L^{-1}. Enhancement factor of proposed method was calculated as the ratio of calibration curve after magnetic solid phase preconcentration to that obtained without preconcentration. An enhancement factor of 63.5 was obtained for only 10 mL sample that can be improved using higher volumes of samples. The relative standard deviations (RSDs) resulted from four replicate extractions of solutions containing 10 μg L^{-1} and 100 μg L^{-1} of lead ions were 3.6 % and 2.8 %, respectively.

A comparison between the figures of merit of the proposed method and some of the recently published methods for extraction and determination of Pb^{2+} ions is summarized in Table 5. Table shows that the enhancement factor and detection limit obtained in the proposed method were better in comparison with other mentioned methods. The proposed method, applied in the present work, has some advantages in comparison with the other extraction methods including low consumption of organic solvents

Table 5. Comparison of the characteristic data between recently published extraction methods and the developed method.

Method	SV (mL)[d]	LOD (μg L^{-1})	R.S.D %	EF	Detection	Ref.
CPE[a]	5	7.2	4.0	–	FAAS[e]	[19]
CPE	20	1.1	4.31	55.6	FAAS	[20]
CPE	100	2.86	6.8	43	FAAS	[21]
On-line SPE[b]	–	0.3	1.5	20	ICP-OES	[22]
Copercipition	10	0.3	–	50	FAAS	[23]
Batch MSPE[c]	10	0.04	2.8	63.5	FAAS	Proposed method

[a] Cloud point extraction   [b] Solid phase extraction   [c] Magnetic solid phase extraction   [d] Sample volume   [e] Flame atomic absorption spectrometry

Table 6. Analytical results for determination of Pb in real water samples.

Sample	Pb added (μg L^{-1})	Concentration (mean, *n* = 3) Pb found (μg L^{-1} ±RSD)	Recovery (%)
Tap water [a]	0.0	–	98
	10.0	9.8 ± 0.2	
Well water [a]	0.0	–	102
	10.0	10.2 ± 2.1	
River water [b]	0.0	1.4 ± 0.3	98
	10.0	11.6 ± 1.2	
Mineral water [c]	0.0	–	99
	10.0	9.9 ± 1.2	
Mineral water [d]	0.0	–	96
	10.0	9.6 ± 1.8	
Mineral water [e]	0.0	–	109
	10.0	10.9 ± 1.9	
Bojagh lagoon water [f]	0.0	1.8 ± 0.1	98
	10.0	11.6 ± 2.4	
Anzaly lagoon water [g]	0.0	2.3 ± 0.9	96
	10.0	12.8 ± 2.1	

[a] Collected from the Semnan city in Iran   [b] River water sample collected from Sefid Rood (Guilan-Iran)   [c] Bottled mineral water was obtained from Damash company   [d] Bottled mineral water was obtained from Kohrang company   [e] Bottled mineral water was obtained from Damavand company   [f] Bojagh lagoon water collected from Kiashahr, Guilan, Iran   [g] Anzali lagoon water collected from Bandare Anzaly, Guilan, Iran

and reagents, easy access, simplicity and low cost of the extraction device, minimum carry over and cross-contamination as well as producing a clean extraction phase for the analysis. Also, the extractant can be easily synthesized in the lab and can be reused for several times.

3. 12. Determination of Lead in Real Samples

The accuracy of the proposed method was studied by analyzing the various environmental water samples including well, tap, mineral, river and lagoon waters. For sampling, the water samples were collected in cleaned polyethylene bottles and pH of samples was adjusted to p-Hs lower than 2 with addition of nitric acid. All of samples were kept at 4 °C before extraction. The lead content of each sample was determined with the optimized proposed method. In order to validate the performance of the proposed method, recovery values were obtained by spiking the samples with lead ions at 10 µg L^{-1} concentration level. After that, the samples were analyzed using the proposed method and the relative recovery percents based on the difference of lead in spiked and initial samples were calculated (Table 6). As could be seen, the recoveries for the spiked samples are in acceptable range (90–110 %). The good agreement between the spiked and found values indicates the successful applicability of the present method for determination of lead in real samples.

4. Conclusion

The use of SDS-coated MNPs system as an alternative to other methods of separation and preconcentration of lead in environmental samples offers several advantages including experimental convenience, safety and being an inexpensive method. The use of MNPs endued the MSPE method with high extraction capacity and enhancement factors. The magnetic separation greatly improved the separation rate while avoiding the time-consuming column passing or filtration. The proposed method gives low limit of detection as well as good RSD and linearity. It is possible to obtain a better preconcentration factor by larger volumes of samples.

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Povzetek

V predstavljeni raziskavi smo sintetizirali nanodelce magnetita z velikostjo pod 47 nm in jih uporabili za predkoncentracijo Pb^{2+} ionov iz vodnih raztopin. Za predkoncentracijo Pb^{2+} ionov smo površino sintetiziranih nanodelcev modificirali z natrijevim dodecilsulfatom (SDS) kot anionskim surfaktantom. Sintetizirali smo nov kompleksant (2-((E)-2-amino-4,5-dinitrofenilimino)-metil)-fenol in ga uporabili za tvorbo zelo stabilnega kompleksa s Pb^{2+} ioni. Svinčevi ioni so tvorili komplekse, ki smo jih kvantitativno ekstrahirali z SDS-magnetitnimi nanodelci. Po separaciji adsorbenta z magnetom smo adsorbent spirali z 0,5 % (v/v) HCl v dimetilsulfoksidu (DMSO) pred analizo s plamensko atomsko absorpcijsko spektrometrijo (FAAS). Za študij in optimizacijo različnih eksperimentalnih parametrov smo uporabili ortogonalni eksperimentalni načrt (OAD). Pri optimalnih pogojih smo dosegli obogatitveni faktor do 63,5 za ekstrakcijo iz le 10 mL vzorčne raztopine, relativni standardni odklon (RSD %) metode pa je bil pod 2,8 %. Umeritvena premica je bila linearna v območju 1–300 μg L^{-1} s primerno linearnostjo ($r^2 > 0.998$). Meja zaznave (LOD), določena kot S/N = 3, je bila za 10 mL vzorca 0,04 μg L^{-1}. Na koncu smo uporabnost predlagane metode uspešno potrdili s predkoncentracijo in določitvijo sledov svinčevih ionov v okoljskih vzorcih, pri čemer smo dobili zadovoljive rezultate.