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ORIGINAL PAPER

Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] Magnetic Mesoporous Nanocomposite: Dispersive Solid-Liquid Micro Extraction of Pb^{2+} Ions

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Abstract

In the present study, Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] magnetic nano-particles (MNPs) as a new, effective and selective solid phase is reported for the preconcentration of lead ions by using of dispersive solid-liquid micro extraction (DSLME) as a rapid method. The Fe_3O_4@MCM-41 nanocomposite with charged sulfonate groups can be synthesized by the formation of sulfonic functionalized organic-inorganic MCM-41 mesoporous structure on the surface of magnetite nanoparticles. The encapsulated ZrO_2 nanoparticles into network of Fe_3O_4@MCM-41─SO_3H MNPs fabricated by covalently bound with implanted of charged sulfonate groups (-SO_3^-). The structure and morphology of the prepared sorbent were characterized by FT-IR, XRD, VSM, BET and TEM techniques in order to show that they comprised of both magnetite silica mesoporous structures with incorporated sulfonate groups and encapsulated ZrO_2 nanoparticles. The synthesized solid phase was utilized for the preconcentration of lead ions prior to determination by atomic absorption spectrophotometry. The calibration graph 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 detection limits of this method was 0.03 ng mL^{-1}. The obtained results showed that, the method can be successfully applied to the selective extraction and determination of the lead ionsin different samples of water.

Keywords Organic/inorganic mesoporous nanocomposite · ZrO_2 nanoparticles · Solid phase extraction · Lead ions

1 Introduction

The presence of heavy metals in environmental has a serious problem that has an adverse impact on public health and economy even at low concentrations. The metallurgy, electrolysis, electroplating, mining, and surface finishing industries are the most important reason of discharge of heavy metals in environmental [1]. Strict environmental regulations on the discharge of heavy metals and rising demands for clean water with extremely low levels of heavy metals make it greatly important to develop various efficient methods for determination of trace amounts of heavy metals in environmental water samples [2, 3] Lead is recognized as a heavy metal poison and among the list of priority heavy-metal pollutants by most national Environmental Protection Agencies, Pb is a notorious one of the high toxicity and carcinogenicity [4]. Up to now, several conventional technologies such as chemical precipitation (such as liquid-liquid micro-extraction (LLME)), adsorption (such as solid phase extraction (SPE)), membrane filtration and biological treatments have been applied for sequestration of lead ions from water [1]. Adsorption has proven to be one of the most attractive options and development of a specific sorbent has been regarded as the crucial factor in adsorption process. Hence, in the past decades, inorganic metallic nano-particles especially magnetic nano-particles including iron oxides [5–7], manganese oxide [8], cerium hydroxide [9] and activated alumina [10] have been proven to be efficient adsorbents for lead [11–13].

The miniaturization of iron oxide from the bulk (macroscale) to nanoscale effects unique physical properties. Recently, magnetic nanoparticles (MNPs) offer innovative prospects in current nanotechnology. In view of many

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applications, including magnetic fluids [14], catalysis [15, 16], biotechnology/biomedicine [17], magnetic resonance imaging [18, 19], data storage [20] and environmental remediation [21, 22]. Many efforts have been made to disperse the magnetic NPs in a matrix. Matrix-dispersed MNPs can be created in different states and relatively easy ways, e.g. dispersed and embedded into an amorphous or ordered guest matrix, grafted on larger particles and etc. to produce various magnetic nanocomposites. Nanocomposite materials not only render the material with an improved stability of the nanostructure building blocks, but may additionally introduce new physical and biological properties and multifunctional behavior.

Since the discovery of ordered mesoporous silicas (OMS) in 1992 [23], a variety of inorganic−organic hybrid mesoporous materials with high specific surface area have been widely used as adsorbents, catalysts, and supports in chemical, biochemical, and petrochemical applications [24]. These materials with distinct order of the channels ranging from 2 to 50 nm, uniform pore structure, and synergistic effect between the immobilized entities and the physicochemical nature of silica framework make them have gradually become a promising platform for designing new sophisticated matrixes. In other words, the grafting of target molecules onto the pore walls of mesoporous silica has provided numerous opportunities in a broad range of applications [25]. The above mentioned synergistic effect in nanocomposites consisting of hybrid organic–inorganic mesoporous materials creates features that are uncommon in most conventional matrixes.

The development of magnetic mesoporous particles, with large specific surface areas and good textural property is currently an area of extensive research that allows their use as adsorbents [26]. Application of mesoporous materials and magnetic nanocomposites as sorbent is an interest research area. Hence, various types of methods are performed using sorbent organic or inorganic sites grafted on magnetic nanoparticles (MNPs).

In the present study, wish to introduce an efficient method by using Fe_3O_4@MCM-41-SO_3^-[ZrO_2] MNPs as a new method with application of a new organic/inorganic magnetic nano-composite for the extraction of lead ions from aqueous solution by dispersive solid-liquid micro extraction (DSLME) method. For this propose, we fabricated an efficient hybrid nanomaterial by encapsulating ZrO_2 nanoparticles within magnetic mesoporous material beads covalently bound with negatively charged sulfonate groups. Moreover, we think that the negatively charged sulfonate groups immobilized onto the MCM-41 matrix would favor enhancement of the diffusion of positively charged lead ions inside the adsorbent through electrostatic attraction and the ZrO_2 nanoparticles due to their specific sorption affinity toward lead ions.

2 Experimental

2.1 Materials and Apparatus

All the chemicals including tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, 3-mercaptopropyl trimethoxy silane (MPTMS), NaOH $ZrOCl_2$ and NaF, are of analytic grade. Stock solution of lead ions was prepared by dissolving $Pb(NO_3)_2$ into doubly distilled water.

For the characterization of the synthesized nano-composite various instrumentation methods such as X-ray Diffractometry (XRD), Transmission Electron Microscopy (TEM), Fourier Transform Infrared (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET) and Vibrating Sample Magnetometery (VSM) were used. The crystal phases and crystallinity of the synthesized MNPs were analyzed by X-PERTPRO X-ray diffraction (PANalitical) and measured with Cu–Ka radiations in the 2θ range of 1.5–70. The quality and functional groups of the synthesized nanoparticles were characterized by a Shimadzu Fourier transform infrared (FT-IR) spectrometer (Japan, 470) in the range of 400–4000 cm^{-1}. The size and morphology of the synthesized nanoparticles were studied by a PHILIPS transmission electron microscope (TEM, CM10 HT 100KV). The BET surface areas and pore diameters were determined by recording nitrogen adsorption/desorption isotherms at 77 K using a static volumetric technique (Quantachrome Autosorb) and the degas temperature for the sample was 250 °C. For determination of lead ions an atomic absorption spectrophotometer (Shimadzu, model AA-680) was used.

2.2 Preparation of Organic/Inorganic Fe_3O_4@MCM-41—SO_3H Magnetite Nanocomposite

According to our previous works [27–30], the synthesis of Fe_3O_4@MCM-41─SO_3H magnetic nano-composite mainly includes three steps. *(i) Synthesis of* Fe_3O_4 *MNPs:* Fe_3O_4 MNPs were chemically synthesized with a precipitated method. *(ii) Synthesis of* Fe_3O_4*@MCM-41─SH nano composite:* For this purposed, TEOS (7.0 mL) and 3-mercapto propyl trimethoxy silane (5.0 mL) mixed with 50 mL distillated water and stirred for 60 min at 40 °C, then a mixture of the synthesized Fe_3O_4 MNPs, NaOH and NaF were added to the solution mixture and stirred at 40 °C for 1 h. Finally, cetyltrimethylammonium bromide (CTAB) was added to the mixture and stirred at 40 °C for 2 h again. After 2 h, the magnetic composite was hydrothermally treated at 120 °C in an autoclave. At the end of this process, the resultant solid was filtered, washed with distilled water and dried. The template was removed by solvent extraction. *(iii) Synthesis of* Fe_3O_4*@MCM-41─(*SO_3*H) nano composite:*For this purpose, the thiol groups of Fe_3O_4@MCM-41—SH magnetic nanocomposites were oxidized by a mixture of ethanol / *n*-hexane at a 1:1 ratio and 10 mL of 30% hydrogen peroxide. This procedure was repeated twice.

For the synthesis of Fe_3O_4@MCM-41—(SO_3^-) nano composite the Fe_3O_4@MCM-41—SO_3H nano-composite immersed into 1000 mL of binary NaOH−NaCl solution at 25 °C for 3 h.

2.3 Preparation of Fe_3O_4@MCM-41—(SO_3^-)[ZrO_2] Hybrid Nanocomposite

For encapsulation of ZrO_2 nanoparticles within the magnetic mesoporous network (Fig. 1), 1.0 g of the synthesized Fe_3O_4@MCM-41—(SO_3H) MNPs was slowly added into 50 mL of $ZrOCl_2$ and HCl mixture [1]. The mixture was sonicated at 70 °C for 4 h. Next, the resulting solid was separated and sonicated into 500 mL of binary NaOH−NaCl (0.1 mol L^{-1}) solution at 25 °C for 5 h, then $Zr(OH)_4$ was precipitated onto the network of sulfonated magnetic mesoporous nanocomposite. Finally, the resulting material was subjected to washing with ultrapure water till pH reached 5–6 and heated at 80 °C for 6 h to obtain the hybrid nanocomposite (Fe_3O_4@MCM-41—(SO_3^-)[ZrO_2]).

2.4 Extraction Procedure

As it is mentioned previously the focus of this study is on the extraction of lead ions via a dispersive solid-liquid micro extraction (DSLME) method by using Fe_3O_4@MCM-41—(SO_3^-)[ZrO_2] magnetic nano-composite as an effective and selective sorbent. All nano composites used in the extraction process has been the magnetic core. To ensure that this happens after the completion of the synthesis process the nano-particles with magnetic property were separated by a strong super magnet from other particles.

The DSLME as a new rapid and green method was used for preconcentration of lead ions from aqueous solutions. For this purpose aliquots of the solution containing lead ions (50 mL with 100 μg L^{-1} concentration) were adjusted to the appropriate pH (pH 7.0). 5.0 mL hot water (90 °C) containing 0.6 mg mL^{-1} of solid phase (Fe_3O_4@MCM-41—(SO_3^-)[ZrO_2]) was rapidly injected into the sample solution using a 10 mL syringe and then mixed at room temperature for 30 s to absorb lead ions. Subsequently, and in order to isolate the solid phase from solution a Nd-Fe-B strong super magnet was used and the supernatant solutions were decanted. Finally, the preconcentrated ions were eluted from the Fe_3O_4@MCM-41—(SO_3^-)[ZrO_2] NPs with 1.0 mL of 0.5% HCl in water and this solution was introduced into FAAS for determination of Pb^{2+} concentration.

To achieve the maximum extraction efficiency of lead ions from aqueous solution, various parameters affecting the extraction were optimized. Hence, solution pH, contact time of magnetic sorbent and the amount of the sorbent as important parameters were studied. All the optimization experiments were done at Falcon tubes with 50 mL volumes and 100 μg L^{-1} of lead ions were used for the optimization.

The effect of pH on the process exerts have profound influence on the adsorptive of lead cation, because that the negative charg of sulfonic groups on the surface of Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] MNPs is a main factor affecting for the adsorption of analytes within the sorbent surface. Hence, the effect of the pH of the solution on the adsorption of lead ions onto sorbent was studied at a pH range of 4.0–8.0.

In order to study the influence of Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] (mg mL^{-1}) amounts on the extraction efficiency of Pb^{2+} ions, different amounts of the Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] nano composite in the range of 0.1 to 1.0 mg mL^{-1} were used.

3 Results and Discussion

In the present study, a new rapid method for the extraction and preconcentration of lead ions was suggested. This strategy involves: (i) synthesis of Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2]

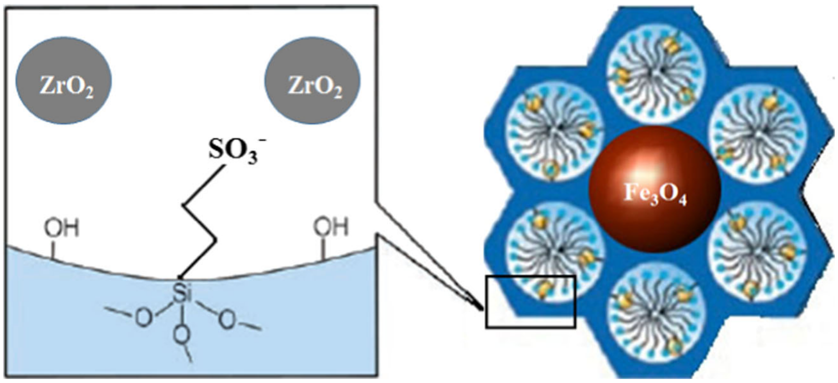

Fig. 1 The structure of Fe_3O_4@MCM-41—(SO_3^-)[ZrO_2] MNPs

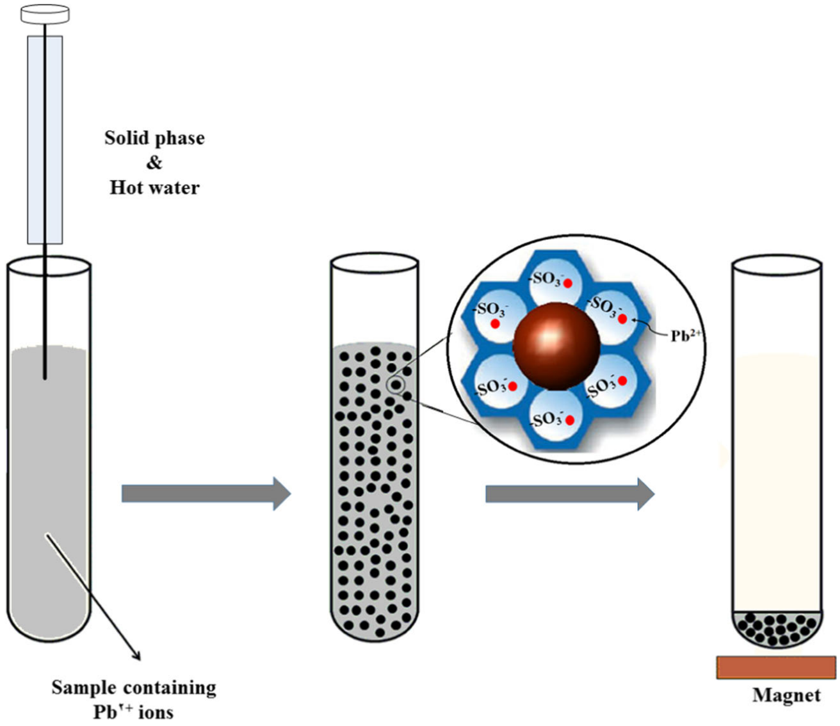

Fig. 2 Preconcentration procedure of Pb^{2+} ions by DSLME method

magnetic nanocomposite as a new sorbent and (ii) application of the synthesized nanocomposite in the DSLME method (Fig. 2).

3.1 Optimization of Variables

3.1.1 Influence of pH

The results showed that maximum extraction of Pb^{2+} ions occurred at pH ranges of 6.0–7.0 (Fig. 3). Hence, pH 7.0 was chosen as the optimum for subsequent experiments.

3.1.2 Influence of Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] Amount

The results (Fig. 4) showed that the adsorption is maximum when the amount of sorbent is 0.6 mg mL^{-1}. Therefore, 0.6 mg mL^{-1} of Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] was selected as optimal for Pb^{2+} ions.

3.1.3 Influence of Contact Time

The decrease of contact time of adsorption system is one of the novelity of proposed method for perconcentration of lead ions in comparison with traditional methods. The study of contact

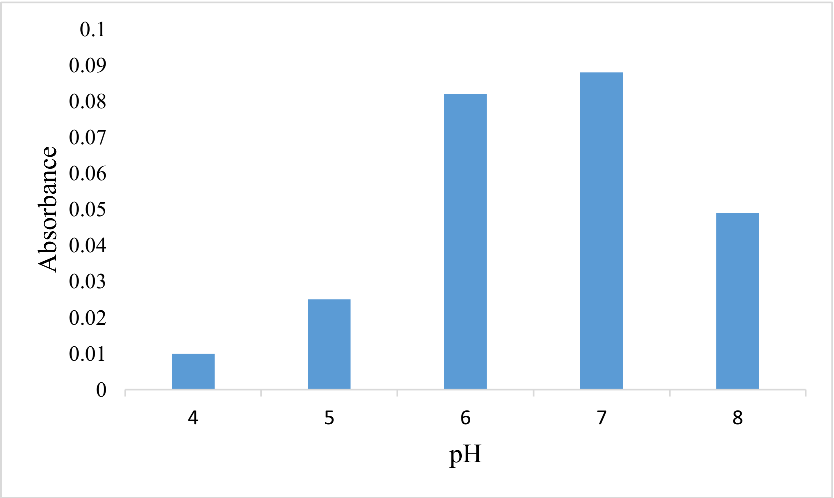

Fig. 3 Effect of pH on the solid phase extraction for lead determination

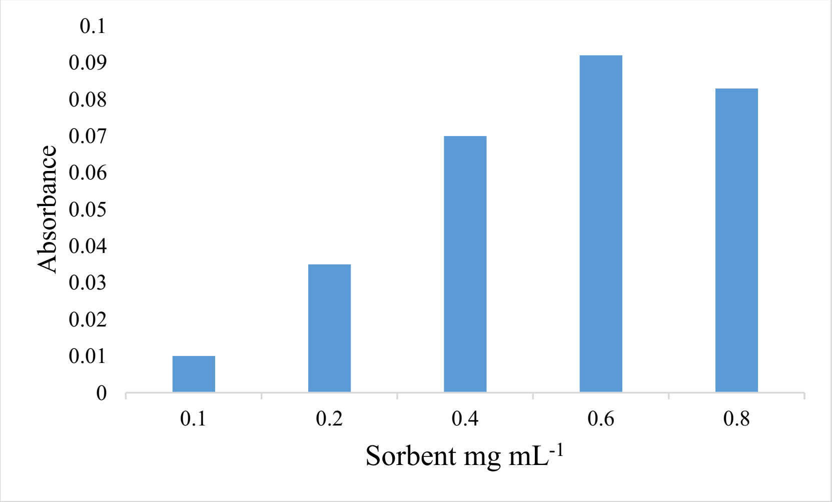

Fig. 4 Effect of magnetic sorbent amounts on the preconcentration of lead ion

time of adsorption system of lead ions for DSLME method showed that the adsorption of lead ion is stable with contact time lower than 30 secend (Fig. 5).

3.2 Characterization of the Synthesized Magnetic Nanocomposite

The magnetic hybrid organic/inorganic mesoporous nanoparticles (Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2]) were evaluated via FT-IR, BET, XRD, TEM and VSM techniques.

Figure 6 displays the FT-IR spectra of Fe_3O_4@MCM-41-(SO_3^-) and Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2]. The FT-IR analysis showed similar spectra in both nanocomposites that confirms the synthesized nanocomposites. The O–H stretching vibrations of surface -OH and sorbed water presented as broad peaks at 3000–3700 cm^{-1} and a sharper peak at 1640 cm^{-1}. The bands at wave numbers of ~ 570 and 430 cm^{-1}, are corresponded to the Fe-O vibrations in tetrahedral and octahedral sites that confirms the Fe_3O_4 as magnetic core (Fig. 6a). An intense peak at 1000–1250 cm^{-1} corresponded to the Si–O stretch in the amorphous silica shell. An intense peak at 430 cm^{-1} can be related to the Zr–O stretching vibration in the amorphous silica shell that confirms the encapsulation of ZrO_2 (Fig. 6b).

The XRD patterns are shown in Fig. 7 for the ordered magnetic mesoporous NPs and encapsulation of ZrO_2 NPs. The peaks with 2θ at 29.72, 35.57, 43.17, 57.15 and 62.77 indicated the magnetite nanoparticles (Fig. 7a). Three observed peaks with 2θ of 30.17, 50.18 and 60.03 are corresponded to diffraction peaks of crystalline ZrO_2 nanoparticles (Fig. 7b). The organic/inorganic mesoporous MNPs indicated three peaks with 2θ at 1.5–10, which are characteristic peaks of MCM-41. The peresence of both peaks of Fe_3O_4 nanoparticles and ZrO_2 nanoparticles in the XRD pattern indicates the accuracy of the synthesis of Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2].

The TEM images confirms the synthesized magnetic core/shell mesoporous nanocomposites and encapsulation of ZrO_2 NPs. Figure 8a showsthe magnetic mesoporous NPs (Fe_3O_4@MCM-41-SO_3H) as a magnetic core/shell nano-

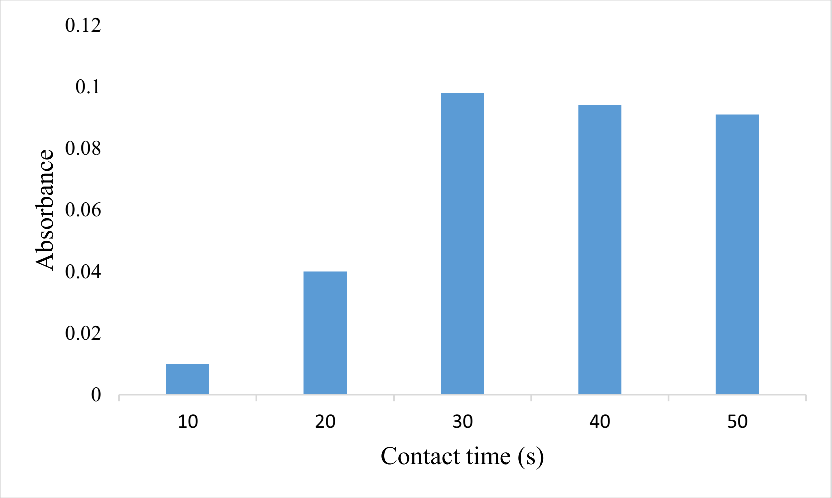

Fig. 5 Effect of contact time of sorbent on the preconcentration of lead ion

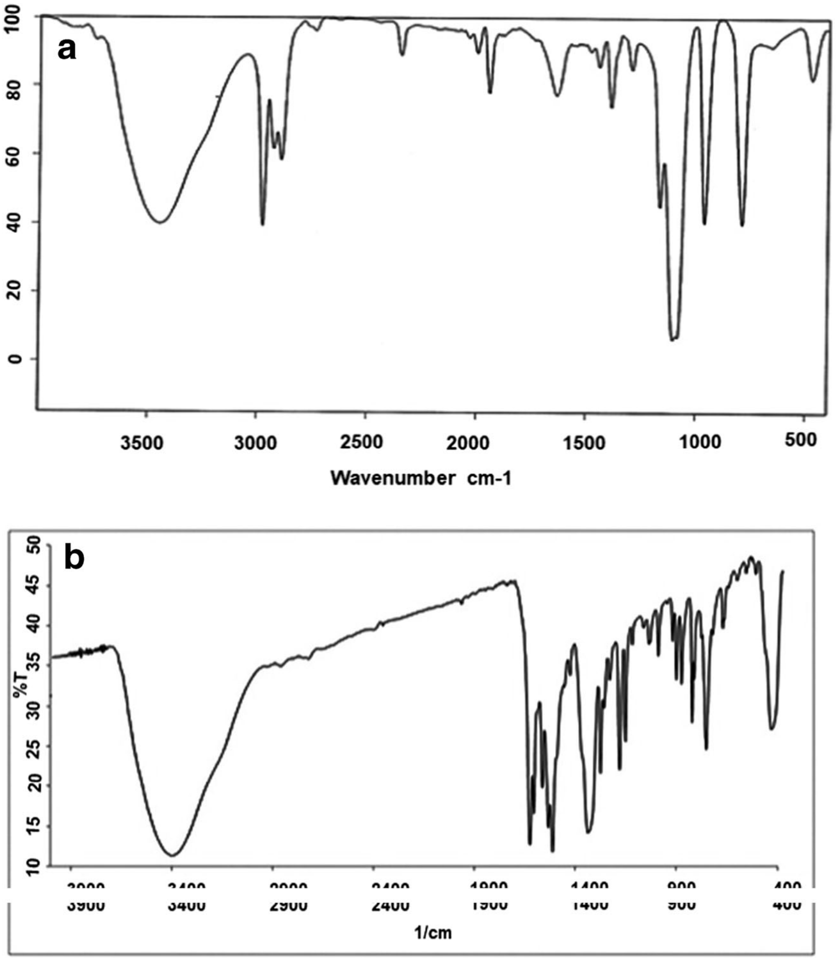

Fig. 6 FT-IR spectra of (**a**) Fe_3O_4@MCM-41-SO_3H and (**b**) Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2]

composite with the particle size of 30–50 nm. The TEM Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] is shown in Fig. 8b and confirms that the ZrO_2 NPs were encapsulated into the network of silica mesoporous. The ZrO_2 NPs dispersed on the network of Fe_3O_4@MCM-41-(SO_3^-) bed with the particle size of 2–3 nm.

In the present study, for easy and rapid separation of solid phase from solution, the solid phase was synthesized with magnetic property. Hence, it is most important that the synthesized solid phase possess sufficient magnetic and super paramagnetism. The magnetic hysteresis curves of the synthesized nano solid phases that were measured by vibrating

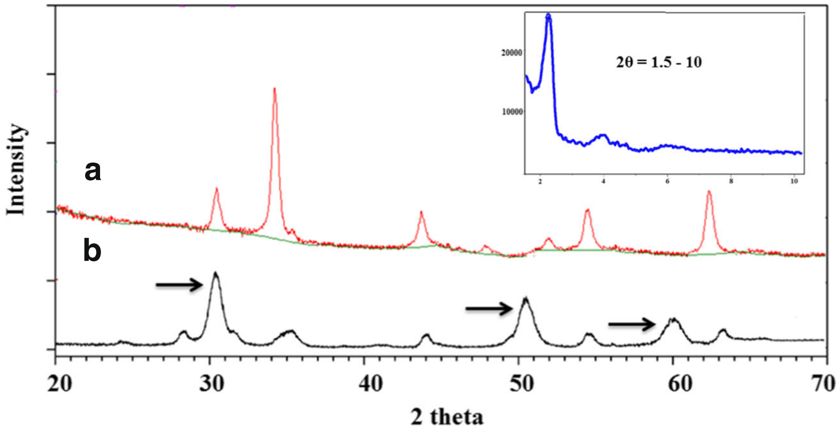

Fig. 7 X-ray diffraction patterns of (a) Fe_3O_4@MCM-41-SO_3H and (b) Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2]

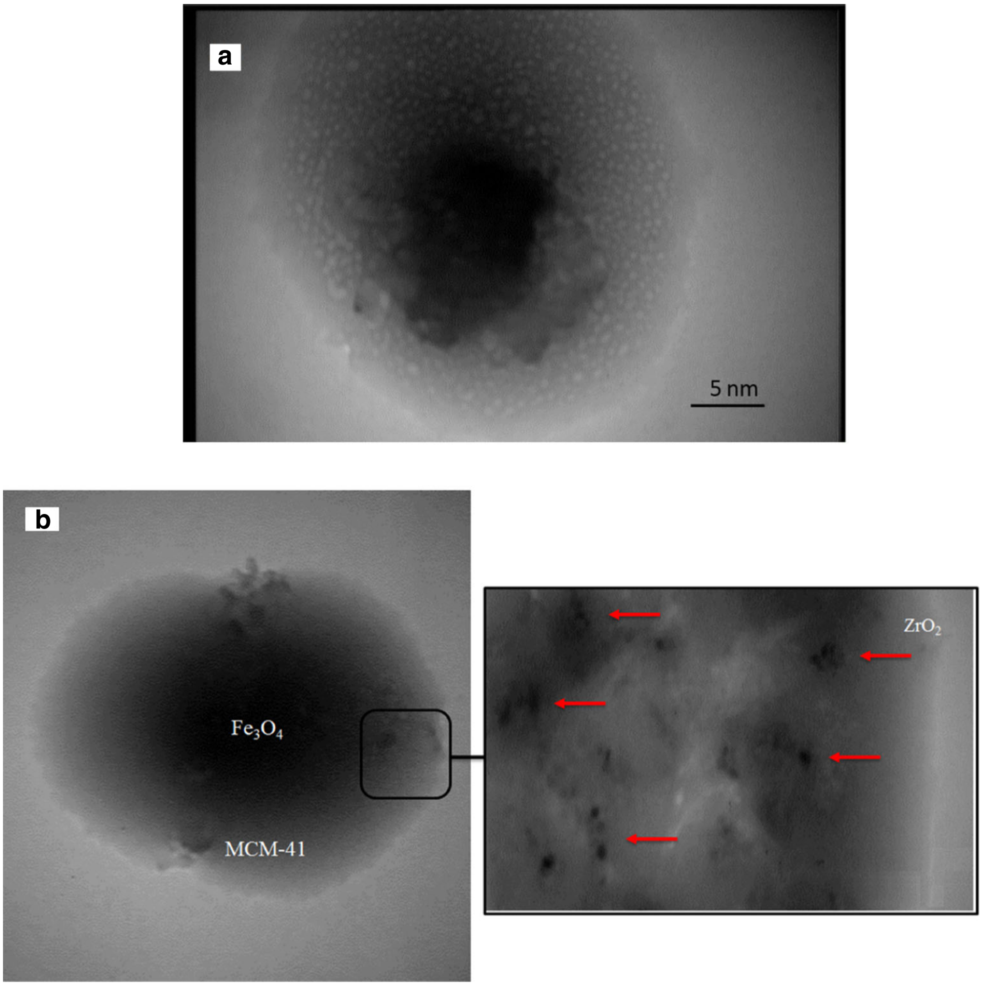

Fig. 8 TEM images of (**a**) Fe_3O_4@MCM-41-SO_3H and (**b**) Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2]

sample magnetometer (VSM) are shown in Fig. 9. The core/shell Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] nano composite exhibited typical superparamagnetic behavior, as evidenced by a zero remanence and coercively on the magnetization loop. The large saturation magnetization of sorbent was 45 emu g^{-1}.

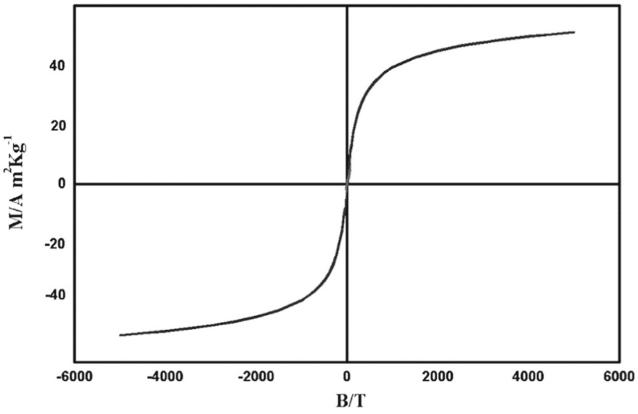

Fig. 9 Magnetic hysteresis curves of the synthesized solid phase

The BET method also confirms the synthesis of Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2] nanocomposite. The impregnation of ZrO_2 nano-particles into the network of the synthesized magnetic mesoporous NPs lead to a decrease in the pore volume from 1.32 to 0.82 cm^3/g and decrease the average pore diameter. This is expected as tethered ZrO_2 NPs extended into the pores, reducing their diameter and volume (Fig. 10).

3.3 Desorption Conditions

After extraction process, for separation of Pb^{2+} ions from the sorbent, different acidic solvents were tested in order to separate metal aggregates. So, water, chloroform, acetonitrile, methanol, ethanol and acetone with acidic pH were selected as eluent solvent. For study the influence of eluent solvent on desorption of Pb^{2+} ions from sorbent, different solvents with 0.5% (*v*/v) HCl were used (Fig. 11).

The results showed that desorption is maximum when the solvent was water, ethanol and methanol. Therefore, water was selected as the eluent solvent, because water is more affordable, cheaper and safer than other solvents.

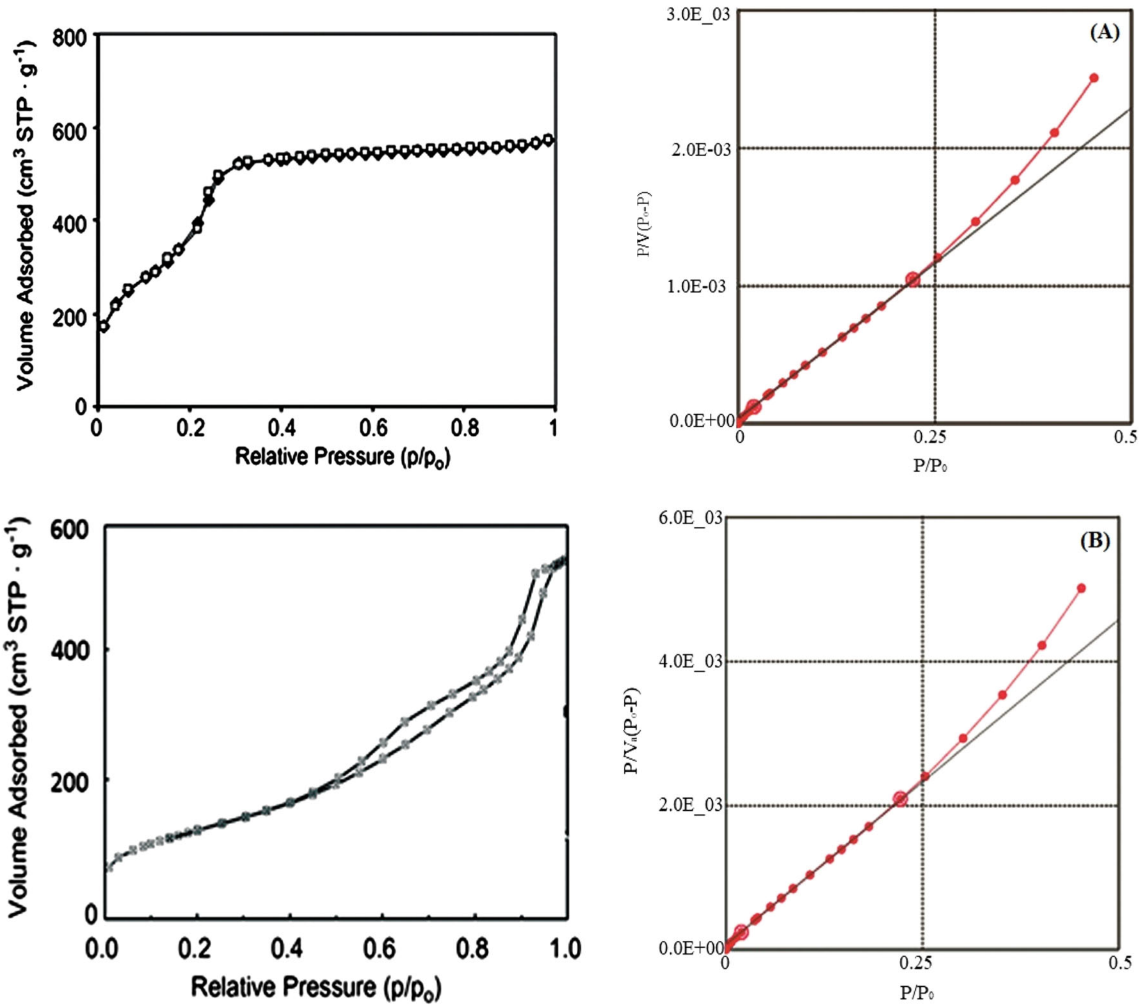

Fig. 10 Nitrogen adsorption isotherms/BET of (**a**) Fe_3O_4@MCM-41-SO_3H and (**b**) Fe_3O_4@MCM-41-(SO_3^-)[ZrO_2]

3.4 Interferences

As is known, the common cations including Fe(III), Ca(II), Mg(II), Na(I) are ubiquitous in natural water or wastewater and always bring about serious competitive influence on adsorption of lead ion and other toxic metal ions [1]. Thus, it is a prerequisite to evaluate the sorption preference of Fe_3O_4@MCM-41─(SO_3^-)[ZrO_2] toward the lead ion. In the present study, Fe(III), Ca(II), Mg(II), and Na(I) ions were selected as the model competing cations and the synthesized nanocomposite without ZrO_2 (Fe_3O_4@MCM-41─(SO_3^-)) was involved for comparison. From the results, the divalent Ca(II) and Mg(II) resulted in a decrease in Pb(II) removal by DSLME, while the adsorption was not influenced by the presence of mono and trivalent Na(I) and Fe(III). Comparatively, Fe_3O_4@MCM-41─(SO_3^-)[ZrO_2] solid phase exhibited higher efficiency than Fe_3O_4@MCM-41─(SO_3^-) in the presence of Ca(II) and Mg(II). This is because that the sulfonates groups sequester Pb(II) ions through nonspecific electrostatic interactions, and other coexisting ions would compete for the active sorption sites, whereas the ZrO_2 nano-particles in the synthesized solid phase are believed to sequester Pb(II) by specific inner-sphere complexation.

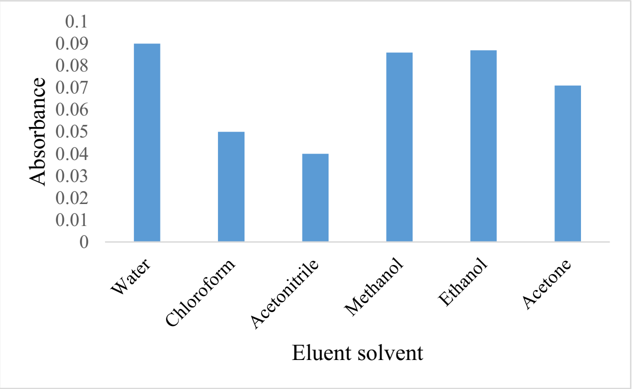

Fig. 11 Effect of different solvents on the desorption process

Table 1 Analytical performance of DSLME method for the lead ions determination

Element	EF[a]	LOD(μg L^{-1})[b]	Correlation coefficient (r^2)[c]	RSDs (%)[d]
Pb^{2+}	71.5	0.03	0.998	2.2

[a] Enrichment factor for 10 mL sample (100 μg L^{-1})

[b] limit of detection, the LOD of the proposed method was calculated from $C_{LOD} = 3S_b/m$

[c] Under the optimized conditions with linear dynamic range of 1.0–300 μg L^{-1}

[d] For solutions containing 100 μg L^{-1} of ions

3.5 Figures of Merit of the Proposed Method

The analytical features of the proposed method such as enhancement factor, limit of detection, precision, linear range of calibration curve and relative standard deviations were examined. The calculated results are shown in Table 1.

The results showed that the enhancement factor and detection limit obtained in the proposed method were better than other methods. The synthesized nan-composite and proposed method, applied in the present work, has some advantages in comparison with the other extraction methods including selectivity, low consumption of organic solvents and reagents, easy access, simplicity and low cost of the extraction device, minimum carry over and cross-contamination as well as producing of a clean extraction phase for the analysis. Also, the extractant can be easily synthesized in the lab and can be reused for several times.

3.6 Determination of Lead Ions in Real Samples

In order to check the accuracy of DSLME method for various real samples, Pb^{2+} ions were extracted in different water samples including Rasht tap water, Sefid Rood and Zardjob river waters and Bojagh lagoon water (Table 2). For this purpose, the water samples were collected and pH of samples were adjusted to pHs lower than 2 with addition of nitric acid. The reliability of method was checked by spiking sample. For this purpose, the all water samples spiked with 10 μg L^{-1} of lead ions and were extracted by the proposed DSLME procedure.

The good agreement between the spiked and found values indicates the successful applicability of the present method for determination of lead ions in real samples.

4 Conclusion

In the present study, for the first time a nano hybride of ZrO_2 and Fe_3O_4@MCM-41─(SO_3^-) as a new solid sorbent for preconcentration of lead ions by DSLME method as a rapid method was reported. This preconentration method offers an eco-friendly alternative to other techniques, because this technique employs only a very small amount of organic solvent. Also, the synthesized solid phase successfully performed for determination of lead ions in water samples. The proposed solid phase extraction shows interesting results such as inexpensively, recyclability, fastness, simplicity, and sensitivity. The presence of $–SO_3^-$ and ZrO_2 groups on the surface of the MCM-41 mesoporous magnetite nanoparticles offers a

Table 2 Analytical results for determination of Pb in real ware samples

Sample	Concentration(mean, $n = 3$)(μg L^{-1})		
	Pb added	Pb found(±RSD)	Recovery (%)
Tap water [a]	0.0	–	98
	10.0	9.8 ± 0.2	
Well water [a]	0.0	–	101
	10.0	10.1. ± 2.1	
Sefid Rood River water [b]	0.0	2.4 ± 0.3	96
	10.0	12.9 ± 1.2	
Bojagh lagoon water [b]	0.0	3.7 ± 0.1	102
	10.0	13.4 ± 2.4	
Zarjoob river water [c]	0.0	10.4 ± 0.9	97
	10.0	21.1 ± 2.1	

[a] Collected from the Rasht city in Iran

[b] River water sample collected from Sefid Rood (Guilan-Iran)

[c] River water collected from Rasht, Guilan, Iran

simple and cheap nanocomposites that can be used as a selective adsorbents for removal of pollutants. This nanocomposite have a lot of potential as a bed for the synthesis of different metal nano-catalyst and for molecular recognition.

The combination of the properties of Fe_3O_4 MNPs, mesoporous materials and ZrO_2 within a single material exhibited comparable or better activities to other mesoporous materials for adsorbtion of lead ions. This nano-composite offers many possibilities to tailor the material for a wide range of applications including use as adsorbent for determination of organic and inorganic pollution, catalyst, hydrophilic and hydrophobic drug carrying therapies via magnetic targeting as well as selective drug extraction from complex biological environments, offering a combination of high load with narrow pore size distribution.

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