Extraction, Preconcentration and Spectrometric Determination of Al (III) and Cr (III) Ions using Modified MnFe$_2$O$_4$ Nanoparticles as an Efficient Adsorbent

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ABSTRACT

An efficient and reusable adsorbent, namely 3-mercaptopropionic acid modified tetraethyl orthosilicate (TEOS) grafted MnFe$_2$O$_4$ nanoparticles (MPA-TEOS-MnFe$_2$O$_4$ NPs) was synthesized and used for the extraction and preconcentration of trace amount of Al (III) and Cr (III) ions in water samples. MnFe$_2$O$_4$ NPs were prepared by chemical co-precipitation of manganese (II) and iron (III) salts in alkaline medium and then, modified by TEOS to create an inert layer preventing nanoparticle agglomeration. The TEOS-MnFe$_2$O$_4$ NPs were then modified with MPA to produce an adsorbent with carboxylic acid functional groups which have tendency to hard metal ions such as Al (III) and Cr (III). The prepared adsorbent was characterized by SEM, XRD, VSM and FT-IR techniques. The Al (III) and Cr (III) ions were measured by graphite furnace and flame atomic absorption spectrometric techniques, respectively. Various factors affecting extraction/desorption efficiency of target ions were investigated and analytical characteristics of the method were determined and detection limits of 0.5 and 0.2 ng mL^{-1} with preconcentration factor of 69 and 72 were obtained for Al (III) and Cr (III) ions, respectively. The results revealed that the adsorbent has high capacity and good reusability for extraction/preconcentration of target metal ions in tap and drinking water samples.

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INTRODUCTION

High concentration of metal ions in human body can cause serious issues because they have very high toxicity for human health as well as the environment [1]. For example, aluminum ions (Al (III)) are a toxic element in high level and humans can expose to this ion by using food, drinking water and Al-containing medicines. This ion is one of the causative factors in several neuropathological and clinical diseases, especially in patients with chronic renal failure. It can also accumulate in bones leading to renal osteodystrophy [2]. Water-soluble chromium (Cr) compounds are also very toxic and highly irritants of nasopharynx, larynx, lungs, and skin. In water sources, Cr (VI) can be simply reduced to Cr (III) [3]. With rapid development of industry, large amounts of wastewater containing heavy metal ions have been produced by metal-plating facilities, tanneries, power generation facilities, paper industries, mining operations and fertilizer industries which destroy the environment and harm human health and can contaminate drinking

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water resources [4]. Therefore, determination of such toxic metal ions is a very important issue [5, 6].

According to the literature, many methods have been used for preconcentration of metals ions such as, ion exchange [7], membrane filtration [8], liquid-liquid extraction [9, 10], single drop micro-extraction [11], and cloud point extraction [12, 13]. Solid phase extraction (SPE) procedure using adsorbents modified with suitable ligand is one of the most promising methods for preconcentration of trace amount of heavy metals ions in different matrices [14-17]. Among these adsorbents, nanoparticles (NPs) have attracted scientific and industrial interest. Because they possess high surface-to-volume ratio resulting high sorption capacity and rapid kinetics [18]. In addition, large volume of solvents can be treated in a short period because of their Brownian motion. For example, 15 g of nano-magnetite with diameter of 12 nm can be used to treat 50 L of arsenic ions with the concentration of 500 μg L^{-1} instead of 1.4 kg of bulk iron oxide [19]. Up to now, various nanomaterials such as hematite, magnetite, spinel ferrites, graphene oxide, carbon nanotubes, and metal oxides have been used for decontamination and determination of metal ion pollutant from aqueous solutions [20-22]. Among them, magnetic spinel ferrite NPs are very interesting due to the fact that these nanomaterials exhibit higher surface area and are stable due to high chemical resistance to oxidation. MnFe$_2$O$_4$ NP is a member of spinel ferrite NPs which is relatively stable, and has high saturation magnetization which is in favor of separation [5]. However, it may tend to aggregate in aqueous media and decreasing its adsorption capacity due to its high surface energy. These weaknesses influence its potential for removal of toxic pollutants. Thus, grafting or coating with organic or inorganic layers is performed to overcome these problems. Silica is considered to be one of the best materials used for modification of NPs, due to its surface chemistry, stability, and adsorption capacity.

In this study, 3-mercaptopropionic acid (MPA) modified tetraethyl orthosilicate (TEOS) grafted MnFe$_2$O$_4$ NPs (MPA-TEOS-MnFe$_2$O$_4$ NPs) is prepared and used as an efficient adsorbent for the extraction and preconcentration of Al (III) and Cr (III) in aqueous solutions. Parameters affecting the adsorption and desorption efficiency of the analytes are optimized and the method is applied to the analysis of trace amounts of these metal ions in tap and drinking water samples.

EXPERIMENTALS
Materials and reagents
Ferric chloride hexahydrate (FeCl$_3$.6H$_2$O), manganese nitrate (Mn(NO$_3$)$_2$), aluminum sulfate (Al$_2$(SO$_4$)$_3$, chromium nitrate (Cr(NO$_3$)$_3$.9H$_2$O), TEOS, MPA, sodium hydroxide, glycerol (about 78%), sodium chloride, and methanol were purchased from Merck (Darmstadt, Germany). All chemicals and reagents were of analytical grade and used without further purification. Deionized water was used through the experiments. The stock solution of each ion with concentration of 1000 mg L^{-1} was prepared from their above-mentioned salt and working standard solutions were prepared by appropriate stepwise dilution of the stock solutions.

Instrumentation
Concentration of Al (III) ions were determined by SPECTRAA 20 plus Varian graphite furnace atomic absorption spectrometry (Palo Alto, CA, USA). The Cr (III) ions were measured using WFX-210 Rayleigh flame atomic absorption spectrometry (Beijing, China). Scanning electron microscopy (SEM) of the adsorbent was performed by S-4160 Hitachi Field emission scanning electron microscope (Tokyo, Japan). Phase characterization of the adsorbent was performed by Ital Structures (Riva Del Garda, Italy) APD 2000 X-ray diffractometer (XRD) using Cu K$_a$ radiation source with wavelength of 1.540598 A^o and reflection scan mode. Chemical interactions between MnFe$_2$O$_4$ NPs and the modifiers were studied by a WQF-510A Rayleigh FT-IR spectrometer (Beijing, China) in the range of 400-4500 cm^{-1}. The pH was adjusted using a Metrohm 827 mV/pH meter (Herisau, Switzerland).

Preparation of the modified MnFe$_2$O$_4$ NPs
The MnFe$_2$O$_4$ NPs were prepared via a chemical co-precipitation method based on the previously reported method with a slight modification [23]. Briefly, manganese nitrate (0.1 mole) and ferric chloride hexahydrate (0.2 mole) were dissolved in deionized water under N$_2$ atmosphere with vigorous stirring. Then, NaOH (0.2 mole) was rapidly added into the solution with the final volume of 50 mL followed by vigorous stirring at 85 °C. The mixture was stirred for 15 min under the same condition, and then, was washed three times with 200 mL deionized water and once with 100 mL methanol. Then, the obtained powder

was calcined in a horizontal electrical furnace at 900 °C. The precipitate was then dispersed in an aqueous solution of TEOS 10% v/v, 80 mL followed by 60 mL glycerol. The suspension was stirred at 90 °C for 2 h under nitrogen atmosphere. After cooling down to room temperature, the suspension was washed sequentially three times with 200 mL deionized water, two times with 200 mL methanol and three times with 200 mL deionized water. After that, TEOS-MnFe$_2$O$_4$ NPs were homogeneously dispersed in MPA (150 mL, of 1.0% w/v) and sonicated for 2 h. The resulting NPs were washed five times with 250 mL of deionized water and dried as black powder at 45 °C in an oven.

General magnetic SPE procedure

The magnetic SPE was as performed in batch mode as follows: a portion of sample containing 50 mg mL^{-1} of target metal ions was transferred into a 200 mL beaker and its pH was adjusted to 7.0 with 0.1 M HCl or 0.1 M NaOH and its final volume was adjusted to 150 mL with deionized water. Then, 100 mg of the adsorbent was added and the mixture was stirred for 10 min. After that, the adsorbent was settled down using a strong supermagnet and upper solution was decanted. Then, the supermagnet was removed; an eluent containing 2 ×1 mL of 1.0 M HNO$_3$ was added to the solution and it was stirred for 10 min. Finally, the supermagnet was used again to settle the adsorbent and the upper solution was transferred to the determination instrument.

Sample preparation

A pre-washed acid-leached polyethylene flask was used to real samples collection and the samples were pretreated with a nitric acid solution with pH 1.5 immediately after collection to prevent adsorption of metal ions on the flask wall. The samples were filtered before analysis using a 0.45 mm pore size filter. Then, 100 mL of each water sample was transferred to a 150-mL volumetric flask and the pH of sample was adjusted to 6.0 with 0.1 M HCl/NaOH. Then, the sample was diluted to the mark and subjected to the general magnetic SPE procedure.

RESULT AND DISCUSSION

Hard metal ions are known to have a great tendency toward the complexing agents with hard coordination sites like oxygen. The synthesized MPA-TEOS-MnFe$_2$O$_4$ NPs have carboxyl end groups (i.e. oxygen donor atoms) and show good characteristics to form stable complexes with hard metal ions such as Al^{3+} and Cr^{3+}.

Characterization

XRD analysis of the modified MnFe$_2$O$_4$ NPs is presented in Fig. 1 and confirms the crystalline phase of ferrite part in MnFe$_2$O$_4$ which is very close to the JCPDS No. 74-2403 [24]. As can be seen, the most intensive lines of 311 and 440 diffraction planes are observed at peak position of 36.47 and 61.44°. The XRD pattern shows the adsorbent has cubic structure and the sharp peaks represent the crystalline order and high crystalline structure of MnFe$_2$O$_4$ NPs. There were no additional peaks, showing the existence of impurity in the prepared adsorbent.

The saturation magnetization curve of MPA-TEOS-MnFe$_2$O$_4$ NPs is presented in Fig. 2. As can be seen, the adsorbent has saturation magnetization
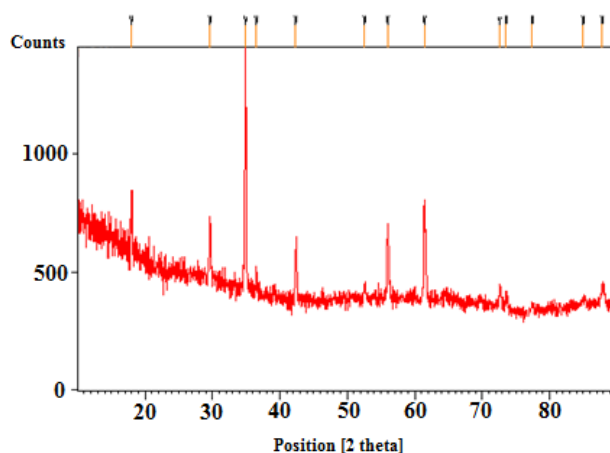

Fig. 1: The XRD pattern of modified MnFe$_2$O$_4$ NPs.

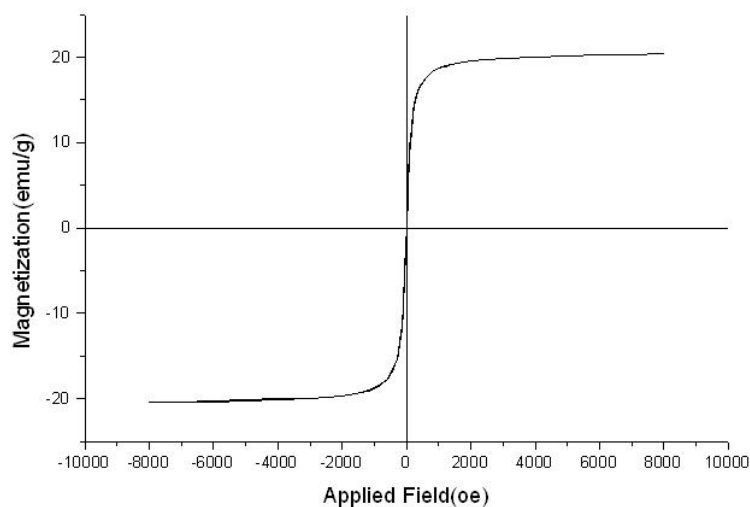Fig. 2: VSM analysis of the modified MnFe₂O₄ NPs.

of about 22 emu g⁻¹ indicating enough magnetic responsiveness for manipulation with strong magnet. In this study, MNPs is expected to be held in place by an external magnetic field and the carrier releases the drug in a controlled manner.

The SEM image of the MnFe₂O₄ NPs is represented in Fig. 3. As can be seen, the particles have relatively uniform structure and quasi-spherical in shape and they have mean diameter of about 20 nm ± 2.

Fig. 4 represents FT-IR spectrum of the modified MnFe₂O₄ NPs. As can be seen, two strong absorption bands at about 547 and 451 cm⁻¹ are due to the stretching vibration of Fe-O bond [25, 26]. The absorption band at 1096 cm⁻¹ corresponds to the stretching vibration of Si-O band and absorption band at 3437 cm⁻¹ is due to the OH groups of MAA units or existence of surface water in sample powder. The absorption peak at 1640 cm⁻¹ belongs to the vibrational band of C=O in MPA modifier. Furthermore, two vibrational bands at about 2922 and
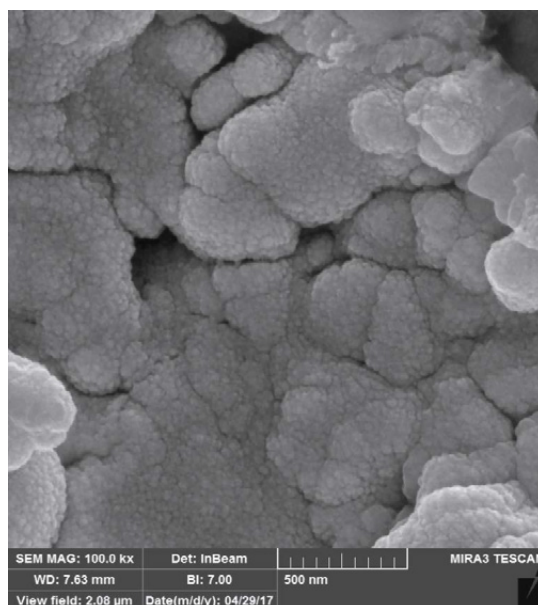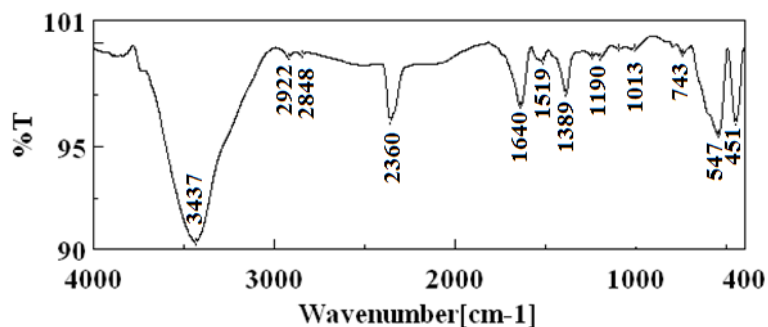

Fig. 3: SEM images of the MnFe₂O₄ NPs.

Fig. 4: FT-IR spectra of the modified MnFe₂O₄ NPs.

2848 cm^{-1} correspond to the asymmetric stretching of $-CH_2$ group and the intense characteristic band at 1389 cm^{-1} is assigned to bending vibration of -CH group. The results confirm successful synthesis of the modified $MnFe_2O_4$ NPs.

Effect of pH

The pH value of the solution plays a critical role in any SPE procedure. To study the effect of solution pH on the extraction of metal ions, 150 mL of Al (III) and Cr (III) solutions with the concentration of 50 ng mL^{-1} were transferred into a beaker and its pH was adjusted to 2.0-9.0. Then, 100 mg of the adsorbent was added and it was subjected to the recommended SPE procedure. The results are presented in Fig. 5. As can be seen, the adsorption efficiency of both ions is increased with the increase of pH value from 2.0 to 7.0 and then, it remains constant. The pK_a value of 3-mercaptopropionic acid is 4.3 for its carboxylic acid group [2]. Below this pH, most carboxylic groups on the surface of adsorbent are in neutral form and complexation between target ions and the adsorbent cannot be occurred. At pH higher than pK_a, negatively charged functional groups of the adsorbent are in the favor of ion adsorption due to the complex formation. Experimental results indicate that the adsorbent is quantitatively (>90%) adsorbed to the analytes in the pH ranged from 7.0 to 9.0. Thus, pH 7.0 was selected for all subsequent experiments.

Desorption conditions

In most magnetic based SPE of metal ions, mineral acids with/without a complexing agent are the most commonly used eluent for desorption of these ions from the adsorbent. Hence, various desorbing reagents such as 0.1 M of HNO_3, HCl, and $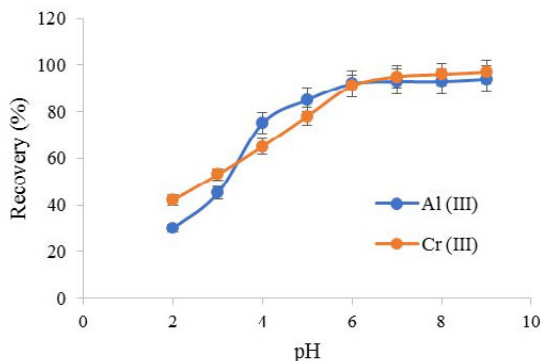H_2SO_4$ solutions, along with some organic solvents such as ethanol and acetonitrile were examined for quantitative recovery of 50 mg mL^{-1} of target metal ions in the solution. As can be seen from Fig. 6, most of acidic solutions revealed higher elution efficiency and HNO_3 has the maximum recovery. So, it was selected as the eluent. Furthermore, the effect of eluent volume on the quantitative recovery of 50 mg mL^{-1} of target ions was also studied. The results revealed that the minimum volume of eluent required for quantitative desorption is 2.0 mL (2 ×1 mL). Therefore, 2.0 mL of 1.0 M HNO_3 was selected as the optimum eluent in the next experiments.

Effect of sample volume

The possibility of using higher sample volumes causes enriching low concentrations of metal ions and obtaining higher preconcentration factor. Hence, the maximum applicable sample volume must be determined. Therefore, different sample volumes namely, 25, 50, 100, 150, and 200 mL which have 50 mg mL^{-1} of each target ion were examined according to proposed SPE procedure. The results indicate that quantitative recoveries are obtained for 25 to 150 mL of sample solutions, and in higher volumes the recovery is decreased. The larger volumes can cause analyte loss from the adsorbent surface. Thus, 150 mL was selected as the optimum value for sample volume in the next experiments.

Effect of extraction and desorption times

The conventional SPE procedures usually need centrifugation or filtration of sample solutions to separate the adsorbent from the sample. However, magnetic NPs can be easily and rapidly separated from the sample using an external supermagnet. In order to obtain the optimum experiment time, the effect of extraction and desorption times on the recovery of target ions were investigated. The experimental results
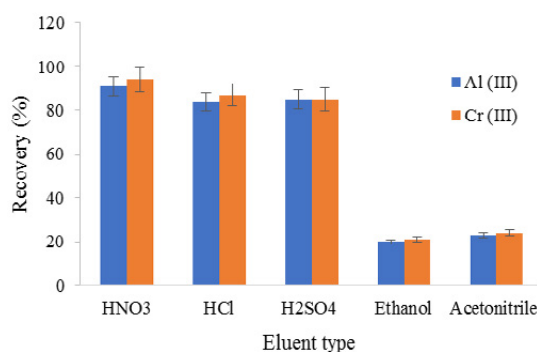

Fig. 5: Effect of pH on the recovery of 50 mg mL^{-1} of Al (III) and Cr (III) solution.

Fig. 6: Effect of various eluents on the recovery of 50 mg mL^{-1} of Al (III) and Cr (III) solution.

Table 1: Determination of Al (III) and Cr (III) in water samples (n= 5).

Sample	Added (ng mL⁻¹)		Found (ng mL⁻¹)		Recovery (%)	
	Al (III)	Cr (III)	Al (III)	Cr (III)	Al (III)	Cr (III)
Tap water	0	0	12.1	7.1	-	-
	50	50	55.3	53.1	89	93
	200	200	193.0	194.7	91	94
	400	400	379.1	390.8	92	96
Drinking water	0	0	21.5	11.8	-	-
	50	50	64.3	56.8	90	92
	200	200	203.8	201.2	92	95
	400	400	391.9	395.3	93	96

indicate that 10 min is sufficient for achieving both quantitative adsorption and desorption of metal ions with recovery >90%. Since, the magnetic adsorbent can completely separate from the solution in less than 1.0 min due to its super paramagnetism property, the whole SPE procedure can be performed within about 30 min which effectively shortens the traditional column-passing SPE.

Adsorbent amount and reusability

NPs have higher surface area to volume ratio with respect to the common micro-sized adsorbents, which offers short diffusion route, rapid extraction dynamics and high extraction capacity to them. Thus, satisfactory separation can be obtained with low amount of these type of adsorbents. To investigate a suitable amount of modified $MnFe_2O_4$ NPs for the adsorption of Al (III) and Cr (III) ions without scarifying the recovery%, different amounts of the adsorbent in the range of 50-200 mg were examined. The results revealed that the extraction efficiency is increased by increasing adsorbent amount and reaches maximum in 100 mg, then it remains constant. Thus, a minimum of 100 mg was used as the optimum amount of magnetic adsorbent and used in the following experiments.

For testing the reusability of the modified $MnFe_2O_4$ NPs, the adsorbent used in the general SPE procedure was washed twice with 50 mL of the eluent and three times with 50 mL of deionized water. Then, it was reused in the same SPE procedure for recovery of the analytes. The results revealed that the adsorbent can be re-used up to five times without sacrificing the analytical performance with RSD <5%.

Analytical characteristics

The optimum experimental conditions were applied for determination of analytical characteristics of the proposed method. The linear range was 5-500 mg mL⁻¹ for the target metal ions with R^2 better than 0.998. The detection limit was evaluated as the concentration corresponding to three times of blank

standard deviation for five times blank evaluations and were obtained 0.5 and 0.2 ng mL⁻¹ for Al (III) and Cr (III) ions, respectively. The precision of the methods was presented as relative standard deviations (RSD%) of five times determination of a solution with concentration of 100 mg mL⁻¹ with respect to each target metal ion and it was found 3.7 and 3.1% for Al (III) and Cr (III) ions, respectively. The preconcentration factor was defined as $PF=V_s/V_e \times R\%$, which V_s is sample volume, V_e is eluent volume, and R% is percent recovery. According to the results, Al (III) and Cr (III) have PE of 69 and 72 respectively. To evaluate the adsorbent capacity, 100 mg of $MnFe_2O_4$ NPs was added to 150 mL of various concentrations of target ions and the supernatant was analyzed after 30 min. The initial concentration of ions was increased until reaching plateau level. The maximum adsorption capacity was found to be 54 and 52 mg g⁻¹ for Al (III) and Cr (III), respectively which is enough adsorption capacity for adsorption of metal ions. The results represent good analytical characteristics of the proposed method.

Application of the method

The proposed magnetic SPE procedure was applied to the determination of trace amounts of Al (III) and Cr (III) ions in tap and drinking water samples. Calibration curves using matrix-match technique with triplicate analysis of five spiked samples were obtained and analysis of real samples was performed using these equations. Recovery results are presented in Table 1. As can be seen, the mean recoveries are in the range of 89-96% indicating the suitability of the prepared sorbent for extraction and preconcentration of trace amounts of Al (III) and Cr (III) in real water samples.

CONCLUSION

In this research, MPA modified TEOS coated $MnFe_2O_4$ NPs was synthesized and successfully applied as an efficient adsorbent for the extraction and preconcentration of Al (III) and Cr (III) ions in water samples. The adsorbent was characterized by XRD,

VSM, SEM and FT-IR techniques and parameters affecting the extraction/preconcentration recovery of the analytes were evaluated. According to the results, the procedure can apply in neutral pH which offer minimal sample pretreatment and the prepared adsorbent has characteristics of high capacity, high preconcentration factor and fast adsorption and desorption. The proposed method has advantages of simplicity, short analysis time and low cost in comparison with conventional SPE methods.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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