



Selective solid-phase extraction and analysis of trace-level Cr(III), Fe(III), Pb(II), and Mn(II) ions in wastewater using diethylenetriamine-functionalized carbon nanotubes dispersed in graphene oxide colloids



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ABSTRACT

Multi-walled carbon nanotubes (MCNTs) were dispersed in graphene oxide (GO) colloids to be further functionalized with diethylenetriamine (DETA), resulting in GO-MCNTs-DETA nanocomposites for the solid-phase extraction and analysis of Cr(III), Fe(III), Pb(II), and Mn(II) ions at the trace levels in wastewater. Inductively coupled plasma optical emission spectrometry (ICP-OES) indicates that this new solid-phase sorbent could facilitate the maximum static adsorption capacities of 5.4, 13.8, 6.6 and 9.5 mg g⁻¹ for Cr(III), Fe(III), Pb(II), and Mn(II) ions, respectively, showing the adsorption capacity up to 95% within about 30 min. Moreover, the detection limits of the GO-MCNTs-DETA-based analysis method were found to be 0.16, 0.50, 0.24 and 0.38 ng mL⁻¹ for Cr(III), Fe(III), Pb(II), and Mn(II) ions, respectively, with the relative standard deviation of lower than 3.0% (*n*=5). Importantly, common coexisting ions showed no significant interference on the separation and pre-concentration of these heavy metal ions at pH 4.0. Subsequently, the GO-MCNTs-DETA sorbent was successfully employed for the separation and analysis of trace-level Cr(III), Fe(III), Pb(II), and Mn(II) ions in wastewater samples yielding 75-folds concentration factors.

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1. Introduction

The separation and analysis of trace-level heavy metal ions in wastewater has become more and more important [1]. Due to most heavy metal ions like Cr(III), Fe(III), Pb(II), and Mn(II) ions can present very low concentrations in environmental samples, their separation and sensitive determination necessitate the use of sorbents with highly-effective pre-concentration or trace enrichment [2–4]. As a well-known pre-concentration or separation technique, the solid-phase extraction (SPE) method can provide simple operation and flexible working conditions [5]. Compared with the most traditional methods, SPE enjoys some advantages of rapid phase separation, high recovery, high enrichment factor, cost-effectiveness, and low consumption of solvents, and especially it can be incorporated with various techniques for on-line or off-line analysis [6–9].

In a typical SPE procedure, the choice of appropriate sorbents is a critical factor for achieving high recovery and enrichment factor [10]. In recent decades, carbon nanotubes (CNTs), first discovered by Iijima [11], have been increasingly applied in this field due to they possess high surface area, mechanical strength, and chemical stability. Remarkably, with unique characteristics and strong adsorption ability [12], CNTs have been used to remove different kinds of pollutants such as phenols [13], pesticides [14], diazinon [15], tetracyclines [16], gallium [17], copper [18–20], mercury [21,22], nickel [23], lead [24], cadmium [25–27], and zinc [28,29] from real samples. For example, Zhang et al. [17] applied Ga(III) ion-imprinted multi-carbon nanotubes as solid-phase extraction sorbent for selective extraction gallium ion from fly ash. The maximum static adsorption capacity of the imprinted sorbent for Ga(III) was 58.5 μmol g⁻¹. Liu et al. [27] applied L-cysteine-functionalized CNTs as a selective sorbent for Cd(II) enrichment. The mercapto content in this sorbent was 3.0 mmol g⁻¹. Nevertheless, the application of raw or oxidized-CNTs for the enrichment of metal ions is still quite limited, especially for SPE. Moreover, the poor dispersion of CNTs in water might prevent them from the

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large-scale applications in aqueous media. Additionally, it is expected that CNTs may be modified with some organic compounds so as to achieve more selective solid-phase extraction of metal ions. However, to the best of our knowledge, few studies have been reported so far.

In this work, multi-walled CNTs (MCNTs) were first dispersed in graphene oxide (GO) colloids and further modified with diethylenetriamine (DETA), resulting in the GO–MCNTs–DETA nanocomposite to serve as the novel SPE sorbent materials for the extraction of Cr(III), Fe(III), Pb(II), and Mn(II) ions in wastewater. Several extraction variables and desorption conditions were optimized. Compared with other SPE sorbents, the developed GO–MCNTs–DETA sorbent could possess higher extraction efficiency for Cr(III), Fe(III), Pb(II), and Mn(II) ions. A new analysis method was thereby developed for the sensitive determination of these ions in wastewater samples.

2. Experimental

2.1. Apparatus

Inductively coupled plasma spectrometer (PE 4300DV, USA) was used for determining metal ions. The operation conditions were those recommended by the manufacturer, and the wavelengths selected for Cr(III), Fe(III), Pb(II), and Mn(II) ions were 267.716 nm, 259.940 nm, 216.999 nm, and 279.482 nm, respectively. Moreover, a BT100-2J peristaltic pump (The Baoding longerpump Co., Ltd, Hebei, China) was applied in the separation/pre-concentration process. Additionally, a self-made glass micro-column (45 mm × 2.5 mm i.d.) was used in the experiments.

2.2. Reagents and solutions

Standard labware and glassware used were cleaned with HNO₃ and further rinsed with deionized water, according to a common procedure [30]. Metal ions (1.0 mg mL⁻¹) were prepared by dissolving analytical grade salts using diluted hydrochloric acid prior to use. Diethylenetriamine (DETA, chemical company, Beijing, China) was used for modifying multi-walled carbon nanotubes (MCNTs, Chengdu Institute of Organic Chemistry, Academia Sinica). N,N-dicyclohexylcarbonodiimide (DCC, Lanzhou Institute of Chemical Physics, Academia Sinica) and graphene oxide (GO, Graphene Supermarket, USA) nanosheets were employed to prepare the sorbent materials. All other reagents are of analytical grade.

2.3. Synthesis of the sorbent

First, 10 g MCNTs, which were first purified by concentrated HCl (36.5%) and then sonicated in a water bath for 24 h, were suspended in 300 mL H₂SO₄ (98%) and HNO₃ (70%) mixture at the volume ratio of 3:1 to be sonicated in a water bath for 24 h at 50 °C. The resultant MCNTs–COOH were collected on a polytetrafluoroethylene filter, and then washed separately for four times with water and methanol. The yielding MCNTs were dried overnight at room temperature and finally recovered from the filter by scraping them off.

The GO-dispersed MCNTs (GO–MCNTs) were prepared with the mass ratio of GO nanosheets to MCNTs of 1:10. An aliquot of 5.0 g GO–MCNTs was added to the mixture of 5.0 g DCC in 150 mL DETA, and then stirred at 120 °C for 48 h. The mixture was separated and washed separately with toluene and methanol, dried at 80 °C for 8 h, forming the GO–MCNTs modified with DETA (GO–MCNTs–DETA). In addition, the DETA-modified MCNTs (MCNTs–DETA) were prepared according to the same procedure.

2.4. Procedures

2.4.1. Batch method

A series of standard solutions of 1.0 µg mL⁻¹ Cr(III), Fe(III), Pb(II), and Mn(II) ions were prepared and separately transferred into a 10-mL beaker, of which the pH value was adjusted using 0.10 mol L⁻¹ HNO₃ and 0.10 mol L⁻¹ NH₃ · H₂O. Following that, an aliquot of 30 mg GO–MCNTs–DETA sorbent was introduced. Following that, the mixture was shaken vigorously for 30 min to facilitate the adsorption of metal ions. Furthermore, ICP–OES was carried out for directly determining these metal ions desorbed by centrifuging and eluting with HCl at the optimum concentrations and volumes.

2.4.2. Column method

An aliquot of 50 mg sorbent and 50 mg glass beads (40–60 mesh) were used to prepare the homogenous mixture to be packed in the glass microcolumn that were plugged with a small portion of glass wool at both ends. Then, HNO₃ solution (pH 4.0) and deionized water were sequentially passed through to equilibrate, clean, and neutralize the resulting micro-columns. After adjusting the pH value to about pH 4.0, each of the ion samples was introduced into the column at a flow rate of 1.5 ml min⁻¹ (controlled by a peristaltic pump). Further, these metal ions adsorbed on the column were eluted by 2.0 mol L⁻¹ HCl. Subsequently, the ion analytes in the elutions were separately determined by ICP–OES.

3. Results and discussion

3.1. Synthesis and characterization of DETA-modified GO–MCNTs

3.1.1. Synthesis of DETA-modified GO–MCNTs

It is well-known that the dispersion stability of MCNTs in water is unsatisfactory. GO colloids that are amphiphilic with an edge-to-center distribution of hydrophilic and hydrophobic domains could be potentially used as the dispersants [31,32]. Herein, purified MCNTs were dispersed into the GO colloids to obtain improved aqueous dispersion serving as the SPE sorbent of GO–MCNTs with large specific area and mechanical strength. Moreover, DETA was chosen as the modifier for the GO–MCNTs, resulting in GO–MCNTs–DETA nanocomposite. An improved selective adsorption capacity could be thus expected for the new SPE sorbent for extracting and analyzing the meaningful heavy metal ions of Cr(III), Fe(III), Pb(II), and Mn(II) ions.

3.1.2. Characterization of DETA-modified GO–MCNTs

Transmission electron microscopy (TEM) was utilized to characterize the so prepared GO–MCNTs–DETA in comparison with MCNTs–DETA (Fig. 1). One can note from the representative TEM images that MCNTs–DETA highly entangled by van der Waals force could be partly coagulated and stacked in water, showing dense, robust, and network structure (Fig. 1a). In contrast, GO–MCNTs–DETA nanocomposites could present much improved aqueous dispersion and stability (Fig. 1b)

3.2. Optimization of extraction and analysis conditions

3.2.1. Effects of pH

It is well recognized that the acidity might exert two effects on the metal adsorptions. Firstly, protons in acid solution can protonate the binding sites of the chelating molecules. Secondly, hydroxide in basic solution might precipitate most of the metal ions. Accordingly, the effects of pH values on the adsorption capacities of GO–MCNTs–DETA for Cr(III), Fe(III), Pb(II), and Mn(II) ions were

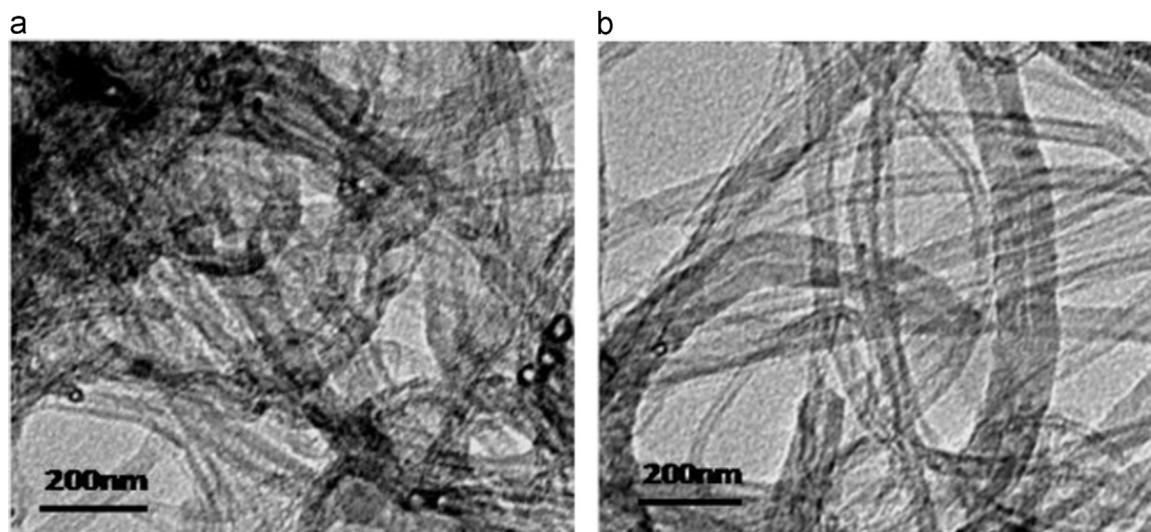


Fig. 1. TEM images of (a) MCNTs-DETA and (b) GO-MCNTs-DETA nanocomposites.

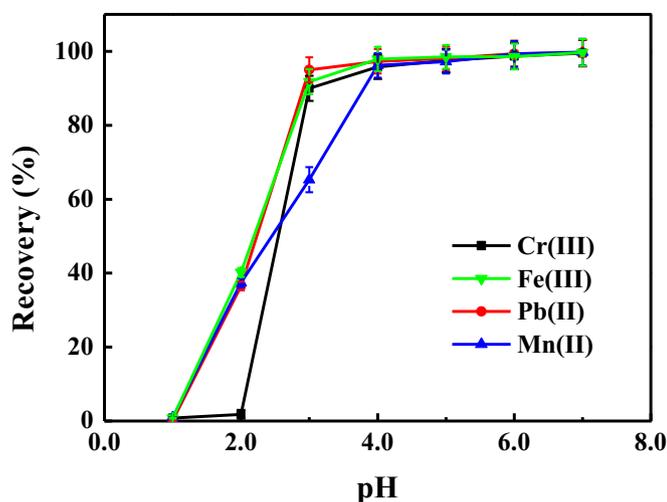


Fig. 2. Effects of pH values on the analyte recovery of Cr(III), Fe(III), Pb(II), and Mn(II) ions ($1.0 \mu\text{g mL}^{-1}$) in the buffer solutions of different pH values. Other conditions: 30 mg GO-MCNTs-DETA sorbent, shaking time 30 min, temperature 25°C .

investigated over the pH range from 1.0 to 7.0 by the batch procedure. As can be seen from Fig. 2, the sorption amounts of Cr(III), Fe(III), Pb(II), and Mn(II) ions were very low when the pH values were lower than 2.0, presumably due to that the protonation of partial nitrogen in the sorbents might cause a decrease in their bonding capabilities for these metal ions. However, when the pH values increased up to 4.0, their ion sorption of the SPE sorbent could increase dramatically till they reached the sorption balance. To avoid the possible hydrolyzation of metal ions at higher pH values, pH 4.0 was chosen thereafter in the experiments for the simultaneous determination of these metal ions.

3.2.2. Effects of shaking time

The shaking time is another important factor in governing the practical applications of the GO-MCNTs-DETA for the selective extraction of Cr(III), Fe(III), Pb(II), and Mn(II) ions. In this work, different shaking time ranging from 2 to 40 min was studied for the GO-MCNTs-DETA sorbent, where the extraction percentages of Cr(III), Fe(III), Pb(II), and Mn(II) ions ($1 \mu\text{g mL}^{-1}$) were recorded. The results are shown in Fig. 3. It is found that the adsorption of Cr(III) and Fe(III) ions were over 95% sorption during the first 10 min, indicating that sorption toward the kinetic equilibrium is quite

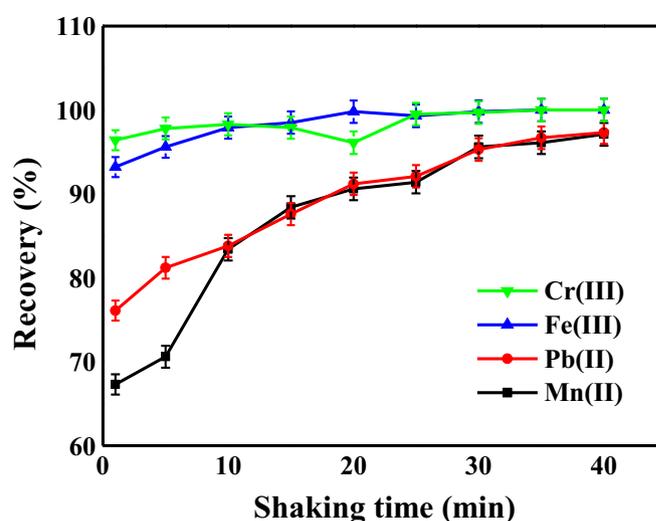


Fig. 3. Extraction percentages of Cr(III), Fe(III), Pb(II), and Mn(II) ions ($1.0 \mu\text{g mL}^{-1}$) at different shaking time ($n=3$). Other conditions: 30 mg GO-MCNTs-DETA sorbent, temperature 25°C .

fast. But the sorption of Mn(II) and Pb(II) ions ($> 95\%$) needs more than 30 min. In order to determine them in a simultaneity way, the shaking time of 30 min was thus chosen as the optimum time of sorption equilibrium.

3.2.3. Effects of the mass of sorbent

To test the effects of extractant mass on the quantitative retention of metal ion analytes, different amounts of GO-MCNTs-DETA sorbent ranging from 5.0 to 40 mg were added into the metal ion solutions by following the batch procedure. The results are shown in Fig. 4. Obviously, quantitative recoveries for Cr(III) and Fe(III) ions were obtained in the range of 15–40 mg of sorbent. Yet, quantitative recoveries for Mn(II) and Pb(II) ions were obtained in the range of 25–40 mg of sorbent. Accordingly, 30 mg of GO-MCNTs-DETA sorbent was selected for all further studies for purpose of the determination simultaneity.

3.2.4. Effects of flow rates

The effects of the flow rates of sample solutions containing Cr(III), Fe(III), Pb(II), and Mn(II) ions through the packed volume was investigated under the optimum conditions (pH value, eluent, etc.)

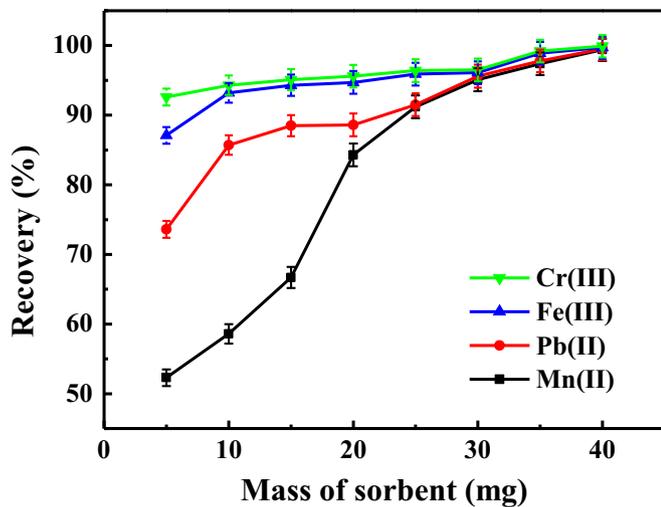


Fig. 4. Effects of sorbent mass on the metal ion analyte recovery of Cr(III), Fe(III), Pb(II), and Mn(II) ions (pH 4.0, $1.0 \mu\text{g mL}^{-1}$). Other conditions: shaking time 30 min, temperature 25°C .

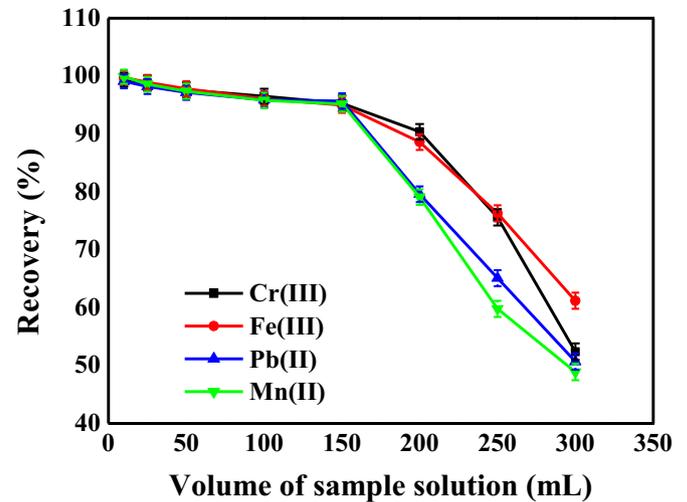


Fig. 6. Effects of the sample volumes on the analyte recoveries of Cr(III), Fe(III), Pb(II) and Mn(II) ions (pH 4.0, $1.0 \mu\text{g mL}^{-1}$). Other conditions: 30 mg GO-MCNTs-DETA sorbent, shaking time 30 min, temperature 25°C .

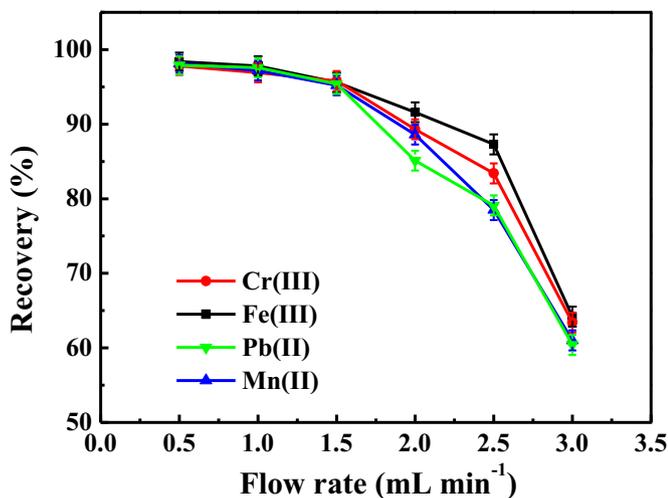


Fig. 5. Effects of the flow rates on the analyte recoveries of Cr(III), Fe(III), Pb(II), and Mn(II) ions (pH 4, $1.0 \mu\text{g mL}^{-1}$). Other conditions: sample volume 50 mL, temperature 25°C .

by the column method (Fig. 5), where the flow rates were adjusted in the range from 0.50 to 3.0 mL min^{-1} . As expected, the flow rates could present a significant influence on the sorption of Cr(III), Fe(III), Pb(II), and Mn(II) ions, showing that too low flow rates would not be attempted because of the longer extraction time. However, at flow rates greater than 1.5 mL min^{-1} , there was a decrease in the percentage of metal ion sorption, probably due to that the metal ions could not sufficiently equilibrate with the SPE sorbent. Thus, a flow rate of 1.5 mL min^{-1} was selected as the optimum flow rate in this work.

3.2.5. Maximum sample volume, elution condition, and enrichment factors

In order to explore the possibility of concentrating the low-level analytes from the large volumes of mixtures, the effects of sample volumes on the retentions of metal ions were investigated. For this purpose, 10, 25, 50, 100, 150, 200, 250, and 300 mL of sample solutions containing $1.0 \mu\text{g}$ of Cr(III), Fe(III), Pb(II), and Mn(II) ions were pumped through the micro-column at the optimum flow rate. As shown in Fig. 6, the quantitative recoveries ($> 95\%$) were obtained for the sample volumes of 150 mL of four metal

ions. Therefore, 150 mL of sample solution was adopted for the pre-concentration of metal ion analytes in samples. Moreover, the elution condition was studied by the batch and column procedure, where various concentrations and volumes HCl were used for the desorption of retained Cr(III), Fe(III), Pb(II), and Mn(II) ions. The results showed that 2.0 mL of 2.0 mol L^{-1} HCl was sufficient for up to 95% recovery for the investigated metal ions. Accordingly, 2.0 mL of 2.0 mol L^{-1} HCl was used as the eluent in the experiments. Additionally, considering that the maximum sample volume is 150 mL, the high enrichment factor was calculated to be about 75.

3.2.6. Adsorption capacity of GO-MCNTs-DETA

The capacity of the adsorbent is an important factor in determining the adsorbent dosage required for quantitatively removing a specific amount of metal ions from the solutions [33]. The adsorption capacities of various metal ions probably differ due to their size, degree of hydration, and the value of their binding constant with the ligands anchoring at the sorbent matrix. Therefore, the capacity study was commonly adopted as reported by Maquieira et al. [34]. In the present work, the adsorption capacities of the GO-MCNTs-DETA sorbent for Cr(III), Pb(II), and Mn(II) ions with different ion concentrations ($1.0\text{--}40 \text{ mg L}^{-1}$) were examined by the proposed procedure (batch method) at pH 4.0 (Fig. 7a). Meantime, considering the risk of hydrolysis of Fe(III) ions, effects of initial Fe(III) volume on the adsorption quantity (Q) of GO-MCNTs-DETA were tested alternatively (Fig. 7b). Breakthrough curves were gained by plotting the concentrations (mg L^{-1}) or volumes (mL) vs. the micrograms of Cr(III), Pb(II), and Mn(II) ions adsorbed per gram of GO-MCNTs-DETA (Fig. 7a and b). Of note, the adsorption capacities were calculated by the following equation: $Q = (C_0 - C_e)V/W$, where Q represents the adsorption capacity (mg g^{-1}), C_0 and C_e represent the initial and equilibrium concentration of Pb(II) (mg L^{-1}), respectively, W is the mass of GO-MCNTs-DETA particles (g) and V is the volume of metal ion solution (L).

From the breakthrough curves, the maximum adsorption capacities of GO-MCNTs-DETA for Cr(III), Fe(III), Pb(II), and Mn(II) ions are found to be 5.4, 13.8, 6.6, and 9.5 mg g^{-1} , respectively. The SPE results indicate that GO-MCNTs-DETA could present considerably high adsorption capacities for Cr(III), Fe(III), Pb(II), and Mn(II) ions.

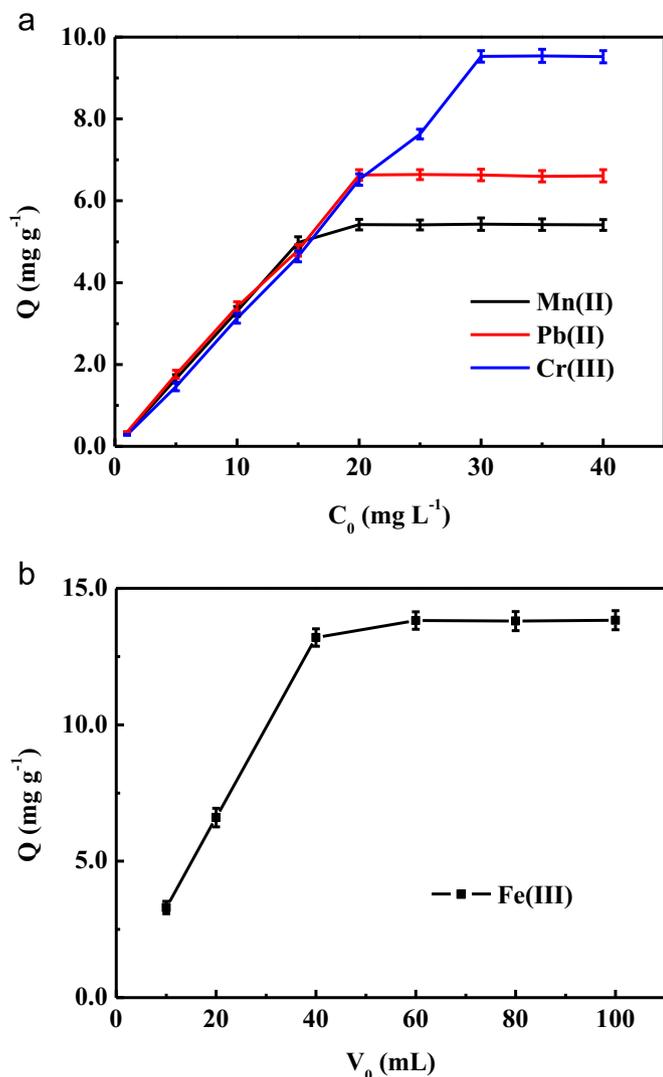


Fig. 7. (a) Effects of initial concentrations (C_0) of Cr(III), Pb(II), and Mn(II) ions on the adsorption quantities (Q) of GO-MCNTs-DETA using sample volume of 10 mL at pH 4.0; (b) effects of initial volumes (V_0) of Fe(III) ions on the adsorption quantities (Q) of GO-MCNTs-DETA using the sample concentration of 10 mg L⁻¹ at pH 4.0.

3.2.7. Effects of coexisting ions

The effects of common coexisting ions on the GO-MCNTs-DETA adsorption for Cr(III), Fe(III), Pb(II), and Mn(II) ions were studied by the batch procedure. As shown in Table 1, interestingly, the

Table 1

Effects of coexisting ions on the percent recoveries of the GO-MCNTs-DETA sorbent for Cr(III), Fe(III), Pb(II), and Mn(II) ions (1.0 μg mL⁻¹) by elution with 2 mol L⁻¹ HCl.

Co-existing ions (μg mL ⁻¹)		Recovery percentages of analytes (%)			
		Cr(III)	Fe(III)	Pb(II)	Mn(II)
K ⁺	2000	98.69	99.55	99.48	97.26
Ca ²⁺	2000	100	100	96.31	98.62
NO ₃ ⁻	2000	99.34	99.45	100	99.16
Na ⁺	2000	99.17	100	96.29	100
Mg ²⁺	2000	100	95.66	98.54	99.43
Ni ²⁺	500	100	98.93	99.01	96.45
Cu ²⁺	500	95.16	100	96.34	98.34
Zn ²⁺	500	100	100	99.90	99.43
Co ²⁺	500	96.82	99.57	97.03	99.18
Cd ²⁺	500	100	100	98.85	98.62
Hg ²⁺	100	98.25	99.06	97.18	98.46

2000-fold excess of K(I), Ca(II), Mg(II), Na(I), NO₃⁻ 500-fold Ni(II), Co(II), Cd(II), Cu(II), Zn(II) and 100-fold Hg²⁺ ions showed no significant effects on the extraction and analysis process for Cr(III), Fe(III), Pb(II), and Mn(II) ions. Yet, the reasons behind the low adsorption capacities of GO-MCNTs-DETA sorbent for the common coexisting ions remain unclear, which are being studied in our laboratory.

3.2.8. Detection precisions and limits

Under the optimized testing conditions, eleven portions of standard samples of Cr(III), Fe(III), Pb(II), and Mn(II) ions were enriched and analyzed simultaneously by using GO-MCNTs-DETA sorbent. The detection limits, estimated by 3σ rule, of the method, which were defined by International Union of Pure and Applied Chemistry, were found to be 0.16, 0.50, 0.24 and 0.38 ng mL⁻¹ for Cr(III), Fe(III), Pb(II), and Mn(II) ions, respectively. The relative standard deviations (RSDs) of the eleven replicate determinations were all lower than 3.0% for 1.0 μg mL⁻¹ Cr(III), Fe(III), Pb(II), and Mn(II) ions. The results indicate that the developed analysis method could show a favorable analysis precision for probing trace-level Cr(III), Fe(III), Pb(II), and Mn(II) ions in samples.

3.2.9. Application of the GO-MCNTs-DETA-based analysis method

The proposed extraction and analysis method using GO-MCNTs-DETA sorbent was applied for the determination of Cr(III), Fe(III), Pb(II), and Mn(II) ions in wastewater samples, with the ICP-OES data summarized in Table 2, where the standard addition method was applied. Accordingly, the proposed method could allow for the precise extraction and analysis of trace-level Cr(III), Fe(III), Pb(II), and Mn(II) ions in real samples of wastewater. Moreover, this method was applied to probe separately Cr(III), Fe(III), Pb(II), and Mn(II) ions in river sediment samples and the certified reference materials (GBW08301, China). The ICP-OES analysis results are shown in Table 3, which were compared with the certified values using a *t*-test at 95% confidence limits.

4. Conclusions

MCNTs were successfully dispersed in GO nanocolloids and further functionalized with DETA, resulting in GO-MCNTs-DETA nanocomposites serving as the novel SPE sorbent materials for the extraction of trace-level Cr(III), Fe(III), Pb(II), and Mn(II) ions in wastewater. This new solid-phase sorbent could facilitate the maximum static adsorption capacities of 5.4, 13.8, 6.6 and

Table 2

Analytical results of Cr(III), Fe(III), Pb(II), and Mn(II) ions in wastewater samples ($n=5$).

Wastewater samples	Added	Found (μg L ⁻¹)	Recovery percentages (%)
Cr(III)	0	4.53 ± 0.06	–
	5.0	9.39 ± 0.11	97.2
	10.0	14.22 ± 0.09	96.9
Fe(III)	0	5.38 ± 0.08	–
	5.0	10.15 ± 0.16	95.4
	10.0	15.65 ± 0.21	102.7
Pb(II)	0	6.26 ± 0.10	–
	5.0	11.24 ± 0.09	99.6
	10.0	16.38 ± 0.23	101.2
Mn(II)	0	3.52 ± 0.06	–
	5.0	8.46 ± 0.10	98.8
	10.0	13.26 ± 0.13	97.4

Table 3

Determination of Cr(III), Fe(III), Pb(II), and Mn(II) ions in certified sample (GBW 08301) ($n = 5$, $p = 95\%$).

Analyte	Found by present method	Certified Value
	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$
Cr(III)	87 ± 6.7	90 ± 8
Fe(III)	39248 ± 134	39400 ± 1300
Mn(II)	963 ± 31	975 ± 34
Pb(II)	81 ± 11.3	79 ± 12

9.5 mg g^{-1} for Cr(III), Fe(III), Pb(II), and Mn(II) ions, respectively, showing the adsorption capacity up to 95% within about 30 min. Moreover, the detection limits of the GO–MCNTs–DETA-based analysis method were found to be 0.16, 0.50, 0.24 and 0.38 ng mL^{-1} for Cr(III), Fe(III), Pb(II), and Mn(II) ions, respectively, with the relative standard deviation of lower than 3.0% ($n = 5$). Importantly, common coexisting ions showed no significant interference on the separation and pre-concentration of these heavy metal ions at pH 4.0. The introduction of GO nanocolloids could significantly improve the aqueous dispersion of hydrophobic MCNTs supports so as to achieve more effective and stable anchoring of DETA for selectively binding with the meaningful metal ions. Compared with other SPE sorbents, the developed GO–MCNTs–DETA sorbent could present much higher extraction efficiencies for Cr(III), Fe(III), Pb(II), and Mn(II) ions. Moreover, GO–MCNTs–DETA could facilitate the ICP–OES determination of trace-level Cr(III), Fe(III), Pb(II), and Mn(II) ions in wastewater samples with acceptable accuracy and precision. Such a new SPE sorbent holds a great promise of potential applications in the highly-effective enrichment and sensitive analysis of metal ions in different aqueous media.

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