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Use of tetraethylenepentamine-functional Fe_3O_4 magnetic polymers for matrix solid phase dispersion extraction and preconcentration of Cr(VI) in water samples at ultratrace levels

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ABSTRACT

A new method that utilizes tetraethylenepentamine-functional Fe_3O_4 magnetic polymers (TEPA-NMPs) as a solid-phase extractant for matrix solid phase dispersion extraction (MSPD) has been developed for preconcentration of Cr(VI) at ultratrace levels prior to the measurement by flame atomic absorption spectroscopy (FAAS). The separation/preconcentration conditions of Cr(VI) was investigated, including the pH value, shaking time, adsorption temperature, sample volume, desorption conditions and interfering ions. The results showed the adsorption properties of the TEPA-NMPs were highly pH dependent. The data of adsorption kinetics obeyed pseudo-second-order rate mechanism well. Adsorption thermodynamic studies suggested that the adsorption processes of Cr(VI) onto the TEPA-NMPs was endothermic and entropy favored in nature. Under the best experimental conditions, the enhancement factor was 125 times, the detection limit of the method was 0.16 μg L^{-1} and the relative standard deviation was 1.9% (n=7). Furthermore, the developed method was validated by comparing with Graphite Furnace atomic absorption spectrometry (GF-AAS) method, and has been applied for the determination of ultratrace Cr(VI) ions in the river and tap water samples with satisfactory results, which revealed the sensitivity of the proposed TEPA-NMPs MSPD-FAAS method was comparable with that of GF-AAS method.

1. Introduction

Chromium is considered to be necessary for the production of electroplating and metal finishing processes, tanning of leather, pigment and chemical industry, *etc.* [1–3], but there is public concern about chromium (VI) presence in water, field, and food due to its already probed carcinogenic and/or mutagenic effects on living organisms [1]. Recently, a series of in vitro and in vivo studies have already demonstrated that Cr(VI) induces an oxidative stress through enhanced production of reactive oxygen species (ROS) leading to genomic DNA damage and oxidative deterioration of lipids and proteins [4,5]. In addition, Cr(VI) has become one of the most frequently detected ground water at hazardous waste sites. Owing to these two contrasting effects, precise and accurate determination of Cr(VI) especially at ultratrace levels in environmental samples is required urgently for environmental protection, food and agricultural chemistry.

However, the direct determination of Cr(VI) at ultratrace levels is limited due to their low concentrations. Therefore, in ultratrace analysis, a preconcentration and/or separation are necessary to improve sensitivity and selectivity of determination [6].

Various preconcentration techniques such as solvent extraction [7], ion-exchange [8], and coprecipitation [9] have been applied for extraction of trace levels of the heavy metal ions from environmental samples. However, these methods often require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems [10]. Recently, solid-phase extraction (SPE) and matrix solid phase dispersion (MSPD) are the most common technique used for separation and enrichment of various inorganic and organic analytes due to their advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques [11–18]. Although SPE and MSPD both have so many advantages listed above in the extraction of trace levels of analytes from environmental samples, MSPD is much easier than SPE due to analytes extracted by mixing sample solution with an SPE sorbent rather than passing it through an SPE column.

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In SPE and MSPD procedure, the choice of appropriate adsorbent is a critical factor to obtain full recovery and high enrichment factor [14,16,19]. In the case of Cr(VI), many kinds of adsorbents for wastewater treatment have been developed, such as polyelectrolyte-modified multi-walled carbon nanotubes [20], activated alumina [21], iron phosphate [22] and treated sawdust [23], ethylenediamine-functionalized Fe_3O_4 magnetic polymers [24] but few of them are used for preconcentration of Cr(VI) at ultratrace levels. Recently, Kim et al. reported a kind of hybrid mesoporous material used to extract and preconcentrate Cr(VI) in water samples at ultratrace levels [13]. Although the SPE on hybrid mesoporous material yielded satisfactory analyte recovery, its enrichment fact for Cr(VI) was only 16 times. Once these adsorbents mentioned above were used for MSPD procedure, there would be some other problems, e.g., how to separate the adsorbed adsorbent quickly and shorten the separation time from the solution. Therefore, to explore more suitable adsorbents which can overcome the difficulty mentioned above and have strong adsorption ability for MSPD extraction and preconcentration of Cr(VI) at ultratrace levels has become a new great challenge.

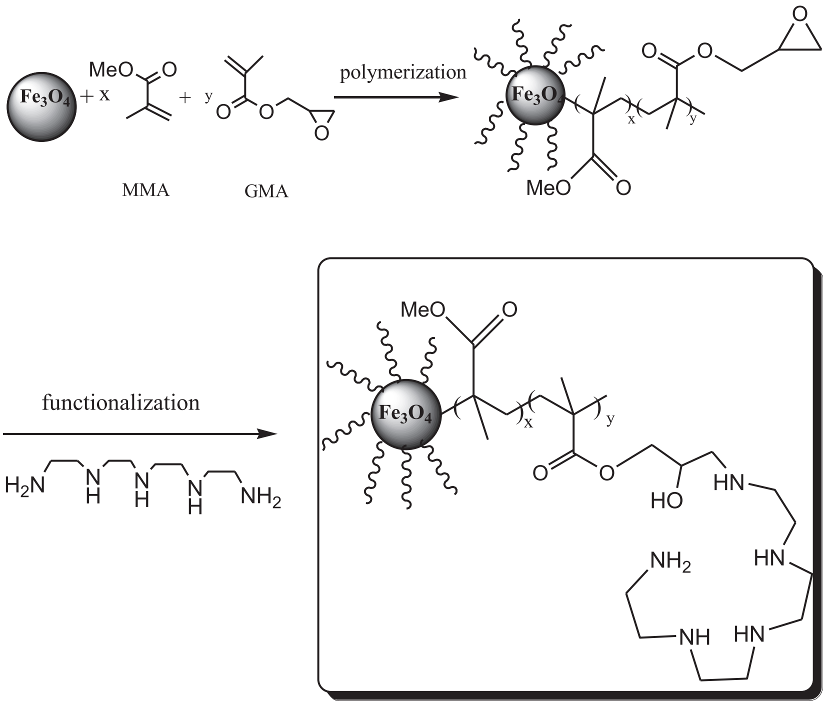
In recent years, magnetic polymeric particles, due to their large surface area, high number of surface active sites, and relatively rapid and easy magnetic separation via magnetic field, have been used in biomedical and bioengineering [25–27]. Moreover, owing to their unique characteristic and strong adsorption ability, magnetic polymeric particles also offer a high potential in several areas of application such as adsorbent for removal and/or preconcentration of many kinds of inorganic and organic pollutants such as pesticides and metal ions [28–30]. In our previous work, a kind of core-shell structured tetraethylenepentamine (TEPA)-functionalized nano magnetic polymer adsorbents, named as TEPA-NMPs had been prepared by improved co-polymerization method followed by ring-opening reaction [31]. The TEPA-NMPs had been verified to be very promising particles for the removal of Cr(VI) in wastewater. The maximum adsorption capacity of TEPA-NMPs to Cr(VI) was found to be 370.4 mg g^{-1} at 35 °C and pH of 2.0. And so, TEPA-NMPs are expected to be more selective and much stronger adsorption ability than other adsorbents reported in the literature for the MSPD extraction of Cr(VI) at ultratrace levels. However, to the best of our knowledge, few such studies have been reported so far.

The focus of the present research is development and validation of rapid methods for the analysis of Cr(VI) present in the water samples at ultratrace levels using MSPD followed by FAAS analysis. In MSPD, the solid phase adsorbent is thoroughly mixed with sample solutions. Dynamic mixing uses less sorbent and provides faster extractions compared to classical SPE. Cr(VI) is concentrated on the adsorbent and can be eluted in concentrated solution. In this work, the TEPA-NMPs used as selective adsorbent in MSPD for separation and preconcentration of Cr(VI). Parameters that can affect the adsorption and recovery efficiency of Cr(VI), such as pH value, the shaking time, the sample volume *etc*, were assessed and optimized from laboratory batch tests. Then, the method was applied to the analysis of water samples with satisfactory results, which suggests that this method can be complimentary to MSPD for separation and preconcentration of metal ions in water samples.

2. Experimental

2.1. Materials and reagents

Reagents of analytical and spectral purity were used for all experiments and double distilled deionized water was used throughout. Standard labware and glassware used were repeatedly cleaned with HNO_3 and rinsed with double distilled water, according to a published procedure [32]. Standard stock solutions of chromium(VI) at a concentration of 1000 mg L^{-1} was prepared by dissolving a known quantity of spectral pure grade chemicals potassium dichromate ($K_2Cr_2O_7$) (The Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) in double distilled water with the addition of hydrochloric acid (The Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and further diluted daily prior to use. TEPA-NMPs used in the experiment were prepared in our laboratory according to the reported procedure [24,31]. The TEPA-NMPs were well multidispersed with an average diameter of around 30 nm, which were much smaller than the EDA-MPs with the average diameter



Scheme 1. Preparation procedure of TEPA-NMPs.

Table 1
Instrumental conditions for Cr(VI) determination, graphite furnace temperature program and parameters of GF-AAS method.

Spectrometer parameter				
(a)				
Wavelength				357.9 nm
Slit width				0.7 nm
Lamp current				8 mA
Background correction				Deuterium lamp
Sample volume				20 μL
Stage	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon gas flow (L min^{-1})
(b)				
Drying I	110	5	30	250
Drying II	160	15	30	250
Ashing	800	10	20	250
Atomization	2300	0	5	0
Cleaning	2250	1	3	250
Parameters				
(c)				
Linearity range				0.5–20 μg L^{-1}
detection limit				0.1 μg L^{-1}

Table 2
Instrumental conditions for Cr(VI) determination and parameters of FAAS method.

Spectrometer parameter	
(a)	
Wavelength	357.9 nm
Slit width	0.2 nm
Lamp current	8 mA
Burnet height	9 mm
Background correction	Deuterium lamp
Parameters	
(b)	
Linearity range	50–1250 μg L^{-1}
detection limit	20 μg L^{-1}

ranged from 300 to 600 nm. The percentages of nitrogen of TEPA-NMPs was found to be 9.89%, which was much higher than the EDA-MPs with the percentages of nitrogen ranged from 1.80% to 3.87%. And so, the maximum adsorption capacity of TEPA-NMPs to Cr(VI) was found to be 370.4 mg g^{-1}, which was much higher than the EDA-MPs with the maximum adsorption capacity ranged from 32.15 to 61.35 mg g^{-1}. The preparation procedure of TEPA-NMPs was illustrated in Scheme 1.

2.2. Instruments and apparatus

Determination of Cr(VI) after adsorption were performed with a PE AA800 Graphite Furnace atomic absorption spectrometry (GF-AAS) equipped with a graphite furnace atomizer THGA-600 and an auto-sampler (AS 800). Deuterium background correction was employed to correct nonspecific absorbance. Peak height was chosen as the analytical signal. The instrumental parameters and temperature program for the GF-AAS are tabulated in Table 1. Determination of Cr(VI) after MSPD extraction and preconcentration were performed with a flame atomic absorption spectroscopy (FAAS) (Shimadzu AA-6701F atomic absorption flame emission spectrophotometer). The instrumental parameters for the FAAS are tabulated in Table 2.

2.3. Sample preparation

River water was collected from Yaojiang River, Yongjiang River and Fenghua River, Ningbo, China. The pH value of water sample was adjusted to 5.5 with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH prior to use, filtered through a nylon membrane (0.45 μm), and then stored in pre-cleaned polyethylene bottles prior to use. Tap water samples taken from our research laboratory (Ningbo Municipal Center for Disease Control and Prevention, Ningbo, China) were analyzed without pretreatment.

2.4. Adsorption procedure

Batch adsorption studies were performed by mixing 0.02 g TEPA-NMPs with 250 mL $K_2Cr_2O_7$ solution of varying concentration from 1.0 to 100 μg L^{-1} in a 500 mL stopper conical flask. 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH solutions were used for pH adjustment. To investigate the effect of pH, 250 mL of 5, 20, 50 and 100 μg L^{-1} Cr(VI) with pH ranging from 2.0–9.0 were mixed with 0.02 g TEPA-NMPs for 24 h to reach equilibrium. For the effect of shaking time studies, under pH value of 5.5, 0.02 g TEPA-NMPs was added into 250 mL of 5, 20, 50 and 100 μg L^{-1} Cr(VI) with contact time ranging from 1–120 min, and samples was taken for Cr(VI) concentration measurements at specific time intervals. For the thermodynamics studies, 0.02 g TEPA-NMPs was added into 250 mL of 5, 20, 50 and 100 μg L^{-1} Cr(VI) with temperature ranging from 283.15 to 323.15 K. When the maximum volume was investigated, different volumes of 100 μg L^{-1}Cr (VI) increased from 50 to 300 mL at pH 5.5 were mixed with 0.02 g TEPA-NMPs for 60 min to reach equilibrium.

2.5. Elution procedure

Under the adsorption conditions, 0.02 g TEPA-NMPs were mixed with 250 mL $K_2Cr_2O_7$ solution at 5, 20, 50 and 100 μg L^{-1} in a 500 mL stopper conical flask. After adsorption, the resulting adsorbents (Cr(VI)-TEPA-NMPs, *hereinafter*) were isolated under magnetic field and washed with water. Then, batch elution studies were performed by eluting the Cr(VI)-TEPA-NMPs with 2.0 mL NaOH solutions of varying concentration from 0.01 to 2.0 mol L^{-1}.

2.6. MSPD extraction and preconcentration procedure

The concentrations of Cr(VI) at 5, 20, 50 and 100 μg L^{-1} were prepared by appropriate dilution of the stock solutions (1000 mg L^{-1}) with double distilled water, Yaojiang River, Yongjiang River, Fenghua River and Tap water, respectively. Batch adsorption studies were performed by mixing 0.02 g TEPA-NMPs with 250 mL Cr(VI) solution mentioned above in a 500 mL stopper conical flask. The pH value of Cr(VI) solution was adjusted to 5.5 with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH. The mixture was shaken vigorously for 60 min to facilitate adsorption of Cr(VI) onto the adsorbents. After adsorption, the concentration of Cr(VI) in the solution was directly determined by GF-AAS. The Cr(VI)-TEPA-NMPs were isolated under magnetic field and washed with water. Then, the Cr(VI)-TEPA-NMPs was eluted by using 2.0 mL NaOH solutions at 0.5 mol L^{-1} prior to the determination of Cr(VI) in the aqueous solution by FAAS.

3. Results and discussion

3.1. Effect of pH

The pH of the solution plays a unique role on metal-chelate formation and subsequent extraction. The reaction between Cr(VI) and the adsorbent (TEPA-NMPs) can be influenced by changes of pH value. Firstly, protons in acid solution can protonate binding sites of the chelating molecules. Secondly, hydroxide in basic solution may complex and precipitate Cr(VI). Therefore, pH of a solution is the first parameter to be optimized.

In order to investigate the effect pH value on the recovery, 250 mL of 5, 20, 50 and 100 μg L^{-1} Cr(VI) with pH ranging from 2.0 to 9.0 were mixed with 0.02 g TEPA-NMPs for 24 h to reach equilibrium. The adsorption experiments were in triplicates and the results were shown in Fig. 1. It can be seen that the adsorption quantity of Cr(VI) increased from 26.3% to 98.6%, 30.5% to 99.1%, 59.8% to 99.2%, and 62.1% to 99.4% gradually with an increase of pH value from 2.0 to 5.5 for the concentration of Cr (VI) at 5, 20, 50 and 100 μg L^{-1}, respectively. Above pH 5.5, the adsorption quantity of Cr(VI) decreased with the increase of pH value in the studied pH ranges. Furthermore, the adsorption quantity of Cr(VI) increased with the increase of the initial concentration of Cr(VI) from 5 to 100 μg L^{-1}, which resulted from the high maximum adsorption capacity of TEPA-NMPs to Cr(VI) (370.4 mg g^{-1}).

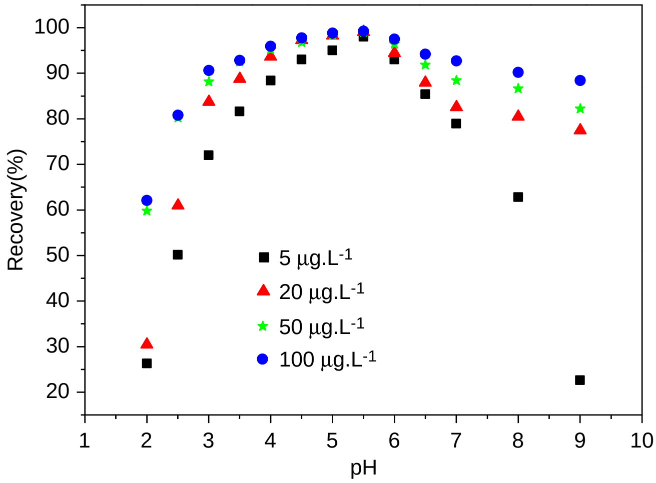


Fig. 1. Effect of pH value on the recovery of Cr(VI) by TEPA-NMPs.

The dependence of Cr(VI) on the pH can be explained from the perspective of surface chemistry in an aqueous phase. The surfaces of TEPA-NMPs are generally covered with amino groups that vary in form at different pH levels. According to our previous work, the adsorption mechanism of Cr(VI) adsorption onto TEPA-NMPs was related with electrostatic attraction, ion exchange and coordination interactions as described in Eqs. (1) and (2), respectively (Scheme 2).

$$-NH_3^+ + HCrO_4^- \rightarrow -NH_3^+ \cdots\cdots HCrO_4^- \quad (1)$$

$$-NH_3^+Cl^- + HCrO_4^- \rightarrow -NH_3^+HCrO_4^- + Cl^- \quad (2)$$

Under acidic conditions, amino groups were easier to be protonated, and the chance of the ion exchange and electrostatic attraction was much more than the coordination interactions. With increasing of the pH value from 2.0 to 5.5, the concentration of H^+ was decreased gradually, and the chance of the coordination interactions was increased, which compensated the loss of the removal efficiency resulting from electrostatic attraction and ion exchange with the increasing of the pH value. And so, the adsorption quantity of Cr(VI) increased gradually with an increase of pH value from 2.0 to 5.5. Above pH 5.5, the concentration of H^+ was decreased rapidly, and so the ability of $-NH_2$ to be protonated was much weakened; at the same time the concentration of OH^-, which competed with $HCrO_4^-$, was increased, both of these reasons resulting in the adsorption quantity of Cr(VI) decreased.

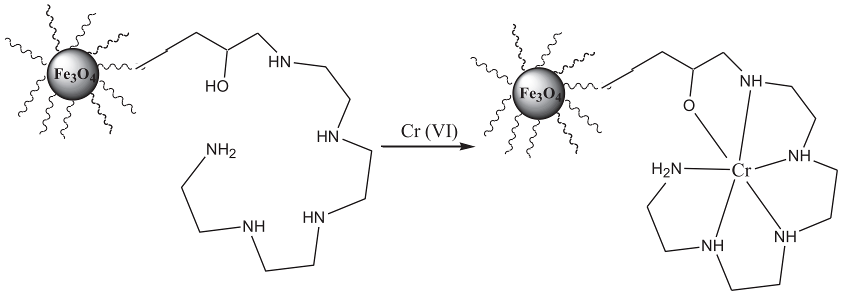
At pH 5.5 it was possible to carry out the determination of Cr(VI). So, pH 5.5 was chosen as the optimum pH for further studies.

3.2. Effect of shaking time

The shaking time is an important factor in determining the possibility of application of TEPA-NMPs for the selective extraction and preconcentration of Cr(VI) ions. In order to investigate the effect shaking time on the adsorption properties, 250 mL of 5, 20, 50 and 100 μg L^{-1} Cr(VI) solution with pH value at 5.5 were mixed with 0.02 g TEPA-NMPs. The results showed that the rate of Cr(VI) uptake was initially quite high, followed by a much slower subsequent adsorption quantity leading gradually to an equilibrium condition.

The adsorption kinetic data obtained from batch experiments have been analyzed using a pseudo-second-order rate equation [33] as

$$t/q_t = 1/k_2 q_{e\cdot c}^2 + t/q_{e\cdot c} \quad (3)$$



Scheme 2. Coordination interactions between TEPA-NMPs and Cr(VI).

where q_t is the amounts of Cr(VI) adsorbed onto adsorbent any time t(mg g^{-1}) and k_2 is the second-order rate constant at the equilibrium (g mg^{-1} min^{-1}). Thus, by plotting t/q_t against t, the values of k_2 (slope^2/intercept), $q_{e.c}$ (1/slope) and $k_2 q_{e\cdot c}^2$ (the initial adsorption rate (mg g^{-1} min^{-1}), 1/intercept) can be determined graphically from the slope and intercept of the revealed plots.

In this work, the pseudo-second-order rate equation of Cr(VI) adsorbed onto TEPA-NMPs was $t/q_t = 0.4973t + 0.8572$ ($R^2 = 0.9999$), which indicated that TEPA-NMPs has rapid adsorption kinetics. Hence, 60 min of stirring was enough to reach maximum values of separation and preconcentration of Cr(VI) ions. Therefore, it is suitable for application in the preconcentration of ultratrace Cr(VI) ions.

3.3. Adsorption thermodynamic studies

In order to evaluate the thermodynamic parameters for adsorption of Cr(VI) onto TEPA-NMPs, the adsorption studies were carried out at temperature from 283.15 to 323.15 K, and the adsorption thermodynamic data obtained from batch experiments were analyzed by using Eq. (4) [34]:

$$ln\ K_D = -\frac{\Delta H^\theta}{RT} \cdot \frac{\Delta S^\theta}{R} \tag{4}$$

where ΔH^θ and ΔS^θ are the values of standard enthalpy change, and standard entropy change, respectively. K_D is the distribution coefficient, which is defined as Eq. (5) [34]:

$$K_D = \frac{\text{Amount of Cr(VI) adsorbed on TEPA-NMPs}}{\text{Amount of Cr(VI) in solution equilibrium}} \times \frac{V}{m} \tag{5}$$

In this work, the adsorption thermodynamic equation of Cr(VI) adsorbed onto TEPA-NMPs was $\ln K_D = -4650.7/T + 16.639$ ($R^2 = 0.9661$), and the results were shown in Fig. 2.

It can be seen that adsorption quantity of Cr(VI) increased with the increasing of temperature, which indicated that adsorption of Cr(VI) onto TEPA-NMPs was endothermic and entropy favored in nature. However, with increasing of the temperature 283.15 to 323.15 K, the adsorption quantity of Cr(VI) was increased from 97.32% to 99.58%, 97.81% to 99.74%, 98.29% to 99.79% and 98.58% to 99.81% for the concentration of Cr (VI) at 5, 20, 50 and 100 μg L^{-1}, respectively. And so, at temperature 303.15 K it was possible to carry out the determination of Cr(VI), and temperature 303.15 K was chosen as the optimum temperature for further studies.

3.4. Preconcentration, maximum of sample volume and enrichment factor

The preconcentration condition was carried out by using NaOH solutions of varying concentration from 0.01 to 2.0 mol L^{-1} for elution of Cr(VI)-TEPA-NMPs obtained by using 250 mL of 5, 20, 50 and 100 μg L^{-1} Cr(VI) solution with pH value at 5.5 mixed with 0.02 g TEPA-NMPs for 60 min to reach adsorption equilibrium, and the results were shown in Fig. 3. The obtained results showed that the elute solution of 2.0 mL of NaOH solutions at 0.5 mol L^{-1} was sufficient for complete elution for Cr(VI)-TEPA-NMPs.

In order to obtain reliable and reproducible analytical results and a high concentration factor, it is very important to get satisfactory recoveries for analyte studied in as large a volume of sample solutions as possible. The maximum volume was studied by using the TEPA-NMPs-MSPD procedure with the volume of Cr(VI) solutions (100 μg L^{-1}) ranging from 50 to 300 mL. Following the experimental procedure, the recoveries of the analyte at different volumes were obtained, and the results showed that the maximum volume could be up to 250 mL with the recovery $>$99.8%. Therefore, 250 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. And a high enrichment factor of 125 times was obtained because the final elute solution was 2.0 mL in these experiments.

Furthermore, the similar results were also obtained in the case of other kinds of water, i.e., Yaojiang River, Yongjiang River, Fenghua River and Tap water, respectively.

3.5. Effect of the mass of adsorbent and reusability of TEPA-NMPs

When designing the TEPA-NMPs-MSPD procedure, it is the primary consideration to employ a suitable mass of the TEPA-NMPs without affecting the recoveries. For this purpose, the effectiveness of various mass of adsorbents on recoveries was studied with Tap water sample spiked with Cr (VI) at 5, 50 and 100 μg L^{-1}. The spiked simples were preconcentrated by using different mass of the TEPA-NMPs, and the results were shown in Fig. 4. It can be seen that the mass of TEPA-NMPs adsorbents had an impact on recoveries of Cr (VI), and it was easy to discern a clear trend in the recovery when increasing the mass of adsorbents from 5 to 30 mg.

With the increasing of the mass of TEPA-NMPs adsorbents from 5 to 30 mg, the recoveries of Cr (VI) increased from 90.1% to

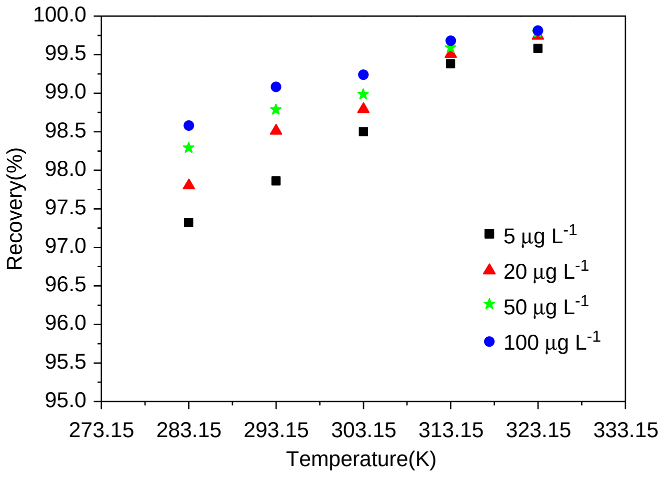


Fig. 2. Effect of temperature on the recovery of Cr(VI) by TEPA-NMPs.

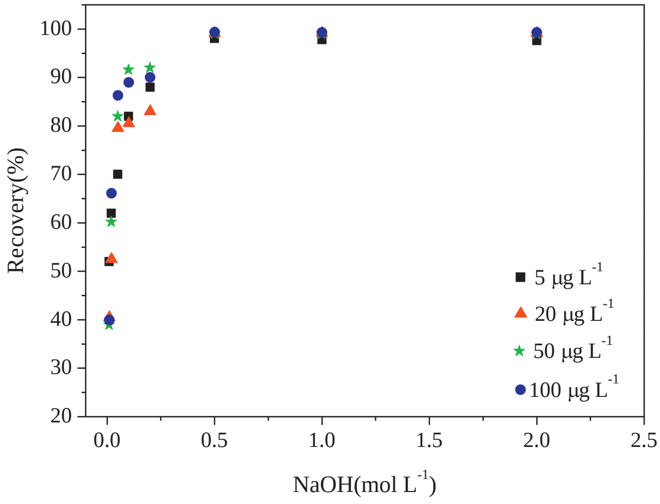


Fig. 3. Effect of the concentration of NaOH solution for elution on the recovery.

102.0%, 81.9% to 100.3% and 76.2% to 101.6% for Cr (VI) at 5, 50 and 100 μg L^{-1}, respectively. And so, it can be seen that the least mass of TEPA-NMPs adsorbents of 20 mg could ensure to obtain satisfactory recoveries ranged from 98.2% to 102.4% for all concentrations of Cr (VI) in this study. Based on the results of the experiments, it can be seen that combination of the least mass of TEPA-NMPs adsorbents in the proportion of 20 mg per 250 mL water sample would ensure efficient preconcentration of Cr (VI).

In order to check the longevity of the adsorbent, TEPA-NMPs were subjected to several adsorption and elution experiments. The capacity of the adsorbent was found to be practically constant (variation of 0.5–2%) after repeated use of more than ten times, thus the multiple use of adsorbent was seen to be feasible.

3.6. *Interferences*

The potential interferences of some ions on the preconcentration and determination of Cr (VI) were investigated. In these experiments, solutions of 100 μg L^{-1} of Cr (VI) containing the interfering ions were treated according to the optimized procedures. The tolerance limit was set as the amount of ions causing recoveries of the examined elements to be less than 90%. The results showed that in excess of 2500-fold K(I), Na(I), Ca(II); 1000-fold Mg(II), Fe(III), Cr(III); 250-fold Mn(II), Ni(II); 100-fold Cu(II), Zn(II), Cd(II), Hg(II) ions had no significant interferences in the preconcentration and determination of the analyses. In addition, a number of common anions like Cl^-, SO_4^{2-}, NO_3^- and F^- were tested. The results showed that they did not interfere at the concentrations up to 100 mg L^{-1}. The phenomenon may be due to the high maximum adsorption capacity of TEPA-NMPs to Cr(VI) (370.4 mg g^{-1}) and the low adsorbing capacity or rates for interfering ions. It can be seen that the presence of major coexisting ions has no obvious influences on the determination of Cr(VI) under the selected conditions.

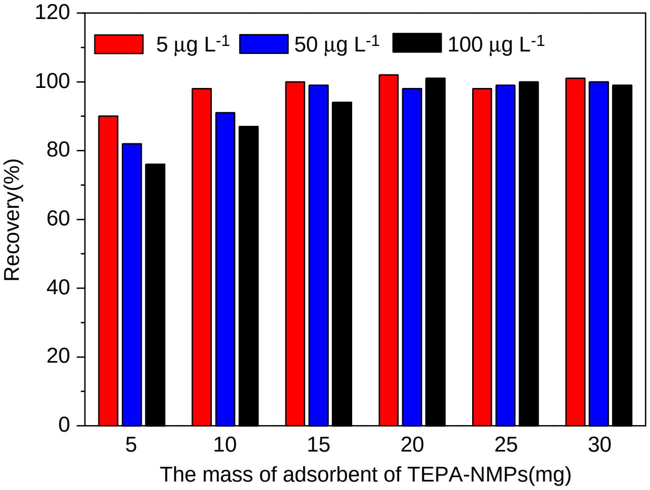


Fig. 4. Effect of the mass of adsorbent of TEPA-NMPs.

3.7. *Detection limits and precision*

In accordance with the definition of IUPAC, the detection limit of the method was calculated based on three times the standard deviation of seven runs of the blank solution. The detection limits (3σ) was found to be 0.16 μg $L^{-1}$for Cr(VI). The relative standard deviations (RSDs) of the seven replicate determinations was 1.9%, which indicated that the method had good precision for the analysis of ultratrace Cr(VI) in water samples.

Comparison of the proposed method with other methods to extract and determine the similar metal ions was shown in Table 3. In the present work, better enhancement factors were obtained for Cr(VI) ions in comparison with those methods. Precision of the proposed method is comparable with on-line CPE and follow injection methods and it is better than on-line SPE methods. In the on-line mode of CPE, heating of sample and trapping of the surfactant-rich phase on a column and elution of the entrapped analytes are need, and these steps are time-consuming and labor intensive. In addition, the detection of the proposed method (FAAS) is much cheaper than the on-line CPE and Flow injection methods (ICP-OES). In comparison with the methods mentioned above, the proposed method is simple, fast and cheap.

3.8. *Application of the method*

The proposed TEPA-NMPs MSPD-FAAS method and GF-AAS method have been applied to the determination of ultratrace Cr(VI) in River water and Tap water samples. The results were listed in Table 4.

It can be seen that the analytical results for all water samples by using TEPA-NMPs MSPD-FAAS method were in agreement with the GF-AAS method. For the analysis of natural River water and Tap water samples, the standard addition method was used, the recoveries of Cr(VI) were in the range of 98%–101%. These results indicated the suitability of TEPA-NMPs for selective MSPD and determination of ultratrace Cr (VI) in environmental water samples.

4. Conclusion

For the first time, magnetic isolate was used in the MSPD with magnetic polymeric particles (TEPA-NMPs) for separation/preconcentration of Cr(VI) at ultratrace in water samples, which can

Table 3
Comparison of the proposed method with other methods to extract and determine the similar metal ions.

Metal ions	System	Method	EF[a]	DL[b] (μg L^{-1})	RSD (%)	Detection	Ref.
Cr	DLLME-SFO	Flow injection	96	0.1	4.1	ICP-OES	[6]
Cr (VI)	Hybrid mesoporous material	On-line SPE	16	0.09	1.8	UV–vis	[13]
Cr(VI)/Cr(III)	PMBP/Triton X-100	Off-line CPE	20	0.81	–	FAAS	[35]
Cr	Chromosorb108/bathocuproinedsulfonic	On-line SPE	80	0.50	1.0	FAAS	[36]
Cr	TTA/Triton X-114	On-line CPE	81	0.2	3.7	ICP-OES	[37]
Cr (VI)	Amberlite IRA-910	Column-in-tip	5.6	0.08	3.5	ET-AAS	[38]
Cr (VI)	C18-PS/DVB beads	SI-BI-LOV	12.9	0.03	3.8	ET-AAS	[39]
Cr (VI)	TEPA-NMPs	Off-line MSPD	125	0.16	1.9	FAAS	This work

[a] Enrichment factor.
[b] Detection limit.

Table 4
Determination of ultratrace levels of Cr (VI) in River water and Tap water samples by using TEPA-NMPs MSPD-FAAS and GF-AAS method.

Sample	TEPA-NMPs MSPD-FAAS			GF-AAS		
	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)
Yaojiang water	0	4.39	–	0	4.28	–
	1	5.41	100.5	1	5.22	98.6
	10	14.50	102.5	10	14.19	97.9
Yongjiang water	0	3.56	–	0	3.48	–
	1	4.65	102.5	1	4.45	99.1
	10	13.42	96.1	10	13.42	98.2
Fenghuajiang water	0	6.21	–	0	6.26	–
	1	7.26	100.8	1	7.28	100.3
	10	16.32	101.8	10	16.25	99.8
Tap water	0	1.06	–	0	0.98	–
	1	2.04	98.1	1	1.99	101.0
	10	11.07	100.9	10	10.97	99.0

separate the adsorbed adsorbent quickly and shorten the separation time from the solution. This simple, fast and cost effective procedure is based on the adsorption of Cr(VI) onto TEPA-NMPs by electrostatic attraction, ion exchange and coordination interactions. The proposed method in comparison with online CPE and on-line SPE has advantages such as simplicity, short extraction time and low cost. It was also of relevance the high sensitivity showed by the GF-AAS method for Cr(VI), providing in case detection limit at $\mu g\ L^{-1}$ level. The preconcentration method allows Cr(VI) determination in different aqueous samples with good accuracy and reproducibility.

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