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Novel surface molecularly imprinted material modified multi-walled carbon nanotubes as solid-phase extraction sorbent for selective extraction gallium ion from fly ash

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ABSTRACT

A new gallium (Ga(III)) ion-imprinted multi-walled carbon nanotubes (CNTs) composite sorbent was synthesized by a surface imprinting technique. The Ga(III) ion-imprinted/multi-walled carbon nanotubes (Ga(III)-imprinted/CNTs) sorbent was characterized by Fourier transform infrared (FT-IR), X-ray diffraction (XRD), nitrogen adsorption experiment, static adsorption experiment, and solid-phase extraction (SPE) experiment. The effects of sample volume, sample pH, washing and elution conditions on the extraction of Ga(III) ion from real sample were studied in detail. The imprinted sorbent offered a fast kinetics for the adsorption of Ga(III). The maximum static adsorption capacity of the imprinted sorbent towards was 58.8 μmol g^{-1}. The largest selectivity coefficient for Ga(III) in the presence of Al(III) was over 57.3. Compared with non-imprinted sorbent, the imprinted sorbent showed good imprinting effect for Ga(III) ion, the imprinting factor (α) was 2.6, the selectivity factor (β) was 2.4 and 2.9 for Al(III) and Zn(II), respectively. The developed imprinted SPE method was applied successfully to the detection of trace Ga(III) ion in fly ash samples with satisfactory results.

1. Introduction

Recently, along with the rapid development of IT technology, semiconductor materials have completed leaps of the first-generation silicide and second-generation gallium arsenide to the third-generation gallium nitride. So gallium and their representatives IIIA compound play a major role in this area [1]. However, exposure to airborne particulates of GaP, GaAs and AlGaAs may result in potential health hazards and toxicity [2]. Even at low gallium doses, gallium and its compounds could be combined with transferrin-bound iron (Tf–Fe) in blood plasma after entering human body and be eventually excreted in urine. As a result, gallium in urine (Ga–U) is regarded as a biological indicator, and gallium concentration in human urine samples as low as 0.02–0.28 ppb has been reported [3]. Meanwhile, many investigations have presented the successful recovery of gallium from various matrices [4]. An inherently safer and cleaner sample treatment procedure must be urgently developed for the analysis of gallium.

Solid-phase extraction (SPE) owing to its flexibility, environmental friendly, absence of emulsion, simplicity, sampling in the field, safety and ease of automation, is a preferred method of separation and enrichment of gallium [5,6]. SPE requests that gallium adsorbent own stronger selective adsorption ability to extract in the composition of the complex simple [7,8]. Consequently, the development of reliable methods for achieving specific and efficient adsorbent of metal gallium is of particular significance. Molecularly imprinted polymers (MIPs) with predetermined selectivity for separation can be achieved separation and enrichment of gallium. In the process of molecular imprinting, appropriate functional monomers are introduced to interact with template molecules, and then the functional groups on the monomers are fixed with chemical cross-linkers [9]. Extraction of the template molecules leaves predetermined arrangement of ligands and tailored binding pocket [10]. Such the imprinted polymer shows a special affinity for the template molecule over other structurally related compounds [11]. For metal ions, molecular imprinting can be interpreted as ionic imprinting [12].

An efficient adsorbent should consist of a stable and insoluble porous matrix having suitable active groups that interact with metal ions. Multi-walled carbon nanotubes (CNTs) are ideal support materials because they have strong interactions, stable under acidic conditions, no swelling and large surface area [13]. Recently, CNTs have been attracted great attention [14]. For example, Liu et

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al. reported using oxidized CNTs (CNTs-COOH) coated on the outer surface of the fused-silica tube as solid-phase microextraction sorbent coupling to high-performance liquid chromatography (HPLC) to detect the substituted aniline compounds [6]. CNTs could serve as the reinforcing element in a polymer or metal matrix in fabricating new advanced materials (CNT-incorporated films) [15,16]. The effective utilization of CNTs depends strongly on the modification modified of CNTs. Especially, metal ion-imprinted–CNTs composite material should improve the selective affinity for the template ion [17–19]. Although some of imprinted materials can exhibit specific interactions with soft Lewis acids without the particular ligand at the prepolymerization [4,12], the selectivity of these materials is usually unremarkable. The reason may be many metals have the ability to bind with functional monomer, however, the stereochemical interactions between the ligand and metal ion were not considered [20].

In this work, Ga(III)-imprinted copolymers were synthesized using Ga(III) ion-8-hydroxyquinoline complex (Ga(III)-8-HQ) as a template molecule, methacrylic acid (MAA) as a monomer, ethyleneglycoldimethacrylate (EGDMA) as a cross-linker and 2,2-azobisisobutyronitrile (AIBN) as an initiator. After removal of Ga(III) ion and 8-hydroxyquinoline, Ga(III)-imprinted/CNTs composite materials were used for solid-phase extraction and preconcentration of Ga(III) ion in fly ash samples. The effect of the extraction efficiency on Ga(III) ion from fly ash lixivium were evaluated and optimized. The characterization of this Ga(III)-imprinted/CNTs composite material and its applicability to selective solid-phase extraction of Ga(III) ion were discussed in detail.

2. Experimental

2.1. Materials and reagents

All the chemicals were in analytical grade. Distilled water was used throughout this work. Gallium, aluminium and zinc were used in the form of $GaCl_3$, $AlCl_3$ and $ZnCl_2$, respectively. Multi-walled carbon nanotubes (CNTs, 95%, diameters ranging from 20 to 40 nm, lengths ranging from 500 to 50 μm) were obtained from Shenzhen Carbon Nanotechnologies Co. Ltd (China). Methacrylic acid (MAA), EGDMA and acrylamide were purchased from Sigma (USA). Aniline, ethoxyethanol, methanol, chloroform, 8-hydroxyquinoline (8-HQ), AIBN, sodium hydroxide (NaOH), hydrochloric acid, ethanol (HPLC grade), acetic acid, thionyl chloride ($SOCl_2$), sodium acetate and N,N′-dimethylformamide (DMF) were obtained from Changsha chemical reagent company (Hunan, China).

2.2. Instrumentation

Flame atomic absorption spectrometry (FAAS) analysis was performed using a Shimadzu AA6300 atomic absorption spectrophotometer (Japan). The AAS instrument was controlled by a SOLAARS operation software. Scanning electron microscopy (SEM) images were obtained on a JSM-6700F field emission scanning electron microscope (Japan). Fourier transform infrared (FT-IR) spectra (4000–400 cm^{-1}) in KBr were recorded using a Magna-560 spectrometer (Nicolet, USA). X-ray diffraction (XRD) was performed on Siemens D 5005 powder X-ray diffractometer. Nitrogen adsorption measurement was performed on an Omnisorp 100CX (Coulter, USA) apparatus.

2.3. Pretreatment of CNTs

A typical free radical reaction using AIBN as a radical initiator was adopted to obtain carboxylic acid-functionalized CNTs (CNTs/COOH). Briefly, crude CNTs (0.5 g) and 0.1 g AIBN were dispersed in 50 mL of toluene under sonication for 10 min. Then the mixture was stirred continuously at 75 °C for 4 h under the protection of nitrogen. Cooled to room temperature, the mixture was filtered through a 0.22 μm polycarbonate membrane and washed thoroughly with toluene for four times. The filtered solid was dried under vacuum, obtaining AIBN-modified CNTs black solid.

AIBN-modified CNTs (0.5 g) were dispersed in 50 mL of NaOH methanol solution (10 mol L^{-1}) at 60 °C for 48 h under reflux. After completion of the reaction, the resulting solid was collected by filtration, washed repeatedly with 6 mol L^{-1} HCl for several times until the pH value of the filtrate was 3, again washed thoroughly with distilled water, and dried under vacuum at 70 °C for 8 h, obtaining carboxylic acid-functionalized CNTs (CNTs/COOH).

CNTs/COOH (0.5 g) was suspended in 30 mL of $SOCl_2$ at 60 °C for 24 h under reflux. The mixture was filtered and the solid was washed with DMF for several times to remove the excess $SOCl_2$ and dried under vacuum to obtain CNTs/COCl. Then, CNTs/COCl (0.5 g), 10.0 mL of aniline and 2.0 g of acrylamide were dispersed in 50 mL of DMF. The mixture suspensions were stirred at 45 °C for 24 h and then collected by centrifugation and washed with DMF. Finally, the product was dried overnight in a vacuum desiccator to obtain vinyl and phenyl group functionalized CNTs (CNTs/V/P).

2.4. Preparation of Ga(III)-imprinted/CNTs sorbent

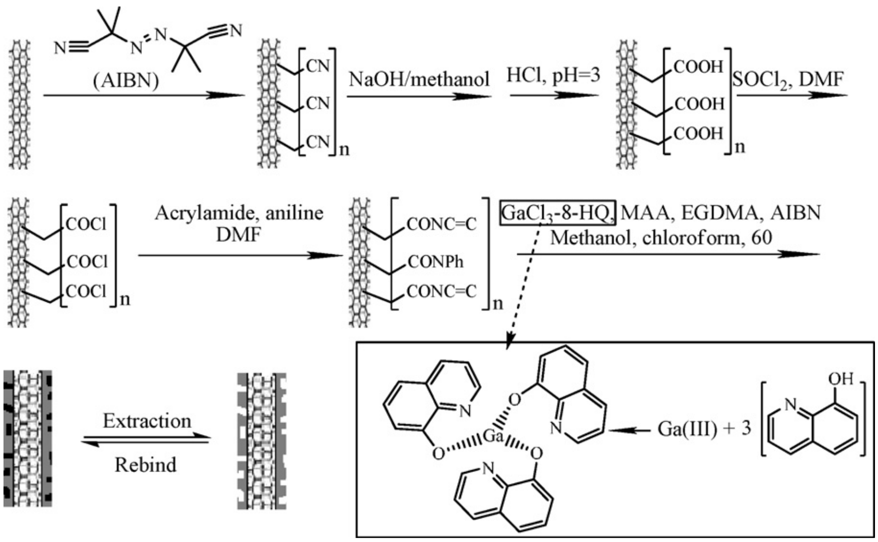
Using Ga(III) ion complex of 8-HQ as a template, Ga(III)-imprinted/CNTs sorbent was prepared by selective polymerizing MIPs onto the CNTs/V/P surface. The amount of $GaCl_3$, 8-HQ, MAA, EGDMA and AIBN are described in Table 1 . Briefly, CNTs/V/P was added to the mixing solvent of 20 mL of chloroform and 20 mL of methanol and purged with N_2 under magnetic stirring. The pre-prepared mixture of $GaCl_3$, 8-HQ and MAA dissolved by 10 mL of chloroform were added to the reactor and mixed for 30 min to form a complex of template molecule and functional monomer. Then, EGDMA and AIBN were added. The reaction was allowed to process at 60 °C for 24 h. The resulting products were collected by centrifugation and washed thoroughly with ethanol to discard the reagents. Then, the composites were eluted by the mixing solvent of ethanol and acetic acid (9:1, v/v) for several times to extract the template. The obtained polymers were finally rinsed with ethanol to remove the remaining acetic acid and dried in a vacuum desiccator for 24 h before use.

For comparison, non-imprinted polymers (CNTs/NIPs) were prepared by the same procedure, only without the addition of $GaCl_3$ in the polymerization process.

2.5. Static adsorption test

The effect of pH on the adsorption of Ga(III) ion was tested by equilibrating 10 mg of the Ga(III)-imprinted/CNTs sorbent with 10 mL of sample solutions containing 1 mmol L^{-1} of $GaCl_3$ and 3 mmol L^{-1} 8-HQ under different pH conditions. The pH of the solutions was adjusted using acetic acid and sodium hydroxide. Uptake kinetics of Ga(III) ion to the Ga(III)-imprinted/CNTs sorbent was performed by adding 10 mg sorbent to 10 mL of 1 mmol L^{-1} complexing solution at pH 7.3. Samples were collected regularly at appropriate time intervals, separated and analyzed to calculate Ga(III) ion content. To measure the static adsorption capacity, 10 mg of Ga(III)-imprinted/CNTs or non-imprinted/CNTs sorbent was equilibrated with 10 mL of various concentrations of complexing solutions at pH 7.3.

Competitive loading of Ga(III) and Al(III) ions by Ga(III)-imprinted/CNTs or non-imprinted/CNTs sorbent was discussed in a mixing solution of Ga(III), Al(III) and 8-HQ at pH 7.3. A 120-mg portion of Ga(III)-imprinted/CNTs or non-imprinted/CNTs sorbent



Scheme 1. Synthesis route of Ga(III)-imprinted/CNTs sorbent.

was equilibrated with 10 mL of the mixing solution containing 1.0 mmol L^{-1} of Ga(III), 1.0 mmol L^{-1} of Al(III) and 6 mmol L^{-1} of 8-HQ.

In all above batch experiments, the mixtures were mechanically shaken for 30 min at room temperature, and then separated centrifugally. The supernate was measured by FAAS. The amount of ion absorbed by the sorbent (Q) was calculated by subtracting the amount of free ion in the supernate from the amount of complex compound initially added with the formula as follows:

$$Q = \frac{(C_0 - C_e)V}{m}$$

where C_0 and C_e are the initial and final concentrations of metal ion in the aqueous solution, respectively; V is the volume of metal ion complexes compound solution and m is the mass of Ga(III)-imprinted/CNTs.

2.6. Solid-phase extraction of Ga(III) ion

A total of 200 mg of sorbent (imprinted or non-imprinted) was poured into the SPE column. A polyethylene frit was placed at both ends to prevent loss of the sorbent during the sample loading. HCl (1 mmol L^{-1}) was passed through the column at 0.1 mL min^{-1} for 8 h to eliminate Ga(III) ion before used. Before loading the sample, the SPE cartridges were conditioned by passing 10 mL buffer solution (pH 7.3) at a flow rate of 1 mL min^{-1}. Then, 3 mL of fly ash sample solution containing 1 mmol L^{-1} Ga(III) ion and 3 mmol L^{-1} 8-HQ was passed through the column at flow rate of 1.0 mL min^{-1} (controlled by a peristaltic pump). The column was washed with 3 mL ethanol/distilled water (3:7, v/v) and then eluted with 10 mL of ethanol/acetic acid (9:1, v/v) for three times at a flow rate of 0.5 mL min^{-1}. Three times extracted solutions were merged and placed in a water bath at 80 °C, and then concentrated to 2.0 mL under a gentle stream of N_2.

2.7. Sample preparation

A 1.0-g portion of the fly ash sample calcined at 550 °C and quantificational $GaCl_3$ (4.5 or 0.45 mg) were dispersed in 5.0 mL of 6 mmol L^{-1} HCl. Then the mixture was shaken mechanically for 12 h at room temperature. Separated centrifugally, the supernatant was mixed with 10.0 mL of chloroform solution containing 8-HQ (accordance with the gallium ion concentration ratio, 3:1) under continuous shaking, and then filtered through a 0.22 μm filter film. The filtered fluid was transferred into a 25-mL volumetric flask to obtain 1 mmol L^{-1} Ga(III) ion sample solution in fly ash.

3. Results and discussion

3.1. Preparation of Ga(III)-imprinted/CNTs sorbent

CNTs were selected as an attractive structural material for the development of novel analytical device because of the good tensile strength, strong chemical stability, immense aspect ratio, poor solubility and ideal p-electron conjugated structure [14]. However, the p-electron conjugated structure of original CNTs had been slightly damaged after carboxyl functionalized [21]. Further repair of conjugate structure in this paper was necessary. Aniline is an ideal patch for repair of conjugate structure because of the big π bond in phenyl and amine group. The condensation reaction based on amine group of aniline and acyl chloride group of CNTs were the reason for the formation of covalent bond. The procedure of preparation of the Ga(III)-imprinted/CNTs sorbent was described in Scheme 1. AIBN was used for the carboxyl function of CNTs because of its strong catalytic action, low oxidizing ability, which prevents it from cutting off CNTs. The effect of the mass ratio of AIBN and CNTs was investigated. The result showed when the mass ratio increased from 20% to 100%, the reflux temperature fixed at 75 °C, the percent grafting of the final CNTs/COOH did not change significantly. Therefore, the

Table 1
Preparation conditions of the imprinted and non-imprinted sorbent.

Polymers	CNTs/V/P (mg)	$GaCl_3$ (mg)	8-HQ (mg)	MAA (μL)	EGDMA (μL)	AIBN (mg)	Chloroform (mL)	Methanol (mL)
MIP[a]	100	352.2	871.0	701	7929	20	30	20
NIP[b]	100	–	872.1	698	7928	20	30	20

[a] Ga(III)/imprinted/CNTs sorbent.
[b] Non-imprinted/CNTs sorbent.

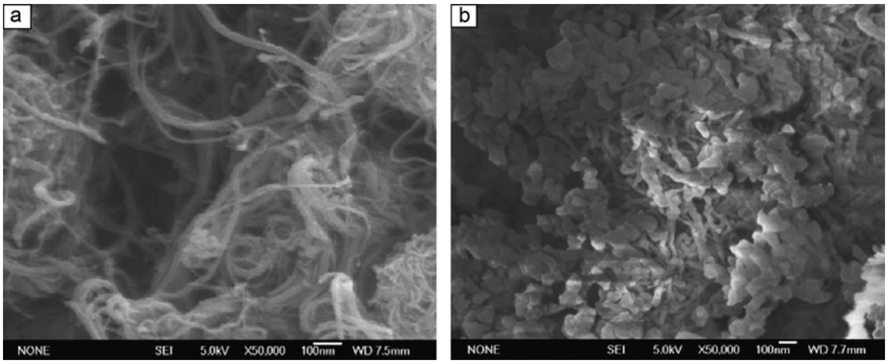


Fig. 1. The SEM microphotographs of crude CNTs (a) and Ga(III)-imprinted/CNTs sorbent (b).

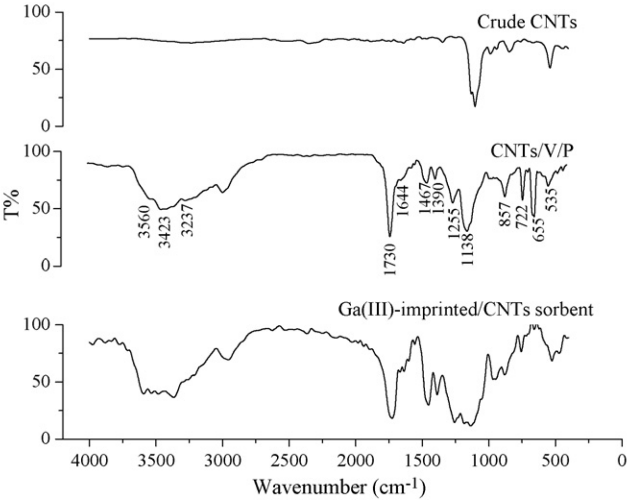


Fig. 2. FT-IR spectra of the crude CNTs, CNTs/V/P and Ga(III)-imprinted/CNTs sorbent.

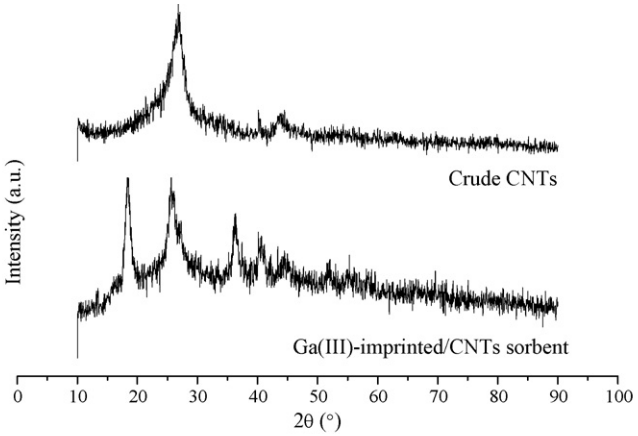


Fig. 3. X-ray diffraction patterns of the crude CNTs and Ga(III)-imprinted/CNTs sorbent.

Table 2
Comparison of imprinted and non-imprinted sorbent from nitrogen sorption measurements.

Sorbent	Specific surface area ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)	Mean diameter (nm)
MIP	168.7	0.63	6.9
NIP	162.8	0.59	4.3

mass ratio (AIBN:CNTs = 20%) was chosen for carboxyl functionalized in this work.

Grafted carboxyl group, the CNTs surface was introduced with the vinyl and phenyl groups, which has been previously discovered to interact with acrylate on the surface of solid supports by the covalent bonding [17]. Thus, vinyl and phenyl groups grafting on the CNTs surface could direct copolymerized with functional monomers and cross-linkers. The morphology of sorbent was detected by scanning electron microscope (SEM). As shown in Fig. 1, the crude CNTs are in the form of small bundles or individual tubes, and the average thickness and length are about 30 nm and several micrometers, respectively. The diameter of the imprinted sorbent increases obviously was observed at the same magnification.

3.2. Characteristic of FT-IR spectra and X-ray diffraction

IR spectra were obtained from the CNTs, CNTs/V/P, Ga(III)-imprinted/CNTs sorbent to ascertain the presence of aniline and acrylamide in the functionalized CNTs. As shown in Fig. 2, comparing with the crude CNTs, the observed absorption peak from 4000 to 400 cm^{-1} indicated –OH (3560 cm^{-1}), –NH (3423 and 1644 cm^{-1}), –C═C (1644 cm^{-1}) and –Ph (3237 and 1450 cm^{-1}) stretching vibrations in CNTs/V/P. It suggests that vinyl and phenyl groups were grafted onto the surface of the CNTs after modification. The bands from 1823 to 1345 cm^{-1} resulted from –C═O and –C═C stretching vibrations. A characteristic feature of the Ga(III)-imprinted/CNTs sorbent compared with CNTs/V/P and crude CNTs is the stronger of vibrations bonds around 3000 and 1250 cm^{-1}. This is because of cross-linking polymerization reaction resulting from a variety of groups vibrations.

XRD was used to confirm the crude CNTs and Ga(III)-imprinted/CNTs sorbent formation. The obtained spectrums are presented in Fig. 3 for crude CNTs and Ga(III)-imprinted/CNTs sorbent. The peak at about $2\theta = 26^\circ$ relates to CNTs constituent. The other peaks in spectrums of Ga(III)-imprinted/CNTs sorbent confirm MIPs layer grafted onto the surface of CNTs.

3.3. Nitrogen sorption measurement

Table 2 listed the porosity and surface area of these sorbents, which were determined by nitrogen sorption measurements. It can be seen from Table 2 that specific surface areas, total pore volume and mean diameter of the Ga(III)-imprinted/CNTs sorbent were no-obvious different from those of the non-imprinted/CNTs sorbent. Therefore, the difference of adsorption between the imprinted sorbent and non-imprinted sorbent in the subsequent study could not be attributed to the morphological difference, but to the imprinting effect.

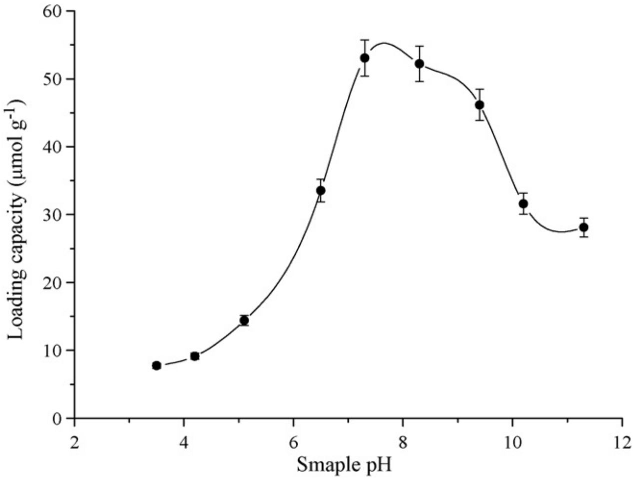


Fig. 4. Effect of sample pH on the adsorption of Ga(III)-imprinted/CNTs sorbent toward the Ga(III) ion complexes. *Experimental conditions*: the mass of sorbent was 10 mg; sample volume was 10 mL; Ga(III) ion initial concentration was 1 mmol L^{-1}; adsorption time was 12 h.

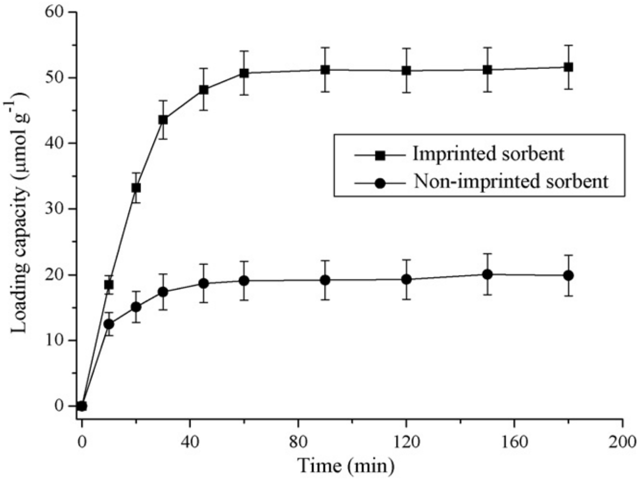


Fig. 5. Adsorption dynamic of Ga(III) ion complexes on Ga(III)-imprinted/CNTs sorbent and non-imprinted/CNTs sorbent. *Experimental conditions*: the mass of sorbent was 10 mg; sample volume was 10 mL; Ga(III) ion initial concentration was 1 mmol L^{-1}; adsorption time was 12 h; pH was 7.3.

3.4. Effect of sample pH

The effect of sample pH on the adsorption of Ga(III)-imprinted/CNTs sorbent towards Ga(III) ion was investigated by varying the pH between 3.5 and 11.5 and the results were shown in Fig. 4. The adsorption of Ga(III) ion increased with the pH increment from 3.5 to 7.3. A low loading capacity of 7.5 μmol g^{-1} at pH 3.5 to the maximum of 54.8 μmol g^{-1} at pH 7.3 was observed. When the pH increased from 7.3 to 9.5, loading capacity remained greater than 50 μmol g^{-1}.When the pH increased from 9.5 to 11.5, loading capacity of Ga(III) ion reduced rapidly. The loading capacity increased in the pH range 3.5–7.3 owing to the protonation of 8-HQ reduced to form complexes with metal ions [5,12,22], and reduced rapidly in the pH range 9.5–11.5 due to weak precipitation of the metal hydroxide. So the pH ranging from 7.0 to 8.5 was chosen in further experiments.

3.5. Dynamic adsorption

The adsorption kinetics of Ga(III)-imprinted/CNTs sorbent towards Ga(III) ion were investigated by changing the adsorption time from 10 to 180 min, and the initial concentration of Ga(III) ion and 8-HQ were kept constant at 1.0 and 3.0 mmol L^{-1}, respectively. The fitted curves of the dynamic adsorption were presented in Fig. 5. The imprinted sorbent exhibited much higher capacity than that of the non-imprinted sorbent. For the imprinted sorbent, adsorption capacity increased rapidly in the early 30 min, and then the rate of adsorption increased slowly until obtaining an equilibrium adsorption capacity. Due to a large number of imprinted cavities of Ga(III) ion complex existed on the surface of imprinted sorbent, the template complex was easy to reach the specific binding sites at the early time [23]. When the imprinted cavities were filled up, the rate of adsorption dropped significantly and adsorption process achieved equilibrium [6].

3.6. Adsorption capability

The adsorption capability of Ga(III)-imprinted/CNTs or non-imprinted/CNTs sorbent towards Ga(III) ion complex was investigated under the complex initial concentration ranging from 0.1 to 1.0 mmol L^{-1}. As shown in Fig. 6(a), the Ga(III)-imprinted/CNTs sorbent exhibited a higher adsorption capacity for the complex than that of non-imprinted sorbent in the studied initial concentration range. At the low concentration range (0.1–0.5 mmol L^{-1}), the osmotic pressure of the template complex was not enough to saturate the specific binding cavities. However, when the complex concentration increased to 0.7 mmol L^{-1}, all the specific imprinted sites were almost occupied by Ga(III) ion complex and the adsorption capacity of the sorbent reached the highest.

In this paper, Langmuir model was used for evaluation of the Ga(III) ion complex adsorption on imprinted sorbent. The Langmuir equation is follows [6]:

$$\frac{C_e}{Q} = \frac{C_e}{Q_{\max}} + \frac{1}{(bQ_{\max})}$$

where C_e is the equilibrium concentration of Ga(III) ion complex (mmol L^{-1}), Q (μmol g^{-1}) is the adsorption capacity of complex at equilibrium concentration, $Q_{\max}$ is the theoretical maximum adsorption capacity (μmol g^{-1}), and b is the Langmuir adsorption equilibrium constant (mL mol $^{-1}$). The linear plot of C_e/Q versus C_e for the imprinted sorbent was shown in Fig. 6(b). The equilibrium constant (b) and theoretical maximum adsorption capacity ($Q_{\max}$) were calculated. The adsorption capacity $Q_{\max}$ of imprinted and non-imprinted sorbent was 58.8 and 37.1 μmol g^{-1}, respectively; equilibrium constant b for the G(III)-imprinted/CNTs sorbent was 8.1 mL mol^{-1}, whereas that for the non-imprinted sorbent was 1.3 mL mol^{-1}. Thus, the promotion of binding activity by the present imprinting is attributed to the increase in the binding constant, not to simple in crease in the number of binding sites.

3.7. Adsorption specificity

To investigate the adsorption specificity of Ga(III)-imprinted/CNTs sorbent, static adsorption experiment was carried out for the binding of Ga(III) ion, Al(III) ion and Zn(II) ion in a 8-HQ buffered solution. As shown in Fig. 7, the Ga(III)-imprinted/CNTs sorbent exhibited good adsorption selectivity for Ga(III) ion. The adsorption capacity of the Ga(III)-imprinted/CNTs sorbent binding Ga(III) ion was much higher than that of other ion. As competitive ion, due to the spatial structure of these complexes with 8-HQ were not complementary to the imprinted sites, it had less chance to be adsorbed on the imprinted sorbent. In contrast, the adsorption of the non-imprinted sorbent towards Ga(III) ion much less than that of imprinted sites since the non-imprinted sorbent had not generated specific recognition sites due to the absence of Ga(III) ion during the preparation process. Therefore, the physical adsorption

Table 3
Imprinting factor (α) and selectivity factor (β) of the sorbent.

Adsorbate	Q_{MIP}	Q_{NIP}	α	β
Ga(III)	51.6	19.9	2.6	
Al(III)	23.1	20.5	1.1	2.4
Zn(II)	19.8	21.7	0.9	2.9

was the primary factor for the NIP. Additionally, imprinting factor (α) and selectivity factor (β) were used to evaluate the specific recognition property of the imprinted sorbent and the results were listed in Table 3. The imprinting factor is defined as follows:

$$\alpha = \frac{Q_{MIP}}{Q_{NIP}}$$

where Q_{MIP} and Q_{NIP} are the adsorption capacity for the imprinted sorbent and non-imprinted sorbent, respectively. The selectivity factor is defined as follows:

$$\beta = \frac{\alpha_{tem}}{\alpha_{con}}$$

where α_{tem} is the imprinting factor toward the template molecule and α_{con} is the imprinting factor toward the contradistinctive ion. The α toward Ga(III) ion is 2.6, which is greater than that toward Al(III) (1.1) and Zn(II) ion (0.9). The β value were 2.4 (Al(III)) and 2.9 (Zn(II)), which indicated the Ga(III)-imprinted/CNTs sorbent adsorption for both of two ions was low equally.

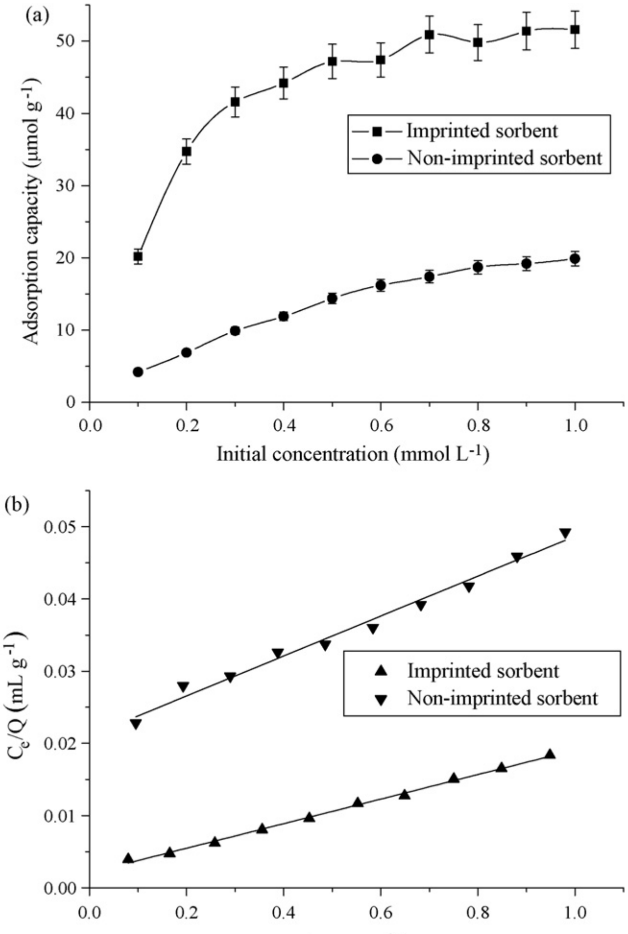


Fig. 6. Adsorption isotherm of Ga(III) ion complexes on Ga(III)-imprinted/CNTs sorbent and non-imprinted/CNTs sorbent (a), linearized according to the Langmuir model (b). *Experimental conditions*: the mass of sorbent was 10 mg; sample volume was 10 mL; adsorption time was 12 h; pH was 7.3.

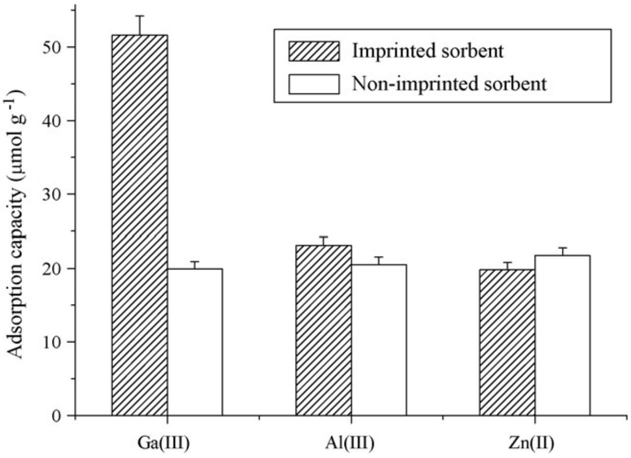


Fig. 7. Selective adsorption of Ga(III), Al(III) or Zn(II) ion complexes of 8-HQ on the Ga(III)-imprinted/CNTs sorbent and non-imprinted/CNTs sorbent. *Experimental conditions*: the mass of sorbent was 10 mg; the concentration of each competitive ion was1 mmol L^{-1}; sample volume was 10 mL; adsorption time was 12 h; pH was 7.3; adsorption time was 4 h.

3.8. *Competitive loading*

Competitive loading studies were performed with Ga(III) and Zn(II) ions to investigate the selectivity of the Ga(III)-imprinted/CNTs sorbent in a dynamic adsorption environment. Al(III) ion was chosen as the competitive species for Ga(III) ion because both ions have the same charge and belong to the same main group elements. Moreover, both ions bind well with 8-HQ. Table 4 summarized the parameters involving the percentage uptake, adsorption capacity, distribution coefficient (K_d), selectivity coefficient of the sorbent towards Ga(III) ion (k), and the relative selectivity coefficient (k'). The k value of the imprinted sorbent increased significantly than that of the non-imprinted sorbent. This indicated that the Ga(III)-imprinted/CNTs sorbent rebinding Ga(III) ion is superior to rebinding Al(III) ion in the dynamic adsorption process. This because the spatial structure of Ga(III)-8-HQ complex, which agree with the imprinted cavity and specific binding sites of imprinted sorbent formed orderly during the preparation period. However, in the non-imprinted sorbent, the functional binding sites arranged random and disorderly, resulted in unremarkable selectivity performance.

3.9. *Solid-phase extraction of Ga(III) ion*

The applicability of Ga(III)-imprinted/CNTs accumulating on Ga(III) ion was evaluated by a traditional SPE method. The SPE three steps including loading, washing and eluting were optimized to achieve good sensitivity and precision of the extraction and elution of Ga(III) ion.

The washing step is a most crucial procedure for maximizing the specific interactions between the analytes and binding sites, and reducing the non-specific adsorption. Thus, various ethanol/distilled water ratio were investigated in washing step. The results were shown in Fig. 8. It was found that with the increase of ethanol in the washing solutions, the recoveries of Ga(III) ion by the imprinted SPE column decreased rapidly from 96.4% to 60.4%, while the recoveries of Ga(III) ion in non-imprinted SPE column was decreased slightly from 57% to 50%. These results showed the solubility of the complex affects its reserved capacity on the imprinted SPE column. It implicated a like dissolves like occurred in desorption process. A stronger solubility solvent for the com-

Table 4
Competitive Loading of Ga(III) and Al(III) ion complexes by the Ga(III)-imprinted/CNTs sorbent and non-imprinted/CNTs sorbent.

Sorbent	Initial solution (mmol L^{-1})		Uptake%		Capacity (μmol L^{-1})		K_d[a] (mL g^{-1})		k[b]	k'[c]
	Ga(III)	Al(III)	Ga(III)	Al(III)	Ga(III)	Al(III)	Ga(III)	Al(III)		
MIP	1.0	–	98.4	–	82.0	–	5125	–	–	6.3
	1.0	1.0	97.5	40.5	81.3	33.8	3250	57	57.3	
NIP	1.0	–	85.2	–	71.0	–	480	–	–	
	1.0	10.	80.6	31.3	67.2	26.1	346	38	9.1	

[a] K_d, distribution coefficient, $K_d = [(C_0 - C_e)/C_e] \times$ [volume of solution (mL)]/[mass of sorbent (g)].
[b] k, selectivity coefficient, $k = K_d(\text{Ga})/K_d(\text{Al})$.
[c] k', relative selectivity coefficient, $k' = k_{MIP}/k_{NIP}$.

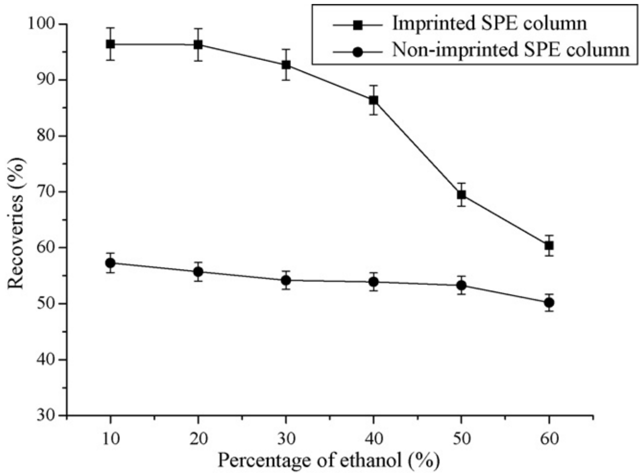


Fig. 8. Effect of ethanol in washing step to SPE column. Experimental conditions: SPE column is 100 mm × 4.6 mm i.d.; loading sample volume was 3 mL; sample concentration was 1 mmol L^{-1}; sample pH was 7.3; flow rate was 1.0 mL min^{-1}; each washing volume was 3 mL; each eluting solution is ethanol/acetic acid (9:1, v/v) and the volume was 10 mL.

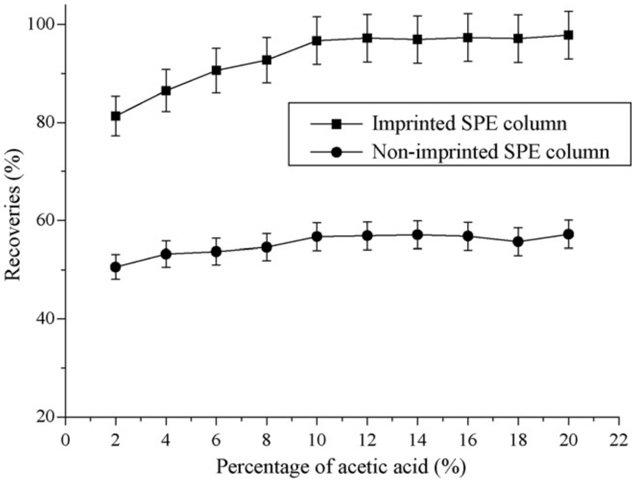


Fig. 9. Effect of acetic acid in elution step to SPE column. Experimental conditions: SPE column is 100 mm × 4.6 mm i.d.; loading sample volume was 3 mL; sample concentration was 1 mmol L^{-1}; sample pH was 7.3; flow rate was 1.0 mL min^{-1}; each ethanol/distilled water (3:7, v/v) volume was 3 mL; each eluting solution volume was 10 mL.

plex can reduce the retention of Ga(III) ion complex. However, the lower portion of ethanol in mixture solvent (1:9, v/v) led to a large reservation of impurity, resulting the selectivity of imprinted SPE column is inferior. Thus, a rational volume ratio of ethanol/distilled water (3:7, v/v) was selected as the washing solvent.

The purpose of elution step is to remove the reloading Ga(III) ion as complete as possible. The acidity of elution solvent, which was regulated by changing ethanol/acetic acid ratio, plays an important role in complex extraction. The results were shown in Fig. 9. In contrast to non-imprinted SPE column (the recoveries of Ga(III) ion augment from 50.6% to 57.2%), the recoveries of Ga(III) ion on the imprinted SPE column displays an obvious dissimilarity with the increase acidity of augment from 81.3% to 97.8%. These results indicated that the imprinted SPE column had high selectivity for Ga(III) ion. Additionally, the higher acidity of elution solvent is, the better elution effect is. There are two possible factors for the phenomena. Firstly, the complexing reaction is taken place more effectively in an alkaline solution than in an acidic solution [24,25]. Conversely, a solution containing acetic acid disassembled Ga(III) ion complex easily, as a result of eluted Ga(III) ion easily. Secondly, Polarity of elution solution affected the adsorbability which was in form of hydrogen bond [26] and π–π conjugate [27]. The polarity of elution solution increases with the increment of acetic acid. Therefore, the adsorbability of Ga(III) ion complex on imprinted sorbent got smaller and smaller.

3.10. Enrichment Ga(III) ion from fly ash lixivium

In this research, 6.0 mmol L^{-1} HCl which exhibited a good ability for dissolved metallic oxide, was selected to lixiviate Ga(III) ion from fly ash. Blank sample was extracted by imprinted sorbent in the same SPE method. For 3 mL blank sample extracted, Ga(III) ion had been not detected by FAAS until the blank sample volume increase to 15 mL. Thus, in order to obtain the recoveries of imprinted sorbent, a certain amount of Ga(III) ion were added into blank lixivium. After adding a certain amount of Ga(III) ion, the Ga(III) ion lixivium were extracted by the imprinted sorbent or the non-imprinted sorbent. The results of FAAS analysis are presented in Table 5. The recoveries of Ga(III) ion in two spiked level were 87.3% and 94.5% for imprinted SPE column, and that for the non-imprinted SPE column were 20.7% and 36.5%, respectively. The comparison of the imprinted SPE elution fractions with the non-imprinted SPE elution fractions and the direct analysis of the spiked lixivium demonstrated the high degree of enrichment for the imprinted sorbent to Ga(III) ion.

3.11. Performance of the method

The enriched Ga(III) ion standard solution using the method in this paper was detected by FAAS. The enrichment factor obtained by the slopes of the linear portion in comparison with the direct detection of Ga(III) ion standard solution was 43. The detection limit (LOD) is obtained using the 3S criterion and is found to be 3.03 ng mL^{-1}. The quantification limit (LOQ) calculated by the 10S criterion was 10.17 ng mL^{-1}. The relative standard deviation (RSD) for five repetition extractions of 1.0 μg L^{-1} Ga(III) ion standard solution was 4.71%. The linear range of the calibration graph was 1.5–150 ng mL^{-1}.

Table 5
Recoveries of Ga(III) ion in fly ash samples.

Adding (mg g^{-1})		Found (mg g^{-1})		Recoveries (%, Mean ± reproducibility, $n = 5$)	
MIP	NIP	MIP	NIP	MIP	NIP
4.50	4.50	4.25	1.64	94.5 ± 3.1	36.5 ± 3.5
0.45	0.45	0.43	0.16	87.3 ± 2.7	20.7 ± 3.2

Table 6
Comparison other methods with our method in this paper.

Pretreatment methods	Analytical system	Selective	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	Linear range (ng mL^{-1})	Ref.
Imprinted SPE	FAAS	Yes	3.03	10.17	1.5–150	This paper
Supercritical CO_2 extraction	GFAAS[a]	No	1.03	3.14	2.5–250	[28]
Anion-exchange resin	GFAAS[a]	No	0.003	–	–	[29]
NaOH-based extraction	XRD[b]	No	–	–	–	[4]
Dissolving $Ga(NO_3)_3$	CE[c] and UV[d]	No	2.87	–	7.2–717.2	[30]
Dissolving gallium salt	Ion-selective electrode	Yes	–	–	–	[31]
Preconcentration–separation	FAAS	Yes	6.0	–	20–3000	[32]
Fused with KOH or iron carrier	ICP-OES[e]	No	6.0 or 5.0	–	–	[33]
Direct detection	ICP-MS[f]	No	16.0	–	140–0.160	[34]
Ion-exchange chromatography	LC[g]	No	–	–	–	[35]

[a] Graphite furnace atomic absorption spectroscopy.
[b] X-ray diffraction.
[c] Capillary electrophoretic.
[d] Ultraviolet.
[e] Inductively coupled plasma optical emission spectroscopy.
[f] Nductively coupled plasma mass spectroscopy.
[g] Liquid chromatography.

4. Conclusions

In this study, a new procedure for the synthesis of Ga(III)-imprinted/CNTs sorbent was developed by a surface imprinting technique. It has been proved that the imprinted sorbent showed a good selectivity for the imprinted molecule by both functional groups and dimensional structure of specific binding site. Furthermore, as solid extraction material, the imprinted sorbent was applied successfully for extraction of Ga(III) ion from fly ash lixivium followed by FAAS detection. Some methods have been used for the determination of gallium summarized in Table 6. Each method has its advantages and limitations. Comparing with these methods, the method developed in this paper was sufficiently accurate and precise to be used for Ga(III) ion analysis in fly ash samples, and performed better characteristics such as selectivity and cleanliness of the extracts.

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