



## Adsorption of chromium(III), mercury(II) and lead(II) ions onto 4-aminoantipyrine immobilized bentonite

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### ABSTRACT

In this work, the immobilization of 4-aminoantipyrine onto bentonite was carried out and it was then used to investigate the adsorption behavior of Cr(III), Hg(II) and Pb(II) ions from aqueous solutions. The separation and preconcentration conditions of analytes were investigated, including effects of pH, the shaking time, the sample flow rate and volume, the elution condition and the interfering ions. Under optimum pH value (pH 4.0), the maximum static adsorption capacity of the sorbent was found to be 38.8, 52.9 and 55.5 mg g<sup>-1</sup> for Cr(III), Hg(II) and Pb(II), respectively. 2.0 mL of 2% thiourea in 1.0 M HCl solution effectively eluted the adsorbed metal ions. The detection limit (3σ) of this method defined by IUPAC was found to be 0.12, 0.09 and 0.23 ng mL<sup>-1</sup> for Cr(III), Hg(II) and Pb(II), respectively. The relative standard deviation (RSD) was lower 3.0% (n = 8). The developed method has been validated by analyzing certified reference materials and successfully applied to the determination of trace Cr(III), Hg(II) and Pb(II) in water samples with satisfactory results.

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### 1. Introduction

Heavy-metal pollution occurs in many industrial wastewater such as those produced by metal plating facilities, mining operations, battery manufacturing process, the production of paints and pigments, and the glass production industry. Many of these metal ions are reported to be toxic, carcinogenic and tend to bioaccumulate in aquatic organisms even when present in low concentrations [1].

For determination of heavy metal ions in the practical samples, many analytical techniques have been used. These include: graphite furnace atomic absorption spectrometric (GFAAS) [2], X-ray fluorescence spectrometry (XRF) [3], inductively coupled plasma atomic emission spectrometry (ICP-AES) [4] and inductively coupled plasma mass spectrometry (ICP-MS) [5]. However, GFAAS is difficult to determine multi-elements simultaneously, while the sensitivity of XRF is lower than that of ICP-AES. ICP-MS has been acknowledged as one of the most powerful techniques for ions determination, but the equipment is still too expensive for many institutions. In comparison, ICP-AES is a timesaving, simple, and well-available technique for the determination of heavy metal ions [6]. However, the direct determination of heavy metal ions at trace levels is limited due to their low concentrations and matrix effects.

This limitation can be overcome by the use of a separation and preconcentration step [7].

Several treatment technologies have been developed for preconcentration heavy metals from solution such as precipitation and coprecipitation [8], adsorption [9], ion-exchange [10], and solid phase extraction (SPE) [11–14], etc. Among these techniques, SPE is the most common approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs and extraction time for sample preparation. SPE has been preferably applied using natural, synthetic, and modified inorganic, organic supports.

Numerous substances have been applied as solid-phase extractants, such as chelating resin [15], bentonite [16], activated carbon [17], cellulose [18] and biological substances [19]. The volcanic ash weathering product: bentonite (BNT), includes montmorillonite (MMT) as the main active constituent in variable compositions depending upon its origin [20]. MMT: a member of the smectite family, having two SiO<sub>4</sub>-tetrahedral sheets sandwiching a central AlO<sub>6</sub>-octahedral sheet (type 2:1) [21]. Due to the isomorphic substitution of the Mg and Al atoms for the Al and Si atoms, respectively, the aluminosilicate layers are negatively charged hence they accommodate exchangeable cations such as Na<sup>+</sup>, Ca<sup>2+</sup> and/or Mg<sup>2+</sup> in the interlayered-spacing for the sake of charge compensation [22]. So bentonite has recently been employed in many separation applications with or without modification [23,24].

The natural clay minerals have the relatively low adsorption capacity. Therefore, they should be pretreated to improve their adsorption ability. In this work, bentonite was functionalized with

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4-aminoantipyrine as extractants for heavy metals, specifically for chromium, mercury and lead. The new sorbent showed high adsorption capacity and short equilibrium time toward Cr(III), Hg(II) and Pb(II). Common coexisting ions did not interfere with the determination of aim ions. Then, the method was applied to preconcentrate trace Cr(III), Hg(II) and Pb(II) from water samples with satisfactory results.

## 2. Experimental

### 2.1. Instruments and apparatus

All metal ions were determined by an IRIS Advantage ER/S inductively coupled plasma atomic emission spectrometer (TJA, USA). The instrumental parameters were recommended by the manufacturer. The wavelengths selected were as follows: Cr 283.563 nm, Hg 194.227 nm and Pb 216.999 nm. Fourier Transform Infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) in KBr were recorded on a Nicolet NEXUS 670 FT-IR spectrometer (Madison, WI, USA). A VarioEL element analyzer, Elementar Analysensysteme (Hanau Germany), was used for elemental analysis. The specific surface areas of bentonite and 4-aminoantipyrine/bentonite were determined using a chemiSorb 2750 automatic temperature-programmed chemisorption analyzer (Micromeritics Instrument corp, USA). A pHs-3C digital pH meter (Shanghai Lei Ci Device Works, Shanghai, China) was used for the pH adjustments. An YL-110 peristaltic pump (The General Research Academe of Colored Metal, Beijing, China) was used in the column procedure. A self-made glass column (50 mm  $\times$  2.5 mm i.d.) was used in this study.

### 2.2. Reagents and standard solutions

All chemicals were of analytical reagent grade otherwise stated. Doubly distilled water was used throughout. All glassware was kept in 10% nitric acid for 24 h and then rinsed with doubly distilled water prior to use. Bentonite was purchased from Zhejiang Linan Bentonite Chemical Factory (Zhejiang, China). Bentonite cation exchange capacity (CEC) has been characterized by the methylene blue method was  $112.0\text{ cmol kg}^{-1}$ . 4-Aminoantipyrine (AAP, Beijing Hengye Zhongyuan Chemical Co. Ltd., Beijing, China) was used in this work.

The stock standard solutions of Cr(III), Hg(II) and Pb(II) ( $1.0\text{ mg mL}^{-1}$ ) were prepared by dissolving spectral pure grade chemicals  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{HgCl}_2$  and  $\text{Pb}(\text{NO}_3)_2$  (The First Reagent Factory, Shanghai, China) in doubly distilled water with the addition of hydrochloric acid (The First Reagent Factory, Shanghai, China). The working standard solutions were prepared by diluting stock standard solutions with  $0.5\text{ mol L}^{-1}$  HCl.

### 2.3. Sample preparation

The certified reference materials (GBW08301, river sediment and GBW08501, Peach Leaf, provided by the National Research Center for Certified Reference Materials, China) were digested according to literature [25]. A portion (50 mg) of the sample was accurately weighed into a 50 mL beaker and aqua regia (12.0 mL concentrated hydrochloric acid and 4.0 mL of concentrated nitric acid) was added to the sample. The beaker was covered with a watch glass and the mixture was evaporated on a hot plate at  $95^\circ\text{C}$  almost to dryness. Then 8.0 mL of aqua regia was added to the residue and the mixture was again evaporated to dryness. After cooling resulting mixture was filtered through a  $0.45\text{ }\mu\text{m}$  polytetrafluoroethylene millipore filter. The sample was diluted to 10.0 mL with doubly distilled water and the addition of hydrochloric acid.

### 2.4. The detection limit determination

According to the definition of International Union of Pure and Applied Chemistry, the detection limit of the method was calculated based on three times the standard deviation of eight runs of the blank solution [26].

### 2.5. Modification process

The bentonite surfaces were activated by refluxing in a concentrated hydrochloric acid for 4 h to remove any adsorbed metal ions, then filtered and repeatedly washed with doubly distilled water to neutral and dried in an oven at  $70^\circ\text{C}$  for 8 h to remove surface-adsorbed water. Then 10.0 g of dry activated bentonite was suspended in 100 mL dry toluene containing 10 mL of 3-chloropropyltrimethoxysilane and refluxed at  $115^\circ\text{C}$  for 8 h. The product was filtered, washed with toluene, ethanol and diethyl ether and dried in an oven at  $80^\circ\text{C}$  for 8 h. The product was bentonite-bound 3-chloropropyl phase (BNT-CP).

For the synthesis of bentonite-bound 4-aminoantipyrine, BNT-CP (5.0 g) and 4-aminoantipyrine (2.0 g) were suspended in 80 mL of ethanol. This mixture was refluxed at  $80^\circ\text{C}$  for 12 h. The final product (BNT-AAP) was filtered, washed with ethanol and dried under vacuum at  $80^\circ\text{C}$  for 8 h. The synthetic route of BNT-AAP is illustrated in Fig. 1.

### 2.6. Characterization

The modified bentonite was confirmed by IR analysis. Fig. 2 shows the FT-IR spectra of BNT-CP and BNT-AAP, respectively. The absorption peaks of BNT-CP (Fig. 2(a)) were observed between  $3627.13$  and  $3434.47\text{ cm}^{-1}$ , which was due to H–O–H stretching vibration bands of water molecules weakly hydrogen bonded to the

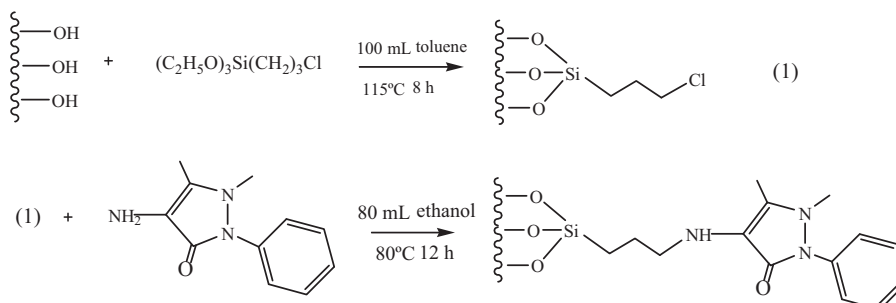


Fig. 1. Synthetic route of the BNT-AAP.

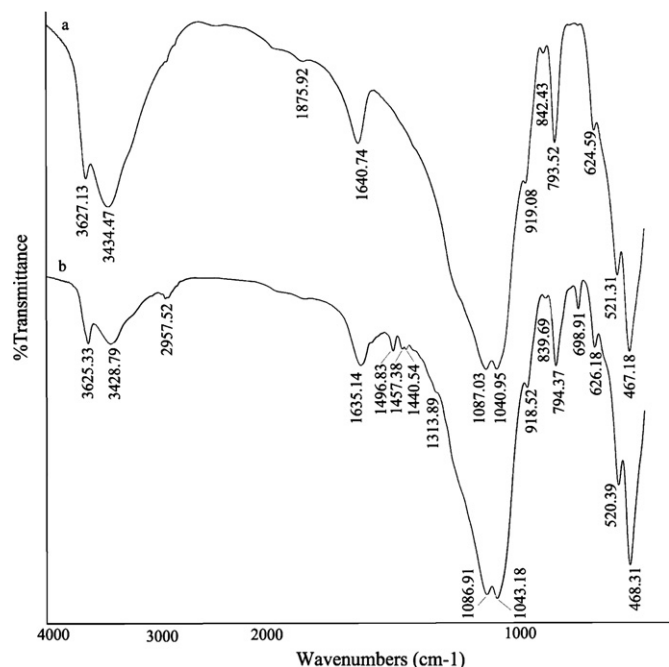


Fig. 2. FT-IR spectra of BNT-CP (a) and BNT-AAP (b).

Si–O surface in the bentonite. The band of the OH bending vibration was observed at  $1640.74\text{ cm}^{-1}$  whereas the Al–Al–OH bending frequency was observed at  $919.08\text{ cm}^{-1}$ . This might be considered characteristic of a di-octahedral montmorillonite 2:1 layer [27,28]. The Si–O coordination bands at  $1087.03$  and  $1040.95\text{ cm}^{-1}$  were observed as a result of the Si–O vibrations. The deep band at around  $1040\text{ cm}^{-1}$  represented the stretching of Si–O in the S–O–Si groups of the tetrahedral sheet. The bands at  $467.18$  and  $521.31\text{ cm}^{-1}$  were due to Si–O–Al (octahedral) and Si–O–Si bending vibrations for BNT-CP [29].

When BNT-CP was modified with 4-aminoantipyrin, the IR of BNT-AAP showed remarkable spectral changes. As shown in Fig. 2(b), the band at  $2957.52\text{ cm}^{-1}$  could be assigned to the C–H stretching vibration. The C–C and C–N ring stretching (skeletal) vibrations in the BNT-AAP were observed at  $1496.83$ ,  $1457.38$ ,  $1440.54$  and  $1313.89\text{ cm}^{-1}$  (four bands) and the ring bending vibration obtained at  $698.91\text{ cm}^{-1}$  [30], but these bands were not observed in BNT-CP. This might be acceptable evidence for the immobilization of 4-aminoantipyrine onto bentonite.

Elemental analysis indicated 3.77% carbon and 1.501% hydrogen in BNT-CP and 9.04% carbon, 1.58% nitrogen and 1.426% hydrogen in BNT-AAP. It could be calculated that 1 g bentonite contained 0.08 g 4-aminoantipyrine.

The specific surface areas of bentonite and 4-aminoantipyrin immobilized bentonite were  $34.0$  and  $24.9\text{ m}^2\text{ g}^{-1}$ , respectively. The relatively low surface areas of the organobentonites indicated external surface only, no internal surface area was accessible to nitrogen gas [31].

Consequently, the above experimental results showed that bentonite was successfully modified by 4-aminoantipyrine.

## 2.7. General procedures

### 2.7.1. Batch procedure

A series of standard or sample solutions containing Cr(III), Hg(II) and Pb(II) were transferred into a 25 mL beaker, and the pH value was adjusted to the desired value with  $0.1\text{ mol L}^{-1}$  HCl and  $0.1\text{ mol L}^{-1}$   $\text{NH}_3\cdot\text{H}_2\text{O}$ . Then the volume was adjusted to  $10.0\text{ mL}$  with doubly distilled water. Amount of  $30\text{ mg}$  of BNT-AAP was

added, and the mixture was shaken vigorously for 30 min to facilitate adsorption of the metal ions on the sorbent. The concentrations of the metal ions in the solution were determined by ICP-AES directly. Then the sorbent was eluted with  $1.0\text{ mol L}^{-1}$  HCl and 2% thiourea solution. The concentrations of the desorbed metal ions were measured by ICP-AES.

### 2.7.2. Column procedure

Amount of  $30\text{ mg}$  of functionalized bentonite sorbent was packed in a self-made glass column ( $50\text{ mm} \times 2.5\text{ mm}$  i.d.) plugged with a small portion of glass wool at both ends. In order to equilibrate, clean and neutralize the column before using, 10%  $\text{HNO}_3$  solution and doubly distilled water were successively passed through it. Portions of sample solutions containing Cr(III), Hg(II) and Pb(II) were prepared, and the pH value was adjusted to 4.0 with  $0.1\text{ mol L}^{-1}$  HCl and  $0.1\text{ mol L}^{-1}$   $\text{NH}_3\cdot\text{H}_2\text{O}$ . Each solution was passed through the column at a flow rate of  $2.0\text{ mL min}^{-1}$  controlled with a peristaltic pump. Then column was eluted with  $1.0\text{ mol L}^{-1}$  HCl and 2%  $\text{CS}(\text{NH}_2)_2$  solution and the analytes in the eluent were determined by ICP-AES.

## 3. Results and discussion

### 3.1. Effect of initial pH

Suspension pH is of prime importance for efficient retention of the trace elements on the sorbent [32]. Its influence strongly depends on the nature of the sorbent used. Careful optimization of this parameter is thus crucial to ensure quantitative retention of the trace elements and in some cases selective retention. According to the batch procedure, several metal ions, viz. Cr(III), Fe(III), Co(II), Ni(II), Hg(II), Mn(II), Cu(II), Zn(II), Cd(II) and Pb(II) were tested at different pH values (from 1.0 to 7.0). As shown in Fig. 3, the results expressed that quantitative extraction (>95%) for Cr(III), Hg(II) and Pb(II) was obtained when the pH exceed 4.0. Since more metal-binding sites could be exposed and carried negative charges, with subsequent attraction of metal ions with positive charge and adsorption onto the sorbent surface. In order to avoid metal precipitation appeared at higher pH values, so a pH of 4.0 was selected as the optimum condition. Other ions had insignificant adsorption on BNT-AAP at pH 4.0 indicating the high selectivity of this sorbent for Cr(III), Hg(II) and Pb(II).

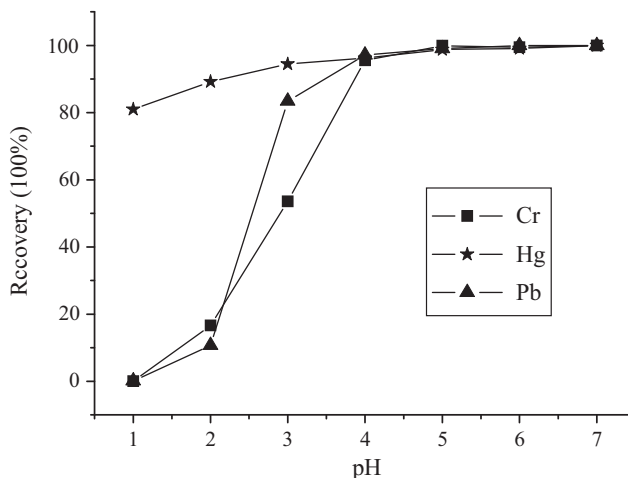
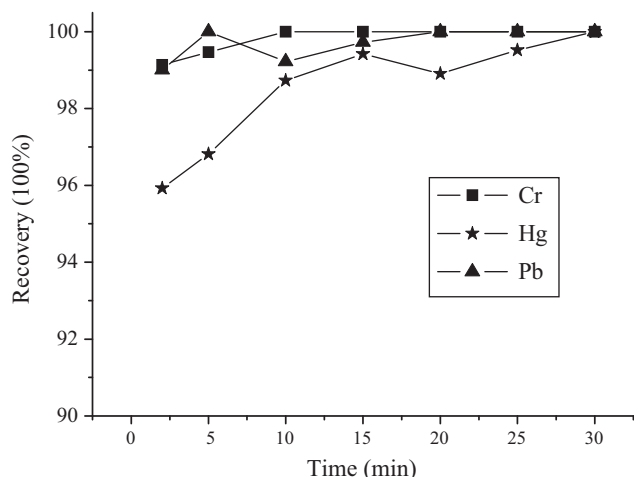


Fig. 3. Effect of pH on adsorption of  $1.0\text{ }\mu\text{g mL}^{-1}$  Cr(III), Hg(II) and Pb(II) on BNT-AAP. Other conditions: shaking time 30 min; sorbent mass 30 mg; temperature  $25\text{ }^\circ\text{C}$ .



**Fig. 4.** Effect of time on adsorption of  $1.0 \mu\text{g mL}^{-1}$  Cr(III), Hg(II) and Pb(II) on BNT-AAP. Other conditions: pH 4.0; sorbent mass 30 mg; temperature  $25^\circ\text{C}$ .

### 3.2. Effect of shaking time

The shaking time is an important factor in determining the equilibration rate and flow rate for further study. In this work, different shaking time (range from 2 to 30 min) was studied for the extraction of Cr(III), Hg(II) and Pb(II) by BNT-AAP. As shown in Fig. 4, Cr(III), Hg(II) and Pb(II) binding was fast, occurring within the first 2 min of contact. The reason might be that the active donor atoms (N and O) on the modified bentonite surface are so oriented that their accessibility is not difficult and consequently fast interaction with the free metal ions present in solution is feasible. Therefore, BNT-AAP had rapid adsorption for Cr(III), Hg(II) and Pb(II).

### 3.3. Effect of flow rate

Another important parameter in adsorption is the flow rate of the sample solution, which influence the adsorption of cations to the sorbent surface and the time of complete analysis. Therefore, the effect of the flow rate of sample solution was examined under the optimum conditions by passing 10 mL of sample solution through the column with a peristaltic pump. The flow rates were adjusted in range of  $0.5\text{--}4.0 \text{ mL min}^{-1}$ . It was found that quantitative recovery ( $>95\%$ ) of Cr(III), Hg(II) and Pb(II) was obtained in flow rate of  $0.5\text{--}2.0 \text{ mL min}^{-1}$ . A flow rate  $<1.5 \text{ mL min}^{-1}$  was not employed to avoid the long extraction time. However, over  $2.0 \text{ mL min}^{-1}$ , the recovery of the analytes decrease with the increase of the flow rate, probably because the metal ions do not equilibrate sufficiently with the sorbent. Thus, a flow rate of  $2.0 \text{ mL min}^{-1}$  is selected in this work.

### 3.4. Effect of eluent concentration and volume

The nature of the eluent is of prime importance and should optimally meet three criteria: efficiency, selectivity and compatibility [33]. Based on this, 10.0 mL of various concentrations of HCl and  $\text{CS}(\text{NH}_2)_2$  for the desorption of retained Cr(III), Hg(II) and Pb(II) from the sorbent. As could be seen in Table 1, satisfactory results were not obtained for Hg(II) by only using HCl as eluent (recovery  $<85\%$ ). In comparison, HCl +  $\text{CS}(\text{NH}_2)_2$  were found to be the suitable eluent for stripping off the adsorbed Hg(II). The reason might be that thiourea and Hg(II) had more stronger coordinating ability than that of BNT-AAP, so the coordination linkage of chelated Hg(II) was easily disrupted and subsequently Hg(II) ions were released from the BNT-AAP into the desorption medium. Thus, the  $1.0 \text{ mol L}^{-1}$

**Table 1**

Effect of concentration of eluent for Cr(III), Hg(II) and Pb(II) adsorbed on sorbent.

Eluent concentration <sup>a</sup>	Recovery (%)		
	Cr(III)	Hg(II)	Pb(II)
1.0 M HCl	87.72	52.65	92.67
2.0 M HCl	95.37	59.52	97.25
3.0 M HCl	97.56	76.28	99.06
4.0 M HCl	99.23	84.97	98.86
1.0 M HCl + 1% $\text{CS}(\text{NH}_2)_2$	98.94	92.61	99.81
1.0 M HCl + 2% $\text{CS}(\text{NH}_2)_2$	99.14	97.58	99.70

<sup>a</sup> 10.0 mL.

**Table 2**

Effect of volume of eluent for Cr(III), Hg(II) and Pb(II) adsorbed on sorbent.

Eluent volume (mL) <sup>a</sup>	Recovery (%)					
	2.0	3.0	4.0	5.0	6.0	7.0
Cr(III)	98.35	98.06	99.22	98.97	100	100
Hg(II)	98.72	98.97	99.14	99.42	98.84	99.28
Pb(II)	98.26	98.74	98.63	99.87	100	100

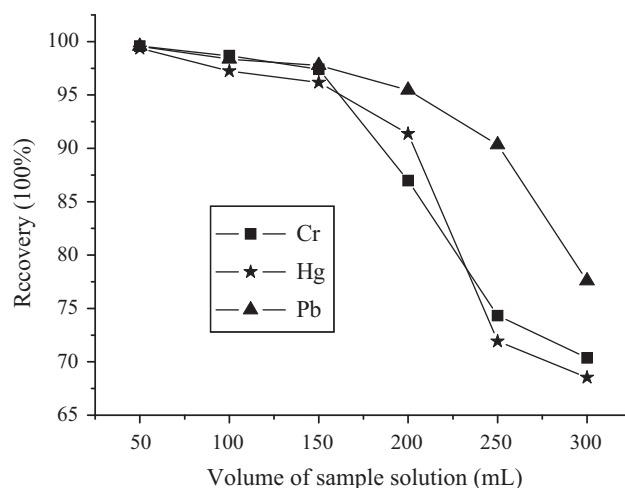
<sup>a</sup>  $1.0 \text{ M HCl} + 2\% \text{CS}(\text{NH}_2)_2$ .

HCl and 2%  $\text{CS}(\text{NH}_2)_2$  was sufficient for complete elution (recovery  $>95\%$ ).

The effect of eluent volume on the recovery of Cr(III), Hg(II) and Pb(II) was also studied by keeping the HCl concentration of  $1.0 \text{ mol L}^{-1}$  and the  $\text{CS}(\text{NH}_2)_2$  concentration of 2%. As can be seen in Table 2, quantitative recovery could be obtained with 2.0 mL of  $1.0 \text{ mol L}^{-1}$  HCl and 2%  $\text{CS}(\text{NH}_2)_2$ . Therefore, 2.0 mL of  $1.0 \text{ mol L}^{-1}$  HCl and 2%  $\text{CS}(\text{NH}_2)_2$  was used as eluent in further experiments.

### 3.5. Maximum sample volume and enrichment factor

In order to achieve a high preconcentration factor, metal ions in the large sample volume has been quantitatively adsorbed and desorbed by a small stripping volume. The effect of sample volume on metal adsorption was studied by 50–300 mL  $1.0 \mu\text{g mL}^{-1}$  of Cr(III), Hg(II) and Pb(II) through the column at the optimum flow rate. As shown in Fig. 5, the results showed that the maximum sample volume could be up to 200 mL with the recovery  $>95\%$ . The high enrichment factor of 100 was obtained because the eluent volume was 2.0 mL.



**Fig. 5.** Effect of the sample volume on recovery of  $1.0 \mu\text{g mL}^{-1}$  at pH 4.0. Other conditions: sorbent mass 30 mg; temperature  $25^\circ\text{C}$ .

### 3.6. Adsorption capacities

The capacity of the sorbent is an important factor because it determines how much adsorbent is required to quantitatively remove a specific amount of metal ions from the solutions [34]. According to the batch procedure, 30 mg of sorbent was equilibrated with 10.0 mL of Cr(III), Hg(II) and Pb(II) sample solution adjusted to pH 4.0 of various concentrations for 1 h. In order to reach the “saturation”, the concentration of Cr(III), Hg(II) and Pb(II) was increased till the plateau value (adsorption capacity value) obtained. The variation in sorption capacities of various metal ions probably arises due to their sizes, degree of hydration and binding constants of their complexes with the matrix. Therefore, the maximum adsorption capacity of BNT-AAP was found to be 38.8, 52.9 and 55.5 mg g<sup>-1</sup> for Cr(III), Hg(II) and Pb(II), respectively.

Moreover, the capacity of BNT-AAP comparable to that of bentonite modified with hydroxy-aluminum is 24 mg g<sup>-1</sup> for Cr(III) [35]. On the other hand, the capacity of the other clay minerals such as montmorillonite is 21.7 mg g<sup>-1</sup> for Pb(II) [36], 46.1 mg g<sup>-1</sup> for Hg(II) [37] and 5.13 mg g<sup>-1</sup> for Cr(III) [38]. The capacity of modified hectorite is 54.7 mg g<sup>-1</sup> for Hg(II) [37]. These comparable results demonstrated that BNT-AAP showed relatively high adsorption capacity toward Cr(III), Hg(II) and Pb(II).

### 3.7. Effects of coexisting ions

The effect of different cations and anions on the adsorption of Cr(III), Hg(II) and Pb(II) on BNT-AAP were studied using the batch procedure. The tolerance limit was set as the amount of ions causing recoveries of the examined elements to be less than 90%. As shown in Table 3, in excess of 2000 µg mL<sup>-1</sup> of K<sup>+</sup> and Na<sup>+</sup>, 500 µg mL<sup>-1</sup> of Ca<sup>2+</sup>, Mg<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>, 50 µg mL<sup>-1</sup> of Ni<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup> and Fe<sup>3+</sup> did not interfere with the separation and determination of Cr(III), Hg(II) and Pb(II). The possible factor for this reason is the 4-aminoantipyrine functionalized group inherent selectivity. The results demonstrated that BNT-AAP expressed a high adsorptive selectivity towards Cr(III), Hg(II) and Pb(II).

### 3.8. The detection limits and analytical precision

Under the selected conditions, eight portions of standard solutions were enriched and analyzed simultaneously following the recommended procedure. The detection limit (3σ) was found to be 0.12, 0.09 and 0.23 ng mL<sup>-1</sup> for Cr(III), Hg(II) and Pb(II), respectively. The relative standard deviation (RSD) was lower than 3.0% (Cr(III): 2.7%, Hg(II): 2.1% and Pb(II): 1.6%), which revealed that the method presented good precision for the analysis of trace Cr(III), Hg(II) and Pb(II).

**Table 3**

Effect of foreign ions on adsorbing recovery of 1.0 µg mL<sup>-1</sup> of Cr(III), Hg(II) and Pb(II) on the sorbent (GBW08301 and GBW08501).

Coexisting ion	Concentration (µg mL <sup>-1</sup> )	Recovery of analytes (%)		
		Cr(III)	Hg(II)	Pb(II)
K <sup>+</sup>	2000	98.46	96.93	100
Na <sup>+</sup>	2000	97.65	96.73	98.58
Ca <sup>2+</sup>	500	95.22	97.68	94.63
Mg <sup>2+</sup>	500	97.95	98.27	93.19
PO <sub>4</sub> <sup>3-</sup>	500	99.13	96.64	98.78
SO <sub>4</sub> <sup>2-</sup>	500	96.46	96.89	99.43
Ni <sup>2+</sup>	50	98.72	97.70	95.17
Cd <sup>2+</sup>	50	97.37	94.91	96.72
Zn <sup>2+</sup>	50	95.12	97.35	98.45
Mn <sup>2+</sup>	50	98.47	96.84	97.74
Co <sup>2+</sup>	50	98.59	98.95	98.52
Cu <sup>2+</sup>	50	95.23	96.37	95.57
Fe <sup>3+</sup>	50	96.62	97.42	97.41

**Table 4**

Analysis results for the determination of Cr(III), Hg(II) and Pb(II) in standard reference materials.

Ion	Found by present method <sup>a</sup> (µg g <sup>-1</sup> )	Certified value (µg g <sup>-1</sup> )	<i>t</i> -Test <sup>b</sup>
GBW08301			
Cr(III)	91.1 ± 3.5	90.0 ± 4.0	0.89
Hg(II)	0.31 ± 0.3	0.22 ± 0.2	0.85
Pb(II)	77.6 ± 3.7	79.0 ± 6.0	1.07
GBW08501			
Cr(III)	0.91 ± 0.06	0.94 ± 0.07	1.41
Hg(II)	0.049 ± 0.005	0.046 ± 0.006	1.70
Pb(II)	0.95 ± 0.06	0.99 ± 0.04	1.89

<sup>a</sup>  $\bar{x} \pm s$  ( $n = 8$ ),  $\bar{x}$ : average value for eight determinations;  $s$ : standard deviation;

<sup>b</sup>  $t_{0.05,8} = 2.31$ .

**Table 5**

Analysis results for the determination of Cr(III), Hg(II) and Pb(II) in environmental samples.

Ion	Added (µg L <sup>-1</sup> )	Found <sup>a</sup> (µg L <sup>-1</sup> )	Recovery (%)
Top water			
Cr(III)	0	2.07 ± 0.14	
	5	7.32 ± 0.09	103.5
	10	12.14 ± 0.10	100.6
Hg(II)	0	– <sup>b</sup>	
	5	5.12 ± 0.09	102.4
	10	9.83 ± 0.14	98.3
Pb(II)	0	3.15 ± 0.15	
	5	8.02 ± 0.08	98.4
	10	13.49 ± 0.10	102.6
Yellow River water			
Cr(III)	0	3.02 ± 0.13	
	5	8.26 ± 0.08	103.0
	10	12.93 ± 0.10	99.3
Hg(II)	0	1.82 ± 0.11	
	5	6.71 ± 0.07	98.4
	10	11.74 ± 0.12	99.3
Pb(II)	0	3.56 ± 0.11	
	5	8.72 ± 0.09	101.9
	10	13.38 ± 0.08	98.7

<sup>a</sup> The value following “±” is the standard deviation ( $n = 3$ ).

<sup>b</sup> Not detected.

### 3.9. Application of the method

Certified reference materials (GBW08301 and GBW08501) were used for method validation. Applying the *t*-test, the  $t_{0.05}$ , three values for certified reference materials of GBW08301 and GBW08501 were listed in Table 4. As could be seen, there did not exist statistical differences between determined values and certified ones. The analytical results for the standard materials were in good agreement with the certified values.

The proposed method has been also applied to the determination of trace Cr(III), Hg(II) and Pb(II) in water samples. As could be seen in Table 5, the recoveries of Cr(III), Hg(II) and Pb(II) were in range of 98–104%. The results demonstrated that BNT-AAP was used for determination of trace Cr(III), Hg(II) and Pb(II) in water samples with satisfactory results. Therefore, the proposed method was reliable and successful.

## 4. Conclusions

A simple, sensitive and reliable method was established for the determination of trace Cr(III), Hg(II) and Pb(II) in water samples using 4-aminoantipyrine modified bentonite as a solid-phase extractant. The optimum enrichment acidity was 4.0 and the important characteristics of BNT-AAP were short extraction time and high enrichment factor. The maximum adsorption capacity of BNT-AAP was found to be 38.8, 52.9 and 55.5 mg g<sup>-1</sup> for Cr(III), Hg(II) and

Pb(II), respectively. In addition, the preparation of BNT-AAP was relatively simple and rapid. This new developed method has been validated by analyzing certified reference materials and successfully applied to the analysis of trace Cr(III), Hg(II) and Pb(II) in water samples. The precision and accuracy of the method are satisfactory.

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