



## 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 isomorphous 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

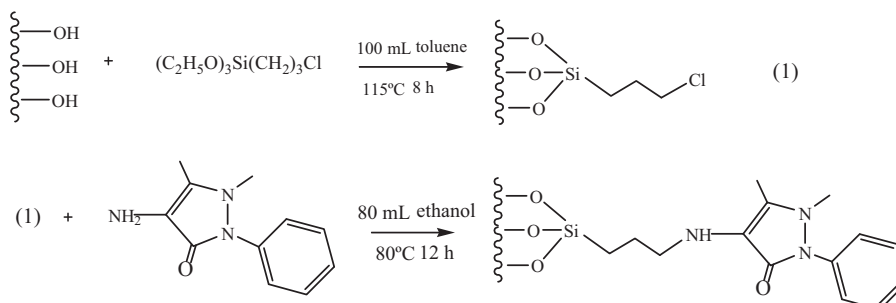


Fig. 1. Synthetic route of the BNT-AAP.

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