



Study on solid-phase extraction and flame atomic absorption spectrometry for the selective determination of cadmium in water and plant samples with modified clinoptilolite

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ARTICLE INFO

Article history:

Received 15 April 2009

Received in revised form 30 June 2009

Accepted 30 June 2009

Available online 5 July 2009

Keywords:

Solid-phase extraction

Natural zeolite

Clinoptilolite

Flame atomic absorption spectrometry

Cadmium

Sorption mechanism

ABSTRACT

A sensitive, simple separation and solid-phase procedure, which is sorption and desorption of cadmium on modified clinoptilolite zeolite (with surfactant and neothorine), for preconcentration of cadmium prior to analysis by FAAS is described. The sorbent has exhibited good sorption potential for cadmium at pH 5. Cadmium was eluted from the column by nitric acid which resulted in preconcentration factor of 160. Thermodynamic behaviors for the process are investigated and adsorption process is interpreted in term of Freundlich equation. A detection limit of 0.015 ng mL^{-1} was obtained and it is shown that calibration curve is linear from 0.01 to $4.0 \mu\text{g mL}^{-1}$ in the final solution. Furthermore, the effects of various parameters such as pH, flow rate of the sample and eluent solution were studied. This method was successfully applied for determination of cadmium in various plant and real water samples.

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1. Introduction

The levels of heavy metals circulating in the environment have seriously increased during the last few decades due to human activity. In particular, the toxicity of cadmium for plants, animals and human life is well documented by several studies that have been carried out. Among the environmental trace elements, cadmium presents the most insidious and widespread health hazard. When inhaled, cadmium completely absorbs in the lungs; it is also known that not only cadmium induces arterial hypertension and affects on the kidneys, but also some toxic effects attributed in the past to lead (proteinuria) [1–3].

Consequently, the development of reliable methods for the removal and determination of cadmium in environmental samples is a significant subject. Among the spectral methods, FAAS method is simple, rapid, reliable, low cost and present in almost all analytical laboratories. On the other hand, FAAS is highly selective (as atomic lines are sharp) but not that sensitive compared to widely accepted and costlier ICP-MS, ICP-AES and GF-AAS. Hence, combining a preconcentration step prior to FAAS determination is often resorted by various researchers [4–9]. In recent years, differ-

ent preconcentration techniques such as coprecipitation [10] and solid-phase extraction [11–13] have been used for analyte sample enrichment.

Solid-phase extraction of traces of heavy metal ions is widely used in preconcentration methodology. Batch and column procedures are the two important parts of the solid-phase extraction. Various solid materials such as activated carbon [14], cellulose [15], naphthalene [16], amberlite XAD-2 resin [17], Polymeric adsorbent resin [18] and synthetic zeolites [19] have been used for solid-phase extraction. Some of these adsorbents are suitable for preconcentration of metal ions, but their methods of preparation are time-consuming and involve rigid control of conditions.

Natural zeolites have been intensively studied recently because of their applicability in removing by utilizing the ion exchange phenomenon [20–24]. The main reason of the interest for natural zeolite-bearing materials is the increasing demand of low-cost ion exchange and adsorbent materials in such fields as energy production, pollution control and metal recovery as well as their wide availability on the earth [25].

Clinoptilolite with the simplified formula $(\text{Na}, \text{K})_6 \text{Si}_{30} \text{Al}_6 \text{O}_{72} \cdot n\text{H}_2\text{O}$ is the most abundant natural zeolite and may serve as cost-effective sorbent. Although clinoptilolite is commonly used as a cation exchanger, it can be modified to increase its total organic carbon content in order to enhance sorption of anionic and organic compound [26,27].

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In the present paper an attempt is made to investigate the adsorption of cadmium ions from real water and plant samples on surfactant modified clinoptilolite loaded with neothorin. The significance of this work is the possibility of using a cheap natural adsorbent for concentration of trace amounts of cadmium ions in a regime of solid-phase extraction. Moreover, in our study, it is aimed to investigate the thermodynamic of adsorption and obtain the best conditions for maximum removal of cadmium.

2. Experimental

2.1. Apparatus

A Varian model spectrAA220 flame atomic absorption spectrometer was used for the analysis. The instrumental conditions were selected as suggested by manufacturer (current: 4.0 mA, wavelength: 228.3 nm, the bandwidth of the slit: 0.5 nm). The flame composition was acetylene with a flow rate of 2.0 L min⁻¹ and air with a flow rate of 10.0 L min⁻¹. The suggested flow rate for Nebulizer ranges between 4 and 6 mL min⁻¹. The 5.0 mL min⁻¹ was used for all experiments. A metrohm 713 pH meter (Switzerland) was employed for pH measurements. For preconcentration procedures a glass column (500 mm × 10 mm) equipped with Teflon tap was used.

2.2. Reagents and solutions

Cadmium nitrate (Merck, Darmstadt, Germany) solution was prepared by dissolving the analytical grade sample in distilled water and standardized by known methods. A 0.001 mol L⁻¹ solution of neothorin (Fluka, Steinheim, Germany) in distilled water was prepared. Benzyltrimethyltetradecylammonium chloride (BDTA, 98% purity, Merck) dissolved in distilled water to obtain a 0.050 mol L⁻¹ solution. Alkali metal and various metal (Merck) solutions were used for studying of anionic and cationic interferences. Buffer solution of pH, 4–5.5, was prepared by mixing 0.1 mol L⁻¹ sodium acetate and 0.1 mol L⁻¹ acetic acid solutions in appropriate ratio. Natural clinoptilolite zeolite was obtained from Semnan region in the center of Iran.

2.3. Zeolite modification

The clinoptilolite tuff was ground and sieved to a size range of 0.110–0.125 mm. Prior to use, the zeolite was treated with 100 mL of 1 mol L⁻¹ of sodium acetate/acetic acid buffer (pH 5) and then rinsed with water to remove any residual carbonate. The pretreated minerals were dried at 60 °C overnight and stored in polyethylene containers. The ammonium ion has a high affinity for clinoptilolite and it can be used to replace other cations. Thus, H-clinoptilolite was prepared from the ammonium form of clinoptilolite by calcination at 380 °C for 2 h [28–30].

Clinoptilolite was saturated with zinc to obtain a uniform substrate and avoid entrance of analyte into pores of zeolite after elution with HNO₃ by shaking 10 g of clinoptilolite for 2 h with 100 mL of 100 µg L⁻¹ zinc solution. This was followed by 2 rinses with 4 mol L⁻¹ nitric acid and 3 rinses with distilled water and finally a drying stage is imposed onto them.

Natural zeolites have negatively charged surfaces that can be modified by cationic surfactants to increase their total organic carbon in order to enhance sorption of nonionic organic compound. The zinc-saturated clinoptilolite was modified with BDTA. Surfactant modification consisted of 10 g of clinoptilolite with 250 mL of the BDTA solution (0.050 mol L⁻¹) for 24 h at 25 °C. It is shown that this time is sufficient for complete reaction of BDTA on clinoptilolite. The BDTA-modified clinoptilolite was placed on a paper filter

in a büchner funnel, rinsed with 30–50 mL of distilled water and air-dried.

A glass column (500 mm height × 10 mm internal diameter) equipped with Teflon tap was loaded with 1.00 g of the modified clinoptilolite. Then 4 mL of 0.001 mol L⁻¹ solution of neothorin was passed through it at flow rate of 1 mL min⁻¹. Prior to sample loading, the column was preconditioned by passing a buffer solution.

2.4. Procedure for the sorption of cadmium on the column

An aliquot of the solution containing 0.05–20 µg of cadmium was taken in a beaker and 2.0 mL of buffer solution with pH 5 was added to it and then diluted to 50 mL with distilled water. This solution was passed through the column at flow rate 1.0 mL min⁻¹. After passing this solution, the column was washed with 3 mL of distilled water. The adsorbed cadmium on the column was eluted with 5.0 mL of 2.5 mol L⁻¹ nitric acid, at flow rate 0.7 mL min⁻¹. The eluent was collected in a 5.0 mL volumetric flask and cadmium was determined by flame atomic absorption spectrometry.

2.5. Sorption isotherm models

Analysis of equilibrium data is important for developing an equation that can be used to compare different materials under different operational conditions. Moreover, it is used to design and optimize an operating procedure [31].

The sorption equilibrium data for Cd on modified clinoptilolite zeolite is analyzed in terms of the Freundlich and Langmuir isotherm models. The relative coefficients of these models were calculated using linear least-squares fitting. The Freundlich isotherm based on sorption on a heterogeneous surface is as follows [32]:

$$q_e = K_F C_e^{1/n} \quad (1)$$

where q_e is the amount adsorbed at equilibrium (µg g⁻¹) and C_e is the equilibrium concentration (mg L⁻¹). K_F and n are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively. The linearized form of Freundlich sorption isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

By plotting $\ln q_e$ versus $\ln C_e$, K_F and n can be determined if a straight line is obtained.

The Langmuir sorption isotherm $q_e = (q_m b C_e)/(1 + b C_e)$ on linearization becomes: $C_e/q_e = (C_e/q_m) + (1/q_m b)$ where q_e is the amount adsorbed at equilibrium (mg g⁻¹), C_e the equilibrium concentration (mg L⁻¹), b a constant related to the energy or net enthalpy of adsorption (L mg⁻¹) and q_m is the maximum adsorption capacity (mg g⁻¹). By plotting C_e/q_e versus C_e , q_m and b can be determined.

3. Results and discussion

3.1. General results

Influence of pH on extraction of cadmium is shown in Fig. 1. Based on the results, the maximum sorption is in the pH range of 4.0–6.2. In subsequent studies, the pH was maintained at approximately 5. At pH values below 4.0 the concentration of hydroxonium ions in the solution would be high and prevent any adsorption onto the active sites on the substrate surface. Similarly, in basic solution (pH > 7) the concentration of OH⁻ ions would be high, leading to precipitation of the cations as their corresponding hydroxides rather than their adsorption on to the adsorbent surface. The effect of sample flow rate was also examined under the optimum conditions. The flow rates were adjusted in range of 0.2–3.0 mL min⁻¹.

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