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Talanta

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Ion-imprinted silica adsorbent modified diffusive gradients in thin films technique: Tool for speciation analysis of free lead species



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ARTICLE INFO

Article history:

Received 17 July 2015

Received in revised form

27 October 2015

Accepted 1 November 2015

Available online 9 November 2015

Keywords:

Diffusive gradients in thin films

Lead

Ion-imprinted

Water

ABSTRACT

A new diffusive gradients in thin films (DGT) device, using Pb(II) ion-imprinted silica (IIS) as the binding agents and commercial cellulose acetate dialysis (CAD) membrane as the diffusion layer (CAD/IIS-DGT), has been developed and evaluated for sampling and measurement of free Pb(II) species. The CAD/IIS-DGT devices were successfully applied to the measurement of free Pb(II) species in synthetic solutions, in natural freshwaters and in industrial wastewaters. The CAD/IIS-DGT provides reliable results over pH range of 4.5–6.5 and a wide range of ionic strength from 1.0×10^{-3} to 0.7 mol L^{-1} . The concentrations of the free Pb(II) species in synthetic solution containing different concentrations of ligands measured by CAD/IIS-DGT showed a good agreement with the value measured by Pb-ion selective electrode. Field deployments of the CAD/IIS-DGT devices allowed accurate measurements of the concentrations of free Pb(II) species.

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1. Introduction

Chemical species of an element are critical factors influencing their mobility, bioavailability, and toxicity to organisms [1]. Dissolved free ions are considered as the chemical species that are directly available to organisms, as opposed to the fraction of contaminants adsorbed to particulate or colloidal material [2]. However, accurate and reliable measurement of free ion concentration in the natural environment remains a challenge due to the co-existence of various chemical forms and its low concentrations [3].

Lead (Pb), one of the most toxic heavy metals, is accumulated throughout the food chain and is becoming a serious threat to our environment [4]. Available analytical techniques, such as ion selective electrode [5], cathodic stripping voltammetry [6], permeation liquid membranes method [7], Donnan membrane technique [8], cation exchange resin method [9], dialysis [10] and liquid membrane technique [11], have been developed to measure the concentration of free Pb(II) ion. Most of these methods suffer from chemical interferences, poor detection limits, competition effects, equilibrium shift or long equilibration time [12–14].

The diffusive gradients in thin films (DGT) technique is a promising tool for in situ speciation of metals in environments [15–17]. The DGT

device contains a diffusion layer, conventionally a polyacrylamide hydrogel, and a binding agent, typically the Chelex-100 resin [17]. Conventional DGT design allows the determination of free ions of metals, labile inorganic and organic compounds, excluding large particles and colloids (which are not quantified) [18]. Many adsorbents have been developed as the binding agent for the measurement of different pollutants or different species of an element, including silver iodide for sulfur [19], half-dried amorphous zirconium oxide for reactive phosphate [20], 3-mercaptopropyl functionalized silica for methylmercury [21] and As(III) [22], ammonium molybdophosphate for cesium [23], manganese dioxide for uranium [24] and radium [25], activated carbon for gold [26], and precipitated ferrihydrite for As(V), Se(VI), V(V), and Sb(V) [27]. Chemical speciation analysis of metals can be performed by DGT device with the different binding agents. For the speciation measurement of Pb(II), some functional materials such as Chelex-100 resin [18], polymer-bound Schiff base [28], poly(ethyleneimine) [29], and carboxymethyl cellulose sodium [30], were used as the binding agents. A vast majority of DGT binding agents published to deal with Pb(II) only focus on the measurement of labile fraction of Pb(II) ions [28–34]. Less attention has been devoted to developing DGT device for the specific measurement of free species of Pb(II) occurring in aquatic environments. Therefore, it is necessary to develop new specific sorbents as DGT binding agent for the measurement of free Pb(II) species.

Recently, ion-imprinted materials have received increasing attention as sorbent for the pre-concentration, separation and removal

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of heavy metals from aqueous solution [35]. The studies suggested that ion-imprinted sorbents have higher selective affinity for the template ion due to the hole-size and coordination-geometry theory [36]. By using free Pb(II) ion as the template, the imprinted sorbent exhibits high selective affinity for free Pb(II) ion, while inorganic and organic complexes of Pb(II) in environment can not match with the imprinted cavity of free Pb(II) ions due to their large size.

In this research, a new configuration of DGT for measuring concentration of free Pb(II) species was developed by using ion-imprinted silica (IIS) as binding agent and cellulose acetate dialysis (CAD) membrane as diffusion layer (CAD/IIS-DGT). The validation of CAD/IIS-DGT for the measurement of free Pb(II) species was studied. The effects of pH and ionic strengths on the performance of CAD/IIS-DGT were investigated. Furthermore, the application of CAD/IIS-DGT in water samples was assessed.

2. Experimental

2.1. Materials

CAD membrane (12,000 MWCO) was purchased from Shanghai Yuanju biological Technology Co., Ltd., Shanghai, China and were pretreated followed the procedure by Li et al. [37]. 3-(2-Aminoethylamino) propyltrimethoxysilane (APS), acrylamide, bis-acrylamide, ammonium peroxydisulfate, tetramethylethylenediamine (TEMED) and humic acid (HA, molecular weight 13,000) were obtained from Sigma-Aldrich. Silica gel (80–120 mesh) was purchased from Qingdao Ocean Chemical Co., (Qingdao, China). The other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All chemicals used in this work were of analytical grade and all solutions were prepared with deionized water.

2.2. Preparation and characterization of ion-imprinted silica

IIS and non-imprinted silica (NIS) sorbents were prepared according to the steps described in Ref. [38]. The preparation process carried out is described (as shown in Supporting Information). The sorbents were characterized by Fourier transmission infrared (FT-IR) spectroscopy (Spectrum One, Perkin-Elmer) through KBr pellets with a resolution of 1 cm^{-1} in the range of $400\text{--}4000\text{ cm}^{-1}$, and by Shimadzu SSX-550 scanning electron microscope (SEM) at the desired magnification operating at 30 kV. The specific surface area was obtained from nitrogen adsorption isotherms at 77 K by a surface area analyzer (ASAP 2010C, Micromeritics, USA).

2.3. Adsorption experiments

Batch experiments were carried out to optimize the effects of pH (1.5–6.5), initial concentrations of Pb(II) ions ($50\text{--}600\text{ mg L}^{-1}$), and contact time (5–120 min) on the adsorption of Pb(II) ions by the sorbents. Dosage of the sorbents was 4 g L^{-1} . The solution pH was adjusted with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions. The solution mixture was stirred at $25 \pm 1\text{ }^\circ\text{C}$. After adsorption, the suspension was filtered with a $0.45\text{-}\mu\text{m}$ syringe filter, and the final concentration of Pb(II) ions in solution was analyzed using atomic fluorescence spectroscopy (AFS, model AFS 8220, Beijing Haiguang Instruments Co. Ltd.) [39]. The blanks solution were below the instrument detection limits of $10\text{ }\mu\text{g L}^{-1}$ for Pb(II) ions. The amount of Pb(II) ions adsorbed onto the sorbents in solution was calculated using the following equation:

$$q = (C_0 - C_e) V / 1000 W \quad (1)$$

where q represents the experimental value of adsorption capacity

(mg g^{-1}), C_0 and C_e represent the initial and final concentrations of metal ions (mg L^{-1}), W is the mass of sorbent (g), V is the volume of metal ion solution (L).

2.4. Preparation of binding gel

Binding gels were prepared as reported by Zhang and Davison [17]. Briefly, 1.5 g of the IIS was added to 10 mL pre-gel solution (15% acrylamide and 0.3% DGT cross-linker) and this solution was mixed well on a vortex mixer for 3 min. Then 70 μL of 10% freshly prepared ammonium persulfate and 25 μL TEMED were added. The solution was mixed and cast between two glass plates with a spacer separating the plates. The glass assembly was placed in an oven at $45\text{ }^\circ\text{C}$ for 1 h, and afterwards the binding gel was peeled off and the 2.5 cm diameter disks of binding gel was cut and stored in deionized water. The thickness of the hydrated gel was $0.50 \pm 0.05\text{ mm}$.

2.5. Measurement of diffusion coefficients of Pb(II) ions

Diffusion coefficients of Pb(II) through the CAD membrane were measured using both diffusion cell and DGT devices. A previously described diffusion cell which consisted of two compartments connected by a 2 cm diameter circular window containing a $85\text{ }\mu\text{m}$ thick CAD membrane was used to measure the diffusion coefficients of Pb(II) ions through the CAD membrane (Fig. S1, Supporting information). 100 mL of carrier solution was introduced into one compartment (known as the receptor solution) and 100 mL of carrier solution containing the Pb(II) ions was introduced into the other (known as the source solution). To test the effect of ionic strengths on diffusion coefficients of Pb(II) ions through the CAD membrane, ionic strengths of both solutions in the range of $0.001\text{--}0.7\text{ mol L}^{-1}$ were adjusted with addition of different mass of NaNO_3 . Variation in temperature was less than $\pm 1\text{ }^\circ\text{C}$ during the course of each experiment. Diffusion coefficients (D_{cell}) were calculated from the slope of a linear plot of measured mass of Pb(II) ions diffused through the CAD membrane versus time, using Eq. (2) [40],

$$D_{\text{cell}} = \text{slope} \cdot \Delta g / C \cdot A \quad (2)$$

where A is the exposed area of CAD membrane (3.14 cm^2), Δg is the thickness of CAD membrane (0.085 cm), and C is the concentration of Pb(II) ions initially present in the source compartment of the diffusion cell.

Diffusion coefficients were also measured by immersing DGT devices in known concentrations of solutions for known time. 5 L of solutions containing 10 mg L^{-1} of Pb(II) ions and different concentrations of NaNO_3 solution in the range from 0.001 to 0.7 mol L^{-1} were prepared at pH 5. After 24 h exposure, the mass of Pb(II) ions accumulated by DGT devices were measured. When using DGT devices, D_{DGT} was calculated using Eq. (3), where M is the mass of Pb(II) ions accumulated during deployment time (t), C_b is the concentration of Pb(II) ions in bulk solution [40]

$$DDGT = M \cdot \Delta g / A \cdot C_b \cdot t \quad (3)$$

2.6. Performance of CAD/IIS-DGT

Elution efficiencies were tested by exposing triplicate binding gel discs to 10 mL of solutions containing 10 mg L^{-1} Pb(II) ions at pH 5 with stirring for 2 h. And then the binding gels were removed from the solutions and eluted using four different concentrations (1, 2, 3 and 6 mol L^{-1}) of HNO_3 solution at $90\text{ }^\circ\text{C}$. The

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