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Separation and recovery of lead from a low concentration solution of lead(II) and zinc(II) using the hydrolysis production of poly styrene-co-maleic anhydride

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ABSTRACT

The Pb—Zn separation/preconcentration technique, based on the complex formation reaction of Pb(II) and Zn(II), using a copolymer poly(styrene-co-maleic anhydride) (PSMA), without adding any carrier element was developed. The effects of several experimental parameters such as solution pH, temperature and adsorption time were studied. The experimental results show that the PSMA resin–Pb equilibrium was achieved in 2 min and the Pb(II) loading capacity is up to 641.62 mg g^{-1} in aqueous solution under optimum conditions, which is much higher than the Zn(II) loading capacity within 80 min. The adsorption test for Pb(II) indicates that PSMA can recover Pb(II) from a mixed solution of Pb(II), Zn(II) and light metals such as Ca(II) and Mg(II) with higher adsorption rate and larger selective coefficient. A further study indicates that PSMA as chelating resins recovering Pb(II) can be regenerated via mineral acid (6 M H_2SO_4). PSMA was synthesized by radical polymerization and tested as an adsorbent for the selective recovery of Pb(II). In addition, the formation procedure and structure of Pb–PSMA complex were also studied. Both the PSMA and the Pb–PSMA complex were characterized by means of FTIR spectroscopy, elemental analysis, gel permeation chromatography (GPC) and atomic absorption spectrometry (AAS).

1. Introduction

Lead presents a threat to human health and environment when it exists in or is discharged into water resources because of its high toxicity and carcinogenicity, and it is not biodegradable in nature [1–4]. The development of high-performance adsorbents for removing lead from wastewater and drinking water is considered as a research priority in the environmental protection field [5–11]. However, lead and zinc ions are usually found to coexist in minerals and wastewater, which makes the separation of them to be difficult. Therefore, the separation and recovery of lead from the mixture of lead and zinc is very urgent.

A vast literature body now exists that deals with lead separation [12–14], but the methods are either costly or ineffective. The use of polymer-bonded ligands in selective lead removal has been the subject of many research articles [15–18] and reviews [19–21], and there are many articles describing the use of polymer-supported ligands such as xanthate [22], thiourea [23], pyridine-based thiols [24], and dithiozone [25] for highly selective lead removal. However, these materials also adsorb other metal ions in significant quantities. Therefore, development of new and more effective adsorbents for selective recovering Pb(II) has become essential, at the same time they should be cost effective.

In our previous work, we have reported the synthesis of MMC (macromolecular metal complexes) containing rare earth metals with polymeric ligands and their application as florescent materials [26,27]. As part of our continuing investigation into the development of MMC, herein we evaluate the Pb—Zn separation through formation of Pb–PSMA complex and the lead loading capacity of PSMA under competitive and noncompetitive conditions. Adsorption experiments reveal that the maximum adsorption capacity of PSMA for Pb(II) is 641.62 mg g^{-1}, which is much higher than that of other polymer resins for Pb(II) reported in previous references, for example, 21.91 mg g^{-1} in Ref. [15] and 117.9 mg g^{-1} in Ref. [18]. At the same time, the PSMA resin does not adsorb Zn(II) and light metals (such as Ca(II) and Mg(II) ions) within 80 min, so the high adsorption selectivity of the PSMA resin to Pb(II) can efficiently separate lead from zinc. A detailed structure and properties of both PSMA and Pb–PSMA complex was also performed. The results indicate that the as-prepared Pb–PSMA complex possesses three-dimensional network structure, which does not dissolve in water or typical organic solvents, revealing that the PSMA resin can be used as a potential chelating adsorbent to recover lead from a mixed solution. For the purpose of developing practical approach for separating lead from zinc in industrial solutions, the adsorption behavior of the PSMA resin for Pb(II) and Zn(II) has been investigated.

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2. Experimental

2.1. Instruments

Vibration spectra from 4000 to 400 cm^{-1} were recorded on a Thermo Nicolect Mattson 2110 spectrometer (KBr discs). Element analysis for C and H was carried on an Elemental Vario-EL elemental analyzer. Metal contents were determined on a Hitachi 180-80 polarized Zeeman atomic adsorption spectrometer (AAS). The average molecular weight of PSMA was estimated by a SN-01A gel permeation chromatography (GPC), using THF as fluent.

2.2. Materials

Styrene (supplied by Sigma–Aldrich, Shanghai, China) was washed with 10% aqueous sodium hydroxide to remove the inhibitor, and followed by washing with water until it was neutral. All the other chemicals used in this work were purchased from Alfa Aesar (Beijing, China) and used as received without further purification, and they were of analytical reagent grade. Stock standard solutions of 1 mg mL^{-1} Pb^{2+}, Zn^{2+} and a Pb^{2+}, Zn^{2+} mixture containing light metal ions (Ca^{2+} and Mg^{2+}) were prepared by dissolving the appropriate amount of analytical or spectrograde metal-nitrates in de-ionized water, respectively.

2.3. Preparation of the PSMA resin

PSMA resin was obtained by free radical copolymerization of maleic anhydride and styrene with benzoyl peroxide as initiator at 70 °C. The synthetic route of PSMA is shown in Fig. 1, and the details of the synthetic procedure are described in the literature [28]. The average molecular weight was evaluated by GPC method. The molar ratio of maleic anhydride to styrene in PSMA, calculated from the elemental analysis, is 1:2, so the content of maleic anhydride in PSMA is 3.162 mmol g^{-1}.

2.4. Adsorption capacities

1 g of dried PSMA resin was put into 35 mL of dilute KOH (0.1 M) solution; the mixture was stirred at room temperature until it dissolved completely. The resulting polymeric potassium carboxylate (K-PSMA) solution was adjusted to pH 6–7, and then added to a $Pb(NO_3)_2$ aqueous solution containing 1.02 mg mL^{-1} Pb(II) ion. The mixture was stirred continuously, the concentration of Pb(II) ion was determined by AAS at different intervals (such as 2 min, 5 min, 30 min, 60 min and so on) till it remained unchanged. The formed precipitates (Pb–PSMA) were separated from the solutions by centrifugation, then washed with water to remove aqueous Pb(II) and any other impurities, finally washed with ethanol and dried in a vacuum desiccator. The adsorption capacity Q (mg g^{-1}) was calculated according to the following formula (1):

$$Q = \frac{(C - C_0)V}{2W} \quad (1)$$

where C_0 (mg mL^{-1}) and C (mg mL^{-1}) represent the initial concentration of Pb(II) and the equilibrium concentration of Pb(II) in supernatant after adsorption, respectively; V is the volume of the solution used for adsorption (mL); and W is the weight of the resin (g). The formation procedure and structure unit of the Pb–PSMA complex are shown in Fig. 2.

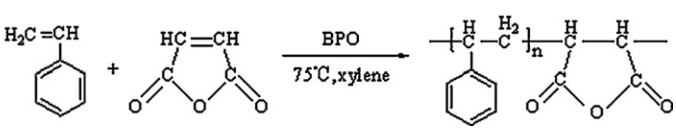

Fig. 1. Synthetic route of the PSMA resin.

Table 1
Elemental analysis of PSMA resin and Pb–PSMA complex.

	C	H	O	Pb
PSMA	72.05	5.34	22.61	
Pb–PSMA	46.93	4.25	35.76	13.04

2.5. Adsorption selectivity

To determine the adsorption selectivity of PSMA to Pb(II), the resin was placed in a binary mixed solution of Pb(II) and Zn(II) ions, in which the concentration of each metal ion was equal moles. Then, accurate amount of K-PSMA solution was put into this binary mixed solution and stirred continually. Finally, the Pb–PSMA complex was separated by centrifugation, and the concentrations of the metal ions in the binary mixture were determined by AAS.

2.6. Desorption and repeated use of the PSMA resin

For desorption of Pb(II), the Pb–PSMA complex was treated with 6 M H_2SO_4 solution. After filtration and being washed with water, the PSMA resin was dried under vacuum at 60 °C for repeated use. The detailed procedure is similar to the previous report [29], here, we do not expatiate it.

3. Results and discussion

3.1. Characterization of Pb–PSMA complex

3.1.1. Elemental analysis

The maleic anhydride content in the PSMA resin was determined by being titrated against potassium hydroxide aqueous solution (0.1 M) and further validated by elemental analysis. It was calculated with Eq. (2) as shown below:

$$\text{MA content (mmol g}^{-1}) = \frac{(V_1 - V_2)C}{2W} \quad (2)$$

where MA is maleic anhydride, V_1 and V_2 are the volume (mL) of KOH consumed by the resin and blank, respectively; C is the concentration of KOH aqueous solution; and W is the weight of the PSMA resin used. The content of maleic anhydride in the PSMA resin is 3.16 mmol g^{-1}. The elemental analysis results of the PSMA resin and Pb–PSMA complex were shown in Table 1.

The data in Table 1 show that the mole ratio of the maleic anhydride in the PSMA resin to Pb(II) is near to 1:1. This means that the mole ratio of carboxyl in K-PSMA to Pb(II) is near to 2:1.

3.1.2. Infrared spectra analysis

The bonding mode of Pb(II) to PSMA was examined by comparing the FTIR spectra of Pb–PSMA complex with that of the PSMA resin. As shown in Fig. 3, the FTIR spectra of Pb–PSMA complex are quite different from those of PSMA resin. The characteristic bands of the PSMA resin and Pb–PSMA complex are listed in Table 2. The results indicate that Pb–PSMA complex still has a weak absorption band at 1700–1705 cm^{-1} ascribed to $\nu_{C=O}$ of the uncoordinated carboxylic group. However, the absorption intensity of this band is

Table 2
FTIR spectra data of PSMA resin and Pb–PSMA complex (cm^{-1}).

complexes	ν_{O-H}	$\nu_{C=O}$	ν_{as} COO^-	ν_s COO^-	$\Delta\nu_{as\text{-}s}$
PSMA	2923/3434	1705			
K-PSMA	2924/3423		1563	1403	160
Pb–PSMA	2926/3433	1704	1544	1401	143