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Chelating adsorption properties of PEI/SiO_2 for plumbum ion

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Abstract

In this paper, a novel adsorption material PEI/SiO_2 with strong adsorption ability towards heavy-metal ions was prepared. In preparation of PEI/SiO_2, functional macromolecule polyethyleneimine (PEI) was grafted onto the surfaces of silica gel particles via the coupling effect of γ-chloropropyl trimethoxysilane (CP). The adsorption properties of PEI/SiO_2 for Pb^{2+} ion were studied by both static and dynamic methods. The experimental results show that PEI/SiO_2 possesses very strong adsorption ability for Pb^{2+} ion, the saturated adsorption amount could reach to 17.5 mg g^{-1}, and the empirical Langmuir isotherm was found to describe well the equilibrium adsorption data. The pH and grafting amount of PEI have great influence on the adsorption amount. The Pb^{2+} ions adsorbed on PEI/SiO_2 are eluted easily by diluted hydrochloric acid solution.

Keywords: Polyethyleneimine; Silica gel; Chelating adsorption; Plumbum ion

1. Introduction

Chelating resins are cross-linked polymers that contain chelate functional groups and are insoluble in water and other solvents. Among chelating resins, the nitrogen-type chelating resins have excellent adsorption property for heavy-metal ions [1–3], and are applied widely in separation, enrichment and removing of heavy-metal ions. Especially, the multi-amino chelating resins may form multidentate chelates owing to a great deal of amino groups existing in the molecules, and display excellent adsorption property for heavy-metal ions, together with their fine hydrophilicity. So they are being studied and developed widely [4,5]. In preparing the chelating resins of multi-amino group type, chemically modifying method for cross-linked polystyrene or other cross-linked polymers with multi-ethylene–multi-amine are often adopted [6–8], or cross-linked or non-cross-linked natural polymer chitosan containing many amino groups are also often used [9–11], especially, the latter method are used more extensively. However, there are some problems, for example, for the former method, prolixity of reaction steps and restricted chelating property; for the latter method, difficulty of graining and poor mechanical strength of chitosan, and restricted chelating property owing to the limited percentage of amino groups in chitosan molecule, and so on.

Polyethyleneimine (PEI) is a kind of water-soluble polyamine, and there is a large quantity of nitrogen atoms of amino groups on the line-type macromolecular chains of PEI, which can produce very strong chelating action [12–14], so PEI is a kind of new trapping agent for heavy-metal ions and has high adsorption amount even if under the condition of high content of alkaline-earth metal ions. The character of PEI has attracted wide attention of investigators, and its applications in adsorption separation fields of heavy-metal ions are developing. For example, some researchers coat PEI on the surfaces of ion exchange resin or silica gel particles to remove heavy-metal ions from water medium [15–17]. However, this is a physical treatment method, and the adsorption efficiency is limited. Others graft PEI onto the surface of fiber to improve the adsorption property of the adsorption fiber [18]. In this study, PEI was grafted onto the surface of silica gel particles via the coupling effect of γ-chloropropyl trimethoxysilane (CP), and the strong chelating property and hydrophilic nature of PEI were combined with high specific area and good mechanical strength of silica gel, and the novel chelating adsorption material PEI/SiO_2 was prepared. The experimental results show that PEI/SiO_2 displays excellent adsorption property for Pb^{2+}, and is easy to be regenerated and has the fine reusing repeatedly property. The elementary study results have revealed the outstanding character of the composite chelating adsorption material PEI/SiO_2, and it will have

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wide applications in the removing, enriching and separating of heavy-metal ions. Therefore, it is an important path for preparing functional composite-type particle material that functional macromolecule is grafted onto inorganic particle surface, and the concentrating effect of functional groups of the macromolecules is combined with good mechanical strength and low cost of inorganic particles.

2. Experiments

2.1. Materials and instruments

Silica was purchased from Ocean Chemical Limited Company (Qingdao, China). PEI was purchased from Qianglong Chemical Limited Company (Wuhan, China, AR grade).

Used instruments in this study were as follows: Unic-2602 UV spectrophotometer (Unic Company, American), Perkin-Elmer1700 infrared spectrometer (Perkin-Elmer Company, American), DDS-11Ar digit conductivity meter (Leici Instrument Limited Company of Shanghai, China), PHS-2 acidimeter (The Second Analytical Instrument Factory of Shanghai, China), 721 spectrophotometer (The Third analytical Instrument Factory of Shanghai, China).

2.2. Preparation and characterizing of adsorption particles of PEI/SiO_2

The preparation process of the PEI/SiO_2 was as follows. Firstly, silica gel articles were treated for activating by using aqueous solution of methane sulfonic acid as activation reagent. Secondly, activated silica gel was reacted with γ-chloropropyl trimethoxysilane (CP) at 80 °C by using xylene as solvent into which a little water was added, and chloropropylation of silica was realized and CP-SiO_2 was prepared. Finally, CP-SiO_2 was added into PEI aqueous solution with a certain concentration, reaction was carried out at 90 °C for 6 h, PEI was grafted onto silica gel surface in coupling manner, and the adsorption particles of PEI/SiO_2 were prepared. The amount of amino groups on PEI/SiO_2 was determined with conductivity titration method by using hydrochloric acid as titrant, and the grafting amount (g/100 g) of PEI was calculated further.

2.3. Static adsorbing of PEI/SiO_2 towards Pb^{2+} ion

2.3.1. Measure of kinetic adsorption curve

Aqueous solution (100 mL) of Pb^{2+} with concentration (C_0) of 100 mg L^{-1} was added into conical flask, then, 0.2 g of PEI/SiO_2 was added into a conical flask directly. The conical flask was placed in a shaker at a pre-settled temperature and pH and shaken. After an interval of time, the concentration (C_t) of Pb^{2+} solution was determined. The adsorption amount (Q) was calculated according to

$$Q = \frac{V(C_0 - C_t)}{m} \quad (1)$$

where V is the volume of the solution (L); m is the weight of absorbent PEI/SiO_2 (g).

2.3.2. Measure of adsorption isotherm with static method

Aqueous solution (100 mL) of Pb^{2+} with concentration (C_0) of 20, 40, 60, 80, 100, until 200 mg L^{-1} were added into each conical flask, respectively, then, 0.2 g of PEI/SiO_2 was added into a conical flask directly. The conical flasks were placed in a shaker at a pre-settled temperature and pH and shaken. After the adsorption reached equilibrium, the equilibrium concentration (C_e) of Pb^{2+} solution was determined. The equilibrium adsorption amount (Q_e) was calculated according to

$$Q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

2.4. Examination of influences of various factors on adsorption property of PEI/SiO_2

Varying the pH of each sample solution by buffer solutions, the influence of pH on the adsorption property of PEI/SiO_2 was examined. Varying the temperature of shaker, the influence of temperature on the adsorption property of PEI/SiO_2 was examined. Varying the grafting amount of PEI on silica gel, the influence of grafting amount on the adsorption property of PEI/SiO_2 was examined.

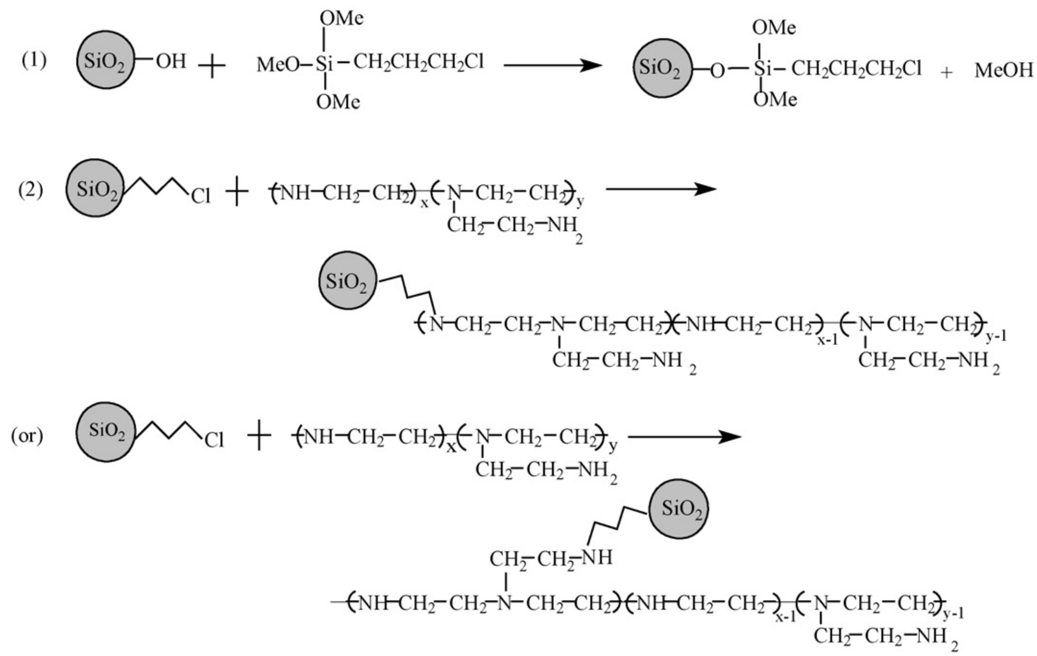
2.5. Dynamics adsorption and elution experiment of PEI/SiO_2

PEI/SiO_2 (1.5 g) were filled in a glass column with 8 mm of diameter, and the bed volume was 2 mL. The Pb^{2+} solution with concentration of 1 g/L and pH 6 was allowed to flow gradually through the column at a rate of five bed volumes per hour (5 BV/h). Collecting one bed volume of effluent, the concentration of the Pb^{2+} was determined, and the dynamics adsorption curve was measured. The leaking adsorption amount and the saturated adsorption amount were also calculated. Elution experiment were performed by using diluted hydrochloric acid solution with concentration of 0.01 mol/L as eluting agent, and the flow rate of the eluting agent was controlled at 1 BV/h, then, the eluent with one bed volume was collected, the concentration of the Pb^{2+} was determined, and the elution curve was plotted.

3. Results and discussion

3.1. Reaction process of preparing composite particles of PEI/SiO_2

The molecules of commercial PEI often have branch chains (Branched PEI), and it contains primary, secondary and ternary amino groups in a ratio of approximately1:2:1 [19] (its chemical structure can be seen from Scheme 1). γ-Chloropropyl trimethoxysilane (CP) was chosen as coupling agent to link silica gel and functional macromolecular PEI. After activating treatment, a great deal of silanol groups produce on silica gel particle surfaces, and γ-chloropropyl trimethoxysilane reacts with silanol groups to form modified silica gel (it can be called chloropropylation silica gel, CP-SiO_2). The chloropropyl groups on



Scheme 1. Synthesis route of composite chelation material PEI/SiO_2.

CP-SiO_2 react further with amine groups on PEI chains, macromolecule PEI is grafted onto silica surface in coupling mode, so that the composite particles of PEI/SiO_2 are formed finally. The coupling grafting reactions occur possibly on all of the active sites of the primary amine groups and secondary amine groups in PEI molecule, so there are two types of coupling grafting reactions. The reaction processes to prepare the composite material PEI/SiO_2 can be expressed in Scheme 1.

The infrared spectrums of PEI/SiO_2 are shown in Fig. 1. The characteristics absorptions of flex vibration and bend vibration of N–H bond appear at 3641 and 1701 cm^{-1}, respectively, and the characteristics absorptions of bend vibration of C–N bond appear at 1488 and 1560 cm^{-1}. The appearances of these absorption bands show that PEI macromolecules have been grafted onto silica gel surface, and PEI/SiO_2 particles have been formed.

3.2. Kinetic adsorption curve

The kinetic adsorption curve is shown in Fig. 2. The adsorption rate of PEI/SiO_2 for Pb^{2+} ion is fast, and the adsorption reaches to equilibrium in 30 min. It was implied that PEI/SiO_2 possesses very strong chelating adsorption ability for Pb^{2+} ions.

3.3. Adsorption isotherm of PEI/SiO_2 for Pb^{2+} ion

The adsorption isotherms of Pb^{2+} ion on PEI/SiO_2 are shown in Fig. 3. When the equilibrium concentrations of the Pb^{2+} ion reach to a certain value, the equilibrium adsorption amount change nearly no longer, namely the adsorptions become saturated. The adsorption isotherm is typical unimolecular layer

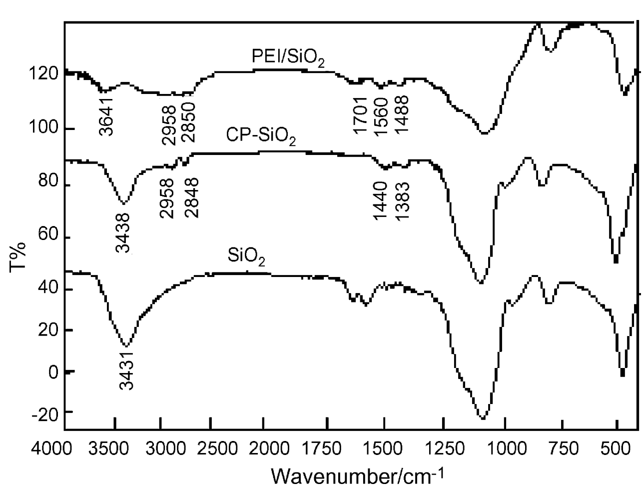


Fig. 1. FTIR spectrum of PEI/SiO_2.

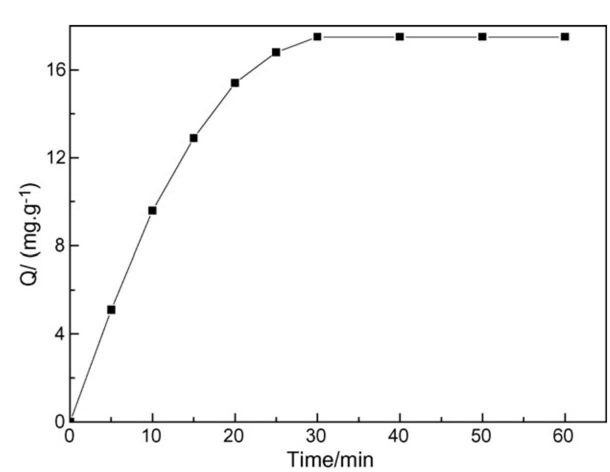


Fig. 2. Kinetic adsorption curve of Pb^{2+} ion on PEI/SiO_2.

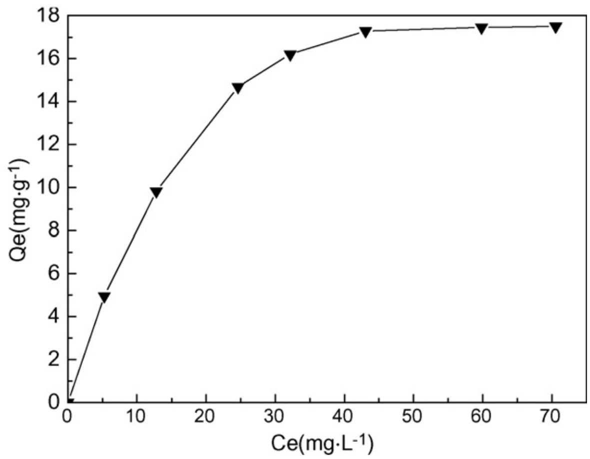


Fig. 3. Adsorption isotherms of Pb^{2+} ion on PEI/SiO_2. Grafting amount of PEI on SiO_2: 3.21 g/100 g; temperature: 24 °C; time: 30 min; pH 6.

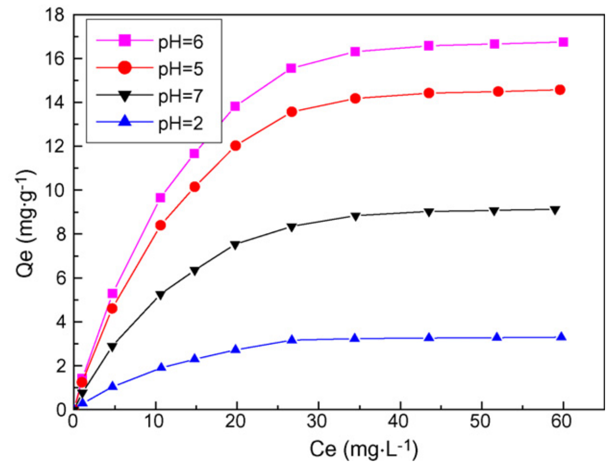


Fig. 5. Adsorption isotherms of Pb^{2+} at different pH. Grafting amount of PEI on SiO_2: 3.21 g/100 g; temperature: 24 °C; time: 30 min.

adsorption of Langmuir type. Langmuir equation is as follows:

$$Q_e = Q_m \frac{kC_e}{1 + kC_e} \quad (3)$$

or

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{kQ_m} \quad (4)$$

where Q_∞ (mg g^{-1}) is the saturated adsorption amount; k is the combine constant. The data in Fig. 3 are regressed linearly according to Eq. (4) and Fig. 4 is obtained. It was indicated fully in Fig. 4 that the Pb^{2+} ion is adsorbed on the PEI/SiO_2 chemically in coordination bond and monomolecular layer.

3.4. Influences of different factors on adsorption property of PEI/SiO_2

3.4.1. Influences of pH

The adsorption isotherms of Pb^{2+} on PEI/SiO_2 at different pH are shown in Fig. 5. It was seen that the adsorption amount of Pb^{2+} is various at different pH. As pH < 6, the adsorption amount of Pb^{2+} increases with the enhancing of pH; as pH 6, the adsorption amount reaches to maximum; whereas as pH > 6, the adsorption amount decreases. In acidic solution, most of N atoms of the amino groups in the macromolecular chains of PEI are protonated [19], the protonation degree of N atoms of amino groups decreases with the decline of acidity, so that the adsorption amount of Pb^{2+} increases with the rising of pH value. As pH > 6, the hydrolytic action of Pb^{2+} will occur, so the adsorption amount again decreases.

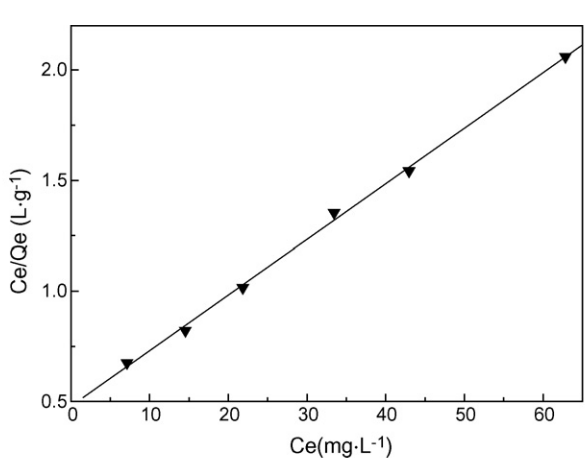


Fig. 4. Plot of equilibrium amount Q_e vs. equilibrium concentration C_e.

3.4.2. Influences of temperature

The adsorption isotherms of Pb^{2+} on PEI/SiO_2 at different temperature are shown in Fig. 6. The adsorption amount of Pb^{2+} ion increases with the rising of temperature, and the influence of temperature on the adsorption amount is greater. The saturated adsorption amount at 46 °C is 19.16 mg g^{-1}, which is far greater than 17.5 mg g^{-1} of the saturated adsorption amount at 24 °C. The fact that the adsorption amount of Pb^{2+} increases with the rising of temperature implies that the chelation adsorbing of PEI/SiO_2 towards Pb^{2+} is an endothermic process.

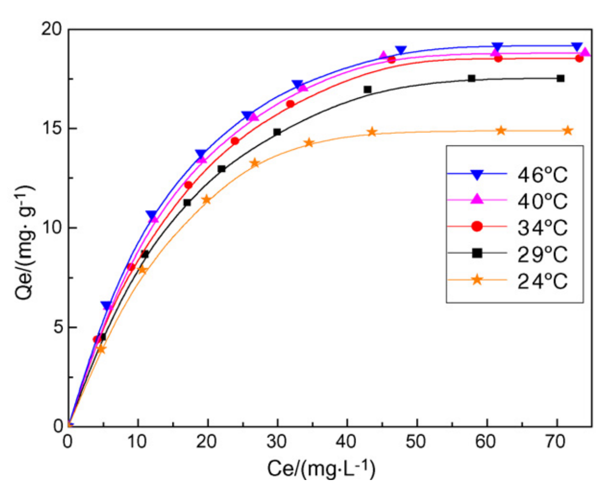


Fig. 6. Adsorption isotherms of Pb^{2+} at different temperature. Grafting amount of PEI on SiO_2: 3.21 g/100 g; time: 30 min; pH 6.

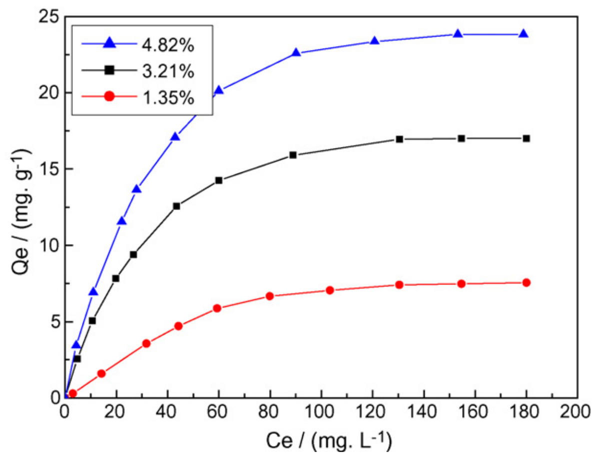


Fig. 7. Adsorption isotherms of Pb^{2+} at different grafting amounts of PEI on SiO_2. Temperature: 24 °C; time: 30 min; pH 6.

3.4.3. Influences of PEI grafting amount

The adsorption isotherms of Pb^{2+} on PEI/SiO_2 at different grafting amount are shown in Fig. 7. The adsorption property of PEI/SiO_2 increases remarkably with the increase of the grafting amount of PEI on SiO_2. The specific weight of the PEI/SiO_2 is greater, however, the saturated adsorption amount of Pb^{2+} on PEI/SiO_2 with a grafting amount of 4.82 g/100 g is as high as 23.82 mg g^{-1}, and the concentrating effect of functional groups (amino group) on polyamine macromolecule chains has been fully displayed.

3.5. Dynamic adsorption curve

The dynamic adsorption curve of PEI/SiO_2 for Pb^{2+} is shown in Fig. 8. When Pb^{2+} solution passes through PEI/SiO_2 column, leaking appears at 5BV, the leaking adsorption amount is 7.65 mg g^{-1}, and the saturated adsorption amount is 16.86 mg g^{-1}. The dynamic adsorption amount is similar with the static adsorption amount.

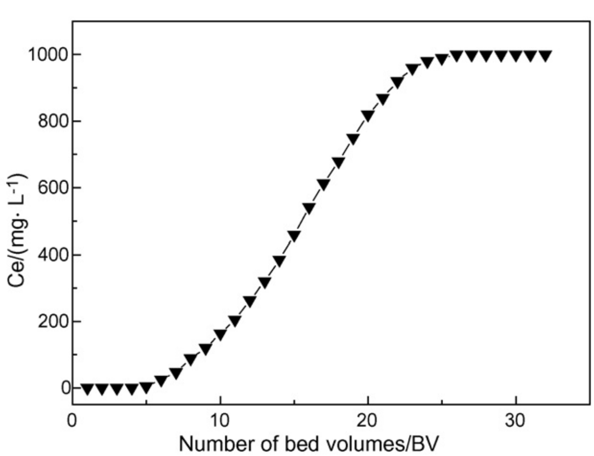


Fig. 8. Breakthrough curve of Pb^{2+} ion on PEI/SiO_2 column. BV of PEI/SiO_2 column: 2 mL; temperature: 24 °C; initial concentration of ion: 1 g/L; flow rate: 5 BV/h.

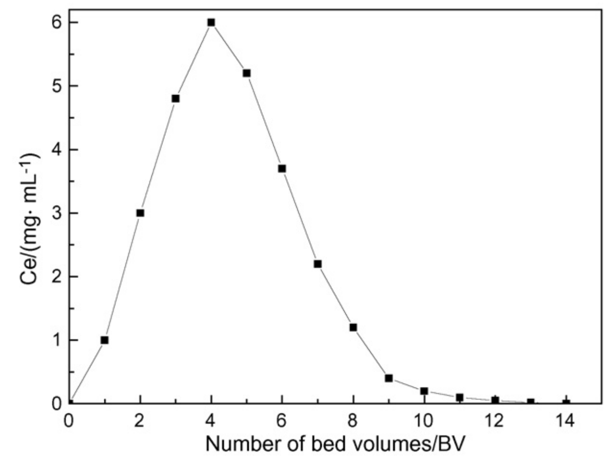


Fig. 9. Elution curves of three ions from PEI/SiO_2. Eluent: 1 mol/L of hydrochloric acid aqueous solution; flow rate: 1 BV/h; BV of PEI/SiO_2 column: 2 mL; temperature: 24 °C.

3.6. Elution curve

The elution curve of PEI/SiO_2 is shown in Fig. 9, and the desorption ratio was calculated as follows [20]:

$$\text{desorption ratio} = \frac{\text{amount of metal ion desorbed to the elution medium}}{\text{amount of metal ion sorbed on PEI/SiO}_2} \times 100\% \quad (5)$$

The calculating results show that for Pb^{2+}, within 10 bed volumes, it is eluted from PEI/SiO_2 with the desorption ratios of 98.40%. The above data show that the elution effect of hydrochloric acid solution for Pb^{2+} ion is excellent, and the reason for this is that in strong acidic solution the amino groups on PEI macromolecules are all protonated nearly, and the N atoms have lost the ability of coordination with heavy-metal ions completely.

4. Conclusions

Polyethyleneimine (PEI) was grafted onto the surface of silica gel particles via the coupling effect of γ-chloropropyl trimethoxysilane (CP), and the novel adsorption material PEI/SiO_2 with strong adsorption ability towards Pb^{2+} ion was prepared. The adsorption material PEI/SiO_2 possesses very strong chelating adsorption ability for Pb^{2+} ion, and the saturated adsorption amount could reach to 17.5 mg g^{-1} for Pb^{2+} ion. The isothermal adsorption data fit to Langmuir equation, and the adsorption is typical chemical adsorption with monomolecular layer. The pH value and grafting amount of PEI has great influence on the sorption.

PEI/SiO_2 will have wide applications in the removing, enriching and separating of Pb^{2+} ion. This is an important path for preparing functional composite-type particle material that functional macromolecule is grafted onto inorganic particle surface so that the concentrating effect of functional groups of the macromolecules is combined with good mechanical strength and low cost of inorganic particles.

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