Journal of Hazardous Materials 173 (2010) 438–444

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Novel negatively charged hybrids. 3. Removal of Pb^{2+} from aqueous solution using zwitterionic hybrid polymers as adsorbent

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ARTICLE INFO

Article history:
Received 14 July 2009
Received in revised form 21 August 2009
Accepted 21 August 2009
Available online 27 August 2009

Keywords:
Zwitterionic hybrid polymers
Adsorption
Pb^{2+} removal
Heavy metal
Kinetics

ABSTRACT

Using zwitterionic hybrid polymers as adsorbent, the adsorption kinetics and isotherm, thermodynamic parameters of ΔG, ΔH and ΔS for the removal of Pb^{2+} from aqueous solution were investigated. It is indicated that the adsorption of Pb^{2+} ions on these zwitterionic hybrid polymers followed the Lagergren second-order kinetic model and Freundlich isotherm model, demonstrating that the adsorption process might be Langmuir monolayer adsorption. The negative values of ΔG and the positive values of ΔH evidence that Pb^{2+} adsorption on these zwitterionic hybrid polymers is spontaneous and endothermic process in nature. Moreover, the zwitterionic hybrid polymers produced reveal relatively higher desorption efficiency in 2 mol dm^{-3} aqueous HNO_3 solution, indicating that they can be recycled in industrial processes. These findings suggest that these zwitterionic hybrid polymers are the promising adsorbents for Pb^{2+} removal and can be potentially applied in the separation and recovery of Pb^{2+} ions from the waste chemicals and contaminated water of lead-acid rechargeable battery.

1. Introduction

With the wide application of lead-acid rechargeable battery in everyday life and the rapid development of electronic industry, water pollution caused by Pb^{2+} ions has become a major environmental issue. As one of high toxic heavy metal ions, lead cannot be biodegraded and easily accumulate in human body to induce lead poisoning [1,2]. Removal of lead ions from aqueous solution is thus significantly important and highly needed. To remove or eliminate such type of toxic heavy metals from water resources, various techniques have been developed in the past. Among these, adsorption using inorganic/polymer hybrid materials as adsorbents is regarded as one of the most effective, low-cost and environmental friendly methods to remove this pollutant from wastewater. Consequently, a variety of innovative approaches have been developed for Pb^{2+} removal [1–5]. For example, Pan and co-workers [2] prepared a novel hybrid sorbent ZrP-001 by loading zirconium phosphate (ZrP) onto a strongly acidic cation exchanger D-001 and investigated the sorption behaviors for Pb^{2+}, Zn^{2+} and Cd^{2+} ions. It is indicated that the sorption order followed $Pb^{2+} \gg Zn^{2+} \approx Cd^{2+}$. Tao et al. [5] investigated the removal of Pb (II) from aqueous solution using chitosan/TiO_2 hybrid film adsorbent.

As one important type of inorganic/organic charged hybrid materials, zwitterionic hybrid polymer has drew much attention in recent years [6–8]. This type of hybrid polymer not only combines the advantages of organic and inorganic materials, but also exhibits some distinguished properties, such as structural flexibility, thermal and mechanical stability. Its unique feature such as pendent-side structure of ionic groups of opposite sign on the polymer chains allows its application in the separation and recovery of heavy metal ions from contaminated water via electrostatic effect. However, little work is done so far to remove and recover Pb^{2+} ions from aqueous solution or wastewater using zwitterionic hybrid polymers as a sorbent.

Recently, many efforts have been made to prepare and characterize zwitterionic hybrid polymer and membranes [7,9–11]. In the previous article [11], a series of zwitterionic hybrid polymers were prepared from the ring-opening polymerization of pyromellitic acid dianhydride (PMDA) and phenylaminomethyl trimethoxysilane (PAMTMS), and a subsequent sol–gel process. Their application for Cu^{2+} removal from aqueous solution was examined. It is indicated that their adsorption for Cu^{2+} ions followed Lagergren second-order kinetic model and Langmuir isotherm model. To continue the previous job and have an insight into the adsorption properties of zwitterionic hybrid polymers for heavy metal ions, herein, the application of zwitterionic hybrid polymers for Pb^{2+} removal is investigated as the model metal for the separation and recovery of heavy metal ions from aqueous solution. Meanwhile, the adsorption kinetics and isotherm, thermodynamic parameters such as ΔG, ΔH and ΔS were calculated to evaluate the adsorp-

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doi:10.1016/j.jhazmat.2009.08.097

tion properties of Pb^{2+} ions. Such investigation expects to be used in the disposal of contaminated water from lead-acid rechargeable battery.

2. Experimental

2.1. Materials

Phenylaminomethyl trimethoxysilane (PAMTMS, purity: ≥95.0%) was purchased from Silicone New Material Co. Ltd of Wuhan University (Wuhan, China) and used without further purification. Pyromellitic acid dianhydride (PMDA, purity: ≥99.5%), bromoethane (C_2H_5Br, purity: ≥98.0%) were purchased from National Pharmaceutical Group Corp. of China (Shanghai, China) and used as received. Other reagents were of analytical grade.

2.2. Preparation of zwitterionic hybrid polymers

The composition and cation-exchange capacities (CIECs) of zwitterionic hybrid polymers used in this case were listed in Tables 1 and 2, respectively. The preparation procedure of these zwitterionic hybrid polymers was discussed in detail in a previous paper [11]. The preparation involved three steps (as illustrated in Scheme 1) and was described briefly as follows.

Firstly, proper PMDA was dissolved in 15 ml DMF solution and stirred vigorously for 1 h at room temperature, and then the prescribed amount of PAMTMS solution was added dropwise into the above-prepared DMF mixed solution within 1 h (the ratio of PMDA and PAMTMS was listed in Table 1). Subsequently, the DMF mixed solution was stirred vigorously for additional 30 min to perform the ring-opening polymerization of PMDA and PAMTMS. After that, a homogeneous sol could be observed. During this process, the sol–gel reaction occurs between Si and O to produce the Si–O–Si bonds in the hybrid precursor. Followed, excess bromoethane (C_2H_5Br) was added to conduct the quaternary amination reaction of tertiary amine groups for 24 h to create the positively charged group in the polymer chains. Finally, the obtained product was washed and dried at 70 °C to acquire the final zwitterionic hybrid polymer.

2.3. Adsorption experiments

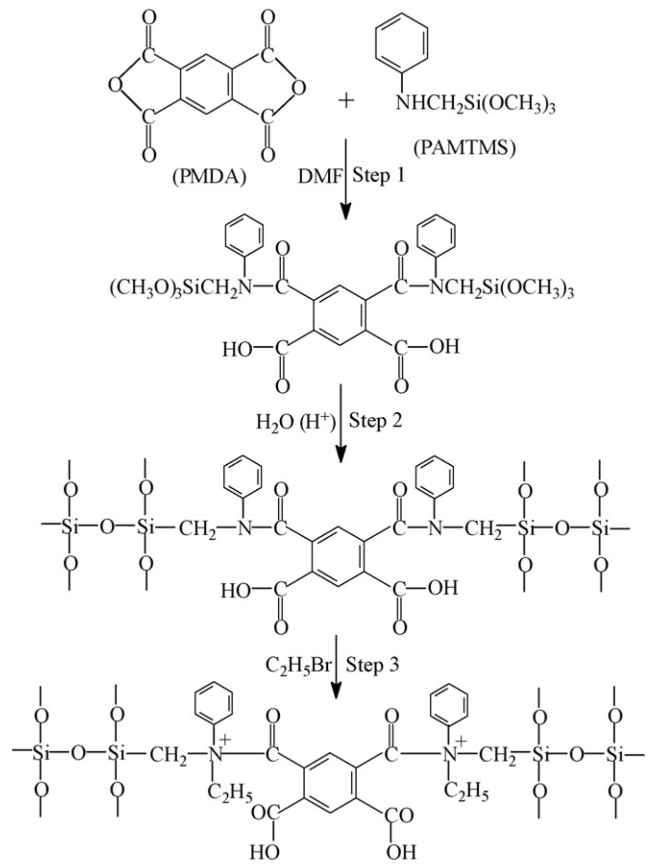
The adsorption experiments of zwitterionic hybrid polymers for Pb^{2+} ions were conducted in similar way as our previous studies, in which aqueous solution containing Cu^{2+} and Pb^{2+} ions were used as the adsorption medium [12]. The procedure can be described briefly as follows: about 1.0 g of particle sample was immersed in a 0.01 mol dm^{-3} aqueous $Pb(NO_3)_2$ solution at pH 5 for 24 h; subsequently, it was taken out and washed with deionized water. An EDTA solution (0.01 mol dm^{-3}) was used to determine the adsorption capacity ($q_{Pb^{2+}}$) of Pb^{2+} ions.

Table 1
Composition of the investigated zwitterionic hybrid polymers.

Sample	PMDA (g)	PAMTMS (ml)	C_2H_5Br (ml)
A	10.12	5	30
B	10.12	2.5	30
C	15.18	2.5	30
D	20.24	2.5	30

Table 2
Cation-exchange capacities (CIECs) of the investigated zwitterionic hybrid polymers.

Sample	A	B	C	D
CIECs (mmol g^{-1})	2.50	4.75	6.51	8.65



Scheme 1. The preparation steps of zwitterionic hybrid polymers; step 1 was the ring-opening polymerization of PMDA and PAMTMS; step 2 was the hydrolysis and condensation of hybrid precursor by sol–gel process; step 3 was the quaternary amination reaction to create the positively charged groups in the polymer chains [11].

The adsorption capacity ($q_{Pb^{2+}}$) of Pb^{2+} ions can be calculated by Eq. (1):

$$q_{Pb^{2+}} = (C_0 - C_R)V/W \quad (1)$$

where V is the volume of aqueous $Pb(NO_3)_2$ solution, C_0 and C_R are the concentration of initial and remaining $Pb(NO_3)_2$, respectively; W is the weight of polymer.

For adsorption kinetic studies, the prepared sample was immersed in 0.01 mol dm^{-3} aqueous $Pb(NO_3)_2$ solution for different adsorption times at pH 5. Meanwhile, the adsorption isotherm was conducted by changing the solution concentration ranging from 0.05 to 0.5 mol dm^{-3} at room temperature for 24 h at pH 5. The adsorption data were analyzed using Lagergren first-order and second-order kinetic model, Langmuir and Freundlich isotherm models. Based on the adsorption data, the thermodynamic parameters such as ΔG, ΔH and ΔS at different temperatures for Pb^{2+} removal were examined. In addition, desorption efficiency of Pb^{2+} ions was also measured using HNO_3, H_2SO_4 and HCl acidic solutions (2.0 mol dm^{-3}), respectively.

3. Results and discussion

3.1. Adsorption kinetics

To determine the dependency of adsorption capacity for Pb^{2+} ions and CIECs of these samples, the adsorption capacity of zwitte-