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Efficient multicyclic sorption and desorption of lead ions on facilely prepared poly(*m*-phenylenediamine) particles with extremely strong chemoresistance ☆

Mei-Rong Huang, Hong-Jie Lu, Xin-Gui Li *

Institute of Materials Chemistry, Key Laboratory of Advanced Civil Engineering Materials, College of Materials Science & Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China

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Abstract

Nitric acid, hydrochloric acid and EDTA were carefully chosen as desorbent to systematically evaluate the adsorption/desorption performance of the Pb^{2+}-adsorbing fine microparticles of poly(*m*-phenylenediamine). The sorption/desorption efficiency was maximized by optimizing desorption condition including the desorbent concentration, contact time, and desorption mode. The variation of the solution pH with Pb^{2+} desorption was recorded to speculate the desorption mechanism. The practical reusability of the microparticles was elaborated through the sorption–desorption cycle experiments in an optimum condition. It was found that the desorption was very rapid with an equilibrium time of several minutes. A strong dependence of the desorbability on the species and concentration of the desorbents was observed. When 20 mM EDTA was chosen as the desorbent, the highest desorptivity was up to 94.2% that was much higher than those using nitric and hydrochloric acids. A successive sorption–desorption study employing nitric acid indicated that the microparticles could be simply regenerated and reutilized for more than 5 cycles together with Pb^{2+} re-adsorption efficiency of about 50% and accumulative Pb^{2+} adsorption capacity of up to 720.4 mg L^{-1}. Facilely prepared, extremely chemoresistant and cost-effective PmPD microparticles would be potentially used for multicyclic sorption of lead ions from aqueous solution.

Keywords: Polyphenylenediamine; Microparticle; Lead ion; Successive multicyclic sorption and desorption; Chemoresistant sorbent; Desorbent; Water purification

1. Introduction

Lead, as well as mercury, cadmium, chromium, and arsenic, is in the group of serious hazardous heavy metals [1,2]. The removal of lead ions from aqueous solution has been traditionally carried out by several techniques [3–5], of which adsorption has shown to be an effective and economically feasible alternative method. In practice, the reuse ability of the adsorbent is becoming one of the comprehensive judgement indexes that affect its practicability. Therefore it is very necessary to study the desorption behavior of the adsorbents.

Most of the desorption studies are mainly focused on several kinds of mineral adsorbents such as soil particles [6–8], inorganic mineral oxides [9–13], and biosorbents [14–16]. The desorption process of the metal ions from the microparticle sorbents is comparably simple and the eluants used in their chemical regeneration including inorganic acid [12,17,18], inorganic salt [15], alkaline [15,19], complex reagent [13,14] and organic acids [12] have been widely reported. The inorganic acid such as nitric acid is the most potential. It has been suggested that the lead ions could be easily removed from carbon nanotubes by altering the pH value of the solution containing nitric acid (HNO_3) or hydrochloric acid (HCl), and the desorption percentage can reach up to 100% at pH 2.0 [20]. An investigation that employs HNO_3, HCl, and EDTA as the desorbent to elute the lead ions from dead Sargassum sp. indicated that EDTA might be the most effective desorbent due to its highest desorptiv-

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* Corresponding author. Fax: +86 21 65980524.
E-mail address: adamxgli@yahoo.com (X.-G. Li).

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ity [16]. Kinetic studies on sorption [21,22] and desorption [13, 23] have also been carried out, and a two-site model including strong and weak adsorption sites demonstrated that the strong sorption equilibrium constant resulted from a small desorption rate constant for the sites [21,22] and the bound ions can be moved from "weak" sites to "strong" sites with increasing aging time [13]. Based on a previous investigation it may be speculated that the desorption behavior is relatively dependent on the sorption sites and the mass transportation in the desorption system [23,24]. In general, the desorption equilibrium could be established very fast. Ultrasonic and stirring treatments have also been considered as an alternative method to more efficiently regenerate the sorbent [20,25,26]. In particular, the ultrasonic irradiation could synergistically enhance the desorption if coupling with a chemical regeneration.

The factors influencing the desorption effect are versatile [8,27], of which the concentration and pH value of the eluant [7,8,20], the contact time [7,13] and the desorption temperature [23] are of great importance. However, literatures on the desorption of heavy-metal ions from polymer sorbents have been rarely found. The desorption mechanism of the ions from the sorbents was not mentioned either.

It has been reported that the poly(*m*-phenylenediamine) (PmPD) microparticles obtained by a chemically oxidative polymerization possess a great potential in removing lead ions from their aqueous solution with the maximum Pb^{2+} adsorbability of 242.7 mg g^{-1} (PmPD) [22]. Another vital advantage is that the PmPD microparticles exhibit extremely high chemoresistance because they are completely insoluble in any solvents including oleum, formic acid, and *N*-methylpyrrolidone [28]. Additionally, the preparation of the microparticles is very simple and facile. Therefore the microparticles as a novel sorbent exhibit high cost effectiveness. However, when they are put into practice, the reusability of the microparticles as good sorbents is becoming one of the key factors that affect their practical performance. Therefore it is crucial to investigate the multicyclic sorption and desorption behaviors of the microparticles. In this paper we attempt to explore the multicyclic sorption and desorption behavior and the possible desorption mechanism of the lead ions from the microparticles using HNO_3, HCl, and EDTA as the desorbents would be proposed. The practical application of the sorbent would also be evaluated on the basis of its performance in successive sorption–desorption cycle experiments.

2. Experimental

2.1. Chemicals

All chemicals were of analysis grade. The lead-ion solution at the lead-ion concentration of 500 mg L^{-1} was prepared by dissolving $Pb(NO_3)_2$ in demineralized water. For the desorption studies, 1 M standard solution of mineral acids (HNO_3 and HCl) and 10 mM standard solution of EDTA were prepared and calibrated with anhydrous sodium carbonate. The various concentrations needed in the experiments can be obtained by diluting the standard solutions.

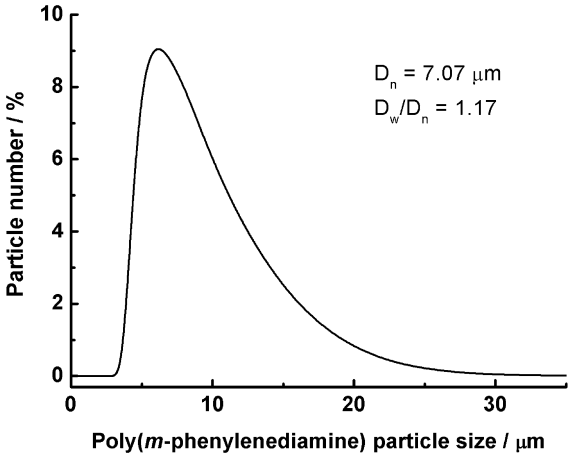

Fig. 1. The size distribution curve of fine poly(*m*-phenylenediamine) microparticles in pure water.

2.2. Preparation of fine poly(m-phenylenediamine) microparticles as sorbents

The fine poly(*m*-phenylenediamine) microparticles were synthesized by a chemically oxidative polymerization in distilled water by using ammonium persulfate as an oxidant [22]. A typical preparation procedure of is as follows: *m*-phenylenediamine (80 mmol) and ammonium persulfate (40 mmol) were dissolved in 100 mL distilled water respectively to prepare monomer and oxidant solutions. Both of them were put into the water bath at 30 °C for over 30 min. The monomer solution was then stirred and treated with the oxidant solution dropwise at a rate of one drop (60 μL) every 3 s for over 30 min at 30 °C. After finishing the dropwise addition of the oxidant solution, the mixture was stirred for 24 h and then the polymer microparticles were filtered and rinsed thoroughly with distilled water to remove the residual oxidant, water-soluble oligomer, and other by-products. The resulting black solid powders, that is, as-prepared PmPD salts, were left to dry in air at 50 °C for 3 days. Fig. 1 showed the size distribution curve of the PmPD salt microparticles analyzed with an LS230 laser particle-size analyzer from Beckman Coulter, Inc. made in USA. Their number–average diameter and size polydispersity index, i.e., weight–average diameter/number–average diameter, were found to be 7.07 μm and 1.17, respectively.

2.3. Batch sorption of lead ions onto fine poly(m-phenylenediamine) microparticles

After poly(*m*-phenylenediamine) microparticles of 500 mg were added to 250 mL lead-ion aqueous solution, the suspension was then stirred for 24 h in the water bath at 30 °C. The microparticles were filtered from the aqueous solution. The solid powders were left to dry in air at 50 °C for 3 days for the desorption experiment. The lead-ion concentration (C) in the filtrate after adsorption was measured by using a complexation titrimetric analysis based on EDTA [29]. In the former case, C was calculated according to equation

$$C = 207200 C_E V_E / V, \quad (1)$$