

Heavy Metal Ions Removal by Nano-sized Spherical Polymer Brushes^{*}

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Abstract Nano-sized spherical polymer brushes (SPBs) consisting of both a polystyrene (PS) core and a brush shell of poly(acrylic acid) (PAA), poly(*N*-acrylcysteamine) (PSH), or poly(*N*-acrylcysteamine-*co*-acrylic acid) (P(SH-*co*-AA)), were prepared by photo-emulsion polymerization. The core-shell structure was observed by dynamic light scattering and transmission electron microscopy. Due to the strengthened Donnan effect, the PAA brush can adsorb heavy metal ions. Effects of the contact time, thickness of PAA brush and pH value on the adsorption results were investigated. Due to the coordination between the mercapto groups and heavy metal ions as well as the electrostatic interactions, SPBs with mercapto groups are capable to remove heavy metal ions selectively from aqueous solutions. The order of adsorption capacity of the heavy metal ions by SPBs with mercapto groups is: $\text{Hg}^{2+} \approx \text{Au}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. The adsorbed heavy metal ions can be eluted from SPB by aqueous HCl solution, and the SPBs can be recovered. After three regenerations the recovered SPBs still maintain their adsorption capacity.

Keywords: Nano-sized spherical polymer brushes; Photo-emulsion polymerization; Heavy metal ions.

INTRODUCTION

Groundwater contaminated with heavy metal ions such as Pb^{2+} and Hg^{2+} is a serious environmental problem. The heavy metal ions are toxic to human beings and also adversely affect the environment^[1]. The removal of heavy metal ions from aquatic ecosystems continues to be an important issue for the science community^[2, 3]. The adsorption and recycling of heavy metal ions, such as mercury and gold, has received considerable attention in industry. Mercapto-functionalized materials are employed as adsorbent agents because of their selective adsorption of some typical cationic metal ions^[4]. Because of the high affinity of the mercapto group for mercury, gold, and lead ions, thiol materials have been often used to remove these heavy metal ions from aqueous solutions^[5, 6].

The structure of spherical polyelectrolyte brushes has several unique properties^[7–10]. Due to the strengthened Donnan effect^[11, 12], the concentration of counter ions inside the brush is much higher than that outside the brush especially at low concentrations. Therefore, in conjunction with ultrafiltration, the spherical polyelectrolyte brushes are ideal candidates for the removal of heavy metal ions. Increasing concerns over the removal of harmful metal ions from aqueous solution have motivated for the development of new methods considering both high selectivity and sensitivity^[13–18]. The coordination of the mercapto groups with the metal ions^[19] has inspired us to combine polyelectrolyte brushes with mercapto groups.

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In this paper nano-sized spherical polymer brushes (SPBs) consisting of both a polystyrene core and a brush shell of poly(acrylic acid), poly(*N*-acrylcysteamine), or poly(*N*-acrylcysteamine-*co*-acrylic acid), were prepared by photo-emulsion polymerization. Effects of contact time, brush thickness and pH value on the adsorption of heavy metal ions by PAA brushes were studied systematically. The adsorption and recovery of Pb^{2+} , Au^{3+} , Hg^{2+} , Cu^{2+} and Ni^{2+} by these three kinds of SPBs were compared.

EXPERIMENTAL

Materials

Dithiothreitol (DTT) and dicyclohexylcarbodiimide (DCC) (both from Alfa) were used as supplied without further purification. Acrylic acid and pyridine were distilled under a reduced pressure prior to use. Mercaptoethylamine (MEA) was obtained by neutralizing $\text{MEA}\cdot\text{HCl}$ (from Alfa) with NaOH followed by freeze-drying. All aqueous solutions were freshly prepared using deionized water (Shanghai RO Micro Q).

Synthesis of *N*-acrylcysteamine

Acrylic acid (0.72 g, 10 mmol) was added to a solution of MEA (1.13 g, 10 mmol) in pyridine (10 mL). Then 2.06 g of DCC, dissolved in 10 mL of pyridine, was introduced into the solution under vigorous stirring (Fig. 1a). After 48 h at 25 °C, the filtered solution was evaporated under reduced pressure. The crude solid product was collected. The crude product was then dissolved in DTT aqueous solution (0.1 mol/L) under stirring and then freeze-dried. The end product was a white powder (yield: 32%). $^1\text{H-NMR}$ (DMSO-d_6 , δ): 2.80 (t, 2H), 3.42 (m, 2H), 8.40 (t, 1H), 6.24 (t, 1H) and 5.60 (d, 2H).

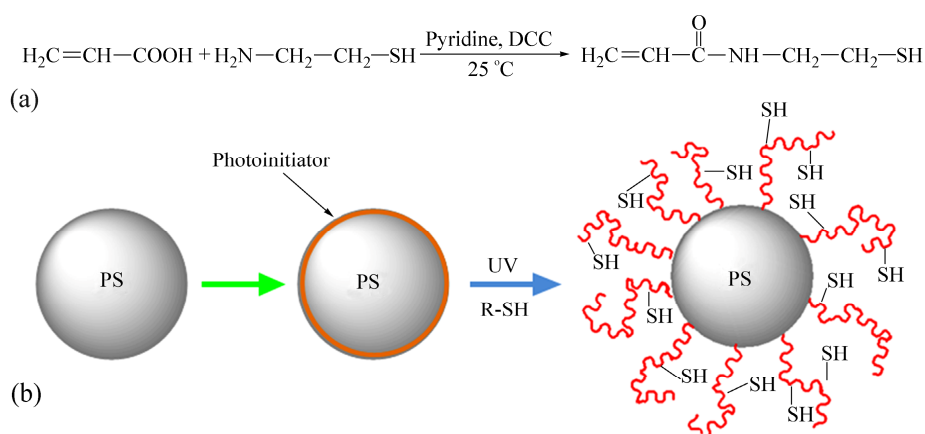


Fig. 1 Schematic procedures for the preparation of (a) *N*-acrylcysteamine and (b) the nano-sized spherical thiol polymer brush

Preparation of Nano-sized Spherical Polymer Brushes

The nano-sized spherical polymer brushes with the shell PAA, poly(*N*-acrylcysteamine) (PSH) or poly(*N*-acrylcysteamine-*co*-acrylic acid) (P(SH-*co*-AA)) were prepared by photo-emulsion polymerization (Fig. 1b)^[12]. The PS core latex was synthesized *via* emulsion polymerization. The well-defined initiator layer was achieved by copolymerization of initiators 2-[*p*-(2-hydroxy-2-methylpropiophenone)]-ethylene glycol-methacrylate (HMEM)^[12] with remnant styrene on the particle surfaces under the “starved condition”. The prepared core latex was purified by dialysis. The grafting of PAA, PSH and P(SH-*co*-AA) chains was carried out in a UV reactor. The purified latex was charged in a UV reactor and diluted to 1 wt% by water. The monomer acrylic acid (AA) and *N*-acrylcysteamine were added and mixed with latex by vigorous stirring. The whole reactor was degassed by repeated evacuation and subsequent addition of nitrogen at least 5 times. Photo-polymerization was initiated by UV/Vis-radiation at room temperature. The prepared latex was purified until the conductivity of outer water was constant.

Adsorption and Regeneration Experiments

In the adsorption experiment of heavy metal ions by SPBs, 10 mg of freeze-dried PAA brushes were added to 100 mL of heavy metal ion solution, the concentration of adsorbed heavy metal ions was monitored by ICP-AES. After soaking in HCl aqueous solution (1 mol/L) at room temperature for 24 h, the brushes were regenerated by ultra-filtration. The regenerated brushes, in the ultrafiltration cell, were recovered by freeze-drying. The metal ions were collected from the elution.

Characterization

^1H -NMR spectra were recorded at room temperature in DMSO-d_6 using a Bruker Avance 500 NMR spectrometer. Dynamic light scattering (DLS, PSS Nicomp 380) was used to determine the size and the size distribution of samples. Transmission electron microscopy (TEM, JEOL-2100F) was employed to observe the morphology of SPBs. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Varian 710 ES) was used to determine the heavy metal ions content.

RESULTS AND DISCUSSION

Structure of SPBs

The particle sizes of PS core and brushes were measured by DLS and the thickness of brush L was determined by subtracting the size of PS core. The thickness of PAA brush, PSH brush and P(SH-co-AA) brush was 20, 22, and 25 nm respectively (Fig. 2). It can be seen from the TEM images that nano-sized spherical polymer brushes

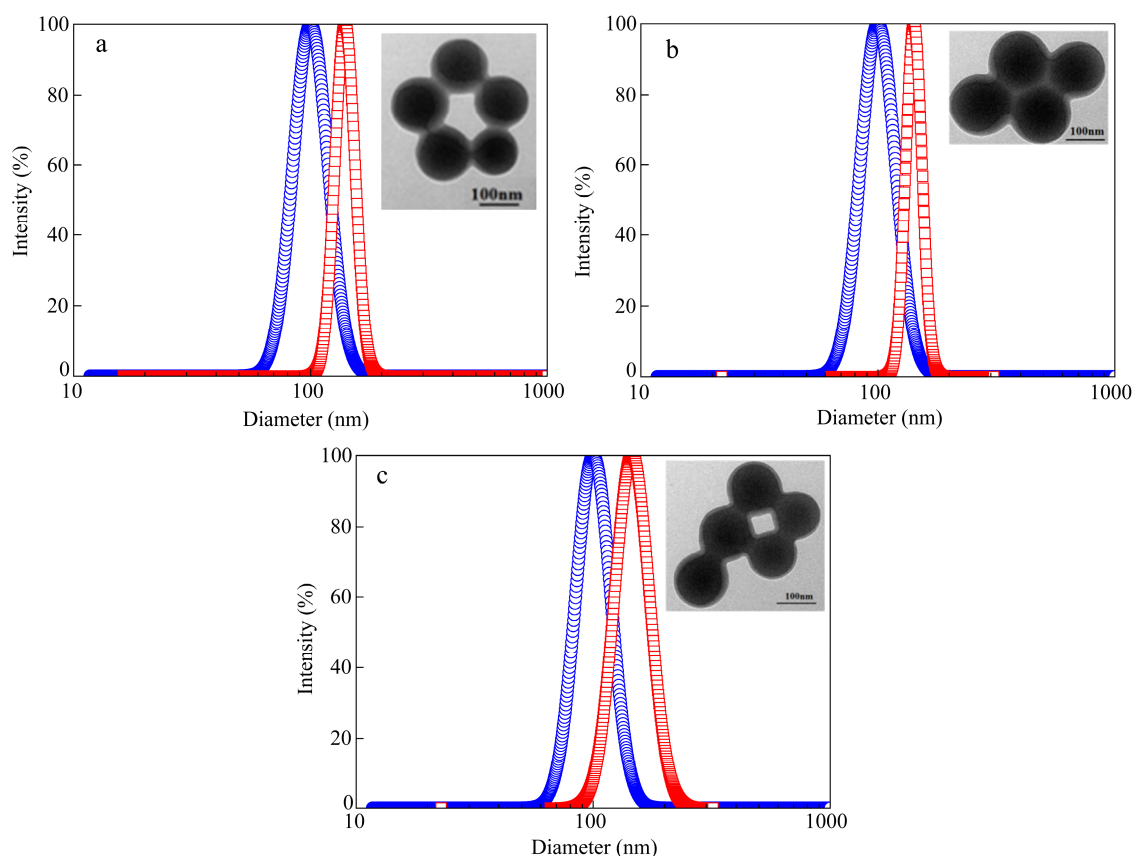


Fig. 2 Size and size distribution of PS core and SPBs determined by DLS: (a) PAA brush with a diameter of 142 nm, (b) PSH brush with a diameter of 146 nm and (c) P(SH-co-AA) brush with a diameter of 151 nm. The insets are the TEM images of SPBs. Symbols denote: (○) core with a diameter of 102 nm, (□) brushes.

show a well-defined spherical structure with a narrow size distribution, although the chains of brushes are hardly visible. According to the elementary analysis of sulfur, the molar ratio of SH and AA groups in the P(SH-co-AA) brush was calculated to be 1:3.

Adsorption of Lead Ions by PAA Brushes

The concentration of lead ions adsorbed by PAA brush was monitored by ICP-AES spectrum. As shown in Fig. 3, the adsorbed amount of lead ions by PAA brushes increased with contact time. The adsorption reached saturation in *ca.* 2 h. After that, the concentration of lead ions in the liquid phase did not change anymore. Due to the strengthened Donnan effect, the concentration of lead ions inside the brush is much higher than that outside the brush.

The adsorption of lead ions by PAA brush in 2 h increased upon increasing the dose, while the adsorption reached a plateau after increasing the dose of PAA brush over 10 mg (Fig. 4). Therefore, 10 mg PAA brushes were chosen for further experiments.

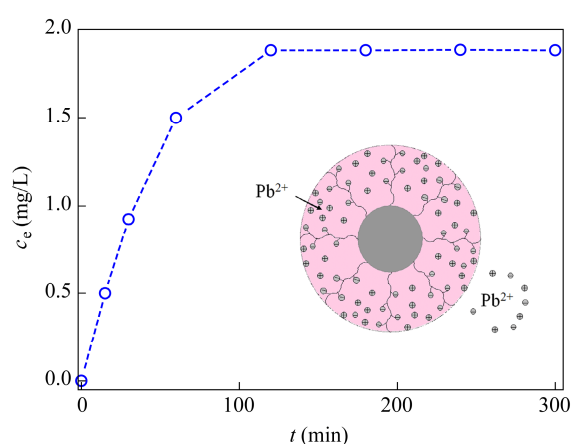


Fig. 3 Lead ions ($c_0 = 2.5$ mg/L) adsorbed by PAA brush as a functional of contact time
 c_0 is the original concentration of heavy metal ions in the solution. c_e is the concentration of heavy metal ions adsorbed by the brushes at the equilibrium (mg/L).

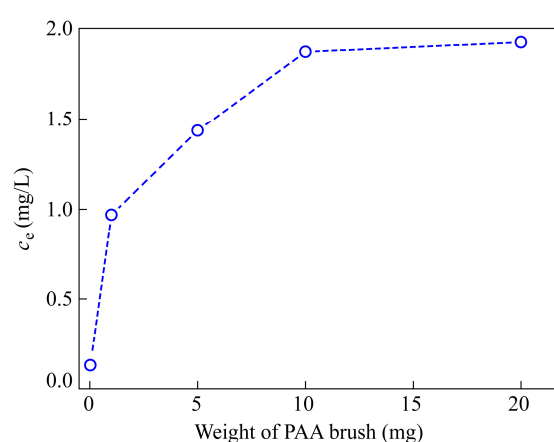


Fig. 4 Lead ions ($c_0 = 2.5$ mg/L) adsorption by PAA brush as a functional of brush amount

As shown in Fig. 5, the adsorption capacity of PAA brush increased with the increasing of brush thickness (L) from 5 nm to 124 nm. The adsorption of lead ions by PAA brushes was determined by the strong electrostatic adsorption of free carboxylic groups in the brush shell. The capacity of electrostatic adsorption increased with the amount of carboxylic groups.

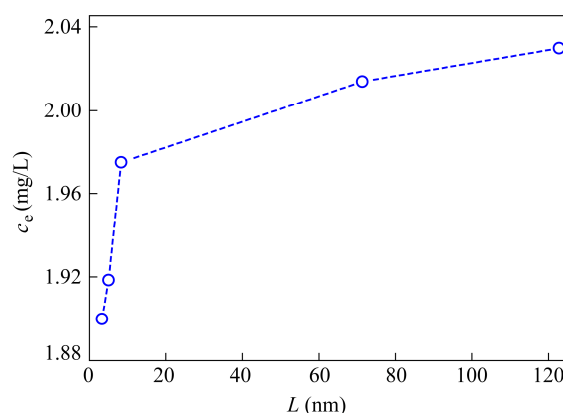


Fig. 5 Lead ions ($c_0 = 2.5$ mg/L) adsorbed by PAA brush as a functional of brush thickness

The diameter of PAA brush are sensitive to pH value because of the polyelectrolyte nature of PAA shell. With the increase of pH value, the diameter of PAA brush reach a plateau after increasing the pH value over 10 (Fig. 6). The initial increase in diameter is largely attributable to the neutralization of PAA chains. And when the PAA chain has been completely neutralized, the diameter becomes independent of pH. Figure 6 shows that the adsorption capacity of PAA brush is sensitive to pH value and reaches the maximum at pH = 6. Due to the steric effect caused by severe shrink of the brush chain, the adsorption of the lead ions is hindered at low pH value. Too high pH value leads to the decrease in adsorption capacity because of the forming of water-insoluble $\text{Pb}(\text{OH})_2$.

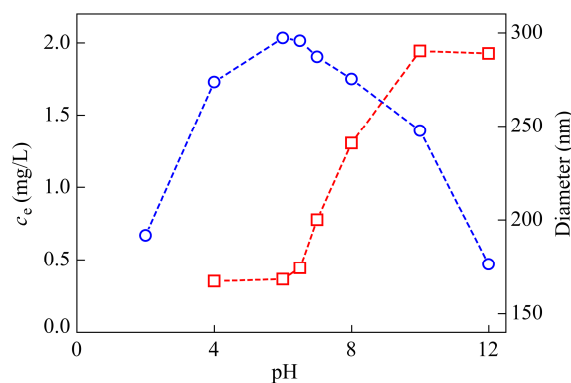


Fig. 6 Lead ions ($c_0 = 2.5$ mg/L) adsorption by PAA brushes and diameter of PAA brushes as a functional of pH value with ionic strength of 0.01 mol/L
Symbols denote: (○) lead ions adsorption and (□) diameter of PAA brush.

Comparison of Different SPBs

The adsorption results of Pb^{2+} , Au^{3+} , Hg^{2+} , Cu^{2+} , and Ni^{2+} by PAA brushes were shown in Fig. 7. The adsorbed amount (%) is defined as the percentage of heavy metal ions adsorbed by the brushes. The adsorption capacity for the divalent ions of Pb^{2+} , Hg^{2+} and Ni^{2+} are similar while that of Cu^{2+} is much lower. However, the adsorption capacity for trivalent ion of Au^{3+} is slightly higher.

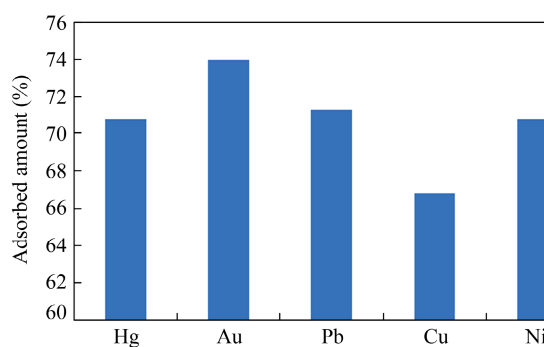


Fig. 7 Adsorption efficiency of different heavy metal ions ($c_0 = 50$ mg/L) by PAA brushes

The adsorption capacity of PAA brushes was almost the same while the mercapto-containing brushes can selectively remove Hg^{2+} , Au^{3+} and Pb^{2+} (Fig. 8). Both the $\text{P}(\text{SH-co-AA})$ and PSH brushes can fully remove Hg^{2+} and Au^{3+} from solution, while the adsorption capacity of Ni^{2+} by PSH brushes is much lower. Due to the coordination between the mercapto groups and heavy metal ions as well as the electrostatic interactions, SPBs with mercapto groups are capable to remove the heavy metal ions selectively from aqueous solutions. The order of adsorption capacity of the heavy metal ions by SPBs with mercapto groups is: $\text{Hg}^{2+} \approx \text{Au}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$.

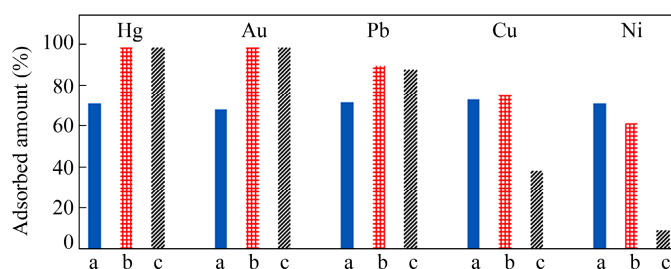


Fig. 8 Comparison of adsorption capacity of different heavy metal ions ($c_0 = 50$ mg/L) by (a) PAA brushes, (b) P(SH-co-AA) brushes and (c) PSH brushes

Regeneration of SPBs

The elution of adsorbed heavy metal ions from SPBs was easily accomplished in an ultrafiltration cell using aqueous HCl solution at room temperature. As shown in Fig. 9, the capacity to adsorb Pb^{2+} remained the same for regenerated PAA brush and P(SH-co-AA) brush while the PSH brush kept about 93%. The same adsorption capacities were obtained for the removal of Hg^{2+} and Au^{3+} by regenerated SPBs.

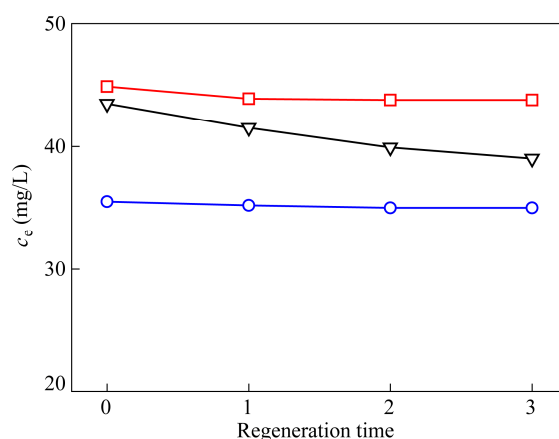


Fig. 9 Lead ions ($c_0 = 50$ mg/L) adsorbed by regenerated brushes
Symbols denote: (○) PAA brush, (□) P(SH-co-AA) brush and (▽) PSH brush

Effective recovery of heavy metals, such as mercury and gold has received considerable attention. As shown in Fig. 10, the recovered amount of mercury and gold is nearly 90% among the three kinds of brushes. Comparing to P(SH-co-AA) and PSH brushes, the recovered amount of mercury and gold by PAA brushes was higher, because the coordination effect between mercapto groups and heavy metal ions is stronger than the electrostatic effect.

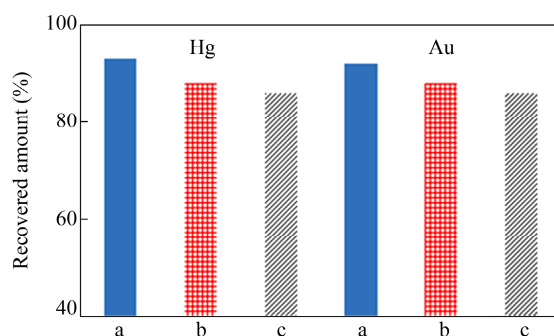


Fig. 10 The recovery of mercury and gold ions by (a) PAA brush, (b) P(SH-co-AA) brush and (c) PSH brush

CONCLUSIONS

Nano-sized spherical polymer brushes with a shell of PAA, poly(*N*-acrylcysteamine) and poly(*N*-acrylcysteamine-*co*-acrylic acid) were successfully prepared by photo-emulsion polymerization. Effects of the contact time, brush thickness and pH value on the adsorption results of heavy metal ions by PAA brushes were investigated. The mercapto-containing brushes can selectively adsorb and concentrate heavy metal ions from aqueous solutions due to the selective coordination of the mercapto groups and heavy metal ions. The order of adsorption capacity of the heavy metal ions by SPBs with mercapto groups is: $\text{Hg}^{2+} \approx \text{Au}^{3+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. The SPBs can be easily recovered by extraction with aqueous HCl solution at room temperature. The adsorption capacities of the brushes remained almost the same even after three cycles of regeneration. These novel nano-sized spherical polymer brushes are ideal candidates for the selective removal and recovery of heavy metal ions.

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