



PVBC microspheres tethered with poly(3-sulfopropyl methacrylate) brushes for effective removal of Pb(II) ions from aqueous solution



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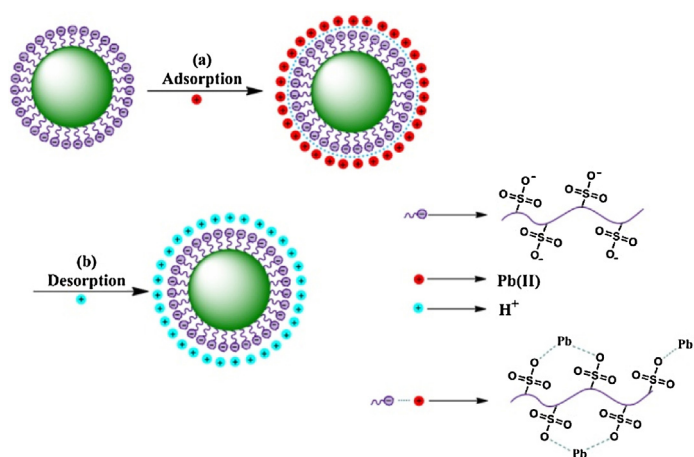
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HIGHLIGHTS

- A novel PVBC resin was prepared by grafting of pH-sensitive polymer chains via ATRP.
- The adsorption kinetics of Pb(II) followed a pseudo-second-order rate model.
- The adsorption isotherms were consistent well with the Langmuir model.
- Thermodynamic parameters revealed an endothermic and spontaneous adsorption process.
- The postulated adsorption mechanism was proposed on the basis of XPS analyses.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel pH-sensitive polystyrene (PS)-type resin was developed by grafting of poly(3-sulfopropyl methacrylate) (PSPMA) brushes onto a cross-linked poly(vinylbenzyl chloride) (PVBC) microsphere via surface-initiated atom transfer radical polymerization (ATRP), and was further utilized as a highly efficient and recyclable sorbent to remove Pb(II) ions from aqueous solutions. The as-synthesized PSPMA-grafted PVBC microspheres were characterized by ATR-FTIR, XPS and SEM. Batch adsorption results revealed that the solution pH had an evident effect on the adsorption capacity of the PSPMA-grafted microspheres towards Pb(II) ions with an optimal sorption pH of above 5.0. The PSPMA-grafted microspheres had rapid adsorption kinetics of Pb(II) ions to reach adsorption equilibrium within 60 min. The Langmuir-fitted adsorption isotherms at pH 5.0 with an initial Pb(II) concentration range of 0.12–0.97 mmol L⁻¹ (i.e. 50–200 mg L⁻¹) revealed a maximum capacity of Pb(II) ions of 0.82 mmol g⁻¹. The calculated thermodynamic parameters demonstrated an endothermic and spontaneous adsorption process of Pb(II) ions on the PSPMA-grafted microspheres. With the inherent stability, high adsorption capacity and good regenerability, the PSPMA-grafted PVBC microsphere resin provides a novel promising PS-type adsorbent for effective removal of heavy metal ions from aqueous solution.

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1. Introduction

Heavy metals contamination of surface and groundwater poses a serious threat to aquatic environments and human health. Owing to their non-biodegradable feature, heavy metals can be accumulated in organisms through the food chain, causing various diseases and disorders. Pb(II) ions, as one of the most toxic heavy metal ions, are discharged by many industries, such as pigments, storage batteries, leaded glass, mining, painting, metal electroplating, coating, smelting, petrochemical, plumbing fuels, photographic materials, matches, and explosives [1]. Even at low concentration levels, Pb(II) exposure may cause various damages to physiological and neurological systems for human beings, especially for children [2]. According to the Environmental Protection Agency (EPA, USA), the permissible Pb(II) concentration in drinking water is less than 0.015 mg L^{-1} [3]. Consequently, it is of great importance to remove Pb(II) ions from aqueous solution prior to being discharged into the environment.

Various strategies, such as chemical precipitation [4], ion exchange [5], membrane filtration [6], reverse osmosis [7], and adsorption [8], have been developed to address the growing need of purifying Pb(II) ions-contaminated aqueous solution. Among them, adsorption has been considered as one of the most efficient and economical technique to remove Pb(II) ions from aqueous solutions due to its simple operation, high selectivity and effectiveness, low cost and without generating secondary pollution. Different types of adsorbents, including activated carbon [9,10], silicates [11] and clay minerals [12], fly ash [13], zeolite, [14], natural biomass (seaweed [15], chitin [16], and chitosan [17]) and polymeric adsorbents [18–21], have been documented to effectively eradicate the toxic Pb(II) ions. Activated carbons are by far the most commonly-used sorbents to treat Pb(II) ions-contaminated wastewater, but they suffer from some drawbacks of costly regeneration, poor selectivity and high attrition rate. The main concerns of the inorganic minerals and natural materials are associated with some limitations of low adsorption capacity, high regeneration cost, and the poor selectivity. Thus, an alternative adsorbent with high adsorption capacity, selectivity and rapid regeneration rate is highly desired to completely purify Pb(II) ions-contaminated wastewater.

Due to their high surface area, excellent mechanical rigidity, adjustable surface chemistry, and ease of regeneration under mild conditions [22], polymeric adsorbents have emerged as a potential alternative to activated carbon. In particular, polymeric adsorbents can be readily regenerated by a simple and non-destructive washing process for recycle adsorption. Natural polymers such as cellulose [23], chitin [16] and chitosan [17,24], and synthetic polymers, such as polystyrene (PS) [18] and poly(hydroxyethyl methacrylate) (PHEMA) [25], have been extensively used to synthesize adsorbents for the Pb(II) removal. However, some polymeric adsorbents are also lack of abundant active sites to sufficiently adsorb pollutants from contaminated aqueous systems. To circumvent the above problem, surface functionalization of polymeric adsorbents has been performed to introduce functional groups onto polymeric matrixes for specific interactions with the target pollutants over the past decades [26–28].

As a typical PS-type synthetic polymer, poly(vinyl benzyl chloride) (PVBC) has been widely utilized to synthesize highly-efficient adsorbents for purifying different pollutants from aqueous solutions [29,30]. The abundant reactive chloromethyl groups of the PVBC surface have been used as anchor sites to introduce specific functional groups, such as amino groups ($-\text{NH}_2$), hydroxyl groups ($-\text{OH}$), carboxylic ($-\text{COOH}$), and sulfonic groups ($-\text{SO}_3\text{H}$) [31]. Surface functional groups of adsorbents not only have a significant effect on the adsorption behaviour, but also dominate the adsorption mechanism. The interaction mechanism between $-\text{COOH}$, $-\text{SO}_3\text{H}$ and phosphonic ($-\text{PO}(\text{OH})_2$) groups and cationic

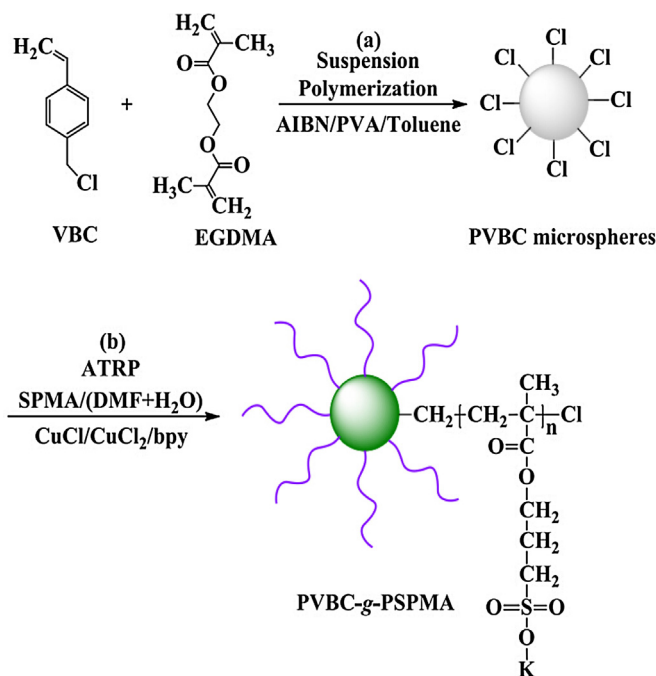


Fig. 1. Schematic illustration of a two-step synthesis process of the PVBC-g-PSPMA microspheres: (a) the synthesis of cross-linked PVBC microspheres via suspension polymerization of VBC and EGDMA, (b) grafting of PSPMA brushes onto the PVBC microsphere surfaces via surface-initiated ATRP reaction (i.e., PVBC-g-PSPMA surfaces).

pollutants have been mainly ascribed to ion exchange and electrostatic interaction, while nitrogen-containing groups, such as amine, hydrazine, thioamide, and imidazoline, are found to chelate heavy metal cations or anionic ions via complexation, electrostatic interactions or hydrogen bonding [32]. Different approaches, including amination [33], quaternization [34], the Gabriel synthesis reaction [35], and grafting reactions [36] have been reported to synthesize the highly-efficient PVBC-based adsorbents. As a newly-developed “controlled/living” radical polymerization method, surface-initiated atom transfer radical polymerization (ATRP) allows to covalently affix well-defined functional polymer brushes on the polymeric adsorbents in a precise and tunable manner [37]. The pendant functional groups, such as $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{PO}(\text{OH})_2$ and $-\text{NH}_2$, on the side chains of polymer brushes can act as adsorptive active sites for various pollutants [38,39]. In our previous study, poly(dimethylamino propyl methacrylate) (PDMA-PMA) brushes were grafted onto the PVBC microsphere surfaces via direct surface-initiated ATRP to remove phenol from aqueous solution [31]. However, to the best of our knowledge, few studies have been devoted to functionalizing PVBC resins via surface-initiated ATRP to trigger specific interactions between adsorbents and pollutants.

Accordingly, the purpose of this study is to graft pH-sensitive poly(3-sulfopropyl methacrylate) (PSPMA) brushes onto the PVBC microspheres via surface-initiated ATRP as a highly efficient and recyclable adsorbent for purifying Pb(II) ions-polluted wastewater. As schematic illustration in Fig. 1, cross-linked PVBC microspheres were first synthesized using a suspension polymerization process, followed by grafting of PSPMA brushes via surface-initiated ATRP. The pH-sensitive sulfonic groups on the PSPMA brushes are expected not only to significantly increase the number of adsorption sites for the enhanced uptake capacity of Pb(II) ions, but also to be readily regenerated for recyclable use. Successful functionalization of PVBC microsphere surfaces was ascertained by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and scan-

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