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Thiol-functionalized polysilsesquioxane as efficient adsorbent for adsorption of Hg(II) and Mn(II) from aqueous solution

Yuzhong Niu *, Rongjun Qu, Xiguang Liu, Lei Mu, Baihui Bu, Yuting Sun, Hou Chen, Yangfeng Meng, Lina Meng, Lin Cheng

School of Chemistry and Materials Science, Ludong University, Yantai 264025, PR China

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ABSTRACT

Thiol-functionalized polysilsesquioxane was synthesized and used for the adsorption of Hg(II) and Mn(II) from aqueous solution. Results showed that the optimal pH was about 6 and 5 for Hg(II) and Mn(II), respectively. Adsorption kinetics showed that the adsorption equilibriums were established within 100 min and followed pseudo-second-order model. Adsorption isotherms revealed that the adsorption capacities increased with the increasing of temperature. The adsorption was found to be well described by the monolayer Langmuir isotherm model and took place by chemical ion-exchange mechanism. The thermodynamic properties indicated the adsorption processes were spontaneous and endothermic nature. Selectively adsorption showed that PMPSQ can selectively adsorb Hg(II) from binary ion systems in the presence of the coexistent ions Mn(II), Cu(II), Pb(II), Co(II), and Ni(II). Based on the results, it is concluded that PMPSQ had comparable high adsorption efficiency and could be potentially used for the removal of Hg(II) and Mn(II) from aqueous solution.

1. Introduction

In recent years, water pollution caused by heavy metal ions is one of the major economic and environmental problems all over the world. Heavy metal ions such as Hg(II), Cd(II), Mn(II), Co(II), and Pb(II) are highly toxic, non-biodegradable, and tend to accumulate in living organisms. Therefore, such metal ions exert deleterious effects on human health and ecological system even at low concentrations [1]. Among these hazardous metal ions, Hg(II) and Mn(II) are widely used in many industries such as battery manufacture, electronics, petroleum refining, metal plating, and mining activities [2,3]. It is well known that Hg(II) has very high tendency for binding to proteins, mainly cause damage to the liver, kidney, and nervous systems [4]. While intake of higher concentrations of Mn(II) can cause *manganese psychosis* which is characterized by neurological disorder and dysfunction of the kidneys [5]. Therefore, the removal and separation of Hg(II) and Mn(II) from aqueous solution is a continuing research objective of environmental pollution control processes.

There are many techniques for the removal and separation of toxic heavy metal ions from aqueous solution, such as chemical precipitation, membrane filtration, solvent extraction, ion exchange, and electrolytic methods [6–9]. However, these techniques are limited for high operational cost, excessive time requirements, and incapable of removing trace level of metal ions [10,11]. In contrast, adsorption is recognized as an efficient and economic method for the removal of metal ions mainly because the adsorption process offers flexibility in design and operation [12]. In addition, the regeneration of adsorbent with economic operation may be possible because adsorption is general reversible [13]. Various adsorbents have been developed to remove metal ions from effluent, such as chelating resins [14], activated carbon [15], silica gel [16], clays [17], and zeolites [18]. And nowadays, seeking for novel adsorbent with low cost and high efficiency has become the main direction of the research [19].

As is well known, the adsorption ability of adsorbent mainly depends on the functional groups used for the binding of metal ions. For the synthesis of a successful adsorbent, it is essential to choose or design efficient functional groups having high affinity toward metal ions. According to Pearson's hard and soft acids and bases concept (HSAB), sulfur group which belongs to soft base, is known to exhibit marked binding affinity to soft acid metal ions such as Hg(II) and Ag(I) [20]. A promising strategy is to take advantage of the high affinity of sulfur group to develop novel adsorbent for removing Hg(II) from aqueous solution [21]. Several sulfur-containing groups, such as thiol, benzoylthiourea, dithiocarbamate, and 1-(2-thiazolylazo)-2-naphthol have been used for the design of various adsorbents [21–24].

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* Corresponding author. Tel.: +86 535 6672176; fax: +86 535 6696281.
E-mail addresses: niuyuzhong@126.com, niuyuzhong@hotmail.com (Y. Niu).

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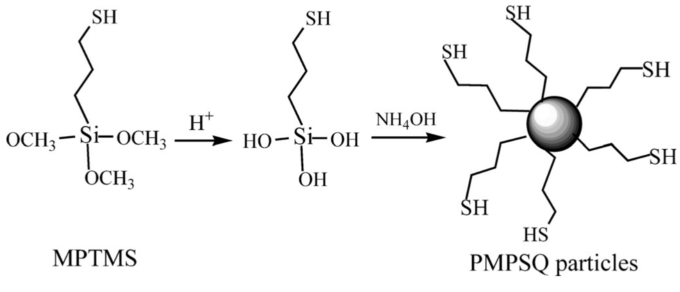
In recent years, considerable attentions have been focused on the preparation and utilization of thiol-functionalized polysilsesquioxane. Vogel et al. [25] reported the synthesis of poly(3-mercaptopropylsilsesquioxane) (PMPSQ) by the two-step sol–gel process. The first hydrolysis and condensation of 3-mercaptopropyltrimethoxysilane (MPTMS) in HCl solution leading to an insoluble oil phase. Then, PMPSQ was obtained by the crosslinking of the oil phase in the ammonia solution. Xin et al. [26] described the synthesis of PMPSQ by the acid- catalyzed hydrolysis and base-catalyzed condensation of MPTMS in aqueous medium with short reaction time. The resulting PMPSQ exhibited excellent adsorption property for Ag(I).

Keeping in view the interesting property of PMPSQ, the present study aimed to synthesize PMPSQ by the sol–gel method and investigate the feasibility of PMPSQ as an efficient adsorbent for the removal of Hg(II) and Mn(II) from aqueous solution. The effect of solution pH, contact time, initial metal ion concentration, temperature and coexisting metal ions on Hg(II) adsorption were systematically investigated. The adsorption kinetics, isotherms, and thermodynamics were also analyzed to reveal the adsorption mechanisms.

2. Experimental

2.1. Materials and methods

PMPSQ was synthesized by the sol–gel method in aqueous medium via the HCl-catalyzed hydrolysis of MPTMS and the following NH_4OH-catalyzed condensation processes as shown in Scheme 1 according to the method described in Ref. [26]. The structure of PMPSQ was confirmed by FTIR and the result was consistent with that described in Ref. [26]. Elemental analysis showed that sulfur content (S%) was 24.758%, which indicated the thiol group content was 7.74 mmol g^{-1}. All solutions were prepared from analytical grade chemicals and distilled water. Stock solutions (0.2 mol L^{-1}) of Hg(II) and Mn(II) were prepared by dissolving appropriate amount of metal(II) chloride. The working and standard solutions with different concentrations were prepared by diluting the stock solution. The buffer solution of pH 1.0–2.0 and pH 3.0–6.0 were obtained by adjusting of HNO_3/H_2O and acetate/acetic acid, respectively. The pH of the solution is monitored with a Seven Multi pH meter (Mettler Toledo Instruments, Co. Ltd., China). FTIR spectra were recorded in the range 4000–400 cm^{-1}on a Nicolet MAGNA-IR 550 (series II) spectrophotometer with a resolution of 4 cm^{-1} by accumulating 32 scans. Elemental analysis was conducted by the Elementar vario EL cube (Elementar Corporation, Germany). The concentrations of metal ions before and after adsorption were determined on a GBC-932 atomic adsorption spectrophotometer (AAS, GBC, made in Australia).



Scheme 1. The synthesis scheme of PMPSQ.

2.2. Saturated adsorption

The adsorption capacity of PMPSQ for metal ions was conducted by the following procedure: about 50 mg of PMPSQ was placed in a 100 mL flask and 20 mL of 0.002 mol L^{-1} metal ion solution was then added. The mixture was shaken in a thermostatic shaker for 12 h at room temperature, then the adsorbent was filtered off and the concentration of metal ion was determined via AAS. The adsorption capacity was calculated according to Eq. (1):

$$q = \frac{(C0 - C)V}{W} \tag{1}$$

where q is the adsorption amount (mmol g^{-1}); C_0 and C are the initial and equilibrium concentration of metal ion, respectively (mmol mL^{-1}); V is the volume of the solution (mL); and W is the weight of PMPSQ (g).

2.3. Effect of pH on adsorption

The effect of pH on the adsorption was performed by equilibrating 50 mg PMPSQ with 20 mL of 0.002 mol L^{-1} metal ion solution in a 100 mL flask for shaking 12 h. The pH of the solution was varied in the range 1.0–6.0 by adjusting with various buffer solutions. The adsorption capacity was calculated.

2.4. Adsorption kinetics

Batch experiment was performed to investigate adsorption kinetics of PMPSQ for Hg(II) and Mn(II) under different initial concentrations. A typical procedure is as follow: a series of 100 mL flasks were charged with 20 mL of metal ion solution and previously buffered to the optimum pH value, then 50 mg of PMPSQ was added to each flask and the mixture was shaken. At different time intervals, the concentration of metal ion was determined and the adsorption capacity was calculated.

2.5. Adsorption isotherms

Adsorption isotherms were investigated by batch experiment. A typical procedure is as follows: a series of 100 mL flasks were charged with 20 mL of metal ion solution with varying concentrations and previously buffered to the optimum pH value. Then about 50 mg of PMPSQ was added into each flask. The mixture was shaken for 12 h at different temperatures and the adsorption capacity was calculated.

2.6. Adsorption selectivity for Hg(II)

The adsorption selectivity of PMPSQ for Hg(II) was carried out by equilibrating 50 mg PMPSQ with 20 mL solution of a binary system containing equal initial concentration (0.002 mol L^{-1}) of Hg(II) and other coexisting metal ion for 12 h at room temperature. The adsorption capacities of Hg(II) and coexisting metal ion were calculated.

3. Results and discussion

3.1. Saturated adsorption

Saturated adsorption capacity for metal ion is generally accepted as one of the most critical parameters to evaluate the adsorption ability of the adsorbent. The saturated adsorption capacity of PMPSQ for metal ions is presented in Fig. 1.

As can be seen from Fig. 1, the adsorption capacities of PMPSQ follow the order of Hg(II) > Mn(II) > Co(II) > Cd(II) > Pb(II) > Cu(II) > Ni(II) > Zn(II). PMPSQ exhibited relative high adsorption