



# Synthesis of silica gel supported salicylaldehyde modified PAMAM dendrimers for the effective removal of Hg(II) from aqueous solution



Yuzhong Niu\*, Rongjun Qu\*, Hou Chen, Lei Mu, Xiguang Liu, Ting Wang, Yue Zhang, Changmei Sun

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

## HIGHLIGHTS

- Silica gel supported salicylaldehyde modified PAMAM dendrimers were synthesized.
- SiO<sub>2</sub>-G0-SA~SiO<sub>2</sub>-G2.0-SA were promising adsorbents for the removal of Hg(II).
- The pseudo-second-order model described adequately the adsorption kinetics data.
- The film diffusion mechanism dominated the adsorption processes of Hg(II).
- Langmuir model provide best correlation of the experimental data.

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## ABSTRACT

A series of silica gel supported salicylaldehyde modified PAMAM dendrimers (SiO<sub>2</sub>-G0-SA~SiO<sub>2</sub>-G2.0-SA) were synthesized and their structures were characterized by FTIR, XRD, SEM, TGA, and porous structure analysis. The feasibility of these adsorbents for the removal of Hg(II) from aqueous solution was first described and the adsorption mechanism was proposed. The adsorption was found to depend on solution pH, the generation number of salicylaldehyde modified PAMAM dendrimers, contact time, temperature, and initial concentration. Results showed that the optimal pH was about 6 and the adsorption capacity increased with the increasing of generation number. Density functional theory (DFT) method was used to investigate the coordination geometries and the chelating mechanism. Adsorption kinetics was found to follow the pseudo-second-order model with film diffusion process as rate controlling step. Adsorption isotherms revealed that adsorption capacities increased with the increasing of temperature. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models were employed to analyze the equilibrium data. The adsorption can be well described by Langmuir isotherm model and took place by chemical mechanism. The thermodynamics properties indicated the adsorption processes were spontaneous and endothermic nature. The maximum adsorption capacity of SiO<sub>2</sub>-G0-SA, SiO<sub>2</sub>-G1.0-SA, and SiO<sub>2</sub>-G2.0-SA were 0.91, 1.52, and 1.81 mmol g<sup>-1</sup>, respectively. The considerable higher adsorption capacity compared with other adsorbents indicates SiO<sub>2</sub>-G0-SA~SiO<sub>2</sub>-G2.0-SA are favorable and useful for the uptake of Hg(II), and can be potentially used as promising adsorbents for the effective removal of Hg(II) from aqueous solution.

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## 1. Introduction

Water pollution caused by heavy metal ions has become a major issue globally due to their persistence and harmful effects upon

aquatic life and human health [1,2]. Hg(II) is one of the most dangerous pollutants because of its high toxicity and accumulative properties within biological systems [3]. It can be released from various natural and anthropogenic sources, such as oceanic and volcanic emissions, fossil fuel combustion, gold mining, battery manufacture, and electronic industry [4]. Bioaccumulation of Hg(II) may inactivate the important cell functions and cause a variety of diseases, including renal dysfunction, serious cognitive and motion disorders, hepatic injury, and minamata disease [5,6]. Therefore,

\* Corresponding authors. Tel.: +86 535 6672176; fax: +86 535 6696281.

E-mail addresses: [niuyuzhong@126.com](mailto:niuyuzhong@126.com), [niuyuzhong@hotmail.com](mailto:niuyuzhong@hotmail.com) (Y. Niu), [rongjunqu@sohu.com](mailto:rongjunqu@sohu.com) (R. Qu).

the development of simple and effective method to remove Hg(II) from aqueous solution is very important for the remediation of Hg(II) pollution.

Several technologies such as chemical precipitation, ionic exchange, adsorption, membrane filtration, and solvent extraction, have been used for the removal of Hg(II) from aqueous solution [7–9]. Compared with other techniques, adsorption is considered to be one of the most promising and widely applied methods owing to its low cost, high efficiency, simple feature to operate, and reversibility [8]. Many kinds of adsorbents have been used for the removal of Hg(II) from aqueous solution, such as activated carbon [10], clays [11], chelating resin [12], cellulose [13], zeolites [14], and silica gel [15]. The design and synthesis of suitable adsorbents with strong affinities and high loading capacity for Hg(II) is still a great challenge.

Recently, the development of silica gel based organic–inorganic hybrid materials for the removal of Hg(II) has become an interesting subject [16–18]. Silica gel is an ideal inorganic solid matrix not only due to its well-modified surface property, excellent thermal and mechanical stability, but also to be relative simple in comparison to polymer resin with rapid adsorption kinetics, good swelling resistance in different solvents, and chemical stability [16]. Different types of functional groups, such as those containing nitrogen, oxygen, and sulfur groups have been used to strategically fabricate such hybrid materials [16–20]. The presence of surface functional group affords these hybrid materials the ability to interact strongly with metal ions. Among various functional groups, polyamidoamine (PAMAM) dendrimer attracted considerable attention due to its excellent properties such as well-defined geometry, high density of nitrogen and oxygen groups, and easy functionalized to enhance the binding ability toward metal ions due to the prevalence of peripheral amine and ester groups [21–25]. The functionalization of amine group with salicylaldehyde have deserved particular attention as the resulting schiff base ligands are known to form stable complexes with metal ions readily, and may give rise to particularly potential adsorbent for Hg(II) [26,27]. So far, no work has been published on the synthesis and application of silica gel supported salicylaldehyde modified PAMAM dendrimers for the removal of Hg(II) from aqueous solution.

In the present work, a series of silica gel supported salicylaldehyde modified PAMAM dendrimers were synthesized by the divergent method. Their structures were characterized by FTIR, XRD, SEM, TGA and porous structure analysis. The feasibility of these hybrid materials for the removal Hg(II) from aqueous solution was assessed by using batch method. The properties concerning the Hg(II) adsorption such as befitting pH, contact time, temperature, and initial Hg(II) ion concentration were evaluated systematically. The adsorption mechanism has been illustrated by using density functional theory (DFT) method and analyzing the adsorption kinetics and isotherms data.

## 2. Experimental

### 2.1. Materials and methods

Silica gel of chromatographic grade (100–200 mesh) was purchased from Qingdao Makall Chemical Institute (Shandong, China) and was activated according to the previous method [21].  $\gamma$ -Aminopropyltriethoxysilane (APES, Qufu Wangda Chemicals Factory, China) and salicylaldehyde (SA, Shanghai Chemical Factory, China) were used without further purification. Methyl acrylate (MA), ethylenediamine (EDA), and toluene were distilled just before use. All the other reagents were of analytical grade. Distilled water was used to prepare all the solutions. Stock solutions of Hg(II) ( $0.2 \text{ mol L}^{-1}$ ) was prepared by dissolving appropriate amount

of mercury(II) chloride with distilled water. The buffer solution of pH 1.0–2.0 and pH 3.0–6.0 were obtained by adjusting of  $\text{HNO}_3/\text{H}_2\text{O}$  and acetate/acetic acid, respectively. The pH of the solution is monitored with a Seven Multi pH meter (Mettler Toledo Instruments, Co. Ltd., China). Silica gel supported hyperbranched PAMAM dendrimers ( $\text{SiO}_2\text{-G0}\sim\text{SiO}_2\text{-G2.0}$ ) were synthesized by divergent method and the  $-\text{NH}_2$  content of  $\text{SiO}_2\text{-G0}$ ,  $\text{SiO}_2\text{-G1.0}$ , and  $\text{SiO}_2\text{-G2.0}$  were determined to be 0.79, 1.50, and  $1.87 \text{ mmol g}^{-1}$  according to the method described in our previous work [21].

FTIR spectra were recorded on a Nicolet MAGNA-IR 550 (series II) spectrophotometer in the range of  $400\text{--}4000 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$  by accumulating 32 scans. The wide-angle X-ray diffraction (WAXD) was determined on a rotating target X-ray diffractometer, D/max-2500VPC (Rigaku Corporation, Japan). The shapes and surface morphology of the samples were examined on a scanning electron microscope (SEM), JSF5600LV (JEOL, Japan). Thermogravimetric analysis (TGA) was performed on a NETZSCH STA409PC (NETZSCH, Germany). Porous structure analysis were characterized by BET and BJH methods through  $\text{N}_2$  adsorption at 77 K using an automatic physisorption analyzer ASAP 2020 (Micromeritics Instruments Corporation, USA). The concentrations of metal ions before and after adsorption were determined on a GBC-932 atomic adsorption spectrophotometer (AAS, GBC, Australia).

### 2.2. Synthesis of silica gel supported salicylaldehyde modified PAMAM dendrimers ( $\text{SiO}_2\text{-G0-SA}\sim\text{SiO}_2\text{-G2.0-SA}$ )

The ideal synthetic routes of  $\text{SiO}_2\text{-G0-SA}\sim\text{SiO}_2\text{-G2.0-SA}$  were illustrated in Scheme 1.

#### 2.2.1. Synthesis of $\text{SiO}_2\text{-G0-SA}$

The modification of  $\text{SiO}_2\text{-G0}$  with SA was carried out via schiff base formation between the amino groups of  $\text{SiO}_2\text{-G0}$  and the active aldehyde group of SA according to the method described in the previous report [25]. A sample of 10.0 g  $\text{SiO}_2\text{-G0}$  was suspended in 150 mL of ethanol and 1.68 mL SA was added. The mixture was stirred and refluxed under nitrogen atmosphere for 6 h. The solid product was isolated by filtration and reflux-extraction in a Soxhlet extraction apparatus by toluene and ethanol for 12 h, respectively. The product was dried at  $50^\circ\text{C}$  under vacuum and  $\text{SiO}_2\text{-G0-SA}$  was obtained.

#### 2.2.2. Synthesis of $\text{SiO}_2\text{-G1.0-SA}$

With the increasing of generation number, the  $-\text{NH}_2$  content and the steric hindrance of the dendrimer increase accordingly, and thus the amount of SA and the reaction time need to be increased to make the reaction process completely. Therefore, a suspension of 10.0 g  $\text{SiO}_2\text{-G1.0}$  and 4.80 mL SA in 150 mL of ethanol was stirred and refluxed under nitrogen atmosphere for 8 h, and then the solid product of  $\text{SiO}_2\text{-G1.0-SA}$  was filtered off. The purification was similar to that of  $\text{SiO}_2\text{-G0-SA}$ .

#### 2.2.3. Synthesis of $\text{SiO}_2\text{-G2.0-SA}$

Similar to that of  $\text{SiO}_2\text{-G0-SA}$ , the amount of SA and the reaction time were also increased. 10.0 g  $\text{SiO}_2\text{-G2.0}$  and 10.29 mL SA was added in 150 mL of ethanol. The mixture was stirred and refluxed for 12 h under nitrogen atmosphere and filtered off. The purification was similar to that of  $\text{SiO}_2\text{-G0-SA}$ , and  $\text{SiO}_2\text{-G2.0-SA}$  was obtained.

### 2.3. Adsorption properties of $\text{SiO}_2\text{-G0-SA}\sim\text{SiO}_2\text{-G2.0-SA}$ for Hg(II)

#### 2.3.1. Effect of pH on adsorption

The effect of pH on the adsorption was carried out by placing 30 mg adsorbent in a series of flasks containing 20 mL of  $0.002 \text{ mol L}^{-1}$  Hg(II) with varying pH in the range of 1.0–6.0 by

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