



Design of a new integrated chitosan-PAMAM dendrimer biosorbent for heavy metals removing and study of its adsorption kinetics and thermodynamics



Zabihullah Zarghami^a, Ahmad Akbari^a, Ali Mohammad Latifi^{b,*}, Mohammad Ali Amani^b

^aInstitute of Nano Science and Nano Technology, University of Kashan, Kashan, Iran

^bApplied Biotechnology Research Center, Baqiyatallah University of Medical Science, Tehran, Iran

HIGHLIGHTS

- Chitosan-PAMAM dendrimer as a new integrated biosorbent were successfully prepared.
- The prepared samples were used as adsorbents for Pb²⁺ removing from aqueous solution.
- Effect of different parameters on adsorption capacity of biosorbents were evaluated.
- Adsorption capacity of sample CS-G3 was 18 times more than sole chitosan.
- Thermodynamic and kinetic models were studied for understanding equilibrium data.

ARTICLE INFO

Article history:

Received 10 December 2015

Received in revised form 12 January 2016

Accepted 14 January 2016

Available online 23 January 2016

Keywords:

Adsorption isotherm

Dendrimer-grafted

PAMAM

Biosorbent

Chitosan

ABSTRACT

In this research, different generations of PAMAM-grafted chitosan as integrated biosorbents were successfully synthesized via step by step divergent growth approach of dendrimer. The synthesized products were utilized as adsorbents for heavy metals (Pb²⁺ in this study) removing from aqueous solution and their reactive Pb²⁺ removal potential was evaluated. The results showed that as-synthesized products with higher generations of dendrimer, have more adsorption capacity compared to products with lower generations of dendrimer and sole chitosan. Adsorption capacity of as-prepared product with generation 3 of dendrimer is 18 times more than sole chitosan. Thermodynamic and kinetic studies were performed for understanding equilibrium data of the uptake capacity and kinetic rate uptake, respectively. Thermodynamic and kinetic studies showed that Langmuir isotherm model and pseudo second order kinetic model are more compatible for describing equilibrium data of the uptake capacity and kinetic rate of the Pb²⁺ uptake, respectively.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

At present, the release of toxic and heavy metals such as Pb²⁺ from several industries, for example, paints, metal plating, electroplating, mining, photograph development, batteries, and alloy industries, results in a number of environmental problems (Arancibia-Miranda et al., 2016; Momcilovic et al., 2011; Machida et al., 2012). The element lead, Pb²⁺ is a neurotoxin that accumulates both in soft tissues and bones and leads to serious damage to the nervous system. In addition, an excessive amount of Pb²⁺ causes blood or brain disorders in mammals. Therefore, it is necessary to carefully eliminate such highly toxic ions from the

environment. Due to environmentally friendly reasons, many attempts have been made to use low cost biomaterials for removing heavy metal ions from wastewater (Yargıç et al., 2015; Luo et al., 2015). Biotechnology as a clean technology has great potential to resolve the environmental concerns. In this regard, bioremediation technique as a crucial method in environmental biotechnology has attracted great deal of researcher's attention. The tools of bioremediation technology include microorganisms, plants and products derived from such as enzymes and various biopolymers.

The application of biopolymers such as bacterial exopolymers, alginate, collagen, chitin and chitosan is one of the emerging adsorption methods for the removal of dyes and heavy metal ions such as U, Cd, Pb, Hg, Cs even at low concentrations (Crini, 2006; Latifi et al., 2012; Newsome et al., 2014; Wang and Chen, 2014)

* Corresponding author. Tel.: +98 21 88617712; fax: +98 21 82482549.

E-mail address: amlatifi290@gmail.com (A.M. Latifi).

due to the presence of amino and hydroxyl groups, which can serve as the active sites (Wu et al., 2001). The presence of a large number of amine groups on the chitosan chain increases the adsorption capacity of chitosan (Evans et al., 2002). Chitosan, a nitrogenous polysaccharide composed mainly of poly(β -1-4)-2-amino-2-deoxy-D-glucopyranose, is produced through the deacetylation of chitin, which is widely spread among marine and terrestrial invertebrates and in lower forms of the plant kingdom (Ngah and Fatinathan, 2006; Chatterjee et al., 2005). In order to improve the chemical and mechanical properties, chitosan can be physically or chemically modified. Chemical modification is the application of chemical treatment on chitosan, which improves its stability in acidic media and enhances the selectivity for metal adsorption. A variety of processes for chemical modification such as crosslinking, grafting, blending, sulfonation, and carboxymethylation can be utilized (Sun and Wang, 2006). In this study, grafting of dendrimer onto chitosan was investigated. Dendrimers are a group of highly branched polymer compounds having different functional groups where they can react with different functional entities of other molecules in nanometer scale. Compared with polymers, dendrimers possess especial physical properties such as viscosity, flexibility, and density distribution (Shimei et al., 2006). For the particular envisaged properties; the distribution of functional groups in the dendrimer skeleton plays a significant role (Astruc et al., 2010; Klajnet and Bryszewska, 2001). Generally, two diverse synthetic strategies are currently explored to synthesize structurally well-defined dendritic polymers, namely the divergent and convergent growth approaches (Tomalia and Frechet, 2002; Newkome and Shreiner, 2008). Herein, different generations of polyamidoamine (PAMAM) dendrimer were successfully grafted to chitosan via step by step divergent growth approach of dendrimer. For investigation of Pb^{2+} adsorption capacity of products, polarographic method was used due to its high sensitivity to low metal ion concentrations. In addition, effect of temperature, pH, solid/liquid ratio, ion initial concentration and other important parameters on adsorption capacity were investigated. Thermodynamic and kinetic studies were performed for understanding equilibrium data of the uptake capacity and kinetic rate uptake, respectively. The equilibrium data were analyzed by applying Langmuir, Freundlich and Temkin isotherm models. The kinetics were evaluated using pseudo-first order, pseudo-second order and intraparticle diffusion equations.

2. Experimental

2.1. Materials

Chitosan with a degree of deacetylation 81.69%, methyl acrylate (MA), ethylenediamine (EDA), $Pb(NO_3)_2$, acetic acid glacial (HOAc) and 37% HCl were purchased from Aldrich. All of the other reagents used were of analytical reagent grade. For purifying of chitosan powder, a typical method was utilized as follows: 4 g of chitosan was dissolved in 20 ml of 0.1 M HOAc. After stirring for 24 h, the solution was filtered through a medium-pore-size sintered glass funnel to remove insoluble substances. Then, 10 ml of 0.1 M NaOH was added drop wise to solution to precipitate chitosan powder. Afterwards, the chitosan powder was separated through a medium-pore-size sintered glass funnel and washed several times with methanol and dried at 50 °C for 24 h. Methyl acrylate (MA) and ethylenediamine (EDA) were refluxed over sodium and distilled just before use.

2.2. Characterization

The crystal structural and compositional properties of products were recorded by X-ray diffraction (Philips-X'PertPro) and FT-IR

(Magna-IR, spectrometer 550 Nicolet with 0.125 cm^{-1} resolution in KBr pellets in the range of 400–4000 cm^{-1}). Pb^{2+} ions concentration in aqueous medium was determined by polarographic method using a Metrohm 797 VA Computrace. Zeta potentials and isoelectric point (point of zero charge) determination of obtained products performed using a Malvern Zetasizer Nano ZS model of zeta potential apparatus. 0.1 wt% adsorbent suspensions were prepared and pH adjustments made using HCl or NaOH. After the pH stabilized, required amount of these solutions transferred to the measuring cell and about 3 values of zeta potential were measured at room temperature. The stock solutions of Pb(II) was prepared by dissolving 1.6 g of lead nitrate in 1000 ml of double distilled water such that each 1 ml of the solution contains 1 mg of divalent metal. The exact concentration of Pb(II) solution was calculated on mass basis and expressed in terms of $mg L^{-1}$ (ppm). The required lower concentrations were prepared by dilution of the stock solution. All precautions were taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions were prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

2.3. Preparation of PAMAM-grafted chitosan

Grafting reaction and propagation of PAMAM dendrimer from purified chitosan powder surface was achieved by two steps, (1) Michael addition of MA to amino groups on the surface, and (2) amidation of terminal groups with EDA (Tsubokawa et al., 1998). Michael addition was carried out as follows: into a 500 ml flask that contained 4 g chitosan powder, 150 ml of methanol and 1 ml of MA were added. The flask was sealed under N_2 gas and the mixture was stirred with a magnetic stirrer at 50 °C. After 24 h, the resulting powder was precipitated by centrifugation (5×10^3 rpm for 20 min) and washed with methanol repeatedly. The obtained product was called CS-G0.5. The amidation of terminal ester groups was carried out as follows: into a 500 ml flask that contained the chitosan powder prepared from previous step, 150 ml of methanol and 10 ml of EDA were added. The flask was sealed under N_2 gas, and the mixture was stirred with a magnetic stirrer at 50 °C. After 24 h, the resulting powder was precipitated by centrifugation (5×10^3 rpm for 20 min) and washed with methanol repeatedly (CS-G1). The propagation for 2nd generation was carried out as follows: into a 500 ml flask, the chitosan powder obtained from the above reactions was treated with 2 ml of MA (twice the volume of the preceding reaction) in 150 ml of methanol (CS-G1.5). After the reaction, the resulting powder was treated with 20 ml of EDA (twice the volume of the preceding reaction) in 150 ml of methanol (CS-G2). Both the Michael addition and the amidation reactions were repeated to propagate the dendrimer from the CS powder surface (CS-G2.5 and CS-G3). The synthesis terms are listed in Table 1.

2.4. Adsorption study

A static adsorption experiment was employed to determine the adsorption capability and thermodynamic and kinetic parameters

Table 1
The synthesis terms of different generations of PAMAM-grafted chitosan.

Sample No.	T (°C)	V methanol (ml)	EDA (ml)	MA (ml)	Chitosan weight (g)
CS-G0.5	50	150	–	1	4
CS-G1	50	150	10	–	4
CS-G1.5	50	150	–	2	4
CS-G2	50	150	20	–	4
CS-G2.5	50	150	–	4	4
CS-G3	50	150	40	–	4

Download English Version:

<https://daneshyari.com/en/article/679259>

Download Persian Version:

<https://daneshyari.com/article/679259>

[Daneshyari.com](https://daneshyari.com)