



Highly effective removal of Cu(II) by a novel 3-aminopropyltriethoxysilane functionalized polyethyleneimine/sodium alginate porous membrane adsorbent



Xue Sun^a, Jian Hua Chen^{a,b,*}, Zhenbo Su^a, Yihong Huang^a, Xinfei Dong^a

^a College of Chemistry and Environmental, Minnan Normal University, Zhangzhou 363000, China

^b Fujian Province University Key Laboratory of Modern Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou 363000, China

HIGHLIGHTS

- Adsorption capacity of the PEI/SA was 7 times more than that of pristine SA membrane.
- The PEI/SA showed excellent adsorption selectivity for Cu(II) ions.
- The adsorption rate was very fast, and adsorption equilibrium time was 60 min.
- Reusability of the PEI/SA was excellent.
- The PEI/SA is an easy operation and efficient adsorbent for removal Cu(II) ions.

ARTICLE INFO

Article history:

Received 5 September 2015
Received in revised form 29 December 2015
Accepted 30 December 2015
Available online 11 January 2016

Keywords:

Sodium alginate
Polyethyleneimine
Porous membrane
Adsorption
Cu(II)

ABSTRACT

In the present paper, we prepared a novel porous membrane adsorbent (PEI/SA) by immobilizing polyethyleneimine (PEI) with sodium alginate (SA), then further functionalized PEI/SA with 3-aminopropyltriethoxysilane and tested its adsorption performance for removing Cu(II). To investigate the adsorption kinetics of Cu(II) onto this newly developed PEI/SA, we performed a series of batch experiments under various conditions: solution pH, adsorbent dose, initial Cu(II) concentration, adsorption temperature, and contact time. The results show that the maximum adsorption capacity of Cu(II) onto the PEI/SA is approximate 329.8 mg/g, which is 7 times more than that of pristine SA porous membrane. We also examined the Lagergren pseudo-first-order and pseudo-second-order kinetic models, the intra-particle diffusion model, and the Crank model to study the mechanism of adsorption process. Kinetics experiments indicate that the pseudo-second-order model displays the best correlation with adsorption kinetics data. The Crank model shows that the intra-particle solute diffusion is the main rate-controlling step. Furthermore, our adsorption equilibrium data could be better described by the Freundlich equation. Effect of ionic strength on adsorption process is weakly. Co-existing Cd(II), Ni(II) and Cr(VI) ions hardly affect the adsorption capacity of PEI/SA towards Cu(II). The reusability experiments show that the PEI/SA has excellent adsorption–desorption efficiencies. The results indicate that the prepared PEI/SA is promising for Cu(II) removal, from the viewpoints of low cost and easy operation.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Recently, rapid industrialization throughout the world has caused the release of various pollutants including heavy metals and organic substances into environment. Unlike most organic wastes, heavy metals are non-biodegradable and can be

accumulated in living tissues, causing various diseases and disorders. Heavy metal ions and their toxic effects have become a major world problem. As a result, environment contamination causing by heavy metal ions has received extensive attention throughout the world. Among various heavy metals, Cu(II) and copper containing materials have number of applications including manufacturing of copper water pipes and brass radiators, as a constituent of fertilizers, pesticides, fireworks and antifouling paints applied on ship hulls [1]. Copper is one of the elements which is essential for human beings, but at higher concentration it affects the health of fauna, flora and humans adversely. Due to the toxicity

* Corresponding author at: College of Chemistry and Environmental, Minnan Normal University, Zhangzhou 363000, China. Tel.: +86 596 2591445; fax: +86 596 2520035.

E-mail address: jhchen73@126.com (J.H. Chen).

of copper, the recommendation of the World Health Organization for the safe amount of Cu(II) is 2 mg/L in drinking water and 0.05–1.5 mg/L in industrial effluent discharge [2]. Therefore, simple, green and high effective methods for Cu(II) removal are should be developed to guarantee the environmental safety and health.

Nowadays, a number of processes have been used to remove or eliminate heavy metal ions from wastewaters including chemical precipitation, electrochemical treatment, ion exchange, and chemical reduction [3–6]. However, these methods are not widely practical due to some drawbacks and limitations including high-energy consumption, high capital investment and running costs, generation of secondary toxic slurries and problems in the disposal of residual metal sludge [7,8]. The removal of Cu(II) from wastewaters by adsorption has attracted more and more researchers attention [9,10]. The main advantages of the adsorption process are high selectivity, less sludge volume produced, simplicity of design, a recovery of heavy metal and the meeting of strict discharge specification. Various materials such as clays, agricultural wastes, biomass, zeolite and synthetic polymers have been used as an adsorbent [11–15]. Recent studies have been focused on the development of cost-effective and efficient adsorbents. An efficient adsorptive material should consist of an insoluble porous matrix and some suitable active groups that can interact with heavy metal ions [16]. During the searching of new adsorption material for high metal ion uptake, composites were found to be most promising candidate because of its simple preparation, easy handling, low cost and excellent properties [17]. Owing to the faster diffusion rate of the metal ions into the internal binding sites in the porous adsorptive membrane than that of adsorptive beads, porous adsorptive membrane is now gaining more and more attention [18–21].

It is well known that biopolymers are abundant, biodegradable, non-toxic, renewable resources and can be modified in a number of ways to enhance their adsorption selectivity and efficiency. Meanwhile, use of biopolymers even makes the adsorption process more environmental friendly. Therefore, cost-effective biopolymers adsorbents have received increasing attention. Among them, polysaccharide type biopolymers such as chitosan [21,22], cellulose [23,24], cyclodextrin [25,26], sodium alginate [27–30] have received more attention. Sodium alginate (SA), for its good membrane forming property and high activity of carbonyl group and hydroxyl group on its chains which are excellent functional groups for anchoring heavy metals through chemical and physical interactions, has been preferred over other materials and attracted considerable attention currently [29,30].

Polyethyleneimine (PEI) is a kind of water-soluble polyamine, and the ratio of primary, secondary and tertiary amine groups on their chains is equal to 1:2:1 approximately [31]. Therefore, PEI can produce very strong chelation ability toward heavy metal ions. PEI has been widely used for modifying various adsorbent, and its application in adsorption separation of heavy metal ions fields are investigating [32–34].

The objective of the present study was to prepare a novel porous membrane adsorbent (PEI/SA) by immobilizing PEI with SA using polyvinylpyrrolidone as a pore former, then functionalized with 3-aminopropyltriethoxysilane (APTEOS). The as-prepared porous membrane adsorbent (PEI/SA) combined the strong chelation ability of amino group towards Cu(II) and the fast diffusion rate of Cu(II) into the internal binding sites in the porous adsorptive membrane. Physico-chemical properties of the PEI/SA were investigated by using scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FT-IR), thermogravimetric analysis (TG) and scanning probe microscope (AFM) methods. The PEI/SA was used for adsorption removal of Cu(II) from wastewater. Batch adsorption experiments were carried out to investigate the effects of adsorption factors, such as solution pH, adsorbent

dose, initial Cu(II) ion concentration, adsorption temperature and contact time on adsorption property of the PEI/SA for Cu(II) ions. By testing various adsorption and kinetics models to fit our experimental data, we also studied the adsorption kinetics and isotherms of the PEI/SA for Cu(II). Meanwhile, the reusability of the PEI/SA for Cu(II) were also investigated.

2. Experimental section

2.1. Materials and analytical method

Sodium alginate (1.05–1.15 Pa s at 10 mg/L, Xilong Chemical Co. Ltd., China), polyethyleneimine ($M_w = 2 \times 10^4$ – 5×10^4 , Qianglong Chemical Limited Company, China), copper nitrate, polyvinylpyrrolidone, hydrochloric acid, Sodium hydroxide (NaOH% ≥ 96.0 , Xilong Chemical Co. Ltd., China), γ -aminopropyl triethoxysilane (0.946 g/mL at 25 °C, Yaohua Chemical Co. Ltd., China), were purchased from Shanghai Chemical Reagent Store (Shanghai, China). All of them are of analytical grade and used without further purification.

A stock solution of 1000 mg/L of Cu(II) was prepared by dissolving certain amount of $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ in 1000 mL deionized water. A series of standard Cu(II) solutions were prepared by appropriate dilution of the stock Cu(II) solution. Solutions of 0.1 M NaOH and HCl were used for solution pH adjustment. The metal ions were determined using a flame atomic absorption spectroscopy (FAAS, GBC-932B, GBC Co. Ltd., Australia), equipped with air-acetylene flame.

2.2. Preparation of porous membrane adsorbent PEI/SA

Four grams of SA was dissolved in 400 mL deionized water following with the addition of 4.0 g PEI. To the above solution, 4.0 mL of 0.01 M HCl and 8.0 mL of APTEOS were dropwisely added in sequence under vigorous stirring with a blender (DSX-120, Hangzhou Electric Instrument Co, Ltd., China) at a speed of 500 rpm. Two hours later, 40.0 mL of aqueous polyvinylpyrrolidone (40.0 g/L) solution was mixed with the above solution under stirring till a homogeneous solution was obtained. The resulted solution was kept in a vacuum oven to remove bubbles, then was cast onto a glass plate (12×12 cm) and dried in an oven at 70 °C for 90 min. The dried membranes were carefully peeled off and immersed in fresh deionized water for 3 times (every time last 8 h). The resulted membranes were further dried in an oven at 70 °C for 180 min, and then stored in a desiccator for further experiments.

2.3. Membrane characterization

FT-IR spectra of the pristine PEI/SA porous membrane and Cu(II)-loaded PEI/SA porous membrane were scanned in the range from 4000 to 400 cm^{-1} by means of ATR-FTIR with an accumulation of 16 scans, resolution of 0.4 cm^{-1} , on a Nicolet-740.

The surface morphology of the pristine SA porous membrane and Cu(II)-loaded PEI/SA porous membrane were also characterized by SEM (Hitachi S-4800), equipped with an energy dispersive X-ray spectroscopy, which was operated at EHT = 4.0 kV.

A CSPM-5500 scanning probe microscope (AFM, Benyuan, China) was used to carry out the morphological characterization of the pristine and Cu(II)-loaded PEI/SA porous membranes, operated in tapping mode. Tapping mode cantilevers (Tap300Al, Budget Sensors) with a spring constant of 40 N/m were used throughout the imaging.

The thermal properties of the pristine and Cu(II)-loaded PEI/SA porous membranes were analyzed using thermogravimetric analysis (Netzsch TG209 F1). Accurately weighted (8 mg) sample was

Download English Version:

<https://daneshyari.com/en/article/145747>

Download Persian Version:

<https://daneshyari.com/article/145747>

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