Chemical Engineering Journal 267 (2015) 132–141

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Preparation of chitosan based electrospun nanofiber membrane and its adsorptive removal of arsenate from aqueous solution

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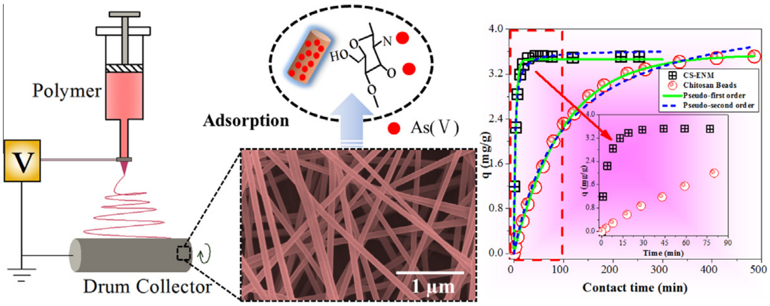
HIGHLIGHTS

- Chitosan electrospun nanofiber membrane (CS-ENM) was synthesized for As(V) removal.
- As(V) adsorption on CS-ENM was very fast and followed pseudo-second-order model.
- As(V) adsorption capacity on CS-ENM was much higher than other chitosan sorbents.
- XPS analysis revealed amine groups on chitosan were involved in As(V) adsorption.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 October 2014
Received in revised form 4 December 2014
Accepted 5 December 2014
Available online 27 December 2014

Keywords:
Adsorption
Arsenic
Electrospinning
Isotherm
Kinetics
XPS

ABSTRACT

In this study, chitosan based electrospun nanofiber membrane (CS-ENM) was prepared as adsorbent for arsenate removal from water. The physicochemical properties of CS-ENM was explored by SEM, TGA and BET analysis. Batch adsorption experiments were systematically carried out to evaluate its arsenate adsorption performance with different process parameters such as solution pH, initial As(V) concentration, contact time, ionic strength, presence of coexisting anions and natural organic matters. XPS was used to investigate the interaction of CS-ENM with arsenate during the adsorption. Results showed that CS-ENM was highly porous with a large specific surface area. Solution pH played a key role in As(V) adsorption onto CS-ENM, and higher adsorption capacity was obtained at lower pH. Kinetics study demonstrated the adsorption equilibrium was achieved within 0.5 h indicating that As(V) uptake by CS-ENM was very fast, and the kinetics process was well fitted by the pseudo-second-order model ($R^2 > 0.99$). The adsorption isotherm experimental data correlated well with Langmuir model, and the maximum adsorption capacity was found to be 30.8 mg/g which was higher than most of the reported chitosan adsorbents. The ionic strength effect study indicated the adsorbed As(V) formed outer-sphere surface complexes with CS-ENM. The existence of CO_3^{2-} and F^- influenced insignificantly to the adsorption of As(V), however the presence of SO_4^{2-}, PO_4^{3-} and humid acid exhibited negative effects on the uptake of arsenate. XPS analysis suggested amine groups on the chitosan backbone were involved in the adsorption of As(V).

1. Introduction

Arsenic is a commonly distributed element in the natural environment, particularly in the ground water. Arsenic contamination in water leads to a number of health problems [1]. People drinking contaminated water with arsenic concentration greater than

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http://dx.doi.org/10.1016/j.cej.2014.12.024

0.05 mg/L are prone to increasing risk of lung and bladder cancer and arsenic-associated skin lesions [1]. Therefore, many technologies have been developed to remove arsenic from water, including coagulation-flocculation, ion exchange, pressure-driven membrane process and adsorption [2]. Because of its high removal efficiency and relative easy operation, adsorption has been recognized as one of the most effective techniques for the treatment of water contaminated with low concentration arsenic. Due to their environmentally friendly nature and low preparation cost, many biosorbents have been developed and tested for the removal of arsenic species from aqueous solution over the past decade, such as bacteria cells [3,4], plant biomass [5] and alginate [6] or chitosan biopolymers [7,8].

Chitosan, an alkaline deacetylated product of chitin, was used extensively in biosorption due to its low cost, high hydrophilicity, nontoxicity and high contents of amino and hydroxyl functional groups, which possess high activity as adsorption sites. The development of chitosan based adsorbents for the removal of metal ions from aqueous solution has been becoming a hot topic in the field of water treatment, due to its excellent properties. Chitosan raw flakes [9,10], crosslinked chitosan beads, magnetic nanoparticles impregnated chitosan beads [11], TiO_2-impregnated chitosan beads [12], molybdate-impregnated chitosan beads [13], chitosan-coated biosorbent [1], and chitosan-immobilized sodium silicate [14] have been prepared and used for the adsorptive removal of arsenic from aqueous environments. As an adsorbent, chitosan is commonly used in the form of flakes, powder or hydrogel beads. It is clear that these physical forms suffer two major drawbacks: the specific surface area is low and the majority of active binding sites are internal, which result in a relatively slow adsorption kinetics and low adsorption capacity [1]. Thus, a way is needed to increase the surface area of chitosan so that the adsorbent can be more effective. Limited studies have been reported on the fabrication of chitosan sorbents with high specific surface area for arsenic removal so far.

One dimensional nanostructure in the form of fibers, wires, rods, belts, or tubes has attracted plenty attention due to their novel properties, high specific surface area and porosity, and diverse applications in the water treatment during the last decade [15]. Electrospinning is currently one of the most promising techniques for mass production of continuous and ultrafine nanofibers [16]. The electrospun nanofiber membrane (ENM) combines the advantages of nanomaterials (high specific surface area) and bulk material (easy separation from water). Haider et al. [17] proposed electrospun chitosan nanofibers for the removal of Cu(II) and Pb(II) ions from aqueous solution. Lee et al. [18] fabricated a novel electrospun composite nanofiber for photocatalytic cogeneration of clean water and energy from dye wastewater. Furthermore, a silver modified electrospun TiO_2 nanofiber was developed for simultaneous filtration and solar photocatalytic disinfection/degradation in water [19].

Chitosan has rigid D-glucosamine repeat units with regularly arranged hydroxyl and amino groups, which leads to poor solubility in common organic solvent and poor electrospinnability [20]. Hence, highly toxic solvents, such as hexafluoroisopropanol (HFIP) and trifluoroacetic acid (TFA), were normally used in the electrospinning of pure chitosan nanofiber [17,21,22]. These organic solvents are harmful to human health and the environment.

The aim of the study is to synthesize a pure chitosan electrospun nanofiber membrane (CS-ENM) in an environmentally friendly way for the adsorptive removal of arsenate from water. We first fabricated electrospun chitosan/poly(ethylene oxide) (PEO) blended nanofiber membrane using 50% acetic acid as solvent. Then, most of the PEO was removed from the blended nanofiber membrane via immerging and washing with water thoroughly. The physicochemical properties of the as-prepared CS-ENM were characterized by scanning electron microscope (SEM) observation, Brunauer–Emmett–Teller (BET) and Thermogravimetric analyzer (TGA) analysis. The adsorption performance and mechanism of arsenate on the CS-ENM were systematically investigated through the batch adsorption experiments and spectral analysis.

2. Materials and methods

2.1. Materials

Sodium arsenate ($Na_3AsO_4\cdot12H_2O$), sodium hydroxide (NaOH), hydrochloric acid (HCl), acetic acid (CH_3COOH), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), disodium hydrogen phosphate (Na_2HPO_4), sodium fluoride (NaF), and potassium perchlorate ($KClO_4$) were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (SCRC, Beijing, China). Humid Acid was ordered from Tianjin Guangfu, China. Chitosan powder with an average molecular weight of 150,000 and 91% degree of deacetylation was purchased from AOXIN, China, and poly(ethylene oxide) particle with an average Mw of 1000,000 was supplied by Changchun Dadi, China. All chemicals, unless otherwise stated, were used as received without further purification. The ultrapure water used in the experiments was supplied by a Milli-Q system (USA). As(V) stock solution (1000 mg/L) was prepared by dissolving appropriate amount of $Na_3AsO_4\cdot12H_2O$ into ultrapure water.

2.2. Preparation of chitosan beads

Chitosan solution was prepared by dissolving 5.0 g of chitosan powder in 95.0 g acetic acid solution. A magnetic stirrer was used to mix the solution until a homogenous solution was obtained. Syringe with 21G needle was filled with the chitosan solution and loaded onto a syringe pump. The syringe pump extruded the chitosan solution droplets into 0.1 M NaOH solution to form homogeneous chitosan beads. The beads were rinsed with deionized water until the pH of filtrate reached around 7.0. After that, the chitosan beads were air dried in room temperature for 72 h, and then further dried at 80 °C in a vacuum chamber for 48 h. The diameter and specific surface area of the dried chitosan beads were measured to be 1.0 mm and 0.34 m^2/g with a Laser particle size analyzer (Malvern Mastersizer 2000, UK) and a BET analyzer (Quantachrome NOVA 1200e), respectively.

2.3. Electrospinning of chitosan based nanofiber membrane

First, the chitosan (4% w/v) and PEO (4% w/v) solutions were prepared separately by dissolving chitosan or PEO in acetic acid (50% v/v), respectively. The chitosan/PEO blend solutions were then prepared by mixing the two master solutions at ratios of 100:0, 97:3, 95:5, 90:10 and 85:15. Homogeneous mixed solutions were obtained after vigorous stirring for 24 h, and the mixed solutions were kept still for 4 h for degassing.

The electrospun nanofibers were synthesized using a simple electrospinning process (Fig. 1). Typically, the blend Chitosan/PEO solution was transferred to a 20 mL plastic syringe with a needle tip (21G). The applied voltage, tip-collector distance and solution flow rate of electrospinning process were 15 kV, 15 cm and 0.2 mL/h, respectively. When the solvent evaporated, a mat-like membrane was obtained on the surface of the collector. After a typical collection time of 3 h, the membrane could be easily torn off from the aluminum foil. The chitosan based electrospun nanofiber membrane (CS-ENM) was then dried in a vacuum chamber,