Journal of Colloid and Interface Science 395 (2013) 205–211

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

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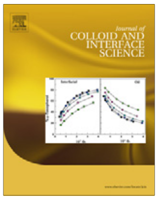

Preparation and sorption studies of glutaraldehyde cross-linked chitosan copolymers

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ARTICLE INFO

Article history:
Received 24 October 2012
Accepted 18 December 2012
Available online 11 January 2013

Keywords:
Adsorption
Biopolymer
Chitosan
Glutaraldehyde
Isotherm, Arsenate anion
p-Nitrophenolate

ABSTRACT

Chitosan–glutaraldehyde copolymer sorbents were synthesized by reacting variable weight ratios (low, medium, and high) of glutaraldehyde with fixed amounts of chitosan. Two commercially available chitosan polymers with low (L) and high (H) relative molecular weights were investigated. The chitosan–glutaraldehyde (Chi–Glu) copolymer sorbents are denoted as **CPL-X** or **CPH-X** where *X* denotes the incremental level ($X = -1, -2, -3$) of glutaraldehyde. The copolymers were characterized using FT-IR spectroscopy and TGA. The solid–solution sorption isotherms in alkaline aqueous solution for the copolymers were characterized using absorbance and emission based spectroscopic methods for *p*-nitrophenol (PNP) and the arsenate oxoanion $\left(HAsO_4^{2-}\right)$ species, respectively. The Sips isotherm model was utilized to obtain sorption parameters at pH 8.5 and 295 K (i.e. sorbent surface area, sorption capacity and removal efficiency) for each copolymer sorbent. The sorbent surface areas for the low molecular weight chitosan copolymers are listed in parentheses ($m^2\ g^{-1}$), as follows: **CPL-1** (124), **CPL-2** (46.7) and **CPL-3** (31.6). The high molecular weight chitosan copolymers are as follows: **CPH-1** (79.8), **CPH-2** (64.7) and **CPH-3** (96.3). The removal efficiencies depend on the pH, temperature, and the relative amounts of sorbate and sorbent. The sorbent removal efficiencies for *p*-nitrophenol ranged between 7.1% and 49%, and the values for $H_2AsO_4^{2-}$ ranged between 31% to 93% for the low and high molecular weight copolymers.

1. Introduction

Water remediation is an important technological challenge due to diverse chemical species (e.g., cleaning agents, personal care products, and pharmaceuticals) with variable concentration ranges of such pollutants in aquatic environments. Access to safe drinking water is necessary for ensuring adequate human health, biodiversity, and healthy ecosystems. Accordingly, the United Nations Environment Program (UNEP) has recognized the importance of safe, clean, drinking water by making it one of the eight millennium goals to reduce the proportion of people without sustainable access by 50% in 2015 [1]. Thus, there is clear need to develop novel materials with improved physicochemical properties for the controlled removal of water borne contaminants.

Water soluble phenolic [2] and inorganic arsenic species [3–6] are an emerging class of contaminants of significant concern to human and ecosystem health because of their relative mobility, toxicity and carcinogenic properties. Such pollutants are known to accumulate in aquatic environments due to their widespread usage. These pollutants pose serious concern for global water security as evidenced by the emergence *cancer belt* region in China [6,7], and arsenic hot-spots across Canada [8]. Adsorption methods are a preferred remediation strategy because of the relatively low cost and efficient removal of contaminants from aquatic environments [9,10]. Natural sorbent materials such as clays, zeolites, activated carbon materials are commonly used for heavy metal removal in wastewater treatment [11]; however, the occurrence of metal oxo-anion species (e.g., Pd, Pt, Mo, V, and As) in aquatic environments has inspired research focused on the development of biomaterial-based sorbents with tunable properties [12,13].

The design of copolymer sorbent materials using biomaterial platforms with variable composition offers a novel "*green*" strategy for the design of sorbents with tunable sorption properties. Renewable biomaterial feedstock's such as chitosan (Chi) and cellulose are abundant platform materials for the design of copolymer sorbents for water treatment applications. Other types of low-cost sorbents such as zeolites, clays, industrial waste (i.e. iron (III) hydroxide and red mud), and low rank coal (i.e. lignite) have been investigated [11,14]. A comparison of the relative cost, availability, and sorption capacity of chitosan with other commercially available sorbents such as activated carbon for heavy metal cations

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0021-9797/$ - see front matter
http://dx.doi.org/10.1016/j.jcis.2012.12.044

(Hg^{2+}, Cr^{6+}, Cd^{2+}, or Pb^{2+}) indicate that chitosan may be a suitable sorbent material [14]. On the other hand, the sorption of heavy metals at neutral or slightly alkaline pH conditions result in the formation of metal oxo-anion species. In comparison to the sorption of metal cations [11], there is a paucity of studies concerning metal oxo-anions [13–16]. The challenges of metal anion recognition is well-described by Steed and Atwood [17]. Amino-polysaccharide-based sorbents (e.g., chitosan) represent suitable materials for binding of metal oxo-anion species because of numerous functional groups (e.g., —OH and —NH_2) because of their suitable H-bond donor and acceptor sites [12,14].

In this paper, we report the synthesis and characterization of chitosan–glutaraldehyde copolymer sorbents with variable glutaraldehyde content and an investigation of their equilibrium sorption properties in aqueous solution. The copolymers were characterized using thermal gravimetric analysis (TGA) and FT-IR spectroscopy. The sorption isotherms were investigated at pH 8.5 and 295 K in aqueous solutions containing an organic anion (*p*-nitrophenolate; PNP) or an arsenate oxoanion $\left(HAsO_4^{2-}\right)$ species at variable concentration. The levels of unbound anion species was evaluated using ICP-OES for $HAsO_4^{2-}$ and UV–Vis spectroscopy for PNP to construct the corresponding isotherms. The Sips isotherm parameters (sorbent surface area and monolayer sorption capacity) of the copolymer sorbents are herein reported.

2. Experimental

2.1. Materials

Glutaraldehyde (Glu), high molecular weight chitosan (Chi-H; 150,000–375,000 g mol^{-1} with ⩾75% deacetylation), and low molecular weight chitosan (Chi-L; 50,000–190,000 g mol^{-1} with ~75–85% deacetylation) were obtained from Aldrich Chem. Co. All materials were used as received without further purification unless specified otherwise.

2.2. Copolymer synthesis

The synthesis of chitosan–glutaraldehyde (Chi–Glu) copolymer materials was adapted from a published procedure, as follows [18]. Approximately 0.40 g of Chi-L was dissolved with stirring in 60 mL of 5.0×10^{-2} M acetic acid in a 100 mL round bottom flask overnight. A variable weight ratio of chitosan/glutaraldehyde (w/w) was employed at low (1/8), medium (1/12), and high (1/17) levels through rapid addition of glutaraldehyde (50% w/v) to a solution of chitosan in aqueous acetic acid. After addition of Glu, the reaction mixture undergoes rapid gelation (~3 min) and the transparent solution becomes a dark yellow–orange color over a 1 h period. The mixture was allowed to stir until complete gelation and then allowed to sit for 1 h before neutralizing with 0.2 M NaOH solution to pH 6–7. The product was washed multiple times with cold Millipore water and cold HPLC grade acetone, followed by drying in a vacuum oven ~56 °C at reduced pressure overnight. The dried products were ground into fine powders before further drying in a pistol dryer under vacuum with P_2O_5 at 50 °C overnight. The products were washed in a Soxhlet extractor with HPLC grade methanol for 24 h followed by a second washing cycle with HPLC grade diethyl ether for 24 h. The products were ground in a mortar and pestle and then passed through a 40-mesh sieve to ensure particles with an upper size limit. A similar procedure was employed for the synthesis of copolymers using chitosan with higher relative molecular weight. The corresponding Chi–Glu copolymers prepared with Chi-L and Chi-H are hereafter denoted as follows: **CPL-1**, **-2**, and **-3**; and **CPH-1**, **-2**, and **-3**; in accordance to the low (1/8), medium (1/12), and high (1/17) chitosan/glutaraldehyde (w/w) ratios employed.

2.3. Characterization

Thermal analysis of the copolymers was performed using thermogravimetry with a TGA (Q50 TA Instruments). Samples were heated in open aluminum pans at 30 °C and allowed to equilibrate for 5 min prior to heating at 5 °C/min up to 500 °C. IR spectra were obtained with a Bio-RAD FTS-40 spectrophotometer wherein samples were analyzed as powders in reflectance mode. Solid samples were prepared by co-grinding copolymers (~5 mg) with pure spectroscopic grade KBr (~50 mg) in a small mortar and pestle. The DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectra were obtained at 295 K with a resolution of 4 cm^{-1} over the 400–4000 cm^{-1} region. DRIFT spectra were recorded with multiple scans in reflectance mode and corrected relative to spectroscopic grade KBr. A Thermoscientific ICP-OES 6000 Series and Varian Cary 100 Scan UV–Vis spectrophotometer were used to measure arsenate emission (λ_{em} = 189 nm) and PNP absorbance (λ_{max} = 400 nm) spectra in aqueous solution, respectively.

2.4. Sorption studies

2.4.1. Arsenate(V) sorption Isotherms

Fixed amounts (~20 mg) of the powdered and sieved sorbents were mixed with 10 mL of adsorbate (Na_2HAsO_4) solution at pH 8.5 in 6 dram vials at variable concentration (45–120 ppm) of adsorbate and equilibrated at room temperature on a horizontal shaker table for 24 h. After shaking, the supernatant solution was filtered through 0.45 μm nylon syringe filters. The initial concentration (C_o) was determined before and after sorption (C_e) at 295 K at pH 8.5. The uptake of the adsorbate was determined as a concentration difference between the initial stock (blank) and final residual adsorbate solutions with Eq. (1). The arsenate concentration (C_o and C_e) was estimated using emission spectroscopy (ICP-OES) at λ_{em} = 189 nm. The protocol for arsenate analyses involved triplicate sample measurements with a 30 s sample flush time with Millipore water between each successive measurement. The sample was introduced using a nebulizer with an axial plasma configuration with the following instrument parameters; calibration mode was set to concentration, flush pump rate ~100 rpm, and an analysis pump rate ~40 rpm with a pump stabilization of 5 s. The RF power was 1150 W with an auxiliary gas flow of 0.5 L min^{-1} and nebulizer gas flow of 0.30 L min^{-1}.

2.4.2. p-Nitrophenolate (PNP) sorption isotherms

Fixed amounts (~20 mg) of the sieved copolymers in powder form were mixed with 10 mL of PNP dissolved in 10 mM aqueous potassium phosphate monobasic buffer using six dram vials at variable PNP concentration (0.2–10 mM). Samples were equilibrated at 295 K on a horizontal shaker table for 24 h. The initial concentration (C_o) was determined before and after sorption (C_e) at pH 8.5. The relative uptake of the adsorbate was determined by difference between the initial blank (C_o) and residual PNP concentration (C_e) in solution using Eq. (1) with UV–Vis absorbance of PNP at λ_{max} = 400 nm.

2.4.3. Arsenate(V) solution preparation

Arsenate solutions were prepared by dissolving ACS grade $Na_2HAsO_4{\cdot}7H_2O$ (Alfa Aesar) into Millipore water at pH 8.5 in 10 mM aqueous potassium phosphate monobasic buffer. The stock solutions were freshly prepared with appropriate dilution as required.

2.4.4. Preparation p-nitrophenolate solutions

Stock solutions of PNP (0.4–10 mM) were prepared by dissolving PNP into 10 mM potassium phosphate monobasic buffer solution at pH 8.5 by adjusting the pH with 2 M NaOH. The molar absorptivity (ε) value for PNP was estimated as ε = 18,478 L mol^{-1} cm^{-1} (pH 8.5;