Carbohydrate Research 344 (2009) 1716–1723

Contents lists available at ScienceDirect

Carbohydrate Research

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

Ethylenesulfide as a useful agent for incorporation into the biopolymer chitosan in a solvent-free reaction for use in cation removal

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ARTICLE INFO

Article history:
Received 26 March 2009
Received in revised form 25 May 2009
Accepted 31 May 2009
Available online 6 June 2009

Keywords:
Chitosan
Solvent-free reaction
Thiol group
Adsorption
Thermodynamic

ABSTRACT

Chitosan (Ch) was chemically modified with ethylenesulfide (Es) under solvent-free conditions to give (ChEs), displaying a high content of thiol groups due to opening of the three member cyclic reagent. Elemental analysis showed a decrease in nitrogen content. This result indicated the incorporation of two ethylenesulfide molecules for each unit of the polymeric structure of the precursor biopolymer. Infrared spectroscopy, thermogravimetry, and ^{13}C NMR in the solid state demonstrated the effectiveness of the reaction, with signals at 30 ppm for ChEs due to the change in the methylene group environment. Divalent metal uptake by chemically modified biopolymer gave the order Cu > Ni > Co > Zn, reflecting the corresponding acidity of these cations in bonding to the sulfur and the basic nitrogen atoms available on the pendant chains. The equilibrium data were fitted to Freundlich, Temkin, and Langmuir models. The maximum monolayer adsorption capacity for the cations was found to be 1.54 ± 0.02, 1.25 ± 0.03, 1.13 ± 0.01, and 0.83 ± 0.03 mmol g^{-1}, respectively. The Langmuir model best explained the cation–sulfur bond interactions at the solid–liquid interface. The thermodynamics for these interactions gave exothermic enthalpic values of −43.02 ± 0.03, −28.72 ± 0.02, −26.27 ± 0.04, and −17.32 ± 0.02 kJ mol^{-1}, respectively. The spontaneity of the systems is given by negative Gibbs free energies of −31.2 ± 0.1, −32.7 ± 0.1, −31.7 ± 0.1, and −32.2 ± 0.1 kJ mol^{-1}, respectively, in spite of the unfavorable negative entropic values of −39 ± 1, −13 ± 1, −18 ± 1, and −49 ± 1 J K^{-1} mol^{-1} due to solvent ordering in the course of complexation. This newly synthesized biopolymer is presented as a chemically useful material for cation removal from aqueous solution.

1. Introduction

Properties, such as abundance, biodegradability, non-toxicity, biocompatibility, biodegradability, bioactivity, and low cost are useful features for choosing biopolymers for valuable applications and they have recently received significant attention, not only because they are renewable, but also because they are more environmental friendly than conventional polymers.[1–3] Cellulose, chitin, and chitosan have related structures and occur in nature, being among the most abundant materials in the world.[4,5]

Among these biopolymers, chitin is natural, abundant, and suitable for developing novel types of materials containing different functions.[6,7] It is biodegradable and is the second most abundant polysaccharide on earth, after cellulose. It is a non-toxic biopolymer made up of acetylglucosamine units, which are widely found in the exoskeleton of shellfish and crustaceans, such crab, lobsters, and shrimps.[8]

Chitosan is a linear copolymer constituted by β-(1→4) linking 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose units obtained through N-deacetylation of chitin under strongly basic conditions. From the structural viewpoint, available amino (NH_2) and hydroxyl (OH) groups present single-pairs of electrons, even though the N-deacetylation is almost never complete.[9] Chitin and chitosan have similar polymeric structures, differing in the amount of acetylated units, as represented by the degree of deacetylation (DD), which is a useful parameter related to this property.[10,11] There is no formal nomenclature for this classification; however, it is expected that chitosan shows a DD value higher than 50%.[12,13]

The more available reactive amino groups on chitosan enable this polysaccharide to substitute chitin in the course of investigations, as an easily synthesized derivative from natural sources, demonstrating a facility for adsorption, in addition to other attractive physical properties.[14–16] On the other hand, when the biopolymeric chitosan is submitted to chemical modification, this is a promising route to yield new biomaterials. Through the inclusion of desirable pendant molecules covalently bonded to the main chain, some characteristic properties are changed and, consequently, many other interesting

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doi:10.1016/j.carres.2009.05.028

areas such as agriculture, medicine, food, industry, and pharmaceutical technology, become possible for technological applications.[17]

In the course of studying the applicability of chitosan and derivatives in many research fields in recent years, little attention has been focused on the study of these biopolymers using solvent-free reactions. The absence of solvent is an excellent reaction alternative, as it leads to an environmental friendly process for acquisition of new polysaccharides, with less expensive methodology. As is known, environmental contamination is a serious problem that is related to possible serious consequences, including contamination of water from various sources. Many traditional treatments have been applied to regenerate contaminated waters from distinct species, including heavy metals. These include ion-exchange, electrodeposition, membrane separation, and adsorption procedures.[2,18]

From these applied methodologies to purify effluents, adsorption seems to be a reliable alternative and many adsorbents have been proposed for this purpose.[19] Various natural or synthetic materials have been tested, and chitosan is being greatly exploited due to its advantages when compared, for example, with active carbon, which is the most intensively used material.[8] Indeed, the success of chitosan is closely related to its binding capacity for cations, mainly using the available amino groups. Thus, chitosan has been explored as one of the most popular adsorbents for metal removal from aqueous solution, because it was proven to have better chelating power than other biopolymers.[19] However, the extent of adsorption depends on its source, its deacetylation degree, the nature of the cation, and the pH of solution.

The available amino and hydroxyl groups in the biopolymer chitosan can be potentially modified to yield new products that usually increase the number of reactive sites to act as chelating centers to adsorb metals, dyes or others species.[20] However, the reactive free active primary amino group also opens the possibility to exploit the chemical reactions involving this group. The hydroxyl groups on carbons 3 and 6 of the ring can also react, to provide even more interesting chemical modifications of this biopolymer.[21]

Taking into account the rigidness of the polymeric chain, resulting in a material insoluble in common solvents, chitosan being soluble only in mineral or some dilute organic acids,[5] investigations are needed to give new biopolymers that enhance solubility. On the other hand, from the viewpoint of the adsorption methodology, chemical modifications, such as a crosslinking process, can be expected to reduce dissolution in acidic media, but with a disadvantage of decreasing sorption capacity.[22,23]

With the aim of synthesizing new chitosan derivatives the present investigation deals with the incorporation of ethylenesulfide molecule in the polysaccharide chain through the reaction of the available amino group. This nucleophilic amino center reacts with the three member cyclic reagent to place pendant chains with sulfur and nitrogen basic sites onto the original structure. An environmentally friendly solvent-free reaction was explored and the activity in adsorbing divalent cations from aqueous solution was studied through various proposed models. The cation–basic center interactions at the solid ≠ liquid interface were also followed calorimetrically and the set of thermodynamic data involved in these interactive processes was determined.

2. Experimental

2.1. Materials

Chitosan (Ch) powder (Primex) with a degree of deacetylation of 82%, determined through infrared spectroscopy, after treating the biopolymer with an alkaline solution.[24] Ethylenesulfide (Es) (Aldrich) reagent was incorporated on chitosan in a solvent-free reaction. Zinc, nickel, cobalt, and copper nitrate solutions were used in the adsorption process in deionized water.

2.2. Equipment and measurements

The carbon, sulfur, and nitrogen content of the precursor chitosan and of the chemically modified biopolymer were determined through elemental analysis on a Perkin Elmer, model 2400, elemental analyzer. FTIR spectra of the samples as KBr pellets were obtained by accumulating 32 scans on a Bomem Spectrophotometer, MB-series, in the 4000–400 cm^{-1} range, with 4 cm^{-1} of resolution. Solid-state ^{13}C NMR spectra of the samples were obtained on a Bruker AC 300/P spectrometer, using the CP–MAS technique, with pulse repetitions of 5 s and contact times of 1 ms; the measurements were at 75.47 MHz, with magic angle spinning of 4 kHz. X-ray diffraction patterns were obtained on a Shimadzu XD-3A diffractometer (35 kv, 25 mA), in the $2\theta = 1.5–50°$ range, with nickel-filtered Cu Kα radiation, having a wavelength of 0.154 nm. Thermogravimetric curves were obtained using a Shimadzu TGA 50 apparatus, under an argon atmosphere at a flow rate of 1.67 $\text{cm}^3\ \text{s}^{-1}$, with a heating rate of 0.167 K s^{-1}. The amount of cation adsorbed was determined using a Perkin Elmer 3000 DV ICP-OES apparatus, considering the difference between the initial concentration in the aqueous solution and that found in the supernatant after the adsorption process. The reproducibility was checked through at least one duplicate run for each experimental point.

2.3. Chemical reaction

To a sample of chitosan (2.0 g) in an appropriate flask protected from humidity, ethylenesulfide in excess (5.6 cm^3) was added in absence of solvent, with magnetic stirring. After 3 h, the solid was separated by filtration and extensively washed with deionized water. The isolated solid, hereafter named ChEs, was dried at 328 K in an oven.

2.4. Adsorption experiments

The new biopolymer (ChEs) was suspended in several metal salt solutions to evaluate its adsorptive capacity. All experiments were performed in duplicate, using a batch process in which nearly 20 mg of the chemically modified biopolymer was introduced into a series of polyethylene flasks containing 10.0 cm^3 of metallic cation solution having concentrations ranging from 7.0×10^{-4} to 7.0×10^{-3} mol dm^{-3}. With the purpose to obtain the time to reach isotherm saturation, kinetic experiments were previously assayed using similar cation solutions. For this determination the amount of cation removal as a function of time well defined a plateau at 4 h.[25] However, the time chosen was 6 h to ensure the best equilibrium condition and the suspensions were stirred in an orbital bath at 298 ± 1 K. The supernatant solutions were separated from the solid through decantation and aliquots were taken to determine the amounts of cation remaining by ICP-OES. The amount of the cation adsorbed in the experiment (mmol g^{-1}) was calculated by Eq. 1, where N_f is the number of moles adsorbed on modified chitosans, n_i and n_s are the number of moles in the initial solution and the supernatant after equilibrium, and m is the mass of the adsorbent used in each adsorption process.[26]

$$N_f = (n_i - n_s)/m \tag{1}$$

To determine the maximum adsorption capacity, N_s, the experimental data related to the number of moles in the supernatant at each point of the titration, C_s, and the N_f obtained were fitted to a modified Langmuir equation (Eq. 2), b being a constant related to the chemical equilibrium at the solid/liquid interface.