Chitosan-glutaraldehyde copolymers and their sorption properties

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ABSTRACT

This study reports the preparation of chitosan-glutaraldehyde (Chi-Glu) copolymers at modified reaction conditions such as the temperature prior to gelation, pH, and reagent ratios. The chitosan copolymers were characterized using infrared spectroscopy (FT-IR), CHN elemental analysis, and thermal gravimetric analysis (TGA). Evidence of self-polymerized glutaraldehyde was supported by CHN and TGA results. The sorption properties of Chi-Glu copolymers were evaluated in aqueous solutions containing p-nitrophenol at variable pH (4.6, 6.6, and 9.0). The sorption properties of the copolymers correlated with the level of the accessibility of the sorption sites in accordance with the relative cross-linker content. The relative sorption capacity of the Chi-Glu copolymers increases as the level of cross-linking increases. Chitosan displays the lowest sorptive uptake while an optimal sorption capacity was concluded at the 4:1 glutaraldehyde:chitosan monomer mole ratio, in close agreement with the three reactive sites (i.e. —OH/—NH) per glucosamine monomer. The PNP dye probe was determined to bind to chitosan through an electrostatic interaction due to the increased sorption capacity of the phenolate anion, as evidenced by the change in pH from 4.6 to 9.0.

1. Introduction

Chitosan was first discovered in 1859 by Rouget when chitin was boiled in concentrated potassium hydroxide and the subsequent product was shown to be soluble in acids (Muzzarelli, 1977). Chitosan is rarely found in nature but can be obtained from hydrolysis of chitin. Each year, approximately 20 million tonnes of shrimp, lobster, and crab shells are discarded as waste by-products (Bruck, Slater, & Carney, 2010). Thus, synthetically engineered chitosan copolymers represent a versatile biomaterial platform for wastewater treatment applications because of its relative availability and amenability to chemical modification. Chitosan is a polysaccharide containing two types of monomer: 2-acetamido-2-deoxy-ᴅ-glucopyranose and 2-amino-2-deoxy-β-ᴅ-glucopyranose. The pK_a of chitosan ranges between 5.5 and 6.5 depending on the degree of deacetylation and its average molecular weight may cover a range of possible values (e.g., $1–5 \times 10^5$ g/mol).

Due to the semi-crystalline nature of chitosan and its relatively low surface area (Piron et al., 1997), it is generally a poor adsorbent of organic dye species in its unmodified form. Therefore, much of the application of chitosan copolymers employs the use of cross-linkers to modify its chemical structure and textural properties by linking at the amine or the hydroxyl sites. Cross-linking between chitosan and glutaraldehyde afford copolymer materials with a porous network with improved adsorption properties (Crini & Badot, 2008). In this manner, chitosan can be structurally modified by forming copolymers with variable morphology (i.e. beads, hydrogels, powders, and films/membranes). Such materials have tunable structure and physicochemical properties as evidenced by their diverse applications; self-repairing materials (Ghosh & Urban, 2009), biopolymer-based membranes for chemical separations (Chen, Zheng, Wang, Lee, & Park, 2002), wastewater and dye remediation (Chiou & Chuang, 2006; Jin & Bai, 2002; Xu, Hein, Loo, & Wang, 2008), and drug delivery systems (Bodnar, Hartmann, & Borbely, 2006; Jafarinejad et al., 2012; Lu et al., 2012; Ma, Qian, Yang, Hu, & Nie, 2010; Shu & Zhu, 2002). Chitosan copolymers derived from cross-linking with glutaraldehyde (Chi-Glu) were applied in dye remediation since adsorption occurs mainly through the deacetylated sites (i.e. primary amine groups). Ion-dipole and H-bonding are considered the primary noncovalent interactions for the adsorption of dyes (Chiou & Li, 2003; Ngah & Fatinathan, 2006; Pratt, Wilson, & Kozinski, 2013).

Chitosan copolymers are typically prepared using a conventional sol–gel process where chitosan is dissolved in dilute acid to form an aqueous solution where the cross-linkers are subsequently incorporated. To obtain beads, the mixture may be added

drop-wise into an alkali solution where the protonated amine groups are neutralized and subsequently precipitated. Precipitation generally occurs rapidly where the resulting beads have uniform diameters (Jin & Bai, 2002). For conventional copolymers, the viscosity of the chitosan solution with the cross-linker increases with time until the gel point is reached; thereafter, the cross-linked chitosan solution forms a gel phase. Gelation depends on various factors but can be accelerated by increasing the pH along with mechanical mixing so that the solution approaches the pK_a of chitosan (Kildeeva, Perminov, Vladimirov, Novikov, & Mikhailov, 2009). An ageing process of the gel sets in where the shear modulus increases with eventual hardening (Kildeeva et al., 2009). An insoluble cross-linked copolymer is obtained once the gel network is dehydrated and neutralized by adding additional alkali solution to precipitate out the copolymer followed by air drying.

The relationship between the gelation process and the degree of cross-linking is poorly understood. The ageing process is known to affect the porosity of the xerogel that forms after drying (Brinker & Scherer, 1990), and ageing may occur over days depending on the type of gel because the overall structure may drastically change (Brinker & Scherer, 1990). For example; the average pore width of titania gel systems (Brinker & Scherer, 1990) increases from 3 to 7 nm after ageing for one day. The dependence of the size of the pores with ageing of the gel likely affects the surface accessibility of the pores and the overall sorption capacity (Brinker & Scherer, 1990; Kyzas et al., 2010). As well, the influence of pH on the morphological properties of gels is anticipated since an increase in the shear modulus of the gel was noted elsewhere (Kildeeva et al., 2009) as the pH increased from 4.1 to 5.6 for a chitosan-glutaraldehyde solution. The textural and chemical properties of the copolymer are related to the overall sorption capacity of the final product.

Therefore, the objective of this paper was to investigate the effect of pH, temperature, and cross-linker content on the sorption capacity of chitosan cross-linked with glutaraldehyde (Chi-Glu). Herein, we describe the synthesis, characterization, and equilibrium sorption properties of aged Chi-Glu copolymers with *p*-nitrophenol (PNP) in aqueous solutions. Dyes such as PNP have been shown to serve as reliable adsorptive probes for studying the physicochemical properties of copolymers in heterogeneous systems at different experimental conditions (Mansri, Memou, & Benabadji, 2013; Wilson, Mohamed, & Headley, 2011).

2. Experimental

2.1. Materials

Sodium hydroxide, potassium phosphate monobasic, *p*-nitrophenol, low molecular weight chitosan (75–85% deacetylated, molecular weight range: 50,000–190,000 kDa), 50%(w/v) glutaraldehyde in water, and glacial acetic acid were obtained from Sigma–Aldrich Canada Ltd. (Oakville, ON). Granular Activated Carbon (GAC; Norit Rox 0.8) was obtained from Norit America and used as received after drying under vacuum. All other chemicals were used as received unless specified otherwise.

2.2. Synthesis of chitosan cross-linked glutaraldehyde copolymers

6.00 g of chitosan (50,000–190,000 g/mol) was dissolved in 600 mL of aqueous acetic acid (5%, v/v). Upon dissolution, glutaraldehyde was diluted with an additional 20 mL (5%, v/v) aqueous acetic acid (pH = 3.3–3.9) and added to the chitosan solution. The amount of glutaraldehyde added was related to the relative mole ratio of chitosan monomer, as shown in Table 1. The solution was stirred overnight at 295 K until a light yellow to orange coloured gel was obtained. The removal of excess water (200–300 ml) under

Table 1

Relative amounts of chitosan glutaraldehyde used for the copolymer synthesis. A theoretical mole ratio of glutaraldehyde to number of amine groups of chitosan ratio (Glu/NH$_2$) is also listed here.

Copolymer product	Mass of chitosan (g)	Volume of glutaraldehyde[a] solution (ml)	Calculated Glu/NH$_2$ mole ratio[b]
CG-1	6.00	3.6	0.670
CG-2	6.00	6.3	1.17
CG-3	6.00	9.0	1.68

[a] Density of glutaraldehyde solution 50% (w/v) is 1.106 g/L.
[b] Degree of deacetylation (75–85% deacetylated) was accounted for in Table 1. An average of 80% deacetylation was used.

vacuum was done with gentle heating at 25–30 °C if gelation did not occur within 24 h. Upon gelation, the mixture was allowed to stand for 24 h to facilitate the ageing process. Upon completion of ageing, a 6 M aqueous sodium hydroxide solution was added slowly over 1 h to the gel with rigorous stirring with a spatula. The gel formed an insoluble brown precipitate and the pH of the supernatant solution was maintained at 7.0. The suspension was left in the solution overnight and a dark brown product was obtained and was isolated with vacuum filtration. A dark brown hydrogel was obtained and broken into smaller pieces with a spatula and ground gently with a mortar and pestle. Gentle drying of the product was carried out for 1 h at 333 K at ambient pressure. The product was periodically removed during the drying process and ground with the mortar and pestle to a fine powder. This procedure of periodic heating and grinding is used to prevent densification of the gel and was repeated until the final product appeared as a fine brown powder which was finally dried for 12 h at 25–30 °C. The final copolymer was then passed through a 40-mesh sieve, followed by washing in a Soxhlet extractor with methanol for 24 h. Finally, a vacuum oven at a temperature of 45 °C and reduced pressure (25 mmHg) was used to remove residual solvents from the copolymer product.

2.3. Copolymer characterization

2.3.1. FT-IR

Fourier Transform IR spectra were obtained using a double beam spectrophotometer (Bruker, model Tensor 27). The sample chamber was purged with nitrogen gas and solid samples were analyzed as KBr pellets in transmission mode. In the case of liquid samples, they were analyzed as a liquid film using a NaF cell.

2.3.2. UV–vis

UV–vis absorbance spectra were obtained using a double beam Varian-Cary (Cary 100) spectrophotometer. Residual dye in aqueous solution was obtained using quartz cuvettes. A calibration curve of absorbance vs. dye concentration was made to determine the linear response region of the Beer–Lambert law and the molar absorptivity (ε) of residual (unbound) PNP at equilibrium for various pH and concentration conditions.

2.3.3. TGA

Thermogravimetry analysis (TGA) of samples was obtained with a TA Instruments analyzer (Model Q50). Nitrogen gas was used for cooling and purging of the sample compartment. Samples were analyzed in open aluminium pans over the temperature range between 30 °C and 500 °C at a nominal heating rate of 10 °C.

2.3.4. CHN analyses

Carbon, hydrogen and nitrogen elemental contents were obtained with a Perkin Elmer 2400 CHN Elemental Analyzer. The combustion oven temperature was above 925 °C while the reduction oven had a temperature over 640 °C. The instrument was