Full Length Research Paper

Synthesis of poly [β-(1→4)-2-amino-2-deoxy-D-glucopyranose]/lead nanocomposite

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Chitosan (poly [β-(1→4)-2-amino-2-deoxy-D-glucopyranose] β-PADG) is a natural polymer with abundant primary amino groups in its molecular structure. Due to its excellent properties such as biocompatibility, biodegradability, nontoxicity, and adsorption properties, it is a potential polysaccharide resource. The present investigation describes the preparation and characterization of novel biodegradable nanocomposite based on complexation of β-PADG with bivalent lead ion. The prepared nano-systems were stable in aqueous media at low pH. The particle size and the size of the complexes were identified by x-ray diffraction (XRD) and UV-vis spectra measurements. It was found that the size of the complexes depended on the concentrations of β-PADG and lead ions. UV-vis spectra of the nanocomposites revealed the presence of metal nanoparticles. At low concentrations, nanosized particles were formed, however, at high concentrations, formation of large aggregates with a broad size distribution was promoted. The results from the XRD measurements showed that the high concentrations of chitosan and Pb2+ ions favored the growth of large complexes. The β-PADG nanocomposite composed of a biodegradable biomaterial with high flocculating and heavy metal binding activity may be useful for various water treatment applications.

Key words: Chitosan, lead ions, nanoparticles, complexation.

INTRODUCTION

Recently, chitosan and other polysaccharides have been used for preparation of nanocomposites. Due to the interaction between the amino groups in chitosan and metal nanoparticles, chitosan was chosen as a protecting agent in synthesis of metal nanoparticles (Huang et al., 2005; Bodnar et al., 2006; Il’ina and Varlamov, 2005). Chitosan is a deacetylated derivative of chitin composed of randomly distributed β-(1→4)-2-amino-2-deoxy-D-glucopyranose, the presence of the pair of free electrons of the amino group is assumed to be the origin of the dative bonds (Yin et al., 2004; Hudson and Smith, 1998; Saifuddin and Kumaran, 2005; Seiichi et al., 1983). This idea is confirmed by the observation of a much weaker fixation in chitin. However, there may be interaction due to the simple phenomenon of adsorption, electrostatic attraction or ion exchange (Yin et al., 2004; Adewuyi et al., 2008; Taboada et al., 2003; Schmuhl et al., 2001). For separation of toxic heavy metal ions, including lead ions, several natural polymers have been investigated and the most valuable properties of these biopolymers are their biocompatibility, biodegradability, and flocculating activity for metal ions (Bodnar et al., 2008; Solpan and Torun, 2005; Taniguchi et al., 2005; Yokoi et al., 1996). Treating waste water using “greener” methods have become an ecological necessity. Chitosan, due to its natural origin are biodegradable and has proven to be a most interesting alternative from several points of view (Clermount, 2005). First, it improves the effectiveness of water treatment while reducing or even eliminating synthetic chemical products and synthetic polymer. Secondly, it potentially reduces the use of alum by up to 60% and eliminates 100% of the polymer from the treated
water thereby improving the system performance (suspended solid and chemical oxygen demand) and significantly reducing odor. The present investigation reports the formation of β-PADG-lead ions nanoparticle composite by chemical reduction method in aqueous solution.

MATERIALS AND METHODS

Chitosan with 100% degree of deacetylation was prepared in our laboratory from snail shell by using the literature methods described earlier (Adewuyi et al., 2008). Pb (NO₃)₂ and NaBH₄ were purchased from Aldrich and used without further purification. Acetic acid (AR) was diluted to a 1% aqueous solution before use. All aqueous solutions were made with ultrahigh purity water.

Preparation and characterization of β-PADG-Pb nanocomposite

2 mg chitosan (β-PADG) was dissolved in 30 mL 1% HOAc solution for 20 h at room temperature, which was then filtered to remove insoluble material. 50 mL distilled deionized water was added to this chitosan solution. Metal nanoparticles were obtained by chemical reduction of metal salts to yield the corresponding zero valent metal nanoparticles with NaBH₄ (Huang et al., 2005, Selichi et al., 1983). Formation of chitosan with Pb²⁺ at diverse stoichiometric ratios and concentrations were made according to the described reaction conditions summarized in Table 1. In a typical procedure, a 50 µL and 20 mM Pb (NO₃)₂ aqueous solution was mixed with 3 ml 2.0 mg/mL chitosan, the mixtures were stirred for 30 min, then freshly prepared aqueous solutions of NaBH₄ (50 µL and 0.2 M) were added quickly to the mixture, and stirred for another 90 min until the entire reduction of metal salts.

The nanocomposites obtained were kept at room temperature for subsequent characterization. Perkin-Elmer 2000 FT-IR (KBr) spectrophotometer was utilized to determine the structure of chitosan and chitosan-lead complex (Adewuyi et al., 2008). The morphology of chitosan and its metal complexes was examined with D/MAX-RC X-ray diffractometer at the CuKa ray (λ=1.54 Å). Measurement was executed from 5-100° with irradiation conditions of 40 kV and 80 mA, and a scanning rate of 2° min⁻¹ of diffraction angle 2θ. UV-vis absorbance spectra were collected using Shimadzu UV-2101PC spectrophotometer.

RESULTS AND DISCUSSION

The structure of chitosan is like cellulose, which is an oxygen-rich natural carbohydrate (polysaccharide) consisting of anhydroglucose units joined by an oxygen linkage to form a linear molecular chain. Traditionally, metal ions were reduced by chemical agents. UV-light in the presence of chitosan which stabilized and controlled the size of the nanoparticles due to the presence of free amino groups (Twu et al., 2008). The amino groups (-NH₂) of linear chitosan chains were cross-linked with lead ions, and formed stable nanoparticles. Complexation was observed and separated or aggregates were obtained depending on the chitosan/Pb²⁺ composition. In neutral and alkali media, chitosan is an uncharged macromolecule, and this may lead to smaller sizes of the chitosan/Pb²⁺ particles unless the concentrations of the components in the mixture are sufficiently high to form intermolecular complexes. In acidic media, the amino groups are protonated and the repulsive electrostatic forces between the positively charged parts affect the physicochemical properties of these particles. The two competing reactions are therefore:

\[
M^{2+} + \text{RNH}_2 \rightleftharpoons \text{M(RNH}_2)_2^{2+} \quad \text{(1)}
\]

\[
H^+ + \text{RNH}_2 \rightleftharpoons \text{RNH}_3^+ \quad \text{(2)}
\]

Figure 1 shows the UV-vis spectra of the (β-PADG) chitosan/Pb nanocomposites with chitosan solution as the reference. The spectra exhibit an absorption band at around 400 - 430 nm, which is a typical plasmon band, suggesting the formation of lead nanoparticles (Murugadoss and Chattopadhyay, 2008; Chen et al., 2007). When the concentration of β-PADG is increased, the intensity of the absorption band decreases with slight change in the center of absorption band. All these changes in UV-vis absorption indicate that the size of lead nanoparticles formed altered with the concentration of chitosan, which operates as a controller of nucleation as well as a stabilizer. This result is comparable with that reported by Bodnar et al. (2008), wherein, a nanocomposite of lead and polygamma-glutamic acid (γ-PGA) was formed. Detail explanation for the change of particle size of lead particles with various concentrations of y-PGA was offered. Similarly, the number of nucleation, the interaction between chitosan and Pb²⁺, and the protective action of β-PADG may be responsible for the particle size change of lead particles prepared in the presence of various concentrations of chitosan.

However, comparing the change in particle size induced by changing β-PADG concentrations with that induced by the change of Pb²⁺ concentrations, that induced by the latter is more pronounced (Figure 2). With increasing concentrations of aqueous Pb (NO₃)₂ from 1 to 20 mM, the intensity of the absorption band increased with increasing concentration of Pb²⁺. These changes in absorption band indicate changes in particle size of lead nanoparticles. The x-ray diffractograms of β-PADG and its Pb²⁺ complexes show that β-PADG has a polymorph.
Figure 1. UV-vis absorption spectra of β-PADG/Pb nanocomposites prepared with various concentrations of chitosan.
of higher crystallinity than the complexes, so complexes have more amorphous domains which allow a better accessibility to reactants and thus a better reactivity. When chitosan is exposed to X-ray diffraction analysis, it gives a diffractogram with five peaks characteristic of crystalline regions (Figure 3) at 9.83, 10.58, 19.78, 22.45 and 27.71°.

**Conclusion**

In this work, the complexation between β-PADG and Pb^{2+} ions at different concentrations of the components was studied using chemical reduction of metal salts to yield the corresponding zero valent metal nanoparticles with NaBH4. Depending on the concentrations of the polymer and the lead ions, chelation of large complexes may occur. UV-vis spectra of the nanocomposites revealed the presence of metal nanoparticles. At low concentrations, nanosized particles were formed, however, at high concentrations, formation of large aggregates with a broad size distribution was promoted. The strong complexation capacity of β-PADG for lead ions indicates a promising sorbent for removal of heavy metals in polluted water.

**REFERENCES**


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