Composites Communications 7 (2018) 7–11

Contents lists available at ScienceDirect

Composites Communications

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

Crosslinked alginate/silica/zinc oxide nanocomposite: A sustainable material with antibacterial properties

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ARTICLE INFO

Keywords:
Alginate
Silica
Zinc oxide
Nanocomposite
Antibacterial activity

ABSTRACT

In the current study silica gel was extracted from rice husk as light and cost effective biomaterial followed by incorporation in crosslinked alginate for preparing nontoxic and functionalized nanocomposite material. Alginate/silica hybrid was investigated as a template for zinc oxide formation. Zinc oxide nanoparticles with diameters of ca. 20 nm were homogenously anchored onto alginate/silica hybrid. The antibacterial activity of the composite was evaluated against gram positive (S. aureus) and gram negative (E. coli) bacteria. The current article shows that the alginate/silica/zinc oxide nanocomposite is promising sustainable and disinfection materials to effectively inhibit bacterial.

1. Introduction

Due to the environmental and societal problems associated with the use of fossil feedstocks, there is an ever growing demand to switch not only fuel production, but also that of material chemistry to sustainable processes using renewable resources [1]. Nanocomposite materials that comprise of natural polymers and inorganic nanoparticles such as metal oxides [2], silicon oxide [3] and calcium phosphate [4] have attracted considerable attention in biomaterials. Among natural polymers, alginate is a water-soluble polysaccharide composed of alternating blocks of guluronic and mannuronic acid. Guluronic block regions are aligned side by side with an ideal shape for the cooperative binding of calcium ions. The gelation of alginate can be carried out under an extremely mild environment using non-toxic divalent cations such as Ca^{2+}, Zn^{2+} or Ba^{2+} forming an ionotropical gel that makes it extremely interesting to be applied in the biomedical field.

Rice husk is an abundantly available agricultural waste material that contains a large amount of siliceous ash. The major constituents of rice husk are cellulose, lignin and ash. Silica represents more than 98% of the ash composition produced from rice husk.

The burning of rice husk in air causes an environmental pollution and possesses a health hazard. The extraction of the silica from rice husk is considered a novel source of silica and reduced the environmental hazards of burnt rice husk. Soluble silicates extracted from silica are recently applied in the industries of glass, ceramics, and cement [5]. Moreover, silica was applied in pharmaceuticals, cosmetics and detergents.

Zinc oxide (ZnO_2) is reported as a safe material with broad antibacterial activities. It has been reported that zinc is relatively non-toxic to humans and animals at low doses (less than 100 mg/day). It is necessary for the proper functioning of living organisms and is involved in the metabolism of proteins and carbohydrates [6]. Moreover, ZnO_2 nanoparticles exhibited much better antibacterial activity than microsized particles. The suggested antibacterial mechanism is mostly due to the release of zinc ions from zinc oxide nanoparticles [7]. For this reason, several attempts have been carried out to investigate new materials with active sites for assistance the formation of zinc oxides nanoparticles. Among these trails, Yan-Wen Wang et al. used graphene oxide to assist homogeneously anchored zinc oxide nanoparticles with 4 nm diameter onto graphene oxide surface. The authors reported that the nanocomposite decelerate zinc oxide dissolution and assist the direct contact between bacteria membrane and zinc oxide. This direct contact induced bacterial death through increasing the penetration and disorganization of bacterial membrane [7].

Recent attempts have carried out for preparing polysaccharides/zinc oxide nanocomposite materials. Among these trials, bacterial cellulose /zinc oxide nanoparticles were prepared using N-methylmorpholine-N-oxide as cellulose solvent. Comparing with pure bacterial cellulose, the composite materials have high mechanical strength, high degradation temperature and improved antibacterial properties. In

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https://doi.org/10.1016/j.coco.2017.11.006
Received 29 December 2016; Received in revised form 20 November 2017; Accepted 23 November 2017

addition, bacterial cellulose/zinc oxide nanoparticles were reported as biocompatible materials with cell adhesion ability [8]. S. Sanuja et. prepared zinc oxide nanoparticles/neem essential oil/chitosan by solution cast technique. The incorporated zinc oxide improved mechanical properties, film transparency and antibacterial properties of the formed composite [9]. From the above results, it is clear that incorporation of zinc oxide nanoparticles into polysaccharides matrix is an essential strategy for preparing new composites with required properties.

The current article aims to prepare full sustainable and environmentally friendly hybrid for biomaterials. Rice husk was used as raw material for silica gel extraction. Alginate, biopolymer, was used as matrix supporting material. Studying the effect of alginate/silica hybrid to assist the formation of zinc oxide nanoparticles was investigated. Moreover, the antibacterial properties of the prepared hybrid against different kinds of bacteria were investigated.

2. Experimental

2.1. Materials

Alginic acid sodium salt from brown algae and zinc acetate dihydrate were supplied from Sigma-Aldrich. All other chemicals of analytical grade and used without further purifications. All reactions were carried out using deionized water.

2.2. Preparation of silica gel from rice husk

Rice Husk supplied from the Egyptian farms was washed with water to remove dust and impurities then dried in an oven at 110 °C for 24 h. Cleaned and dried rice husk was burned in a muffle furnace at 650 °C for 4 h and the obtained ash was collected and sieved to different particle sizes. The ash with particle sizes less than 300 µm was first pretreated with (3% v/v) HCl at liquor ratio of 1:12 for 3 h and then filtered and washed with water three times. Finally the filtrate was refluxed with 1 M NaOH at liquor ratio of 1:12 for 5 h then filtered and washed with 400 ml of boiled distill water. The filtrate was neutralized with 1 N HCl till pH = 7 and left to aging for 24 h.

2.3. Alginate/silica/ZnO nanocomposite preparation

Alginate/silica complex was prepared firstly as follow: Sodium alginate (100 mg) was dissolved in 10 mL deionized water and mixed with silica solution (20 mg). The mixture was dropped in 2% zinc acetate solution and stirred for 2 h. Alginate/silica beads were formed through ionotropic interaction Zn^{2+} with alginate. Moreover, zinc oxide nanoparticles were formed by in-situ precipitation technique by adding 2 M sodium hydroxide solution until the pH reaches 7. Pure zinc oxide was separated and only alginate/silica/ZnO nanocomposite was taken out and washed several times with doubly distilled water before drying.

2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) was done on a Mattson 5000 FTIR spectrometer using KBr discs in the range of 4000–500 cm^{-1}. Scanning electron microscopy was done on Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 20 K. The samples were initially fixed on a carbon tape and then coated with gold by conventional sputtering techniques. Transmission electron microscope (TEM) images were taken with a JEOL JEM-2100 electron microscopy at 100k × magnification, with an acceleration voltage of 120 kV. TEM sample was prepared by placing one dilute drop of prepared hybrid material, dispersed in ethanol using ultrasonic, onto a copper grid and allowing it to dry well. X-ray diffraction (XRD) patterns were recorded with an Empyrean Powder Diffractometer (Cu K_α, 0.154 nm) between 5 and 70° 2θ with a step size of 0.01°/sec. Samples were mounted on a silicon support. Particle size distribution was carried out using a zetasizer instrument (Malvern Instruments, Malvern Worcestershire, UK).

2.5. Antibacterial test

Antibacterial activities of alginate/silica/zinc oxide hybrid was investigated using agar disc diffusion method against Escherichia coli (E. coli) and Staphylococcus aureus (S. Aureus). Different dosages (10, 15, 25, and 30 µL) of alginate/silica/zinc oxide nanocomposite aqueous dispersions were added onto a 10 mm filter paper, dried and sterilized by ultraviolet lamp for 60 min. The sterilized samples were then carefully placed upon the lawns and alginate/silica loaded filter paper was used as control sample. The plates were placed in a 37 °C incubator for 24 h. Then inhibitory action of tested samples on the growth of the bacteria was determined by measuring diameter of inhibition zone.

3. Results and discussion

Polysaccharides/silica hybrids are synthesized in many biosystems such as rice straw. Crosslinking was established to form alginate network, which interconnected with the silica network. This complex network act as carriers for zinc oxide nanoparticles. This hybrid was found to release zinc ions with limited value. The amount of Zn^{2+} released in water was found to be insignificant after 1 day incubation and slightly increase to reach 10 ppm after 5 days of incubation. These results suggest the strong interaction of ZnO with the function groups present inside the internal matrix of the hybrid network. Moreover, it has been reported that zinc is relatively non-toxic to humans and animals at low doses [6]. In addition to its role for allowing light materials, silica has important role on protecting plants from fungal diseases and insects [10]. FT-IR spectra of the silica gel extracted from rice husk is shown in Fig. 1A. Intense bands at 800 and 1200 cm^{-1} attribute to typical peak of Si–O–Si vibrational mode and Si–O–Si skeletal vibration, respectively. Moreover, broad band at 3400–3500 cm^{-1} assigned to the absorbed molecular water. The X-ray diffraction pattern of silica gel extracted from rice husk showed a weak shoulder at 2θ of 14 and two broad reflections at around 20 and 28° as showed in Fig. 1B. Furthermore, Fig. 1C shows that the surface morphology of the silica gel seems homogenous with different sizes in the micrometer and nanometer scales. Extracted silica gel was further evaluated with energy dispersive X-ray spectroscopy which exhibited Si, O, and Na as showed in Fig. 1D.

The FTIR spectra of sodium alginate, alginate/silica and alginate/silica/zinc oxide nanocomposites was recorded to corroborate the success of the mineralization and to obtain information about the structural changes originated during the preparation steps (Fig. 2). Alginate displayed two vibrations at 1596 and 1412 cm^{-1} assigned to an antisymmetric stretch and a symmetric stretch of the carboxylate group. However, the sharp peak at 1047 cm^{-1} can be attributed to the Si–O–Si asymmetric stretching in the alginate/silica hybrid (Fig. 2B). The spectrum of alginate/silica/zinc oxide exhibits broadening the peak observed at ~3420 cm^{-1} which reflects the presence of additional OH groups arising from the zinc oxide nanoparticle surface.

The surface morphology of crosslinked alginate/silica hybrid material before and after zinc oxide nanoparticle mineralization was analyzed by SEM and representative micrographs are displayed in Fig. 3. The alginate/silica crosslinked hybrid appears to be homogenous without evidence for phase separated likely due to the expected hydrogen bonds formed between the sialons and alginate. After zinc oxide mineralization, hierarchical zinc oxide plates with diameter of few micrometers were formed. Moreover, alginate/silica/zinc oxide hybrid was further investigated with energy dispersive X-ray spectroscopy (Fig. 3C). The hybrid exhibits Zn, Si, O and C signals. The presence of Zn confirms the zinc oxide mineralization. However, C is originated from natural polymer and Si originated from silica gel.