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Nano zinc oxide–sodium alginate antibacterial cellulose fibres

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ABSTRACT

In the present study, antibacterial cellulose fibres were successfully fabricated by a simple and cost-effective procedure by utilizing nano zinc oxide. The possible nano zinc oxide was successfully synthesized by precipitation technique and then impregnated effectively over cellulose fibres through sodium alginate matrix. XRD analysis revealed the 'rod-like' shape alignment of zinc oxide with an inter-planar d-spacing of 0.246 nm corresponding to the (1 0 1) planes of the hexagonal wurtzite structure. TEM analysis confirmed the nano dimension of the synthesized zinc oxide nanoparticles. The presence of nano zinc oxide over cellulose fibres was evident from the SEM–EDS experiments. FTIR and TGA studies exhibited their effective bonding interaction. The tensile stress–strain curves data indicated the feasibility of the fabricated fibres for longer duration utility without any significant damage or breakage. The antibacterial studies against *Escherichia coli* revealed the excellent bacterial devastation property. Further, it was observed that when all the parameters remained constant, the variation of sodium alginate concentration showed impact in devastating the *E. coli*. In overall, the fabricated nano zinc oxide–sodium alginate cellulose fibres can be effectively utilized as antibacterial fibres for biomedical applications.

1. Introduction

In the surgical zone, a lot of priorities has been given for protecting a surgical team from the patients' infectious blood and other bodily fluids. The spread of infections like HIV, hepatitis viruses, severe acute respiratory syndrome (SARS), etc., through contamination, has created increased pressure for the protection of the personnel with antimicrobial clothing. Therefore, surgical fabrics should necessarily possess antimicrobial properties (Ambika & Sundrarajan, 2015; Mucha, Hoter, & Swerev, 2002; Vaideki, Jayakumar, Rajendran, & Thilagavathi, 2008). The antimicrobial fabric when applied as wound dressings, it not only act as normal wound dressing but also provide hygienic atmosphere around the wound (Raghavendra, Varaprasad, & Jayaramudu, 2015). Generally, the fibre used in the wound dressing functional clothing contains cellulose, a homopolymer of β-D-glucopyranose units linked together by (1 → 4)-glycosidic bonds (Raghavendra, Jayaramudu, Varaprasad, Sadiku, Ray, & Mohana Raju, 2013). The three-hydroxyl groups in the cellulose acts as bonding sites for the external entities (Gardner, Oporto, Mills, & Samir, 2008).

In recent years, metal nanoparticles were extensively used as antibacterial agents towards many pathogens (Jayaramudu, Raghavendra, Varaprasad, Sadiku, & Raju, 2013; Jayaramudu, Raghavendra, Varaprasad, Sadiku, Ramam, et al., 2013; Raghavendra, Jayaramudu, Varaprasad, Mohan Reddy, & Raju, 2015). Among the various metal nanoparticles, silver nanoparticles were extensively studied because of their potential anti-bacterial properties (Kolya, Pal, Pandey, & Tripathy, 2015). However, the use of silver nanoparticles for medical applications is potentially limited due to their genotoxicity towards mammalian cell and their non-specific biologicaltoxicity (Nagender Reddy, Eladia Maria, & Josef, 2009; Gardner et al., 2008). Alternatively, ZnO serves as an effective entity for devastating the microbial growth. Moreover, the raw material required for synthesis of ZnO is available at lower cost.

ZnO is an interesting transition metal oxide possess good catalytic, electrical, photochemical and optical properties; it is used in the area of bioscience as a biomimetic membrane; it can immobilize and modify proteins because of the fast electron transfer between the enzyme's active sites and the electrode (Gunalan, Sivaraj, & Rajendran, 2012). In addition, ZnO has several advantages: noticeable activity in the pH neutral region (pH = 7–8)

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without the presence of light (Trandafilović, Božanić, Dimitrijević-Branković, Luyt, & Djoković, 2012); it is non-toxic and chemically stable under exposure to both high temperatures and UV (Ambika & Sundrarajan, 2015).

Stabilization of the nanoparticles is an important factor that plays a key role for effective existence of the nanoparticles without aggregation. Natural polysaccharides are extensively used for this purpose. Sodium alginate is one such natural polysaccharide, chemically it is the sodium salt of alginic acid, an unbranched copolymer with homopolymeric blocks of β-1,4-linked-D mannuronic acid and α-1,4-linked-L-guluronic acid (Kolya et al., 2015; Varaprasad et al., 2015). Further, due to its good tissue compatibility, it has been widely used in the field of tissue engineering including regeneration of skin, cartilage, bone and liver and in the treatment of exuding wounds and in enhancing the healing process (Shalumon et al., 2011). Owing to the close relevance to the biomedical field, sodium alginate was particularly chosen for stabilization and binding of the synthesized nano ZnO over cellulose fibre.

Keeping all these perspectives in mind the present investigation was undertaken to fabricate antibacterial cellulose fibres from nano zinc oxide and sodium alginate for effective biomedical applications.

2. Materials

Zinc nitrate ($Zn(NO_3)_2$), sodium alginate (SA) and ammonium hydroxide (NH_4OH) were obtained from Sigma–Aldrich Chemicals Company and were used as received without further purification. Cellulose cotton fibres were purchased from SIMCO thread mills (Salem, Chennai, India). Double distilled water was used in all the experiments. All the reaction processes were carried out at room temperature, under ambient reaction conditions.

2.1. Preparation of nano zinc oxide–sodium alginate antibacterial cellulose fibres

2.1.1. Synthesis of zinc oxide nanoparticles (nano ZnO)

Zinc oxide nanoparticles (nano ZnO) was synthesized by a precipitation technique. In this technique, zinc nitrate (0.05 mol) was completely dissolved in 50 mL of distilled water in a 250 mL beaker under the constant stirring condition at room temperature for 1 h. To this aqueous solution, ammonium hydroxide was slowly added dropwise until a white colour precipitate was formed during which the pH was adjusted to 9. After stirring for 3 h, the precipitate was washed several times with distilled water till the pH of the filtrate was reduced to 7 and boiled for 5 min in order to obtain improved crystallization of the nano zinc oxide. The resultant precipitate was dried at 120 °C for 2 h.

2.1.2. Preparation of nano zinc oxide–sodium alginate cellulose fibres (ZnO–SACNF)

Initially, 0.5, 1.0 and 1.5% of aqueous sodium alginate solutions were prepared individually under constant stirring condition by dissolving the respective amount of sodium alginate in distilled water at room temperature for 4 h. To these solutions, nano zinc oxide (100 mg) was introduced and stirred at the constant stirring condition of 300 rpm for 1 h, then sonicated for 30 min to make the solutions homogeneous. To the prepared solutions, known amount of cellulose fibres were placed in an orbital shaking incubator at 300 rpm for 24 h at room temperature, and finally sonicated for 30 min. A rotation followed by sonication allows the nano zinc oxide to impregnate effectively over the cellulose fibres. Finally, the resulted nano zinc oxide–sodium alginate cellulose fibres (ZnO–SACNF) were taken out, dried at room temperature and utilized for further experimental characterization. Based on the concentration of sodium alginate used for the fabrication of ZnO–SACNF fibres, the fibres were coded as ZnO–$SACNF_1$, ZnO–$SACNF_2$ and ZnO–$SACNF_3$ for 0.5%, 1% and 1.5% sodium alginate solutions, respectively.

Analogous to the above fabricated fibres (ZnO–SACNFs), a set of fibres from cellulose fibres and SA without nano ZnO were also fabricated. These fibres were named as sodium alginate coated cellulose fibres (SACFs) and used as reference samples.

3. Characterizations

Fourier transform infrared (FTIR) spectra of nano ZnO and ZnO–SACNF fibres were obtained from a Perkin Elmer, UATR two, FTIR spectrometer (Beaconsfield, Bucks, UK) in the wavelength range of 4000–500 cm^{-1}. Signal averages were obtained from 25 scans at a resolution of 1 cm^{-1}. SEM micrographs and Energy dispersive spectroscopy analyses for Zinc oxide were carried out using JEOL JEM 7500F SEM (Tokyo, Japan) scanning electron microscope at 2 keV. Microstructure and elemental observations of ZnO–SACNF fibres were carried out by scanning electron microscope energy dispersive spectroscopy (SEM–EDS, Philips XL 30) analyses. Transmission electron microscopes were recorded on JEM-1200EX, JEOL (Tokyo, Japan). The samples were dispersed in 1:1 methanol and water solution, and deposited on a 3 mm copper grid and dried at ambient temperature after removing the excess solution using filter paper. X-ray diffraction measurements were carried out using a Rigakudiffractometer with Cu-Kα radiation and using a scan rate 0.02° s^{-1}. Thermal characteristics of zinc oxide the cellulose nanocomposite fibres were determined from the thermogravimetric analysis (TGA) data, using TGA Q 50 thermal analyzer (T.A. Instruments–Water LLC, Newcastle, DE, USA), at a heating rate of 10 °C/min and passing nitrogen gas at a flow rate of 100 mL/min. Tensile (tensile strength, modulus and % elongation-at-break) properties were determined by using INSTRON 3369 Universal Testing Machine (Buckinghamshire, England). The sample fibres were cut into 1 mm × 100 mm and mechanical properties were studied using 10 kg load cell by maintaining a gauge length of 50 mm, by operating the machine at a crosshead speed of 5 mm/min and at 23 °C.

3.1. Antibacterial test

Antibacterial activity of the cellulose zinc nanocomposite fibres were tested against *Escherichia coli* by following the method adopted by us in our previous research works (Jayaramudu, Raghavendra, Varaprasad, Sadiku, & Raju, 2013; Raghavendra et al., 2013; Raghavendra, Varaprasad, & Jayaramudu, 2015). In brief, the required nutrient agar medium was prepared by mixing peptone (5.0 g), beef extract (3.0 g), sodium chloride (5.0 g) and agar (15.0 g) in 1000 mL of distilled water, and the pH was adjusted to 7.0. The agar medium was sterilized in a conical flask at a pressure of 15 lbs in^{-2} for 30 min and transferred into sterilized Petri dishes in a laminar air flow chamber (Microfilt Laminar Flow Ultra Clean Air Unit, Mumbai, India) for solidification, Later, 50 μL microbial culture was uniformly streaked over the solid surface. Into this inoculated Petri dish, the sample fibres were placed and incubated at 37 °C for 48 h to obtain inhibition zone. Finally, the formed inhibition zone were measured and photographed.

4. Results and discussion

Fabrication of nano zinc oxide cellulose fibres signifies one of the best antibacterial fibres for biomedical applications. During the typical process nano zinc oxide–sodium alginate cellulose fibres (ZnO–SACNF) were fabricated by effective impregnation of sodium