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Zinc impregnated cellulose nanocomposites: Synthesis, characterization and applications

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ABSTRACT

Nanocomposite materials have broad applicability due to synergistic effect of combined components. In present investigation, cellulose isolated from citrus peel waste is used as a supporting material; impregnation of zinc oxide nanoparticles via co-precipitation method. The characterization of nano composite is carried out through Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and Thermo-gravimetric analysis (TGA) resulting less than 10 μm cellulose fiber and approx. 50 nm ZnO NPs. Zinc oxide impregnated cellulose (ZnO–Cel) exhibited significant bacterial devastation property when compared to ZnO NPs or Cellulose via disc diffusion and colony forming unit methods. In addition, the ZnO–Cel exhibited significant total antioxidant, and minor DPPH free radical scavenging and total reducing power activities. The nano composite also showed time dependent increase in photocatalytic by effectively degrading methylene blue dye up to 69.5% under sunlight irradiation within 90 min. The results suggest effective utilization of cellulose obtained from citrus waste and synthesis of pharmacologically important nano-composites that can be exploited in wound dressing; defence against microbial attack and healing due to antioxidative property, furthermore can also be used for waste water treatment.

1. Introduction

The recent advances in nanotechnology are focused on synthesis of controlled shape and size of particles/composites with new biotical activities. Exclusive properties of nanomaterials are attributed to low size, high fraction of surface atoms, and high surface area [1]. Metallic nanoparticles of different oxides have been used in the synthesis of nano-composites. These nano-composites have significant applications in the field of the cancer therapy, cell imaging, drug/gene delivery and biosensing [2]. Owing to numerous functionalities of zinc oxide (ZnO) nanoparticles (NPs) such as photocatalytic activity, physio-chemical stability, UV and infrared absorbing nature, semiconducting behaviour, nontoxic nature towards humans, and antimicrobial activities make them valuable in different industrial applications [3]. Recently ZnO NPs have been reported to possess anticancer activity [4]. Furthermore, Zinc NPs is also used in other paraphernalia including paints, hygiene products and food additives [5].

The uses of non-conductive polymers e.g. cellulose, polythiophene and polypyrole are getting more attention. Cellulose is the most important because it is used in different fields such as clothes and fibres, wood and paper, pharmaceutical and cosmetics industries [6]. Metallic NPs associated with vegetable cellulose as semiconductors has been drastically increased in recent years, [7]. Such composites have high galvanostatic cycling stability, thermal strength, sensitivity, ion absorption capacity due to their respective application as flexible energy devices, nano-fibrous membrane, bio or gas sensors [8]. It is also biocompatible, nontoxic, biodegradable and broadly used in healthcare products and formulation [9]. In bioinorganic nano-composites synthesis, nanoparticles work as reinforcement partner and polymers as scaffolding material [10]. The polymer composites are advantageous over pure polymer due to inadequacy related to their applications [11].

Citrus is one of universally most favorite fruit due to bulk

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productivity, low price and healthy dietary properties. The industrial applications generates large amount of peel and pulp which not only trigger soil pollution but other constrains too. Citrus peel is a rich source of cellulose, hemicelluloses, proteins and pectin [12]. In the present study, cellulose isolated from citrus peel waste is converted into value-added Zinc nano-composite and the future prospects therein are discussed. Zinc-impregnated cellulose nano-composite sheets are characterized by FTIR, XRD, SEM and TGA. Furthermore, antibacterial, antioxidant, and photo-catalytic activities of composite material is evaluated for remarkable application in biomedical and environmental sciences.

2. Experiments

2.1. Material

Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), Sodium hydroxide (NaOH), Hydrogen peroxide (H_2O_2), Toluene (HPLC grade), Dimethyl sulfoxide (DMSO) and ethanol were purchased from Merck. double distilled and deionized water is used in all the experiments, carried out at room temperature or ambient reaction conditions.

2.2. Cellulose isolation from citrus reticulate peel waste

The peel of Kinnow (*Citrus reticulate*) was dried under sun light and grounded into a coarse powered form. Cellulose extraction was carried out following the modified method described by Naz et al. [12]. Briefly, 10 g peel powder was soaked in mixture of toluene and ethanol (2:1) for 12 h and filtered thereafter to remove pigments. The residue was dried and bleached with hydrogen-peroxide at 80 °C in water-bath. This process was repeated until a clear white product was obtained. Finally, the residue was treated overnight with 6% NaOH until the effervescence was observed and filtered again. The residues were re-treated with 6% NaOH for 2 h, neutralized with distilled water, and characterized as extracted cellulose. The obtained residue mixture was finally sonicated for 15–20 min (three times) in ice cold water, dried in vacuum oven at 80 °C for 3 h, and stored for further use.

2.3. Impregnation of Zinc (Zn) into cellulose

The impregnation of ZnO NPs on cellulose was performed with slight modification of the reported method of Maneerung et al. [13]. Citrus cellulose fibres were immersed in 1 mM Zn $(CH_3COO)_2 \cdot 2H_2O$ for 1 h on constant stirring at 200 rpm. The mixture was sonicated for 20 min in water bath, followed by treating with 10 mM NaOH solution for 10 min to reduce Zinc into nanoparticles. Subsequently, the cellulose was washed with ethanol and obtained residue was rinsed with deionized water for 10 min to remove excessive unbound ions/NPs. The synthesized nano composite was vacuum-dried overnight at 30 °C. Finally, different pieces of uneven disc shaped Zinc impregnated citrus cellulosic sheets (ZnO–Cel) are obtained.

2.4. Synthesis of Zinc nanoparticles

Zinc nanoparticles were produced using 1 mM Zn $(CH_3COO)_2 \cdot 2H_2O$ in aqueous solution and 0.01 M NaOH. Similar procedure was followed as described earlier for Zinc impregnation except in absence of cellulose. The synthesised particles were separated at 13,000 rpm for 10 min followed by vacuum drying at room temperature.

2.5. Characterization

Microstructure of ZnO NPs, cellulose, and ZnO–Cel was taken by SEM operating at of 20 keV voltage. The FTIR spectra were recorded in the wave number frequency ranged from 4000 to 600 cm^{-1} with a speed of 16 scans per spectrum using bench-top Spectrum™ 65. XRD measurements were determined using Bruker D8 Advance brand *-2* configuration (generator-detector) X-ray tube copper $S=1.54$ Å and LYNXEYE PDS detector. Thermal characteristic was assessed from the TGA data, using TGA Q50 thermal analyser (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.

2.6. Determination of Zinc release

The synthesized ZnO–Cel films (4–5 cm in size with uneven shapes) were immersed in 20 ml of deionized water for the determination of Zinc release. Every day ZnO–Cel was shifted to a new bottle having 20 ml of deionized water and Zinc ions (released after every single day) were observed by using atomic absorption spectrometer (Varian FS 240AA).

2.7. Antioxidant activities

For antioxidative analysis, ZnO NPs were suspended in DMSO at 4 mg/ml and the mixture was sonicated for 15 min before use. The cellulose paper and Zinc NPs impregnated cellulose were weighted as 200 μg for a reaction mixture of 1 ml and the paper was suspended in the reaction mixture.

2.7.1. DPPH free radical scavenging

Standard 2,2-diphenyl 1-picryl-hydrazyl (DPPH) method was adopted for free radical scavenging potential of samples. For ZnO NPs; solution of 10 μl in DMSO (final concentration 200 μg/ml) was combined with DPPH solution of 190 μl (in methanol). While for cellulose and ZnO–Cel, the samples were directly treated with DPPH solution at 200 μg/ml. After the incubation for 15 min in dark at 37 °C; papers were removed from the reaction mixture and absorbance was measured at 517 nm using spectrophotometer.

2.7.2. Total antioxidant capacity (TAC) assay

TAC was determined by phosphor-molybdenum method [14]. The reagent solution of 1 ml (4 mM ammonium molybdate, 28 mM sodium phosphate and 0.6 M sulfuric acid) was added with 0.1 ml of sample in case of ZnO NPs. In case of paper (cellulose and ZnO–Cel), 200 μg paper was suspended in the reaction mixture. The mixture was incubated at 95 °C for 90 min and then cooled to room temperature. Sample TAC was expressed as ascorbic acid equivalent and the absorbance was measured at 695 nm.

2.7.3. Total reducing power (TRP) assay

The ZnO–Cel and cellulose 200 μg, each were used for TRP while silver nanoparticles were suspended in DMSO at 4 mg/ml. Briefly, samples were mixed with 200 μl phosphate buffer (0.2 mol/l, pH 6.6) and 250 μl potassium ferricyanide $[K_3Fe(CN)_6]$ (1%). The mixture was then incubated at 50 °C for 20 min and then 10% trichloro-acetic acid (200 μl) was added. At room temperature, the mixture was centrifuged at 3000 rpm for 10 min. The upper layer of solution (150 μl) was then mixed with $FeCl_3$ (50 μl, 0.1%). Finally, the absorbance was measured at 630 nm on spectrophotometer. The enhanced absorbance of the reaction mixture showed better reducing power. Blank was prepared by adding 400 μl of DMSO to the above-mentioned reaction mixture instead of the sample. The reducing power of samples was expressed as ascorbic acid (vitamin C) equivalent.