Modification of Tamarind Fruit Shell Powder with In Situ Generated Copper Nanoparticles by Single Step Hydrothermal Method

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ABSTRACT

Tamarind fruit shell powder (TFSP) with particle size of < 50 µm (obtained from cleaned tamarind fruit shells) was modified with in situ generated copper nanoparticles (CuNPs) by simple one step hydrothermal method. The modified TFSP was characterized by scanning electron microscope (SEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and antibacterial tests. The generated stable CuNPs on the surface of the modified TFSP were spherical in shape with an average size of 88 nm. The FT-IR spectroscopy analysis indicated the involvement of the functional groups of the TFSP in the generation and stabilization of the CuNPs. The XRD analysis indicated the presence of both CuNPs and Cu2O nanoparticles in the modified TFSP. The thermal analysis indicated the presence of 5.6 wt% of copper nanoparticles as calculated from the difference of residual char content between the unmodified and modified TFSP. The modified TFSP with in situ generated CuNPs exhibited obvious antibacterial activity against both the Gram negative and Gram positive bacteria and hence can be considered as low cost filler in the preparation of antibacterial polymer hybrid nanocomposites for packaging and medical applications.

1. Introduction

Generation of solid waste materials poses many environmental problems. The amount of solid waste is increasing alarmingly with the growth of the world economy (El-Fadel et al., 1997; Hamer, 2003; Harrison and Hester, 2007; Giusti, 2009). Presently, many countries across the world are facing a huge quantity of agricultural waste which is generated by the industries, domestic and disposal. Considerable amount of solid waste is generated in the form of egg shells, the groundnut shells, tamarind fruit shells (TFS), coconut shells etc., which occupies huge space. One possible solution to at least minimize the pollution by the solid waste is to modify some of its constituents so that the modified materials can be used as fillers in polymer matrices in the preparation of low-cost composites and nanocomposites. In this way, value can be added to part of the solid waste. Tamarind nut powder (TNP) was used in polypropylene carbonate (Senthil Muthu Kumar et al., 2017b) and cellulose (Senthil Muthu Kumar et al., 2018) to make totally biodegradable composite films for packaging applications. In these studies, the researchers initiated to add value to this agro-based waste. Senthil Muthu Kumar et al. (2017a) also used spent coffee bean powder as filler in cellulose matrix and made the composites. They recommended these biocomposites films for environmentally friendly packaging purposes. Tsai et al. (1998) used the agro waste plastic composites in the mode of building materials and in this way, they also widened the usage of agro waste in building construction. Wang and Sun (2002) used wheat straw and corn pith in the preparation of low-density particle board and reported improved properties. Xia et al. (2015) utilized waste leather buff (WLB) as filler in cellulose matrix and made completely biodegradable composite films for packaging applications and recommended them for packaging applications. Ashok et al. (2019) modified the TNP with in situ generated copper nanoparticles by one step
thermal assisted process which exhibited antibacterial activity against both the Gram negative and Gram positive bacteria and suggested them to be used as antibacterial fillers in the preparation of hybrid nanocomposites. Recently, Li et al. (2019) modified tamarind fruit shell powder (TFSP) by in situ generating silver nanoparticles in one step thermal assisted process and reported excellent antibacterial activity against both the Gram negative and Gram positive bacteria. Suguna et al. (2010) used the TFSP as an adsorbent for the removal of manganese from aqueous solutions. They identified the functional groups such as carboxyl, hydroxyl, ester of the TFSP as liable for binding the metallic ions. In the present work, the solid waste of TFs dried and powdered into the TFSP which was later modified by in situ generation of copper nanoparticles (CuNPs) by one step hydrothermal method. The modified TFSP was characterized by scanning electron microscope (SEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and antibacterial tests. The authors selected the TFSP for this purpose as a large quantity of this waste is generated in the fruit processing industries in the developing countries.

2. Materials and Methods

2.1. Materials

The TFs were separated from the fruits, thoroughly washed with water, dried and powdered. The obtained TFSP was sieved to get it with particle size < 50 μm. The CuSO₄·5H₂O made by M/s S.D. Fine Chemicals Limited, Mumbai, India was used as received.

2.2. Preparation of modified TFSP

Modified TFSP with in situ generated CuNPs was prepared by one step hydrothermal method as described by Ashok et al. (2018). For this, 50 mL of 250 mmol/L aqueous CuSO₄·5H₂O solution was prepared and maintained it at 80 °C. To this hot source solution, 3 g of dried TFSP was added and stirred thoroughly at this temperature for 24 h. The color of the TFSP slowly changed from brown to black brown. The modified TFSP was separated, washed with deionized water and then dried in an oven.

2.3. Characterization

The SEM (Zeiss EVO 18) operated at 10 kV was used to record the images and energy dispersive X-ray (EDX) spectrum of the modified TFSP. Using RXI Perkin Elmer FT-IR spectroscopy, the spectra of the unmodified and modified TFSP were recorded in the spectral range of 4000–500 cm⁻¹ at a resolution of 4 cm⁻¹. The X-ray diffractograms of the unmodified and modified TFSP with in situ generated CuNPs were recorded using Bruker Eco D8 X-ray instrument operated at 40 kV and 25 mA in the range of 2θ = 10°–85° at a scanning rate of 4°/min. The primary thermograms of the TFSP and modified TFSP were recorded using Perkin Elmer TGA-7 thermogravimetric analyzer in the temperature range of 50–800 °C at a heating rate of 10 °C/min in nitrogen atmosphere. In this case, 10 mg of the sample was used. To confirm the antibacterial activity of the modified TFSP, the standard disc method was employed (Ashok et al., 2018). The resulting clear zones which indicated the inhibition of both Gram negative (Escherichia coli and Pseudomonas aeruginosa) and Gram positive (Staphylococcus aureus and Bacillus licheniformis) bacteria were photographed and the corresponding zone diameters were measured.

3. Results and Discussion

3.1. Visualization

The tamarind fruit and the separated shell are shown in Fig. 1a. In order to observe the change in color of the TFSP due to the in situ generated CuNPs, the digital image of the modified TFSP was photographed. For comparison, the image of the unmodified TFSP was also photographed. The images of the TFSP and modified TFSP are presented in Fig. 1b and Fig. 1c, respectively. From Fig. 1b, it can be observed that the TFSP was light brown in color. However, as seen in Fig. 1c, the color of the modified TFSP with in situ generated CuNPs was dark blackish brown. The color change preliminarily indicates the in situ generation of the CuNPs in the modified TFSP. For confirmation, the SEM analysis was carried out.

3.2. The SEM analysis

In order to visualize the presence of in situ generated CuNPs on the surface of the TFSP, the SEM analysis was carried out. The SEM images of the modified TFSP are shown in Figs. 2a and 2b at two magnifications. The corresponding EDX spectrum indicating the peak corresponding to copper present in the modified TFSP is shown in Fig. 2c. Using the SEM images, the
Fig. 1  Images of tamarind fruit and separated shell (a); tamarind fruit shell powder (TFSP) (b) and modified TFSP with in situ generated CuNPs (c)

Fig. 2  Scanning electron microscope (SEM) images of the modified TFSP with in situ generated CuNPs using 250 mmol/L aqueous CuSO₄·5H₂O source solution at two magnifications × 25 000 (a) and × 50 000 (b) (Some of CuNPs are indicated by arrows); Energy dispersive X-ray (EDX) spectrum (c) and histogram showing particle size distribution (d)

individual size of the CuNPs was measured through the built in SmartTiff software of the microscope and the histogram showing the particle size distribution is shown in Fig. 2d. From Figs. 2a and 2b, it can be found that roughly spherical CuNPs were in situ generated on the surface of the TFSP particles. The EDX spectrum in Fig. 2c reveals that the nanoparticles generated on the surface of the TFSP particles belong to copper metal. The results in Fig. 2d indicated that the generated CuNPs were in the size range of 61–120 nm. However, most of the CuNPs generated were in the size range of 81–100 nm. The average size of the CuNPs generated on the surface of the TFSP was found to be 88 nm. The SEM images along with the EDX spectrum confirmed in situ generation of the CuNPs on the surface of the TFSP.

3.3. The FT-IR spectroscopy analysis

In order to examine the possible chemical interactions between the TFSP and the generated CuNPs in the modified TFSP, the FT-IR spectroscopy analysis was carried out. The FT-IR spectra of the TFSP and modified TFSP with in situ generated CuNPs are presented in Fig. 3. The spectral analysis of the TFSP was already reported in our previous work on modified TFSP with in situ generated AgNPs (Li et al., 2019). From Fig. 3, it is evident that both the spectra of the TFSP and modified TFSP are similar except the change in intensity of certain bands. The chemical composition as reported in the literature indicates the presence of hydroxyl, carboxyl, amine and ester groups besides the calcium oxalate (Pavia et al., 1996; Suguna et al., 2010). From Fig. 3, it
can be found that the intensity of the peaks at 3324 cm⁻¹ (OH), 1621 cm⁻¹ (CO) and 1314 cm⁻¹ (CO) (Manas et al., 2012) for modified TFSP is lower than those of the TFSP. It indicates the role of these groups in reducing the copper salt into copper nanoparticles. Similar observation was made in the case of modified TFSP with in situ generated AgNPs (Li et al., 2019) and nanocomposite cotton fabrics with in situ generated CuNPs by hydrothermal method (Sadanand et al., 2017). On close examination, we could find two additional peaks at 625 cm⁻¹ and 730 cm⁻¹ which were attributed to the vibrations from cuprous oxide nanoparticles. Similar observation was made by Sukumar et al. (2020) in the case of green-synthesized rice-shaped copper oxide nanoparticles using Caesalpinia bonduc cella seed extract. In order to confirm this further, we carried out X-ray analysis.

3.4. The X-ray analysis

In order to further confirm the in situ generation of the CuNPs and their states in the modified TFSP, the X-ray analysis was carried out. The results of the TFSP and modified TFSP with in situ generated CuNPs are presented in Fig. 4a. The main peaks observed at 2θ = 15° and 23° arose due to the reflections from the planes of calcium oxalate present in the TFSP (Sivasankar et al., 2012). There are also some other common peaks which resulted from the plant materials of the TFSP. On close examination, we can observe additional low intensity peaks in the modified TFSP. These additional peaks may belong to the generated CuNPs in the modified TFSP. In order to analyze the additional peaks which were obscured by the high intensity peaks corresponding to calcium oxalate, the diffractogram of the modified TFSP was expanded in the 2θ = 30°–80° and is presented in Fig. 4b. From Fig. 4b, the additional peaks at 2θ = 42°, 51° and 74° belong to CuNPs (Luo et al., 2012) while those observed at 2θ = 36.4° and 61.5° were due to Cu₂O (Alekseeva et al., 2011). Hence, the modified TFSP had both CuNPs and Cu₂O nanoparticles. Similar observation was made in the case of cellulose nanocomposite films with in situ generated CuNPs by using Osmium sanctum leaf extract as a reducing agent (Sadanand et al., 2016). This is understandable as copper is an oxidizing agent and hence some of the generated CuNPs might have been converted into Cu₂O nanoparticles.

3.5. Thermogravimetric analysis

In order to examine the effect of CuNPs on the thermal stability of modified TFSP, the TGA was carried out. The primary and derivative thermograms of the TFSP and modified TFSP with in situ generated CuNPs are shown in Fig. 5. From Fig. 5, it is found that the degradation for both the TFSP and modified TFSP occurred in three stages. In the first stage (30–122 °C), the weight loss represents the loss of water and other volatiles if any. In this range, the weight loss for the TFSP was found to be 9.6% while for the modified TFSP, it was reduced to 8.0%. It represents a slight lowering of water absorption in the case of modified TFSP due to the in situ generated CuNPs. In the second stage (197–347 °C), the thermal stability of the modified TFSP
was found to be lower than that of the TFSP. During this stage, the organic matter present in both the TFSP and modified TFSP might have been degraded. The lowering of thermal stability in the case of modified TFSP may be attributed to the catalytic nature of the CuNPs in lowering the degradation temperature. Similar observation was made in the case of the cellulose nanocomposite films with in situ generated CuNPs by using Ocimum sanctum leaf extract as a reducing agent (Sadanand et al., 2016). In the 3rd stage (beyond 347 °C), the weight loss in the case of the TFSP was lower than that of the modified TFSP. Though in both cases, char remains in this stage, additionally CuNPs remain leading to higher residual weight at 800 °C. The char content at 800 °C in the case of the TFSP and modified TFSP was found to be 19.4% and 25.0%, respectively and the difference of these two indicated the presence of 5.6 wt% of generated CuNPs in the modified TFSP.

3.6. Antibacterial activity

In order to probe whether the modified TFSP with in situ generated CuNPs possesses antibacterial activity or not, the antibacterial test by disc method was carried against both Gram negative (E. coli and P. aeruginosa) and Gram positive (S. aureus and B. licheniformis) bacteria. In each case, the zone of clearance was photographed and the images are shown in Fig. 6. Using the images presented in Fig. 6, the diameter of the clear zone formed in each case was measured and the values are presented in Table 1. From Fig. 6 and Table 1, it can be found that the TFSP did not form clear zones against all the bacteria tested. It indicated that the TFSP was unable to inhibit the growth of bacteria. On the other hand, the modified TFSP with in situ generated CuNPs formed clear zones with diameters ranging from 33 mm to 36 mm against bacteria under test. On close examination, it can also be observed that in the case of Fig. 6d, there still exists a considerable quantity of B. licheniformis bacteria. It suggested that the modified TFSP was unable to inhibit the growth of B. licheniformis bacteria completely. However, on the whole, the modified TFSP possessed excellent antibacterial activity against both the Gram negative and Gram positive bacteria.

Figure 6  Clear zones formed by TFSP (P) and modified TFSP (Z) with in situ generated CuNPs against Escherichia coli (a); Pseudomonas aeruginosa (b); Staphylococcus aureus (c); Bacillus licheniformis (d) bacteria

Table 1 Diameter (mm) of inhibition zones formed by TFSP and modified TFSP with in situ generated CuNPs against Gram negative (E. coli and P. aeruginosa) and Gram positive (S. aureus and B. licheniformis) bacteria

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample code</th>
<th>Clear zone diameter (mm)</th>
</tr>
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<tbody>
<tr>
<td>TFSP</td>
<td>P</td>
<td>No clear zone</td>
</tr>
<tr>
<td>Modified TFSP</td>
<td>Z</td>
<td>33</td>
</tr>
</tbody>
</table>

4. Conclusions

The tamarind fruit shells which constitute solid waste from tamarind pulp industries were cleaned, dried and powdered. The tamarind fruit shell powder (TFSP) with a particle size < 50 μm was modified with in situ generated CuNPs by one step
hydrothermal method. The SEM analysis indicated that the modified TFSP had spherical CuNPs with an average size of 88 nm. The FT-IR spectral analysis indicated the involvement of the functional groups of the TFSP in reducing and stabilizing the copper salt into the CuNPs. The XRD analysis suggested the presence of both the CuNPs and Cu₂O nanoparticles on the surface of the modified TFSP. The thermal stability of the modified TFSP was found to be slightly lower than that of unmodified TFSP indicating the catalytic activity of the generated CuNPs in lowering the thermal stability. The modified TFSP exhibited excellent antibacterial activity against both Gram negative and Gram positive bacteria. The modified TFSP with antibacterial activity can be utilized as low-cost filler in polymer matrices for the preparation of antibacterial polymer hybrid nanocomposites for packaging and medical applications.

References