Chemistry Research Journal, 2023, 8(5):50-56
Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Preparation and characterization of Copper-Maize Bran Nanocomposite: An Edible-Fibre-Based Natural Nanocomposite

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Abstract
Nano composites are known to have diverse uses. Edible natural polymer nanocomposites are frequently investigated for use in convenient delivery of drugs, vitamins and other essentials in humans. In the current research, a novel nanocomposite was prepared using maize bran and copper II sulphate, and its physical and chemical properties were examined. The successful product earmarked for many applications was characterization using X-ray Diffraction, solid state Infrared, Point of Zero Charge, Water Holding Capacity, Bulk Density and Cation Exchange Capacity processes. X-ray Diffraction comparison of the standard copper nanoparticles and the nanocomposite showed evidence of copper embedded in the matrix of the bran in nanosize. It also revealed the crystallite size of the embedded copper nanoparticles in the matrix of the maize bran at Miller indices (h k l) of (1 1 1), (2 0 0) and (2 2 0) compared to prepared copper nanoparticles at the same Miller indices. Solid State Infrared analysis of the raw maize bran (MB) and the prepared nanocomposite (Cu-MBNc) showed the presence of O–H, C–H, C=O, C=C and C–O on the surfaces of both materials. The Point of Zero Charge of the MB and Cu-MBNc were 4.7 and 5.3 respectively. Water Holding Capacity was 3.14g/g for MB and 3.18g/g for Cu-MBNc. The Bulk Densities were 0.49g/ml for MB and 0.69g/ml for Cu-MBNc, while for Cation Exchange Capacity, the MB yielded 0.0048meq/g and Cu-MBNc yielded 0.0026meq/g. The nanocomposite could be investigated for the delivery of targeted essential medications.

Keywords: Nanoparticles, Nanocomposites, Maize bran, copper, fibre

1. Introduction

Nanocomposites are compounds that combine nano-size particles into the regular material matrix, resulting in a dramatic change in their properties. Nanoparticles possess a tremendously high surface-area-to-volume ratio which, especially at elevated temperatures, provides a tremendous driving force for diffusion. Compared to their bulk size counterparts, their properties are significantly modified [1, 2].

Regardless of its size, a bulk material should have constant physical properties. At the nano-scale, depending on their sizes, different properties are observed. The implication is that properties of the material change as the size reaches nano-scale and as such, the surface to volume percentage of the material becomes important. The percentage of the surface of the bulk material greater than one micron is so negligible in terms of the volume of the bulk of the material [3]. In general, nanocomposites consist of two primary constituents, namely the matrix and the reinforcement. They can be defined by form and materials used in their preparation or synthesis. Literature indicates

that three principal types of nanocomposites have been extensively studied. Depending on the kind of matrix substance, nanocomposites can be grouped as polymer, ceramic or metal [4, 5]. Ceramic nanocomposites include SiO2/Co, Si3N4/SiC, and SiC/Al2O3 [6]; metal nanocomposite materials also include Fe/MgO, Ni/PZT, and Nb/Cu [6], and polymer composites also include Polycaprolctone/SiO2, Poly amide–imide/TiO2, and Polycarbonate/SiO2. Nanocomposites have been used over the years for various applications and their activities have found relevance in many fields and sectors of economies [6].

Although polymers are mostly used in the preparation of nanocomposites, there is limited application and analyses of the use of edible natural polymers in nanocomposite synthesis. Natural polymer materials may come with their attendant challenges of degradation and decomposition, but reinforcement with nanoparticles to enhance their efficiency and performance like the synthetic polymer counterparts in any field may be possible. They could also be envisaged from the angles of compatibility with uses in natural environments.

The use of edible natural fibres in making nanocomposites has the potential to ease the issue of biocompatibility of nanocomposite for drug delivery since the fibres are edible. For instance, edible fibres such as corn or wheat bran have been reported by many researchers and food scientists as being very beneficial to both humans and animals. [7] and [8] both found that the intake of edible fibres helps reduce the danger of developing several diseases such as heart diseases and diabetes. [9] also reported that fibres from oats, beet, wheat, and maize have been used over the years in the formulation of several meat products. Therefore, incorporation of such fibres with edible reinforcers resulting in edible nanocomposites could enhance application of the nanocomposites.

The current study into formulation of edible nanocomposites using maize bran, and its characterization is targeted at a breakthrough in the area of nanocomposite applications, and also to add to the documentation of natural polymer-based nanocomposites. In this study, a novel nanocomposite material using maize bran as the matrix and copper as the reinforcement was therefore prepared and characterized.

2. Materials and Methods

Materials

Materials used in this study were maize bran, distilled water, $CuSO_4.5H_2O$, ascorbic acid solution, hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride, (NaCl), graduated syringe, electronic balance, conical flasks, pipette, pH meter, laboratory oven, Powder Defractometer, Infrared Spectrometer.

Methods

2.1 Synthesis of Copper-Bran Nanocomposite

This was achieved following a standard chemical precipitation method as described in [10] with some modifications. Two separate solutions of $CuSO_4.5H_2O$ and ascorbic acid were prepared by dissolving 20g of $CuSO_4.5H_2O$ in 70ml of distilled water and 48g of ascorbic acid in 140ml of distilled water. Exactly 10g of MB were used to saturate the $CuSO_4.5H_2O$ solution and stirred for 15 minutes, followed by the addition of ascorbic acid solution. The resulting mixture was stirred again for 15 minutes. It was then left covered and undisturbed at room temperature for 24 hours for the copper to settle in the matrix of the maize bran.

After 24 hours, the solution was filtered and the fibre nanocomposite was oven-dried. The dried sample was thoroughly washed with distilled water to remove excess copper on the surface of the nanocomposite. It was oven-dried again, coarse blended and kept in polyethene storage containers and used for the experiment.

2.2 Determination of Physicochemical Parameters

Point of Zero Charge (PZC)

PZC was determined using the method described by [11].

1.0g of the nanocomposite sample was measured into eleven separate conical flasks. Volumes of 10, 15, 20, 25 and 30 ml of 0.1M HCl were pipetted into the first five conical flasks. Into the sixth flask, 30 ml distilled water was placed to serve as control. Into the remaining flasks were poured 10, 15, 20, 25 and 30 ml of 0.1M NaOH. All the conical flasks were allowed to stand for 48 hours after which pH of the solutions were recorded. A graph of pH was

plotted against volume the mixture to obtain the point of zero charge at the point where the graph touches the pH axis.

Water Holding Capacity (WHC)

WHC was determined by adding 30 ml of distilled water to 0.5 g nanocomposite sample. The sample was agitated and left at room temperature for 1 hour. The mixture was decanted, the supernatant discarded, and the residue weighed. The WHC was expressed as mass of water in grams per the mass of dry sample also in grams [12, 13].

Bulk Density (BD)

2.0g of dried sample was placed in a graduated syringe and sufficient pressure was applied to pack the content of the syringe. The volume occupied by the sample was recorded in five (5) replicates. BD was expressed as the mass of sample (g) per volume of dry blended sample (mL) in a measuring cylinder [12, 13]

Cation Exchange Capacity (CEC)

The cation exchange capacity of the sample was determined by converting the cationic functional groups present in 2.0g sample into their acidic form through stirring overnight at 4 °C in 20ml of 2.0M hydrochloric acid (HCl). This was followed by filtration to remove excess HCl. Saturated sodium chloride solution was added and this was followed by extensive washing with distilled water. The washed acidic sample was then titrated with 0.5M potassium hydroxide (KOH). The cation exchange capacity was expressed as milliequivalents per kilogram of dry sample [12, 13].

IR and XRD Analyses

The nanocomposite material was further characterised using Solid State Infrared Spectroscopy and X-Ray Diffraction techniques to find the functional groups associated with the nanocomposite and also to determine the crystallite size of the incorporated copper nanoparticles respectively [14].

3. Results and Discussion

3.1 Physicochemical Parameters

Table 1: Summary of the physicochemical parameters determined in the study.

Sample	PZC	CEC (meq/g)	WHC (g/ml)	BD (g/g)
MB	4.6	0.0048	0.49	3.14
Cu-MBNc	5.3	0.0026	0.69	3.18

Point of Zero Charge: The PZC of the prepared Copper-Bran Nanocomposite was found to be 5.3. This means that at pH below the PZC the surface of the material tends to develop positive charges while above the PZC, it tends to develop negative charges. In comparison, the raw maize bran, before the execution of the nanocomposite had a PZC of 4.6 (Table 1). It can clearly be seen that the modification caused the PZC to increase. This change could be attributed to the presence of the copper nanoparticles within the matrix of the maize bran. PZC is very useful in interaction or adsorption [15] studies as like charges usually repel while unlike charges attract.

Cation Exchange Capacity: The maize bran is indicated to be a better site for cation exchange as it had a capacity of 0.0048meq/g compared to a capacity of 0.0026meq/g of the nanocomposite (Table 1). This change could be due to cationic repulsion since the synthesized composite has nano-size copper particles (cations) trapped in its matrix and so there would likely be limited space to admit other cations. The ionic interactions are also useful parameters in the use of nanocomposites [15].

Water Holding capacity and Bulk Density: The nanocomposite had better water holding capacity and bulk density than the maize bran. The nanocomposite had 0.69g/ml and 3.18g/g bulk density and water holding capacity respectively as against 0.49g/ml and 3.14g/g for same parameters in the maize bran (Table 1). This better potential for performance of the prepared nanocomposite could be attributed to the presence of the copper nanoparticles that have been incorporated into the matrix of the maize bran.

The maize bran is indicative of a better site for cation exchange as it had a capacity.

X-Ray Diffraction

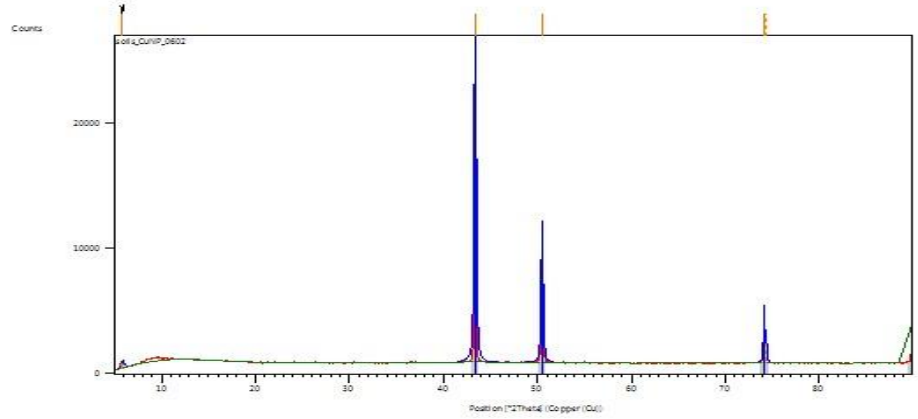

Fig 1: XRD spectrum of Cu nanoparticles

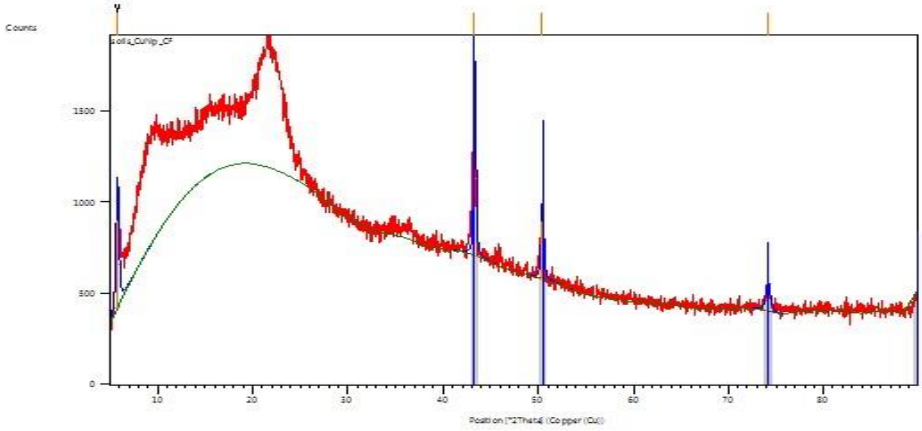

Fig 2: XRD spectrum of nanocomposite

The crystallite size of incorporated copper nanoparticles in the matrix of the maize bran to make the nanocomposite was determined by comparing it with the crystallite size of standard copper nanoparticles. In table 2 below, the crystallite sizes of the nanocomposite and particles have been compared.

Table 2: Crystallite size of nanocomposite compared to nanoparticles

Crystallite Size (nm)		
Relative Intensities (%)	**Copper-Maize Bran-Nanocomposite**	**Copper Nanoparticles**
100	36.17	36.18
37.79	27.87	37.17
14.55	21.07	51.84

The XRD results were generated at relative intensities of 100%, 37.79% and 14.55% respective Miller indices (h k l) of 1 1 1, 2 0 0, and 2 2 0. The peaks due 111 and 200 are comparable to previous work on ZnO by Viswanathan et al. [16] resulting in a hexagonal wurtzite structure otherwise trigonal in the current work. The XRD was used to indicate the successfully incorporation of copper nanoparticles within the bran. From table 2 it can conveniently be concluded that the synthesized nanocomposite had copper nanoparticles embedded in the matrix. Growth of the crystal in the matrix of the maize bran was somehow apparently hindered by the walls of the bran. This is probably why the crystallite sizes of the nanocomposite are less than those of the nanoparticles.

Functional Groups

Functional groups associated with the raw maize bran and those of the synthesized nanocomposite were determined using solid state infrared spectroscopy (Figures 3&4). This was used to check whether there was any change or modification of the functional groups through the transformation of the maize bran into the nanocomposite. Table 3 below shows the functional groups of both the raw maize bran and the synthesized nanocomposite.

Infrared Analysis

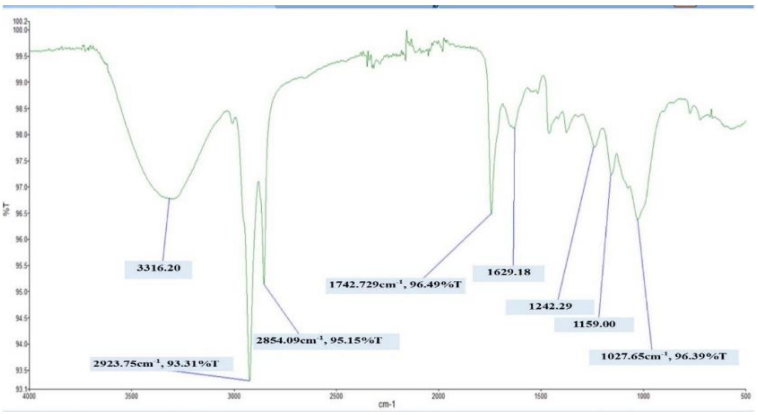

Figure 3: IR Spectrum of Maize Bran

Fig 4: IR Spectrum of Copper-Maize Bran Nanocomposite

Deductions from figures 3 and 4 are summarized in table 3 below.

Table 3: Functional groups of raw maize bran and Nanocomposite

		Wavenumbers (cm^{-1})		
S/No.	**Wavenumber Guide (cm^{-1})**	**Maize Bran**	**Nanocomposite**	**Functional Groups**
1	3500-3000	3301.87	3345.53	OH
2	3000-2500	2923.9	2923.42	C-H
		2854.4	2851.95	
3	2500-2000	-	-	C=C, C=N
4	2000-1500	1710.7	1737.4	C=O, C=C
5	1500-1000	1373.32	1368.85	
		1241.54	1237.08	C-O
		1030.27	1033.82	

There were no changes in the functional groups during the nanocomposite formation as shown by the infrared spectra. Even though the wavenumbers of the raw maize bran and the synthesized nanocomposite look marginally different, they both occur in the same range attributable to the occurrence of the same functional groups. Clearly the nanocomposite preparation process did not transform the functional groups. This implies that, after the incorporation of copper into the maize bran resulting in the nanocomposite material, its authenticity is maintained regardless of the expected reactions [17] [18] between the phytochemicals in the bran and Cu metal. When required, the product could be used without going through any re-modification stress(es). Further proves of the copper nanocomposite formation was found in the lower wavenumbers expressed in Manase et. al. [17][18] in their analyses of Ag nanoparticles. The current wavenumbers were generally lower compared to those of their work. Strong polysaccharide bonding with metals [19] are part of the metal-organic material nanocomposite bonds anticipated. The copper nanocomposite synthesized and characterized has potential in studies and application in drug delivery [20].

4. Conclusion

The synthesis of a copper based nanocomposite using maize bran as the matrix in this work has been achieved and indicated through its characterization. Physical and chemical characterization found indication of altered some parameters in the nanocomposite product. Its Point of Zero Charge is 5.3, Water Holding Capacity is 0.69, while the Bulk Density and Cation Exchange Capacity are 3.18 and 0.0026 respectively. The final point of zero charge difference with the initial material calculated was 0.7 pH points, and this makes the product good for attracting negatively charged species better that the maize bran. The variations are attributed to copper nanoparticles embedded in the matrix of the bran, making resulting in the composite. The synthetic modification process influenced the bulk density and water holding capacity of the maize bran. The nanocomposite has higher bulk density and water holding capacity compared to the maize bran. However, it has a slightly lower cation exchange capacity compared to the raw maize bran.

The X-Ray diffraction results showed crystallite size of the embedded copper nanoparticles. X-ray Diffraction of the nanocomposite at relative intensities of 100, 37.79 and 14.55 % respective Miller indices (h k l) of 1 1 1, 2 0 0, and 2 2 0 indicated crystallite sizes of 36.17, 27.87, and 21.07 respectively. Growth of the crystals, could however have been hindered by the walls of the matrix.

The solid-state Infrared analyses found that OH, C-H, C=C, C=N, C=O, C=C, and C-O functional groups in the bran did not change in the nanocomposite product.

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