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Preparation and Characterization of Nanocellulose-PVA Membranes from Peanut Shells Using Electrospinning

The membrane structure design is critical to the development of high-performance hemodialysis membranes applications and many others in various fields. In this study, bifunctional thin-film Nano fibrous composite membrane was synthesized, consisting of cellulose nanocrystalline (CNC) and poly vinyl alcohol (PVA) hydrogel as a separation layer. CNC was prepared from agriculture waste by 30% hydrolysis followed by sonication. The structural characteristics revealed the nanoscale structure. They showed two diffraction peaks at 15.2209° and 22.5071° indicating typical type I cellulose crystalline planes, transforming cellulose to nano cellulose crystalline structure. Electrospinning was used for prepare nanofibrous membranes from CNC reinforced with PVA to produce nanofiltration membranes. Membranes with ratios 8:2, 7:3 and 5:5 were successfully prepared with the 5:5 CNC:PVA membrane having a fiber network average width of 48.67nm.

Keywords: Nanocellulose; Electrospinning; Nano fibers; polyvinyl alcohol
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1. Introduction

Renewable materials that function well and produce little or no carbon emissions are essential for the sustainable transition away from fossil fuels. The sustainable biopolymer cellulose is present in plant and bacterial cell walls and offers a wide range of possible functions and transformative applications [1]. Its unusual multidimensionality further adds to its appeal. A growing interest has been directed towards one-dimensional nanomaterials such as nanorods, tubes, and wires, however there are four distinct dimensionalities to nanomaterials: zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) [2]. Increased interest in polymeric nanoparticles has been sparked by their novel shape-dependent features, which have promising uses in low-nanoscale packing, extraordinary heat stability, and everyday polymer compounds [3]. The extraction of cellulose is a critical area of research that laboratories throughout the globe are concentrating on in an effort to reduce landfill trash and total waste generation [4]. A biofibrious polymer, cellulose is an inert, flavorless, and odorless substance that is bioproduced by many living things. Additionally, it has functional hydroxyl groups [5,6]. Bacteria, plants, and animals may all provide nanocellulose, a tiny cellulosic substance. Ceramella cellulose, bacterial nanocellulose, and nano-fibrillated cellulose are the three varieties that are available [7]. Nanocellulose has unique chemical and physical characteristics, including a high porosity, a minimal absorption of moisture, and excellent crystallinity. The biomedical sector, electronics, papermaking, packaging, and filtration are just a few of the numerous fields that benefit from its features [8,9]. The electrical, paper, packaging, filtration, and medicinal sectors may all benefit from the enhanced assembly and control capabilities of nanocellulose, a chemically modified material with remarkable features [10]. The anti-fouling, high strength, and stiffness of nanocellulose membranes produced using sustainable nanotechnology make them an attractive material for water filtration [11,12]. A liquid polymer jet is launched onto a grounded collector from a high-voltage source in electrospinning, a process that makes ultra-thin fibers. Because of its capacity to generate nonwoven, continuous fibers with enhanced surface area, it finds extensive use in healthcare, nanotechnology, and tissue engineering [13,14]. Nanocomposites made of PVA are shown in the research using a novel micro-electrospinning mechanism. The purpose of integrating nanocellulose with PVA for membrane creation is to enhance output. Studying the effects of sustainable materials on society and the environment is the primary goal of this study.

This study proposes a new model of home-based micro-electrospinning for preparation of nanocomposites by PVA. The objective is to significantly enhance production by combining the properties of nanocellulose and PVA for membrane formation and explore practical cases. In this study, the authors have tried to understand the electrospinning process completely and characterized all resulting CNC/PVA composite membrane in a detailed manner as well as evaluated its properties and potential application. These goals will also fast-track substantial advancements in a burgeoning discipline - sustainable materials - whose membranes have important social and environmental impacts.

2. Experimental Part

Sodium hydroxide and sulfuric acid were purchased from BDH Chemicals, sodium hypochlorite from Sigma-Aldrich, Poly vinyl alcohol (PVA) was purchased from Sigma-Aldrich.

According to the protocol used in [15] for the experiment, the raw material (peanut shells) was collected, cleaned with distilled water and dried at room temperature. The sample turned into a fine powder via processing. The fine powdered raw ingredients were then collected and stirred for 4 hours at 80°C in 2% NaOH digestion. It was then repeatedly cleaned, filtered, dried, and bleached. Until reached to pH 7. The hydrolysis procedure was then carried out by mixing 10 g of powder from the final sample designated with 100 ml of 35% sulfuric acid with strong stirring. The suspension was filtered, collected and sonicated by Ultra Sonicator (UP400S) with amplitude 80. The suspension nanocellulose (NC) solution was collect and stored before being stored for further processing. Figure (1). illustrates the procedure of preparing nanocellulose from peanut shells.

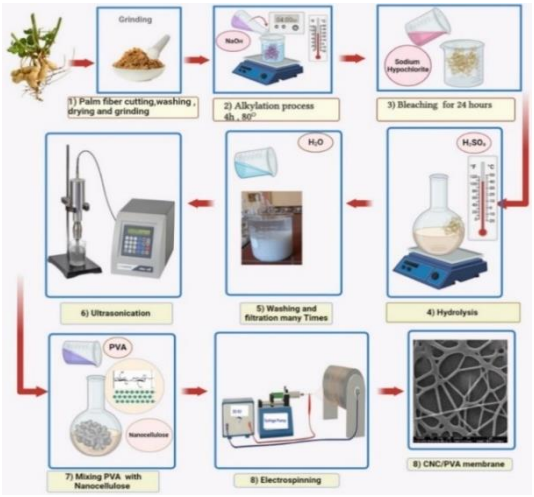


Fig. (1) Synthesis steps of nanocellulose from peanut shells

A 10% PVA in 100 mL of distilled water (w/v) mixture was prepared a heated and stirred for two hours at 85°C using a magnetic stirrer. The PVA solution was then infused) CNC fiber as ratio of 8:2, 5:5, and 7:3. The liquid was heated to 40°C and stirred for an hour using a magnetic stirrer to produce a homogeneous CNC and PVA solution. The solution was then left to stand for an hour to remove any trapped air bubbles. In order to ensure that the solution was thoroughly blended, it was ultrasonicated agitated for five minutes. It was stabilized for one hour before electrospinning.

Before beginning the electrospinning process, the region must be thoroughly cleaned to prevent dust or other impurities from adhering to the nanofiber membrane. The first step involved performing electrospinning at room temperature. A series of trial-and-error tests were also performed with a membrane nanofiber collector distance of 10-15 cm and an applied voltage in the 25-35 kV range. An aluminum foil collector was attached to a blunt-tipped needle with high-voltage positive and negative electrodes.

Mixture of 5% PVA in 100 mL of distilled water (w/v) was heated and stirred for two hours at 85°C using a magnetic stirrer. The PVA solution was then enriched with 5% CNC ramie fiber. The liquid was heated to 40°C and stirred for an hour with a magnetic stirrer to produce a homogeneous CNC and PVA solution. The solution was then allowed to stand for an hour to remove any trapped air bubbles. In addition, the solution was ultrasonically agitated for five minutes to ensure that it was thoroughly blended. It was stabilized for the final hour before electrospinning [16].

Nanofibrous materials are produced using the diverse and creative electrospinning technique [17]. It involves drawing and stretching a polymer solution or melting it into ultrafine fibers, often in the nanometer range, using an electric field [18]. A polymer solution or melt is put into a reservoir or syringe to start the electrospinning process. A high voltage is then used to charge the polymer solution, which is subsequently rapidly propelled in the direction of a grounded or negatively charged collector [19]. The solvent in the polymer solution evaporates in the jet as it flies through the air, leaving a nanofiber behind. Electrospinning allows for the creation of nanofibers with diameters ranging from a few nanometers to micrometers, matching the topologies of natural extracellular matrix and offering a high surface area-to-volume ratio [4,17,20]. The morphology, diameter, and alignment of the nanofibers may be modified by varying factors like voltage, flow rate, and collector distance, enabling the fabrication of materials with particular characteristics [21,22]. Many different polymers and polymer mixtures may be electrospun to produce a variety of nanofibrous materials with different properties, such as biodegradability, biocompatibility, and mechanical strength [23]. Figure (2) shows a diagram of the electrospinning system that was manufactured in the laboratory to prepare nanomembranes from nanocellulose and PVA.

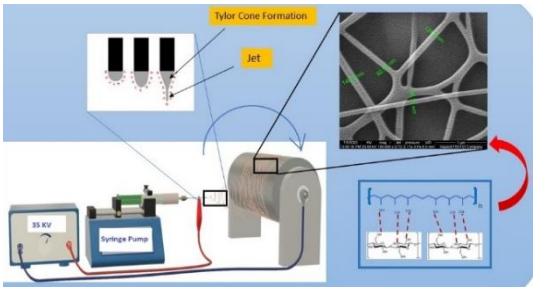


Fig. (2) Electrospinning main components and operations (a) High voltage, (b) Syringe pump, (c) Tylor cone, (d) Collector, and (e) Synthesized membrane

The morphological diameter of CNC fibers prepared from peanut shells was identified by environmental scanning electron microscopy (ZEISS SIGMA VP EM10C). The x-ray diffraction (XRD) is used to determine the crystallite size and form of the material, as well as the lattice strain. In order to investigate the profile of the XRD peaks, which is an analytical formula of Scherer, Williamson-Hall (W-H), and Warren-Averbuch (W-A), integrated extension methods are utilized. The Scherrer's equation is the most widely used for determining crystallite size, although it can only be used when the materials are not under strain [24]. Energy-dispersive x-ray spectroscopy (EDX) is used for chemical analysis, identification of the major elements presents in prepared samples, and assessment of particle size and element ratio. These techniques are necessary to create uniformity and offer helpful data for analytical procedures [25].

3. Results and Discussion

As shown in Fig. (3), the Fourier-transform infrared (FTIR) spectroscopy indicates the absorption bands of CNC prepared from peanut shells and CNC/PVA. The peak at 3301.64 cm^{-1} is related to the stretching of the O-H band. The peak at 2919.97 cm^{-1} is attributed to the C-H stretching vibration, which becomes less intense when CNC prepared [26]. The C=O stretching is responsible for the peak at 1719.56 cm^{-1}, while the peak at 1247.6 cm^{-1} indicated (C-O) aryl group stretching. Peaks between 1421 and 1370 cm^{-1} were attributed to the vibration of aromatic ring CH_2, C-H, and C-O groups. Peaks at 1021 and 1247.6 cm^{-1} are caused by C-H rocking vibration deformation [27].

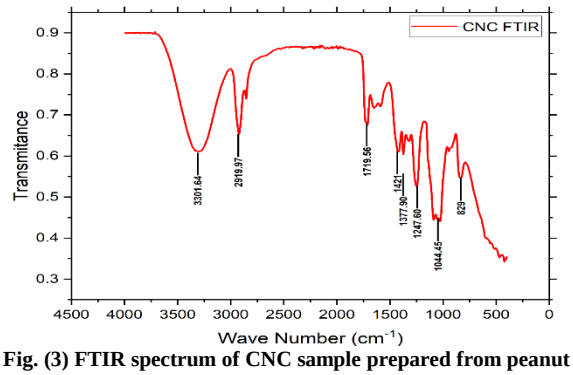


Fig. (3) FTIR spectrum of CNC sample prepared from peanut shells

The XRD patterns of CNC prepared from peanut shells showed two diffraction peaks, which indicate the crystal transformation of cellulose, as shown in Fig. (4). The diffraction peaks indexed to (101), (002) corresponded to the clear peaks at 2θ of 15.2209° and 22.5071°, which are typical of type I cellulose crystalline planes, respectively, indicating the typical crystalline characteristics of natural cellulose. These observations indicated better specific crystalline domains and were confirmed by the increase in CrIn as shown in table (1).

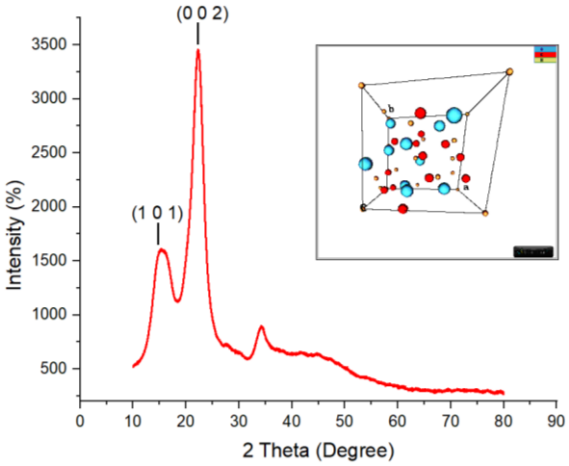


Fig. (4) XRD pattern of CNC prepared from peanut shells

Table (1) XRD parameters of CNC sample prepared from peanut shells

No.	Position (2θ)	Crystallite Size (nm)	Area (nm)
1	15.2209	35.89013	1723.94
2	22.5071	37.59784	5978.31

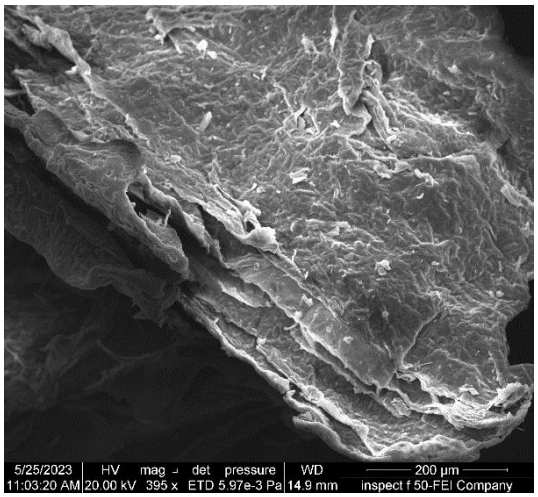
Debye-Scherrer's formula shown in Eq. (1) provides a strong yet easy method for extracting important nanoscale structural information from XRD patterns, relating diffraction phenomena to physical crystal characteristics and synthesis-structure relationships such as crystal size and area of nanoparticles. It connects the intrinsic growth of diffraction peaks attributed to tiny crystals to a unique one that can be measured directly (FWHM). The peaks get wider as the crystals become smaller. This gives information on microstructural features [28]

$$\mathrm{FWHM}(2\theta) = \frac{\beta\lambda}{D\cos\theta} \qquad (1)$$

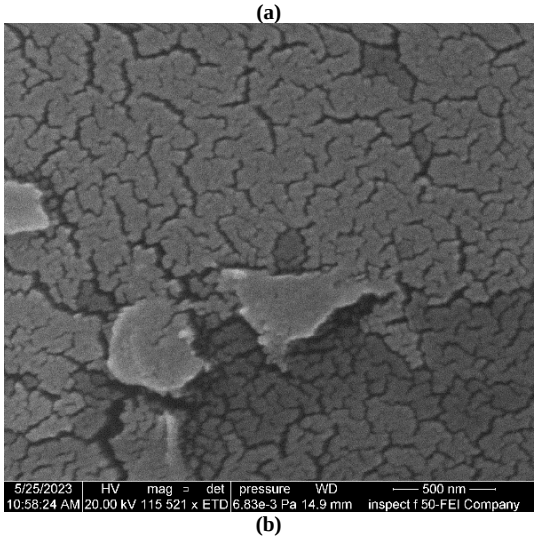
where FWHM is the full width at half maximum of the peak, 2θ is the scattering angle in radians, λ is the wavelength, D is the crystallite size of cubes with monodisperse sizes, and β is a constant that typically takes a value between 0.89 and 0.94 depending on the function used to fit the peak

The interpretation of D must thus be treated carefully for diverse reflections and crystallite shapes. D denotes the volume-averaged crystallite size in polydisperse systems.

The morphology and size of CNC prepared from peanut shells are depicted in Fig. (5). The FE-SEM images revealed the nanocrystalline structure of the prepared cellulose. The FE-SEM image of membranes containing 5:5 CNC and PVA shows that the fiber diameter of the prepared membrane appears to be perfect and sparkling with an average diameter of 48.67nm as shown in Fig. (6).



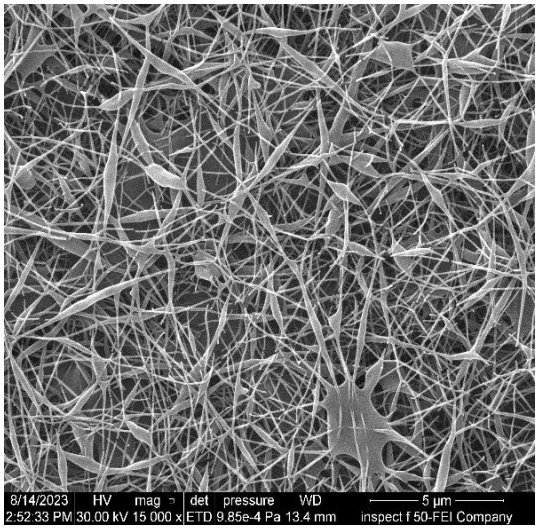
(a)



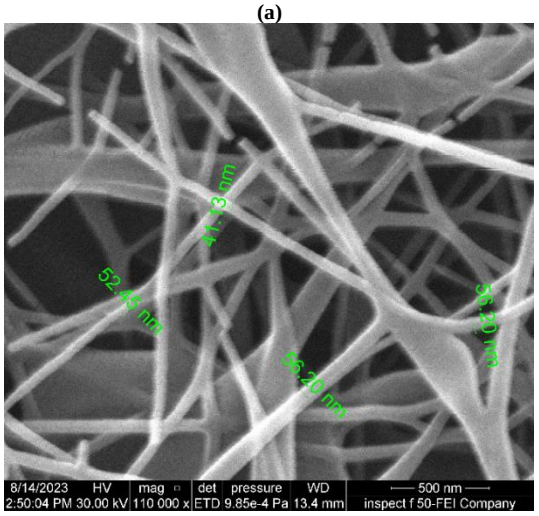
(b)

Fig. (5) FE-SEM images of CNC prepared from peanut shells at (a) 395X and (b) 521X

Optimizing electrospinning characteristics is a critical component of regulating and improving nanofiber synthesis, allowing for customizing of their features and characteristics. Several essential parameters are involved, and their changes can have a major impact on the resultant nanostructure [23]. Some of the implications of modifying electrospinning parameters on nanofiber creation are discussed in this part. It is observed that particles with a smaller diameter are formed when electrospinning is exposed to a high electrical potential, more precisely one that is more than 15 kV. This is mainly because of a Taylor cone formation, a phenomenon has a cone form, which is essential in defining the size of the produced fibers. Remarkably, the Taylor cone gets more pronounced as the voltage is raised over this threshold, leading to a greater decrease in the diameter of the resulting particles [29]. As a result, fibers with a smaller diameter are produced during the electrospinning process at higher voltage settings; this characteristic is linked to the improved and well-defined formation of the Taylor cone. Also, arrangement of needle and the collector drum in the electrospinning instrument plays major roles in formation of CNC nanofiber. A significant distance, usually in the range of 15-20 cm or more, between the needle and the collector drum promotes the development of a more spherical morphology in the formed particles. This is because the longer flight time of the ejected material allows for a more controlled and uniform deposition onto the collector surface. This spatial arrangement is important for controlling the morphology of the resulting nanofibers during the electrospinning process [17].



(a)



(b)

Fig. (6) FESEM image of membrane CNC-PVA (5:5)

Electrospinning method is used for fabricating membranes as it employs a polymer solution. All sorts of factors come into play during the process, including the polymer solution concentration, solvent characteristics, processing conditions, temperature, humidity, spinneret design, post-treatment methods, and polymer qualities themselves. Thicker fibers and higher viscosity are possible outcomes of increasing polymer concentrations; the formation and shape of the fibers are influenced by solvent qualities such as volatility, polarity, and compatibility with the polymer. The shape of the fibers may also be influenced by the spinning parameters, which include the voltage supplied, the flow rate, and the distance

between the spinneret and collector. The ultimate structure of the membrane is affected by the collecting substrate choice, which in turn affects the orientation and alignment of the fibers.

4. Conclusions

The fabrication of CNC from peanut shells which were utilized to prepare composite nanofiber membranes with Poly vinyl alcohol has been successfully conducted using electrospinning method. XRD patterns of CNC prepared from peanut shells shows two diffraction peaks indexed to (101), (002) corresponded to the clear peaks at 15.2209° and 22.5071° which are typical of type I cellulose crystalline planes and have better specific crystalline domains and were confirmed by the increase in CrIn. The diameter of the fiber membrane prepared from CNC and PVA appears to be perfect and sparkling with an average diameter of 48.67 nm.

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