International Journal of Advanced Interdisciplinary Sciences

Vol.1, Issue.1, 2021, 127-143

Nanocellulose Based Biosorbents for Drug Delivery and Dye Removal Applications

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Abstract

Herein, we were successfully exploited the applications such as effluent dye removal and pH responsive drug delivery using TEMPO oxidized nanocellulose fibers (TNCF). TNCF of width, 23-26 nm and a few hundred nm lengths were prepared from Banana fiber (BPSF) via. TEMPO oxidation followed by ultra-sonication. The high entangling nature and pH responsivity of carboxylated TNCF hydrogel were employed to demonstrate drug delivery application using a model protein, HSA (human serum albumin). A drug loading efficiency of 84.89 % and drug releasing efficiency of 65.75 % were achieved in specific release media, PBS (pH=6.5) in 5 hours. The ultra-light nanocellulose aerogels were prepared using a simple freeze-drying and high porous aerogels having a maximum porosity of 99.2 % were obtained. Furthermore, PVA-TNCF aerogel having BET surface area, 73.92 m^2/g was prepared by crosslinking both polymers with glutaraldehyde. The removal of methylene blue (MB) dye was demonstrated using the as-prepared TNCF/PVA aerogels which exhibited 91.63 % dye removal efficiency from an aqueous medium within 48 hours.

Key words: Drug delivery, Nanofibrillated cellulose, Dye removal.

Article History: Received 17 September 2021; Revised 1 December 2021; Accepted 2 December 2021; Published 6 December 2021.

1. Introduction

Cellulose is one of the most plentiful natural polymers in nature which composed of cellobiose units, and the glucose molecules are linked together by β-1, 4-glycosidic linkages. Cellulose fibers are also called as semi-crystalline polysaccharide. It is having width ranging from 5 to 20 μm and length ranging from 0.5 to several millimetres. The presence of the hydroxyl groups and its ability to form hydrogen bonds leads to the formation of fibrillar and semicrystalline packing which provides the important physical properties of these materials. Celluloses in different bioresources may vary in packing of individual fibrils due to the differences in biosynthetic conditions yielding different morphological structures [1-4]. According to these morphological features, cellulose fibers can be dissociated to cellulose nanocrystals (CNCs), nanofibrillated cellulose (NFC) (less than 100 nm width), bacterial nanocellulose (BNC).

Nanofibrillated Cellulose (NFC) refers to cellulose fibers that have been purposely fibrillated to get agglomerates of cellulose microfibril units. In 1970s, Turbak, Snyder and Sandberg were first to report the extraction of NFC by high-pressure homogenization (HPH) of dilute slurries of softwood cellulose fibers. NFC is produced by the defibrillation of cellulosic fibers by the application of an intense high mechanical shearing force to overcome fiber- fiber hydrogen bonding into the crystalline and amorphous parts.

Saito et al. were the first to report 2,2,6,6 tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation of cellulose fibers facilitated the extraction of NFC [5]. Cellulose based-hydrogel matrices are nowadays ideal materials for biological applications such as tissue engineering, drug delivery etc. due to their intrinsic properties like non-toxicity, biocompatibility, tunable and porous microstructure, and good mechanical properties.

Generally, NFC hydrogels can be prepared from the NFC suspensions through simple mechanical treatments, but nowadays it is described as, when fibrils with a high negative charge on their surface may provide good results in the formation of hydrogels. This is why because; cellulose-based hydrogels have a main drawback of low solubility in both water and most of the organic solvents. Fall et al. has proved that, by lowering the pH, hydrogel may formed surprisingly from NFC suspensions readily by the reduction in surface charge [6]. Considering therapeutic applications, oral administration of the medicine is more convenient and safer. But it is a great challenge since oral administration of these kind of drugs are questioned by chemical, enzymatic, and absorbance barriers in the alimentary tract [7]. Scientists are still facing the challenge of developing effective as well as safe oral administration of medicines for therapeutic proteins. Hypothetically, a hydrogel system for

oral administration should be, pH responsive enough to protect the proteins from the acid environment in stomach, biocompatible and capable of releasing proteins into the intestine [8].

So such kind of stimuli-responsive polymeric hydrogels has proved to have higher potential as a candidate of biomaterials for protein delivery [9]. Several new types of cellulose derivatives like hydroxypropyl cellulose (HPC), hydroxyethyl cellulose (HEC) etc., have been synthesized to expand the stimuli responsivity. Chemical modifications, including sulfonation, esterification, etherification, silylation, amidation, etc., have been also widely used to functionalize, nanocelluloses [10]. Nanocellulose made from different raw materials can also show diverse drug delivery effects and mechanism. In this work, pH responsivity of the carboxylated-TNCF hydrogel is explored to demonstrate drug delivery application using a model protein, HSA (human serum albumin).

Also, foams/aerogels have attracted considerable attention toward various applications such as lightweight, thermal insulation, oil/water separation, catalyst support, sensing, energy storage etc. Nanocellulose derived from natural resources was utilized as fillers to prepare foams/aerogel since it is having the distinctive structure and properties such as bio-compatibility, web-like structure, high aspect ratio etc [11, 12]. NFC suspension of interconnected cellulose fibrils (10−100 nm in diameter) having gel-like properties gives solid weight contents of only few weight percent [13]. Therefore, replacing water by air using freeze-dry technique results in porous materials which are called as aerogels with long entangled cellulose nanofibers which are having high surface area and porosity, and can absorbs liquids in large quantity. The morphological structure and the stability of the aerogels are adjusted by controlling the concentration of NFC in the gel before freeze-drying [14].

Cellulose nanofibers can effectively be a nanofiller for polymer nanocomposite aerogels, and also can improve the stability of NFC aerogels by combining with other biopolymers, thereby showing unlimited opportunities to generate valuable engineering materials from a renewable resource for several kinds of applications such as biomedical, waste water treatment etc.

Coming to waste water treatment applications, the porous networks of NFC aerogels allow fast diffusion of ions and molecules, which in turn to good adsorbing performance. Nevertheless, one disadvantage of cellulose-based aerogels is that they have the tendency to dismantle and again disperse in water. This calls attention to the necessity of chemical cross-linking in the aerogels which allow them not to leach apart or redisperse in water. NFCs are well suited with several varieties of synthetic and natural polymers but the disadvantage of NFC is that, it is hydrophilic in nature and most of polymers are hydrophobic in nature. In

order to overcome this, several surface modifications are done by different chemical treatments or physical methods [15].

NFCs have also been collaborated with different sets of polymer matrices, including elastomers, water-soluble polymers, latexes, biodegradable polymers etc. NFCs were also known as reinforcing fillers for a water-soluble and biocompatible polymer, PVA. The hydrophilic property of the PVA provided good result in intensified compatibility between the fibers and polymer matrix [16].

In the second part of the present work, PVA-TNCF aerogel was prepared by crosslinking both polymers with the help of glutaraldehyde. The common pollutant dye methylene blue (MB) removal was demonstrated using prepared TNCF/PVA aerogel.

2. Experimental Section

2.1 Materials used

Bio-extracted banana pseudo-stem fibers (BPSFs) were used for NCF extraction. TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (99 %), sodium hypochlorite (14 % active chlorine) and sodium bromide (99%) were purchased from Sigma-Aldrich. Poly (vinyl alcohol) (PVA) and glutaraldehyde (GA) also were provided by Sigma-Aldrich. Human serum albumin (HSA) and phosphate buffered saline (PBS) were also provided by Sigma-Aldrich. Methylene blue was also purchased from Sigma-Aldrich. All other chemicals, such as sulphuric acid, hydrochloric acid, sodium hydroxide and acetic acid were of analytical grade.

2.2 Preparation of TEMPO-oxidised nanocellulose fibers (TNCF)

a) Mercerisation: To assist the defibrillation of the fibers for synthesising nano fibrillated cellulose (NFCs) and to remove all the non-cellulosic contents, this step is usually used. 10 g of bioextracted banana pseudo-stem fiber (BPSF) was weighed accurately and soaked in 15 wt% NaOH. The mixture was stirred for 4hours.

b) Bleaching: The mercerised fiber was mixed with 1.7 wt% sodium chlorite. The pH was lowered to 4 by the addition of acetic acid. The mixture was taken in a round bottomed flask fitted with a condenser, refluxed at a temperature of 150°C and continues the heating until the yellow colour of the fiber turns to white. The chlorine gas was allowed to evaporate. The product obtained was filtered and washed thoroughly and it is dried.

c) Tempo-Mediated Oxidation: TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated oxidation of cellulose fiber followed by sonication, facilitates the complete defibrillation of cellulose nanofibrils in water. Holocellulose fibers obtained after the bleaching process were undergone to TEMPO oxidation. 0.5g of hollow cellulose, 0.032 g of TEMPO, 0.32 g of

NaBr were drawn to a RB flask and dissolved in double distilled water. 10 mL of NaClO was added slowly to the mixture maintaining continuous stirring. In order to get a 1:300 fiber-to-liquor ratio, remaining required amount of double distilled water were added accordingly. The pH of the solution was maintained in between 10-11 using NaOH solution. The mixture after reaction was then transferred to ultrasonication bath for the defibrillation process of cellulose fibers. The mixture was then quenched using ethanol (3-5ml) to arrest the oxidation process. Then it was neutralised using HCl, centrifuged and washed several times. The remaining gel like matter after washing was then freeze-dried, and kept for further use.

2.3 Study of encapsulation efficiency of TNCF

Human Serum Albumin (HSA) was used as a model protein for entrapment studies. Conjugation of HSA with TNCF hydrogel was achieved by simple mixing of two suspension and consequent reduction in pH to produce hydrogel. In brief, 10 mL mixture containing 0.325 wt% well dispersed TNCF and HSA (6.25 g/ml) at pH= 6.5 was kept overnight for mixing under stirring at room temperature (25±2 °C). Further, the pH of the mixture was made to 3 using acetic acid that resulted in gelation of HSA encapsulated TNCF nanocomposite. The solution was centrifuged and the supernatant was analysed for estimating the amount of unbound protein present. Absorbance at 207 nm was recorded for the calculation of encapsulation efficiency for TNCF-HSA conjugate using the formula

$$Entrapment\ efficency\ (\%) = \frac{(Total\ drug\ added - Drug\ in\ the\ supernatant)X100}{Total\ drug\ added}$$

The HSA loaded TNCF pellet (TNCF/HSA hydrogel) obtained after centrifugation was collected and redispersed in 1ml DI water. 200 µL of this solution was drop casted on a glass slide and dried in an oven. For HSA release study we kept the dried glass slide in 20ml phosphate buffered saline (PBS, pH 7) and stirred continuously for 5 hours. The amount of HSA released was determined by UV-Vis spectroscopy by the analysis of the releasing media at chosen time intervals. Absorbance at 207 nm was found to calculate the amount of model drug released.

$$Protein\ release\ (\%) = \frac{Amount\ of\ protein\ released\ at\ time\ t}{Total\ amount\ of\ protein\ loaded} \times 100$$

2.4 Preparation of PVA-TNCF Aerogel

Different concentrations of TNCF aerogels were prepared by varying the weight ratios of TNCF. Various weight percentage (0.25, 0.5, 0.75, 1, 1.25, 1.5) of dried TNCF were dispersed in 15ml vial and kept in bath sonicator for even dispersion. The dispersions were then kept in freezer at-40 °C overnight. The refrigerated dispersion was set for freeze drying process and the TNCF aerogel was obtained.

0.5 g of PVA (average mol. wt. 3000-7000) was dissolved in DI water and stirred for the PVA to be properly dissolved in the solution. The TNCF (0.0375 g, 0.75 %) and PVA solution (5 mL, 0.5 g in 5 ml) were combined together and drawn to a beaker with continuous stirring for 1 h. Then, sulfuric acid (1 vol%, Sigma-Aldrich) and glutaraldehyde solution (25 wt %, Sigma-Aldrich) were added to the PVA/TNCF solution. Then the mixture was undergone to mechanical stirring for 1 h. The obtained aqueous gel was cross-linked in an oven at 75 °C for 3 h. The cured aerogel was stored overnight and freeze dried. After freeze drying, PVA-TNCF aerogel was obtained. The aerogels were characterized and used for dye absorption experiments.

2.5 Dye Absorption Experiment

A piece of PVA-TNCF aerogel is kept in 10^{-5} M methylene blue solution. Amount of dye absorbed is calculated through UV-Vis spectroscopy using the equation,

$$Dye\ absorption\ efficiency\ (\%) = \frac{Initial\ conc.of\ MB\ solution - Final\ conc.of\ MB\ solution}{Initial\ conc.of\ MB\ solution} X\ 100$$

Desorption studies were conducted accordingly by washing the aerogel with a mixture of ethanol and water for 2 hours and dried in oven for recycling studies.

3. Results and Discussion

3.1 Preparation and characterization of TNCF from BPSF

Nanocellulose fibers were recovered from bio extracted lignocellulosic BPSF, which has a cellulose content of 63-64 wt%. Using scanning electron microscopy, the removal of non-cellulosic components from raw BPSF fibers was examined at each stage of purification (**Figure 1**).

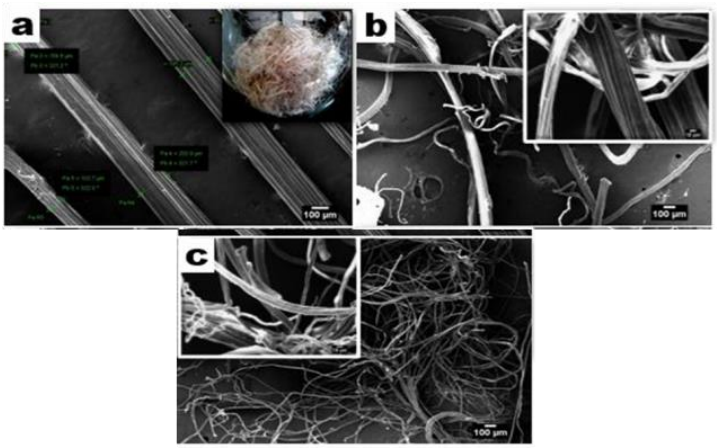

Figure 1. SEM micrographs of, a) bio extracted BPSF, b) after mercerization, c) after bleaching

TEMPO catalysed oxidation has been used to separate nano fibrils from microfibers, followed by high-intensity ultrasonication to disintegrate them. The use of TEMPO-mediated oxidation as a pre-treatment method for the isolation of highly lengthy, customized NFCs has been reported.

The formation of TEMPO-oxidised cellulose nanofibers was confirmed by FT-IR spectra (**Figure 2**), which showed a prominent peak at 1596 nm that corresponded to C=O stretching, which is consistent with previous evidence [46] as the primary hydroxyl groups of cellulose were converted to carboxylic groups. The O-H stretching has a peak of 3335 nm, while the C-H bending and C-O stretching have peaks of 1410 nm and 1040 nm, respectively. Because of the repulsive electrostatic force between the negatively charged ions of nanofibrillated cellulose, carboxyl functionality on nanocellulose resulted in a highly stable aqueous solution. Furthermore, TEMPO oxidation resulted in the removal of noncellulosic components such as lignin, wax, and other substances.

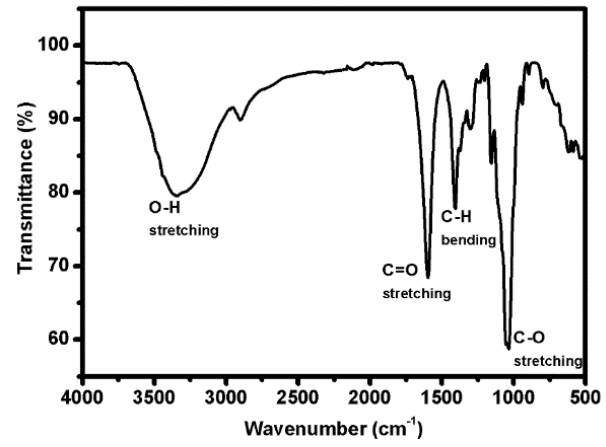

Figure 2. FT-IR spectra of TNCF.

XRD analysis of purified holocellulose and TNCF (**Figure 3**) revealed that TEMPO-mediated nanocellulose isolation does not influence crystallinity, which is not always the case with acid-catalyzed nanocellulose. As a result, it is indeed possible that the amorphosity of untreated lignocellulosic fibers is less effectively maintained even in the nano-domain, resulting in lengthy fibrils.

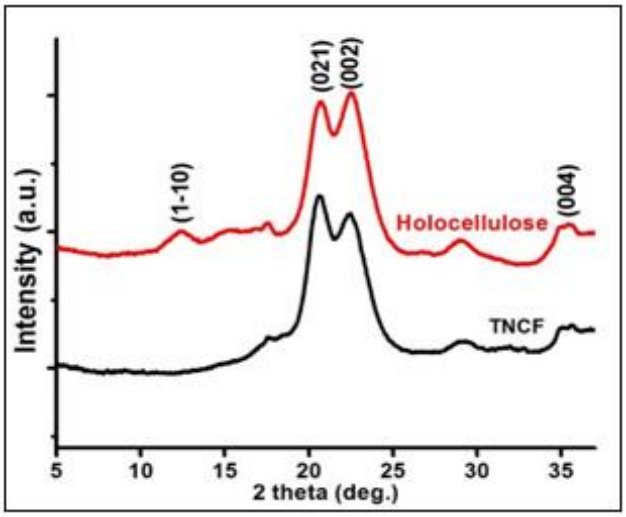

Figure 3. XRD of micron sized holocellulosefibers and TEMPO oxidized NFCs.

Microscopic techniques such as SEM, TEM, and AFM were used to characterise the morphology of the TNCF obtained (**Figure 4**). Individualized nanofibers, or NFCs, with a width of 23-26 nm and a length of a few micrometres (as determined by AFM and TEM), might be generated by ultrasonically treating oxidised celluloses in water.

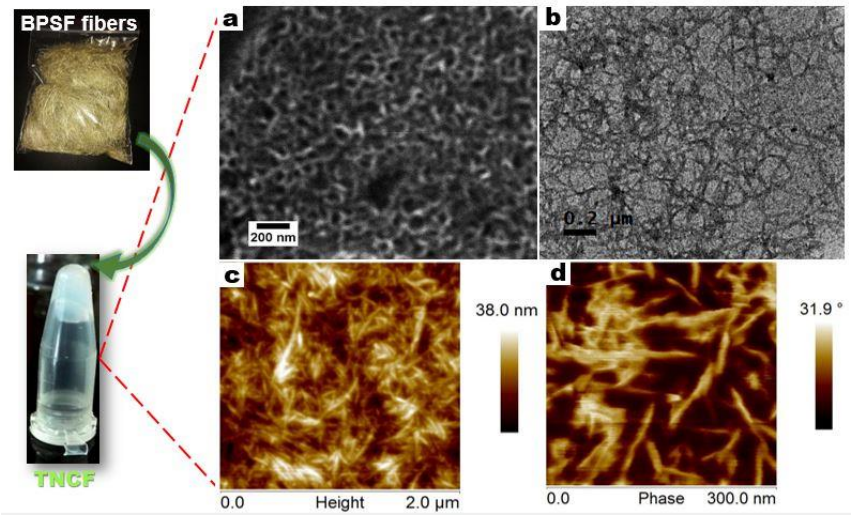

Figure 4. Photographs ofhighly dispersed TNCF suspension and TNCF hydrogel has been shown (a) SEM image of TNCF, (b) TEM, (c) AFM height image and corresponding phase image (d).

3.2 Characterization of TNCF hydrogel

Because of their simplicity of tuning the network strength and wide range of surface functionalization, cellulose hydrogels are commonly employed as excipients in drugs to control the rate of drug release and so reach the correct drug concentration. TNCF hydrogels were loaded with HSA, a naturally occurring protein found in the human serum, as the model medication utilising a physical adsorption method in the current investigation. Because it has a large number of surface negative charges (carboxyl functionalities created during TEMPO oxidation) and a strong affinity for water, an aqueous TNCF solution that forms hydrogels under reduced pH was used to encapsulate the drug. The positively charged protein bonded efficiently to the negatively charged TNCF in the first phase of mixing TNCF solution with HSA. Without the use of any binding agents, further drop of pH brings the conjugated TNCFs together to create hydrogels with a robust network. Reduced pH enables the surface carboxyl groups of cellulose chains to protonate, increasing the Vander Waals attraction inside individual fibers. In the severe acidic environment of the stomach, the pH responsiveness of TNCF aerogel protects HSA proteins from being released. Furthermore, the stable fiber network built around the drug particles would protect the particles from the liquid environment found in the human body and aid in the disintegration of drug molecules, forming a barrier to their diffusion. The hydrogel reverted itself to sol state, releasing medicine at a pH of nearly neutral (pH = 6.5). **Figure 5** shows photos of HSA-loaded TNCF after sol-gel transformation.

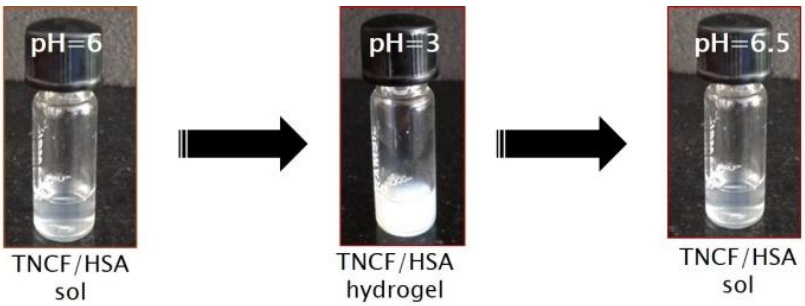

Figure 5. Sol-gel transformation of TNCF/HSA system

UV-Visible spectra were used to determine the amount of drug in the starting sol and the supernatant, as well as the amount of protein bound. Overall drug loading performance was obtained to be 84.89 %. The fine network and entangled structure of nanocellulose with a large fiber surface area could explain the high protein binding efficiency in nanocomposites. Furthermore, the carboxyl functionalities that were introduced, as well as the highly

negatively charged surface, provided an increased number of binding sites for protein conjugation.

UV-Vis has been used to examine the protein released from nanocomposites in PBS buffer at pH 6.5 for any changes in peak wavelength (207 nm) when compared to TNCF bound proteins. A protein release profile (**Figure 6**) was plotted for up to five days based on the data. According to the release profile, 37.81 % medication was released in the first 1 hour and 65.75 % after 5 hours. The facile rupture of the TNCF/HSA hydrogel network at neutral pH, resulting in drug release into solubilizing solutions, could explain the relatively high releasing efficiency observed.

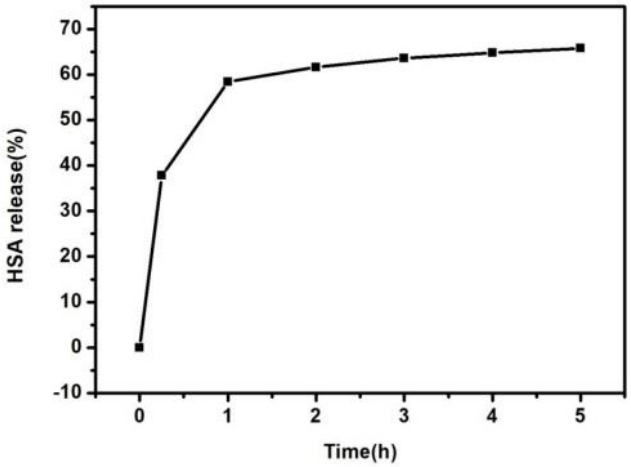

Figure 6. Drug releasing profile of HSA in PBS medium (pH=6.5)

When FTIR spectra of HSA/TNCF compared with standard peaks of HSA, peaks of HSA are appearing in the spectrum which concludes the binding of HSA with TNCF (**Figure 7**). HSA/TNCF shows all the characteristic amide bands at about 1652 and 1542 nm. The slight shifts and all those changes in the intensity of band in the IR spectrum confirm the proper loading/binding of HSA in TNCF.

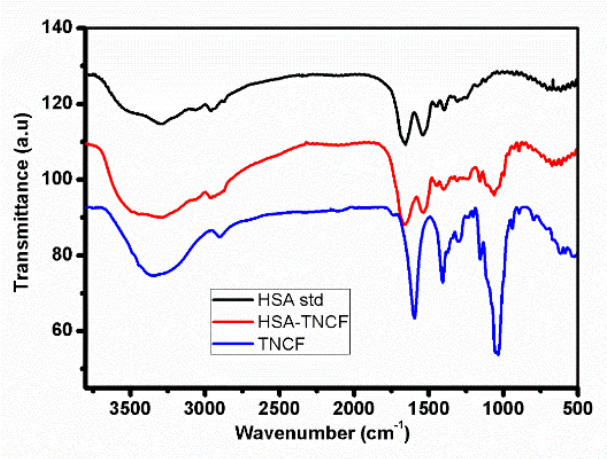

Figure 7. Comparison of FTIR Spectra of HSA (control) with HSA/TNCF and TNCF alone.

It is indeed important to note that freeze-drying a sample can cause some of the microstructures of the cellulose fiber network to collapse, which are effectively maintained in hydrogels. As a result, both percolation and protein release will be inhibited in the former, whilst big open pores allow for simple passage of the latter. Furthermore, because TNCF is a cytocompatible material, it is safe and non-toxic to administer to humans, and the chains may be broken down by digestive enzymes into normal metabolites in the gastrointestinal tract. With this research, we were able to show that a highly cytocompatible nanocomposite created using the physical conjugation method had a higher proportion of protein binding and easier release of HSA proteins.

3.3 Preparation and characterisation of TNCF Aerogel

The characteristics of TNCF aerogels which were prepared by freeze-drying technique strictly depend upon freezing time and temperature. The porosity varies according to the freezing temperature and strength of the TNCF aerogel. Aerogels with different TNCF concentration like 0.75, 1.00, 1.25 wt % were prepared (**Figure 8**). For each percentage, the calculated the porosity and density are given in **Table 1.** The morphology of aerogels was analysed by SEM.

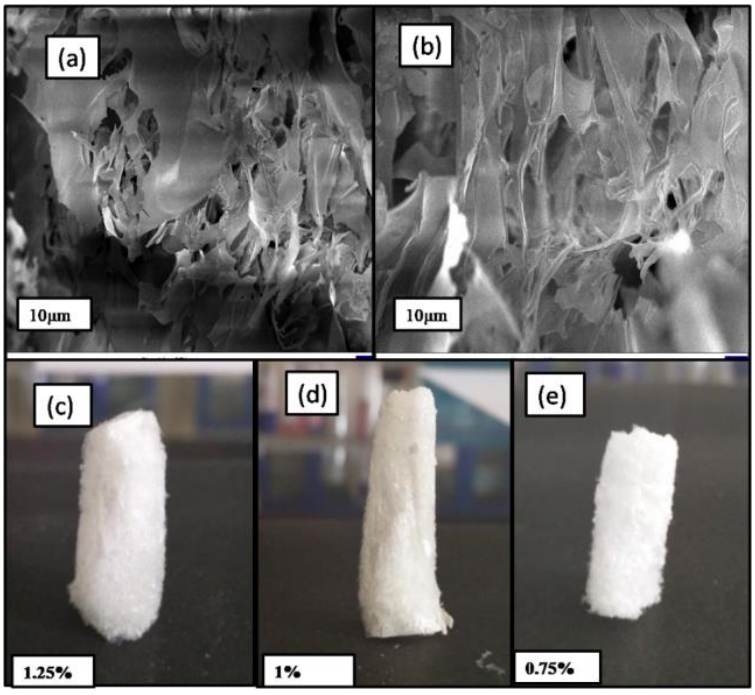

Figure 8. a) and b) Representative SEM micrographs of TNCF aerogel with 1.25 wt% TNCF concentration at different magnifications; photographs of TNCF aerogels prepared with conc. c)1.25 wt.%, d)1 wt.% and e) 0.75 wt.%.

Table 1. Calculation of porosity of TNCF

Conc. Of TNCF Suspension (Wt.%)	Density (g/cm^3)	Porosity (%)
0.75	0.012	99.2
1.00	0.021	98.7
1.25	0.015	99.1

3.3.1 Preparation and Characterisation of PVA-TNCF Aerogel

Fabricating biodegradable NFC-PVA composite may be a possible way to label the constraints of NFC and PVA. These composites should have excellent mechanical properties because of strong hydrogen bonding between NFC and PVA. PVA-TNCF aerogels, were successfully prepared using freeze-drying method. Glutaraldehyde was used as cross-linking agent since hydroxyl groups in PVA are tend to form hydrogen bonds and acetal bonds with other components such as cellulose and aldehydes.

ATR-FT-IR was used to study the changes in the functional groups of TNCF and PVA after crosslinking. When comparing with the ATR-FT-IR spectrum of TNCF aerogel (**Figure 9**), the sharp C-O stretching peak of primary alcohols present in TNCF at 1038 cm^{-1} was mostly disappeared in TNCF- PVA aerogel which point to the consumption of these groups by glutaraldehyde for network formation. It was also favored by the comparable decrease in the amount of hydroxyl groups (broad peaks at 3348 and 3416 cm^{-1} correspond to O-H stretching) with the addition of GA. Also, an additional peak for PVA-TNCF aerogel is observed at 1245 cm^{-1} indicates to C-O-C stretching which confirm the acetal formation during cross linking. Thus, we infer that GA have been shown to crosslink both cellulose and PVA, separately.

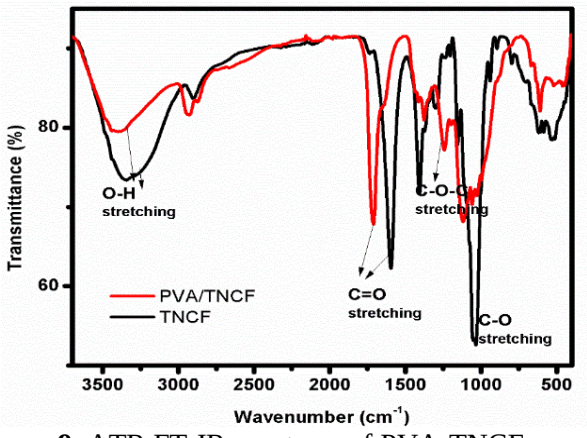

Figure 9. ATR FT-IR spectrum of PVA-TNCF aerogel.

Figure 10 shows the morphological features of prepared PVA-TNCF aerogel. Photograph of PVA-TNCF aerogel and the scanning electron micrographs of PVA-TNCF aerogel in different magnifications are given showing the porosity of TNCF aerogels were sacrificed to some extent in order to reinforce the composite. Both the density and strength of the aerogel has been increased when combined with PVA compared with the TNCF aerogel.

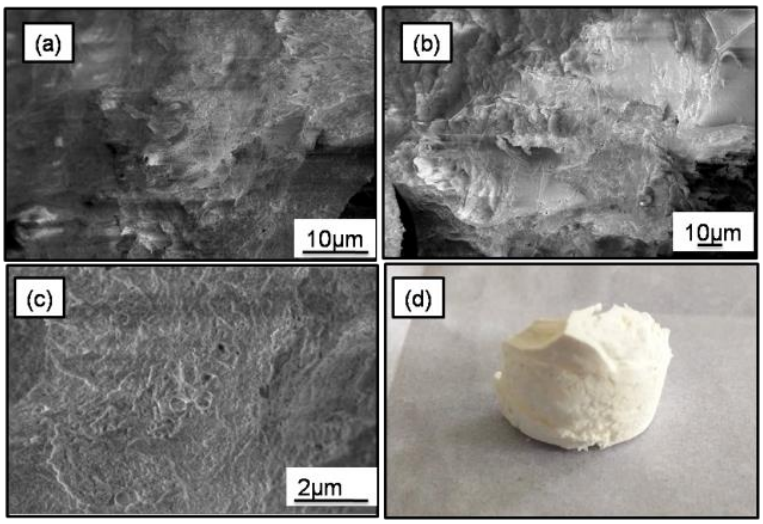

Figure 10. SEM images of the PVA-TNCF aerogels with magnifications (a) and (b) 10 µm, (c) 2µm and d) corresponding photograph.

It was evident that the addition of more amount of crosslinker favoured the reaction at both the edges of GA molecule and decreased the free volume of the material, which facilitates the aqueous stability of the aerogel. Under optimal processing conditions, very little shrinkage was observed in these aerogels. 0.75 wt% TNCF and 10 wt% PVA were mixed together and hence the porosity was relatively low due to the high concentration of PVA. The density calculated for PVA-TNCF aerogel was 0.1089 g/cm^3. BET specific surface area was quantified from nitrogen adsorption isotherms and is found to be 73.92 m^2/g for the prepared composite aerogel.

3.3.2 Dye absorption of PVA-TNCF aerogel

During the experiments it was clearly evaluated that the prepared PVA-TNCF aerogels possess a large polar liquid-holding capacity without any distinguishable changes in the structure. Therefore we speculate dye removal capacity of the prepared composite of a common pollutant, an anionic dye, Methylene blue (MB). Dye absorption experiment was performed by dipping PVA-TNCF aerogel (192.5mg) in 10^{-5} M MB solution for two

days.The **Figure 11** illustrate the visualization of MB dye absorption of PVA-TNCF aerogel from an aqueous medium at different stages of dye removal.

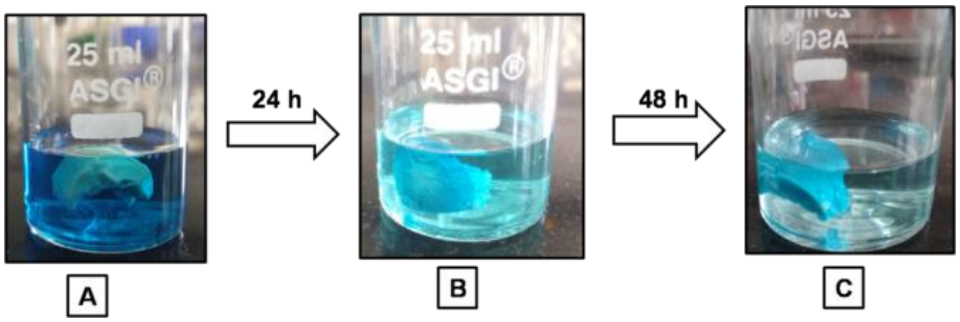

Figure 11. MB absorption of PVA-TNCF aerogel at (a) initial stage, (b) 24 hrs and (c) 48 hrs.

The UV-Visible spectra (**Figure.12**) of the dye solution was recorded at definit time intervals to quantify the MB removal from the aqeous medium. A peak at 661nm is assigned in the UV-Visible spectra represents the absorption peak of MB solution. Absorbance at the initial concentration of MB solution (10^{-5} M) is 1.8537 and it gradually reduced to 0.1552 at the final stage after 48hours. A 91.63 %. dye removal efficiency was calcultaed from the data. The high dye removal efficiency can be attributed to the highly porous nature and high affinity of prepared PVA-TNCF aerogel towards a polar cationic dye like MB enabling the large volume absorption capacity.

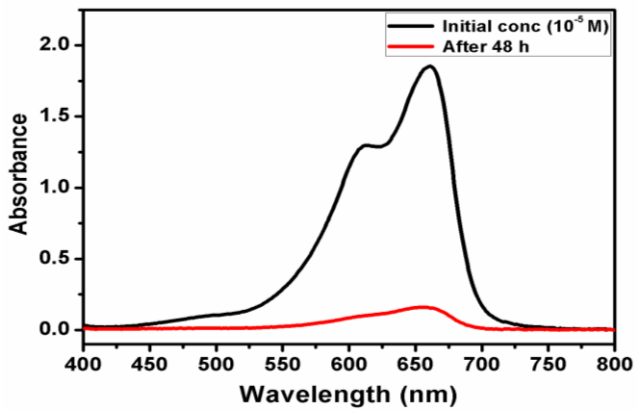

Figure 12. UV-Visible spectra of MB solution at the initial concentration (10^{-5}M) and after 48 hours

Since one of the main intentions of this work was to explore whether the aerogels could be reinforced while keeping up their water absorption capacity, it was important to refine from

the findings that made above that, blending of PVA and GA cross linking had a small negative impact on the absorption capacity of the aerogels.

The reusability of the aerogels was evaluated by repeating the adsorption–desorption cycles up to three times (**Figure 13**). The aerogel lost stability on its third cycle. And two successful adsorption studies were conducted. Second cycle concludes by giving the less efficiency up to 65 % and the third cycle ends up with an efficiency of 26.1 %. And it is clear that the first cycle of dye absorption provides the higher efficiency results.

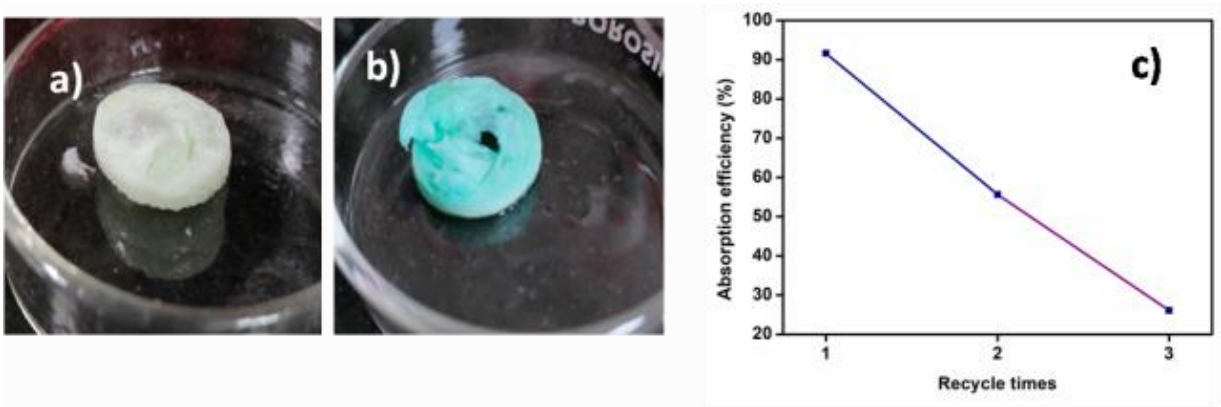

Figure 13. a) represents the first recycled PVA TNCF aerogel using ethanol b) represents the second absorption cycle of methylene blue dye c) gives the decreased adsorption efficiency as a function of the recycle times.

4. Conclusion

TEMPO oxidised nanocellulose fibers (TNCF) with a width of 23-26 nm and lengths of a few hundred nm were successfully prepared from banana fiber (BPSF) using TEMPO oxidation and ultrasonication. The TNCF was investigated using SEM, TEM, AFM, XRD, and FT-IR. Furthermore, the carboxylated TNCF hydrogel's strong entangling nature and pH responsiveness were used to demonstrate drug delivery application utilising HSA as a model protein (human serum albumin). By sol-gel transformation of aqueous TNCF solution at acidic pH with a loading efficiency of 84.89 %, a physical adsorption approach was used to encapsulate therapeutic protein. In 5 hours, the drug releasing efficiency in the release medium of PBS (pH= 6.5) was determined to be 65.75 %. As a result, TNCF hydrogels serve as a highly biocompatible and effective protein/drug carrier matrix for the sustained and gradual administration of surface bound proteins at almost neutral pH.

Another study used a simple freeze-drying procedure to make ultralight nanocellulose aerogels. By freeze-drying varying proportion of TNCF aqueous dispersions, highly porous

aerogels (with a maximum porosity of 99.2 %) were made easily. By crosslinking both polymers with glutaraldehyde, a PVA-TNCF aerogel was generated. The surface area of BET was found to be 73.92 m^2/g. The removal of methylene blue (MB), a common pollutant dye, was utilized to demonstrate a cross-linked TNCF/PVA aerogel. It displayed 91.63 percent dye removal effectiveness from an aqueous medium within 48 hours. In summary, the present study demonstrates the use of nanocellulose-based bio-sorbents in the water treatment process for effluent removal of dye.

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