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Green synthesis of Metal-Organic framework based Hybrid Nanocellulose/ Nano silver composites derived from watermelon peel waste for effective removal of heavy metals from textile effluent

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ABSTRACT

Cellulose, a widely available carbon polymer found in various plant, animal, and bacterial sources, constitutes a significant portion of fruit and vegetable waste also. In tune with the current research, cellulose is also being extensively developed as a nano material, i.e. nano cellulose crystals (CNC). CNCs are advanced version of cellulose particles at nanometer scale and have additional properties other than natural and biodegradable attributes like high surface area, nano size effect, non-toxic, high mechanical strength, thermal stability, hydrophilic, possibility of functionalization due to presence of hydroxyl groups on surface. Nano cellulose has been extensively used in the field of food packaging materials, wastewater treatment, and drug delivery and as a catalyst. Nano cellulose and its hybrid nano composites are among the emerging nanomaterials of this century employed for wastewater remediation application specifically to remove heavy metals from industrial effluents. Recently, with the modification of surface properties of CNC with metal or metal oxide nanoparticles via ex-situ simple blending method, metal-organic framework based hybrid nano composites are synthesized for abundant application worldwide. Biodegradable watermelon peel waste derived nano cellulose (CNC)/nano silver (AgNPs) nano composite synthesized herein is applied as an adsorbent for the removal of heavy metals to purify waste water or textile effluent, mitigating problem of water pollution as well as solid fruit peel waste management. During the study, CNCs were prepared by ultrasonication and acid hydrolysis of isolated cellulose. Pure Cellulose is isolated from natural watermelon peel waste through chemical pre-treatment in which all non-cellulosic components were removed subsequently. Silver nanoparticles (AgNPs) were also synthesized by green biological method from leaf extract of *Nyctanthus arbour tristis.* CNCs were characterized by FTIR, XRD and FESEM to analyze purity of cellulose, crystallinity of CNCs and morphology and size of CNCs respectively. Excellent potential of CNC/AgNPs hybrid nano composites towards water purification application is successfully explored in this study via AAS adsorption estimates and FESEM and EDX analysis of CNCs/AgNPs adsorbent (before and after adsorption of heavy metal ions). Adsorption of heavy metals such as lead, cadmium and copper from textile effluent by CNCs/AgNPs is estimated with 88.68%, 35.44% and 88.04% removal efficiency. This recent development on low cost, natural waste derived sustainable production of novel metal-organic framework based CNCs/AgNPs adsorbent encourages sustainable waste management practices specially towards circular economy concept (3R's) which suggests waste reduction, recycling, and reuse of waste in the production of eco-friendly materials for cleaner environment.

Keywords: *Watermelon peel waste, Nanocellulose/Nano silver hybrid nanocomposites, Solid waste management, Water Remediation, Circular Economy concept, 3R's Approach*

Introduction

The agro-climate of India is very diverse, encouraging the cultivation of numerous horticultural crops which include fruit trees, vegetables, ornamental plants, medicinal herbs, flowers and aromatic plants, and spices. Horticulture crops incorporate mostly fruits and vegetables and India is second largest producer of fruits and vegetables in the world (Govt of India & Department of Agriculture and Farmers Welfare, 2023). One of the most cultivated fruit crops includes watermelon which is a summer crop, mostly grown *in the hot and arid regions of Rajasthan* because of its cool, refreshing taste and thirst quenching ability; thus it has been considered favourite fruit during summer season. Watermelon is abundant of vitamins and minerals such as iron, potassium, magnesium, and phosphorus. Even though the watermelon rind is also edible and nutritious, when the juice has been extracted, the remaining rind, seeds, and peel are typically either composted or dumped in open spaces (Nayak and Bhushan, 2019). Approximately 45% of household and fruit processing industrial solid wastes is generated from unwanted parts of watermelon like its rind, peels, seeds etc. which may cause serious environmental pollution if not disposed properly (Sobukola, *et al*., 2008), (Joshi, 2020). Fruit peel waste as main source of municipal solid wastes (MSW) has become crucial environmental issue. At present, the two main techniques to dispose municipal solid wastes are landfill and incineration. However, inappropriate management of landfill will result in emission of methane and carbon dioxide. Although, these fruit wastes are good source of fiber, pectin, cellulose, hemicellulose, lignin etc. The previously calculated chemical composition of watermelon peel waste from various research articles is summarized in Table 1.

Table 1. Chemical Composition of Watermelon Peel Waste

Composition (% Dry mass)	Water melon peel waste (WPW)
Cellulose	49.23
Hemicellulose	12.56
Lignin	7.25
Pectin	17.4-27.86
Total sugar	56
Protein	11.17

Subsequent removal of these kinds of low or moderately high molecular weight substances leaves cellulose alone (Szymanska-Chargot *et al*., 2017). Cellulose is a well-known natural, structural organic polymer, widely available through extensive vegetation and known for excellent mechanical strength. Apart from planet's predominant structural natural polymer, cellulose has variety of features that includes bio based renewable material, low priced, non-toxic, biodegradable, lower density, substantial strength and mechanical characteristics which make it a very attractive. Owing to eco-friendly nature, cellulose utilisation for the production of novel nano material is gaining attraction (Naz, Ahmad, Akhtar, Ahmad, Ali, & Zia, 2016). Such nano material is referred as nano cellulose which is obtained from reduction of cellulose to nano size by chemical or mechanical treatment.

Extraction of Nano cellulose can be effective way to reduce solid fruit and vegetable peel waste or we can say solid waste is recycled into value added nano sized material or nano materials, i.e. nano cellulose with help of chemo mechanical treatment (Kargarzadeh *tt al*., 2017). The nano cellulose has high surface to volume area, aspect ratio and nano size effect makes them superior from native cellulose fibers. Further, the nano cellulose has mechanical strength, flexibility, blending, biodegradability, chirality, and thermal stability, possibility of functionalization due to presence of hydroxyl groups on surface and low thermal expansion. Nano cellulose has vast application in various fields (Trache *et al*., 2020).

Among different applications of Nano cellulose crystals (CNC), its implementation in wastewater treatment is highly promising. Adsorption is effective method in wastewater treatment compared to other approaches; due to its low capital cost and can remove most of the pollutants and easy regeneration. Enhanced adsorption capacity of nano cellulose based nano composites is obtained as a result of surface modification by attaching new chemical species on the surface. Surface modification led to increase in available active binding sites which will ultimately improve ion-exchange characteristics and promote metal backbone uptake (Yu, *et al*., 2013). The surface modification of nano cellulose with silver nanoparticles has recently gained great attention in wastewater remediation due to its bactericidal, fungicidal, carcinogenic, anti-inflammatory attributes (Wei *et al*., 2015). Synthesized Metal or metal oxide nanoparticles (NPs) are generally unstable if no capping agent is added in reaction mixture. Now days, nano cellulose as a capping agent or template or in the form of stabilizer is used to produce nanoparticles. Presence of hydroxyl groups on the surface of CNCs favours capping of NPs. Additionally, prepared nano cellulose/silver nano particle hybrid nano composite will have dual properties of both nanomaterials in single entity due to its combined effect, such nanomaterials are termed as Metal-organic Frameworks (Khalil *et al.*, 2017). However, CNC/AgNPs hybrid nano composites have been not studied much for water purification application till now; thus, attracting considerable interest in detecting potential of hybrid nanocomposites in removal of inorganic and organic contaminants from wastewater (O'Connell *et al.*, 2008). Utilization of metal-organic frameworks (MOFs) as an adsorbent is breakthrough in water purification treatments. MOFs are highlighted in this particular application due to its characteristic qualities such as large specific surface area, easy-to-use cavities and water stability, can be reproduced in bulk (Rojas and Horcajada, 2020). In this way, such sustainable approach of using one kind of waste to control/minimise the bad effect of another kind of waste may help to mitigate the environmental issues.

Water pollution in India is a significant environmental issue that affects human health as well as country's ecosystems. In India with 1,95,813 habitations in the country reported to have poor water quality due to extensive water contamination causing serious health problems and nearly half a million or more deaths were caused by water pollution. Numerous types of wastewater generated are reported to contain a wide range of contaminants and noxious wastes, including inorganic anions, heavy metals, dyes, detergents, phenols, humus substances, other persistent organic pollutants, bacteria, and viruses, among others (Schweitzer and Noblet, 2018). Contaminated water resources may lead to the rise of a global water crisis. Recycling and reusing the treated waste water was found to be inevitable step to confront the situation of water scarcity (FAO and UN-Water, 2024). Novelty of this research includes first time extraction of nano cellulose from watermelon peel waste and till date, no research work is published which has used metal-organic framework based nano cellulose/nano silver hybrid nano composites for water remediation application. This study is stepping stone in implementing circular sustainable economy using 3R's approach (Reduce, Recycle, Reuse) towards clean environment (Kohli and Gourav, 2024) as nano cellulose source chosen here natural waste (watermelon peel waste) reduces this solid waste from environment, recycle peel waste into value added product like nano cellulose and reuse of waste derived nano cellulose for water remediation.

Materials and Methods

Materials

Watermelon peels and *Nyctanthus arbour tristis* (harsingar) leaves were collected from local domestic sites and textile effluent for adsorption study of heavy metals is collected from local industrial area of Jodhpur, Rajasthan. All other chemicals used were of high purity, analytical grade and of standard make. Water used is double distilled water while Whatman filter paper is used for all filtration.

Extraction of Nanoellulose (CNC) from watermelon peel waste (WPW)

Nanocellulose production follows two crucial steps- (i) step-1: Chemical Pre-treatment and (ii) step-2: mechano-chemical treatment.

Step-1: Chemical pre-treatment to isolate cellulose from WPW

The pre-treatment step is necessary for taking out ashes, waxes, and noncellulosic compounds in order to isolate pure cellulosic products. It is investigated that on applying multi-stage chemical treatment using acid and base to remove pectin and hemicellulose and using oxygen and peroxide compounds as delignifing agents, allowed the safe removal of lignin and other non-cellulosic components without degradation of the cellulose, pure cellulose fibres are obtained (Hu and Ragauskas, 2012). Fractioning process of cellulose is presented via flow chart in Figure 1.

The resulting white residue indicates isolation of pure cellulose, which was washed several times with hot distilled water until a neutral pH of the filtrate was obtained. Collected cellulose is dried in oven for 20 minutes at 60 °C to carry out further defibrillation and its characterization.

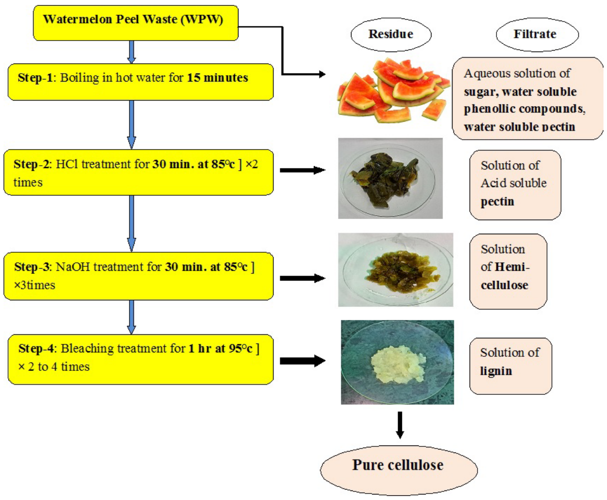

Fig. 1. Flow chart of chemical pre-treatment to isolate cellulose

Step-2: Chemical and mechanical treatment to defibrillate cellulose fiber into nanocellulose

Step-2 is used to extract nanocellulose from pre-treated cellulose fibres. The nano cellulose fibrils may be isolated from the natural waste using chemical and mechanical methods which expose the pulp to high shear forces, ripping the larger wood-fibres apart into nano fibers. Most commonly used chemical treatment in step-2 is acid hydrolysis with sulphuric acid or hydrochloric acid (Kumar, Negi, Choudhary, & Bhardwaj, 2020). Various Chemical treatments are described earlier and mechanical treatments such as high-pressure homogenization, Micro fluidization, micro-grinding, high-intensity Ultrasonication, electrospinning, cryocrushing and steam explosion can be employed. Generally acid hydrolysis process is used to isolate crystalline part of cellulose from amorphous domain and ultrasonication process is used to enhance defibrillation of cellulose into nano cellulose (Chen *et al.*, 2011).

The isolated cellulose from WPW was used to prepare cellulose nano crystals (CNCs) using 60%(w/v) H_2SO_4 during acid hydrolysis followed by Ultrasonication as shown in Fig. 2. 5g of preserved WPW cellulose was suspended in 100 ml of pre-heated 60 wt. % H_2SO_4 solutions, and continuously stirred for 45 min at 45 °C. The reaction was stopped by adding 100 ml of cold distilled water. Excess H_2SO_4 from the hydrolysed WPW nano cellulose suspension was removed by several washings

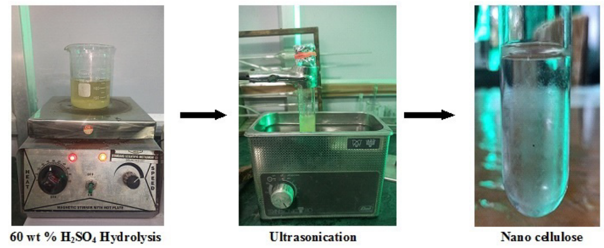

Fig. 2. Extraction of Nano cellulose Crystals

using distilled water. The pH of CNCs suspension was adjusted to 7 using 10% aqueous solution of sodium bicarbonate. Finally, 5% (w/v) CNCs suspension was prepared and then sonicated at 20 Hz for 30 min. These prepared watermelon peel waste derived CNCs suspensions (WNC) were kept at 4 ºC for further characterization.

Development of Metal-organic framework based hybrid nano composites

Step-1: Green synthesis of silver nanoparticles (AgNPs)

Biological method is most trending, feasible, eco-friendly, and sustainable green method among others, it involves natural resource extract such as leaf extract, bark extract, flower extract, fruit extract etc (Borase *et al.*, 2014). In recent study, we have used leaf extract of *Nyctanthus arbour tristis* (Harsingar plant) as reducing agent in biological method to prepare silver nanoparticles (AgNPs).

Take some harshingar leaves and rinse with distilled water then make paste in pestle-mortar. Paste is transferred in round bottom flask, also add 60 ml distilled water in it and allow refluxing for 30 minutes at 40-60 ºC. After 30 minutes it is allowed to cool and filtered, obtained filtrate is leaf extract. Now we make 0.001M silver nitrate ($AgNO_3$) solution which was stored in dark brown coloured amber bottle to avoid light effect. The mechanism of formation of AgNPs involves (i) chemical reduction process where silver ion reduced to zero oxidation state silver, (ii) nucleation step- generate AgNPs by adhesion of some zero valent silver. Here, in the first step we add $AgNO_3$ and leaf extract (as a natural reductant) in 1:1 ratio for biological reduction, change in colour of $AgNO_3$ solution from colourless to dark brown is observed which shows formation of AgNPs.

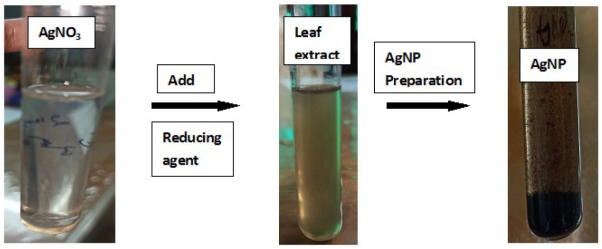

Fig. 3. Green synthesis of nano silver particles (AgNPs)

Sstep-2: Preparation of Hybrid nanocellulose/ AgNPs composites

AgNPs are generally prepared by the reduction of $AgNO_3$ and stabilizing it with capping agents to minimize the aggregation of nanoparticles. Thus, Nano cellulose can be used as a capping agent which is environmentally friendly method to immobilize and stabilize AgNPs in aqueous solutions (Kaushik and Moores, 2016)**.** The presence of a large surface area and a highly reactive primary OH group on the surface of nano cellulose is believed to play an essential role in the synthesis and capping of inorganic nanoparticles. Most common method of simple blending or immersing cellulose nano crystals (CNC) into previously prepared AgNPs solution is used for nano composites preparation (Musino, Rivard, Landrot, Novales, Rabilloud and Capron, 2021), (Suman *et al*., 2014). Ex-situ simple blending is easy to apply but to make homogenous mixture; continuous stirring is required (Sarkar *et al*., 2012). In this study, equal amount of both nanocellulose and silver nanoparticles were blend together for 45-60 minutes with continuous stirring. We obtain homogenous hybrid nano composite suspension after 45 minutes of contact time (Figure 4 &5).

Sample Preparation for Adsorption Study

Preparation of standard stock solution of heavy metals and dye

Preparation of $CuSO_4$ solution

To make 1000 ppm of copper sulphate solution 3.92 g $CuSO_4.5H_2O$ is added in 1000 ml distilled water at pH 4-5. Blue colour solution is prepared.

Preparation of $Pb(NO_3)_2$ solution

To make 1000 ppm of lead nitrate solution we add

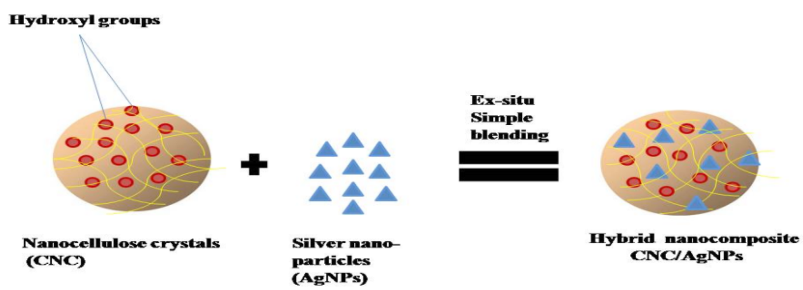

Fig. 4. Schematic Ex-situ synthesis of CNC/AgNPs hybrid nano composites

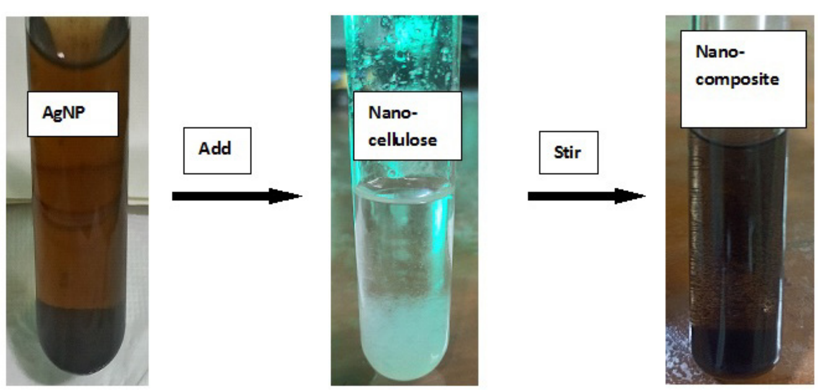

Fig. 5. Hybrid Nano cellulose/ nano silver composite formation

1.6 g of $Pb(NO_3)_2$ in 1000 ml distilled water at pH 6. White coloured solution is prepared.

Preparation of $CdCl_2$ solution

1000 ppm of cadmium chloride solution is prepared by adding 1.63 g of $CdCl_2$ in 1000 ml distilled water at pH 4-5. Colourless solution is obtained.

Collection of Textile sample containing heavy metals

Industrial effluent sample of textile factory is collected from Sangaria industrial area of Jodhpur. This textile effluent contains heavy metals like Pb, Cd, Cu, Ni, Zn, Fe etc

Batch Adsorption Study Experiments

Adsorption of Cu^{+2} by WNC/AgNPs Nanocomposite

Take 50 ml of 1000 ppm $CuSO_4$ solution in beaker then add 20 ml of watermelon peel waste derived nanocellulose/ nano silver particles (WNC/AgNPs) hybrid nano composite adsorbent in it and allow stirring for 45 minutes at room temperature and filtering with whatman filter paper. Change in colour of solution from blue to light blue is observed. It means adsorption takes place.

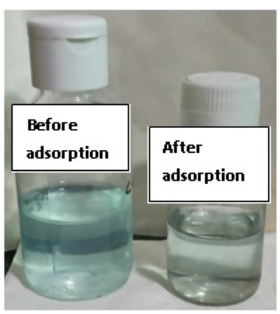

Fig. 6. Colour of $CuSO_4$ solution before and after Adsorption

Adsorption of Cd^{+2} by WNC/AgNPs Nanocomposite

Take 50 ml of 1000 ppm $CdCl_2$ solution in beaker then add 20 ml of WNC/AgNPs hybrid nano composites suspension (as an adsorbent) in it and allow stirring for 45 minutes at room temperature. No colour change can be seen as $CdCl_2$ solution is colourless.

Adsorption of Pb^{+2} by WNC/AgNPs Nanocomposite

Take 50 ml of 1000 ppm $Pb(NO_3)_2$ solution in beaker then add 20 ml of hybrid WNC/AgNPs nano composites suspension in it and allow stirring for 45 minutes at room temperature. No colour change is observed as $PbNO_3$ is colourless solution.

Adsorption of contaminants (Cu^{+2}, Cd^{+2}, Pb^{+2}) from Textile Sample

Take 50 ml of textile effluent in the beaker then add 20 ml of hybrid WNC/AgNPs nano composites suspension in it and allow stirring for 45 minutes at room temperature then filter it and filtrate is labelled as TSW. Blue coloured solution becomes gray in colour indicating adsorption.

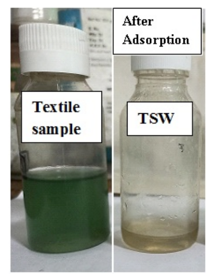

Fig. 7. Colour of Textile Sample before and after Adsorption

Characterization Techniques

Fourier Transform Infrared Spectroscopy (FTIR)

Information regarding chemical structure and structural composition of cellulose and other fractions of watermelon peel waste and WNCs derived from WPW can be obtained from FTIR instrumental analysis. The samples were loaded on KBr discs, and spectral signals were recorded from two wave number ranges from 600–4000 cm^{-1} and from 200-650 cm^{-1} with an average of 32 scans at a resolution of 8 cm^{-1} using Cary 630 spectrometer (Agilant Technologies, USA), and the obtained spectra were smoothened using software Agilant Micro Lab. FTIR spectra of samples collected at different steps are merged with the help of Origin software.

Field Emission Scanning Electron Microscopy (FESEM)

The surface morphology of the raw waste, cellulose, nano cellulose and composites were analyzed using a scanning electron microscope (Novo Nano FESEM 450 (FEI)). Raw WPW in powder form is used whereas cellulose and nano cellulose as dried film is used for sampling. All the samples were placed on aluminium stub using carbon tape and gold-coated using a vacuum sputter coater (Quorum Q150T ES) prior to FESEM analysis, and all the images were taken at specific magnifications based on better visibility.

Powder X-ray Diffraction (XRD)

XRD studies helps to know the structural changes of WNCs prepared from WPW. The crystal size, and crystallinity index (CI) were estimated from the spectra given by XRD (Panalytical X-pert Pro) equipped with Cu-Kα radiation unit *(λ=1.54060 Å)* operated at a voltage of 30 kV, and current of 10 mA. The dried samples were mounted on the quartz substrate, and scans were collected in 2θ° range of 10°-50° at a scanning speed of 2°/min. XRD analysis were carried out in duplicate for each material. The diffraction peaks were smoothened and analyzed using Origin Pro 8.5.0 (Origin Lab Corporation, USA) software. The Crystalline Index (CI) was calculated using the equation (1), given by Segal *et al.*

$$CI\ P\%\ (I_{200} - I_{AM}) / I_{200} \quad .. \quad (1)$$

Where, I_{200} is the height of the 200 peak (at 2λ of 22.5°) and I_{AM} is the minimum height (plateau) between the 200 and 110 peaks (at 2λ of 15.5°). The Scherrer equation (eq-2) was used to calculate the crystal size t (nm) of cellulose-I structure in respect of (200) plane:

$$Crystal\ size(t) = \frac{k\lambda}{\beta 1/2\ cos\theta} \quad .. \quad (2)$$

Where, K is the correction factor and usually taken to be 0.91, θ is the radiation wavelength, λ is the diffraction angle, and $\beta_{1/2}$ is the corrected angular width (in radians) at half maximum intensity.

Atomic Absorption Spectrophotometer (AAS)

The quantitative determination of heavy metal ions in textile effluent was determined using the absorption of light by free atom in gaseous state with atomic absorption spectrophotometer instrument, ECIL Flame-AAS instrument.

Results and Discussion

FTIR Analysis of Watermelon Peel Waste (WPW)

The FT-IR spectra of raw fiber, HCl treated fiber, NaOH treated fiber, cellulose fiber, and Nano cellulose fiber (NC) from watermelon peel waste, is compared respectively from 4000 to 500cm^{-1} wavenumber range in respect to changes occur in fibre's structural components during chemical pretreatment and acid hydrolysis process, as shown in Figure- 8.

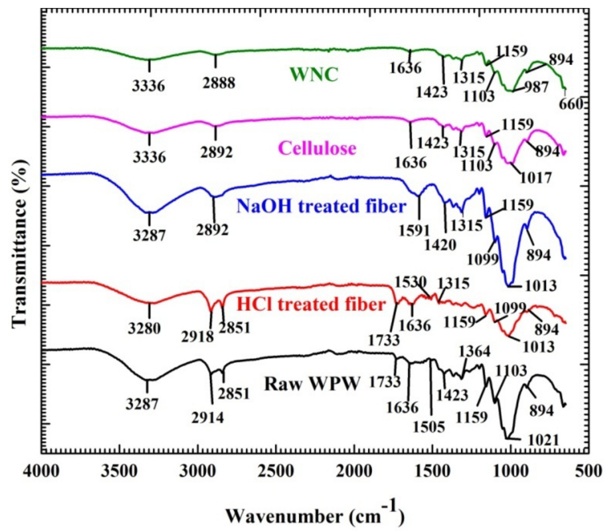

Fig. 8. FTIR Spectra of Watermelon Peel Waste (WPW)

FTIR spectra were obtained to recognize the functional groups present on the WPW surface. FTIR spectrum profiles of raw WPW broadly confirm the presence of pectin, hemicellulose, lignin, cellulose, phenol, carboxylic acid, alcohol, alkanes, alkyl halide, amines, and amino acids. After Hydrochloric acid treatment on raw WPW, specific peak of pectin, 2914 cm^{-1} is removed. After NaOH treatment, hemicellulose is removed along with remaining pectic polysaccharides. It is confirmed by absence of 1733, 1505, 1530 and 2918 cm^{-1} peak in WPW. After alkaline treatment, in delignification process all lignin content is removed as specific peak of lignin 1591 cm^{-1} is absent and pure cellulose is isolated. Spectrum of isolated celluloses showed characteristic bands at 1017 cm^{-1} and 894 cm^{-1} assigned to C–O stretching vibration and the glycosidic-C_1 H deformation, respectively. The stretching absorption band centred at 3280-3336 cm^{-1} represents the OH or NH group in a WPW. The band observed at around 2892 cm^{-1} is assigned to stretching vibrations of $-CH_3$ or $-CH_2$ groups in carboxylic acid and its bending vibration is observed at around 1364 cm^{-1}. The spectral band observed in the region 1636 cm^{-1} are due to the O–H bending due to adsorbed water, 1423 cm^{-1} is due tosCH_2 scissoring motion in cellulose), 1364 cm-1 (C-H bending), 1336 cm^{-1} (O-H in plane bending), 1315 cm^{-1} (CH_2 wagging), 987-1021 cm^{-1} (C–O–C pyranose ring stretching vibration), 894 cm^{-1} (associated with the cellulosic β-glycosidic linkages), <"1159 cm^{-1} (C–C ring stretching band), and at 1103 cm^{-1} (the C–O–C glycosidic ether band). The peaks at 1159 cm^{-1} and 894 cm^{-1} in cellulose microfibers from WPW indicated an increase in the cellulose components after removal of lignin, and hemicelluloses by chemical treatments. WPW derived nano cellulose (WNC) has spectral band at 660 cm^{-1} indicating crystal nature of WPW cellulose and WNC (Naduparambath *et al.*, 2018).

FESEM Analysis of Raw watermelon Peel Waste, WPW derived cellulose and Nanocellulose

The raw WPW in Figure-9(a) appeared as sea sponge or flowers and flakes like structure with smooth surface and not having particular shape due to presence of lignin, hemicelluloses, pectin, waxes, and other extractives. Dimension of raw WPW is around 10-20 µm. After (HCl) acid treatment, the flakes structure of raw fiber was completely disturbed and smooth surface became rough. The alkali-treated fiber revealed that the NaOH treatment caused partial removal of non-cellulosic component i.e. hemicellulose from the raw WPW. During the delignification step, NaOCl will remove almost all the residual lignin, thereby separated them into individual cellulose microfibers (Prasanna and Mitra, 2020). These obtained individual cellulose microfibers had dimension of 29-50 nm (Figure-9b). These obtained individual cellulose microfibers contained bundles of WNCs, interconnected by amorphous and crystalline regions along the microfibers. During the sulfuric acid hydrolysis (60%) and ultrasonication treatment for WNCs, β-1,4-glucopyranose linkage was broken, and the amorphous regions of cellulose were destructed and thereby the considerable size reduction seen in individual nano sized crystals having dimension of 5-15 nm in a very dense web like network as shown in Figure-9c. It is found from FESEM analysis that nanocellulose has porous traps and having fibrous web-like network with rough morphology which may be helpful for nanocomposite formation and adsorption application.

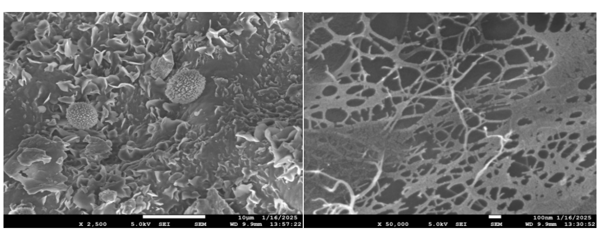

Fig. 9(a). Raw WPW **Fig. 9(b).** WPW Cellulose After delignification

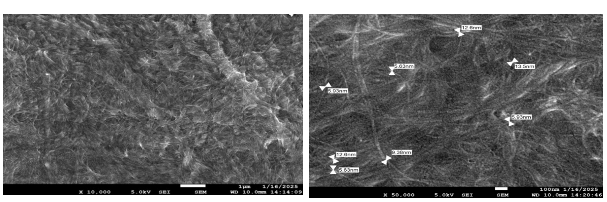

Fig. 9(c). WNC After acid hydrolysis and Ultrasonication

Fig. 9. FESEM micrographs of (a) Raw WPW (b) WPW derived cellulose (c) WNC (WPW derived nano cellulose)

X-Ray Diffraction (XRD) Analysis: Degree of Crystallinity of WPW derived Nanocellulose

XRD analysis is carried out to know the nature of obtained nano cellulose that means crystalline and amorphous nature. Nano cellulose exhibited crystalline peaks at 12.5°, 15.5°, 22.5°, 24° and 32° that is associated with typical structure of α-cellulose or cellulose-I type. In Nano cellulose, the main sharp peak at 22.5° correspond to the distance between hydrogen-bonds in cellulose I and the other broad peak at 15.5° corresponds to the convoluted peak from I_{α} and the third smallest peak at ~32° or 34° corresponds to 1/4 of the length of one cellobiose unit ordered along the fiber direction (French, 2013). The Nano cellulose crystals exhibit characteristic assignments of 1-10, 110, 200, and 004 planes along 2θ angles 12.5°, 15.5°, 22.5°, and 32° respectively. The XRD peaks of WNC with cellulose I_{β} pattern miller indices can be seen in Figure 10.

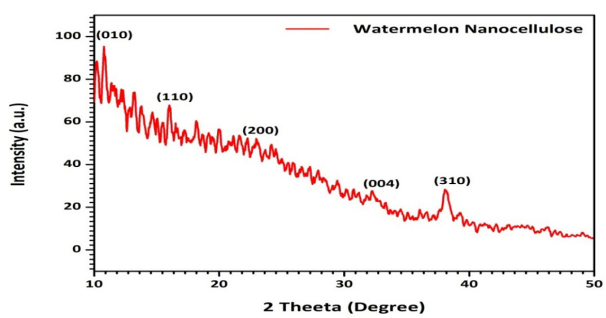

Fig. 10. X-Ray Diffract gram of Waste derive nano cellulose Crystals (WNC)

Small shoulders at 38° peak (310) in WNC are due to amorphous reflections. Peak at 10.81° (010) in WNC is due to α-cellulose crystalline peaks. The crystallinity index WNCs was obtained as 61.59%, determined by equation-(1) shows crystalline nature of nanocellulose crystals. Natural waste derived Nano cellulose has a well pronounced crystalline structure, due to hydrogen bonding and Vander Waals interactions, existing between adjacent cellulose molecules. Average crystal size of WNC is found to be 22.21 nm determined by equation – (2) that means in the range of 1-100 nm confirming nano crystal formation not nanofibers.

$$\text{CI P\% } (I_{200} - I_{AM}) / I_{200} \quad \text{.. (1)}$$

$$\text{Crystal size (t)} = \frac{k\lambda}{\beta 1/2 \cos t} \quad \text{... (2)}$$

From various research studies, we get to know that the crystalline values of nano cellulose are mostly dependent on the data evaluation procedure of measurement, pre-treatment used for cellulose isolation, duration of acid hydrolysis process, and source of raw materials. Calculated XRD spectrum parameters (using Origin Pro 8.5.0 software) are shown below in Table 2.

Adsorption study of Hybrid Watermelon Nano cellulose /Silver nano composites (WNC/AgNPs) in removal of heavy metal ions

Water pollution in India is a significant environment issue that affects human health as well as country's ecosystem (leading to scarcity of potable water). Hazardous contaminants enter into water through Textile, dyes & manufacturing industries, pharmacological waste, power plant effluents etc. The industrial effluents are reported to contain a wide range of contaminants including inorganic anions, heavy metals, dyes, detergents, phenols, humus substances, other persistent organic pollutants, bacteria, and viruses. Heavy metals are toxic elements at low concentration having density greater than 5g per cubic. These include platinum & zinc group of periodic table (like Ni^{+2}, Pt^{+2} , Zn^{+2}, Cd^{+2}, Hg^{+2}), mineral acid, inorganic salt, and trace elements like Cu^{+2}, Pb^{+2}, As^{+2}, Cr^{+2}, Fe^{+2} etc. Heavy metals like Chromium, Cadmium, Lead, Copper, and Nickel are frequently used in the textile industry, primarily for producing pigments in dyes. The release of these metals into water bodies from textile wastewater is a significant source of pollution. Cadmium and Lead are classified as carcinogens whereas copper can accumulate in the body's organs and cause serious health problems. Adsorption is one of the best methods used for water remediation due to its low cost, high capacity, and ability to remove chemical impurities in high concentrations. Nowadays, advances in adsorbent formation are in trend because it is the simplest and fastest removal method**.** Recent developments in water purifying adsorbents increases use of hybrid inorganic-organic (Abouzeid *et al*., 2019) or metal-organic framework (Mon *et al*., 2018) like nano cellulose/silver nano hybrid nano composites (Yu *et al*., 2020) to increase surface area of adsorption and efficiency of adsorption by overall removal of impurities whether it is chemical or biological

AAS Analysis of Laboratory prepared Standard Metal ion Sample

In present study, Adsorption behaviour of WNC/AgNPs nano composites towards Pb^{+2}, Cd^{+2} and Cu^{+2} present in standard solution (prepared in lab at room temperature), is studied using single metal ion concentration, each having initial concentration of 1000 ppm. Results are calculated by ECIL Atomic Absorption Spectrophotometer at wavelength 214.7 nm, 228.9 nm and 321.9 nm for Pb^{+2}, Cd^{+2} and Cu^{+2} respectively are shown below in Table 3.

20 ml of nano composites suspension and 50 ml of 1000 ppm standard heavy metal solution is taken in each metal ion adsorption study, at room temperature. Optimized pH for each adsorption experiment is maintained at 8. Heavy metal removal effi-

Table 2. Calculated XRD Parameters of Waste derived Nanocellulose

Nano cellulose source	Crystalline peaks 2θ	FWHM or β	Crystallite size (nm)	Average crystal size (nm)	Crystalline Index or % Crystallinity
WNC	10.81	0.2103	**39.64**	**22.21**	**61.59**
	16.02	0.2379	**35.23**		
	22.96	0.4817	**17.58**		
	32.17	1.5832	**5.46**		
	38.12	0.6687	**13.14**		

ciency or % adsorption is calculated using equation (3).

% Adsorption or % removal efficiency = $(C_o–C_f)/C_o \times 100$ .. (3)

In which, C_o and C_f are the metal ions initial concentration (mg/l) and final concentration (mg/L) respectively. According to Table 3, maximum adsorption of lead (77.8) followed by copper (74.55) then Cadmium (38.45 %), is discovered.

AAS Analysis of Textile Sample (TSW)

Adsorption behaviour of WNC/AgNPs nano composites towards Pb^{+2}, Cd^{+2} and Cu^{+2} present in textile sample (TSW) at room temperature, is studied using industrial effluent having all heavy metals in particular amount. Results are calculated by ECIL Atomic Absorption Spectrophotometer at wavelength 214.7 nm, 228.9 nm and 321.9 nm for Pb^{+2}, Cd^{+2} and Cu^{+2} respectively are shown below in Table 4.

20 ml of nano composites suspension and 50 ml of textile sample (TSW) is taken in each metal ion adsorption study, at room temperature. Optimized pH for each adsorption experiment is maintained at 8. Heavy metal removal efficiency or % adsorption is calculated using equation (3). According to table-4, maximum adsorption of Lead (89.68%), followed by copper (88.04%) then cadmium (35.44 %) is discovered.

AAS analysis of both standard metal ion sample and textile sample gave similar results for Hybrid WNC/AgNP nano composites which follow trend of uptake of metal ions as follows-

Adsorption capacity of WNC/AgNPs Nanocomposite: Pb^{+2}> Cu^{+2}> Cd^{+}

FESEM Analysis of WNC/AgNPs Nanocomposite

Figure 11 illustrates morphology of adsorbent (WNC/AgNPs) before heavy metal ion adsorption where square shaped silver nanoparticles adhere to rough and porous surface of nano cellulose which is helpful for adsorption. Figure 12 represents porous structure of nano cellulose filled with nano sized round shaped heavy metal ions due to adsorption. It is clearly observed that the metal ions aggregated

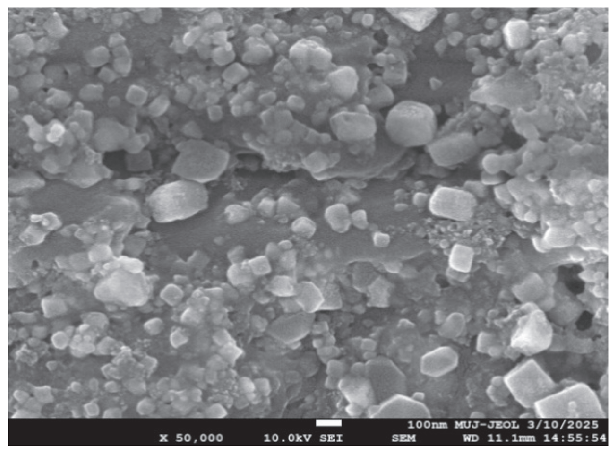

Fig. 11. FESEM micrograph of WNC/AgNPs before Adsorption

Table 3. % Removal efficiency of heavy metal ions from Standard samples using WNC/AgNPs nano composites

Adsorption Behaviour of WNC/AgNPs			
Standard solution of heavy metal ions	Initial Concentration of heavy metal ions (mg/L)	Final Concentration of heavy metal ions after adsorption (mg/L)	Heavy metal Removal efficiency (%)
$PbNO_3$	1000	222	77.8
$CdCl_2$	1000	615.5	38.45
$CuSO_4$	1000	254.5	74.55

Table 4. % Removal efficiency of heavy metal ions from Textile sample (TSW) using WNC/AgNPs nano composites

	Adsorption Behaviour of WNC/AgNPs		
Textile sample containing heavy metal ions (TSW)	Initial Concentration of heavy metal ions (mg/L)	Final Concentration of heavy metal ions after adsorption (mg/L)	Heavy metal Removal efficiency (%)
Pb^{+2}	1.706	0.176	89.68
Cd^{+2}	0.237	0.153	35.44
Cu^{+2}	0.276	0.033	88.04

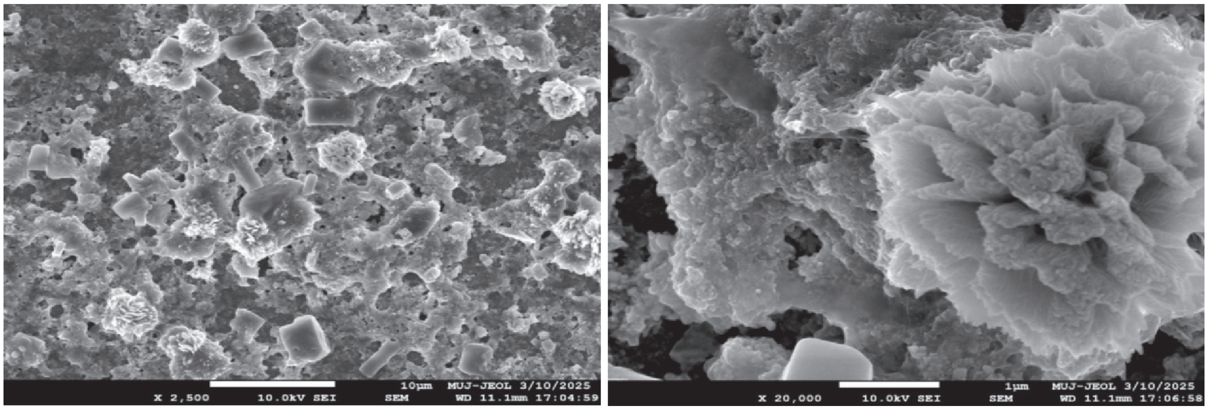

Fig. 12. FESEM micrographs of WNC/AgNPs (after Adsorption) at different magnification

Table 5. EDX data of Hybrid Nanocomposite WNC/AgNPs after Adsorption

Element	Weight %	Atomic %
C K	25.1	39.1
O K	43.4	50.8
Si K	9.7	6.5
S K	0.3	0.2
Cu L	3.3	1.0
Ag L	10.6	1.8
Cd L	0.3	0.1
Pb M	7.3	0.7

over the nano composite surface and rough morphology of cellulose nano flowers is observed which confirms the adhesion of metal ions after adsorption process.

EDX spectrum (Figure 13) depicts peaks of Pb, Cd and Cu, confirms adsorption of these heavy metal ions on surface of hybrid nano composite. Along with heavy metal ions, EDX analysis also confirms presence of peaks of C & O from nano cellulose structure, Si peak of glass slide (used for sampling), and Peak of Ag for AgNPs. Table 5 reveals % weight composition of developed hybrid nano composites WNC/AgNPs after adsorption of heavy metals from textile sample. EDX data also confirms maximum weight % of Lead among other heavy metals is adsorbed on surface of hybrid nano composite WNC/AgNPs.

Conclusion

Production of cellulose nano crystals (NCs) from watermelon peels has been studied for the first time, and characterized to get better insight into their nanostructure and crystalline nature. FTIR characterization proved isolation of pure cellulose and removal of all non-cellulosic components present in raw fiber. XRD also confirms presence of characteristics peaks of cellulose only and all peaks indicated

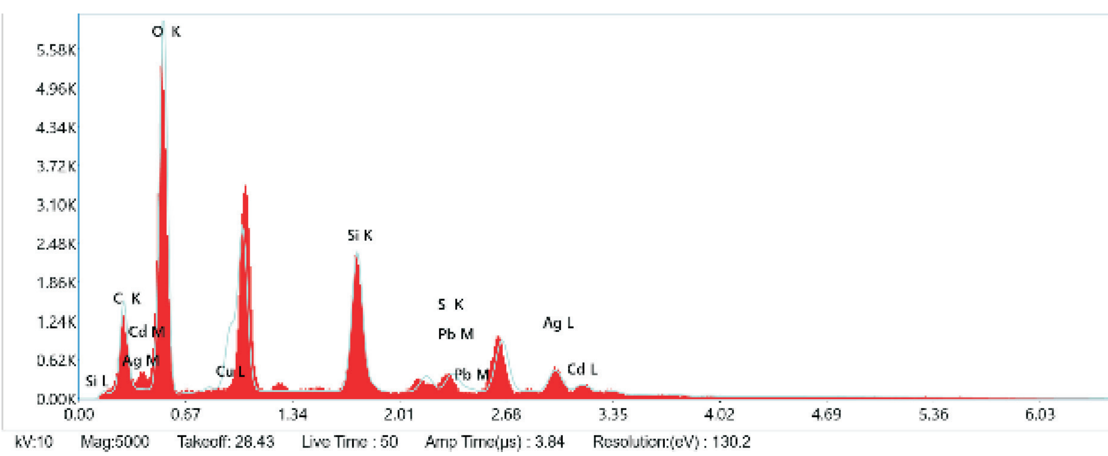

Fig. 13. EDX Spectrum of WNC/AgNPs after Adsorption

presence of Cellulose I structure. XRD study revealed that WNC showed crystallinity index value 61.59 % and crystal size of 22.21 nm. FESEM analysis study is giving insight into morphology of nano cellulose produced from watermelon peel waste. The WNC were agglomerated but clearly seen 'nano flower-shaped' forming web like network having dimension in range of 5-15 nm and length of 100 to 500 nm. It is found from FESEM analysis that nano cellulose has porous traps and showing fibrous web-like network with rough morphology which will be helpful for nano composite formation and adsorption application.

In general, Cellulose to nano cellulose transformation requires costly and energy consuming chemical and mechanical treatments on industrial scale production. But, this study confirms that cost-effective, mild chemical and less energy consuming ultrasonication treatment is enough for production of nano cellulose because cellulose obtained herein is already in nano dimensions. Applications of nano cellulose in environmental remediation have recently aroused much attention with great potential at large scale industrial level, as a new generation of nano structured adsorbents from renewable resources. However, in nano cellulose-based adsorbents, the surface functionalization is a key step to promote the adsorption of a specific class of contaminant and enhance the adsorption efficiency. To this end, nano cellulose/ nano silver hybrid nano composites (WNC/AgNPs) is developed by ex-situ simple bending for heavy metal adsorption from textile effluent. Result analysis from FESEM confirmed the presence of uniformly distributed square shaped AgNPs on surface of nano cellulose. XRD analysis showed addition of 1 extra peak characteristic to AgNPs at 38.1°. Thus, both results were signalling towards successful fabrication of hybrid nano composites. In present study, adsorption efficiency hybrid nano composites towards removal of heavy metals like Pb^{+2}, Cd^{+2}, Cu^{+2} present in standard as well in textile effluent is evaluated by AAS. High Adsorption efficiency or % removal of Pb^{+2}, Cu^{+2}, Cd^{+2}, by WNC/AgNPs nano adsorbent from textile effluent is observed which is 89.68, 88.04, 35.44 respectively. Lead and cadmium efficiently removed from textile effluent with this nano material. FESEM and EDX data confirms the presence of aggregation of heavy metal ion on the surface of nano composites after adsorption and their particular peak in EDX. Desirable results of % removal of all heavy metals at high initial concentration of 1000 ppm is due to increased surface area of adsorbent by synergistic effect of nano cellulose and nano silver which increases availability of OH^- groups on surface for interaction with contaminants.

This research is based on research work which is mitigating dual problem with one nano material and implementing circular sustainable economy using 3R's approach (Reduce, Recycle, Reuse) towards cleaner environment. That means, source of nanomaterials used in this study are fruit peel waste which is low cost, natural, biodegradable, non-toxic, easily available at residence & juice shops as domestic and municipal solid waste and using them to prepare novel nanomaterials leads to mitigating the problem of solid waste management. Another major problem is water pollution led by textile industries; they discharge industrial effluents (containing heavy metals and dye) in water bodies and make water unfit for drinking purpose. Now days, availability of drinking water is at verge. Therefore, nanomaterials synthesised herein is applied for removal of heavy metals to purify waste water or industrial effluent, mitigating problem of water pollution. Excellent potential of WNC/AgNPs hybrid nano composites towards water purification application is successfully explored in this study. Till date, no research work is published which has used nano cellulose/nano silver hybrid nano composites for water remediation except one or two study and First time 1000 ppm of initial concentration of heavy metals is used with minimum concentration of adsorbent (hybrid nano composites) for adsorption study which paved way to use this nano composites for water remediation of highly contaminated water.

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Declaration

Competing Interest
The authors have no relevant financial or non-financial interests to disclose.

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