Synthesis of nanocelluose from paper recycling based paper mill sludge

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Abstract

Paperboard mill results in the production of huge quantity of solid waste material, namely, the sludge. The volume and its high moisture content makes sludge difficult to handle, transport or store for a long duration. This paper has characterized the generated paperboard mill sludge and further used for synthesis of nanocellulose using 90% citric acid solution at 80^{o}C for a duration of 4 hours. The synthesized nanocellulose had a width of 13–25 nm and length of 450–490 nm, with a ζ-potential value of -29.5 mV. When compared to a commercially available microcrystalline cellulose sample, the thermal analysis exhibited better observation.

Keywords: Paperboard mill, sludge, waste management, nanocellulose

1. INTRODUCTION

Revolutionary increase in technological advancements and population has compelled in an exorbitant surge in the solid wastes generated from industries which try to meet the needs of the people (Karak *et al.,* 2012). Global municipal solid wastes production is anticipated to reach 2.2 billion tonnes annually by 2025.

The solid waste sludge from the primary and secondary effluents treatment is the primary by-product of the pulp and paper industry(Kamali & Khodaparast, 2015). At present, 44% of the waste that ends up from pulp and paper mills results in debris without an appropriate sustainable solution, with 35 per cent of that material becoming a waste and 56 per cent of that material being used for recuperation of energy. The disposal process at landfills is exorbitant and hazardous for the ecosystem. Therefore, identifying innovative options for utilising this sludge gains greater concern in the paper manufacturing industries. Alternatives to sludge treatment are being explored far and wide. The cardboard and paper products are primarily produced from wooden substrates, subsequently they consist of 40 to 80 percent cellulose, between 5 and 15 per cent hemicellulose, and only trace amounts of polyphenolic lignin (Nair *et al.,* 2018). Paper-based waste products are frequently recycled (approximately 2.4 times) (Zhang *et al.,* 2015), but during the recovery process, the fibres are reduced in size by mechanical weathering, leading to massive quantities of small fibres (approximately 40 per cent) (de Alda, 2008), known as repurposed paper sludge. Global municipal solid waste is anticipated to reach 2.2 billion tonnes yearly by 2025 (Moya *et al.,* 2017) and 4 billion tonnes by 2100 (Pour *et al.,* 2018).

The pulp and paper mills have been reported to produce 100 tonnes of sludge for a quantity of 550 tonnes of beneficial pulp produced. Although pulp and paper wastes may not be unsafe, appropriate techniques for disposal are nevertheless necessary for managing the land, the environment, and related issues (Monte *et al.,* 2009). Through waste recovery, the sludge can be employed for managing industrial wastes as a resource, thereby reducing the irreversible damage that waste causes to the ecosystem and human health while producing alternatives to landfilling (Diamantis *et al.,* 2013).

The Indian Paper Manufacturers Association (IPMA) has reported that the size of the Indian Paper and Paperboard market is 16.1 million tonnes in 2019. In India, the demand for packaging paper board segment is expected to grow at a CAGR of 8.9 per cent, and it may reach upto11.1 million tonnes in fiscal year 2020-2021. In India, there are more than 600 pulp and paper factories with 8.5 million tonnes yearly output capacity. Furthermore, according to (Velusamy *et al.,* 2016), an average of 300 m^3 of water was utilised to make one tonne of paper.

The Indian Tobacco Company - Paper boards and Specialty Paper Division (ITC-PSPD) situated at the foothills of Western Ghats at Thekkampatti village, Mettupalayam Taluk, Coimbatore, Tamil Nadu, is a leader in the production of high-quality duplex paperboard from waste papers. The factory has a daily production output of about 300 kilo tonnes of duplex board and uses about 8 metric litres of water. Each day, the factory releases between 2400 and 2600 litres of effluent and 15 to 20 tonnes of sludge. This paper focusses on the viable and sustainable options available for the safe handling of the huge quantities of sludge.

The optimum procedure to generate nanocellulose is by breaking down sources of cellulose, like plants, wood, tunicate, and algae, by employing mechanical or chemical methods to create cellulose nanofibres (CNFs), or using acidic medium hydrolysis to generate cellulose nanocrystals (CNCs) (Adu *et al.*, 2018). The production of materials such as thin films for food packaging, nanocomposites, biomedicines using drug delivery systems and artificial implants, acoustics, cosmetics, hygiene products, water-treatment, and smart materials can all benefit from the utilization of nanocellulose as essential building blocks (Bharimalla *et al.*, 2015).

2. MATERIALS AND METHODS

2.1. Characterization of paperboard mill sludge:

The analyses of the primary sludge collected from the effluent treatment plant of the paperboard mill was subsequently dried in shade, passed through a 2 mm sized nylon mesh sieve, and packed into polythene bags for storage. The physico-chemical properties of the sludge was studied using standardized methodologies as detailed in the table 1.

Table 1. Methodology for physico-chemical analysis of paperboard mill sludge

Sl. No.	Particulars	Unit	Remarks	Reference
1.	pH	-	Sample: water suspension of 1:2.5	(Jackson, 1973)
2.	EC	dS m^{-1}	Sample: water suspension of 1:2.5	(Jackson, 1973)
3.	Bulk density	mg m^{-3}	Wet cylinder method	(Chopra & Kanwar, 1976)
4.	Particle density	mg m^{-3}	Wet cylinder method	(Chopra & Kanwar, 1976)
5.	Organic carbon	Per cent	Wet digestion	(Piper, 2019)

6.	Total N	Per cent	Diacid extract (5:2- H_2SO_4 : $HClO_4$)- semi automatic kjeldahl distillation method	(Jackson, 1973)
7.	Total P	Per cent	Triacid extract (9:2:1- HNO_3: H_2SO_4 : $HClO_4$) Vanadomolybdate yellow colour method	(Jackson, 1973)
8	Total K	Per cent	Triacid extract- neutralized with ammonia- Flame photometer	(Jackson, 1973)
9.	Total Ca and Mg	Per cent	Versenate titration method	(Jackson, 1973)
10.	Total Na	Per cent	Tri acid extract (flame photometer)	(Jackson, 1973)
11.	Organic carbon	Per cent	Chromic acid wet digestion method	(Walkley & Black, 1934)
12.	Total Fe, Mn, Zn, Cu	mg kg^{-1}	Atomic Absorption spectrophotometer (triple acid extract)	(Jackson, 1973)
13.	Total Cr	mg kg^{-1}	Atomic Absorption spectrophotometer (triple acid extract)	(United States. Environmental Protection Agency. Methods Development *et al.*, 1974)

2.2. Isolation of cellulose:

A combination of citric acid - hydrochloric acid hydrolysis technique was used in order to isolate the cellulose from the sludge. In a 250 mL Erlenmeyer flask, 3.0 g of sludge along with 90:10 of citric acid (135 mL, 3 M) and concentrated hydrochloric acid (15 mL) (on volume basis) across a range of reaction durations using a mechanical mixer (750 rpm) was used to produce the cellulose by hydrolysis. Here, 1 g of the sludge was allowed to react with 50 mL of citric:hydrochloric acid mixture at 80^{o}C for 2, 3, 4, 5 and 6 hours of duration. The resulting suspension was then recurrently centrifuged with the deionized water to the point it reached close to neutral pH after it reached ambient room temperature. The isolated celluloses were confirmed using FT-IR.

2.3. Synthesis and analysis of nanocellulose:

Cellulose obtained from hydrolysis was then subjected to ball milling using zirconia balls for reduction to desirable sizes that ultimately results in the production of nanocellulose (Fig. 1.). The morphology of the nanocellulose was confirmed using SEM (Quanta 250 - FEI, Hillsboro, OR, USA) that were sputter-coated (a coating of either gold or palladium on the sample) to avoid charging. The sample chamber of the ESEM (Environmental Scanning Electron Microscope) was mounted with powder sample dispersed on a double-sided conductive carbon tape that was fastened to the stub. The sample was ultrasonically treated for 30 minutes to determine the dimensions of the sludge-derived nanocellulose. Following this, 10 µL of the sample suspension was dropped on the copper grid structure of the TEM, which was then allowed to dry at room temperature and observed under TEM (FEI, Hillsboro, OR, USA) at a voltage gradient of 100 kV. Fourier Transform Infra-Red spectrometry (FTIR) was used along with a diamond-tipped ATR device (Shimadzu, Japan) at wave numbers of 4000 to 400cm^{-1}, the functional molecules prevalent in the nanocellulose were detected. Zeta potential analysis was carried out with 0.5 mg of sample was added to 20 ml of deionized water, and the resulting mixture was agitated using a mechanical shaker at 180 rpm for two hours. The solution was subjected to sonication that separated the particles into colloids, later on it was filtered using Whatman no. 42. Particle size analyzer (Horiba Scientific Nanopartica SZ-100, Japan) was used to derive the zeta potential from the supernatant of the filtered solution (Uçar *et al.*, 2015). Thermogravimetic analysis was done by employing a thermogravimetric analyzer (NETZSCH STA 449 F3 Jupiter, Selb, Germany). A platinum crucible containing 5 mg of nanocellulose was cautiously packed with the sample before being heated at temperatures ranging from 30 to 600 degrees Celsius. The rate of heating was held constant at 20 °C min^{-1} while nitrogen-rich atmosphere was maintained.

3. RESULTS AND DISCUSSION

The organic composition of agriculture based industrial wastes make them suitable for use in agriculture for improving the soil organic matter content. In addition to being nutrient-rich, the industrial sludge is organic which can beneficially enhance the chemical and physical properties of the soil, boosting plant ability to grow and thrive.

3.1. Paperboard mill sludge characterization

The major characteristics in a sample of paperboard mill sludge are provided in table 2. The sludge sample was observed to have a very moisture content of 79 per cent. The sludge was mechanically dewatered in a filter press to reduce the moisture content, for the ease of handling and transportation. It had neutral pH of 7.60 accompanied with an electrical conductivity of 1.65 dS m^{-1}. This conductivity level is well below the mark of 2.00 dS m^{-1}as prescribed by the Central Pollution Control Board. The nutrient content of the sludge was observed to have 4 per cent of total nitrogen content, 0.15 per cent of total phosphorus content and 0.05 per cent of total potassium content. The presence of these nutrients plays a vital role in metabolism of the microorganisms. The organic carbon content of the sludge sample was 33.50 per cent. Similar results were also reported by (Abdullah *et al.*, 2015). This implied that the C:N ratio of the sludge sample was 8.88, which can be improved by the inclusion of other agricultural wastes such as plant biomass, coconut husk, fronds, that are readily available in and around wastewater treatment plant. The calcium content was 1.26 per cent, magnesium at 0.54 per cent and sodium at 0.63 per cent, respectively. This could be due to the presence of calcium compounds such as calcium and magnesium carbonates which are generally used during process of paper finishing.

As for the heavy metals in the paperboard mill sludge, lead alone was observed to be present (78 mg kg^{-1}). And other heavy metals such as chromium, cadmium and nickel were below detectable levels. In general, the heavy metal concentration of pulpboard mill sludge is often low enough to justify constraints on the application rates to soil (Cabral & Vasconcelos, 1993).

Table 2. Characterization of paperboard mill sludge

S. No.	Parameter	Value
	Physical Parameters	
1.	Bulk Density (g cm^{-3})	2.00
2.	Particle Density (g cm^{-3})	3.25
	Physico-chemical Parameters	
3.	Moisture (per cent)	78.7
4.	pH	7.60
5.	EC (dS m^{-1})	0.65
6.	Ca (per cent)	1.26
7.	Mg (per cent)	0.54
8.	Na (per cent)	0.63
9.	Total Nutrients (per cent)	
	Nitrogen (N)	4.00
	Phosphorus (P)	0.15
	Potassium (K)	0.05
10.	Heavy metals (mg kg^{-1})	
	Chromium (Cr)	BDL

	Cadmium (Cd)	BDL
	Lead (Pb)	38
	Nickel (Ni)	BDL
11.	Compositional Analysis (per cent)	
	Lignin Content	23.18±0.1
	Cellulose	36.57±0.9
	Hemicellulose	16.25±0.5
	Ash	20.00±0.2
	Extractives	4.00±0.5

*Samples were analyzed under moist free basis
*Values represent an average of three values

3.2. Isolation of cellulose:

Generally, the cellulose extraction from lignocellulosic substrates is achieved by using strong acids such as sulphuric acid. It is worth mentioning here, that use of such strong acids further poses risk to the environment, because the decanted acid portion needs safe handling and disposal. Hence, the present study has been attempted to use citric acid, which is a weak acid compared to sulphuric acid – a strong mineral acid.

Cellulose was extracted from the paperboard mill sludge with citric acid (9:1 ratio) treatment through hydrolysis. Maximum cellulose yield of 65 per cent was observed in the process involving 80^{o}C for 4 hours duration. Citric acid derived celluloses were observed to have comparable with the observations of (Ruiz-Caldas *et al.,* 2023) which were derived from used cotton clothing.

3.3. Nanocellulose synthesis and characterization:

Celluloses isolated from the citric acid hydrolysis were down-sized using ball milling employing zirconia balls.

3.3.1. SEM Imaging:

The images of nanocellulose obtained after ball milling had the characteristic rod-like structure, with dimensions of 450-490 nm in length and 13-25 nm in breadth based on the SEM imaging (Fig.1a).

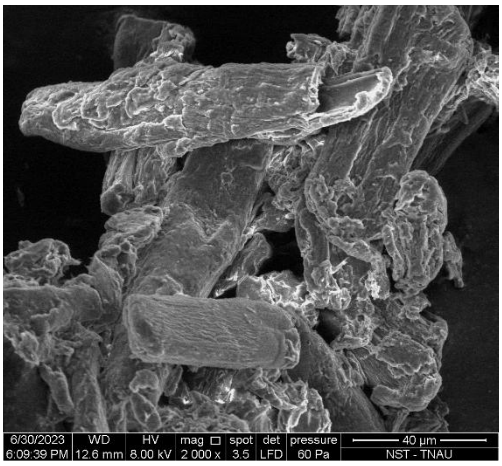

Fig. 1a. SEM image of nanocellulose

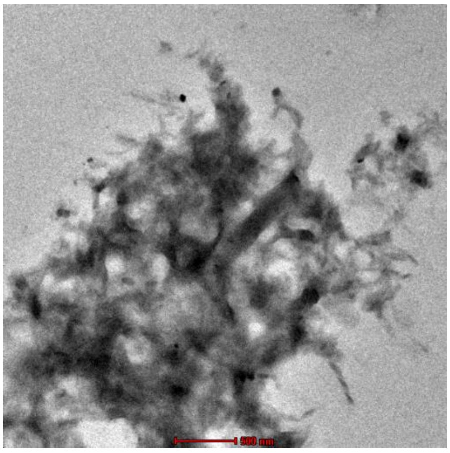

Fig. 1b. TEM image of nanocellulose

3.3.2. TEM Imaging:

As per the observations of the TEM image, the nanocellulose had slightly elongated masses. The diameters of the fibrils varied from 22 to 45.5 nm (Fig. 1b). The average length was shorter as the reaction time increased which was supported by the findings of (Yu *et al.,* 2016).

3.3.3. FT-IR:

In FT-IR spectra, it was noted that the O-H stretching vibrations around 3341 cm^{-1}, the C-H stretching vibrations at 2898 cm^{-1}, the H-C-H and O-C-H in-plane bending vibrations at 1429 cm^{-1}, and the C-H deformation vibrations at 1376 cm^{-1} were representative peaks of celluloses (Fig.2.). The results of FT-IR were comparable with the observations made by (Nasir *et al.,* 2022). The presence of carboxyl groups (-COOH) on the surface of the nanocelluloses, created by means of esterification involving the hydroxyl groups of cellulose and the carboxyl groups of citric acid, was clearly demonstrated by the appearance of a carbonyl peaking at 1735 cm^{-1}. Similar observations were reported by (Ji *et al.,* 2019; Ruiz-Caldas *et al.*, 2023; Yu *et al.*, 2016).

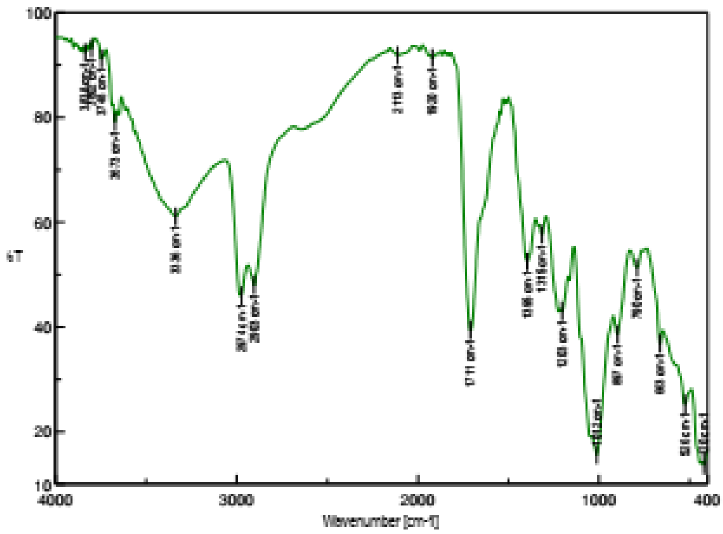

Fig. 2. FT-IR of nanocellulose obtained using citric acid hydrolysis

3.3.4. Zeta Potential:

Surface charge of the nanocellulose was ascertained using zeta potential measurement. Nanocellulose had a zeta potential value of -29.5 mV for the 0.1 wt% suspension. It is evident that, due to the citric acid carboxyl content, zeta potential of nanocellulose was consistent, indicating that the carboxyl groups had an immediate effect on the negatively charged topography of the substance (Yu *et al.*, 2016).

3.3.5. Thermogravimetric Analysis:

The thermogravimetric analysis method for evaluating thermal stability and breakdown temperatures of sample. The nanocellulose sample in the first stage experienced deterioration at temperatures between 30 °C and 100 °C because of a moisture release. When temperatures were between 305 °C and 353 °C, a considerable weight loss of between 50 and 60 per cent was primarily responsible during the second stage thermal degradation. This is comparatively higher than the TGA of 293.8°C as observed in case of the commercially available microcrystalline cellulose (Bian *et al.*, 2017).

4. CONCLUSION

Based on the current study has made an attempt for eco-friendly synthesis of nanocellulose from paperboard mill sludge using citric acid mixed with hydrochloric acid with the dimensions of 450-490 nm in length and 13-25 nm width, with a ζ-potential value of -29.5 mV indicating its stability. The thermal analysis had better observance as compared to commercially available microcrystalline cellulose sample. The prepared nanocellulose can, thus, be taken forward for further studies such as their use in paper industry, water treatment, etc.

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