CELLULOSE NANO FIBER AEROGELS FOR WATER FILTRATION

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ABSTRACT-Industrialisation of Indian subcontinent in the last decade leads to contamination of our soil and water with oil and dyes. So surface water get contaminated and not able to use for drinking. Science and Technology now focused on sustainable and eco friendly biodegradable materials for adsorbing these contaminants. Over the last decade, so many research groups are engaged to find out a concrete solution for this problem. Results have been reported by researchers about preparation, processing and fabrication of cellulose nano fibre aerogel. The fascinating properties of this material include high surface area, strength, aspect ratio and cost effective in nature suggests a huge potential material for water purification. However due to hydrophilicity of cellulose, it was not able to use in water treatment applications. We extracted cellulose nano fibre from waste biomass of newspaper and freeze dried to obtain aerogel. Surface modifications were done on cellulose aerogel viz. silination of aerogel using trimethoxy silane. This method was induced hydrophobicity in cellulose nano fibre aerogel and thereby can be efficiently used for water purification. This aerogel are low cost, elastic, ultra light, reusable and eco friendly. Adsorbed dye in cellulose aerogel can be easily reused by simple mechanical squeezing. So our work lay foundation for development of biodegradable, eco friendly and sustainable oil, dye, chemical pollutant and bacteria removal applications.

KEYWORDS **Cellulose nanofibril , Malachite green, Methyl blue, Fourier Transform Infra Red Spectrophotometer , Scanning electron microscopy.**

1. INTRODUCTION

Its well known that 40% of plant biomass is cellulose[1]–[7], which is the most available biopolymer[8] in the earth. Disposing the waste bio mass is one of the biggest problem faced by the modern world. This can be easily tackle by extracting cellulose from waste bio mass[9]. Cellulose nanofibril[10] (CNF) aerogels can be easily produced from this cellulose . This is done by preparing nano cellulose fibre aqueous suspension by supercritical drying or freeze-drying[11] . Even having all its merits, due to its higher hydrophilicity[12], makes nanocellulose no use in water related applications. So cross linking[8] or surface treatment is required to increase the hydrophobicity[13] of the nanocellulose aerogels[11]. We developed three different methods for increasing the hydrophobicity and found that all these methods are excellent for water treatment[14].

1.1 LITERATURE SURVEY

The extraction of cellulose from plant consists of several methods. It include grinding[15] , cryocrushing[16], high intensity ultrasonic treatments[17], homogenization[18], acid hydrolysis[19], steam explosion[20], electrospinning[21] and enzymatic[18] pre-treatments. The dimensions and morphologies of cellulose nano fibre depends upon pre-treatment and degree of fibrillation[22].

So many researchers are going on for the elimination of dyes[23] from industrial waste water[24]. Activated carbon[25] extracted from waste agricultural material was used for the exclusion of direct navy blue[25] 106 (DNB-106) from wastewater[26]. Synthesized maghemite nanoparticles had showed good adsorption rate of congo red[27] compared to most of other adsorbents and can be used for the exclusion of congo red in a wastewater management process . Biological[28] treatment of agricultural[25] residues with phanerochaete chrysosporium[29] shows excellent dye adsorption[30]

Most of the commonly used water based inks can be removed by TEMPO[28] oxidized nano fibrillated cellulose had developed with different core chemical structure. Nanocellulose fibrils fabricated by means of TEMPO oxidized macroporous honeycomb cellular structure surrounded with mesoporous[31] thinwalls. The high specific surface and surface carboxyl content of these aero-gels capable of removing cationic malachite green[12] (MG) dye from waste water . CNF aerogel fibrila surface modified by trimethylammonium chloride functional group[10] which is produced by freeze drying and cross linked using aliphatic trisocyanate.

This aerogel exhibits excellent properties for absorbing anionic dyes and increases the hydrophobicity of CNF. A biopolymer-based aerogel by freeze-drying a hydrogel[32], synthesized from cross linking carboxymethylated chitosan and bifunctional hairy nano crystalline cellulose through a Schiff base reaction[8]. It is mostly effective in adsorbing negatively charged dyes[33]. CNF with anionic groups[34] which is focused on tunable hydrophilicity.

For extraction of anionic carboxylated CNF, acid hydrolysis was used. Here hydronium ions from HCl or RCOOH dissociation of amorphous domain of cellulose, the bare crystalline cellulose chains with carboxyl groups by catalysing the etherification of hydroxyl groups. This leads to the increased precipitation of carboxyl groups which provides added active adsorption sites[19].

1.2 CELLULOSE

Figure 1 shows the structure of cellulose which is an organic material with the formula $(C_6H_{10}O_5)_n$, is the most important part of cell wall in a plant which is used for production of aerogel, paper etc. It consists of polysaccharide having many thousands of linear linked D glucose[35] units which is illustrated in figure 2. It's a bio polymeric material having good properties and structure. It is generally distributed in vascular plants, where it plays a fundamental structural role for the cell walls.

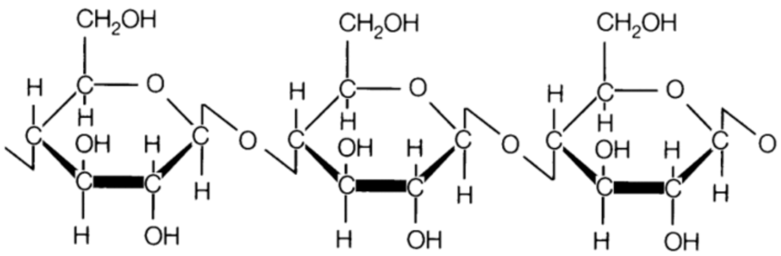


Figure 1 Structure of cellulose

Cellulose was first extracted from plan substance by a French scientist Anselme Payen in 1830 and determined its chemical formula. It was used to extract first thermoplastic polymer.

1.3 NANOCELLULOSE

Nanocellulose has been in use from 1980s . It was derived from plant fibre and mainly consists of lignin[36], cellulose and hemicellulose[37]. Cellulose is ordered in micro fibrils which gave the mechanical property[18] for the fibre. It's the main constituent for numerous natural fibres such as jute[38], flax, hemp, sisal etc. One third of the plant tissues[39] consists of cellulose and it can be restocked by means of photosynthesis[40].

Compared with paper, nanocellulose has much smaller diameter (<10 nm) that makes it interesting, larger surface area higher aspect ratio[16]. Thus, cellulose at nano level, exhibit special physical and chemical properties that makes them interesting for environmental[20] friendly products and find applications in electronics, medicine, construction[41], cosmetics, packaging[42] etc. Another significant property of nanofibres is that light scattering can be suppressed[43].

Here waste biomass of newspaper were chosen as the source of cellulose, which are easily available and rich in cellulose (70-80%). Finding new sources for developing nanocellulose is very important as the morphology and properties of the nanocellulose depends largely on the source and the extraction processes applied. Plant extracts have tremendous medical properties[44] and have been a part of traditional remedies.

2. EXPERIMENTAL SECTION

2. 1 MATERIALS

2.1.1 WASTE BIOMASS OF NEWSPAPER

The waste biomass of newspaper were rinsed well with water to eliminate dirt and other pollutants. It was dried and cut into small pieces of about 1 cm length. These were then dried in the oven overnight. It was then grounded using a blender. The powder was then separated into 100µm particles using a micro-sieve shaker and then finally stored in a sealed polythene bag.

2.1.2 OTHER CHEMICALS

Sodium hydroxide pellets and sodium hypochlorite were purchased from Sigma Aldrich, India.

2. 2 EXTRACTION OF CELLULOSE NANOFIBERS (CNF)

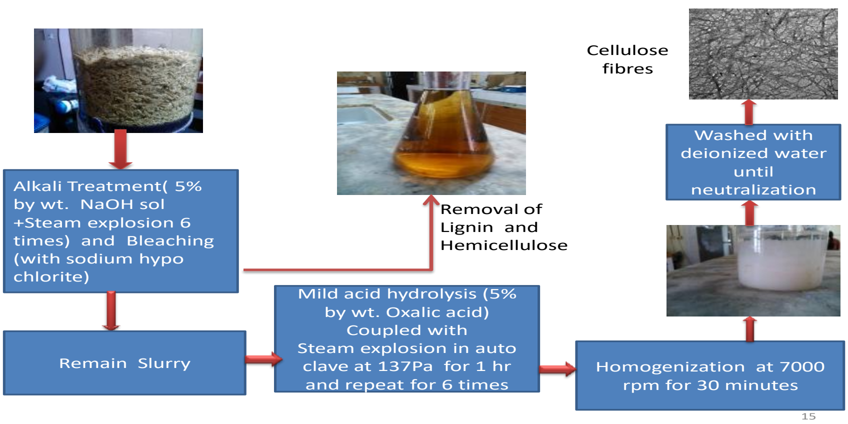


Figure 3 Extraction of CNF

Figure 3 illustrates the extraction of nano cellulose fibres. Alkali Treatment of waste bio mass newspaper with 5% by wt. of NaOH solution followed by steam explosion in a laboratory autoclave (KAUC-A1) 6 times and bleached with sodium hypo chlorite. Lignin and hemicellulose is drained off and remain slurry is mild acid hydrolysis (5% by wt. Oxalic acid) coupled with steam explosion in auto clave at 137Pa for 1 hour and repeat this procedure for 6 times. Homogenization of this cellulose at 7000 rpm for 30 minutes. Finally the residue was washed with deionised water until neutralization of cellulose.

2. 3 FABRICATION OF CNF AEROGELS

CNF suspensions having 3% by weight were freeze dried in a lyophilizer to a temperature of -80^{o}C and a pressure of 0.1bar. After 24 hours CNF aerogels are obtained.

2. 4 SILANE MODIFICATION OF CNF AEROGELS

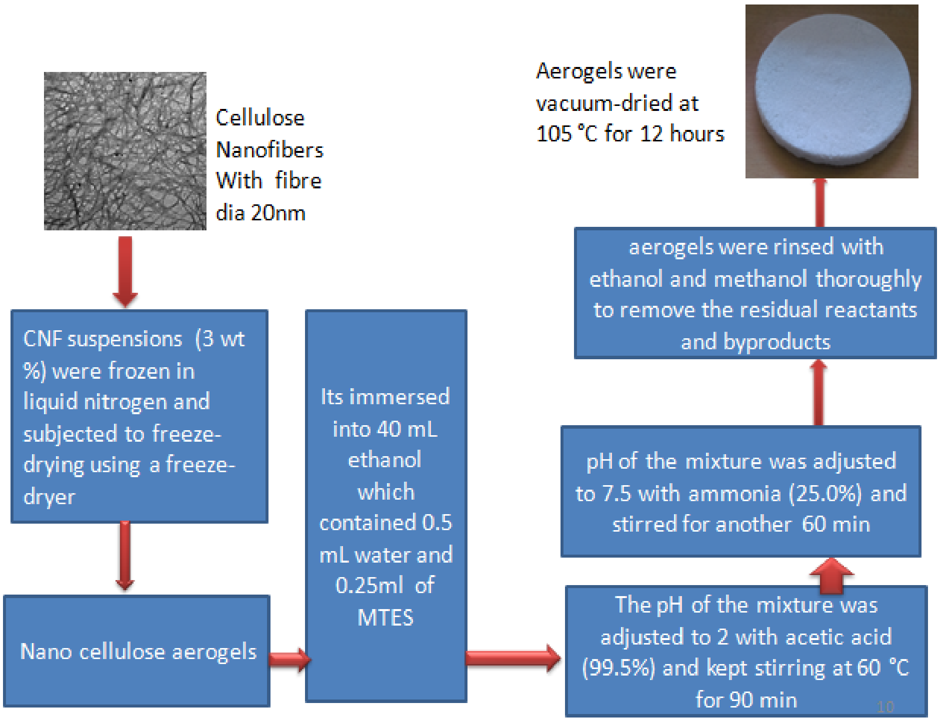


Figure 4 Silination of CNF aerogel

Figure 4 shows the flow chart for silane modification of CNF aerogel. Take 5% silane (trimethoxy silane) in 40 ml ethanol in a round bottom flask (preferably 150 ml size). Then add 0.5 ml of water in to this solution. Reduce the pH of solution to 2 with the help of acetic acid. After reaching pH of the solution to 2.5, place the aerogels into the round bottom flask. Subsequently this round bottom flask with re-fluxing condenser should be set at 60 ^{o}C for 90 min in an oil bath. Remove the condenser after 90 minutes and add ammonium hydroxide solution to rise the pH to 7.5, leave the set-up at 60 ^{o}C for 1 h in the oil bath. Afterward, decant the solution from the round bottom flask and wash the samples few times with ethanol to eliminate the polymerized silane and unreacted silane from the samples. Dry it in oven for 12 hours to get modified samples. Chemistry of silination shown in figure 5.

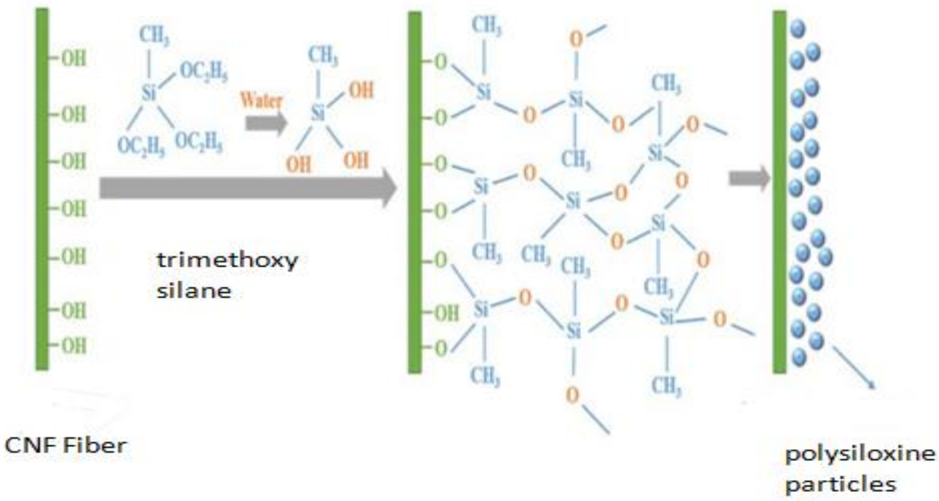


Figure 5 Chemistry of silination

When CNF fibre is mixed with trimethoxy silane as explained above, H atoms are substitute with Si atoms on the surface of aerogel which causes polysiloxine layer leads to increase of hydrophobicity.

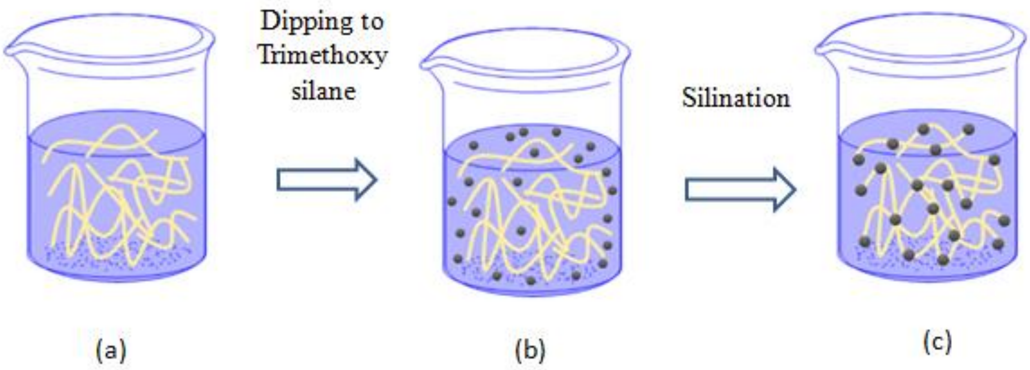
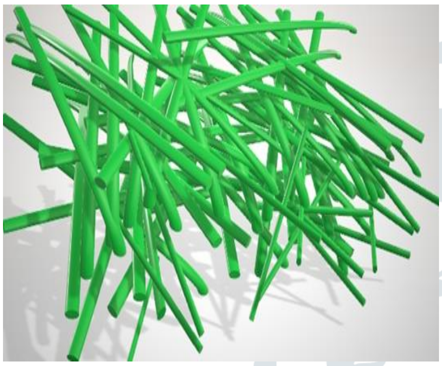


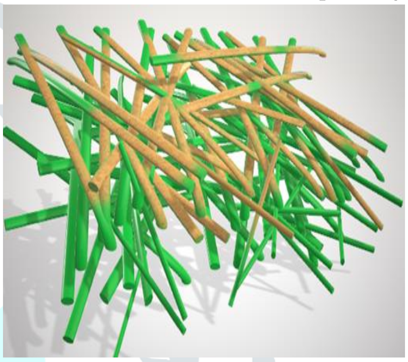
Figure 6 Morphology before and after silination

Morphology of the aerogel before silination[45] shows as in figure 6(a) in which fibers of cellulose in the beaker is freely embedded with water. Figure 6(b) shows trimethoxy silane is mixed with CNF and baking it in a hot chamber for 12 hours makes Si is precipitated on the surface of fibres. It's shown in figure 6(c). This reaction did not affect the porosity of the aerogel.



Nano cellulose fiber aerogel

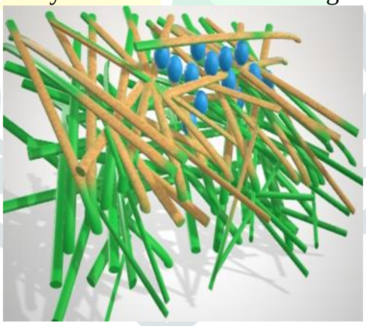
Figure 7(a)



Surface modified nano cellulose fiber aerogel

Figure 7(b)

Figure 7(a) shows CNF fibres of aerogel. Surface modification using trimethoxy silane illustrates figure 7(b). When this aerogel was applied for filtration of water having methyl blue was as shown in figure 7(c).



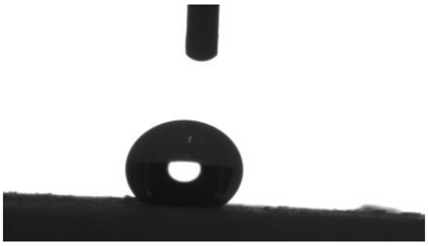
Methyl Blue colour filtered using Nano cellulose fiber aerogel

Figure 7(c)

Methyl blue colour was sieved in between space of CNF fiber and was due to the inter atomic attraction between negatively charged CNF aerogel and positively charged methyl blue colour.

3. RESULTS AND DISCUSSION

3.1 CONTACT ANGLE STUDIES



Water contact angle is 143 °

Figure 8 Contact angle studies

Figure 8 shows the water contact angle of the silinated CNF aerogel. Water contact was analysed using Drop Shape Analyzer DSA100E. Normal CNF is highly hydrophilic and it absorbed water and no contact angle was observed. When water was applied to silinated aerogel, a water contact angle of 143° is observed. It shows that this aerogel was hydrophobic due to silination process.

3.2 TEST RESULTS OF THE WATER SAMPLE

Table 1 Test results of river water before and after purification

Sl No	Parameter	Unit	Value			Permissible Limit
			Raw water*	Purified water at 500 l	Purified water at 1000l	
1	pH		5.1	7	7	6.5-8.5
2	Color		Slight gray	Colorless	Colorless	Colorless
3	Dyes		Traces	No traces	No traces	No traces

* Raw water collected from meenachil river, kottayam, Kerala.

Table 1 showed the test results of raw water was taken from meenachil river near kottayam and chemical test of water was done at rubber board regional testing centre, kottayam. The test result showed that most of the parameters were controlled by CNF aerogels. The pH of filtered water was neutral and colorless. There was no traces of dyes in the filtered water. There was not much difference in the parameters in the test sample taken at 500 liters and 1000 liters.

4. CONCLUSION

Mechanically robust aerogel with hydrophobic and higher porosity was fabricated via lyophilization coupled with silination on the surface. It was observed that the contact angle of the fabricated silane modified aerogel displayed a contact angle of 143°. This higher hydrophobicity due to the presence of the polysiloxine particles on the surface of the CNF aerogel during the silane modification. Adsorption of oil and textile dyes by this CNF aerogel makes it huge application in water treatment plants. After saturation of pores, the adsorbed oil and dyes can be easily cleaned by squeezing the aerogel. So this CNF aerogel can be reused multiple times.

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