Silane Modified Cellulose Nano Fiber Aerogel for Treatment of Textile Dye Mixed Waste Water

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ABSTRACT

Due to rapid increase in world population, urbanization, industrialization, agricultural actions, excessive application of chemicals resulted in pollution of environment. Contamination of ground and surface water with synthetic dyes is a severe environmental hazard and is a threat to mankind and aquatic life. Organic and inorganic wastes leads to increased quantity of polluted water which increases health concerns of human and other living organisms. Release of textile dyes into surface water can cause harmful effect to ecology and mankind.. Textile industries and other dyeing industries such as plastic, paper, leather, printing and food are main industrial waste water sources. Textile dyes are mainly chemical compounds which can join itself to water bodies to impart colour. Nano fibrillated cellulose have good adsorption property owing to their higher surface area and higher active sites for interaction. The elimination of toxic textile dyes were due to electrostatic attraction between the positively charged dyes and the negatively charged nano fibrillated cellulose. So it is considered as a good material for removal of dyes. . It is found that by silanation reaction using trimethoxylsilane super hydrophobicity can be attained..

KEYWORDS Cellulose nanofibril , direct navy blue, Fourier Transform Infra Red Spectrophotometer, Malachite green, Scanning electron microscopy, Tetramethylpiperidine-1-oxyl radical.

1. INTRODUCTION

Its well known that 40% of plant biomass is cellulose[1]–[7], which is the most available biopolymer[8] in the earth. Cellulose nanofibril[9] (CNF) aerogels can be easily produced from cellulose . This is done by preparing nano cellulose fibre aqueous suspension by supercritical drying or freeze-drying[10] . Even having all its merits, due to its higher hydrophilicity[11], makes nanocellulose no use in water related applications. So cross linking[8] or surface treatment is required to increase the hydrophobicity[12] of the nanocellulose aerogels[10]. We used trimethoxy silane for increasing the hydrophobicity and found that it as an excellent material for water treatment[13]. Over 10,000 different commercially available pigments[14] and dyes are exist in the world. About $7x10^5$ tonnes per year of pigments and dyes are manufactured yearly. For production of plastic, textile, carpet, printing, food, paper, cosmetics, dyes and pigments are used to obtain colour. But about 15% of dyes are leftover and mixed with water streams. This leads to reduction of reoxygenation capacity and colour to water which is difficult to treat with conventional methods. . Due to the growing use of dyes, the dye wastewater is fetching an environmental threat, and the extraction of these pollutants from wastewater is challenging.

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 researches 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[14] treatment of agricultural[25] residues with phanerochaete chrysosporium[28] shows excellent dye adsorption[29]

Most of the commonly used water based inks can be removed by TEMPO[14] 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[30] thinwalls. The high specific surface and surface carboxyl content of these aero-gels capable of removing cationic malachite green[11] (MG) dye from waste water . CNF aerogel fibrila surface modified by trimethylammonium chloride functional group[9] 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[31], 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[32]. CNF with anionic groups[33] 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

Fig. 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.

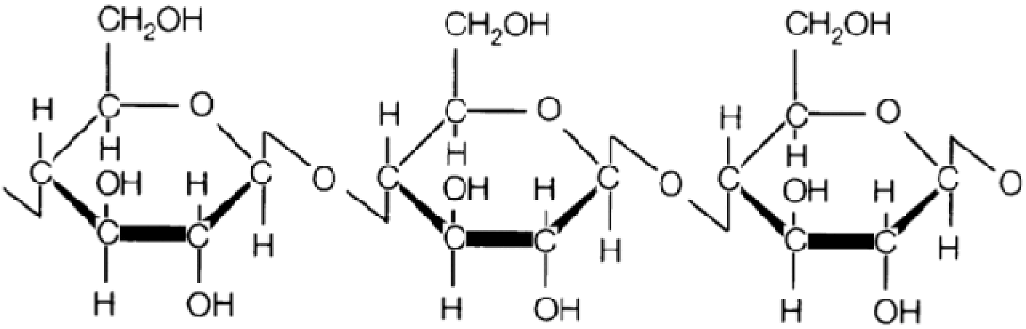


Figure 1 Structure of cellulose

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. Here pineapple leaves 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.

2. EXPERIMENTAL SECTION

2.1 MATERIALS

2.1.1 PINEAPPLE LEAVES

The pineapple leaves are 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)

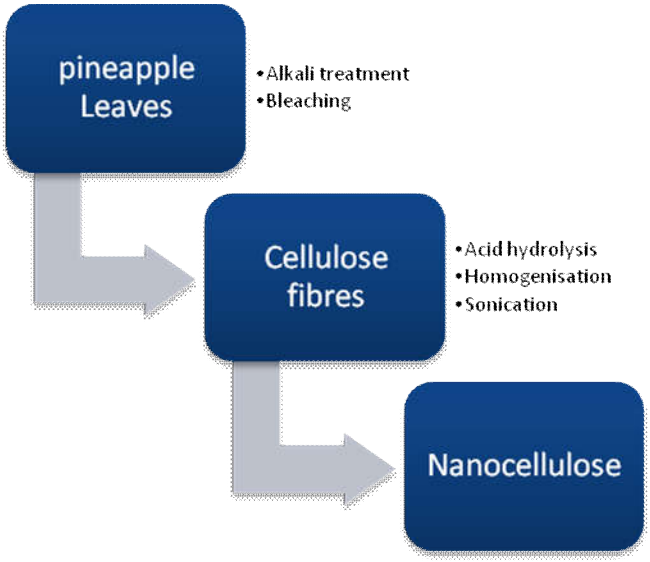


Figure 2 Extraction of CNF

Fig. 2 illustrates the extraction of nano cellulose fibres. Alkali Treatment of pineapple leaves 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 AND SILANE MODIFICATION OF CNF AEROGELS

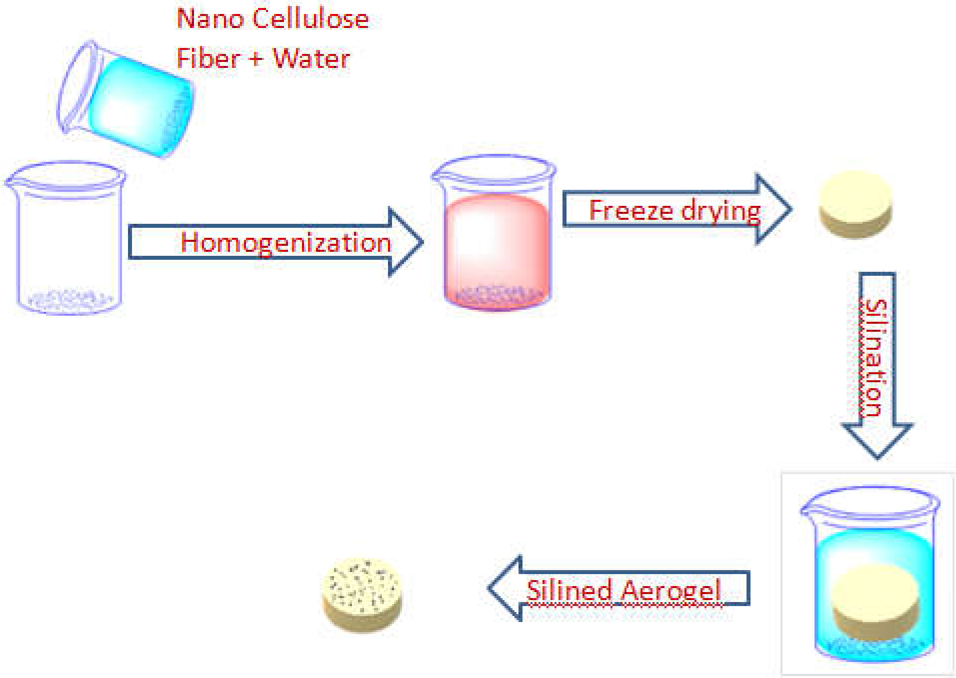


Figure 3 Silination of CNF aerogel

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

2.4 CHEMISTRY OF SILINATION

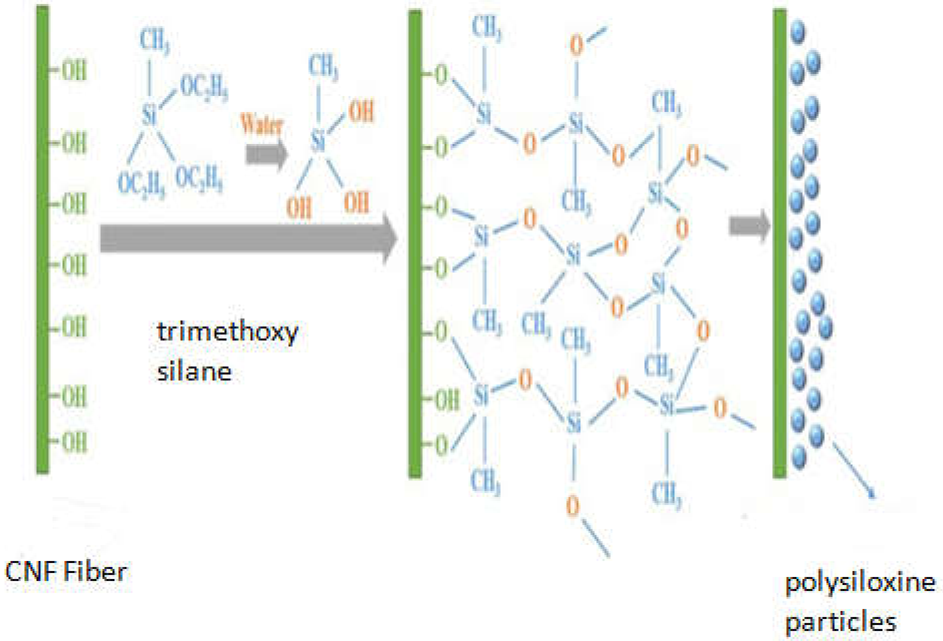


Figure 4 Chemistry of silination

Fig. 4 shows chemistry behind silination reaction. 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.

2.5 MORPHOLOGY BEFORE AND AFTER SILINATION

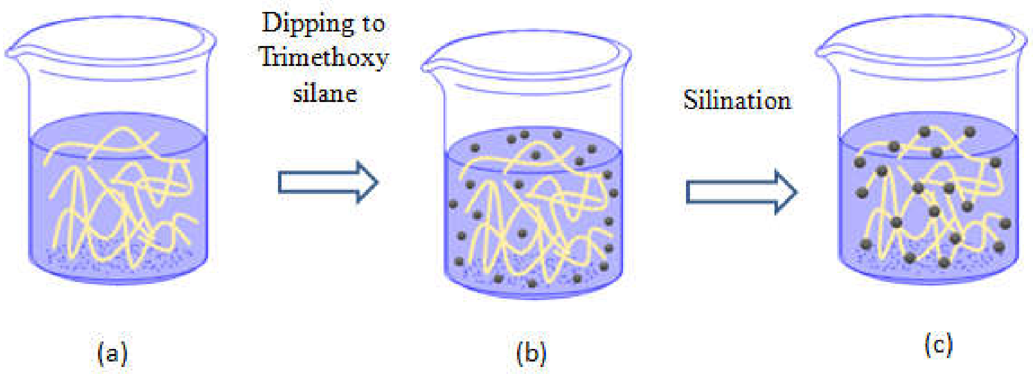


Figure 5 Morphology before and after silination

Morphology of the aerogel before silination[34] shows as in fig. 5(a) in which fibers of cellulose in the beaker is freely embedded with water. Fig. 5(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 fig. 5(c). This reaction did not affect the porosity of the aerogel.

2.6 METHYL BLUE DYE ADSORBED CNF AEROGEL

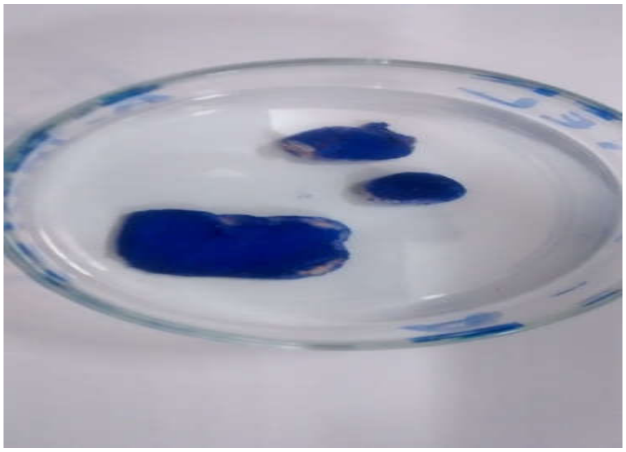


Figure 6 Methyl blue dye absorbed nano cellulose fiber aerogel

Fig. 6 shows methyl blue dye absorbed by silinated CNF fibres of aerogel. When this aerogel was dipped into water having methyl blue, the aerogel adsorbs all colour and gave water colourless.

2.7 ADSORPTION CAPACITY VS TIME GRAPH

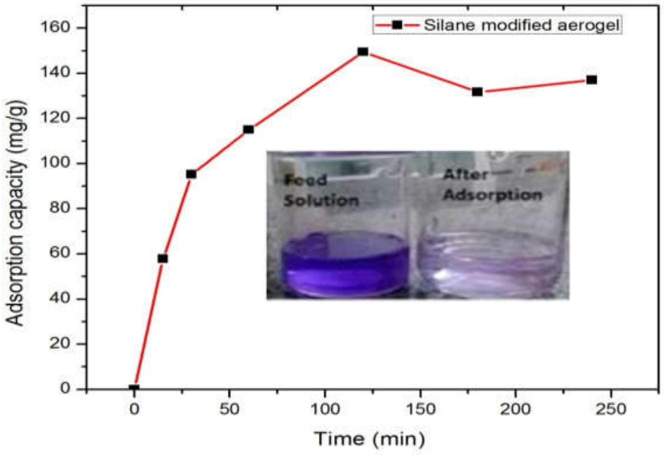


Figure 7 Adsorption capacity vs time graph for silane modified CNF aerogel

Fig. 7 shows the adsorption capacity of the silane modified aerogel. The dye removal efficiencies of the dye increased to 150 mg/g at 125 minutes and decreased gradually with the increases in time. Increase in adsorption may due to greater quantity of vacant lively sites of adsorbent were extra available for the adsorption at the lesser preliminary concentration. As the absorption amplified, the soaked sites made it not easy to confine dye molecules. So after 150mg/g of adsorption capacity suddenly decreases the adsorption rate.

3 RESULTS AND DISCUSSION

3.1 SEM ANALYSIS OF RAW CNF AEROGEL

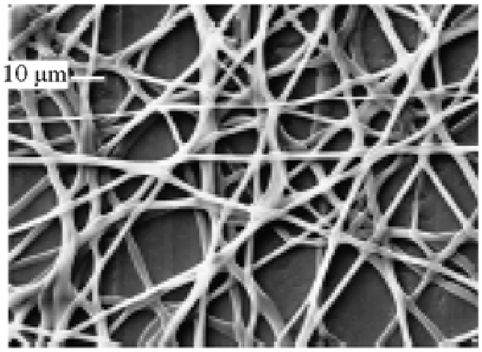


Figure 8 SEM image of CNF aerogel 10 µm

Fig. 8 shows the SEM images of CNF aerogel before surface treatment. There are net like structure such that above 90% porosity can be obtained. So water can be easily flow through the cross section and sieving will be effected. Due to hydrophobicity this structure will be destroyed. To overcoming this problem surface treatment was done.

3.2 SEM ANALYSIS OF SILANE MODIFIED CNF AEROGEL

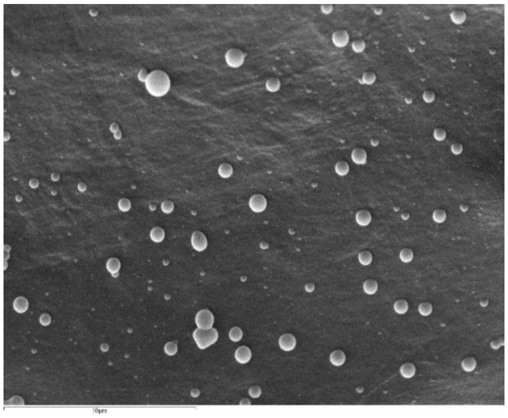
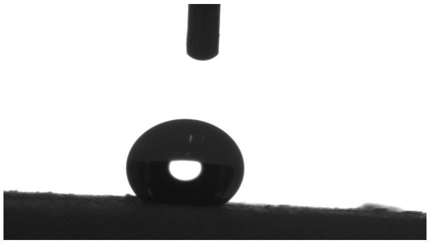


Figure 9 SEM image of silane treated CNF aerogel 50 µm

Fig. 9 shows the SEM images of CNF aerogel after silination with 100µm was evaluated and found that some of polysiloxine[34] particles having diameter of 150µm appeared on the surface of the aerogel. There was no change in inner structure of CNF aerogel which means there are no change in its porosity.

3.3 CONTACT ANGLE STUDIES



Water contact angle 143 °

Figure 10 Contact angle studies

Fig. 10 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^o was observed. It shows that this aerogel was hydrophobic due to silination process.

3.4 TEST RESULTS OF THE WATER SAMPLE

Table 1 Test results of methyl blue mixed 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
5	Odour		Slight rotten egg smell	Odourless	Odourless	Odourless
13	Coliform Bacteria	ml	520 coliform / 100ml	No traces	No traces	10 coliform / 100ml
14	Pesticides		Traces	No traces	No traces	0.001
15	Dyes		Traces	No traces	No traces	No traces

* Raw water collected from meenachil river

Table 1 shows the test results of raw water which was collected from meenachil river near kottayam and methyl blue dye mixed with an initial concentration of 58.46×10^{-6} M. 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 after treatment of 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 It was found that after silination, this aerogel selectively absorbs methyl blue textile dye. This was due to electrostatic attraction between the positively charged dye and negatively charged CNF aerogel. After saturation of dyes in the pores, it can be oozed out by squeezing the aerogel. So it could be reused. It was found that the demonstrated aerogel do not loss its hydrophobicity by the passage of time.

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