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Nanocellulose Based Functional Constructs for Clean water and Microwave Suppression

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Nanocellulose Based Functional Constructs for Clean water and Microwave Suppression

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Statement of Originality

I, Deepu Ambika GOPAKUMAR, formally submit the dissertation entitled "Nanocellulose based functional constructs for clean water and microwave suppression" to University of South Brittany (UBS), Lorient, France for the academic degree of Doctor of philosophy in Engineering Sciences. The work presented here was carried out from November 2014 till February 2017 at the International and Inter University Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam, India, Chemistry Department, Federal University of Uberlandia, Brazil and Laboratoire Ingenierie des Mateiriaux de Bretagne, UBS, Lorient Cedex, France. I hereby certify that this submission is solely my work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person, except where due reference is made in the thesis itself. Neither the dissertation, nor any sections thereof, has been previously submitted for a degree or other qualification to any other University or Institution. Any contribution made to the research by others, with whom I have worked at UBS or elsewhere, is unambiguously acknowledged in the thesis.

Deepu Ambika GOPAKUMAR
Lorient, France
24-05-2017

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General Introduction

The contamination of water is one of the serious issue that we are facing globally. This is mainly due to the various pollutants like toxic textile dyes, heavy metals, bacteria, virus etc. which can cause severe adverse effects to human beings, aquatic life and the ecosystem. Generally these pollutants are coming from biological and physical process but the impact of water pollution depends on several factors like ecological impact of the pollutant, abundance of pollutant and the use of the water. Unfortunately the most of the water pollution is derived due to the industries, agriculture and land-based activities of human. Considering the shortage of the usable water and the progressive pollution as a recognized global threat, the necessity to develop cutting-edge technology to address these major issues for water purification is very important for a clean environment. Membrane assisted water purification technology is one of such innovative approaches for creating a better healthier environment. .Thus, advanced technologies for filtration are an essential part of meeting the current and future needs for water innovations in the development of novel approaches to remove the minute contaminants like textile dyes from water. Considering the energy efficiency and ease of operation, membrane assisted filtration technology is anticipated to dominate among the water purification technologies. Among the water pollutants, toxic textile dye waste is an important pollutant to consider due to the emergence of the substantial number of modern textiles into the market. It is evident that after agriculture, the textile dyeing

and finishing industry has generated a large water pollution problem. Among the common removal techniques, microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) using pressure driven technologies have received very much interest due to their high performance and low cost. Conventionally these membranes for water treatment are produced by phase inversion techniques, where it is very difficult to achieve uniform pore size and water flux. Here, the membranes produced via electrospinning has numerous advantages like higher effective porosity with continuously interconnected pores, high surface area etc. when compared with the membranes fabricated via phase inversion technique. Moreover, membranes fabricated via electrospinning have an excellent particle rejection property. These properties make electrospun membranes as an excellent platform for microfiltration applications, however the average porosity of the membranes fabricated from electrospinning is too big to eliminate minute contaminants like viruses and textile dyes via size exclusion. So in order to remove the minute contaminants like textile dye, an extra adsorption mechanism is important. One of the typical approaches to remove the toxic textile dyes from waste water is to enhance the electrostatic charges of the membrane to increase the adsorption capability.

Another problem that we are facing globally is the electromagnetic wave pollution arising due to outrageous usage of electronic gadgets operating at different frequencies. Extensive use of electrical and microelectronic systems for domestic, industrial and other application functioning in radio frequency band remains to be a severe concern. The electromagnetic radiations from such electronic equipment's affect the performance of other near or far region electromagnetic fields which is called electromagnetic interference (EMI), and is emerging to be a serious issue for

circuit designers. For the safety of the sensitive circuits, light weight EMI shielding materials are very essential to shield the workspace from radiations emitted out from other electronic devices. EMI which can cause intolerable deterioration of equipment performance due to the unwanted radiated signals. If these concerns are not properly rectified, it may severely affects to the safety operation of many electronic devices. More over the electromagnetic waves from the sensitive electronic equipment's are reflected or absorbed by the human body. Thus misdirected radiations emitted out from the electronic devices may have adverse effect on human health. In the operation of microprocessor controlled devices, the use of high frequency signals may be emitted out of the equipment to the neighbouring environment can adversely affect the proper functioning of nearby equipment. So in order fix this issue, a proper shielding mechanism has to be given to the electronic devices to shield the both incoming and outgoing electromagnetic waves. Conventionally, metals were used to shield EM waves but are highly undesirable due to their inherent drawbacks such as higher weights, corrosive nature and difficulty of processing into intricate shapes. In this context, we need to address this insensible and unnoticed pollutant by designing electromagnetic shields based on conducting polymer nanocomposites thereby converting this undesirable energy into heat energy. Intrinsic conducting polymers (ICPs) like polyaniline (PANI) is an effective candidate for EMI shielding due to their tuneable conductivities, light weight and corrosion resistance as compared with typical metals. Moreover, the absorption dominant shielding characteristic of PANI compared to metals makes, PANI as an effective shielding material for many practical applications. This makes PANI as attractive alternative materials for EMI shielding. However, the existence

of the conjugated system in PANI enhances the rigidity of the polymer molecule, resulting in poor film-forming capability. Cellulose nanofibers as an effective substrate have been proposed as a solution for this obstacle. By combining the cellulose nanofibers with PANI, the poor formability and frangibility of PANI can be alleviated to produce a conducting composite that is capable to shield electromagnetic radiations via absorption dominated mechanism.

The present study make use of nanocellulose as a sustainable solution for water purification and electromagnetic suppression. Cellulose nanofibers extracted from sunflower stalks were chosen to prepare membrane and flexible nanopapers for water purification and electromagnetic wave suppression respectively. Here we intended to produce a unique absorbent material from cellulose nanofibers (CNFs) via non-solvent assisted procedure using Meldrum's acid as esterification agent in order to enhance the absorption towards the toxic textile dye like crystal violet. In this work we also fabricated a series of conductive cellulose nanopapers via in-situ polymerization with polyaniline (PANI) to attenuate electromagnetic radiations specifically in a small bandwidth of the microwave frequency region (8.2 -12.4 GHz). We firmly believe that these finding offers a new platform for make use of cellulose nanofibers extracted from bio-mass for the water purification and electromagnetic wave suppression applications.

Chapter 1

Bibliographical Review

1. Introduction

Our society are increasingly demanding products made from renewable and sustainable resources that are biodegradable, non-petroleum based and have low environmental, animal/human health and safety risks. There is a growing trend to use bio-fibers as fillers and/or reinforces in plastics composites. Their flexibility during processing, highly specific stiffness, and low cost make them attractive to manufacturers. As a renewable material, cellulose and its derivatives have been widely studied, focusing on their biological, chemical, as well as mechanical properties. The materials based on cellulose and its derivatives have been used for more than 150 years in a wide variety of applications, such as food, paper production, biomaterials and pharmaceuticals. Cellulose is one of the most abundant biopolymers on earth, occurring in wood, cotton, hemp and other plant-based materials and serving as the dominant reinforcing phase in plant structures. Natural cellulose based materials (wood, hemp, cotton, linen, etc.) have been used by our society as engineering materials for thousands of years and their use continues today as verified by the enormity of the world wide industries in forest products, paper, textiles, etc.

In recent years, there is an increasing interest in the development of biodegradable and /or plant derived composite materials which sometimes referred to as “green

composites because of the strong global demand for creating renewable sources. Its industrial use is mainly for making paper and cardboard but recently it has also attracted significant interest as a source of biofuel production. The scientists believe that cellulose nanofibers have a high potential to be used as transparent and extremely strong films in many different areas. Now a days, scientists are focused on the isolation, characterization, and search for applications of novel forms of cellulose, variously termed nanocrystals, whiskers, nanofibrils and nanofibers, such isolated cellulosic materials with one dimension in the nanometre range are referred to generally as nanocelluloses. These nanocelluloses combine important cellulose properties such as high specific strength and modulus, hydrophilicity, wide chemical modification capacity etc. with specific features of nanoscale materials. This is mainly caused due to the very large surface area of these materials. Nanocelluloses can be classified in three main subcategories namely 1) cellulose nanofibers (CNFs) 2) cellulose nanocrystals (CNCs) and 3) bacterial nanocellulose (BC). Surface functionalization on nanocellulose allows the tailoring of particle surface chemistry to facilitate self-assembly, controlled dispersion within a wide range of matrix polymers.

1.1 Cellulose , its sources, chemical composition and physical properties

The primary occurrence of cellulose is existing lignocellulosic material in forests, with wood as the most important source. Other cellulose-containing materials include agriculture residues, water plants, grasses and other plant substances and various sources of cellulosic fibers are shown in the Table 1.1. Besides cellulose, they contain hemicelluloses, lignin and a small amount of extractives. Chemical compositions of some typical cellulose-containing materials are shown in the Table 1.2. The most common sources of cellulose for industrial use are wood pulp and cotton linter.

Cellulose is a long chain of linked sugar molecules that gives wood its remarkable strength. It is the main component of plant cell walls, and the basic building block for many textiles and for paper. Cotton is the purest natural form of cellulose.

Various sources (Nano cellulosic fibers)	**References**
Wood	Yano et al. (2007), Chen et al.(2011)
Cotton, Cotton liner	Teixeira et al. (2010), Li et al. (2014), Chen et al. (2014).
Potato tuber cells	Dufresne et al. (2000)
Cladodes and spines from Opuntia ficus-indica	Malainine et al. (2003)
Prickly pear fruits of Opuntia ficus-indica	Habibi et al. (2008)
Lemon and maize	Mouro et al. (2003)
Soybean	Wang et al. (2007)
Wheat straw and soy hulls	Alemdar et al. (2008), Kaushik et al. (2011)
Hemp	Wang et al. (2007)
Coconut husk	Rosa et al. (2010)
Branch-barks of mulberry	Li et al. (2009)
Pineapple leaf	Cherian et al. (2010)
Banana rachis	Zuluaga et al. (2009)
Banana plant	Deepa et al. (2011)
Banana peels	Pelissari et al. (2014), Tibolla et al. (2014)
Waste news paper	Takagi et al. (2013).
Sisal	Moran et al. (2008)
Pea hull	Anderson et al. (2009)
Sugar beet	Dufresne et al. (1999), Vignon et al. (1997), Meng Li et al. (2014).
Isora fiber	Chirayil et al. (2014)

Table 1.1: Various sources of nanocellulosic fibers Copyright 2012. Reproduced with permission from the Elsevier.

Source	Cellulose %	Hemicellulose %	Lignin%
Hard wood	43-47	25-35	16-24
Soft wood	40-44	25-29	25-31
Bagasse	40	30	20
Coir	32-43	10-20	43-49
Corn cobs	45	35	15
Corn stalks	35	25	35
Cotton	95	2	1
Flax (retted)	71	21	2
Flax (unretted)	63	12	3
Hemp	70	22	6
Jute	71	14	13
Kenaf	31	26	18
Ramie	76	17	1
Sisal	73	14	11
Sunn	80	10	6
Wheat straw	30	50	15
Banana fibers	63-64	19	5

Table 1.2: Chemical composition of some typical cellulose containing materials. Copyright 2012. Modified with permission from the Elsevier.

Natural fibres can be considered as naturally occurring composites consisting mainly of cellulose fibrils embedded in lignin matrix. The cellulose fibrils are aligned along the length of the fibre, shown in figure1.1, which renders maximum tensile and flexural strengths in addition to providing rigidity. The reinforcing efficiency of natural fibre is related to the nature of cellulose and its crystallinity. The structure

and the morphology of cellulose have been the studied and the key subject for a large amount of work. Basically it is a polydisperse linear polymer consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by 1,4-b-D-glycosidic linkages at C_1 and C_4 position 1 shown in figure1.2 [1].The degree of polymerization (DP) is around 10,000. Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose.

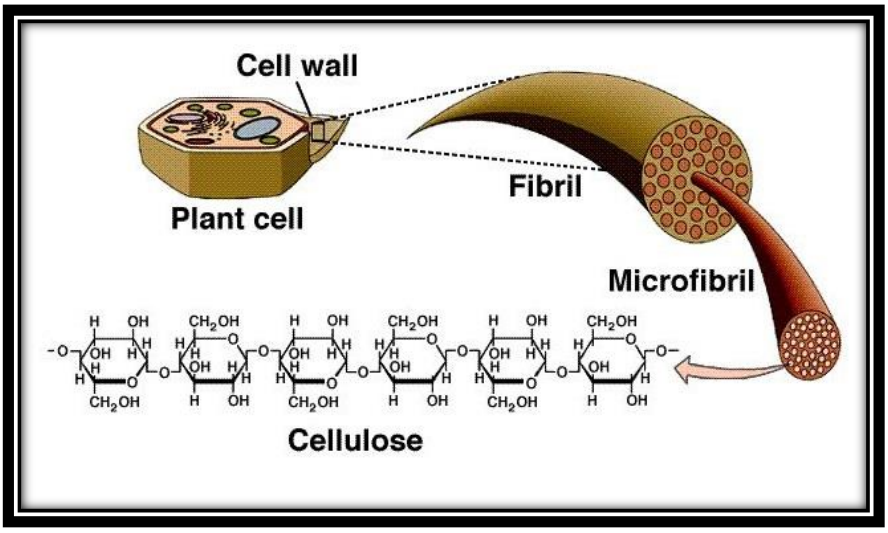

Figure 1.1: Arrangement of Fibrils, Microfibrils and Cellulose in Cell walls.

There are four different polymorphs for cellulose: Cellulose I, II, III and IV. Cellulose I is occurs in native cellulose found in nature, and it occurs in two allomorphs, I_α and I_β. Cellulose II or regenerated cellulose emerges after re-crystallization or mercerization with aqueous sodium hydroxide and it is the most stable crystalline form [2]. The major difference between these two forms of cellulose is the layout of their atoms: Cellulose II has antiparallel packing, whereas the chains in cellulose I run in a parallel direction [2]. Cellulose III_I and III_{II} are

obtained by ammonia treatment of Cellulose I and II respectively, whereas modification of Cellulose III led to Cellulose IV structure.

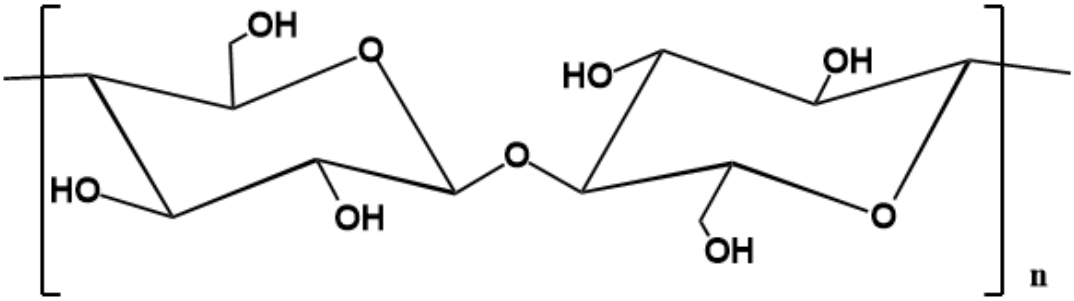

Fig1.2: Chemical Structure of Cellulose.

Over the past decades, natural cellulose materials have been used as an energy source, for building materials, paper, textiles and clothing etc. [3]. For engineering applications new features such as uniformity and durability are required in natural cellulose. These features can be shown by cellulose elementary building blocks called cellulose microfibrils with nano dimensions, which is the base reinforcement unit that strengthens all structures in plants, trees etc. Thus the extraction of the nanocellulose from native cellulose and their use as reinforcement agent in polymer composite materials has gained considerable interest due to its unique features such as high strength and stiffness, low weight and biodegradability [4].

1.2 Cellulose nanofibers (CNFs) and Cellulose nanocrystals (CNCs)

Two main types of nanocelluloses are (i) cellulose nanocrystals and (ii) cellulose microfibrils or nanofibers. The major difference between the CNCs and CNFs are lies in their amorphous portions and dimensions. The CNCs have nano dimensions in both length and diameter wise, whereas CNFs have length in micro dimension and diameter is in the nano dimensions as shown in the figure 1.3 CNFs can be manufactured by various process like grinding, homogenization, steam explosion

etc. whereas CNCs by strong acid like sulphuric acid and it destroys all the amorphous portion (dis-ordered region) and lead to the nanocrystal structure. Both CNCs and CNFs can be isolated from the plant cell walls. The abundant availability of plant bio-mass and their superior mechanical properties of nanocellulose including CNCs and CNFs as a desirable reinforcing material for polymer nanocomposites [2].

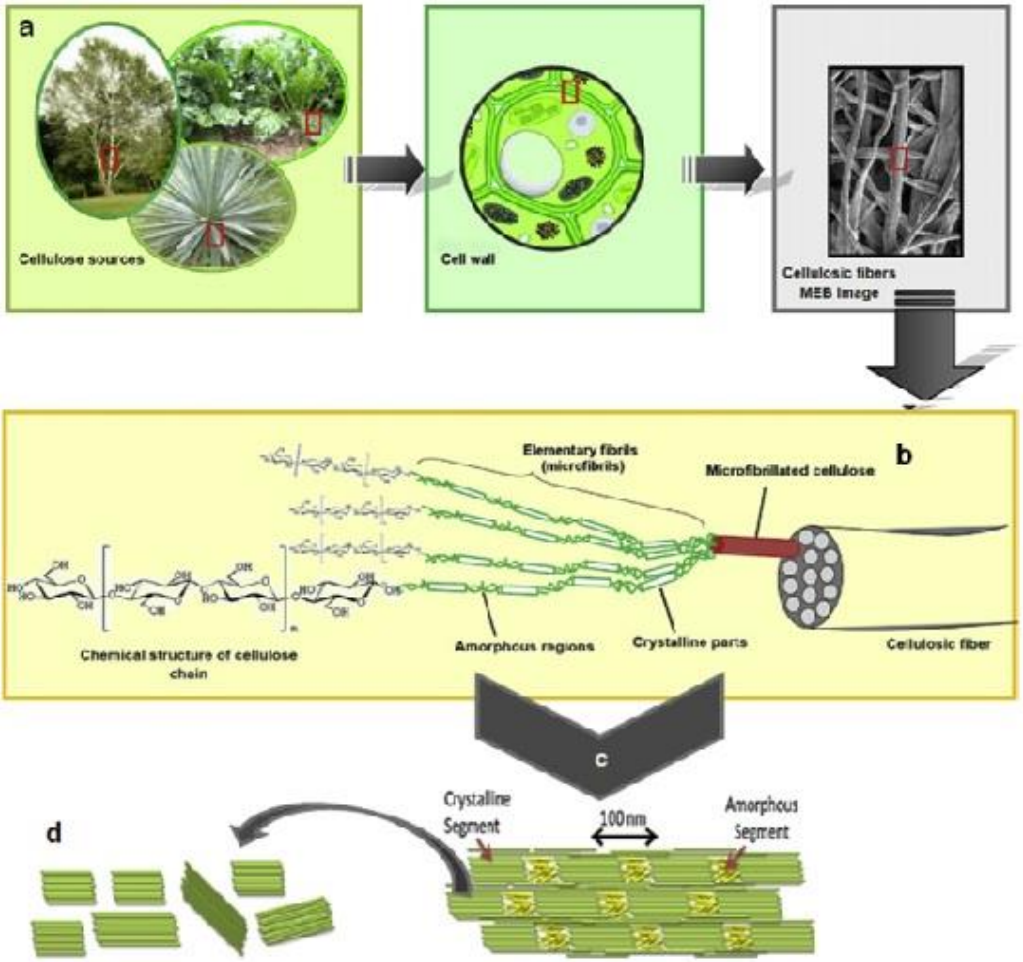

Figure 1.3: Schematics of cellulose fibre structure with emphasis from the (a) cellulosic plant sources and (b) cellulose fibre to the (c) cellulose nanofibers (CNFs) bundles consisted of crystalline and amorphous regions and to the (d) cellulose nanocrystals (CNCs) [3]. Copyright (2015). Reproduced with permission from Elsevier Ltd.

1.3 Isolation and Extraction techniques for cellulose nanofibers (CNFs)

Many studies have been done on isolation and characterization of cellulose nanofibers from various sources. Cellulose nanofibers can be extracted from the cell walls by simple mechanical shearing or by combination of both chemical and mechanical routes. Isolation of the CNF from renewable sources is becoming an important area of the research. The use of the novel nature based materials has gained the considerable attention among the scientists due to their high strength, bio compatibility etc. There are several methods or extraction techniques have been employed for the extraction of the cellulose nanofibers from the plant cell wall.

1.3.1 High pressure Homogenization:

This is the widely used method for the large scale production of cellulose nanofibers. This process has been extensively used by the dairy and food industry mainly to stabilize food emulsion. During this process, the cellulose fibers are pumped at high pressure and fed through a spring loaded valve assembly. As this valve opens and closes at a very fast rate, the fibers are exposed to a large pressure drop with shearing and impacting forces. This combination of forces will lead to a high degree of micro fibrillation of cellulose fibers. The extent of the cellulose fibrillation depends on the number of homogenization cycles and the applied pressure. The higher the pressure, the higher the efficiency of disruption per pass through the machine. Methods for producing micro fibrillated cellulose (MFC) were first reported by Herrick et al. [4]. They have passed the dilute cellulosic wood pulp-water suspensions through a mechanical homogenizer, in which a large pressure drop facilitated micro fibrillation**.** Li et al. extracted the cellulose nanofibers from de- pectinated sugar beet pulp by the combination of chemical treatments and high

pressure homogenization. The diameter of the obtained cellulose nanofibers was from several nm to 70 nm. They showed that the crystallinity of nanofibers increased significantly after treatments [5]. Chen et al. also reported a method to fibrillate raw dried cotton fibers into individual cellulose nanofibers by chemical purification and pre-treatment by a high speed blender combined with high pressure homogenization (nanofibrillation). The resultant nanofibers were found to have a diameter of approximately 10-30 nm and high aspect ratios [6]. Cellulose nanofibers were isolated by Pelissari et al. from banana peels using a combination of chemical treatments, such as alkaline treatment, bleaching and acid hydrolysis. It was done by passing the suspensions of chemically treated fibers through a high pressure homogenizer [7].

1.3.2 Grinding

In grinding process, cellulose fibers are forced through a gap between two specially modified grooved discs, one is static and other is revolving at about 1,500 rpm. In this process, the cell wall structure is broken down by the high shearing forces and it resulting in nanosized individualized fibers. The extent of fibrillation is dependent upon the distance between the discs, the morphology of the disc channels and the number of passages through the grinder. Abe et al. obtained cellulose nanofibers with a uniform width of 15nm from wood by the grinding treatment in an undried state. They reported the nanocellulose fibre diameter with diameter of 15nm. This study demonstrated that grinding is a powerful quiet simple method for the production of cellulose nanofibers from plant fibers [8]. When homogenized cellulosic pulp was subjected to a grinder treatment by Iwamoto et al. the fibril

bundles were further fibrillated and 10 repetitions of the grinder treatment resulted in uniform nanofibers 50-100 nm wide [9].

1.3.3 Cryocrushing:

Cryocrushing is an alternative method for producing nanofibers where fibers are frozen using liquid nitrogen, and then high shear forces are applied. This process involves the acting of the high impact forces on the frozen fibers, ice crystals exert pressure on the cell walls, causing them to rupture and then led to the formation of microfibrils. Cryocrushing combined with a high pressure fibrillation process was used by Wang et al. for the isolation of nanofibers with diameters in the range 50-100 nm from soybean stock [10]. Alemdar et al. also reported the extraction of cellulose nanofibers from wheat straw and soy hulls by mechanical treatment involving cryocrushing. They investigated the chemical composition, morphology, physical and thermal properties of the nanofibers to study their usability in bio-composite applications. They showed that the produced wheat straw nanofibers' diameters were in the range of 10–80 nm with lengths of a few thousand nanometres [11]. Chakraborty et al. also reported a novel technique to produce cellulose microfibrils through mechanical methods. The technique involved a combination of severe shearing in a refiner, followed by high-impact crushing under liquid nitrogen [12].

1.3.4 High Intensity Ultrasonic Treatments:

This process comprises of combination of chemical pre-treatment and high-intensity ultrasonication. The ultrasonic impact can gradually disintegrate the micron-sized cellulose fibers into nanofibers. Before ultra-sonication the plant fibers are being purified to prepare the cellulose fibers by mild acid hydrolysis followed by alkali treatment and bleaching treatment. This process comprises of the removal of non-

cellulosic materials like lignin, hemicelluloses etc. After chemical pre-treatment, the purified cellulose fibers are soaked in distilled water. About 110 ml of solution containing chemical-purified cellulose fibers are then placed in an ultrasonic generator of 20-25 KHz in frequency. The ultrasonication is conducted for 30 min to isolate the nanofibers. Li et al. prepared nanocellulose fibers by pre-treating cellulose in NaOH/urea/Thiourea solution and then defibrillating the fibers by ultrasonication. They achieved the high yield of 85.4%. The obtained nanocellulose fibers were about 30 nm in diameter with cellulose II crystal structure. They possess high thermal stability with an onset of thermal degradation at 270 °C and a maximum degradation temperature of 370 °C [13]. Chen et al. reported that the cellulose nanofibers were individualized from poplar wood by explosive chemical pre-treatment and high-intensity ultrasonication. When the output power of ultrasonic treatment used for the chemical-purified cellulose fibers was greater than 1000W, cellulose nanofibers were 5–20 nm in width and several microns in length were obtained [14].

1.3.5 Steam Explosion process:

This process comprises of short time vapour phase cooking at temperatures in the range of 180-210°C, followed by explosive decompression and sudden release of pressure. In this process the cellulosic biomass is pressurized for a short period of time in an autoclave with water steam, and then explosively discharged to atmospheric pressure which results in a sudden disintegration of the starting material into a fibrous dispersed solid. This process results in a substantial breakdown of lignocellulosic structure, hydrolysis of the hemicellulose fraction, depolymerisation of the lignin components and defibrillation**.** Deepa et al. reported the extraction of

the cellulose nanofibers from the banana plant by the steam explosion process in an autoclave [15]. Chirayil et al. employed the steam explosion process for extracting cellulose nanofibers from isora fibre in an autoclave. This technique involves alkaline treatment, bleaching, acidic steam treatment and homogenization. The results showed that the prepared cellulose nanofibers have nanofibrillar network like structure with high crystallinity and good thermal stability [16]. Cherian et al. also reported that the steam explosion process was successful for the extraction of cellulose nanofibrils from pineapple leaf fibres for the first time. Steam explosion coupled with mild acid treatment on the pineapple leaf fibres was found to be effective in the depolymerisation and defibrillation of the fibre to produce nanofibrils of these fibres [17].

1.3.6 Electrospinning:

Electrospinning is quite simple method operates on the principle that a solution is extruded –electrospun under the action of a high electric field. Once the voltage is high enough, a charged stream of matter is ejected following a rather complicated loop. During this process, the solvent evaporates leaving behind randomly oriented nanofibers accumulating on the collector. Cellulose nanofibers have been produced by using electrospinning technique by dissolving cellulose fibers in solvents, such as ethylene diamine, with a salt selected from the group consisting of potassium thiocynate, potassium iodide. Only few fundamental studies are currently dedicated to this method. Ma et al. prepared cellulose acetate (CA) nanofibers with fibre diameter ranging from 200 nm to 1 µm by electrospinning technique and solvent employed was acetone/DMF/trifluoroethylene (3:1:1) mixture [18].

1.3.7 Enzymatic Pre-treatments:

This process enables the manufacture of cellulose nanofibers with significantly reduced consumption [19]. In nature, cellulose is not degraded by a single enzyme but a set of cellulases are involved. These can be classified as A- and B- type cellulases, which are able to attack highly crystalline cellulose and C- and D- type cellulases, which generally require some disorder structure in order to degrade cellulose. Paakko et al. and Henriksson et al. reported that endoglucanase pre-treatment facilitates disintegration of cellulosic wood fiber pulp into cellulose nanofibers [19-20]. Another work was done by Tibolla et al. and they isolated cellulose nanofibers from banana peel bran using chemical treatment (involves alkaline treatment, bleaching and acid hydrolysis) and enzymatic treatment (alkaline treatment and hydrolysis with xylanase). Nanofibers produced from chemical treatment and enzymatic treatment had an average diameter of 10.9 and 7.6 nm and a length of 454.9 and 2889.7 nm respectively. They showed that the nanoparticles isolated from both of the treatments have potential application as reinforcing elements in composites [21].

1.4 Surface chemistries on nanocellulose

One of the drawback of nanocellulose with polar surfaces is poor dispersiblity/ compatibility with non-polar solvents or resins. Therefore applications largely limited to aqueous or polar systems. To overcome this problem it is necessary to reduce the entanglement of the fibrils to improve their dispersion in matrix by chemical or surface modification. Cellulose has 3 alcoholic hydroxyl groups in each of its AGUs & chemical modification can be exclusively performed on these hydroxyls with practical relevance. Chemical modification can be conducted both in

heterogeneous& homogeneous conditions. Due to high crystallinity cellulose can be only dissolved in limited solvents, so many modifications have been conducted in heterogeneous conditions. Since chemical reactions occur only at the surface layer in heterogeneous conditions, the gross structure of the cellulose sample can largely maintained. Because of a natural advantage of an abundance of hydroxyl groups at the surface of cellulose Nano particles, different chemical modifications have been done such as esterification, catonization, Acetylation, oxidation, silylation, polymer grafting, etc. shown in figure 1.4.

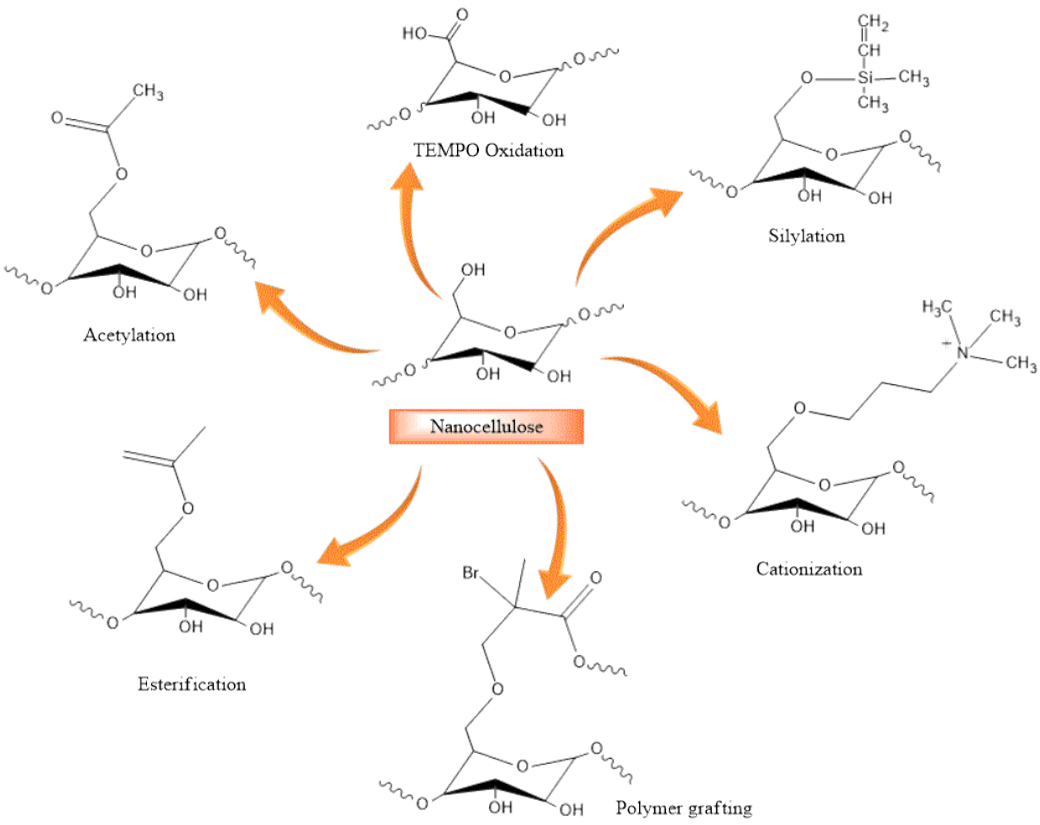

Figure 1.4: Common modification chemistries on nanocellulose surfaces

1.4.1 TEMPO Oxidation

This Procedure involves the application of a stable nitroxyl radical, the 2, 2, 6, 6-tetra methyl piperidine-1-oxyl (TEMPO) in the presence of NaBr & NaOCl. In this process, carboxylic acid groups at the surface of fibrillated cellulose and catalytic amounts of TEMPO & NaBr were dissolved in polysaccharide solution at pH 10-11 & oxidation was started by addition of NaClO solution as a primary oxidant. The C6 primary hydroxyls of cellulose can be entirely & selectively converted to C6 sodium carboxylate groups by TEMPO- mediated oxidation. TEMPO-mediated oxidation of nanocrystals obtained from acid hydrolysis of cellulose fibres was first reported by Araki et al. and they prepared a sterically stabilized cellulose microcrystal suspension by grafting of polyethylene Glycol (PEG) using TEMPO oxidation procedure [22]. In TEMPO oxidation newly installed carbonyl groups that imparted negative charges at the cellulose Nano crystal surface & thus induced electro static stabilization as shown in the figure1.5. Another work was reported by Saito et al. and they prepared homogeneous suspensions of invidualized microfibrils from TEMPO-catalysed oxidative of native cellulose. They found that, after treatment the native cellulose were readily disintegrated into long individual microfibers by a treatment with wearing blender, yielding transparent and highly viscous suspensions. They concluded that, compared to the conventional technique which disintegrate cellulose fibers into microfibrillar suspensions using mechanical treatment, a combination of TEMPO-mediated oxidation and homogenizing treatment presents the advantage to disintegrate into microfibrils with small widths using a much lower input [23].

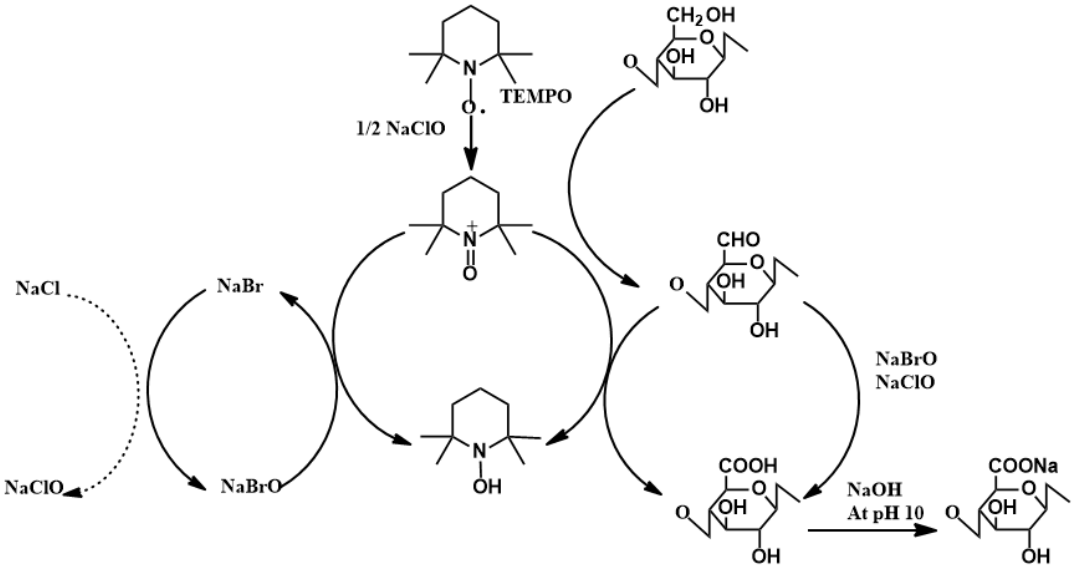

Figure 1.5: Scheme of TEMPO mediated oxidation mechanism of the hydroxymethyl groups of nanocellulose

1.4.2 Acetylation

Acetylation is a chemical modification method, which introduce acetyl group (CH3-C (=O) - on to the surface of the nanocellulose as shown in the figure1.6, in order to convert the hydrophilic character of nanocellulose into hydrophobic [24-26]. The acetylation of cellulose depends on the accessibility and susceptibility of the OH groups in the amorphous and crystalline regions within the cellulose polymer chain [27]. The Acetylation has several advantages when compared to other chemical treatments for nanocellulose. Acetylation provides good dispersiblity of cellulose fibers in the polymer matrix during compounding, low costs, ease of use, shorter process duration and environmental friendliness. The main limitation of the nanocellulose in practical composite application is the self-agglomeration due to the presence of large surface hydroxyl groups, thereby resulting in crack or failure of the composites. Mukherjee et al. done surface acetylation of the nanocellulose using acetic anhydride and dimethyl formamide to reduce the agglomeration and they

found that after acetylation the dispersion of acetylated nanocellulose had improved in PLA matrix [28].

Figure 1.6: Chemical modification of nanocellulose with acetic anhydride and DMF (N, N-dimethyl formamide.

1.4.3 Silyation

Silane is a chemical compound with chemical formula SiH_4. Silanes are used as coupling agents to let glass fibers adhere to a polymer matrix, stabilizing the composite material. Silane coupling agents may reduce the number of cellulose hydroxyl groups in the fibre– matrix interface. In the presence of moisture, hydrolysable alkoxy group leads to the formation of silanols. The silanols then reacts with the hydroxyl group of the fibre, forming stable covalent bonds to the cell wall that are chemisorbed onto the fibre surface [29]. Therefore, the hydrocarbon chains provided by the application of silane restrain the swelling of the fibre by creating a cross-linked network due to covalent bonding between the matrix and the fibre. The reaction scheme is given in the figure 1.7. Silane coupling agents were also found to be effective in modifying natural fibre–polymer matrix interface and increasing the interfacial strength. Abdelmouleh et al. done the surface modification of cellulosic fibers using organo functional silane coupling agents in an ethanol/water medium. They found the presence of SI-O-cellulose and Si-O-Si bonds on the surface of the cellulose and there by imparting the hydrophobic character to the cellulose fibers which was confirmed via water contact angle studies [30].

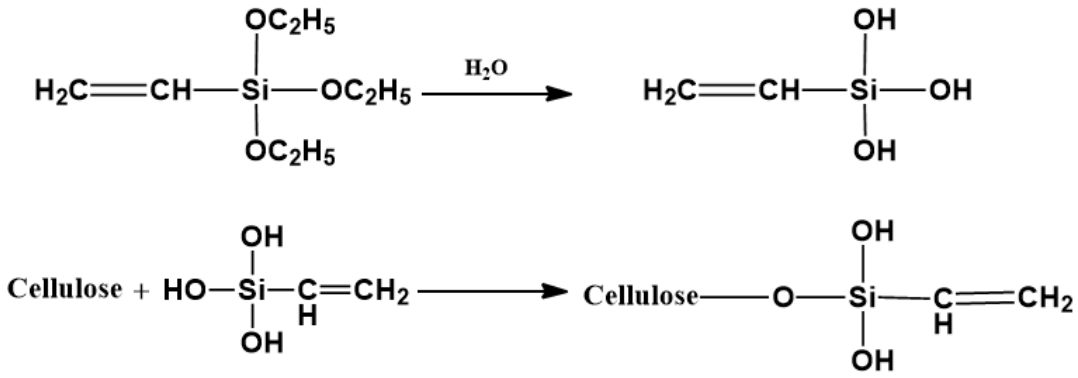

Figure 1.7: Silyation of Nanocellulose

1.4.4 Esterification

The simultaneous occurrence of cellulose hydrolysis and acetylation of hydroxyl groups have been reported. Fischer esterification of hydroxyl groups simultaneously with the hydrolysis of amorphous cellulose chains has been introduced as a viable one-pot reaction methodology that allows isolation of acetylated CNCs in a single-step process as shown in the figure 1.8 [31, 32].

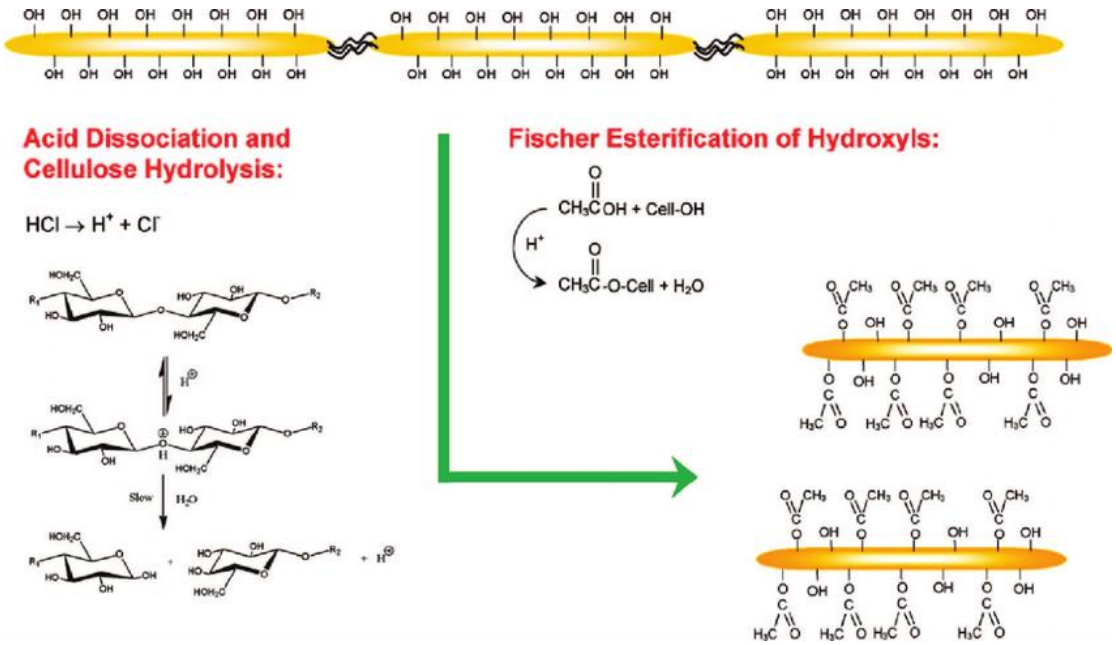

Figure 1.8: Reaction scheme illustrating the simultaneous occurrence of cellulose hydrolysis and esterification of hydroxyl groups using a mixture of acetic and hydrochloric acid as example

This procedure can be applied to access various esters of nanocellulose as demonstrated by the authors. However, a strict control of the esterification degree using this method is quite tough. In a similar approach, Herrick et al. have proposed in the early development of nanocellulose, the simultaneous acetylation of NFCs during the mechanical shearing using as processing media a mixture of acetic acid and acetic anhydride with sulphuric acid as catalyst instead of water [33].

1.4.5 Polymer Grafting

Surface chemical modification of cellulose nanoparticles can be achieved by covalently attaching small molecules, as well as polymers. The general objective of this chemical modification is to increase the polar character of the nanoparticle and have a better compatibility with hydrophobic polymer matrices. Two main approaches can be used to graft polymers onto surfaces, i.e., “grafting onto” or “grafting from”. The first method was extensively used for the fibers or the NCC particles and not for the NFC. The “grafting onto” approach consists of: (i) mixing the cellulosic nanoparticles with an existing polymer and a coupling agent to attach the polymer to the nanoparticle surface; or (ii) activating the cellulose substrates (or the polymer) and grafting one (or the other) onto the other one. The second strategy, i.e., “grafting from” approach, consists of mixing the cellulosic nanoparticles or the activated cellulosic nanoparticles with a monomer and an initiator agent to induce polymerization of the monomer from the nanoparticle surface. Ljungberg et al. done graft maleated PP (PPgMA) on to the surface of extracted nanocrystals. They found that in the linear region, the mechanical properties above the glass-rubber transition were found to be drastically enhanced for the nanocomposites as compared to the neat polypropylene matrix [34]. Habibi et al. grafted poly caprolactone on to the

surface of cellulose nano crystals via ring opening polymerization (ROP) using stannous octoate (Sn(oct) as a grafting & polymerization agent. They confirmed the grafting efficiency of the composite via long term stability of the suspension of PCL-grafted cellulose nanocrystals in toluene. They found the significant improvement in terms of young modulus and storage modulus [35].

1.4.6 Catonization

There are three kinds of methods to prepare cationic modified fibers. The first method is direct cationize fibers to get the cellulose fibre amine derivatives. The second method is cationic pre-polymer of short chain coupled to the fibre surface to obtain high surface charge density fibre. The third method is graft copolymerization of cationic polymers to the fibre; cationic monomer and neutral monomers are connected to the fibre surface by free radical copolymerization. All these three methods can make the fibre cationic, but the connection types of cationic and fibers are different, and finally the fibre morphology and performance are also different [36] There are few ways of introduction of cationic groups in cellulose by chemical reaction, for instance, attaching quaternary ammonium groups by using of 2,3-epoxypropyl trimethylammonium chloride (EPTMAC) [37- 39]. One end of the cationic reagent is quaternary ammonium salt, showing cationic character, and the other end of the structure is an epoxy group. Hasani et al. introduced epoxy propyl trimethyl ammonium chloride (EPTMAC) on the surface of nanocellulose, so that the nanocellulose was imparted positive charges [38]. Such surface catonization procedure was conducted through a nucleophilic addition of the alkali-activated cellulose to epoxy groups of EPTMAC. This modification resulted in the stable

aqueous suspensions of nanocellulose with unexpected thixotropic gelling properties.

1.5 Water purification as a comprehensive challenge for future and electrospun nanofibers as an advanced solution

The contamination of water is due to the excess amount of substance which can cause severe adverse effects to human beings, aquatic life and the ecosystem. Generally the pollutants are coming from physical, biological and physical process but the impact of water pollution depends on several factors like ecological impact of the pollutant, abundance of pollutant and the use of the water. Unfortunately the most of the water pollution is derived due to the industries, agriculture and land-based activities of human. The figure 1.9 a clearly shows the distribution mode of water on earth and it is shown that the oceans contain around 97 % of all water and only remain 3% is available as fresh water. Out of the 3% fresh water 79% is confined in glaciers and icecaps as saline water at the same time the rest of water is produced via the water cycle. Figure 1.9 b shows that surprisingly the remaining freshwater, almost all of it exists as ground water and not accessible. Of all the freshwater on earth, only about 0.3 percent is contained in rivers and lakes and usable for human's daily life. Despite such limited capacity of usable water, the human kind is also polluting the water thereby minimizing the available fresh usable water [40].

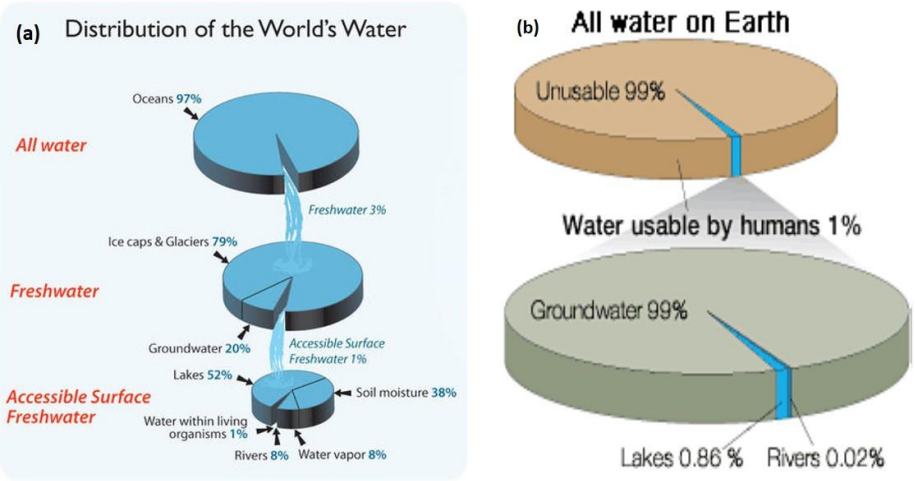

Figure 1.9: a) Distribution of earth's water and b) Scarcity of the water usable for human needs

According to the World Health Organization, in 2008 approximately 880 million people in the world (or 13% of world population) did not have access to improved (safe) drinking water as shown in the figure 1.10 (World Health Statistics, 2010) [41].

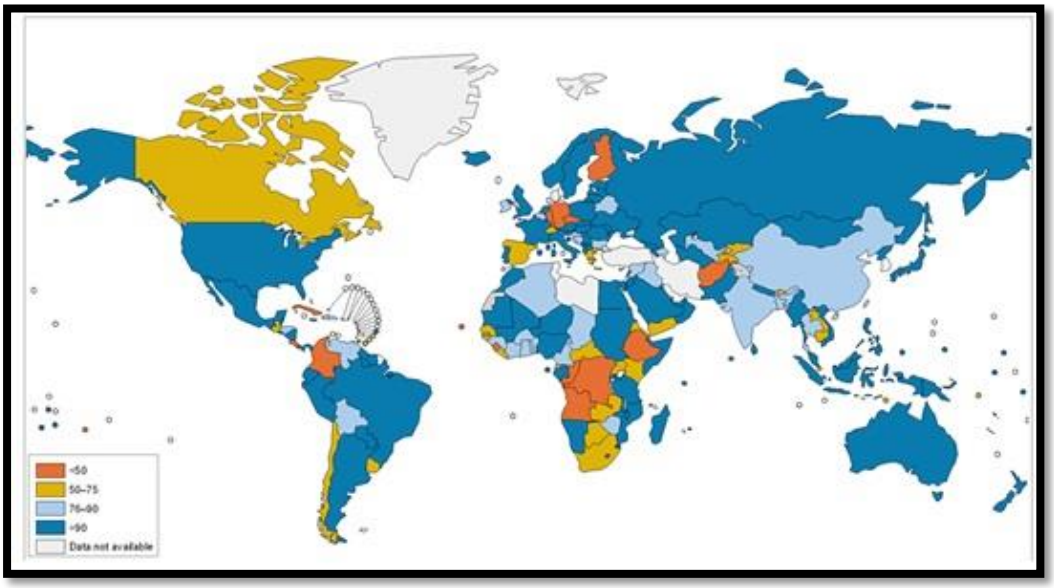

Figure 1.10: Proportion of Population by Country Using Improved Drinking Water Sources in 2008 ***Source: World Health Organization*** [41]

At the same time, about 2.6 billion people (or 40% of world population) lived without improved sanitation as shown in the figure 1.11, which is defined as having access to a public sewage system, septic tank, or even a simple pit latrine. Each year approximately 1.7 million people die from diarrheal diseases associated with unsafe drinking water, inadequate sanitation, and poor hygiene, e.g., hand washing with soap [41].

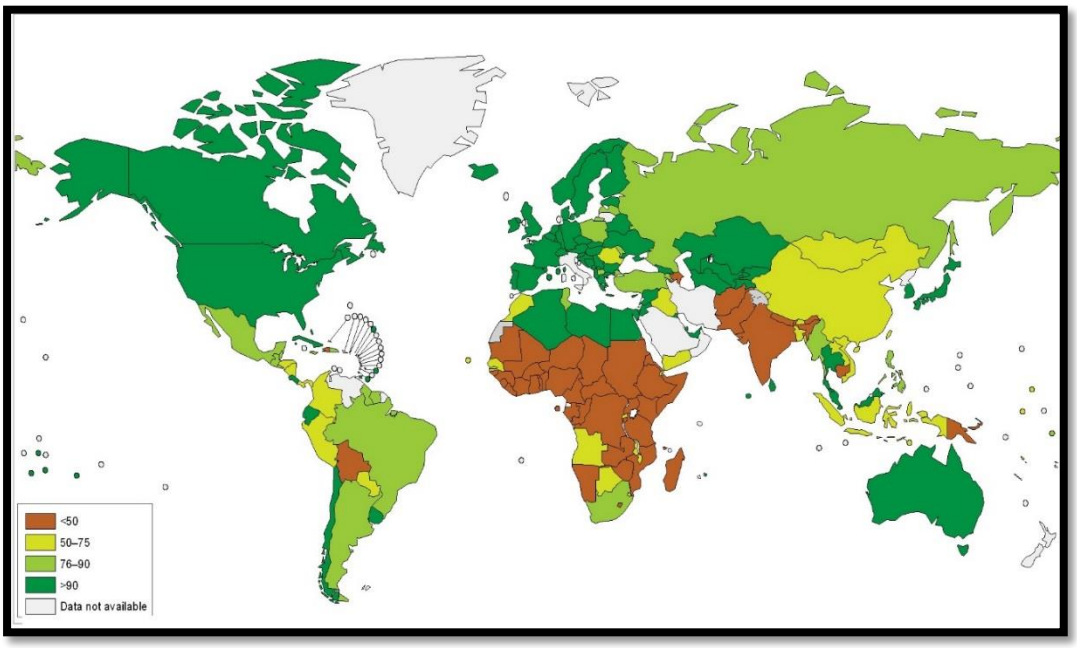

Figure 1.11: Proportion of Population by Country Using Improved Sanitation Facilities in 2008 ***Source: World Health Organization*** [41]

Considering the shortage of the usable water and the progressive pollution as a recognized threat to the world's environment, the attention must be switched, as quickly as possible, towards addressing these critical challenges and directing global research to develop advanced technology and devices for creation of a clean environment. Filtration technology is one of such advanced approaches for making a healthier and cleaner environment. For instance, tapping alternative sources of water, such as seawater, rainwater, wastewater effluent etc. and removal of available

contaminants through a filtration process to increase the water quality can be a potential solution for the problem of water shortage. Thus, advanced technologies for filtration are an essential part of meeting the current and future needs for water innovations in the development of novel technologies to desalinate the water. Membrane technology is expected to continue to dominate the water purification technologies owing to its energy efficiency.

1.5.1 Next Generation filtration Media: Electrospun Membranes

There are several methods such as melt fibrillation [42], Island-in-sea [43], and gas jet [44] etc. for producing nanofibers from high-volume production methods. However, their usefulness is limited by combinations of restricted material ranges, possibly fibre assembly, and cost and production rate. Here, electrospinning has an advantage with its comparative low cost and relatively high production rate. The ability to form porous fibers through electrospinning means that the surface area of the fibre mesh can be increased tremendously, which property makes the electrospun membranes as promising candidate for filtration applications. High porosity, interconnectivity, micro scale interstitial space and large surface to volume ratio that nonwoven electrospun nanofiber meshes are an excellent material for membranes water filtration [45].Fortunately, membrane separation is one of the most efficient methods to remove the contaminants from water, whose properties of porosity, surface charge, hydrophilic/phobic nature etc., play a vital role in filtration. Among them, electrospun three dimensional porous nanofibrous filtering membrane has received considerable attention because of their high porosity, good interconnectivity and high specific surface area [46]

1.5.2 Nanocellulose as an sustainable solution for water purification

Nanocellulose can be tailored into novel and significantly improved physical and chemical properties. The unique features of nanocellulose include small diameter, high surface –to-volume ratio, abundant hydroxyl groups for easy functionalization, good mechanical properties and good chemical resistance. These excellent properties make nanocellulose as a huge potential candidate for waste water treatment. In an aqueous environment, the high surface area and high aspect ratio of nanocellulose are beneficial for the formation of an ultrafine three-dimensional network structures which can be explored for removal and absorption of various pollutants in the water. Since cellulose is hydrophilic in nature, cellulose has been used an antifouling hydrophilic coating to increase the flux of the membranes. Cellulose tends to exhibit a high adsorption capacity for pollutant after suitable chemical modification on its surface with the aim of incorporating molecules that contain basic groups, particularly those that are rich in nitrogen, sulphur and oxygen [47]. Cellulose nanofibers have been intensively studied due to their natural abundance, ease of functionalization and structural diversity [48, 49]. Nanotechnologies have been touted as having great potential for reducing costs and improving efficiency in pollution prevention, treatment and clean up [50]. Nanocellulose has generated interest in this area as an active sorbent material for contaminants and as stabilizer for other active particles. The easily functionalizable surface of nanocellulose allows for the incorporation of different chemical moieties that may enhance the binding and adsorption efficiency against the pollutants in water such as dyes, toxic heavy metals etc. Cellulose nanomaterial are a promising alternative adsorbent due to its high surface area-to-volume ratio, low cost, high

natural abundance, and inherent environmental inertness. Moreover, CNFs easily functionalizable surface allows for the incorporation of chemical moieties that may increase the binding efficiency of pollutants to the CNFs. Carboxylation of CNFs is by far the most studied method for increasing their sorptive capacity. The sorption of organic contaminants has also been demonstrated with modified CNF matrices. The inherent hydrophilicity of CNFs can be reduced to improve the affinity of the material for hydrophobic compounds. The rapid progress made in the nanosciences, especially with nanocellulose; offer a potential new type of material for use in water treatment in the form of nanoparticles. Nanocellulose is efficient absorbent materials due to its high surface area to volume ratio, low cost, highly natural abundance and inherent environmental inertness. The manipulation of the surface chemistry of nanocellulose can be achieved by inclusion of both organic and inorganic functionalities; thereby it could acts as a water repellent such that it could remove oils that were spread on the surface of the water.

Nanocellulose based microfiltration membranes for water treatment has gained considerable interest in nowadays. The dimensions of nanocellulose and the strength of the material can be exploited in the fabrication of membranes for water treatment. Membranes can greatly benefit from the high strength of nanocellulose. At low loadings of a few wt% nanocellulose can increase the tensile strength of polymer membrane up to 50% [51, 52]. At low nanocellulose loading (< 4 wt %), membranes show increased porosity, larger pore size and greater surface hydrophilicity which lead to greater water permeability. The addition of nanocellulose to polymer membrane has generally been shown to increase membrane hydrophilicity, thereby reducing the antifouling problems of the membrane. All these properties such as

membrane surface hydrophilicity, greater permeability, greater selectivity and greater resistance to bio-fouling make nanocellulose as a promising candidate for waste water treatment applications.

1.5.2.1 Cellulose nanofibers (CNFs) based microfiltration membrane for water purification

The dimensions of CNFs and their strength can be exploited in the fabrication of membranes for water treatment. Recently many studies have been reported on the CNFs based nanofibrous microfiltration membrane for water treatment. Wang et al. prepared CNFs based microfiltration membranes capable of removing bacteria, virus and heavy metals. They demonstrated a two-layered nanoscale PAN/ micro scale PET fibrous scaffold containing infused ultra-fine functional CNFs. They showed that the demonstrated membrane could simultaneously remove bacteria, viruses or toxic heavy metal ions. They found that, the demonstrated membrane with the addition of a substantial amount of charged groups (positively charged carboxylate groups or negatively charged amine groups) on the extremely large surface area of ultra-fine cellulose nanofibers was facilitated completely removing of bacteria (*E.coli*), reaching a log-reduction value (LRV) of 4 for MS2 virus removal shown in Table 1.3 and had the adsorption capability of 100mg chromium (Cr) (VI) or 260 mg lead Pb (II) per gram of cellulose nanofiber, while maintaining a high permeation rate (1300L/m^2h/Psi). They concluded that the demonstrated membranes were unique as they could simultaneously remove toxic contaminants (virus, heavy metals) from polluted water with relatively large pores as well as bacteria by size exclusion [53].

PET/PAN layer thickness (µm)	Max. pore size (µm)	Mean flow pore size (µm)	Cellulose nanofiber loading (mg/cm^2)	LRV for *E.coli bacteria*	LRV for MS2 virus
100+40	0.78± 0.03	0.66 ± 0.01	0	6	0
100+ 40	0.73± 0.01	0.38 ± 0.01	0.2 ± 0.05*	6	0
100+ 40	0.78± 0.01	0.32 ± 0.01	0.2 ± 0.05**	6	>4

*Cellulose nanofibers without PVAm grafting

** Cellulose nanofibers with PVAm grafting.

Table 1.3: Retention of MS2 of composite membranes [53]. Copyright (2013). Reproduced with the permission from Elsevier Ltd.

Another CNFs based nanofibrous microfiltration membrane was fabricated by Ma et al. and they prepared ultrafine CNFs via TEMPO/NaBr/ NaClO oxidizing method and fabricated thin film nanofibrous composite (TFNC) membranes by using prepared ultrafine CNFs. They showed that CNFs top barrier layer surface appeared to be relatively smooth as shown by SEM given in figure 1.12. This resulted in a lower tendency to trap unwanted materials on the CNFs barrier surface, thereby reducing the fouling problem.

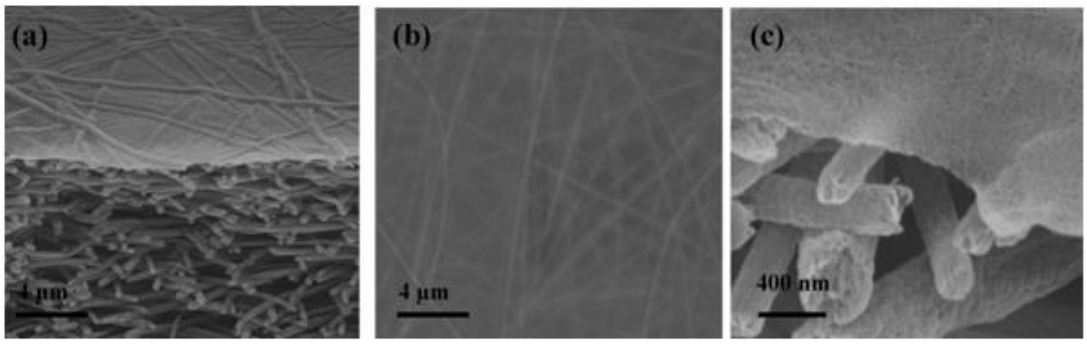

Figure 1.12: SEM images of (a) cross-sectioned view of TFNC membrane with cellulose nanofiber barrier layer; (b) top view of TFNC membrane; and (c) magnified cellulose nanofiber barrier layer of TFNC membrane [54].Copyright (2011). Reprinted with permission from American Chemical Society.

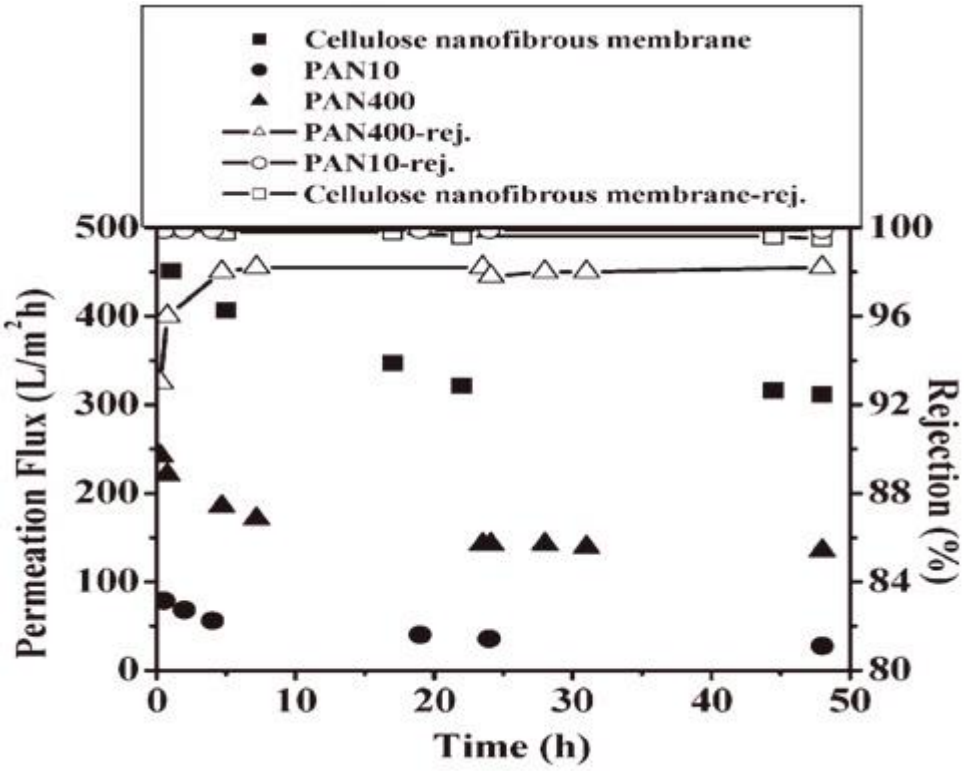

Figure 1.13: Permeation flux and rejection ratio of TFNC membrane containing cellulose nanofiber barrier layer (0.10 ± 0.02 µm thickness, prepared from 0.05 wt% aqueous suspension) as a function of time; measurement carried out a constant pressure of 30 psi and temperature of 37º C based on ultrafiltration of oil/water emulsions. (The ultrafiltration performance of commercial PAN10 and PAN400 membranes was also included for comparison [54].Copyright (2011). Reprinted with permission from American Chemical Society.

They found from MS2 bacteriophage testing that the demonstrated TFNC membrane had very high virus adsorption capacity due to very high surface-to- volume ratio and negatively charged surface of CNFs. They reported that, the ultrafine cellulose nanofibers- based TFNC membrane had 10-fold higher permeation flux with above 99.5% rejection ratio, when compared with two commercial UF membranes (PAN10 and PAN 400) shown in figure 1.13. They led to a conclusion that the ultrafine CNFs –based TFNC membranes could surpass conventional membrane systems in different water purification applications [54].

1.5.2.2 Cellulose nanocrystals (CNCs) based microfiltration membranes for water purification

The CNCs enhanced mechanical properties, low defects, high surface area to volume ratio; CNCs have been successfully added to a wide variety of microfiltration membranes for water purification. Additionally, CNCs are particularly attractive nanoparticles because they have low environmental, health and safety risks, are inherently renewable, sustainable and have the potential to be processed in industrial-scale quantities at low costs. Cao et al. reported robust poly acrylonitrile nanofibrous membrane reinforced with jute cellulose nanowhiskers for water purification. They developed a novel double layer of poly acrylonitrile (PAN) electrospun nanofibrous membranes (with an average fibre diameter of 173 nm) reinforced with TEMPO (2,2,6,6- tetra methyl piperdine-1-oxyl radical) selectively oxidized jute cellulose nanowhiskers (with a diameter in the range of 3-10 nm). They showed that the introduction of cellulose whiskers into the composite membrane had improved the mechanical properties, such as tensile strength increased to 10 MPa for single layer composite membrane and 14 MPa for double layer composite membrane, shown in figure 1.14. This can interpreted by the strong hydrogen bonding of cellulose nanowhiskers network formed on the surface of PAN nanofibrous electrospun membrane.

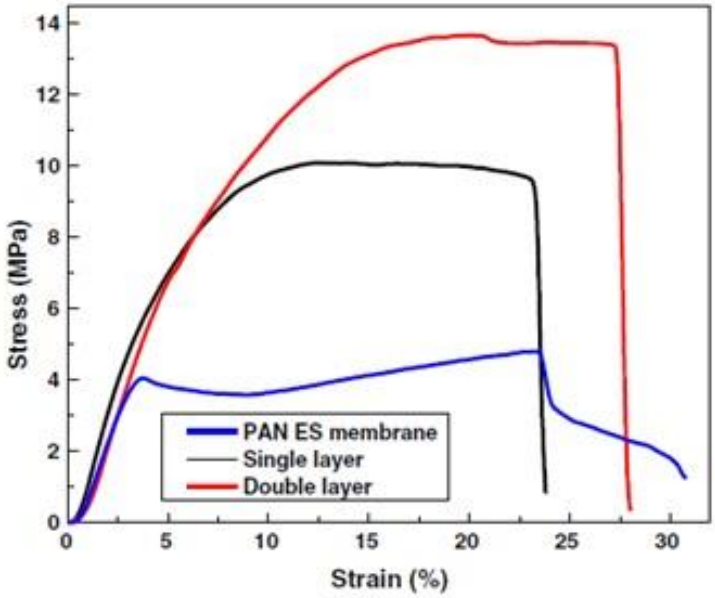

Figure 1.14: Stress-strain curves for PAN ES films, PAN ES films reinforced with cellulose nanowhiskers and double layers of PAN ES films reinforced with cellulose nanowhiskers [46]. Copyright (2013). Reproduced with permission from Elsevier Ltd.

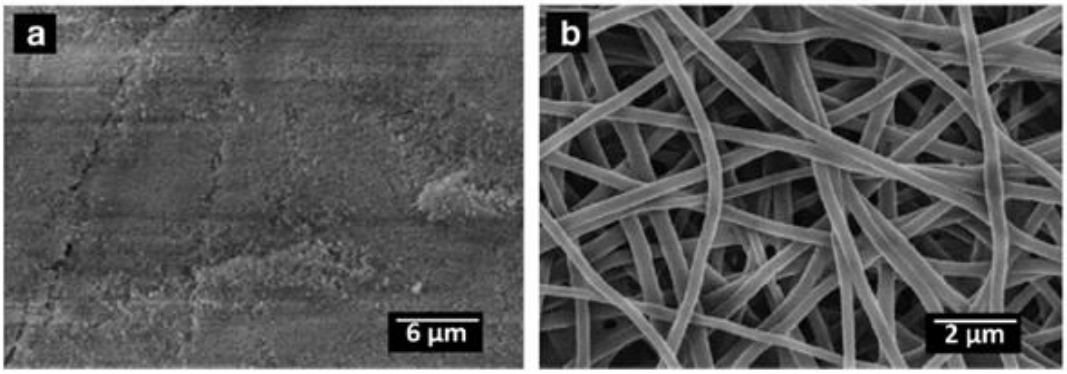

Figure 1.15: FESEM images of PAN fibrous composite membrane after filtration of silica nanoparticles, top surface (a) and bottom surface (b) [46]. Copyright (2013). Reproduced with permission from Elsevier Ltd.

They had done silica nanoparticles removal and oil/water separation on the fabricated membranes. From the FESEM images shown in figure 1.15, from the top surface of the filtrated membrane they observed that the nanoparticles formed a thick film, but from the bottom surfaces of composite membrane surface there was no nanoparticles and they found that the fabricated membrane successfully removed

the silica nanoparticles with 7-40 nm from the simulative waste water. They also reported that the composite membrane had the rejection ratio above 99.5% against the oil/water mixture. Moreover, they observed that the oil concentration of the filtrate was less than 5.5 ppm, which definitely satisfied with the environmental standard for waste water discharge (< 10 ppm) [46]. Another interesting work was reported by Ma et al. and they demonstrated a multi-layered nanofibrous microfiltration (MF) membrane system with high flux, low pressure drop and high retention capability against both bacteria and bacteriophages (a virus model) by impregnating ultrafine cellulose nanowhiskers (diameter about 5 nm) into an electrospun polyacrylonitrile (PAN) nanofibrous scaffold supported by poly (ethylene terephthalate) (PET) non-woven substrate. They reported that young's modulus and ultimate tensile strength for the cellulose nanowhiskers based nanofibrous membrane were 375± 15 & 14.3±0.4 MPa, respectively, which were about two times higher than those (i.e., 226± 20 & 8.5 ± 0.3 MPa) of the unmodified membrane containing only electrospun scaffolds. This was due to the stabilization of the electrospun scaffold by the formation of cross-linked cellulose nanowhiskers mesh, in agreement with the SEM images shown in figure 1.16.

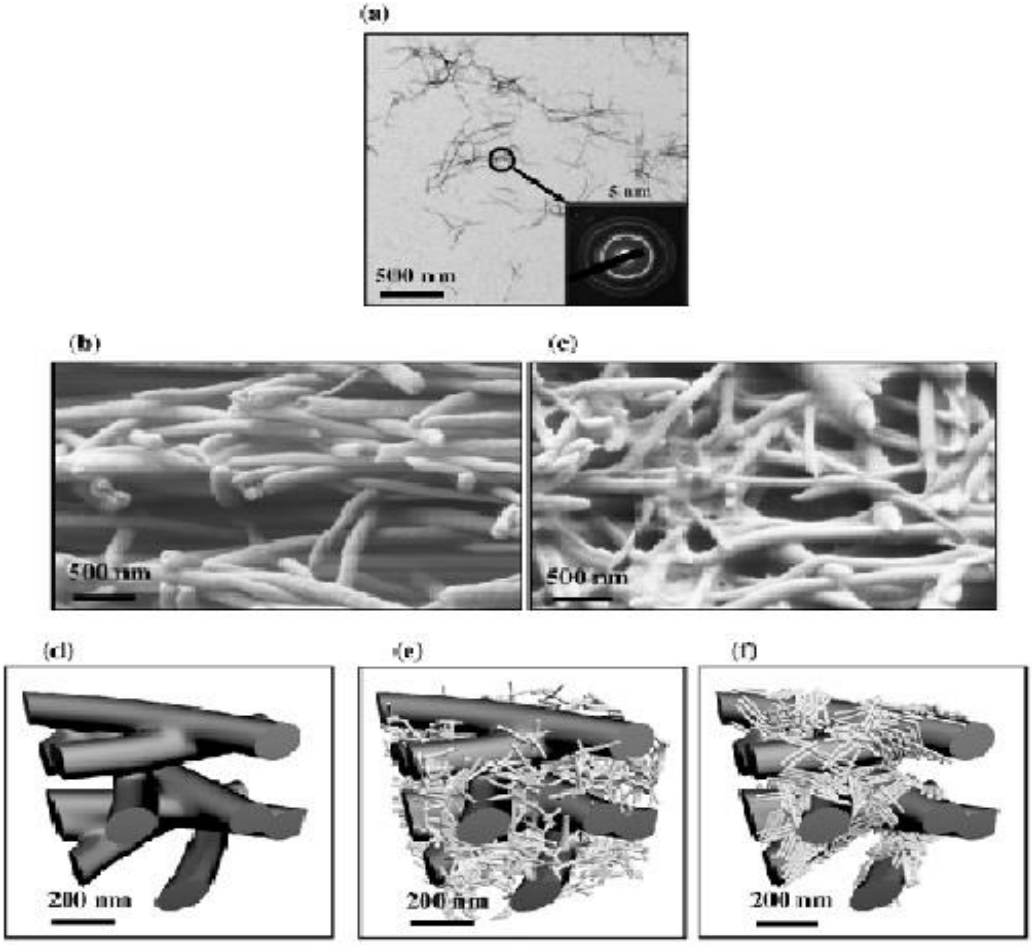

Figure 1.16: (a) TEM image of cellulose nanowhiskers fabricated by the TEMPO/NaBr/NaClO oxidation method. (The inset shows the electron diffraction pattern.) (b) SEM images of cross-sectional views of PAN electrospun nanofibrous scaffold and (c) cellulose nanowhisker-modified PAN electrospun nanofibrous scaffold. Schematic representations of electrospun nanofibrous scaffolds: (d) scaffold before nanowhisker infusion; (e) infused nanowhiskers forming loose cross-linked mesh; and (f) nanowhiskers collapsed onto the scaffold, forming bundles [55]. Copyright (2012). Reprinted with permission from American Chemical Society.

They observed that cellulose nanowhisker-based MF membrane exhibited 16 times higher adsorption capacity against positively charged dye over a commercial nitro cellulose-based membrane and this experimental membrane also showed full retention capability against bacteria, for example, *E.coli* & B. diminuta (log

reduction value (LRV) larger than 6) and decent retention against bacteriophage *MS2* (LRV larger than 2) [55].

1.6 EMI Shielding as a global challenge for future and intrinsically conducting polymers based on cellulose nanopapers as an advanced solution

Widespread use of electric and electronic systems for household, industrial, communication and other application makes it necessary for circuits to operate in close proximity of each other. Often these circuits affect performance of other near or far region electromagnetic fields. This interference is thus called electromagnetic interference (EMI), and is emerging to be a major problem for circuit designers. In addition the use of integrated circuits are being put in less space close to each other, thereby increasing the problem of interference [56]. EMI which can cause unacceptable deterioration of equipment performance due to the unwanted radiated signals [57]. If these issues are left unattended, it may cause severe damage to communication system and safety operation of many electronic devices. More over the EMI also causes a lot of health issues such as symptoms of languidness, insomnia; nervousness and headache on exposure to electromagnetic waves [58-60]. In the operation of microprocessor controlled devices the use of high frequency signals may be transmitted out of the device to the surrounding environment can severely affect the functioning of nearby equipment. So in order to prevent this, an electronic devices must be shielded in such a way that both incoming and outgoing interferences should be filtered [61].

ICPs are new alternative candidates for EMI shielding applications due to their lightweight, corrosion resistance, ease of processing, and tuneable conductivities as compared with typical metals. More importantly, the dominant shielding

characteristic of absorption other than that of reflection for metals render ICPs more promising materials in applications requiring not only high EMI shielding effectiveness but also shielding by absorption, such as in stealth technology. Intrinsically conducting polymers (ICPs) are attractive alternative materials for EMI shielding.

1.6.1 EMI Shielding Theory

Shielding effectiveness is the ratio of impinging energy to the residual energy. When an electromagnetic wave pass through a shield, absorption and reflection takes place. Residual energy is part of the remaining energy that is neither reflected nor absorbed by the shield but it is emerged out from the shield. All electromagnetic waves consist of two essential components, a magnetic field (H) and an electric field (E) as shown in figure 1.17. These two fields are perpendicular to each other and the direction of wave propagation is at right angles to the plane containing the two components. The relative magnitude depends upon the waveform and its source. The ratio of E to H is called wave impedance. EMI shielding consists of two regions, the near field shielding region and far field shielding region. When the distance between the radiation source and the shield is larger than $\lambda/2\pi$ (where λ is the wavelength of the source), it is in the far field shielding region. The electromagnetic plane wave theory is generally applied for EMI shielding in this region. When the distance is less than $\lambda/2\pi$, it is in the near field shielding and the theory based on the contribution of electric and magnetic dipoles is used for EMI shielding [62].

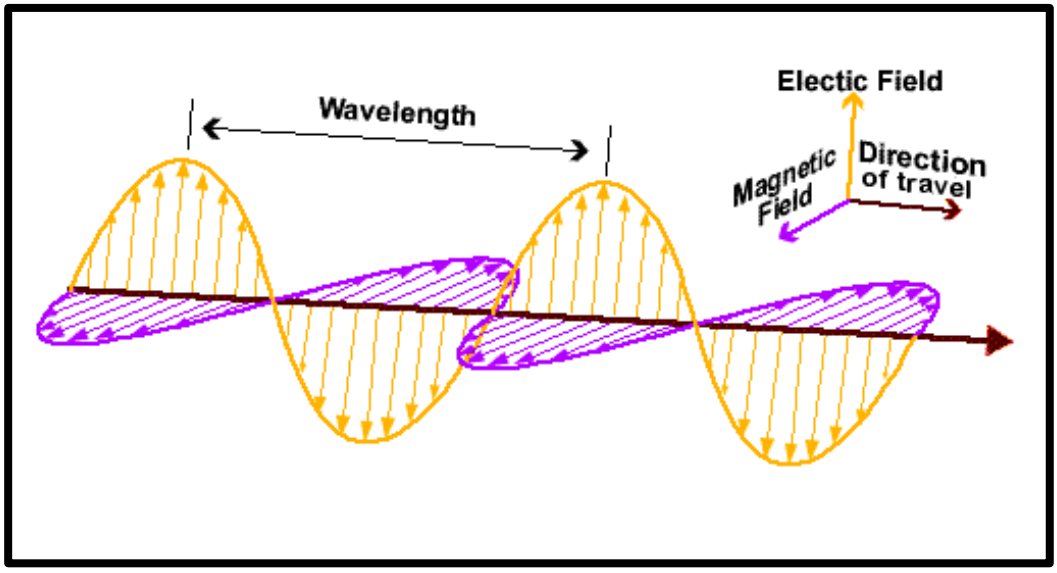

Figure 1.17: Electromagnetic radiation vector

Shielding effectiveness (SE) is the ratio of the field before and after attenuation of electric and magnetic field and can be expressed as

$$SE = 20 \log (E_t/E_i) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$SE = 20 \log (H_t/H_i) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where E and H are electric and magnetic fields and the subscripts t and i refer to the transmitted and incident waves. E is measured in volts/m and H in amps/m. SE is a function of frequency [63].

The attenuation of an electromagnetic wave occurs by three mechanisms as shown in figure 1.18. They are Absorption (A), Reflection (R) and Multiple reflections (B). Thus shielding effectiveness is the sum of all the**se** three terms SE = A+ R+ B.

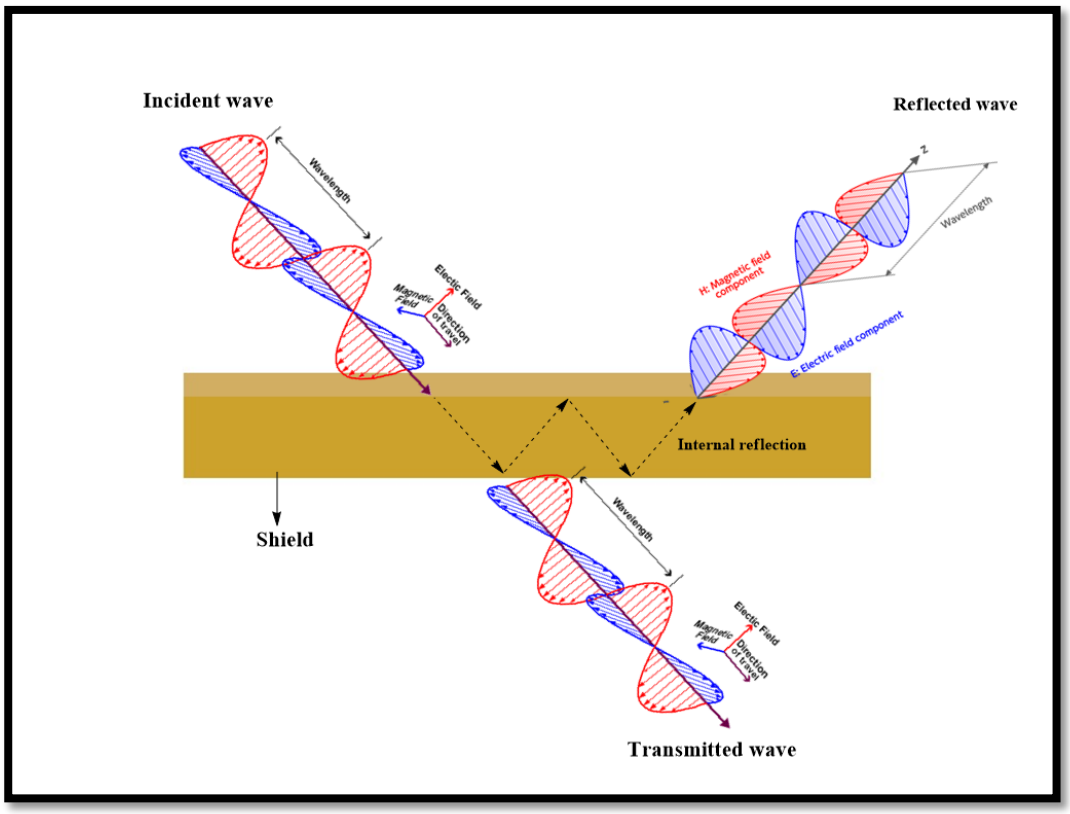

Figure 1.18: Attenuation of an electromagnetic wave by a shield.

1.6.2 Polymers as EMI shielding material

Generally polymers are natural insulators and do not reflect or absorb EMI. Most of the energy waves are not obstructed by polymers and enter or leave the housing rapidly which causes interference problems. In order to shield EMI, several technical approaches have been extensively used to improve the electrical conductivity of polymers by the way of 1) Conductive coating of plastics, 2) Compounding with conductive fillers and 3) Intrinsically conducting polymers.

1.6.3 Conductive coating of plastics

Metallic plating [64, 65] and coating on plastics are well established techniques for decorative, automotive appliance and plumbing products. However, metallized plastics are also used for conductive applications. For EMI shielding purpose

following methods are used for metalizing the plastic surface. There are different coating techniques have been employed to make conductive coating on the plastics. They are Foil laminates and tapes, Ion plating, Vacuum metallization, Zinc flame spraying, Zinc arc spraying, Cathode sputtering, Conductive paints, Electro less plating and Electroplating [66-68]. Main disadvantage of the above mentioned techniques are, these process are secondary to the moulding operation and hence demand additional surface preparation and special equipment.

1.6.4 Compounding with conductive fillers

Conventional polymers are excellent electrical insulators having resistivity in the range of 10^{15} -10^{18} Ω cm and it is possible to make it conductive by the incorporation of a conducting material. Several extensive studies have been done to enhance the conductivity of the polymers by incorporating the conductive nano fillers like, graphene, carbon nanotubes, carbon black, carbon nano fibers etc. Li et al. investigated electromagnetic interference shielding of single –walled carbon nanotube epoxy composites. Their results indicated that the SWNTs can be used as effective light weight EMI shielding materials. They found that the epoxy composites with 15 wt % of SWNT have the highest EMI shielding effectiveness with 49 dB at 10 MHz [69]. Thomassin et al. investigated the EMI reduction of polycaprolactone/ MWNT nanocomposites foams. Carbon nanotubes were dispersed within PCL by melt blending and by co-precipitation. They found that the PCL composites with very low vol% of MWNTs had high EMI shielding efficiency in the range of 60-80 dB [70]. Yang et al. developed a novel carbon nanotube – polystyrene (PS) foam composite for EMI shielding. They found that even at low concentration of CNT (7wt%) the composite had an efficient EMI in the range of 20

dB and they concluded that such a CNT-PS foam composite can be used commercially as a shielding material against electromagnetic radiation. The primary EMI shielding mechanism of such CNT-PS foam composites was demonstrated and ascribed to the reflection of electromagnetic radiation [71]. Yousefi et al. developed a self-aligned RGO/epoxy nanocomposites with highly anisotropic mechanical and electrical properties for EMI shielding application. The large rGO sheets and their alignment into a layered structure play an important role in achieving a dielectric constant of over 14000 with 3 wt% of rGO at 1 kHz. They found that the demonstrated nanocomposites had very high dielectric constant and can be served as an effective EMI shielding materials due to their high charge absorbing characteristics with a remarkable EMI SE of 38 dB [72]. Zhang et al. fabricated graphene-PMMA nanocomposites by blending and then foamed by using an environmentally benign subcritical CO_2 foaming technique for EMI shielding application. They found that the graphene-PMMA foam with a low graphene loading of 1.8 vol % exhibited not only a high conductivity of 3.11 S/m, but also a good EMI shielding efficiency of 13-19 dB at the frequencies from 8 to 12 GHz. The EMI shielding efficiency was mainly attributed to the absorption rather than the reflection in the investigated frequency range. Moreover they concluded that, this work provides a promising methodology to fabricate tough and lightweight graphene-PMMA nanocomposites microcellular foams with superior electrical and EMI shielding properties [73].

1.6.5 Intrinsically conducting polymers (ICPs)

Since the discovery of ICPs in the late 1970s [74] EMI shielding, as well as electrostatic discharge, have been well projected and evaluated by many early papers

[75-78]. Applications of ICPs and their composites (or blends) owing to the higher electrical conductivity of these polymers in doped states have been extensively studied subsequently by many researchers. [79-81].

ICPs are termed organic polymers that possess the electrical, electronic, magnetic, and optical properties of a metal while retaining the mechanical property, process ability, etc. Since the first ICP, polyacetylene (PA), was successfully synthesized in 1977 by Shirakawa et al. [74] great interests have been aroused and a series of ICPs,[82] such as polyaniline (PANI), polypyrrole (PPY), polythiophene (PTH), poly(p-phenylene-vinylene) (PPV) (Figure 1.19) have been synthesized subsequently and studied extensively.

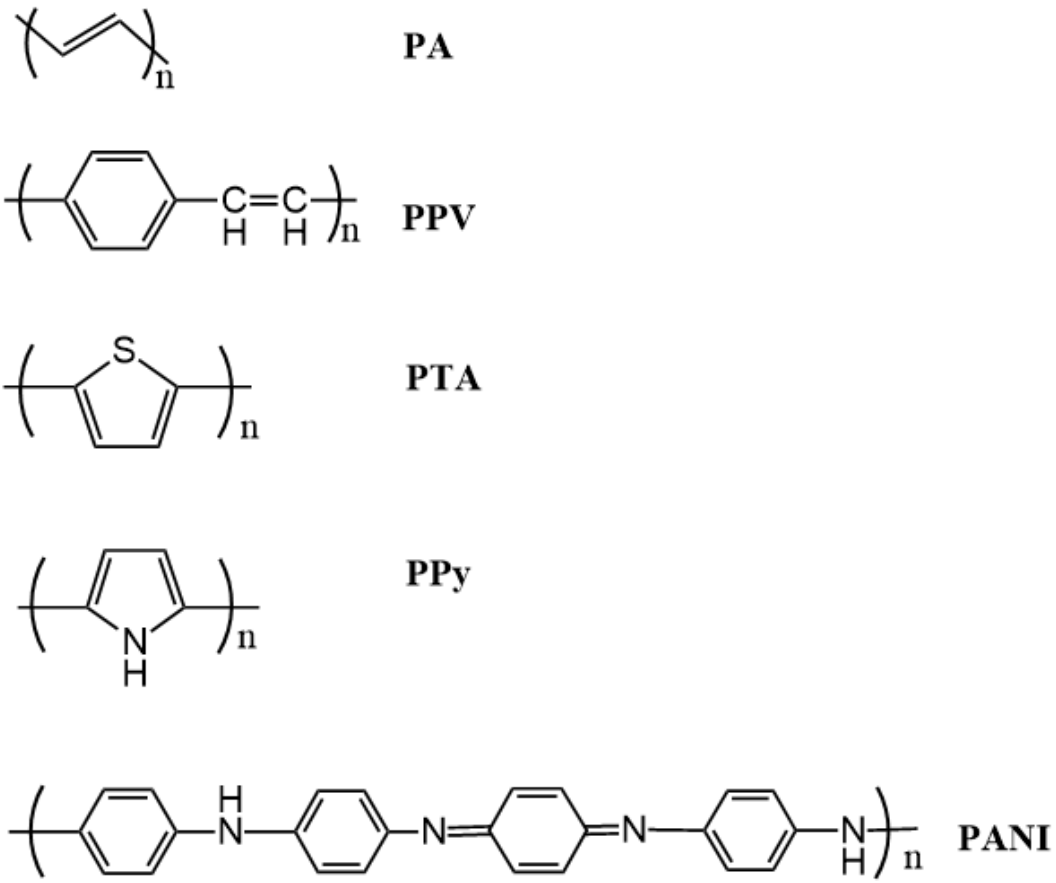

Figure 1.19: Molecular structure of common intrinsic conducting polymers

Kim et al. investigated the EMI shielding of the PET fabric/ polypyrrole (PPy) composite with high electrical conductivity. The composite was prepared by the chemical and electrochemical polymerization of PPy in sequence on a polyester (PET). They found that the fabricated composite shield EMI by absorption as well as reflection and that EMI shielding through reflection increased with the electrical conductivity. The specific volume resistivity of the composite prepared in this study was extremely low as 0.2 O cm and EMI SE was in the practically useful range of about 36 dB over a wide frequency range up to 1.5 GHz. They concluded that, the PET fabric/ PPy composite is practically useful for many applications requiring not only a high EMI SE but EMI shielding by absorption of the wave [83]. Intrinsically conducting hot melt adhesives ICHMAs have been developed by Pomposo et al. based on polypyrrole PPy blends, for use in electronic and telecommunication applications requiring shielding against electromagnetic interference EMI. The conductivity properties, adhesion characteristics and both near- and far-field EMI SE behaviour of these ICHMAs at room temperature are investigated as a function of PPy content. They found that at 300 MHz, the near-field EMI SE values were estimated to remain above 30 dB for the fabricated ICHMAs [79]. Polypyrrole (PPy) was polymerized both chemically and electrochemically in sequence on nylon 6 woven fabrics, giving rise to polypyrrole–nylon 6 composite fabrics (PPy–N) with a high electric conductivity for EMI shielding application was fabricated by Kim et al. and they got an electromagnetic interference shielding efficiency (EMI SE) values were in the range 5– 40 dB and depended on the conductivity and the layer array sequence of the conductive fabric. Moreover they found that, the composites with a high conductivity represented reflection-dominant EMI shielding characteristics,

which were typical of the EMI shielding characteristics of metals [84]. Erdogan et al. investigated the EMI shielding efficiency of the Conductive polythiophene (PTh)/poly (ethylene terephthalate) (PET) composite fibers, which were prepared by polymerization of thiophene in the presence of PET fibers in acetonitrile medium using $FeCl_3$. The effects of polymerization conditions such as oxidant/monomer mol ratio and polymerization temperature and time on PTh content and surface electrical resistivity of PTh/PET composite fibre were investigated in detail. They obtained the EMI shielding effectiveness (SE) in the range of 21 dB, which was suitable for commercial EMI applications [85].

1.6.6 EMI Shielding with Polyaniline (PANI)

PANI possess a fascinating electromagnetic interference shielding mechanism by absorption, leading as a tremendous material especially for military purposes. Unlike other conducting polymers like polypyrrole, polythiophene and polyfuran, the hetro atoms in the PANI contributes to π bond formation thereby become conducting. This makes PANI as a unique conducting polymer among the conductive polymers. The first systematic study of PANI for EMI shielding was reported by Shacklette et al. and they melt blended PANI with polyvinyl chloride (PVC) to form a composite with conductivity of 20 S/cm. EMI SE of the PANI composites, as well as other composites of metal fillers, were measured over a frequency range from 1MHz to 3GHz and theoretically calculated for both near and far field. They obtained far field SE as high as 70 dB for the PANI composite [86]. Trivedi et al. grafted PANI on surfaces of fabrics and measured their EMI SE using the coaxial transmission line method in the frequency range of 1000 kHz to 1 GHz. The results showed that at

higher frequencies (0.1MHz to 1 GHz), the SE is at 16–18 dB; while at lower frequencies, it is more than 40 dB They concluded that, the level of doping and type of dopant, as well as the thickness of the PANI layer, had strong effect on the SE of the PANI grafted fabrics [61]. Saini et al. fabricated polyaniline (PANI)–multi-walled carbon nanotube (MWCNT) for microwave absorption and EMI shielding via insitu polymerization of PANI on MWCNT. Their shielding studies revealed that reflection loss increases slightly from −8.0 to −12.0 dB whereas absorption loss exhibits rapid enhancement from −18.5 to −28.0 dB with the increased CNT loading. They obtained absorption dominated total shielding effectiveness in range of −27.5 to −39.2 dB indicates that these materials could be utilized effectively for the shielding purposes in the Ku-band (12.4–18.0 GHz). Finally they concluded that these PANI coated MWCNTs with large aspect ratio were proposed as hybrid conductive fillers in various thermoplastic matrices for making structurally strong microwave shields [87]. Another study was reported by Koul et al. and they studied the electromagnetic interference shielding effectiveness of conducting polyaniline (PANI) – acrylonitrile–butadiene–styrene (ABS) composites at 101 GHz. They observed that shielding effectiveness of the PANI–ABS composites increases with the increase in the loading levels of the conducting polymer doped with hybrid dopants. The lower loading of PANI doped with hybrid dopants in the moulded conducting composites can be effectively used for the dissipation of electrostatic charge. However, with higher loadings, a shielding effectiveness of 60 dB has been achieved which makes the conducting composites a potential EMI shielding material for its application in encapsulation of electronic equipment's in electronic and in high tech applications [88]. Yuping et al. investigated electrical conductivity and

EMI shielding effectiveness (SE) of the silicone rubber (SR) with different loading levels of HCl –doped polyaniline (PANI-HCl) composites in the low frequency range from 3 to 1500 MHz. They found that the SE of the composites increase and the volume resistivity decrease with increasing mass ratio loading of PAN-HCl in the SR. They obtained the SE of the composites were from 16 to 19.3 dB at 100 mass ratio loading of the PANI-HCl [89].

1.6.7 Cellulose nanopapers derived from bio-mass as an effective substrate for EMI Shielding applications

Intrinsically conductive polymers are promising candidates for EMI shielding applications due to their lightweight, corrosion resistance, ease of processing, and tuneable conductivities as compared with typical metals. More importantly, the dominant shielding characteristic of absorption other than that of reflection for metals render intrinsic conducting polymers more promising materials in applications requiring not only high EMI shielding effectiveness but also shielding by absorption, which is highly desirable in the current scenario. However, the existence of the conjugated system in conductive polymers enhances the rigidity of the polymer molecule, which resulted in the insolubility in most of the organic solvents. Moreover these polymers are not able to form a film by casting or other techniques. This is due to the fact that ability of such polymers to form H bonds is very low. In order to alleviate this problem, several works have been done in recent years to fabricate different conducting polymers composites by blending different polymers with excellent process ability. Among them, cellulose nanofibers from bio-mass as abundant renewable eco-friendly materials have gained considerable interest among scientific community. Cellulose nanofiber based papers or cellulose nanofiber suspensions give adequate H-bonding that films may be easily produced

from the mixture of conducting polymers and cellulose nanofibers. By combining the cellulose nanofibers with conducting polymers, the poor formability and frangibility of conducting polymers can be alleviated to produce a conducting composite that is capable to shield electromagnetic radiations.

Very few works have been reported in this aspect. Fugetsu et al. investigated electrical conductivity and electromagnetic interference shielding efficiency of carbon nanotube/ cellulose composite paper. They observed that the CNTs form a continuously interconnected network on the cellulose fibers. They found that, the paper containing 8.32 wt% CNTs was electrically conductive with a volume resistance of $5.3 \cdot 10^{-1}$ Ω cm. The fabricated composite paper was capable of shielding electromagnetic interference over the tested range of 15–40 GHz, particularly in range of 30–40 GHz, with absorption as the essential shielding mechanism [90]. Marins et al. prepared conducting bacterial cellulose (BC) membranes coated with a high proportion of polyaniline (PAni) were prepared through in situ oxidative polymerization of aniline on the surface of the BC in the presence of acetic acid as the protonating agent. They investigated the effect of two different oxidizing agents, ammonium persulfate (APS) or iron (III) chloride ($FeCl_3$), on the mechanical performance, electrical conductivity, crystallinity, morphology and ability to absorb the electromagnetic radiations. They obtained the shielding effectiveness (SE) of -5 dB for BC/PANI membranes at 8.2-12.4 GHz [91]. Cellulose/ carbon nanotube composite aerogel for highly efficient electromagnetic interference shielding was developed by Huang et al. and they demonstrated a scaffold structure which was well designed from nanofibrillar networks to nanosheet networks by controlling the concentration of cellulose in the

sodium hydroxide/urea solution. The obtained conductive aerogel was first reported as an electromagnetic interference shielding material; it exhibits an electromagnetic interference (EMI) shielding effectiveness of 20.8 dB at frequency range of 8.2–12.4 GHz. They concluded that this type of green conductive aerogel has the potential to be used as lightweight shielding material against electromagnetic radiation, especially for aircraft and spacecraft applications [92]. Similar work was reported by Jian et al. and they developed the environmentally-friendly hybrid aerogels consisting of cellulose and multi-walled carbon nanotubes (MWCNTs). In addition, they obtained high electromagnetic interference (EMI) shielding effectiveness (SE) value of 19.4 dB They concluded that the absorption-dominant shielding mechanism of the fabricated aerogel helps a lot to reduce secondary radiation, which was beneficial to develop novel eco-friendly EMI shielding materials [93].

1.7 Objectives of research

The major objectives of the research thesis are:

1) Extraction of cellulose nanofibers (CNFs) from sunflower stalks by steam explosion coupled with mild acid hydrolysis.

2) To produce a unique green adsorbent material from cellulose nanofibers (CNFs) via a non-solvent assisted procedure using Meldrum's acid as an esterification agent to enhance the adsorption toward positively charged crystal violet dyes.

3) Fabrication of polyvinylidene fluoride (PVDF) microfiltration membrane via Electrospinning process.

4) Fabrication of Meldrum's acid modified cellulose nanofiber-based PVDF microfiltration membrane via vacuum filtration technique and their characterizations.

5) Evaluation of adsorption efficiency of Meldrum's acid modified cellulose nanofiber-based PVDF microfiltration membrane against positively charged dyes.

6) Microfiltration performance of Meldrum's acid modified cellulose nanofiber-based PVDF microfiltration membrane against nanoparticles.

7) Insitu polymerization of aniline on cellulose nanofibers (CNFs)

8) Fabrication of conductive polyaniline (PANI)/ CNFs nanopapers via vacuum filtration technique and their characterizations.

9) EMI shielding performance of PANI/CNF nanopapers.

To accomplish the goals, various experimental techniques and equipment's will be used to characterize the composite membranes and papers such as Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), UV-visible spectro photometer, Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy, X-ray Diffraction (XRD) analysis, Pore size analyser, dielectric measurements and PNA Network analyser.

1.8 References

1) Nevell, Thomas Percy, and S. Haig Zeronian. "Cellulose chemistry and its applications." (1985).

2) Aulin, Christian, Susanna Ahola, Peter Josefsson, Takashi Nishino, Yasuo Hirose, Monika Österberg, and Lars Wågberg. "Nanoscale Cellulose Films with Different Crystallinities and Mesostructures Their Surface Properties and Interaction with Water." *Langmuir* 25, no. 13 (2009): 7675-7685.

3) Lavoine, Nathalie, Isabelle Desloges, Alain Dufresne, and Julien Bras. "Microfibrillated cellulose–Its barrier properties and applications in cellulosic materials: A review." *Carbohydrate polymers* 90, no. 2 (2012): 735-764.

4) Turbak, Albin F., Fred W. Snyder, and Karen R. Sandberg. "Suspensions containing microfibrillated cellulose." U.S. Patent 4,500,546, issued February 19, 1985.

5) Li, Meng, Li-jun Wang, Dong Li, Yan-Ling Cheng, and Benu Adhikari. "Preparation and characterization of cellulose nanofibers from de-pectinated sugar beet pulp." *Carbohydrate polymers* 102 (2014): 136-143.

6) Chen, Wenshuai, Kentaro Abe, Kojiro Uetani, Haipeng Yu, Yixing Liu, and Hiroyuki Yano. "Individual cotton cellulose nanofibers: pretreatment and fibrillation technique." *Cellulose* 21, no. 3 (2014): 1517-1528.

7) Pelissari, Franciele Maria, Paulo José do Amaral Sobral, and Florencia Cecilia Menegalli. "Isolation and characterization of cellulose nanofibers from banana peels." *Cellulose* 21, no. 1 (2014): 417-432.

8) Abe, Kentaro, Shinichiro Iwamoto, and Hiroyuki Yano. "Obtaining cellulose nanofibers with a uniform width of 15 nm from wood." *Biomacromolecules* 8, no. 10 (2007): 3276-3278.

9) Iwamoto, S., A. N. Nakagaito, H. Yano, and M. Nogi. "Optically transparent composites reinforced with plant fiber-based nanofibers." *Applied Physics A* 81, no. 6 (2005): 1109-1112.

10) Wang, Bei, and Mohini Sain. "Isolation of nanofibers from soybean source and their reinforcing capability on synthetic polymers." *Composites Science and Technology* 67, no. 11 (2007): 2521-2527.

11) Alemdar, Ayse, and Mohini Sain. "Isolation and characterization of nanofibers from agricultural residues–Wheat straw and soy hulls." *Bioresource technology* 99, no. 6 (2008): 1664-1671.

12) Chakraborty, Ayan, Mohini Sain, and Mark Kortschot. "Cellulose microfibrils: A novel method of preparation using high shear refining and cryocrushing." *Holzforschung* 59, no. 1 (2005): 102-107.

13) Li, Meng, Li-jun Wang, Dong Li, Yan-Ling Cheng, and Benu Adhikari. "Preparation and characterization of cellulose nanofibers from de-pectinated sugar beet pulp." *Carbohydrate polymers* 102 (2014): 136-143.

14) Chen, Wenshuai, Kentaro Abe, Kojiro Uetani, Haipeng Yu, Yixing Liu, and Hiroyuki Yano. "Individual cotton cellulose nanofibers: pretreatment and fibrillation technique." *Cellulose* 21, no. 3 (2014): 1517-1528.

15) Deepa, B., Eldho Abraham, Bibin Mathew Cherian, Alexander Bismarck, Jonny J. Blaker, Laly A. Pothan, Alcides Lopes Leao, Sivoney Ferreira De Souza, and M. Kottaisamy. "Structure, morphology and thermal characteristics of banana nano fibers obtained by steam explosion." *Bioresource Technology* 102, no. 2 (2011): 1988-1997.

16) Chirayil, Cintil Jose, Jithin Joy, Lovely Mathew, Miran Mozetic, Joachim Koetz, and Sabu Thomas. "Isolation and characterization of cellulose nanofibrils from Helicteres isora plant." *Industrial Crops and Products* 59 (2014): 27-34.

17) Cherian, Bibin Mathew, Alcides Lopes Leão, Sivoney Ferreira de Souza, Sabu Thomas, Laly A. Pothan, and M. Kottaisamy. "Isolation of nanocellulose from pineapple leaf fibres by steam explosion." *Carbohydrate Polymers* 81, no. 3 (2010): 720-725.

18) Ma, Zuwei, M. Kotaki, and S. Ramakrishna. "Electrospun cellulose nanofiber as affinity membrane." *Journal of membrane science* 265, no. 1 (2005): 115-123.

19) Pääkkö, M., Mikael Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen et al. "Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels." *Biomacromolecules* 8, no. 6 (2007): 1934-1941.

20) Henriksson, Marielle, Gunnar Henriksson, L. A. Berglund, and Tom Lindström. "An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers." *European Polymer Journal* 43, no. 8 (2007): 3434-3441.

21) Tibolla, Heloisa, Franciele Maria Pelissari, and Florencia Cecilia Menegalli. "Cellulose nanofibers produced from banana peel by chemical and enzymatic treatment." *LWT-Food Science and Technology* 59, no. 2 (2014): 1311-1318.

22) Araki, Jun, Masahisa Wada, and Shigenori Kuga. "Steric stabilization of a cellulose microcrystal suspension by poly (ethylene glycol) grafting." *Langmuir* 17, no. 1 (2001): 21-27.

23) Saito, Tsuguyuki, Yoshiharu Nishiyama, Jean-Luc Putaux, Michel Vignon, and Akira Isogai. "Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose." *Biomacromolecules* 7, no. 6 (2006): 1687-1691.

24) Stenstad, Per, Martin Andresen, Bjørn Steinar Tanem, and Per Stenius. "Chemical surface modifications of microfibrillated cellulose." *Cellulose* 15, no. 1 (2008): 35-45.

25) Rodionova, Galina, Marianne Lenes, Øyvind Eriksen, and Øyvind Gregersen. "Surface chemical modification of microfibrillated cellulose: improvement of barrier properties for packaging applications." *Cellulose* 18, no. 1 (2011): 127-134.

26) Jonoobi, Mehdi, Jalaluddin Harun, Aji P. Mathew, Mohd Zobir B. Hussein, and Kristiina Oksman. "Preparation of cellulose nanofibers with hydrophobic surface characteristics." *Cellulose* 17, no. 2 (2010): 299-307.

27) Sassi, Jean-François, and Henri Chanzy. "Ultrastructural aspects of the acetylation of cellulose." *Cellulose* 2, no. 2 (1995): 111-127.

28) Mukherjee, Tapasi, Nhol Kao, Rahul K. Gupta, Nurul Quazi, and Sati Bhattacharya. "Evaluating the state of dispersion on cellulosic biopolymer by rheology." *Journal of Applied Polymer Science* 133, no. 12 (2016).

29) Agrawal, Richa, N. S. Saxena, K. B. Sharma, S. Thomas, and M. S. Sreekala. "Activation energy and crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde composites." *Materials Science and Engineering: A* 277, no. 1 (2000): 77-82.

30) Abdelmouleh, M., S. Boufi, M. N. Belgacem, A. P. Duarte, A. Ben Salah, and A. Gandini. "Modification of cellulosic fibres with functionalised silanes: development of surface properties." *International Journal of Adhesion and Adhesives* 24, no. 1 (2004): 43-54.

31) Braun, Birgit, and John R. Dorgan. "Single-step method for the isolation and surface functionalization of cellulosic nanowhiskers." *Biomacromolecules* 10, no. 2 (2008): 334-341.

32) Sobkowicz, Margaret J., Birgit Braun, and John R. Dorgan. "Decorating in green: surface esterification of carbon and cellulosic nanoparticles." *Green Chemistry* 11, no. 5 (2009): 680-682.

33) Herrick, Franklin W., RONALD L. Casebier, J. KELVIN Hamilton, and KAREN R. Sandberg. "Microfibrillated cellulose: morphology and accessibility." In *J. Appl. Polym. Sci.: Appl. Polym. Symp.;(United States)*, vol. 37, no. CONF-8205234-Vol. 2. ITT Rayonier Inc., Shelton, WA, 1983.

34) Ljungberg, N., C. Bonini, F. Bortolussi, C. Boisson, L. Heux, and Jean-Yves Cavaillé. "New nanocomposite materials reinforced with cellulose whiskers in atactic

polypropylene: effect of surface and dispersion characteristics." *Biomacromolecules* 6, no. 5 (2005): 2732-2739.

35) Habibi, Youssef, Anne-Lise Goffin, Nancy Schiltz, Emmanuel Duquesne, Philippe Dubois, and Alain Dufresne. "Bionanocomposites based on poly (ε-caprolactone)-grafted cellulose nanocrystals by ring-opening polymerization." *Journal of Materials Chemistry* 18, no. 41 (2008): 5002-5010.

36) GRUBER, Erich. "Is there a future for chemically modified pulp?." *Ipw. International paperworld* 6 (2002): 73-85.

37) Cai, Xiaolin, Bernard Riedl, and A. Ait-Kadi. "Effect of surface-grafted ionic groups on the performance of cellulose-fiber-reinforced thermoplastic composites." *Journal of Polymer Science Part B: Polymer Physics* 41, no. 17 (2003): 2022-2032.

38) Hasani, Merima, Emily D. Cranston, Gunnar Westman, and Derek G. Gray. "Cationic surface functionalization of cellulose nanocrystals." *Soft Matter* 4, no. 11 (2008): 2238-2244.

39) Montazer, M., R. MA Malek, and A. Rahimi. "Salt free reactive dyeing of cationized cotton." *Fibers and Polymers* 8, no. 6 (2007): 608-612.

40) http://ga.water.usgs.gov/edu/earthwherewater.html

41) Water for Life: Making it Happen (2005) World Health Organization and UNICEF.Retrievedfrom http://www.who.int/water_sanitation_health/waterforlife.pdf

42) Perez, Mario A., Michael D. Swan, and John W. Louks. "Microfibers and method of making." U.S. Patent 6,110,588, issued August 29, 2000.

43) Pike, Richard Daniel. "Superfine microfiber nonwoven web." U.S. Patent 5,935,883, issued August 10, 1999.

44) Reneker, Darrell H. "Process and apparatus for the production of nanofibers." U.S. Patent 6,520,425, issued February 18, 2003.

45) Ramakrishna, Seeram, Kazutoshi Fujihara, Wee-Eong Teo, Thomas Yong, Zuwei Ma, and Ramakrishna Ramaseshan. "Electrospun nanofibers: solving global issues." *Materials today* 9, no. 3 (2006): 40-50.

46) Cao, Xinwang, Meiling Huang, Bin Ding, Jianyong Yu, and Gang Sun. "Robust polyacrylonitrile nanofibrous membrane reinforced with jute cellulose nanowhiskers for water purification." *Desalination* 316 (2013): 120-126.

47) Musyoka, Stephen Makali, Jane Catherine Ngila, Brenda Moodley, Lesley Petrik, and Andrew Kindness. "Synthesis, characterization, and adsorption kinetic studies of ethylenediamine modified cellulose for removal of Cd and Pb." *Analytical Letters* 44, no. 11 (2011): 1925-1936.

48) Fernandes, Susana, Carmen SR Freire, Armando JD Silvestre, Carlos Pascoal Neto, and Alessandro Gandini. "Novel materials based on chitosan and cellulose." *Polymer International* 60, no. 6 (2011): 875-882.

49) Peterson, Joseph J., Markus Willgert, Susanne Hansson, Eva Malmström, and Kenneth R. Carter. "Surface-Grafted conjugated polymers for hybrid cellulose

materials." *Journal of Polymer Science Part A: Polymer Chemistry*49, no. 14 (2011): 3004-3013.

50) Karn, Barbara, Todd Kuiken, and Martha Otto. "Nanotechnology and in situ remediation: a review of the benefits and potential risks." *Environmental health perspectives* (2009): 1823-1831.

51) Lalia, Boor Singh, Elena Guillen, Hassan A. Arafat, and Raed Hashaikeh. "Nanocrystalline cellulose reinforced PVDF-HFP membranes for membrane distillation application." *Desalination* 332, no. 1 (2014): 134-141.

52) Qu, Ping, Huanwei Tang, Yuan Gao, Liping Zhang, and Siqun Wang. "Polyethersulfone composite membrane blended with cellulose fibrils." *BioResources* 5, no. 4 (2010): 2323-2336.

53) Wang, Ran, Sihui Guan, Anna Sato, Xiao Wang, Zhe Wang, Rui Yang, Benjamin S. Hsiao, and Benjamin Chu. "Nanofibrous microfiltration membranes capable of removing bacteria, viruses and heavy metal ions."*Journal of Membrane Science* 446 (2013): 376-382.

54) Ma, Hongyang, Christian Burger, Benjamin S. Hsiao, and Benjamin Chu. "Ultrafine polysaccharide nanofibrous membranes for water purification." *Biomacromolecules* 12, no. 4 (2011): 970-976.

55) Ma, Hongyang, Christian Burger, Benjamin S. Hsiao, and Benjamin Chu. "Nanofibrous microfiltration membrane based on cellulose nanowhiskers." *Biomacromolecules* 13, no. 1 (2011): 180-186.

56) White, Donald RJ, Kenn Atkinson, and J. D. M. Osburn. "Taming EMI in microprocessor systems: The authors propose a systematic approach to limiting the effects of electromagnetic interference." *IEEE Spectrum* 22, no. 12 (1985): 30-37.

57) Jana, P. B., A. K. Mallick, and S. K. De. "Electromagnetic interference shielding by carbon fibre-filled polychloroprene rubber composites." *Composites* 22, no. 6 (1991): 451-455.

58) Yavuz, Özlem, Manoj K. Ram, and Matt Aldissi. "Electromagnetic applications of conducting and nanocomposite materials." *The New Frontiers of Organic and Composite Nanotechnology* (2008): 435.

59) Sittisart, Pongphat, Margaret M. Hyland, Michael A. Hodgson, Chuong Nguyen, and A. Fernyhough. "Developing a Cost-Effective Composite Based on Electroless Nickel-Coated Cellulose Fibres for Electromagnetic Interference Shielding." *Journal of Renewable Materials* 2, no. 4 (2014): 264-269.

60) Sienkiewicz, Zenon. "Biological effects of electromagnetic fields." *Power Engineering Journal* 12, no. 3 (1998): 131-139.

61) Trivedi, Dinesh Chandra, and Sundeep Kumar Dhawan. "Shielding of electromagnetic interference using polyaniline." *Synthetic metals* 59, no. 2 (1993): 267-272.

62) Wang, Yangyong, and Xinli Jing. "Intrinsically conducting polymers for electromagnetic interference shielding." *Polymers for advanced technologies*16, no. 4 (2005): 344-351.

63) Nalwa, Hari Singh. *Handbook of Organic Conductive Molecules and Polymers, Volume 2, Conductive Polymers: Synthesis and Electrical Properties*. Chichester: John Wiley and Sons, 1997.

64) Hochberg, Arie, and Johan Versieck. "Shielding for EMI and antistatic plastic resins with stainless steel fibres." *Plastics, Additives and Compounding* 3, no. 3 (2001): 24-28.

65) Thornton, Steven L. "EMI shielding gasket." U.S. Patent 5,070,216, issued December 3, 1991.

66) Huang, Jan-Chan. "EMI shielding plastics: a review." *Advances in polymer technology* 14, no. 2 (1995): 137-150.

67) Diaz, A. F., and J. Bargon. "Electrochemical synthesis of conducting polymers." *Handbook of conducting polymers* 1 (1986): 81-115.

68) Štefečka, M., M. Kando, H. Matsuo, Y. Nakashima, M. Koyanagi, T. Kamiya, and M. Černák. "Electromagnetic shielding efficiency of plasma treated and electroless metal plated polypropylene nonwoven fabrics." *Journal of materials science* 39, no. 6 (2004): 2215-2217.

69) Li, Ning, Yi Huang, Feng Du, Xiaobo He, Xiao Lin, Hongjun Gao, Yanfeng Ma, Feifei Li, Yongsheng Chen, and Peter C. Eklund. "Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites." *Nano letters* 6, no. 6 (2006): 1141-1145

70) Thomassin, Jean-Michel, Christophe Pagnoulle, Lukasz Bednarz, Isabelle Huynen, Robert Jerome, and Christophe Detrembleur. "Foams of

polycaprolactone/MWNT nanocomposites for efficient EMI reduction." *Journal of Materials Chemistry* 18, no. 7 (2008): 792-796.

71) Yang, Yonglai, Mool C. Gupta, Kenneth L. Dudley, and Roland W. Lawrence. "Novel carbon nanotube− polystyrene foam composites for electromagnetic interference shielding." *Nano letters* 5, no. 11 (2005): 2131-2134.

72) Yousefi, Nariman, Xinying Sun, Xiuyi Lin, Xi Shen, Jingjing Jia, Biao Zhang, Benzhong Tang, Mansun Chan, and Jang-Kyo Kim. "Highly aligned graphene/polymer nanocomposites with excellent dielectric properties for high-performance electromagnetic interference shielding." *Advanced Materials* 26, no. 31 (2014): 5480-5487

73) Zhang, Hao-Bin, Qing Yan, Wen-Ge Zheng, Zhixian He, and Zhong-Zhen Yu. "Tough graphene− polymer microcellular foams for electromagnetic interference shielding." *ACS applied materials & interfaces* 3, no. 3 (2011): 918-924.

74) Shirakawa, Hideki, Edwin J. Louis, Alan G. MacDiarmid, Chwan K. Chiang, and Alan J. Heeger. "Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene,(CH) x." *Journal of the Chemical Society, Chemical Communications* 16 (1977): 578-580.

75) Yoshino, Katsumi, Munehiro Tabata, Keiichi Kaneto, and Toshiyuki Ohsawa. "Application and characteristics of conducting polymer as radiation shielding material." *Japanese journal of applied physics* 24, no. 9A (1985): L693.

76) Laakso, Jukka. "Synthesis and Analysis of some Sulfur and Nitrogen containing conducting polymers including conducting polymer blends of poly (3-

octylthiophene)." *ACTA POLYTECHNICA SCANDINAVICA-CHEMICAL TECHNOLOGY SERIES* 184 (1988): 1-48.

77) Taka, T. "EMI shielding measurements on poly (3-octyl thiophene) blends." *Synthetic Metals* 41, no. 3 (1991): 1177-1180.

78) Mäkelä, T., S. Pienimaa, T. Taka, S. Jussila, and H. Isotalo. "Thin polyaniline films in EMI shielding." *Synthetic Metals* 85, no. 1-3 (1997): 1335-1336.

79) Pomposo, J. A., J. Rodrıguez, and H. Grande. "Polypyrrole-based conducting hot melt adhesives for EMI shielding applications." *Synthetic Metals* 104, no. 2 (1999): 107-111.

80) Desai, Keyur, and Changmo Sung. "Electrospinning nanofibers of PANI/PMMA blends." *MRS Online Proceedings Library Archive* 736 (2002).

81) Koul, S., and R. Chandra. "Newer compatible conducting polymeric composites for elimination of electromagnetic radiations." In *ANTEC... conference proceedings*, vol. 3, pp. 3039-3044. Society of Plastics Engineers, 2004.

82) Heeger, Alan J. "Semiconducting and metallic polymers: the fourth generation of polymeric materials." (2001): 8475-8491.

83) Kim, M. S., H. K. Kim, S. W. Byun, S. H. Jeong, Y. K. Hong, J. S. Joo, K. T. Song, J. K. Kim, C. J. Lee, and J. Y. Lee. "PET fabric/polypyrrole composite with high electrical conductivity for EMI shielding." *Synthetic metals* 126, no. 2 (2002): 233-239.

84) Kim, Seong Hun, Soon Ho Jang, Sung Weon Byun, Jun Young Lee, Jin Soo Joo, Sung Hoon Jeong, and Myung-Ja Park. "Electrical properties and EMI

shielding characteristics of polypyrrole–nylon 6 composite fabrics." *Journal of applied polymer science* 87, no. 12 (2003): 1969-1974.

85) Erdoğan, Meryem Kalkan, Meral Karakişla, and Mehmet Saçak. "Preparation, Characterization and Electromagnetic Shielding Effectiveness of Conductive Polythiophene/Poly (ethylene terephthalate) Composite Fibers." *Journal of Macromolecular Science, Part A* 49, no. 6 (2012): 473-482

86) Shacklette, L. W., and N. F. Colaneri. "EMI shielding measurements of conductive polymer blends." In *Instrumentation and Measurement Technology Conference, 1991. IMTC-91. Conference Record., 8th IEEE*, pp. 72-78. IEEE, 1991.

87) Saini, Parveen, Veena Choudhary, B. P. Singh, R. B. Mathur, and S. K. Dhawan. "Polyaniline–MWCNT nanocomposites for microwave absorption and EMI shielding." *Materials Chemistry and Physics* 113, no. 2 (2009): 919-926.

88) Koul, S., R. Chandra, and S. K. Dhawan. "Conducting polyaniline composite for ESD and EMI at 101GHz." *Polymer* 41, no. 26 (2000): 9305-9310.

89) Yuping, Duan, Liu Shunhua, and Guan Hongtao. "Investigation of electrical conductivity and electromagnetic shielding effectiveness of polyaniline composite." *Science and Technology of Advanced Materials* 6, no. 5 (2005): 513-518.

90) Fugetsu, Bunshi, Eiichi Sano, Masaki Sunada, Yuzuru Sambongi, Takao Shibuya, Xiaoshui Wang, and Toshiaki Hiraki. "Electrical conductivity and electromagnetic interference shielding efficiency of carbon nanotube/cellulose composite paper." *Carbon* 46, no. 9 (2008): 1256-1258.

91) Marins, Jéssica A., Bluma G. Soares, Mayra Fraga, Daliana Müller, and Guilherme MO Barra. "Self-supported bacterial cellulose polyaniline conducting membrane as electromagnetic interference shielding material: effect of the oxidizing agent." *Cellulose* 21, no. 3 (2014): 1409-1418.

92) Huang, Hua-Dong, Chun-Yan Liu, Dong Zhou, Xin Jiang, Gan-Ji Zhong, Ding-Xiang Yan, and Zhong-Ming Li. "Cellulose composite aerogel for highly efficient electromagnetic interference shielding." *Journal of Materials Chemistry A* 3, no. 9 (2015): 4983-4991.

93) Jian, L. I., and W. A. N. Caichao. "Cellulose aerogels decorated with multi-walled carbon nanotubes: preparation, characterization, and application for electromagnetic interference shielding." *Frontiers of Agricultural Science and Engineering* 2, no. 4 (2016): 341-346.

Chapter 2

Materials and Methods

2.1 Introduction

This chapter covers the detailed information regarding the different materials, methods/techniques and experimental techniques employed for the different composite systems based on the cellulose nanofibers (CNFs) with polyvinylidene Fluoride (PVDF) and Polyaniline (PANI). It gives a detailed description of the formulation used for the extraction of cellulose nanofibers from sunflower stalks and the preparation of nanocomposites membranes and papers with two different polymers, PVDF and PANI. This chapter also deals with the fabrication procedure for the cellulose nanofiber based PVDF microfiltration membrane and self-supported cellulose nanofibers based polyaniline conductive papers. This chapter also contains the different characterization techniques employed for the above mentioned nanocomposites systems.

2.2 Materials

Sunflower stalks were procured from Umbria, Italy. The various chemicals used for the extraction of cellulose nanofibers are sodium hydroxide (NaOH), acetic acid (CH_3COOH), sodium hypochlorite, and oxalic acid ($H_2C_2O_4$), purchased from Sigma Aldrich, India. PVDF with Mw (2, 75000 g/mol), 2, 2-Dimethyl-1, 3 dioxane -4, 6-dione (98%) (Meldrum acid) and Iron oxide (Fe_2O_3) nanoparticles, 50-100nm particles size were procured from Sigma-Aldrich, Brazil, while Crystal violet dye

(CV, C_{25} H_{30} N_3 Cl, λ_{max} =584nm, MM= 407.98g/mol) was procured from vetec (Brazil). Aniline, ammonium persulfate (APS) and hydrochloric acid (35%) were purchased from Sigma Aldrich Co. All other chemicals were procured from Sigma Aldrich and used as received.

2.3 Methods of Fabrication

This part gives a detailed description of the formulation used for the extraction of cellulose nanofibers from sunflower stalks and the preparation of nanocomposites membranes and papers with two different polymers, Polyvinylidene Fluoride (PVDF) and Polyaniline (PANI).

2.3.1 Extraction of Cellulose nanofibers via steam explosion coupled with Mild acid hydrolysis

The extraction procedure of cellulose nanofibrils (CNF) was done by a steam explosion treatment [1] that involved 1) alkali treatment with steam explosion; 2) bleaching and 3) mild acid hydrolysis coupled with steam explosion which is given in the figure 1. Initially the sunflower stalks were cut into small pieces with a grinder. A laboratory autoclave, model no: KAUC-A1 which can work with 137Pa was used for steam explosion treatment. 100g of grind piece of stalks were treated with 5wt% NaOH solution and kept in an autoclave with the pressure of 137 Pa with the temperature of 180°C in an autoclave for 1.5 hours. After that, a bleaching of the resultant alkali treated stalk sample was done by treating with 5wt% sodium hypochlorite solution for 1.5 hours. Bleaching was repeated six times until the residue become white in colour. After bleaching, the fibers were thoroughly washed, dried and subjected to mild acid hydrolysis using 5% oxalic acid under a pressure of 137Pa in an autoclave for 20 minutes. The pressure was released immediately and

the process was repeated six times. The fibers were taken out, washed and dispersed in water and homogenized under continuous stirring for 6 hours and the resultant suspension became cellulose nanofiber aqueous suspension. The final product was washed with deionised water by successive centrifugations until neutralization.

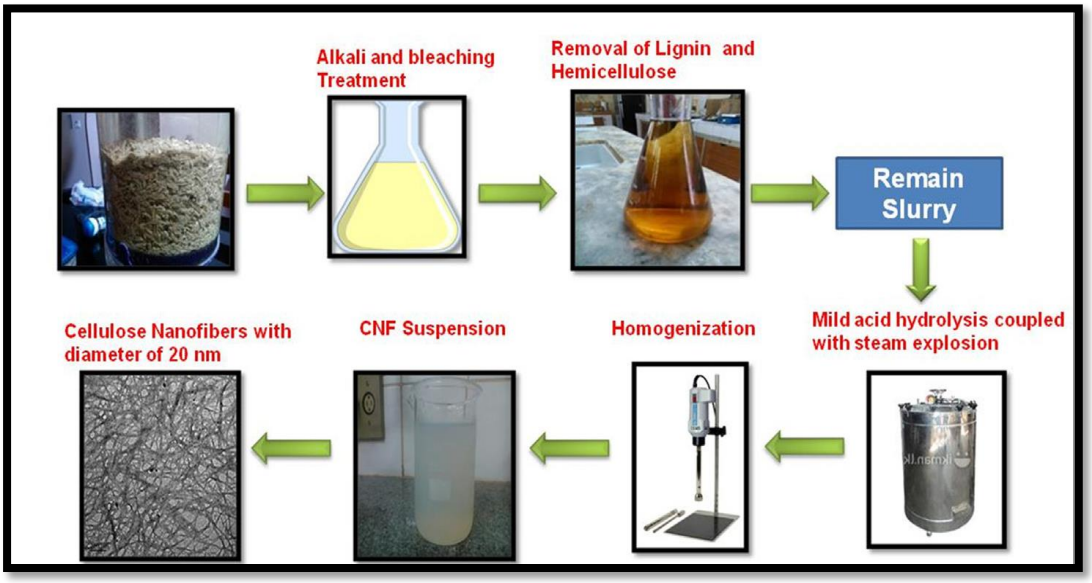

Figure 1: Scheme of the extraction procedure for the extraction of cellulose nanofibers from sunflower stalks [2]. Copyright (2016). Reproduced with permission from Elsevier Ltd.

2.3.2 Surface modification of CNFs using Meldrum's acid

Initially, the extracted cellulose nanofibers (CNFs) (1.3g) and Meldrum's acid (1.3g) were mixed in a mortar and added to a round bottom flask provided with the reflux condenser and heated the whole mixture at 110°C for 4 hours in an oil bath with constant magnetic stirring. After the reaction, the resultant mixture was washed with de-ionized water and acetone to remove the non-reacted Meldrum's acid and then dried in an oven at 90° C for 1 hour.

2.3.3 Preparation of electrospun PVDF microfiltration membranes

17 wt% of PVDF pellets were dissolved in the solvent mixture of (DMF: Acetone) at a volume ratio of 60:40 at 50ºC. The PVDF nanofibrous electrospun membrane was prepared at 15 KV in a relative humidity of 60% at 28ºC at a feed rate of 1 mL/h with a constant tip to collector distance at 15 cm using electrospinning unit (HOLMARC: HO-NEV-02). After the electrospinning process, the electrospun membrane was placed in a hot air oven at 150ºC for 3 hrs to remove any residual solvent and to improve the membrane overall structural integrity before any characterization was performed.

2.3.4 Fabrication of PVDF/Meldrum modified CNFs based Nanofibrous Microfiltration (MF) Membranes

The electrospun PVDF membrane sample in the pattern of a circular shape with 2cm width was clamped in a Glass Filter Filtration Assembly (Holder-47mm), where 0.1wt% concentration of Meldrum acid modified CNFs or unmodified CNFs, pH 7.0 was impregnated into the PVDF electrospun membrane by applying pressure around 200 mm of Hg. Then the sample was heated at 100°C in an oven for 15 minutes to start the cross-linking reaction to immobilize CNF network. The thickness of the prepared membrane was calculated using thickness gauge (7301 MITUTOYO) and it was 170 ± 2 µm.

2.3.5 *In-situ* Polymerization of aniline on cellulose nanofibers

In this work, oxidative synthetic methodology [3] was employed for the synthesis of polyaniline. In order to prepare a set of PANI/CNF ratios of 0.2:1, 0.3:1, 0.5:1, 0.8:1, 0.9:1 and 1:1, different amounts of aniline monomer were dissolved in 40g of CNF suspension (1.15 mg/ml) at room temperature for 1 hour. Then the prepared

solution was cooled down at 1°C in an ice bath, after which APS solution (dissolved in 40 ml of 1 M HCl) with APS/aniline 1.5 wt/wt was added. After 3 hrs, PANI/CNF suspension became dark green colour and suspended. Then the resulting aqueous mixture/ suspensions were washed with deionised water, acetone and 0.1 M HCl in order to obtain the aqueous suspension of PANI/CNF.

2.3.6 Fabrication of PANI/CNF flexible conductive papers

Vacuum filtration technique was used for the fabrication of PANI/CNF flexible composite papers. A filtration assembly with cellulose ester membrane (47 mm in diameter and 0.45 µm pore size) was employed for the vacuum filtration of the PANI/CNF suspension. After this the fabricated paper was washed several times with 1 M HCl to remove all the contaminants. Lastly, the fabricated PANI/CNF composite papers were peeled off from the filter and dried for 48 h.

2.4 Characterization Techniques

2.4.1 Transmission electron microscopy (TEM)

A JEOL JEM 2100 transmission electron microscope (TEM) was employed to evaluate the diameter of the prepared cellulose nanofibers (CNFs). Diluted CNFs suspension was sonicated for 7 minutes to avoid the agglomeration and directly dropped on the copper grid for characterization. The transmission electron microscopy of the extracted cellulose nanofibers from the sunflower stalks were conducted to investigate the dimensions, dispersion and morphology.

2.4.2 Scanning electron microscopy (SEM)

The morphology of PVDF electrospun membrane, PVDF/ Meldrum modified CNFs nanofibrous MF membranes, neat CNF paper and PANI/CNF flexible papers were

examined using a SEM (CARL ZEISS, EVO MA10). The samples were sputtered with gold in an argon atmosphere. The accelerating voltage was 20 kV.

2.4.3 X-ray diffraction analysis (XRD)

X-ray diffraction patterns for prepared CNF, PANI and PANI/CNF samples were obtained with (SHIMADZU XRD-6000). The x-ray diffractograms were obtained at room temperature within in a 2ɵ range from 5 to 40° at a scan rate of 2° min^{-1}.XRD patterns were employed to check whether the Meldrum's acid modified CNFs preserves its cellulose I structure, for that XRD pattern of unmodified CNF and Meldrum's acid modified CNF was obtained with (SHIMADZU XRD-6000). The XRD patterns were collected from 2ɵ= 5-38° at a scan rate of 2° min^{-1}. The crystallinity index (CrI) of the CNF and Meldrum's acid modified CNF were determined by the Segal method as shown in equation 2.1 [4].

$$\mathbf{CrI = [(I_{002} - I_{AM})/I_{002}] \times 100} \qquad \text{..... (2.1)}$$

In this equation, CrI expresses the relative degree of crystallinity, I_{002} is the maximum intensities of the (0 0 2) lattice diffraction at 2θ = 23°, and I_{AM} is the intensity of diffraction at 2θ =18°. I_{002} represents both crystalline and amorphous regions, while I_{AM} represent only the amorphous portion.

2.4.4 Thermogravimetric analysis (TGA)

The thermal stability of the Meldrum's acid modified CNF and CNF samples were determined by TGA measurements performed using a Mettler Toledo Thermogravimetric analyzer (TGA/SDTA 85-F). The amount of sample used for each measurement was 10 mg. All measurements were performed under nitrogen

atmosphere with a gas flow of 100 mL min^{-1} by heating the material from room temperature to 800° C at a heating rate of 10 ° C $min^{-1.}$

2.4.5 Conductimetic titration

The carboxyl group content present in the cellulose nanofibers before and after chemical modification with Meldrum's acid, were determined by conductimetic titration according to Tappi standard T-237 and adaptations of by Sjöström and Alen (1999) [5], as the following procedure: At first 0.5 g of dried cellulose nanofibers was added into 300mL of distilled water and dispersed by mechanical stirring. Then the material was filtered and added 300 mL of 0.1 M HCL and then stirred for one hour. After stirring, the material was filtered and washed with distilled water until the filtrate conductivity less than 5 S/cm. Then the filtered material was added into the mixture of 250 ml of 0.001M NaCl, and 1.5 mL of 0.1M HCl. Then the mixture was stirred and titrated with 0.05 M NaOH (concentration rigorously known), in the conductivimeter. Then plot a conductivity chart v/s volume of NaOH spent to calculate the amount of the carboxyl groups by using the equation 2.2.

$$\textbf{Amount of carboxyl groups in (mmol/100g)} = \frac{(B-A) \times C}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.2)$$

Where, A and B are the volumes (mL) of NaOH in the intersection curves of the graph.

C is the concentration of NaOH solution x 100

W is the weight of dried CNF and Meldrum's acid CNF employed.

2.4.6 Fourier transform infrared spectroscopy (FTIR)

The IR spectra of CNF powder, Meldrum's acid modified CNF, PANI powder and PANI/CNF flexible paper were recorded using (IR prestige-21, FOURIER TRANSFORM INFRARED SPECTRO PHOTOMETER, SHIMADZU). The KBr disk method was employed for obtaining the IR spectra of all samples from 400-4000cm^{-1}. The studies were carried out with a resolution of 2cm^{-1} and a total of 15 scans for each sample.

2.4.7 Water contact angle studies

Water contact angles of electrospun PVDF membrane, PVDF/unmodified CNF nanofibrous MF membrane and PVDF/Meldrum's acid modified CNF nanofibrous MF membrane was measured using SCA20 contact angle analyzer. We used 10µL of de-ionized water for the measurements. Three measurements were obtained for each sample and calculated the average value.

2.4.8 BET measurements

A Micrometrics Surface and Pore Size Analyzer (ASAP2020) was used to conduct N_2adsorption–desorption experiments at 77 K. Before the experiment, the sample was degassed at 573 K for 18 h. The surface area was obtained using the BET model. BET measurements were employed to determine the surface area and average pore diameter of PVDF electrospun membrane and Meldrum modified CNFs based PVDF nanofibrous microfiltration membrane.

2.4.9 UV- Visible spectrophotometer

The nanoparticles removal and dye removal were monitored with (FEMTO Mod. 800X I) by transmittance, absorbance respectively. For the evaluation of the nanoparticles removal, the feed solution and filtrate were poured into PMMA disposable cuvette and transmittance was obtained from 300 to 900 nm while for the assessment of dye removal, the starting and filtrate solution were poured into the PMMA cuvette and absorbance was measured at 590 nm. To calibrate the transmittance and absorbance of the samples, the spectrum of a cuvette filled with water was employed as the reference. Ultraviolet-visible spectroscopy (UV-vis) procedure was applied for the determination of solute concentrations in the starting and final solutions.

2.4.10 Dye adsorption studies

The evaluation of the adsorption efficiency of the nanofibrous MF membranes was done by using the following method. Initially, 0.05 g of unmodified CNF based PVDF nanofibrous MF membrane, Meldrum's acid modified CNF based PVDF nanofibrous MF membrane and PVDF membrane was immersed in 25 ml of CV aqueous solution (10mg/L, pH 7.0) on a shaking bed for 10-240 minutes at ambient temperature. The adsorption efficiency of CV dye was measured as a function of time. The concentration of the CV dye adsorbed on to the membrane was obtained from the concentration change of the CV solution before and after the adsorption steps using UV-visible spectrophotometer by optical adsorption at 590 nm.

2.4.11 Microfiltration performance of the nanofibrous MF membranes

The microfiltration test of the nanofibrous membranes was carried out in Glass Filter Filtration Assembly (Holder-47mm) with a filtration area of 9.6 cm^2.The 0.2wt% of Fe_2O_3 nanoparticles with the size of (50-100 nm) was set as the feed solution. The microfiltration was conducted at a pressure of 200mm Hg.

2.4.12 Electrical conductivity measurements

Four probe methods using a Keitheley 2400 source meter equipped with a gold probe was employed for the DC conductivity measurements for the fabricated PANI/CNF paper. The tests were performed at the ambient atmospheric conditions.

2.4.13 Dielectric studies

The dielectric analysis of the PANI/CNF papers was done using a WAYNE KERR-6500B Precision Impedance Analyser with a frequency range of 30 Hz to 30 MHz. High frequency dielectric measurements were done using a Novocontrol Alpha High-Resolution Dielectric analyser with 10 GHz and 15 GHz resonator having sample dimension of 3cm ×3cm.

2.4.14 EMI shielding performance

EMI shielding values of Fabricated PANI/CNF paper was measured using an Agilent E8362B (10 MHz -20 GHz) two port PNA Network analyser coupled to a Keycom waveguide to measure the scattering parameters at frequency range of 8.2 to 12.4 GHz (X band). The scattering parameters (S_{11}, S_{12}, S_{22} & S_{21}) were recorded and the SE_{Total} of the PANI/CNF nanopapers were calculated with standard equations.

2.5 Conclusion

This chapter has given an insight to all the experiment details, characterization techniques, and different studies for various nano composites used in this thesis.

2.6 References

1) Chirayil, Cintil Jose, Jithin Joy, Lovely Mathew, Miran Mozetic, Joachim Koetz, and Sabu Thomas. "Isolation and characterization of cellulose nanofibrils from Helicteres isora plant." *Industrial Crops and Products* 59 (2014): 27-34.

2) Fortunati, E., F. Luzi, A. Jiménez, D. A. Gopakumar, D. Puglia, S. Thomas, J. M. Kenny, A. Chiralt, and L. Torre. "Revalorization of sunflower stalks as novel sources of cellulose nanofibrils and nanocrystals and their effect on wheat gluten bionanocomposite properties." *Carbohydrate polymers* 149 (2016): 357-368.

3) Yu, Haipeng, Peng Chen, Wenshuai Chen, and Yixing Liu. "Effect of cellulose nanofibers on induced polymerization of aniline and formation of nanostructured conducting composite." *Cellulose* 21, no. 3 (2014): 1757-1767.

4) Segal, L. G. J. M. A., J. J. Creely, A. E. Martin Jr, and C. M. Conrad. "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer." *Textile Research Journal* 29, no. 10 (1959): 786-794.

5) Sjöström, Eero, and Raimo Alén, eds. *Analytical methods in wood chemistry, pulping, and papermaking*. Springer Science & Business Media, 2013.

Chapter 3

Surface Modification of Cellulose Nanofibers via Non Solvent Assisted Procedure using Meldrum's acid: A unique methodology

3.1 Introduction

This chapter provides the details about the surface modification of cellulose nanofibers extracted from sunflower stalks using Meldrum's acid via esterification and their characterization. Until now**,** various surface modifications have been done on the cellulose nanofibers such as TEMPO oxidation [1-8], acetylation [9-12], Silyation [13], esterification [14, 15] and catonization [16]. In most of the above mentioned surface modifications of cellulose nanofibers were done using toxic organic solvents. Among them TEMPO oxidation is attained a considerable attention due to its advantage of surface modification and fibrillation of fiber occurs simultaneously in single process. But an obvious disadvantage of this oxidation procedure is the use of TEMPO and sodium bromide, which both are associated with environmental issues. Moreover, the TEMPO reagent is very expensive to commercialize in the industry level. So there is every need to formulate new chemical design protocols on the surface treatment of cellulose nanofibers via solvent free procedure technique. In this context, we intended to produce a unique adsorbent material from cellulose nanofibers (CNFs) via non-solvent assisted method using Meldrum's acid as an esterification agent. To the extent of our knowledge, preparation of new green based surface modification of cellulose

nanofibers (CNFs) via non-solvent assisted procedure using Meldrum's acid as esterification agent has not been addressed till date. This finding offers a new platform for the surface treatment of cellulose nanofibers using solvent free green technology.

3.2 Morphology of cellulose nanofibers (CNFs)

Transmission electron microscopy (TEM) was employed to investigate and measure the morphology and average fiber diameter respectively of the prepared CNFs from the sunflower stalks. From the TEM image figure 3.1 it allows evaluating that the fibers are in the range of 5-10 nm in diameters. From this image, it is clearly evident that the combination of steam explosion and mild acid hydrolysis is an efficient technique to prepare cellulose nanofibers. Chirayil et al. and Cherian et al. extracted cellulose nanofibers from isorafibers and banana leaf fibers respectively via steam explosion technique. They obtained cellulose nanofibers with the average diameter of 10-20 nm and 15nm from isorafibers and banana fibers respectively [17, 18]. It was anticipated that during steam explosion technique the lingo cellulosic structure undergoes chemical decomposition [19].

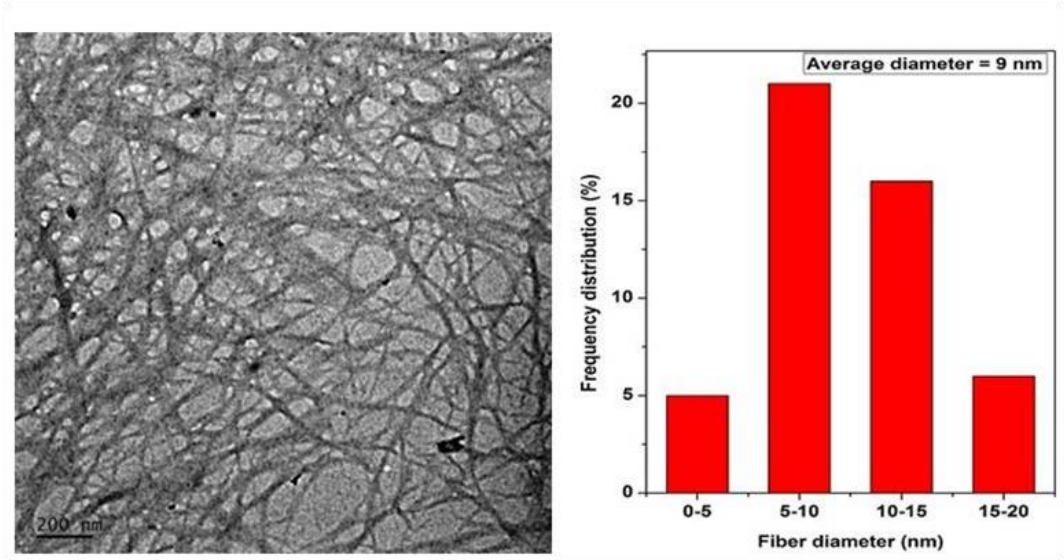

Figure 3.1 TEM image and diameter frequency distributions of cellulose nanofibers extracted from sunflower stalks.

3.3 Characterization of Meldrum's acid modified CNFs.

After the esterification modification by Meldrum's acid on the CNFs the COOH groups were attached to the CNFs surface (Figure 3.2) and it enables the adsorption of the positively charged species like crystal violet dye on to the surface of the modified CNFs.

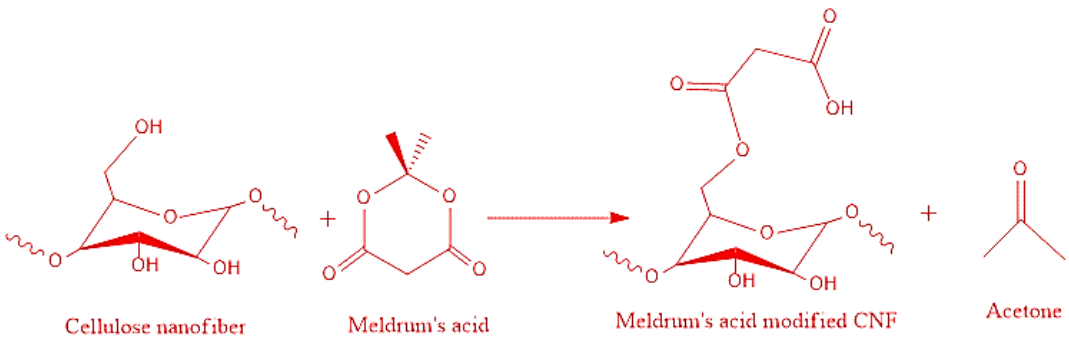

Figure. 3.2 Strategy for the preparation of the Meldrum's acid modified cellulose nanofiber.

3.3.1 FTIR spectroscopy studies

The IR spectra of unmodified CNFs and Meldrum's acid modified CNFs are shown in figure 3.3. From this figure, it is clearly shown that the following changes have occurred in the IR spectra of Meldrum's acid modified CNFs when compared with CNFs. 1) The presence of the band at 2954 cm^{-1}, is regarded as the asymmetric stretching of methylene (CH_2) groups, due to the interaction between the malonyl groups and CNFs. 2) Strong band emerging at 1748 cm^{-1} for Meldrum's acid modified CNFs, attributed to the presence of ester groups formed during the esterification reaction between the malonic acid and CNFs. 3) the band emerging at 1384cm^{-1} for Meldrum's acid modified CNFs, indicates the presence of carboxylate groups. From this FTIR spectrum, it can be concluded that the esterification reaction between Meldrum's acid and CNFs was successful [20].

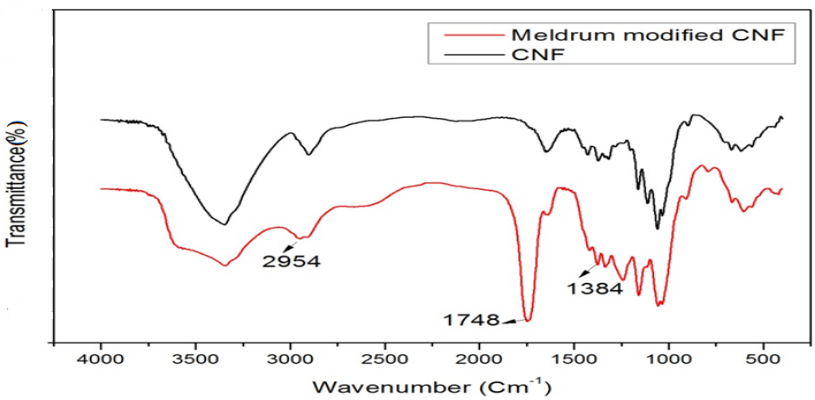

Figure. 3.3 FTIR spectra of Meldrum modified CNF and CNF

3.3.2 XRD Studies

The XRD patterns of the neat CNFs and Meldrum's acid modified CNFs are shown in figure 3.4. Two characteristic peaks at 2ɵ = 16.3° and 2ɵ = 22.6º are observed from the XRD pattern of neat CNFs, which shows the cellulose type I structure [21]. From the X-ray diffraction pattern, it is clearly shown that the Meldrum's acid modification has been affected mainly by the surface hydroxyl groups of cellulose. The XRD profiles of the Meldrum's acid modified CNF is representative of plant-derived cellulose I structure, indicate that the cellulose type I structure is preserved even after the surface modification by Meldrum's acid. The crystallinity index (CrI) of the Meldrum's modified CNFs and CNFs samples were evaluated by using Segal (1959) method, as given in Eq. (1) [22].

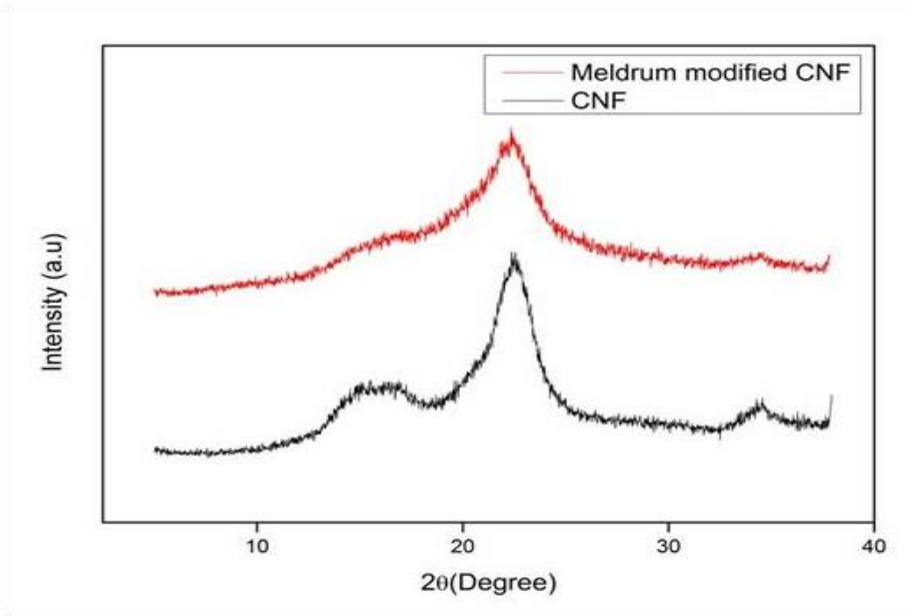

Figure. 3.4 X-ray diffraction pattern of Meldrum modified CNF and CNF

$$CrI = [(I_{200} - I_{AM})/I_{200}] \times 100 \qquad (1)$$

In Eq. (1), CrI expresses the relative degree of crystallinity, I_{200} is the maximum intensities of the 2 0 0 lattice diffraction at $2\theta = 23^o$, and I_{AM} is the intensity of diffraction at $2\theta = 18^o$. I_{200}represent both crystalline and amorphous regions, while I_{AM} represents only the amorphous portion. The obtained Crystallinity Index values of Meldrum modified CNFs and CNFs were 63% and 78% respectively

3.3.3 Morphology of the Meldrum's acid modified CNFs

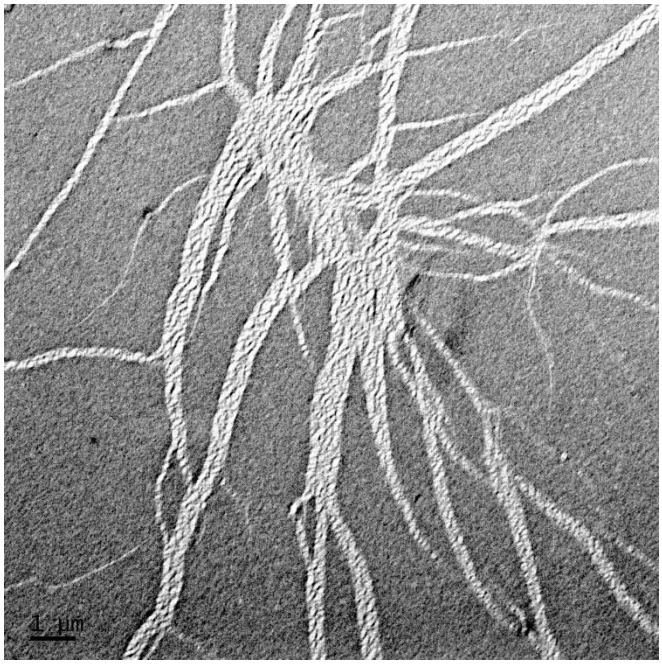

Figure 3.5: TEM image of the Meldrum's acid modified CNF

Figure 3.5 shows the TEM image of the Meldrum's acid modified CNFs. From this image, it can be seen that the fiber structure of the cellulose nanofibers are maintained well even after the surface modification of Meldrum's acid on cellulose nanofibers.

3.3.4 Thermo gravimetric analysis

Meldrum's acid modified CNF and CNF samples were thermo gravimetrically analyzed to compare the degradation characteristics. From the figure 3.6 TGA plot, it can be clearly seen that the Meldrums'acid modified CNF starts to degrade in the range of 150-200° C, whereas in the case of neat CNF degradation starts after 220° C. This difference in the degradation profile could be attributed to the lower hydrogen bonding interactions in the Meldrum's acid modified CNF, because –OH groups are used up during the esterification between the Meldrum's acid and neat CNF. Moreover in the case of modified CNF, the organic moieties protruding outside can act as the initiation sites for degradation.

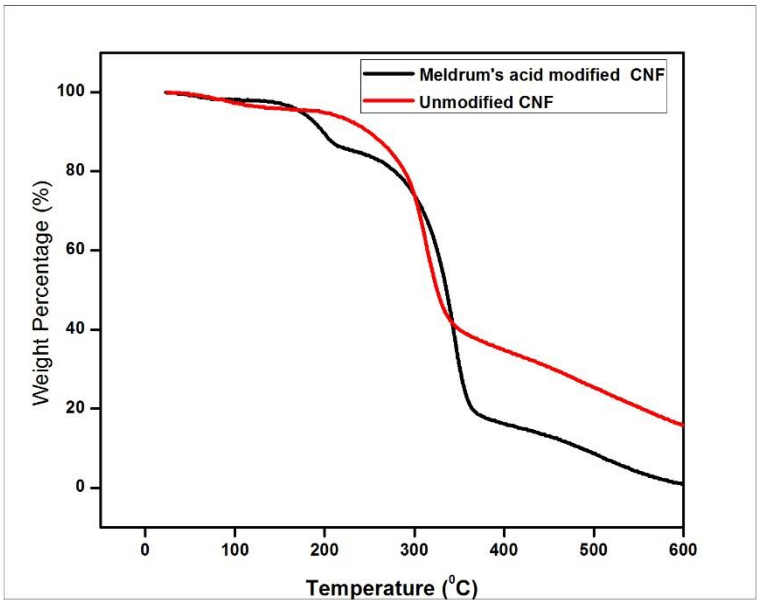

Figure 3.6: TGA analysis of Meldrum's acid modified CNF and CNF

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3.3.5 Determination of the amount of Carboxyl groups on the Meldrum modified CNFs.

Conductimetric titration analysis was employed to calculate the carboxylate content of the extracted cellulose nanofibers and Meldrum's acid modified cellulose nanofibers. The carboxyl group content present in the cellulose nanofibers before and after chemical modification with Meldrum's acid, were determined by conductimetic titration according to the procedure adopted by Sjöström et al. [23].The amount of the carboxyl groups present in the CNF and Meldrum's acid modified CNFs was calculated using the following equation.

$$\textbf{Amount of carboxyl groups in (mmol/100g)} = \frac{(B-A) \times C}{W}$$

Where, A and B are the volumes (mL) of NaOH in the intersection curves of the graph, C is the concentration of NaOH solution x 100 and W is the weight of dried CNF and Meldrum's acid CNF employed. The titration graph, volume of NaOH v/s conductivity (µS/cm) was shown in the figure 3.5.

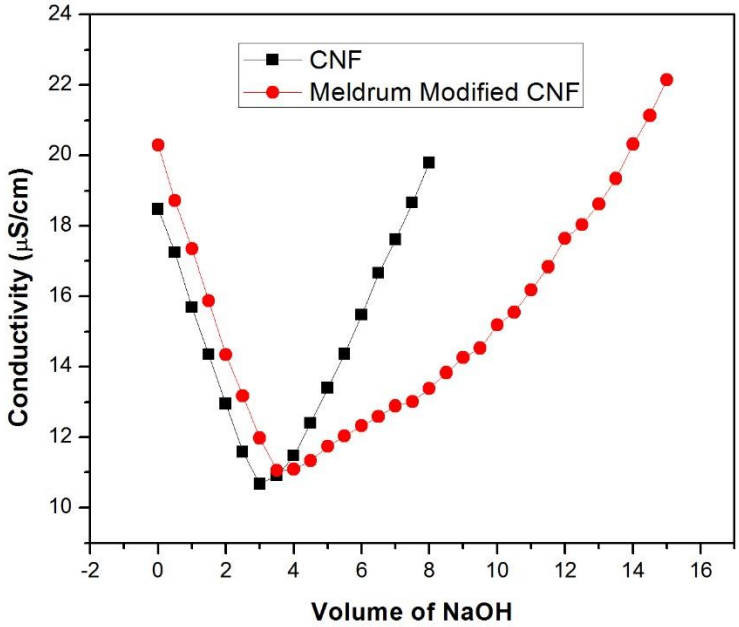

Figure. 3.5 Conductimetic titration of extracted CNF and Meldrum's acid modified CNF

From this figure the values of A, B and C was calculated. It was found that the carboxylate content increased from 8.75 mmol/l00 g for CNF, to 71.35 mmol/100g for the Meldrum's acid modified CNF. The increased amount of carboxyl groups proves the effective esterification reaction of Meldrum's acid on the surface of the cellulose nanofibers.

3.4 Conclusion

This chapter has given the complete details about the surface modification of the cellulose nanofibers using Meldrum's acid and their characterizations. This modified Meldrum's acid cellulose nanofibers were used for the fabrication of nanofibrous microfiltration membrane. From the FTIR spectra of the CNFs and Meldrum's acid modified CNFs, it can be concluded that the esterification reaction between Meldrum's acid and cellulose nanofibers was successful. From the x-ray diffraction

pattern, it was clearly shown that the Meldrum's acid modification has been affected mainly on the surface hydroxyl groups of cellulose nanofibers. The crystallinity index values of both cellulose nanofibers and Meldrum's acid modified CNFs was calculated and it was 78% and 63% respectively. The decrease in the crystallinity index of Meldrum's acid CNFs compared to CNFs was due to the surface modification of CNFs by Meldrum's acid. Conductimetic titration analysis was employed to calculate the carboxylate content of the extracted cellulose nanofibers and Meldrum's acid modified cellulose nanofibers. From the conductimetic titration analysis of both CNFs and Meldrum's acid CNFs, it was found that the carboxylate content increased from 8.75 mmol/l00 g for CNF, to 71.35 mmol/100g for the Meldrum's acid modified CNF. The increased amount of carboxyl groups proves the effective esterification reaction of Meldrum's acid on the surface of the cellulose nanofibers.

3.5 References

1) Saito, Tsuguyuki, Satoshi Kimura, Yoshiharu Nishiyama, and Akira Isogai. "Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose." *Biomacromolecules* 8, no. 8 (2007): 2485-2491.

2) Isogai, Akira, Tsuguyuki Saito, and Hayaka Fukuzumi. "TEMPO-oxidized cellulose nanofibers." *Nanoscale* 3, no. 1 (2011): 71-85.

3) Fukuzumi, Hayaka, Tsuguyuki Saito, Tadahisa Iwata, Yoshiaki Kumamoto, and Akira Isogai. "Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation." *Biomacromolecules* 10, no. 1 (2008): 162-165.

4) Ifuku, Shinsuke, Manami Tsuji, Minoru Morimoto, Hiroyuki Saimoto, and Hiroyuki Yano. "Synthesis of silver nanoparticles templated by TEMPO-mediated oxidized bacterial cellulose nanofibers." *Biomacromolecules* 10, no. 9 (2009): 2714-2717.

5) Ishii, Daisuke, Tsuguyuki Saito, and Akira Isogai. "Viscoelastic evaluation of average length of cellulose nanofibers prepared by TEMPO-mediated oxidation." *Biomacromolecules* 12, no. 3 (2011): 548-550.

6) Saito, Tsuguyuki, Masayuki Hirota, Naoyuki Tamura, Satoshi Kimura, Hayaka Fukuzumi, Laurent Heux, and Akira Isogai. "Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions." *Biomacromolecules* 10, no. 7 (2009): 1992-1996.

7) Fujisawa, Shuji, Yusuke Okita, Hayaka Fukuzumi, Tsuguyuki Saito, and Akira Isogai. "Preparation and characterization of TEMPO-oxidized cellulose nanofibril films with free carboxyl groups." *Carbohydrate Polymers* 84, no. 1 (2011): 579-583.

8) Besbes, Iskander, Sabrine Alila, and Sami Boufi. "Nanofibrillated cellulose from TEMPO-oxidized eucalyptus fibres: effect of the carboxyl content." *Carbohydrate Polymers* 84, no. 3 (2011): 975-983.

9) Ashori, Alireza, Mehran Babaee, Mehdi Jonoobi, and Yahya Hamzeh. "Solvent-free acetylation of cellulose nanofibers for improving compatibility and dispersion." *Carbohydrate polymers* 102 (2014): 369-375.

10) Jonoobi, Mehdi, Jalaluddin Harun, Aji P. Mathew, Mohd Zobir B. Hussein, and Kristiina Oksman. "Preparation of cellulose nanofibers with hydrophobic surface characteristics." *Cellulose* 17, no. 2 (2010): 299-307.

11) Cetin, Nihat Sami, Philippe Tingaut, Nilgül Özmen, Nathan Henry, David Harper, Mark Dadmun, and Gilles Sebe. "Acetylation of cellulose nanowhiskers with vinyl acetate under moderate conditions." *Macromolecular Bioscience* 9, no. 10 (2009): 997-1003.

12) Ifuku, Shinsuke, Masaya Nogi, Kentaro Abe, Keishin Handa, Fumiaki Nakatsubo, and Hiroyuki Yano. "Surface modification of bacterial cellulose nanofibers for property enhancement of optically transparent composites: dependence on acetyl-group DS." *Biomacromolecules* 8, no. 6 (2007): 1973-1978.

13) Abdelmouleh, M., S. Boufi, M. N. Belgacem, A. P. Duarte, A. Ben Salah, and A. Gandini. "Modification of cellulosic fibres with functionalised silanes: development of surface properties." *International Journal of Adhesion and Adhesives* 24, no. 1 (2004): 43-54.

14) Ramírez, Jhon Alejandro Ávila, Camila Juan Suriano, Patricia Cerrutti, and María Laura Foresti. "Surface esterification of cellulose nanofibers by a simple organocatalytic methodology." *Carbohydrate polymers* 114 (2014): 416-423.

15) Herrick, Franklin W., RONALD L. Casebier, J. KELVIN Hamilton, and KAREN R. Sandberg. "Microfibrillated cellulose: morphology and accessibility." In *J. Appl. Polym. Sci.: Appl. Polym. Symp.;(United States)*, vol. 37, no. CONF-8205234-Vol. 2. ITT Rayonier Inc., Shelton, WA, 1983.

16) Hasani, Merima, Emily D. Cranston, Gunnar Westman, and Derek G. Gray. "Cationic surface functionalization of cellulose nanocrystals." *Soft Matter* 4, no. 11 (2008): 2238-2244.

17) Chirayil, Cintil Jose, Jithin Joy, Lovely Mathew, Miran Mozetic, Joachim Koetz, and Sabu Thomas. "Isolation and characterization of cellulose nanofibrils from Helicteres isora plant." *Industrial Crops and Products* 59 (2014): 27-34.

18) Cherian, Bibin Mathew, Alcides Lopes Leão, Sivoney Ferreira de Souza, Ligia Maria Manzine Costa, Gabriel Molina de Olyveira, M. Kottaisamy, E. R. Nagarajan, and Sabu Thomas. "Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibers for medical applications." *Carbohydrate Polymers* 86, no. 4 (2011): 1790-1798.

19) Cara, Cristobal, Encarnación Ruiz, Ignacio Ballesteros, María J. Negro, and Eulogio Castro. "Enhanced enzymatic hydrolysis of olive tree wood by steam explosion and alkaline peroxide delignification." *Process Biochemistry* 41, no. 2 (2006): 423-429.

20) Ferreira, Bruno Christiano Silva, Filipe Simões Teodoro, Aparecida Barbosa Mageste, Laurent Frédéric Gil, Rossimiriam Pereira de Freitas, and Leandro Vinícius Alves Gurgel. "Application of a new carboxylate-functionalized sugarcane bagasse for adsorptive removal of crystal violet from aqueous solution: Kinetic, equilibrium and thermodynamic studies." *Industrial Crops and Products* 65 (2015): 521-534.

21) French, Alfred D. "Idealized powder diffraction patterns for cellulose polymorphs." *Cellulose* 21, no. 2 (2014): 885-896.

22) Segal, L. G. J. M. A., J. J. Creely, A. E. Martin Jr, and C. M. Conrad. "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer." *Textile Research Journal* 29, no. 10 (1959): 786-794.

23) Sjöström, Eero, and Raimo Alén, eds. *Analytical methods in wood chemistry, pulping, and papermaking*. Springer Science & Business Media, 2013.

Chapter 4

Meldrum's Acid Modified Cellulose Nanofiber based PVDF Nanofibrous MF membrane for Dye Water Treatment and Nanoparticle Removal

4.1 Introduction

All plants and animals must have water to survive. With the evolution of various industries, water pollution is one of the biggest problems that the world faces. After agriculture, the textile dyeing and finishing industry has generated a large water pollution problem as most of the chemicals coming from these industries are highly toxic and directly or indirectly affect human health. Since the development of advanced modern textiles and the arrival of new synthetic dyes to the market daily, water pollution due to dye waste is an important issue to study [1]. Biological processes, chemical processes, and the operation of electromagnetic radiation are common removal techniques [2-6]. From these mentioned methods, microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) using pressure driven technologies have gained considerable interest due to their impressively high performance and low cost [7,8]. These conventional ultrafiltration, nanofiltration, and microfiltration membranes for water purification are produced by phase immersion methods like immersion precipitation and thermally induced phase separation, where the torturous path results in the low water flux. Electrospun

membranes have some advantages over the membranes produced via phase immersion methods such as higher effective porosity with continuously interconnected pores, light weight, and high surface area [9, 10]. Therefore, electrospinning is a promising technique for generating continuous fibers with diameters in the range of a few hundred nanometers [11]. They exhibit excellent mechanical strength, water flux, and particle rejection. These properties make electrospun membranes an excellent platform for microfiltration applications [12].

On the other hand, the average porosity of the electrospun membrane is too high to remove smaller objects like viruses and textile dyes by size exclusion [13, 14]. So, to eliminate the minute particles like viruses and textile dyes, an additional adsorption mechanism is essential without affecting the permeability of electrospun MF membranes. One of the typical approaches to remove viruses or dyes from wastewater is to increase the electrostatic charges of the MF membrane to enhance the absorption capability [15]. PVDF (polyvinylidene fluoride) has earned great attention in recent years as a membrane material due to its excellent properties like high thermal stability, mechanical strength, and chemical resistance toward solvents, acids, and base. Compared to other fluoropolymers PVDF can quickly dissolve in most of the organic solvents. These outstanding properties make PVDF membranes have been used as membrane filters for water purification [16-22].

Nanomaterials play a significant role in developing new materials with high efficiency at low cost for water pollution. Among the nanomaterial's, cellulose nanofibers (CNFs) are one of the promising adsorbent materials for water purification due to their low cost, abundant hydroxyl groups, natural abundance, and ecofriendly nature. Moreover, the CNFs have the enormous amount of surface

hydroxyl (OH) groups, which enables a lot of surface chemistries or incorporation of chemical groups that may increase the adsorption toward the various pollutants in water. Until now, a few extensive reports have been published in the area of water purification using nanocellulose by Ma et al. [3, 5]. Most of the works based on nanocellulose in water treatment were reported by the Chemistry Department of Stony Brook University, USA. They demonstrated nanocellulose based membranes for the removal of positively charged dyes, bacteria, and viruses from water. They used (2, 2, 6, 6-tetramethylpiperidin- 1-yl) oxyl (TEMPO) oxidation surface treatment for cellulose nanofibers for almost all of their studies. An obvious disadvantage of this oxidation procedure is the use of TEMPO and sodium bromide, which both are associated with environmental issues. Moreover, the TEMPO reagent is very expensive to commercialize in the industry level. Another work was done by Qiao et al., and they removed cationic dyes using carboxylate functionalized cellulose nanocrystals. They used pyridine as a solvent medium for the carboxylation of cellulose nanocrystals, which is highly toxic in nature [23]. Cao et al. removed silica nanoparticles from the water using poly- (acrylonitrile) nanofibrous membrane reinforced with jute cellulose nanowhiskers, where they used TEMPO surface treatment for the cellulose nanowhiskers [24]. So there is every need to formulate new chemical design protocols on the surface treatment of cellulose nanofibers via a solvent free procedure technique.

In this context, we intended to produce a unique adsorbent material from cellulose nanofibers (CNFs) via non-solvent assisted method using Meldrum's acid as an esterification agent which can remove the dyes from water. To the extent of our knowledge, preparation of new green based adsorbent to adsorbing dyes from CNFs

via a non-solvent assisted procedure using Meldrum's acid as esterification agent has not been addressed to date. This finding offers a new platform for the surface treatment of cellulose nanofibers using solvent free green technology.

4.2 Morphology of PVDF electrospun membrane.

Figure 4.1 showed the SEM images of PVDF electrospun membrane. From the figure, the nanofibrous membrane showed the three-dimensional arrangement of nanofibers with an average fiber diameter of 700 nm. It could be seen that from the SEM figure, nanofibrous membranes with irregular fiber arrangement of PVDF nanofibers.

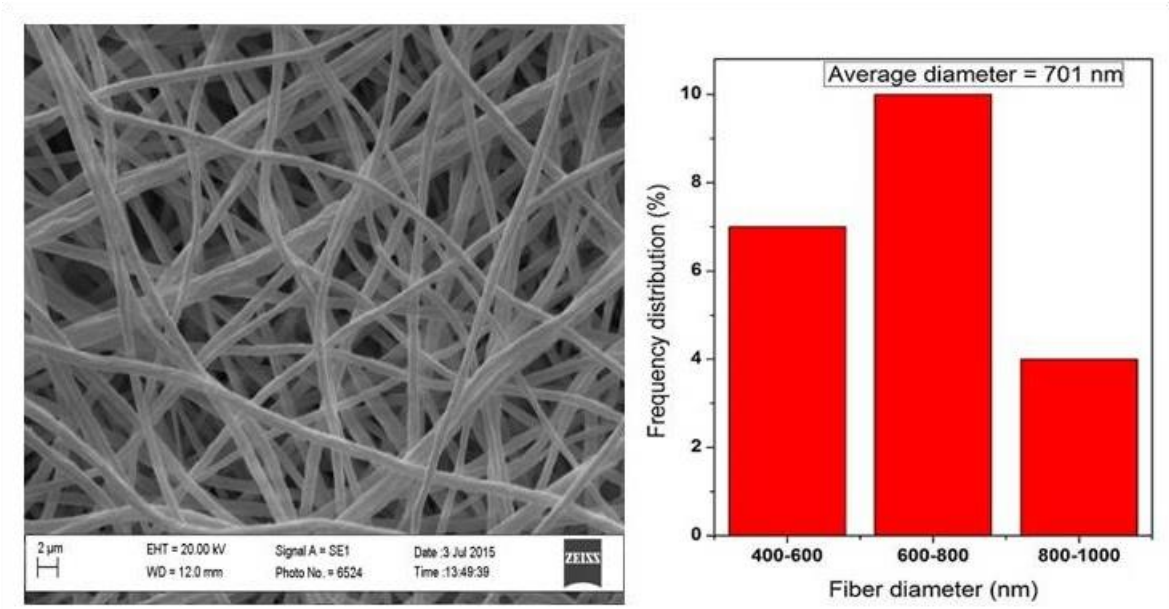

Figure 4.1 SEM image and diameter frequency distributions of PVDF electrospun membrane

4.3 Morphology of modified CNFs based PVDF nanofibrous MF membrane.

Figure 4.2 showed the SEM images of the top view of the modified CNFs based PVDF nanofibrous MF membrane. The top modified CNFs coating seems to be

relatively soft and regular surface which has a higher tendency to remove the trapped foreign particles on the surface, thus enhances the antifouling property of the membrane. Since modified CNFs are very much smaller than the PVDF fibers, at lower magnification, the cellulose nanofiber layer seems to be like the soft thin film. From this, it can be concluded that modified CNFs have been successfully coated over the PVDF electrospun membrane resulting in a nanofibrous microfiltration membrane.

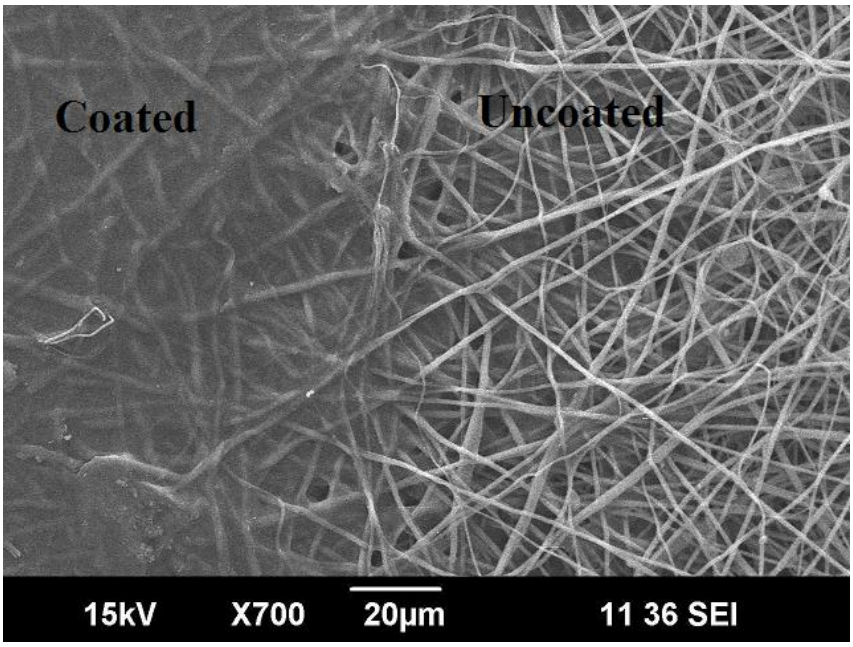

Figure 4.2 SEM image of the top view of Meldrum's acid modified CNFs based PVDF nanofibrous MF membrane (The uncoated membrane part is displayed at the right side).

4.4 Surface area of nanofibrous MF membrane.

Fabrication of Meldrum's acid modified CNF based PVDF nanofibrous MF membrane was done by impregnation of 0.1 wt% of Meldrum's' acid modified CNFs (pH 7.0) into the PVDF electrospun membrane. Compared with the PVDF electrospun membrane this coating of modified CNFs resulted in a substantial

enhancement in the surface area around 11.4%, i.e. from 4.6713 m^2/g to 5.2078 m^2/g for PVDF Electrospun Membrane and Meldrum modified CNFs based PVDF nanofibrous MF membrane respectively from the BET measurements. This increase in the area can improve the efficiency of the adsorption process.

4.5 Contact angle studies

The water contact angle measurements for the PVDF electrospun membrane, Meldrum's acid, modified CNFs based PVDF membrane and unmodified CNFs based PVDF membrane were measured. The water contact angle obtained for the PVDF electrospun membrane, Meldrum's modified CNFs based PVDF membrane and unmodified CNFs based PVDF membrane were 142.6°, 123° and 121° respectively. The water contact angle for both modified CNFs and unmodified CNFs membranes were decreased to 123° and 121° respectively which indicates the enhancement of the wettability of both nanofibrous membranes compared to the PVDF electrospun membrane. It can be noticed that there was the only slight difference between the contact angles of both nanofibrous membranes. The water contact angle measurements confirmed that the fouling problem of the PVDF electrospun membrane could be decreased to some extent by the coating of modified CNFs and unmodified CNFs on to the surface of PVDF electrospun membrane.

4.6 Evaluation of Adsorption capacity of nanofibrous membrane against crystal violet dye

In this study, we used crystal violet (CV) dye as a model of positively charged particles to evaluate the adsorption efficiency of all membranes. To determine the adsorption efficiency, UV-vis spectroscopy was employed. Figure 4.3 illustrates the adsorption efficiency, of 10mg/L CV by PVDF membrane alone, unmodified CNFs

based PVDF membrane and Meldrum's modified CNFs based PVDF membranes towards crystal violet (CV) dye as a function of time. From the figure it was clearly shown that, with the 10mg/L of CV aqueous solution, CV adsorption of PVDF electrospun membrane and unmodified CNFs based PVDF membrane was around 1.368 and 2.948 mg/g of the membrane, whereas it was 3.984 mg/g of the membrane by Meldrum's acid CNFs based PVDF membrane. These observations were comparable with those of Ma et al. who evaluated the adsorption of positively charged CV dye was 3.8mg/g of the membrane using poly (acrylonitrile) (PAN) scaffold nanofibrous membrane with cellulose nanowhiskers [3]. It was found that the adsorption efficiency of Meldrum's modified CNFs based PVDF nanofibrous MF membrane was higher than that of PVDF electrospun membrane and unmodified CNFs based PVDF microfiltration membrane.

This enhancement in the dye adsorption of the Meldrum's modified CNFs based PVDF membrane can be justified by the high electrostatic attraction between the positively charged CV dyes and carboxylate groups (negatively charged) on the Meldrum's acid modified CNFs (mechanism shown in figure 4.4). The adsorption of CV on to Meldrum's acid modified CNFs based PVDF membrane reached equilibrium after 3 h. Therefore, it can be concluded that the adsorption efficiency (using 10mg/L CV aqueous solution) of the Meldrum's modified CNFs based PVDF membrane was about two to three times higher than that of PVDF electrospun membrane. Therefore, the demonstrated membrane is expected to be a very promising adsorbent for dye wastewater treatment and dynamic adsorption in practical applications.

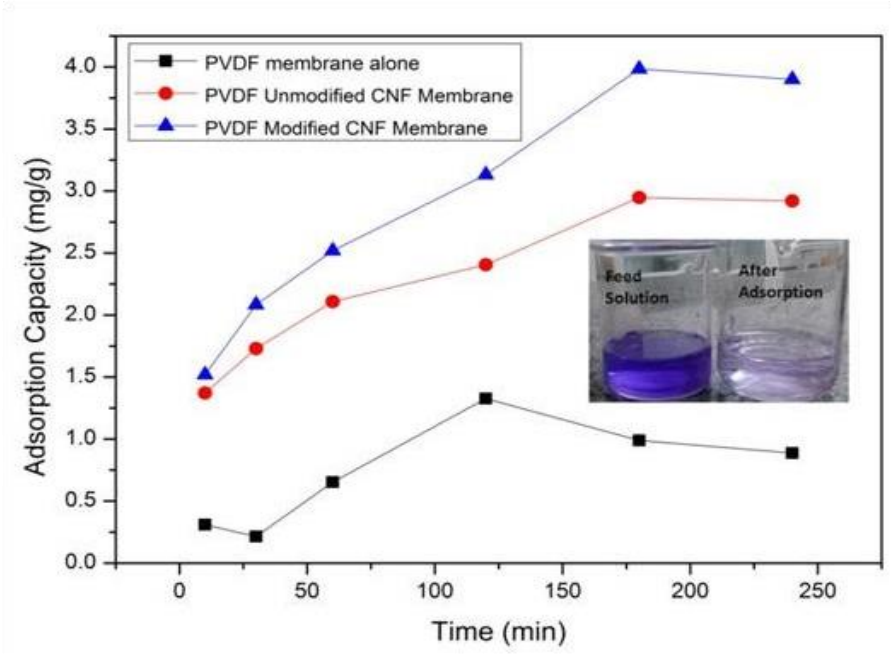

Figure 4.3 The adsorption capacity of PVDF membrane alone, PVDF/ unmodified CNF membrane and PVDF/ modified CNF membranes against time.

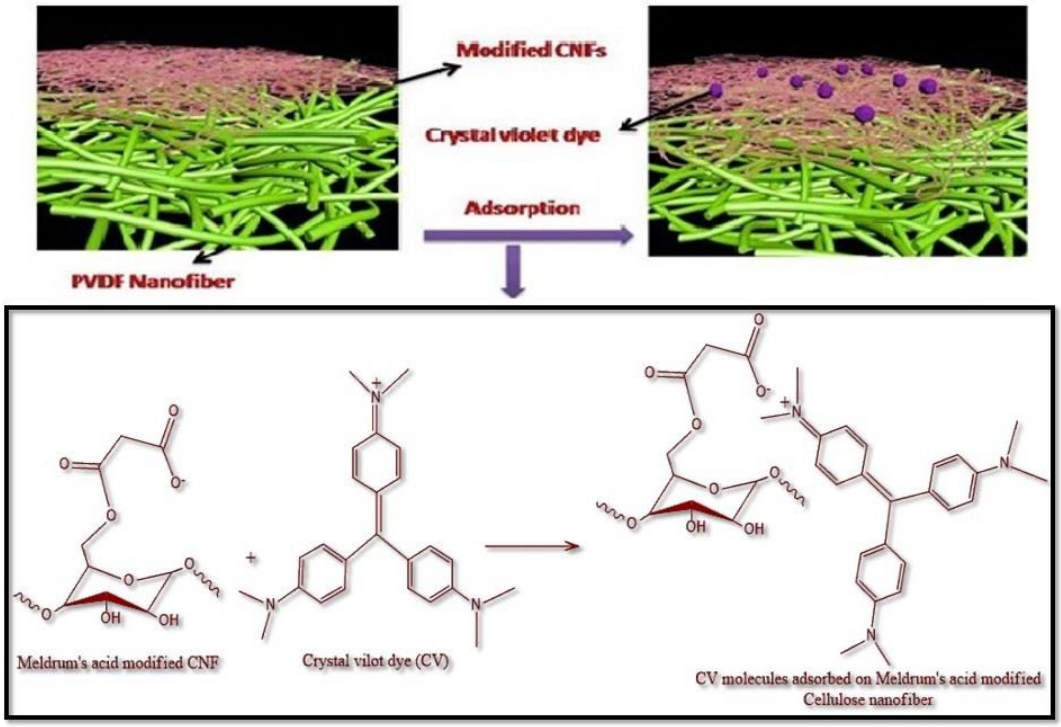

Figure 4.4 Schematic representation of crystal violet removal by Meldrum's acid modified CNFs based PVDF nanofibrous MF membrane and its mechanism

4.7 Microfiltration performance of nanofibrous MF membrane against nanoparticles.

Figure 4.5, 4.6 and 4.7 show the SEM images of the PVDF membrane alone, unmodified CNFs based PVDF membrane and Meldrum's acid modified CNFs based PVDF membranes respectively, top and bottom surfaces, after the removal of Fe_2O_3 nanoparticles. From the top surfaces of the all filtrated membranes showed that the Fe_2O_3 nanoparticles are formed like a clusters on the top surfaces of the membranes as illustrates in figure 4.5a, 4.6a and 4.7a**,** whereas in the bottom surfaces of all membranes as shown in 4.5b, 4.6b and 4.7b, we could not find much Fe_2O_3 nanoparticles. These results indicate that the removal of Fe_2O_3 nanoparticles was similar for all membrane samples studied. Since the work was focused on the Meldrum's modified CNFs based PVDF membrane, we studied the UV-visible spectra of the starting (feed) and final (filtrate) solution of Meldrum's acid modified CNFs based PVDF membrane, which was given in figure 4.8. Figure 4.8 illustrates UV-vis spectra of both starting (feed) and final (filtrate) solution of for Fe_2O_3 nanoparticles. From the final solution, it could be seen that the Fe_2O_3 nanoparticles were effectively eliminated from the starting solution by the Meldrum's modified CNFs based PVDF membrane and the membrane had the good particle rejection ratio against the Fe_2O_3 nanoparticles.

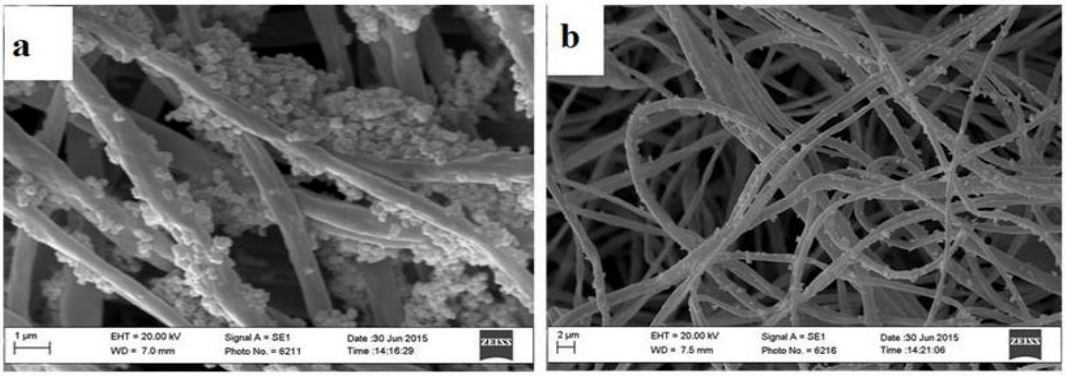

Figure 4.5 SEM images of the top surface (a) and the bottom surface (b) of PVDF electrospun membrane after the filtration of Fe_2O_3 nanoparticles.

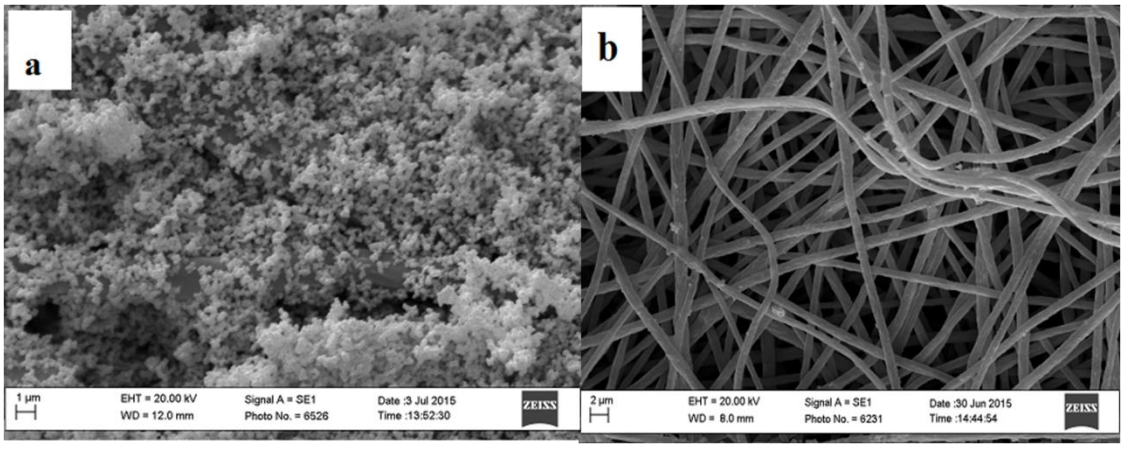

Figure 4.6 SEM images of the top surface (a) and the bottom surface (b) of unmodified CNFs based PVDF electrospun membrane after the filtration of Fe_2O_3 nanoparticles.

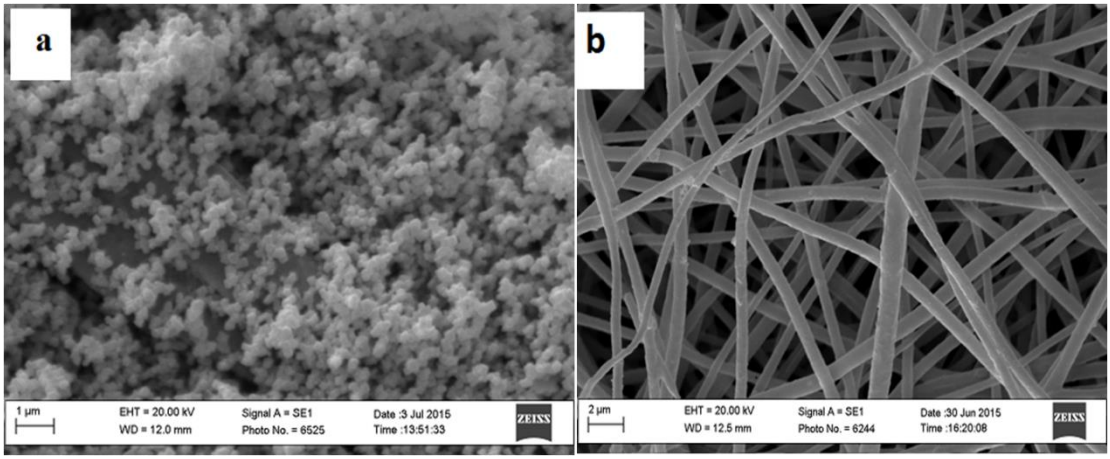

Figure 4.7 SEM images of the top surface (a) and the bottom surface (b) of Meldrum's acid modified CNFs based PVDF electrospun nanofibrous membrane after the filtration of Fe_2O_3 nanoparticles.

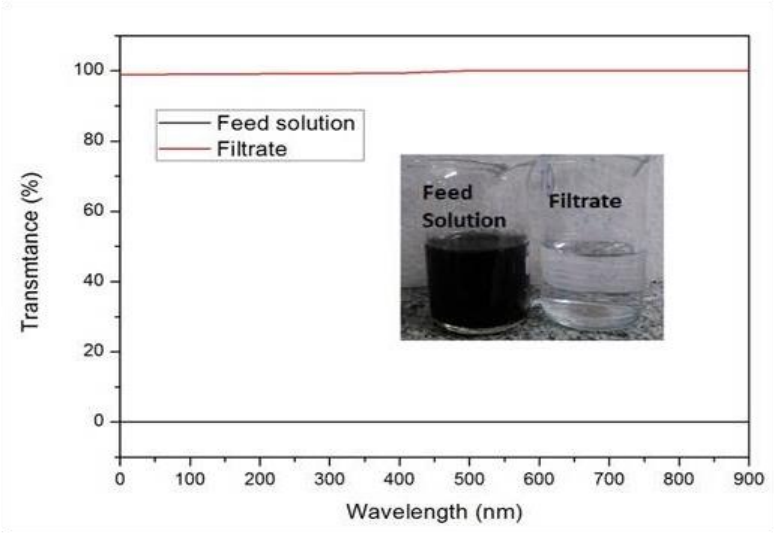

Figure 4.8 UV-visible spectra of feed and filtrate solution of Fe_2O_3 nanoparticles for Meldrum's acid modified CNFs based PVDF membrane

4.8 Conclusion

We have prepared a new adsorbent material for the adsorption of positively charged crystal violet dyes from cellulose nanofibers (CNFs) via non-solvent- assisted methodology using Meldrum's acid as an esterification agent. It is also demonstrated that the Meldrum's modified cellulose nanofibers based PVDF nanofibrous membrane can be successfully used to remove the crystal violet dyes and Fe_2O_3 nanoparticles (with the rejection of over 99%) from the water. It has been shown that with 10mg/L of crystal violet aqueous solution, CV adsorption of PVDF electrospun membrane and unmodified CNFs based PVDF membrane was around 1.368 and 2.948 mg/g of the membrane respectively, whereas it was 3.984 mg/g of the membrane by Meldrum's acid CNFs based PVDF membrane. Meldrum's acid modified CNFs based PVDF membrane showed two or three times higher adsorption than the PVDF electrospun membrane because the high electrostatic attraction between the positively charged CV dyes and carboxylate groups

(negatively charged) on the surface of Meldrum's acid modified CNFs. This demonstrated membrane is unique as they can concurrently eliminate crystal violet dyes and Fe_2O_3 nanoparticles from the water. So they are auspicious for use in water treatment applications. All the experimental results suggested that the Meldrum's modified CNFs were a promising additive for modifying MF membrane. Moreover, this study opens up a new platform for the surface modifications of cellulose nanofibers via solvent-free technique, which can enhance the economic feasibility of the process.

4.9 References:

1) Kant, Rita. "Textile dyeing industry an environmental hazard." *Natural science*4, no. 1 (2012): 22-26.

2) Lewis, Scott R., Saurav Datta, Minghui Gui, Eric L. Coker, Frank E. Huggins, Sylvia Daunert, Leonidas Bachas, and Dibakar Bhattacharyya. "Reactive nanostructured membranes for water purification." *Proceedings of the National Academy of Sciences* 108, no. 21 (2011): 8577-8582.

3) Ma, Hongyang, Christian Burger, Benjamin S. Hsiao, and Benjamin Chu. "Nanofibrous microfiltration membrane based on cellulose nanowhiskers." *Biomacromolecules* 13, no. 1 (2011): 180-186.

4) Chiam, Chel–ken, and Rosalam Sarbatly. "Purification of aquacultural water: conventional and new membrane-based techniques." *Separation & Purification Reviews* 40, no. 2 (2011): 126-160.

5) Ma, Hongyang, Christian Burger, Benjamin S. Hsiao, and Benjamin Chu. "Ultra-fine cellulose nanofibers: new nano-scale materials for water purification." *Journal of Materials Chemistry* 21, no. 21 (2011): 7507-7510.

6) Ambashta, Ritu D., and Mika Sillanpää. "Water purification using magnetic assistance: a review." *Journal of hazardous materials* 180, no. 1 (2010): 38-49.

7) Kavitskaya, A. A., M. D. Skil'skaya, A. I. Kononova, and I. D. Atamanenko. "Ultrafiltration purification of underground water during its various preconditioning." *Journal of Water Chemistry and Technology* 32, no. 6 (2010): 365-369.

8) Geise, Geoffrey M., Hae-Seung Lee, Daniel J. Miller, Benny D. Freeman, James E. McGrath, and Donald R. Paul. "Water purification by membranes: the role of polymer science." *Journal of Polymer Science Part B: Polymer Physics* 48, no. 15 (2010): 1685-1718.

9) Ding, Bin, Moran Wang, Xianfeng Wang, Jianyong Yu, and Gang Sun. "Electrospun nanomaterials for ultrasensitive sensors." *Materials Today* 13, no. 11 (2010): 16-27.

10) Wang, Xianfeng, Bin Ding, Jianyong Yu, and Moran Wang. "Engineering biomimetic superhydrophobic surfaces of electrospun nanomaterials." *Nano today* 6, no. 5 (2011): 510-530.

11) Reneker, Darrell H., and Iksoo Chun. "Nanometre diameter fibres of polymer, produced by electrospinning." *Nanotechnology* 7, no. 3 (1996): 216.

12) Wang, Ran, Yang Liu, Brandon Li, Benjamin S. Hsiao, and Benjamin Chu. "Electrospun nanofibrous membranes for high flux microfiltration." *Journal of membrane science* 392 (2012): 167-174.

13) Gopal, Renuga, Satinderpal Kaur, Chao Yang Feng, Casey Chan, Seeram Ramakrishna, Shahram Tabe, and Takeshi Matsuura. "Electrospun nanofibrous polysulfone membranes as pre-filters: Particulate removal." *Journal of membrane science* 289, no. 1 (2007): 210-219.

14) Ma, Zuwei, Kotaki Masaya, and Seeram Ramakrishna. "Immobilization of Cibacron blue F3GA on electrospun polysulphone ultra-fine fiber surfaces towards developing an affinity membrane for albumin adsorption." *Journal of membrane science* 282, no. 1 (2006): 237-244.

15) Netzer, A., P. Wilkinson, and S. Beszedits. "Removal of trace metals from wastewater by treatment with lime and discarded automotive tires." *Water Research* 8, no. 10 (1974): 813-817.

16) Park, Hyun Hee, Bal Raj Deshwal, Hang Dae Jo, Won Kil Choi, In Won Kim, and Hyung Keun Lee. "Absorption of nitrogen dioxide by PVDF hollow fiber membranes in a G–L contactor." *Desalination* 243, no. 1-3 (2009): 52-64.

17) Chae, So-Ryong, Hiroshi Yamamura, Keiichi Ikeda, and Yoshimasa Watanabe. "Comparison of fouling characteristics of two different poly-vinylidene fluoride microfiltration membranes in a pilot-scale drinking water treatment system using pre-coagulation/sedimentation, sand filtration, and chlorination." *Water research* 42, no. 8 (2008): 2029-2042.

18) Bottino, A., G. Capannelli, and A. Comite. "Novel porous poly (vinylidene fluoride) membranes for membrane distillation." *Desalination* 183, no. 1-3 (2005): 375-382.

19) Park, Sung Yong, Sung Hak Choi, Jae Woo Chung, and Seung-Yeop Kwak. "Anti-scaling ultrafiltration/microfiltration (UF/MF) polyvinylidene fluoride (PVDF) membranes with positive surface charges for Ca 2+/silica-rich wastewater treatment." *Journal of Membrane Science* 480 (2015): 122-128.

20) Kalaiselvi, G., P. Maheswari, D. Mohan, and S. Balasubramanian. "Synthesis and characterization of poly 3-methyl 2-vinyl pyridinium nitrate incorporated polyvinylidine fluoride ultrafiltration membrane for metal ion removal." *Separation and Purification Technology* 143 (2015): 105-114.

21) Buscio, V., M. Crespi, and C. Gutiérrez-Bouzán. "Application of PVDF ultrafiltration membranes to treat and reuse textile wastewater." *Desalination and Water Treatment* 57, no. 18 (2016): 8090-8096.

22) Liu, Fu, N. Awanis Hashim, Yutie Liu, MR Moghareh Abed, and K. Li. "Progress in the production and modification of PVDF membranes." *Journal of membrane science* 375, no. 1 (2011): 1-27.

23) Qiao, Han, Yanmei Zhou, Fang Yu, Enze Wang, Yinghao Min, Qi Huang, Lanfang Pang, and Tongsen Ma. "Effective removal of cationic dyes using carboxylate-functionalized cellulose nanocrystals." *Chemosphere* 141 (2015): 297-303.

24) Cao, Xinwang, Meiling Huang, Bin Ding, Jianyong Yu, and Gang Sun. "Robust polyacrylonitrile nanofibrous membrane reinforced with jute cellulose nanowhiskers for water purification." *Desalination* 316 (2013): 120-126.

Chapter 5

Strategy and Fabrication of in-situ Polymerized PANI/CNF Nano papers

5.1 Introduction

Among the conducting polymers, PANI gained a considerable interest due to its presence of the chemically flexible –NH-group in the polymer backbone which not only take part in the protonation/deprotanation but also contributes to π –bond formation [1], thus ensuring greater environmental stability. PANI can be obtained either by chemical or electrochemical method and does not involve any special precautions [2-4]. Although it is easily synthesised in bulk, its use is restricted due to its unprocessability by normal melt or solution techniques. But the presence of conjugated system in PANI leads to the rigidity of the polymer molecule, resulting in poor film-forming capability. This due to the lack of the ability to form hydrogen bonds and thereby it is difficult to prepare a film by casting and drying. In order to rectify this problem, various studies has been done to fabricate various PANI composites by blending it with various polymers. Cellulose has been recognized as good matrix/substrate for biodegradable batteries, sensors and actuators [5-7]. Cellulose nanofiber based papers or cellulose nanofiber suspensions give adequate hydrogen bonding that films may be easily produced from the mixture of conducting polymers and cellulose nanofibers [8-10].

Yu et al. deposited PANI on CNFs through in situ polymerization. The intertwined CNF/PANI structure forms conductive films exhibiting continuous polymerization

of PANI. They found that the prepared CNF/PANI composite with PANI content 68.6 % showed the highest conductivity under optimized conditions [11]. Another work was reported by Hu et al. and they prepared conductive polyaniline/bacterial cellulose (PANI/BC) nanocomposites membranes by in-situ oxidative polymerization of aniline with ammonium persulfate as an oxidant and BC as a template. The resulted PANI-coated BC nanofibrils formed a uniform and flexible membrane. They found that the PANI nanoparticles deposited on the surface of BC connected to form a continuous nanosheath by taking along the BC template, which greatly increases the thermal stability of BC. They concluded that the content of PANI and the electrical conductivity of composites increased with increasing reaction time from 30 to 90 min [12]. Similar work was done by Liu et al. and they fabricated thin composite films of nanocellulose with PANI inclusions at different loadings via in-situ polymerization where aniline-HCl was polymerized with ammonium peroxydisulfate (APS) as oxidant in aqueous nanocellulose suspension. They found that the thin composite films showed improved combination of flexibility and conductivity [13].

In this chapter we discussed about the fabrication of flexible, lightweight& highly conductive cellulose nanopapers via *in-situ* polymerization of aniline monomer on to cellulose nanofibers. The demonstrated paper exhibits good conductivity due to the formation of a continuous coating of polyaniline over the cellulose nanofibers during *in-situ* polymerization which is evident from SEM, FTIR and XRD analysis. The free hydroxyl groups on the surface of nanocellulose fibers promptly forms intermolecular hydrogen bonding with PANI which makes the cellulose nanopapers even more robust.

5.2 Strategy for the *in-situ* polymerization of aniline monomers onto cellulose nanofibers

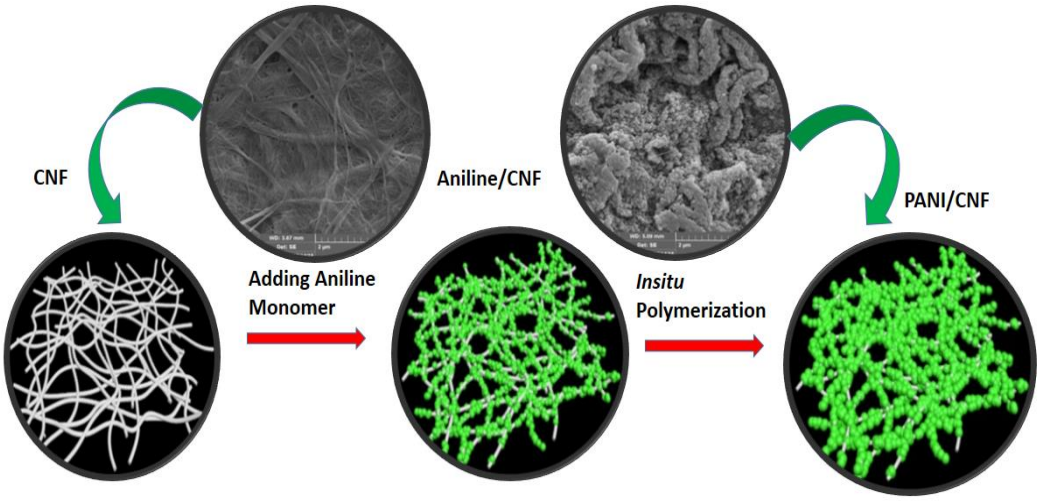

Figure 5.1: Strategy for the *in-situ* polymerization of aniline monomers onto cellulose nanofibers

The scheme in figure 5.1, illustrates the *insitu* polymerization of aniline on the surface of the cellulose nanofibers and thereby the formation of PANI/CNF flexible composite papers. As shown in the figure 5.1, the aniline hydrochloride molecules could be uniformly coated on the surface of the cellulose nanofibers due to the secondary forces of interaction via hydrogen bonding between the amine groups of aniline and the hydroxyl groups of cellulose nanofibers as shown in figure 5.2.The aniline monomers would be polymerized on the surface of cellulose nanofibers, upon the addition of the ammonium persulfate (APS) oxidant. This resulted in the formation of dark black coloured PANI/CNF suspensions and composite papers as shown in figure 5.3. Aqueous suspensions of PANI/CNF composite papers with different PANI ratios were then obtained by washing with distilled water.

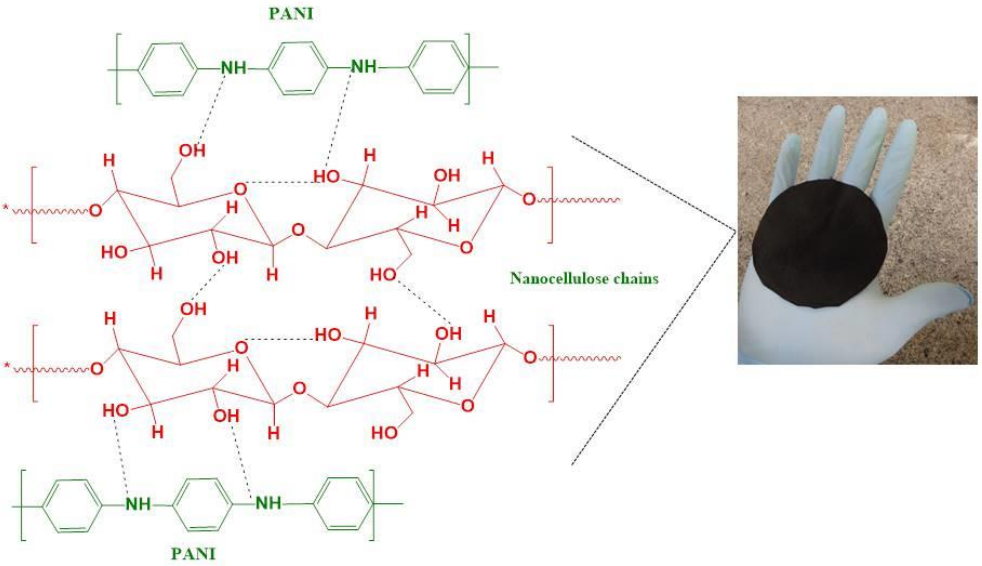

Figure 5.2: Interaction between CNF and PANI inset photographs of PANI/CNF paper.

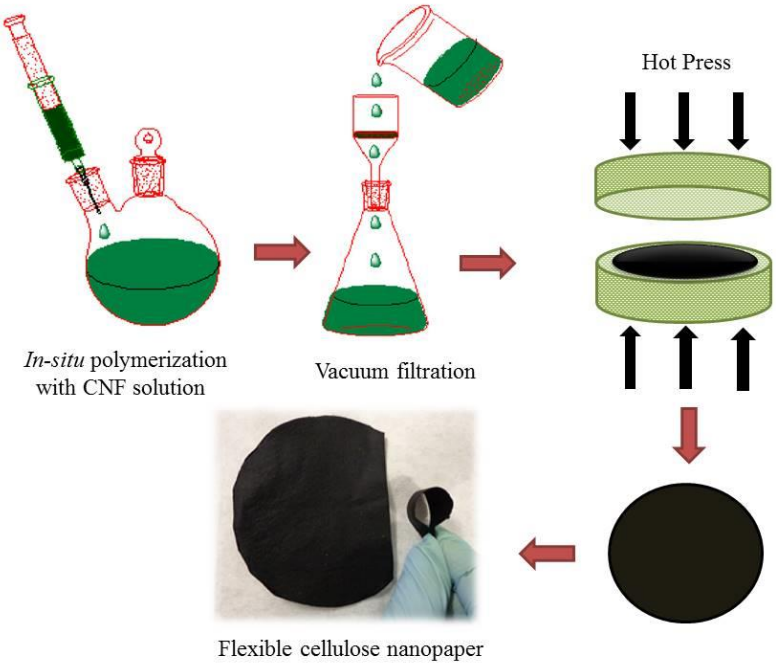

Figure 5.3: Schematic showing the preparation of PANI/CNF composite paper

5.3 Characterization of the Fabricated PANI/CNF composite paper

5.3.1 FTIR studies

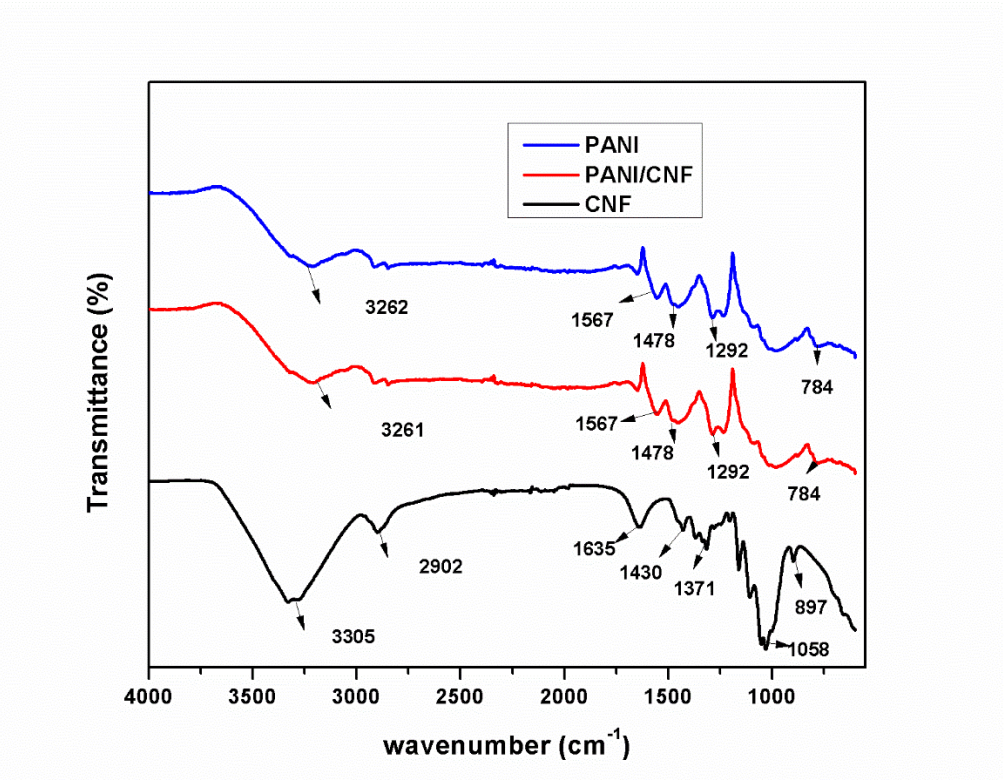

Figure 5.4: FTIR spectra of PANI/CNF and CNF flexible papers

FTIR analysis was carried out to investigate the structure of PANI, CNF and PANI/CNF papers. As shown in figure 5.4, neat CNF shows the absorption peak at 3305 cm-1, which could be attributed to –OH stretching , while those at 2902, 1430, 1371, 1058 and 897 cm-^{1} were attributed to -CH stretching, –CH_2 and –OCH in-plane bending, –CH bending, C–O–C stretching, and vibration of anomeric carbon (C1), respectively [14,15]. In the case of neat PANI, it presents characteristic bands around 3262cm-^{1}, was attributable to N-H stretching mode [16]. The C=C stretching vibration of quinine ring presents at 1567 cm^{-1} and that of benzene ring presents at 1478 cm^{-1}. The presence of benzenoid and quinoid units shows that the

prepared PANI is in its emeraldine form. The FTIR spectrum of PANI/CNF composite papers seems like the entire spectrum of PANI. Compared with the neat CNF paper, the absorption peaks at 3305, 2902, 1430, 1058 and 897 cm^{-1} were disappeared in the case of PANI/CNF composite papers. Moreover the FTIR spectrum of PANI/CNF composite paper has the characteristic transmission peaks at 1292 and 784 cm-1 for C-N stretching and C-H bending at C1 and C4 of the benzene ring indicate that CNFs formed a strong interfacial hydrogen bonding interaction with PANI.

5.3.2 XRD studies

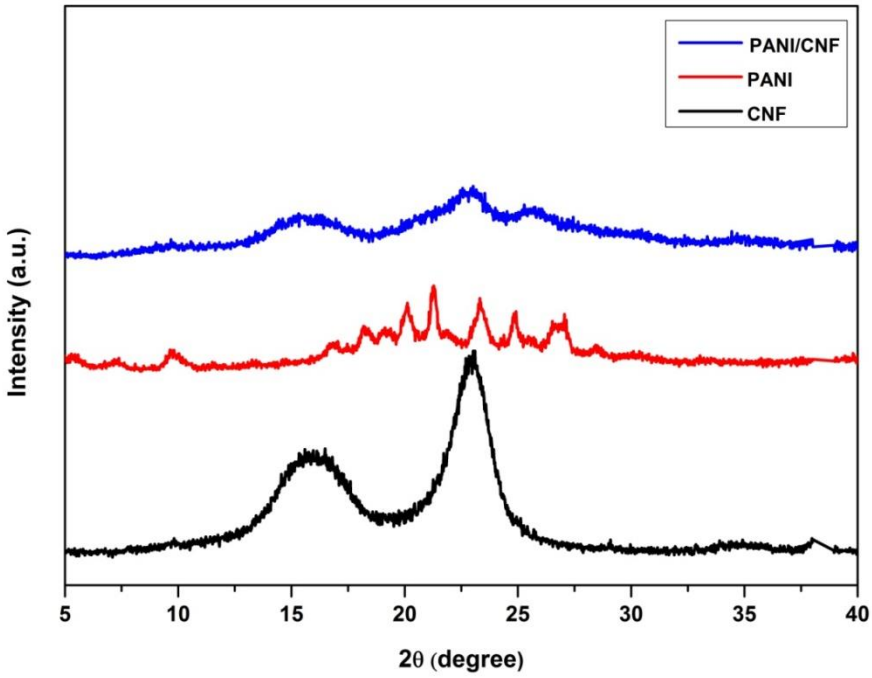

Figure 5.5: XRD patterns of PANI/CNF, PANI, and CNF

The XRD patterns of neat PANI, CNF and PANI/CNF paper are illustrated in figure 5.5. The XRD spectra of CNF shows diffraction peaks around 2ɵ= 16.3° and 2ɵ =

22.6°, which typically attributed to cellulose type I structure [17]. The spectra of pure PANI exhibited a broad background with four peaks at 8.9°, 15.1° and 20.4 ° were due to the periodic arrays parallel to the principal chain [18].The peak at 25.2° was due to the periodic arrays perpendicular to the principal chain. The XRD spectra of PANI/CNF composite paper demonstrated the combination of PANI and CNFs diffraction profiles

5.3.3 Morphological Studies of PANI/CNF flexible composite papers

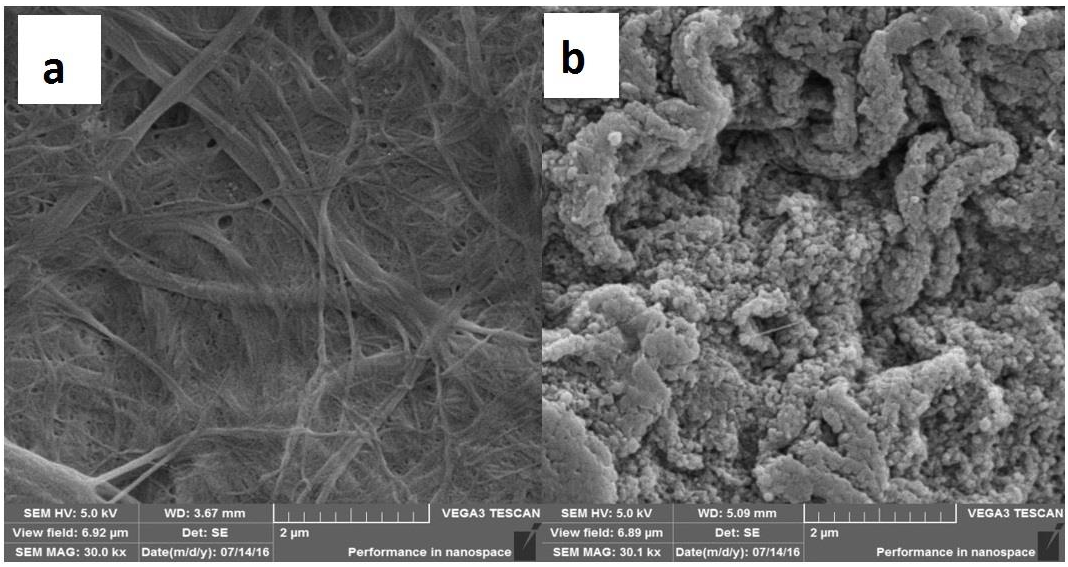

Figure 5.6: SEM images of (a) Neat CNF paper and (b) Fabricated PANI/CNFpaper

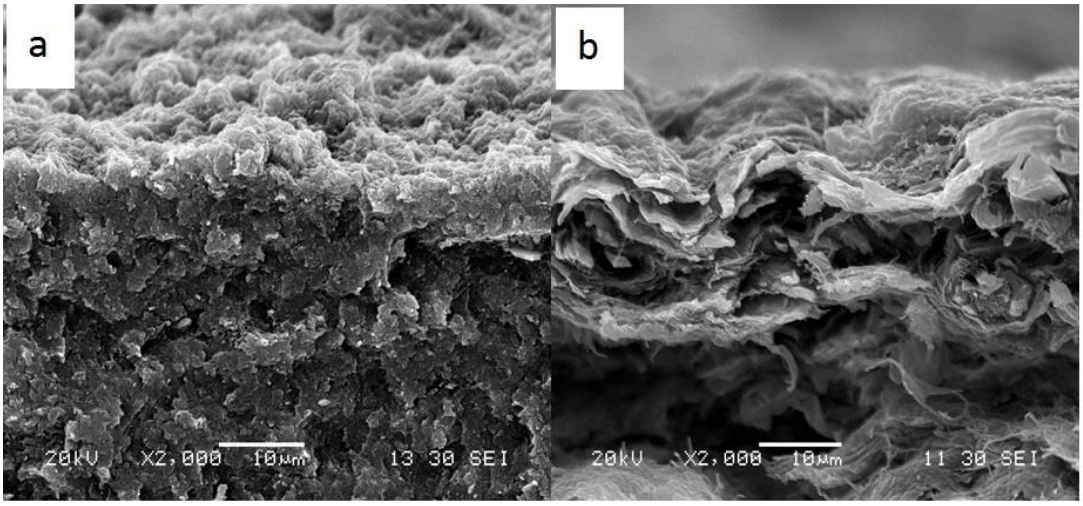

Figure 5.7: SEM images of the cross-section of PANI/CNF flexible paper (a) and neat CNF paper (b).

Figure 5.6(a) illustrates the SEM image of neat CNF paper and figure 5.6(b) illustrates the SEM of in-situ polymerized PANI on CNF paper respectively. By comparing both the figures it could be seen that, during in-situ polymerization the aniline monomer was coated uniformly and polymerised to PANI on the surface of the cellulose nanofibers which resulted in the high conductivity of samples. Additionally, FTIR spectra of CNF and PANI/CNF flexible papers were used to illustrate possible interactions between CNF and PANI in the flexible composite paper. Figure 5.7a and Figure 5.7b shows the cross sectional view of PANI/CNF flexible paper and neat CNF paper respectively. From this figure it is clearly evident that PANI was uniformly coated on the surface of cellulose nanofibers.

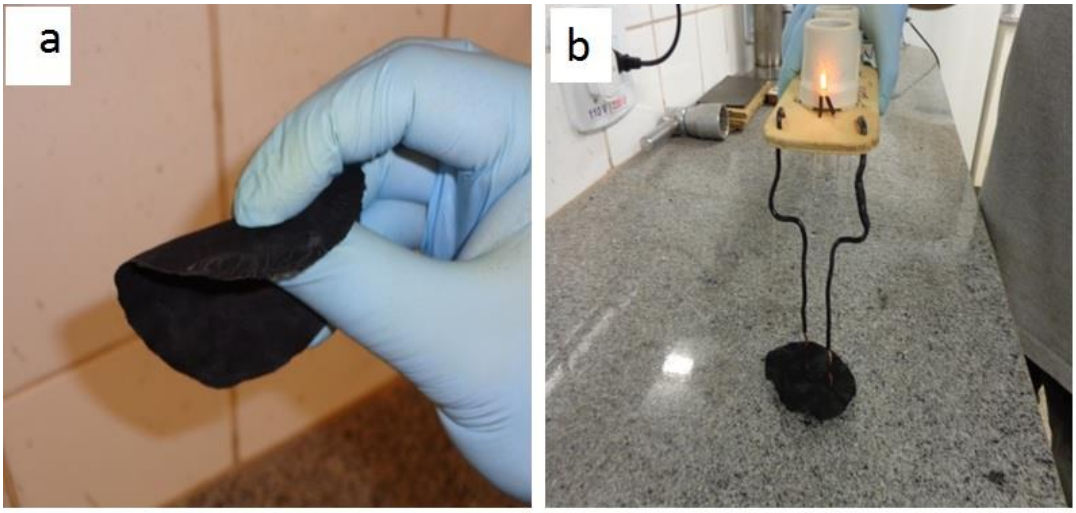

Figure 5.8: Images of (a) Fabricated PANI/CNF paper (b) conductivity demonstration of PANI/CNF paper.

5.3.4 DC Conductivity of the fabricated PANI/CNF paper.

The formation of a continuous network of PANI on the surface of the cellulose nanofibers even at low concentration of PANI/CNF (0.2:1) is a key requirement for the transport of mobile charge carriers [19, 20].The high aspect ratio of cellulose nanofibers and the meticulous use of the secondary forces via H bonding have resulted in a high value of conductivity. The DC conductivity value of the cellulose nanopapers with varying concentration of PANI is given in the Table 5.1 below. The fabricated PANI/CNF papers exhibited a highest value of 3.14×10^{-1} S/cm at 1:1 ratio (PANI: CNF). Figure 5.8a shows the digital image of the flexible PANI/CNF paper and figure 5.8b demonstrates an intuitive evidence of conductivity of demonstrated PANI/CNF paper.

PANI:CNF Ratios	DC conductivity (S/cm)
1: 1	3.14×10^{-1}
1:0.9	2.91×10^{-1}
1:0.8	1.2×10^{-1}
1:0.5	6×10^{-2}
1:0.3	2×10^{-3}
1:0.2	4.5×10^{-4}

Table 5.1: DC conductivity of PANI/CNF papers with varying PANI ratios.

5.3.5 Dielectric properties of the PANI/CNF composite paper

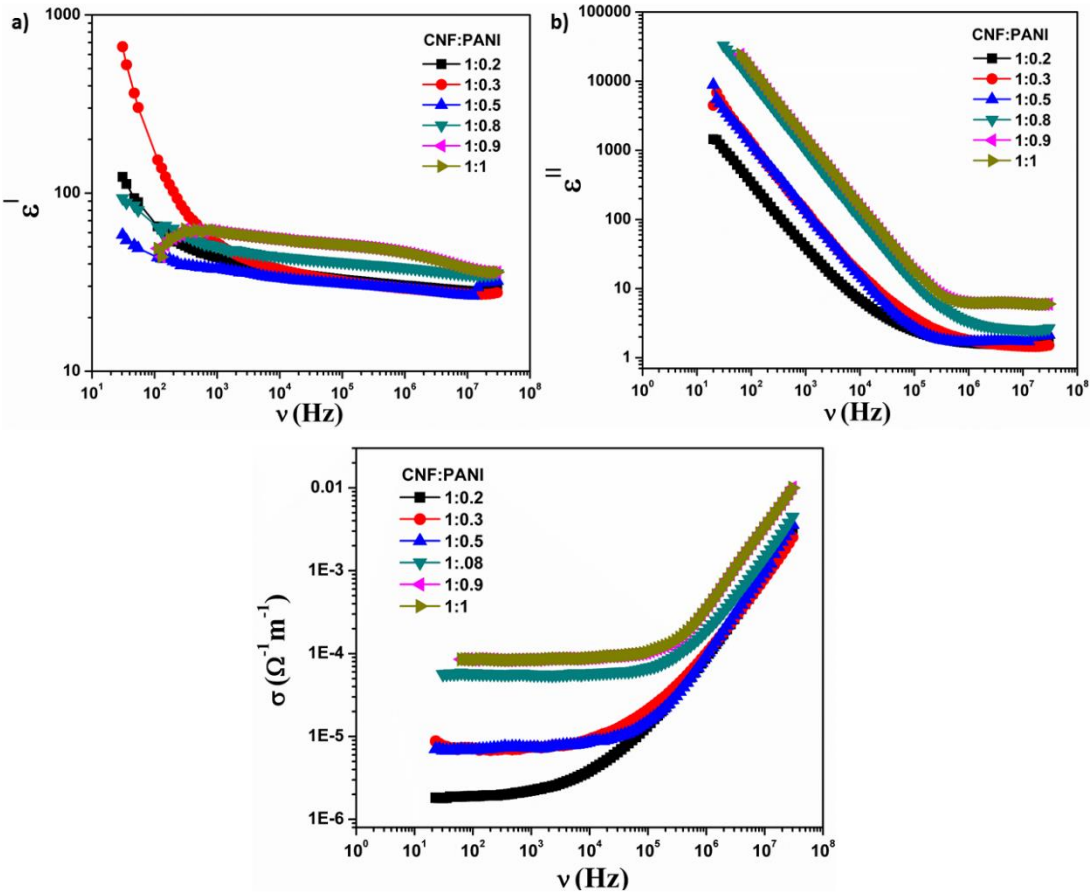

Figure 5.9: Frequency dependence of the (a) dielectric constant (ε^{1}) and (b) dielectric loss (ε^{11}) and (c) ac conductivity of PANI/CNF papers with varying PANI ratios.

According to Maxwell's equations [21], a material's response to electromagnetic radiation is determined by the following parameters; electrical conductivity (σ), electrical permittivity (ε) and magnetic permeability (μ). The real part of permittivity representing the stored energy between the material and the fields while the imaginary parts indicate the dissipated energy. Materials with high dielectric constant can store a substantial amount of electric charge. A material with high dielectric constant and dielectric loss values would show high electromagnetic shielding effectiveness [22]. In the case of polymer nanocomposites, the dielectric constant mainly arises from matrix filler incongruity. Maxwell-Wagner-Sillars (MWS) theory declares that this mismatch results the interfacial polarization at the interface. Frequency dependent dielectric constant and loss factor of PANI/CNF papers with varying PANI ratios are shown in figure 5.9. The dielectric constant of all PANI/CNF papers **(**Figure 5.9a) decreases with increase in frequency. In the case of conducting polymer composites, the frequency dependency is related to the dissipation of charge at the filler-matrix interface. The material's inherent properties are mainly reflected at the higher frequency regions than surface issues related lower frequency region [23]. As shown in figure 5.9a, PANI/CNF (1:1) composite paper shows the maximum ε^1 value compared to other compositions. At 30 MHz, PANI/CNF (1:0.2) composite paper displayed ε' value of about 28 whereas PANI/CNF (1:1) composite paper showed ε' value of 36. This enhancement may be attributed to the decrease in the gap between fillers due to the high filler loading and because of the higher charge accumulation at MWS interface of PANI/CNF (1:1) paper. Figure 5.9b shows that the imaginary permittivity, ε^{11}, increases with increase in PANI loading. Generally, in the case of nanocomposites, the conductive

nanofiller networks acts as charge carriers and increase of these conductive networks results nanocomposites higher loss factor. As expected, PANI/CNF (1:1) paper display higher value of imaginary permittivity with a ε^{11} value of 5.9 at 30 MHz.

The ac electrical conductivity, which is directly related to the loss factor (ε'') is given by the following equation.

$$\sigma_{AC} = 2\,\pi f \varepsilon_0 \varepsilon''$$

Where f is the frequency in Hz and ε_0 is the permittivity of free space ($\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m). As shown in figure 5.9c, σ_{AC} increases with increase in frequency and PANI content. Contrast to DC electrical conductivity, AC conductivity arises from the charge accumulation and interfacial polarization. Significant amount of free charges present in the PANI/CNF (1:1) paper than lower PANI contents donates to the conductivity by hopping mechanism [24]. This may lead to the formation of conducting network among PANI chains. At 30 MHz, PANI/CNF (1:1) composite paper shows σ_{AC} value of 0.009S/m.

Since the frequency of interest for the cellulose nanopapers was mostly X band region, the dielectric response of the CNF/PANI papers was also studied at 10 GHz and 15 GHz respectively. The dielectric properties of PANI/CNF (1:1) composite paper was further evaluated at higher frequencies of 10 GHz and 15 GHz (fig 5.10). The ε' value (1.66 for 10 GHz and 1.26 for 15 GHz) shows the same decreasing trend with respect to frequency dispersion whereas ε'' value (0.47 for 10 GHz and 0.58 for 15 GHz) increases with respect to frequency. At the highest frequency of

electromagnetic waves, the dipoles cannot follow the field variations. This will decrease the permittivity because of the decreased charge accumulation.

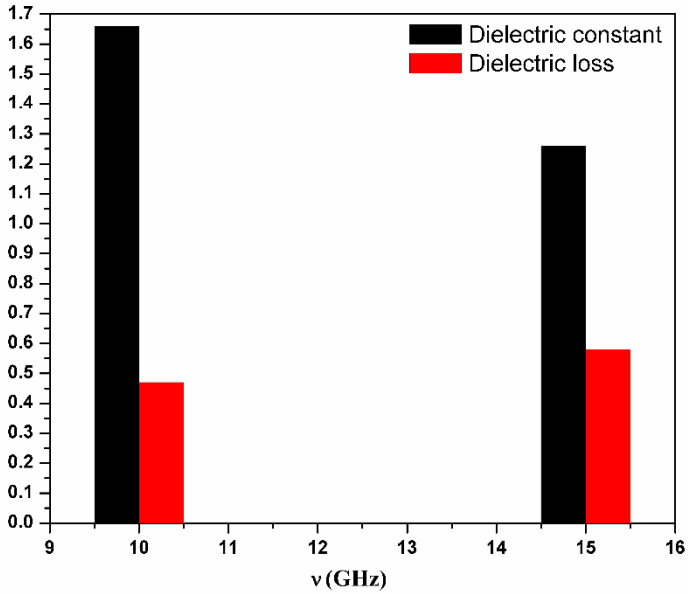

Figure 5.10: Dielectric properties of CNF: PANI (1:1) flexible paper at a frequency of 10 GHz and 15 GHz.

The CNF/PANI paper has showed good permittivity values even in the high frequency region of 15 GHz which makes it an ideal candidate for shielding EM waves at X band region.

5.4 Conclusion:

We reported herein a facile approach for the fabrication of highly processable PANI/CNF suspensions containing various aniline ratios. The PANI/CNF flexible composite papers exhibited high DC conductivity value of 3.14×10^{-1} S/cm with a PANI: CNF ratio of 1:1. It was clearly evident from the SEM images that *in-situ* polymerization of PANI has formed a continuous network on the surface of the cellulose nanofibers. This formation of continuous network was attributed to the

secondary forces of interaction via hydrogen bonding which was confirmed from FTIR studies. From dielectric studies, it was clearly shown that the PANI/CNF (1:1) composite paper shows the maximum ε^{1} value compared to other compositions. At 30 MHz, PANI/CNF (0.2:1) composite paper displayed ε' value of about 28 whereas PANI/CNF (1:1) composite paper showed ε' value of 36. Moreover PANI/CNF (1:1) paper display higher value of imaginary permittivity with a ε^{11} value of 5.9 at 30 MHz.

5.5 References:

1) Brédas, J. L., B. Thémans, J. G. Fripiat, J. M. André, and R. R. Chance. "Highly conducting polyparaphenylene, polypyrrole, and polythiophene chains: An ab initio study of the geometry and electronic-structure modifications upon doping." *Physical Review B* 29, no. 12 (1984): 6761.

2) MacDiarmid, A. G., J. C. Chiang, A. F. Richter, and and AJ Epstein. "Polyaniline: a new concept in conducting polymers." *Synthetic Metals* 18, no. 1-3 (1987): 285-290.

3) Prakash, T. P., and DINESH CHANDRA Trivedi. "Electrochemical modification of electrode by O-phenelynediamine." *Bulletin of Electrochemistry* 4, no. 06 (1988): 587-592.

4) Dhawan, S. K., and D. C. Trivedi. "Preparation of conductive polyaniline solutions for electronic applications." *Bulletin of Materials Science* 12, no. 2 (1989): 153-157.

5) Nyström, Gustav, Aamir Razaq, Maria Strømme, Leif Nyholm, and Albert Mihranyan. "Ultrafast all-polymer paper-based batteries." *Nano letters* 9, no. 10 (2009): 3635-3639.

6) Kim, Jaehwan, Sungryul Yun, Suresha K. Mahadeva, Kiju Yun, Sang Yeol Yang, and Mohammad Maniruzzaman. "Paper actuators made with cellulose and hybrid materials." *Sensors* 10, no. 3 (2010): 1473-1485.

7) Kim, Jaehwan, Sungryul Yun, and Sun-Kon Lee. "Cellulose smart material: possibility and challenges." *Journal of Intelligent Material Systems and Structures* 19, no. 3 (2008): 417-422.

8) Nyholm, Leif, Gustav Nyström, Albert Mihranyan, and Maria Strømme. "Toward flexible polymer and paper-based energy storage devices." *Advanced Materials* 23, no. 33 (2011): 3751-3769.

9) Luong, Nguyen Dang, Juuso T. Korhonen, Antti J. Soininen, Janne Ruokolainen, Leena-Sisko Johansson, and Jukka Seppälä. "Processable polyaniline suspensions through in situ polymerization onto nanocellulose." *European Polymer Journal* 49, no. 2 (2013): 335-344.

10) Auad, María L., Tara Richardson, William J. Orts, Eliton S. Medeiros, Luiz HC Mattoso, Mirna A. Mosiewicki, Norma E. Marcovich, and Mirta I. Aranguren. "Polyaniline-modified cellulose nanofibrils as reinforcement of a smart polyurethane." *Polymer International* 60, no. 5 (2011): 743-750.

11) Yu, Haipeng, Peng Chen, Wenshuai Chen, and Yixing Liu. "Effect of cellulose nanofibers on induced polymerization of aniline and formation of nanostructured conducting composite." *Cellulose* 21, no. 3 (2014): 1757-1767.

12) Hu, Weili, Shiyan Chen, Zhenhua Yang, Luting Liu, and Huaping Wang. "Flexible electrically conductive nanocomposite membrane based on bacterial cellulose and polyaniline." *The Journal of physical chemistry B* 115, no. 26 (2011): 8453-8457.

13) Liu, Dongyan Y., G. X. Sui, and Debes Bhattacharyya. "Synthesis and characterisation of nanocellulose-based polyaniline conducting films." *Composites Science and Technology* 99 (2014): 31-36.

14) Gopakumar, Deepu A., Daniel Pasquini, Mariana Alves Henrique, Luis Carlos de Morais, Yves Grohens, and Sabu Thomas. "Meldrum's acid modified

cellulose nanofiber-based polyvinylidene fluoride microfiltration membrane for dye water treatment and nanoparticle removal." *ACS Sustainable Chemistry & Engineering* 5, no. 2 (2017): 2026-2033.

15) Zhang, Lixia, Lijuan Zhang, Meixiang Wan, and Yen Wei. "Polyaniline micro/nanofibers doped with saturation fatty acids." *Synthetic metals* 156, no. 5 (2006): 454-458.

16) Zheng, W., M. Angelopoulos, Arthur Joseph Epstein, and A. G. MacDiarmid. "Experimental evidence for hydrogen bonding in polyaniline: mechanism of aggregate formation and dependency on oxidation state." *Macromolecules* 30, no. 10 (1997): 2953-2955.

17) French, Alfred D. "Idealized powder diffraction patterns for cellulose polymorphs." *Cellulose* 21, no. 2 (2014): 885-896.

18) Abdiryim, Tursun, Zhang Xiao-Gang, and Ruxangul Jamal. "Comparative studies of solid-state synthesized polyaniline doped with inorganic acids." *Materials Chemistry and Physics* 90, no. 2 (2005): 367-372.

19) Al-Saleh, Mohammed H., and Uttandaraman Sundararaj. "A review of vapor grown carbon nanofiber/polymer conductive composites." *Carbon* 47, no. 1 (2009): 2-22.

20) Sahoo, Nanda Gopal, Sravendra Rana, Jae Whan Cho, Lin Li, and Siew Hwa Chan. "Polymer nanocomposites based on functionalized carbon nanotubes." *Progress in polymer science* 35, no. 7 (2010): 837-867.

21) Huang, Yi, Ning Li, Yanfeng Ma, Feng Du, Feifei Li, Xiaobo He, Xiao Lin, Hongjun Gao, and Yongsheng Chen. "The influence of single-walled carbon nanotube structure on the electromagnetic interference shielding efficiency of its epoxy composites." *Carbon* 45, no. 8 (2007): 1614-1621.

22) Chen, Lin-Feng, C. K. Ong, C. P. Neo, V. V. Varadan, and Vijay K. Varadan. *Microwave electronics: measurement and materials characterization*. John Wiley & Sons, 2004.

23) Beeran, Yasir, Vid Bobnar, Selestina Gorgieva, Yves Grohens, Matjaž Finšgar, Sabu Thomas, and Vanja Kokol. "Mechanically strong, flexible and thermally stable graphene oxide/nanocellulosic films with enhanced dielectric properties." *Rsc Advances* 6, no. 54 (2016): 49138-49149.

24) McQueen, Douglas H., Karl-Michael Jäger, and Michaela Pelíšková. "Multiple threshold percolation in polymer/filler composites." *Journal of Physics D: Applied Physics* 37, no. 15 (2004): 2160.

Chapter 6

Electromagnetic Wave Attenuation Performance of PANI/CNF Nano Papers

6.1 Introduction

In our modern society the electromagnetic shielding of devices functioning in radio frequency band remains to be a severe concern. For the safety of the sensitive circuits, light weight EMI shielding materials are required to shield the workspace from radiations transmitted out from computers and telecommunication equipment. Electromagnetic waves from the sensitive electronic equipment's are reflected or absorbed by the human body. Thus misdirected radiations emitted out from the electronic devices may have an adverse effect on human health [1]. Light weight, flexible polymer nanocomposite materials have been a key interest for EMI shielding and microwave absorption due to many advantages over traditionally used metal sheets [2-4]. Conducting polymers such as polyaniline (PANI), polypyrole (PPY) and polyacetylene (PA) are popular for EMI shielding. Among them, PANI has gained considerable interest due to the controllable electrical conductivity via simple protonation/deprotonation process, good environmental stability [5]. Thus various applications like sensors, biomedical devices, opto-electronics, electro chromic devices and fuel cells, PANI has been explored [6-11]. Furthermore, PANI possess a fascinating electromagnetic interference shielding mechanism by

absorption, leading as a tremendous material especially for military purposes [5]. PANI occurs in various forms and the particular forms find diverse specific technological applications. Leucoemeraldine is the completely reduced form of PANI, which has been used in electro chromic devices. Emeraldine is the insulating form of the PANI, which is the 50% reduced and 50% oxidized form of polyaniline. This emeraldine form has been used in sensors for HCl gas. The doping of the emeraldine form results in the conducting PANI, which has been used in various applications like sensors, EMI shielding and electro chromic devices. Unlike other conducting polymers like polypyrrole, polythiophene and polyfuran, the hetro atoms in the PANI contributes to π-bond formation thereby become conducting. This makes PANI as a unique conductive polymer among the conductive polymers [12].

However, the existence of the conjugated system in PANI enhances the rigidity of the polymer molecule, resulting in poor film-forming capability. This is due to the fact that the ability of such polymers to form H bonds is very low, so thereby it is difficult to form films by casting and drying from such dispersions. To fix this issue, extensive work has been done in recent years to fabricate various PANI composites by blending diverse polymers with excellent mechanical properties and process ability. A variety of polymeric materials with excellent physical properties have been used as good supports for PANI, such as cellulose, rubbers, plastics, and textiles [13-16]. Among them, cellulose nanofibers as abundant renewable eco-friendly materials have drawn more and more attention [17, 18]. Cellulose nanofibers as a substrate have been proposed as a solution for this obstacle. Cellulose nanofiber based papers or cellulose nanofiber suspensions give adequate H-bonding that films may be easily produced from the mixture of conducting

polymers and cellulose nanofibers. By combining the cellulose nanofibers with PANI, the poor formability and frangibility of PANI can be alleviated to produce a conducting composite that is capable to shield electromagnetic radiations.

Cellulose nanopapers (CNPs) are a class of promising functional constructs which can be exploited for varying technological applications ranging from flexible optoelectronic devices [19-21] to nonwoven porous membranes for water purification [22-23] and as fire retarding gas barrier films [24-25]. Such applications are made possible due to superior mechanical properties, high aspect ratio, thermal stability and chemical resistance of nanocellulose fibers which can be sensibly fine-tuned as per the application. Electro Magnetic Interference (EMI) is a serious concern and need of the hour for present day electronics and telecommunication sector. Electro Magnetic (EM) pollution deteriorates the performance and life of electronic gadgets and also adversely affects the human health. Hence, research works are ongoing to develop novel flexible polymeric lightweight materials which can attenuate these unwanted radiations [26-28]. Conventionally, metals were used to shield EM waves but are highly undesirable due to their inherent drawbacks such as higher weights, corrosive nature and difficulty of processing into intricate shapes. Conductive cellulose nanopapers can offer a potential green feasible solution to this problem. Herein, we intent to make use of a series of conductive cellulose nanopapers fabricated via *in-situ* polymerization with polyaniline (PANI) to attenuate electromagnetic radiations specifically in a small bandwidth of the microwave frequency region (8.2 -12.4 GHz).To the best of our knowledge so far, this is the first report on PANI/CNF flexible nanopapers with an effective total

shielding effectiveness of >20 dB which makes it suitable for commercial device applications

6.2 EMI Shielding of the fabricated conductive PANI/CNF paper

The extent of attenuation of incident EM radiation is analysed by measuring the scattering parameters and thereby calculating total shielding effectiveness (SE_T) which is usually expressed as decibels (dB). As per the classical EMI shielding theories, the main criterion for effective microwave attenuation is high conductivity values preferably in the range of 10^{-1} S/m to 1 S/m [29]. However, along with high conductivity values, formation of a continuous network and presence of electrical dipoles in PANI/CNF also contributes to the total shielding effectiveness. It is well established that SE_{Total} is a summation of three different shielding mechanisms i.e shielding by absorption (SE_A), shielding by reflection (SE_R) and shielding due to multiple reflections (SE_{MR}).

$$SE_{Total}(dB) = SE_A + SE_R + SE_{MR} \quad (1)$$

It is also well known that SE_{MR} can be neglected if the absorption component is ≥10 dB or the shield thickness is greater than the skin depth of the samples where the multiple reflections can be neglected because the reflected wave from the internal surface will be absorbed by the shield [4]. Then, the total shielding effectiveness can be re-expressed as equation (2).

$$SE_{Total}(dB) = SE_A + SE_R \quad (2)$$

The total shielding effectiveness, shielding due to absorption and shielding due to reflection can also be expressed in terms of scattering parameters as given in equations (3),(4) & (5).

$$SE_{Total}(\text{dB}) = 10\log\frac{1}{|S_{21}|^2} = 10log\frac{1}{|S_{12}|^2} \quad (3)$$

$$SE_A = 10\log_{10}\left[\frac{(1-S_{11})^2}{{S_{12}}^2}\right] \quad (4)$$

$$SE_R = 10\log_{10}\left[\frac{1}{(1-S_{11})^2}\right] \quad (5)$$

Where, S_{21}& S_{12} are the forward transmission coefficient & reverse transmission coefficient respectively, S_{11} is the forward reflection coefficient were obtained from the vector network analyser (VNA). The SE $_{Total}$ values of the PANI/CNF nanopapers of varying thickness were measured by placing a 30 mm* 30 mm samples inside a waveguide and measurements were taken after calibrating the VNA.

The variation of total shielding effectiveness and the corresponding shielding by absorption and reflection components of the fabricated PANI/CNF papers in X band (8.2-12.4 GHz) is given in figures 6.1& 6.2. A total SEvalue of c.a -23 dB was observed for PANI/CNF paper at 1.00 mm thickness. In all the EMI measurements, CNF to PANI ratio was 1:1 as this composition has shown a maximum DC conductivity value of $3.14x10^{-1}$S/cm. However, it was also observed that as the PANI ratio was increased, nanopapers exhibited poor flexibility and were found to be brittle in nature. It is also evident that the effect of forming a continuous network of PANI on to the surface of cellulose nanofibers has played a pivotal role in enhancing the electrical conductivity and attenuating electromagnetic radiations. Nevertheless, the secondary interactions such as the inter molecular hydrogen bonding between hydroxyl groups of the nanocellulose and the nitrogen of the PANI has been attributed as the key factor for achieving >99% attenuation even at a very low thickness of 1.0 mm. The basic mechanism of EM wave attenuation of PANI is

by absorption mechanism but because of its poor film forming characteristics its application as EM shields is very limited. Thus the combined effects of cellulose nanofibers and PANI has resulted in formation of flexible and robust nanopapers which could be used as EM shields inside electronic devices such as terrestrial communication systems, aerospace communications & radar which operates mostly in X band frequencies. From figure 6.3, it is clearly shown that the PANI/CNF composite paper exhibited a predominant attenuation of microwave radiation by absorption mechanism. The flexible PANI/CNF composite papers demonstrated an attenuation of 87% by absorption and 13 % by reflection mechanism at 8.2 GHz, which is highly desirable as it prevents any further electromagnetic pollution and provides a noise free workspace. A cartoon illustrating the plausible shielding mechanisms of the fabricated PANI/CNF nanopapers is illustrated in figure 6.4. The incident EM waves are simultaneously reflected and absorbed by PANI/CNF nanopapers with an enhanced shielding by absorption mechanism in X band region.

There are only few reports on the use of cellulose nanofibers in combination with conducting polymers for use as EMI shielding materials. Marins et al. made use of bacterial cellulose (BC) membranes *in-situ* polymerised with aniline monomer to form a coating of PANI on the surface of BC membranes. The overall shielding effectiveness of such membranes was found to be -5 dB (nearly 63.38% attenuation) at a thickness of about 0.080 mm in X band region. In contrary, we were able to achieve c.a -23 dB (nearly 99% attenuation) at 1.0 mm thickness in X band region, which is considered to be a suitable value for commercial device applications. Table 6.1, manifests some of the works reported on cellulosic based EMI shielding materials and their corresponding shielding effectiveness, thickness and operating

frequency of the shields. . It is also evident from this data that achieving >20 dB shielding effectiveness in cellulosic substrates is quite a remarkable value which makes the fabricated PANI/CNF nanopapers as commercially viable shields.

Table 6.1: Shielding effectiveness data for some cellulosic based nanocomposites for EMI Shielding application.

SI No	Polymer/filler combination	SE_{Total} (dB)	Thickness (mm)	Frequency	References
1	Cellulose/CNT composite paper	-20	0.45	15-40 GHz	[30]
2	Bacterial cellulose/PANI membrane	-5	0.080	8.2-12.4 GHz	[31]
3	Cellulose/CNT aerogel	-20	2.5	8.2-12.4 GHz	[32]
4	Cellulose/CNT aerogel	-19.4	-	8.2-12.4 GHz	[33]
5	CNF/PANI paper	-16.3	0.75	8.2-12.4 GHz	(This work)
6	CNF/PANI paper	-23	1.0	8.2-12.4 GHz	(This work)

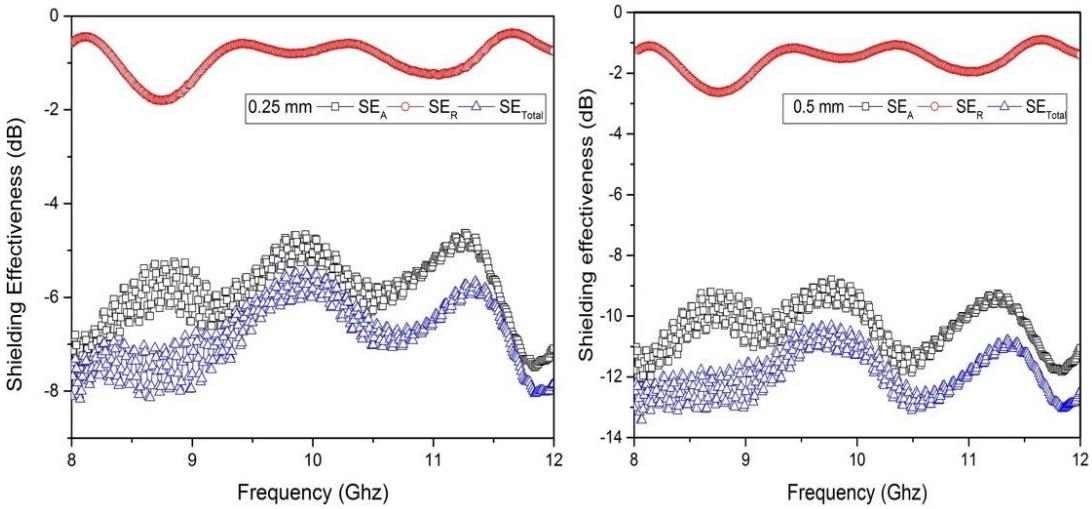

Figure 6.1: EMI shielding effectiveness of PANI/CNF flexible paper at (a) 0.25 mm & (b) 0.50 mm thickness in X band (8.2 -12 GHz)

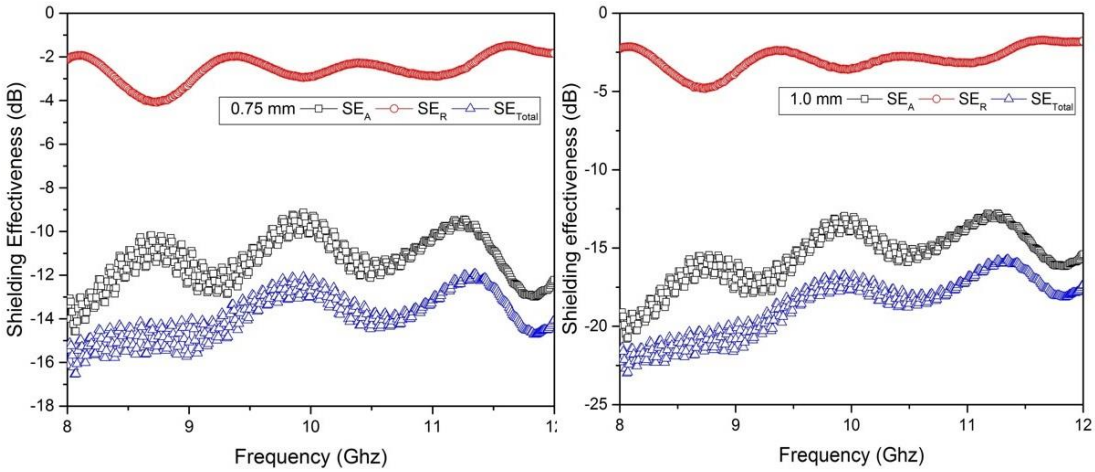

Figure 6.2: : EMI shielding effectiveness of PANI/CNF flexible paper at (a) 0.75 mm & (b) 1.0 mm thickness in X band (8.2 -12 GHz)

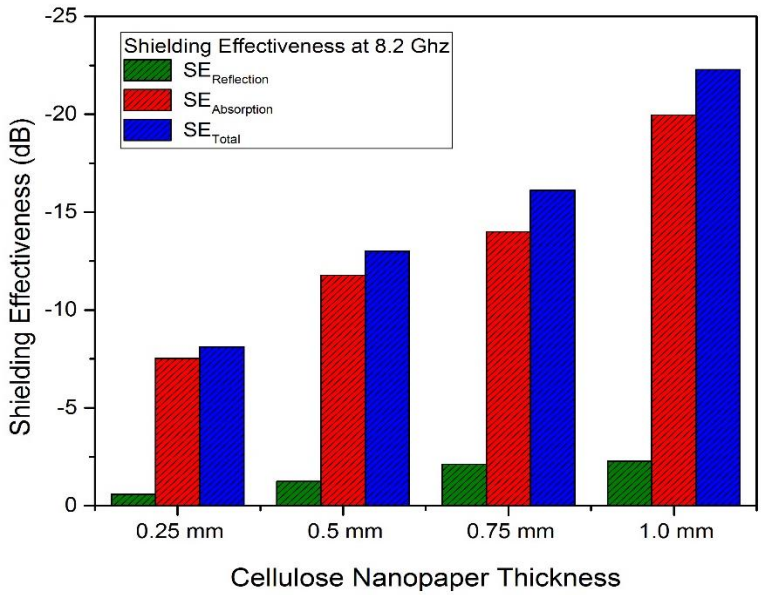

Figure 6.3: Shielding Effectiveness (SE_T, SE_A, SE_R) of fabricated PANI/CNF nanopapers of varying thickness at 8.2 GHz.

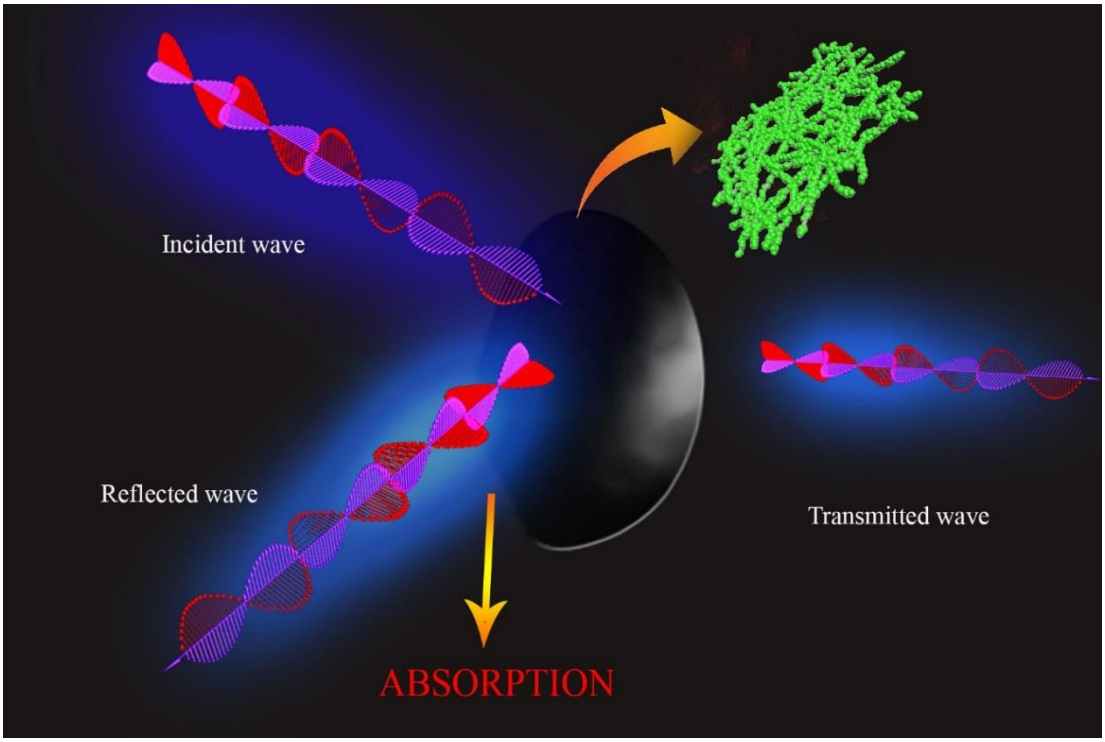

Figure 6.4: Schematic illustration of EMI shielding interference of demonstrated PANI/CNF flexible paper.

6.3 Conclusion

Nevertheless, the PANI coating on the cellulose nanofibers is of paramount importance in attenuating the incident EM waves. The total shielding effectiveness of the composite nanopapers was found to be -16.3 dB and -23 dB at 0.75 mm and 1.0 mm paper thickness respectively at 8.2 GHz. The attenuation of EM waves was governed by a predominant absorption mechanism (c.a 97%) and very less reflection mechanism (c.a 13%). Such nanopapers have given a new arena for designing green microwave attenuators which can shield the incoming radiation by absorption dominated mechanism. Additionally, the demonstrated PANI/CNF flexible paper can be potentially used as material for plethora of applications such as flexible electrodes, sensors, electrically conductive and flexible films and other flexible

paper based devices. The EMI shielding measurements of the demonstrated paper confirmed that, the PANI/CNF flexible composite paper was a good promising candidate for attenuating electromagnetic radiations. We firmly believe that, this study will be an effective platform for developing green microwave attenuators in future.

6.4 References

1. Shen, Bin, Wentao Zhai, Mimi Tao, Jianqiang Ling, and Wenge Zheng. "Lightweight, multifunctional polyetherimide/graphene@ Fe3O4 composite foams for shielding of electromagnetic pollution." *ACS applied materials & interfaces* 5, no. 21 (2013): 11383-11391.

2. Arjmand, Mohammad, Aref Abbasi Moud, Yan Li, and Uttandaraman Sundararaj. "Outstanding electromagnetic interference shielding of silver nanowires: comparison with carbon nanotubes." *RSC Advances* 5, no. 70 (2015): 56590-56598.

3. Zhang, Yi, Zhou Wang, Boliang Zhang, Guang-Lin Zhao, and S. M. Guo. "The electromagnetic interference shielding effectiveness of high aspect-ratio SiC nanofibers/epoxy composites." *RSC Advances* 5, no. 113 (2015): 93499-93506.

4. Al-Saleh, Mohammed H., and Uttandaraman Sundararaj. "Electromagnetic interference shielding mechanisms of CNT/polymer composites." *Carbon* 47, no. 7 (2009): 1738-1746.

5. Bhadra, Sambhu, Dipak Khastgir, Nikhil K. Singha, and Joong Hee Lee. "Progress in preparation, processing and applications of polyaniline." *Progress in Polymer Science* 34, no. 8 (2009): 783-810.

6. Guimard, Nathalie K., Natalia Gomez, and Christine E. Schmidt. "Conducting polymers in biomedical engineering." *Progress in Polymer Science* 32, no. 8 (2007): 876-921.

7. Bai, Hua, Qi Chen, Chun Li, Chanhui Lu, and Gaoquan Shi. "Electrosynthesis of polypyrrole/sulfonated polyaniline composite films and their applications for ammonia gas sensing." *Polymer* 48, no. 14 (2007): 4015-4020.

8. Hong, Siang-Fu, Shou-Chia Hwang, and Lin-Chi Chen. "Deposition-order-dependent polyelectrochromic and redox behaviors of the polyaniline–prussian blue bilayer." *Electrochimica Acta* 53, no. 21 (2008): 6215-6227.

9. Amrithesh, M., S. Aravind, S. Jayalekshmi, and R. S. Jayasree. "Enhanced luminescence observed in polyaniline–polymethylmethacrylate composites." *Journal of Alloys and Compounds* 449, no. 1 (2008): 176-179.

10. Prabhakar, Nirmal, Kavita Arora, Harpal Singh, and Bansi D. Malhotra. "Polyaniline based nucleic acid sensor." *The Journal of Physical Chemistry B* 112, no. 15 (2008): 4808-4816.

11. Lange, Ulrich, Nataliya V. Roznyatovskaya, and Vladimir M. Mirsky. "Conducting polymers in chemical sensors and arrays." *Analytica chimica acta* 614, no. 1 (2008): 1-26.

12. Dhawan, S. K., N. Singh, and D. Rodrigues. "Electromagnetic shielding behaviour of conducting polyaniline composites." *Science and Technology of Advanced Materials* 4, no. 2 (2003): 105-113.

13. Cerqueira, Daniel A., Artur JM Valente, R. Guimes Filho, and Hugh D. Burrows. "Synthesis and properties of polyaniline–cellulose acetate blends: the use of sugarcane bagasse waste and the effect of the substitution degree." *Carbohydrate polymers* 78, no. 3 (2009): 402-408.

14. Chandran, A. Saritha, and Sunil K. Narayanankutty. "An elastomeric conducting composite based on polyaniline coated nylon fiber and chloroprene rubber." *European Polymer Journal* 44, no. 7 (2008): 2418-2429.

15. Lakshmi, K., Honey John, K. T. Mathew, Rani Joseph, and K. E. George. "Microwave absorption, reflection and EMI shielding of PU–PANI composite." *Acta Materialia* 57, no. 2 (2009): 371-375.

16. Jeevananda, T. "Synthesis and characterization of polyaniline filled PU/PMMA interpenetrating polymer networks." *European Polymer Journal* 39, no. 3 (2003): 569-578.

17. Qaiser, Asif A., Margaret M. Hyland, and Darrell A. Patterson. "Surface and charge transport characterization of polyaniline− cellulose acetate composite membranes." *The Journal of Physical Chemistry B* 115, no. 7 (2011): 1652-1661.

18. Cerqueira, Daniel A., Artur JM Valente, R. Guimes Filho, and Hugh D. Burrows. "Synthesis and properties of polyaniline–cellulose acetate blends: the use of sugarcane bagasse waste and the effect of the substitution degree." *Carbohydrate polymers* 78, no. 3 (2009): 402-408.

19. Erlantz Lizundia, Marc Delgado-Aguilar, Pere Mutje´, Eduardo Ferna´ndez . Beatriz Robles-Hernandez, Marı´a Rosario de la Fuente, Jose´ Luis Vilas, Luis M. Leo´n *Cellulose* (2016) 23:1997–2010.

20. Yagyu, Hitomi, Tsuguyuki Saito, Akira Isogai, Hirotaka Koga, and Masaya Nogi. "Chemical modification of cellulose nanofibers for the production of

highly thermal resistant and optically transparent nanopaper for paper devices." *ACS applied materials & interfaces* 7, no. 39 (2015): 22012-22017.

21. Hsieh, Ming-Chun, Changjae Kim, Masaya Nogi, and Katsuaki Suganuma. "Electrically conductive lines on cellulose nanopaper for flexible electrical devices." *Nanoscale* 5, no. 19 (2013): 9289-9295.

22. Mautner, Andreas, Koon-Yang Lee, Tekla Tammelin, Aji P. Mathew, Alisyn J. Nedoma, Kang Li, and Alexander Bismarck. "Cellulose nanopapers as tight aqueous ultra-filtration membranes." *Reactive and Functional Polymers* 86 (2015): 209-214.

23. Sehaqui, Houssine, Seira Morimune, Takashi Nishino, and Lars A. Berglund. "Stretchable and strong cellulose nanopaper structures based on polymer-coated nanofiber networks: An alternative to nonwoven porous membranes from electrospinning." *Biomacromolecules* 13, no. 11 (2012): 3661-3667.

24. Liu, Andong, Andreas Walther, Olli Ikkala, Lyuba Belova, and Lars A. Berglund. "Clay nanopaper with tough cellulose nanofiber matrix for fire retardancy and gas barrier functions." *Biomacromolecules* 12, no. 3 (2011): 633-641.

25. Nair, Sandeep S., J. Y. Zhu, Yulin Deng, and Arthur J. Ragauskas. "High performance green barriers based on nanocellulose." *Sustainable Chemical Processes* 2, no. 1 (2014): 23.

26. Ling, Jianqiang, Wentao Zhai, Weiwei Feng, Bin Shen, Jianfeng Zhang, and Wen ge Zheng. "Facile preparation of lightweight microcellular polyetherimide/

graphene composite foams for electromagnetic interference shielding." *ACS applied materials & interfaces* 5, no. 7 (2013): 2677-2684.

27. Song, Wei-Li, Xiao-Tian Guan, Li-Zhen Fan, Wen-Qiang Cao, Chan-Yuan Wang, Quan-Liang Zhao, and Mao-Sheng Cao. "Magnetic and conductive graphene papers toward thin layers of effective electromagnetic shielding." *Journal of Materials Chemistry A* 3, no. 5 (2015): 2097-2107.

28. Shen, Bin, Wentao Zhai, Mimi Tao, Jianqiang Ling, and Wenge Zheng. "Lightweight, multifunctional polyetherimide/graphene@ Fe3O4 composite foams for shielding of electromagnetic pollution." *ACS applied materials & interfaces* 5, no. 21 (2013): 11383-11391.

29. Dhakate, Sanjay R., Kiran M. Subhedar, and Bhanu Pratap Singh. "Polymer nanocomposite foam filled with carbon nanomaterials as an efficient electromagnetic interference shielding material." *Rsc Advances* 5, no. 54 (2015): 43036-43057

30. Fugetsu, Bunshi, Eiichi Sano, Masaki Sunada, Yuzuru Sambongi, Takao Shibuya, Xiaoshui Wang, and Toshiaki Hiraki. "Electrical conductivity and electromagnetic interference shielding efficiency of carbon nanotube/cellulose composite paper." *Carbon* 46, no. 9 (2008): 1256-1258.

31. Marins, Jéssica A., Bluma G. Soares, Mayra Fraga, Daliana Müller, and Guilherme MO Barra. "Self-supported bacterial cellulose polyaniline conducting membrane as electromagnetic interference shielding material: effect of the oxidizing agent." *Cellulose* 21, no. 3 (2014): 1409-1418.

32. Huang, Hua-Dong, Chun-Yan Liu, Dong Zhou, Xin Jiang, Gan-Ji Zhong, Ding-Xiang Yan, and Zhong-Ming Li. "Cellulose composite aerogel for highly efficient electromagnetic interference shielding." *Journal of Materials Chemistry A* 3, no. 9 (2015): 4983-4991.

33. Jian, L. I., and W. A. N. Caichao. "Cellulose aerogels decorated with multi-walled carbon nanotubes: preparation, characterization, and application for electromagnetic interference shielding." *Frontiers of Agricultural Science and Engineering* 2, no. 4 (2016): 341-346.

Chapter 7

Conclusions and Perspectives

This thesis investigates the applicability of cellulose nanofibers in water purification and EMI shielding. Due to environment and sustainability problems, this century has witnessed remarkable achievements in green technology through the development of eco-friendly bio-composites. Bio-composites are most suitable materials profound in nature for their use in various fields due to their eco-friendly advantages. It is known that recently there has been a substantial interest in the industrial applications of containing bio-fibre. For environmental awareness and the international demand for green technology, bio-nanocomposites have the huge potential to replace present petrochemical based materials. The beneficial engineering properties of bio-fibers are specific strength, low density, high toughness, and good thermal properties as compared to most of the synthetic polymers, reduced tool wear, respiratory irritation and ease of processing. Bio-fibers find many applications in bio medical, food packaging, geotextile, architecture, composites and automotive transportation and general system.

Among the bio-fibers cellulose is the most prevalent natural polymer and has greatly impacted the world and society in broad reaching areas. It was only within the last century that advanced processing and analytical instrumentation allowed

researchers to discover the nanoscale cellulose structures that exhibit extraordinary properties. These cellulose nanostructures are naturally ranging from a few nanometres to microns with excellent mechanical properties. Cellulose nanomaterial's inherent fibrous nature and remarkable mechanical properties combined with low cost, biocompatibility and sustainable source, suggest huge potential as a component in water filtration membranes and green microwave attenuators in future.

In the present study, cellulose nanofibers were successfully isolated from renewable, abundant and low-cost natural source, sunflower stalks by steam explosion coupled with mild acid hydrolysis. This technique comprises of alkaline treatment, bleaching, acidic steam treatment and homogenization. Morphological investigation was performed using transmission electron microscopy (TEM). Comparing the results with other reports, one can conclude that the nature and concentration of acid is of high importance with regard to the morphology of the resulting nanofibers. The first chapter is an updated survey of literature covering the field of cellulose nanofibers, various extraction techniques and its surface modifications. This chapter also describes the applicability of cellulose nanofibers in water purification membranes and electromagnetic interference systems. At the end of this chapter the main objectives are explained. The material details, experimental techniques and characterization methods employed in this study are presented in the second chapter.

The third chapter explains about the surface modification of the extracted cellulose nanofibers via non-solvent assisted method using Meldrum's acid. From literature survey regarding the surface modification of cellulose nanofibers, one can concluded that the most of the surface modifications of cellulose nanofibers were

done using toxic organic solvents. In this context, we intended to produce a unique adsorbent material from cellulose nanofibers (CNFs) via non-solvent assisted method using Meldrum's acid as an esterification agent. To the extent of our knowledge, preparation of new green based surface modification of cellulose nanofibers (CNFs) via non-solvent assisted procedure using Meldrum's acid as esterification agent has not been addressed till date. This finding offers a new platform for the surface treatment of cellulose nanofibers using solvent free green technology. Techniques such as FTIR, XRD and conductimetic titration method have been employed for the characterization of these Meldrum's acid modified cellulose nanofibers. From the FTIR spectra of the CNFs and Meldrum's acid modified CNFs, it can be concluded that the esterification reaction between Meldrum's acid and cellulose nanofibers was successful. From the x-ray diffraction pattern, it was clearly shown that the Meldrum's acid modification has been affected mainly on the surface hydroxyl groups of cellulose nanofibers. From the conductimetic titration analysis of both CNFs and Meldrum's acid CNFs, it was found that the carboxylate content increased from 8.75 mmol/l00 g for CNF, to 71.35 mmol/100g for the Meldrum's acid modified CNF. The increased amount of carboxyl groups proves the effective esterification reaction of Meldrum's acid on the surface of the cellulose nanofibers.

The dye absorption studies and nanoparticle removal from water was carried out for the fabricated Meldrum's acid modified cellulose nanofiber based PVDF nanofibrous microfiltration membrane. Both CNF-based PVDF membranes (Meldrum's acid modified CNFs and CNF) were prepared by successive coating of modified and unmodified CNFs on to the surface of a PVDF electrospun membrane.

All the demonstrated membranes showed high filtration capacity against the Fe_2O_3 nanoparticles. With the 10 mg/L of crystal violet (CV) aqueous solution, CV adsorption of PVDF electrospun membrane, and unmodified CNF-based PVDF membrane was around 1.368 and 2.948 mg/g of the membrane respectively, whereas it was 3.984 mg/g of the membrane by Meldrum's acid CNF-based PVDF membrane. This results was comparable with the reported values in the existing literature. The demonstrated Meldrum's acid modified CNF based PVDF membrane was proven to be the efficient media that can concurrently eliminate the Fe_2O_3 nanoparticles and CV dyes from the water.

Cellulose has been recognized as good matrix/substrate for biodegradable batteries, sensors and actuators. Cellulose nanofiber based papers or cellulose nanofiber suspensions give adequate hydrogen bonding that films may be easily produced from the mixture of conducting polymers and cellulose nanofibers. In this context, in-situ polymerized polyaniline (PANI)/cellulose nanofibers (CNFs) nanopapers with different PANI ratios were fabricated by vacuum filtration method. HCl and ammonium persulfate (APS) were employed as dopant and oxidant respectively. The PANI/CNF flexible composite papers exhibited high DC conductivity value of 3.14×10^{-1} S/cm with a PANI: NFC ratio of 1:1. SEM images revealed that *in-situ* polymerization of PANI has formed a continuous network on the surface of the cellulose nanofibers. This formation of continuous network was attributed to the secondary forces of interaction via hydrogen bonding which was confirmed from FTIR studies. . At 30 MHz, PANI/CNF (1:0.2) composite paper displayed dielectric constant (ε**')** value of about 28 whereas PANI/CNF (1:1) composite paper showed ε'

value of 36. Moreover PANI/CNF (1:1) paper display higher value of imaginary permittivity with a dielectric loss (ε”) value of 5.9 at 30 MHz.

In the sixth chapter comprises of the electromagnetic wave attenuation performance of the fabricated PANI/CNF papers. The total shielding effectiveness of the composite nanopapers was found to be -16.3 dB and -23 dB at 0.75 mm and 1.0 mm paper thickness respectively at 8.2 GHz. The attenuation of EM waves was governed by a predominant absorption mechanism (c.a 97%) and very less reflection mechanism (c.a 13%). Such nanopapers have given a new arena for designing green microwave attenuators which can shield the incoming radiation by absorption dominated mechanism. Additionally, the demonstrated PANI/CNF flexible paper can be potentially used as material for plethora of applications such as flexible electrodes, sensors, and electrically conductive and flexible films and other flexible paper based devices. The EMI shielding measurements of the demonstrated paper confirmed that, the PANI/CNF flexible composite paper was a good promising candidate for attenuating electromagnetic radiations. We firmly believe that, this study will be an effective platform for developing green microwave attenuators in future.

As a future outlook for designing efficient filters based on fully eco-friendly materials like nanocellulose and its functionalized analogues will be a sustainable solution for water purification. In this work we proved that the membranes fabricated from PVDF and surface modified cellulose nanofibers will be a promising candidate for water purification. However these membranes cannot be commercialize at industrial scale. As a future step to commercialize these membranes we need to focus on fully green based cost effective membranes from cellulose by replacing high cost synthetic polymers. As an extension of the EMI

shielding performance, we need to focus on multi-layered approach of cellulose nanopapers in combination with decorated magnetic structures can be effectively used for designing high performance ultra-light weight electromagnetic shields. The multilayer architecture has a significant role in attenuating electromagnetic radiations. The impedance of air shield interface and interlayer interface can be finally tuned to facilitate enhanced absorption of electromagnetic waves. Fabrication of porous aerogel structures based on cellulose and conducting polymers is also a key area to work in future. The porous architecture has a pivotal role in attenuating electromagnetic radiations as the intensity of electromagnetic waves remarkably reduces due to the multiple scattering occurring within the porous network.

Publications

1) Gopakumar, Deepu A., Daniel Pasquini, Mariana Alves Henrique, Luis Carlos de Morais, Yves Grohens, and Sabu Thomas. "***Meldrum's acid modified cellulose nanofiber-based polyvinylidene fluoride microfiltration membrane for dye water treatment and nanoparticle removal.***" *ACS Sustainable Chemistry & Engineering* 5, no. 2 (2017): 2026-2033.

   http://pubs.acs.org/doi/abs/10.1021/acssuschemeng.6b02952

2) Fortunati, E., F. Luzi, A. Jiménez, D. A. Gopakumar, D. Puglia, S. Thomas, J. M. Kenny, A. Chiralt, and L. Torre. "***Revalorization of sunflower stalks as novel sources of cellulose nanofibrils and nanocrystals and their effect on wheat gluten bionanocomposite properties.***" *Carbohydrate polymers* 149 (2016): 357-368.

   http://www.sciencedirect.com/science/article/pii/S0144861716304970

3) Manna, Suvendu, Debasis Roy, Prosenjit Saha, Deepu Gopakumar, and Sabu Thomas. "***Rapid methylene blue adsorption using modified lignocellulosic materials***." *Process Safety and Environmental Protection* 107 (2017): 346-356.

   http://www.sciencedirect.com/science/article/pii/S0957582017300745

4) ***"Eucalyptus Derived Cellulose Nanofiber Based Polyaniline Flexible Papers for Attenuating Microwave Radiations via Absorption dominated mechanism in X Band".*** D. A. Gopakumar, A. R .Pai, Y.B.Pottathara, D. Pasquini, L.C.Morais, M.Luke, N.Kalarikkal, Y.Grohens, S.Thomas submitted to ACS Applied Materials and Interfaces; Manuscript ID: am-2017-111945.

Book Chapters:

1. D.A.Gopakumar, S.Thomas, Y. Grohens." ***Nanocelluloses as Innovative Polymers for Membrane Applications***" In book: Multifunctional Polymeric Nanocomposites Based on Cellulosic Reinforcements, Publisher: William Andrew, 2016.

2. Deepu A. Gopakumar, Suvendu Manna, Daniel Pasquini, Sabu Thomas, Yves Grohens. ***Nanocellulose: Extraction and application of cellulose nanofibers as a sustainable materials for waste water purification;*** In New Polymer Nanocomposites for Environmental Remediation, Elsevier Publishing, (Accepted, to be published in Dec, 2017).

3. Suvendu Manna, Deepu Gopakumar, Debasis Roy, Prosenjit Saha, Sabu Thomas. ***Nanobiomaterials for Removal of Fluoride and Chlorophenols from Water;*** In New Polymer Nanocomposites for Environmental Remediation, Elsevier Publishing, (Accepted, to be published in Dec, 2017).

4. Ajithkumar M. P., Jiji Abraham, Praveen K. M., D.A.Gopakumar., Sabu Thomas, ***Fiber reinforced composites: Macro to nanoscales;*** *Springer Handbook of Functional Polymers* (Accepted)

5. Blessy Joseph, Deepu A. Gopakumar Hanna Maria, Nandakumar Kalarikkal, Sabu Thomas; ***Nanocellulose for healthcare applications*** ; *Encyclopedia of Polymer Applications* (EPA), a multi-volume reference work to be published by the Taylor & Francis Group (Accepted)

6. Deepu A. Gopakumar, Sabu K.T, Sisanth K.S, Avinash R Pai, Sabu Thomas; ***Environmental Science and Engineering Applications of Nanocellulose ;***

Encyclopedia *of Polymer Applications* (EPA), a multi-volume reference work to be published by the Taylor & Francis Group (Accepted)

7. Deepu A Gopakumar, Yasir Beeran, Nandakumar Kalarikkal, Yves Grohens, SabuThomas; ***Development of value added products from natural fibre based composites*****";** *Encyclopedia of Polymer Applications* (EPA), a multi-volume reference work to be published by the Taylor & Francis Group (Accepted)

8. Deepu A. Gopakumar, Vishnu Arumukhan, Daniel Pasiquini, Ben leu, Sabu Thomas, Yves Grohens; ***Nanocellulose based membranes for water purification;*** In Book Nanoscale materials for water purification, to be published by Elsevier Ltd.

Books Edited

1) Deepu A.Gopakumar, Kaveh Hariri Asli, Soltan Ali OgliAliyev, Sabu Thomas, **"*Handbook of Research for Fluid and Solid mechanics: Theory, Simulation and Experiment"*** Publisher: Apple Academy, Canada. ISBN: 978-1771885010.

   https://www.crcpress.com/Handbook-of-Research-for-Fluid-and-Solid-Mechanics-Theory-Simulation/Asli-OgliAliyev-Thomas-Gopakumar/p/book/9781771885010

2) Deepu A. Gopakumar, Sabu Thomas, Daniel Pasquini, Shao-Yuan (Ben) Leu**,** ***"Nanoscale materials for water purification*****"** In press to be published by Elsevier.