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Synthesis of Cellulose Nanofibers from sugarcane bagasse and Iron Oxide Nanocubes, and their composite for Oil spill Remediation.

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Abstract

Every year number of oil spills occur due to various reasons and these spills adversely affects marine environment. It is very much essential to remove this oil from the aquatic environment at earliest. Currently various types of absorbents are used to remove oil from spillage. An effort has been made to synthesis oil absorbent nanomaterial from sugarcane bagasse. This paper briefly explains synthesis and characterization of the prepared material and results obtained. Cellulose nanofibers were prepared from the sugarcane bagasse using acid hydrolysis technique. Iron oxide nanocubes [α-Fe_2O_3] were synthesized by hydrothermal method. The nanocomposites were prepared by stirring and mixing of cellulose nanofiber with iron oxide nanocubes. The structure and morphology of the samples were studied using XRD and SEM, respectively. SEM images confirmed the growth of cellulose nanofibers with iron oxide nanocubes. The oil absorptivity of the cellulose nanofibers was studied.

Keywords:

Cellulose nanofibers;
Sugarcane bagasse;
Iron oxide nanocubes;
Nanocomposite;
Oil Spill remediation.

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1. Introduction

Large reserves of oil and gas are trapped deep beneath the Earth's surface. Seldom, they develop cracks and some of the oil or gas leaks out, which rarely causes any major damage as its part of the nature. In contrast, when the same problem is caused due to human interference it can cause damage to marine ecosystems. Oil spill occurs when any liquid petroleum is released into the environment, especially water bodies, by vehicle, drilling rigs, vessel or pipeline. It is one of the major forms of the water pollution. As oil floats on water, it prevents sunlight to pass through it. The shiny substance on top layer of water is oil which makes it difficult for plants and sea animals to survive. It is highly toxic and can cause massive loss of species living in the sea and birds as it penetrates into their furs [1][2].

Currently various types of absorbents are used to remove oil from spillage. An effort has been made to synthesis oil absorbent nanomaterial from agro-waste. Nanomaterials arebeing increasingly used in various sectors due to its unique, beneficial chemical, physical, and mechanical properties. Here, we have focused on cellulose nanofibers (CNF) and Iron oxide nanocubes, and its composite material. CNF has interesting properties such

as high tensile strength - 8 times that of steel, it can be produced from any cellulose source material such as sugarcane bagasse, coconut husk, cotton, banana leaf, etc. in large quantities in a cost-effective manner, its biocompatibility and can be easily surface modified, and most important its oil absorption and desorption property[3][4]. Iron oxide nanocubes has antimicrobial and super paramagnetic properties [5][6]. So far to our knowledge, there has been no literature reported on cellulose nanofibers and iron oxide nanocube composite. This makes our work as the first report using nanocomposites for oil spill remediation.

2. Experimental Procedure

The procedure for the synthesis of cellulose nanofibers, Iron Oxide nanocubes and their composite are given below.

2.1. Synthesis of cellulose nanofibers

The materials required to synthesize cellulose nanofiberswere sugarcane bagasse, Sodium Hydroxide, Sodium Chlorite, glacialacetic acid, nitric acid and concentrated sulphuric acid for pre-treatment and hydrolysis. Initially, the sugarcane bagasse is washed, chopped, dried and sieved. Secondly,Pre-treatment is done of the sugarcane bagasse for the removal of lignin and hemicelluloses,which is done by alkaline method and bleaching, followed by acid hydrolysis using sulphuricacid to obtain cellulose nanofibers [4].

2.1.1. Alkaline Treatment

Sodium hydroxide was used for the alkaline pre-treatment of cellulose nanofibers [7]. Thesieved bagasse were dispersed in distilled water and stirred for 2hrs, filtered andwas repeated once again. Later, the residue was dispersed in 2% sodium hydroxide andstirred for 2hrs at 80°C, followed by filtration using Whatmann filter paper and washed with thedistilled water. This procedure is repeated once more and the bagasse was dried at 50° C for24hrs.

2.1.2. Bleaching Treatment

The alkali treated fibres were bleached using sodium chlorite distilled watersolution and glacial acetic acid was added drop wise, while heating at 70°C for 1hr under constantstirring. By this method, the leftover lignin was removed. The mixture was cooled in ice bath,filtered and washed with cold water. At last, the bleached fibers were treated with nitricacid solution and then washed with distilled water.

2.1.3. Acid Hydrolysis

Isolated cellulose from the sugarcane bagasse was hydrolysed with sulphuric acid. The hydrolysis process was quenched by adding distilled water to thesulphuric acid, and the solution was added drop wise to the bagasse with constant stirring at 50°C. Later, the mixture was centrifuged for 15mins at 3000rpm and thenultrasonicated.The obtained hydrolysed pulp was dried and collected [4].

2.2. Synthesis of Iron Oxide Nanocubes

Iron Oxide nanocubes were synthesized using hydrothermal process. The chemicals required forthe process were aqueous iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and triethylamine. $Fe(NO_3)_3 \cdot 9H_2O$ and triethylamine were dissolved in 100mL of distilled water to form ahomogeneous solution. Later, the solution was stirred vigorously for 5 – 10 minutes. Thissolution was transferred in the Teflon lined autoclave and was filled with water up to 80% of thetotal volume, and heated at 160°C for 24hrs. After it cooled down at

room temperature, theresulting products were filtered using Whatmann filter paper and washed with water andanhydrous ethanol for several times. The obtained product was dried for 5hrs at 50°C [8].

2.3. *Preparation of the nanocomposite*

Composites of cellulose nanofibers and Iron oxide nanocubes were dispersed in distilled water. Later the mixture was stirred for 30 mins at 800rpm.The resulting products were dried at 50°C in the hot air oven.

2.4. *Antibacterial evaluation*

The Staphylococcus aureus bacteria subculture was prepared and incubated for 24hrs. Agar wasmade using the nutrient agar and autoclaved for 40mins. The sub cultured Staphylococcus aureusbacteria were swabbed uniformly across a culture plate. A filter-paper disk, impregnated with the cellulose nanofibers and iron oxide nanocubes were placed on the surface of the agar. This was then placed in the hot air oven [9].

3. Results and Discussion

3.1. *Powder X-ray Diffraction analysis*

The PXRD pattern of the synthesized Cellulose Nanofibers and Iron Oxide nanocubes are shownin figure 1a. The crystallinity index of the isolated cellulose nanofibers were analysed by X-raydiffraction. The peak for the cellulose nanofibers is between 22° to 24°.The crystallinityindex of the prepared cellulose nanofiber was calculated by peak height method which is an empirical method being the most common and simple method to determine thedegree of crystallinity. In this approach, the X-ray apparent crystallinity (%) of cellulose iscalculated from the following equation:

$$C = 100.\ [(I_{200} - I_{non\text{-}cr})/I200]$$

Where,C expresses the apparent crystallinity [%] defined by Segal and co-workers [10],I_{200} gives the maximum intensity of the peak corresponding to the plane in the sample with theMiller indices 200 at a 2ø angle of between 22- 24 degrees, and $I_{non\text{-}cr}$represents the intensityof diffraction of the non-crystalline material. The crystallinity index of the obtained nanofiberswas 69.47%. The diameters of the cellulose nanofibers were found to be 15.65nm.

XRD pattern of the prepared Iron oxide nanocubes is shown inFigure 1b. The crystalline size of the prepared nanocubes was found to be 5.63nm,using Scherrer equation, and i.e. $D = 0.9\lambda/\beta\cos\theta$. The interplanar spacing was found to be 1.45A° and 2.18A° for the corresponding (h k l) values (300) and (113)respectively, a= 5.0229A°and c= 13.4030A° from the XRD pattern. It is concluded that all the diffraction peaks readilyindexed as the pure rhombohedralα-Fe2O3 (JCPDS file Card, no. 33-0664). The narrow peakssuggests that the α-Fe2O3 samples were higher crystalline. No other peaks were observed,indicating high purity of the as-prepared samples [8].

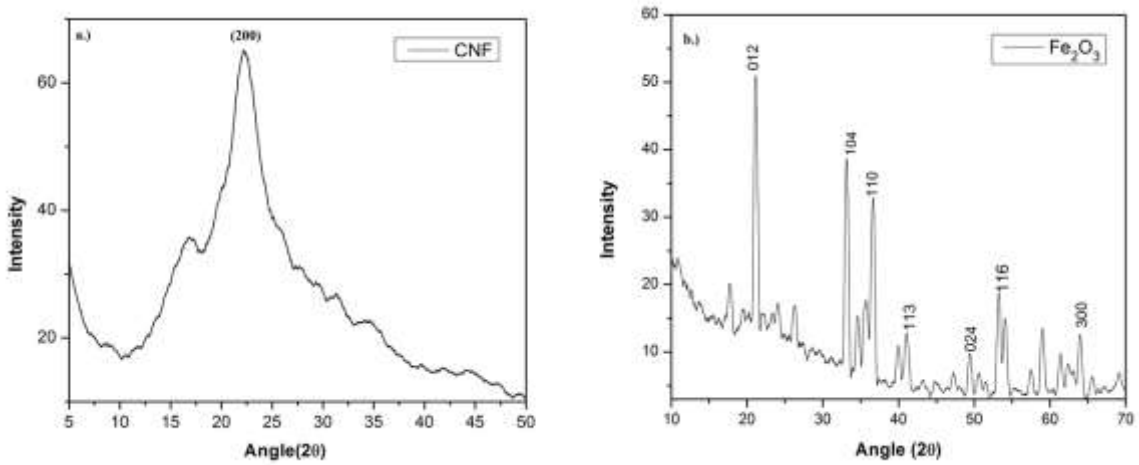

Figure 1a) X-ray diffraction spectra of cellulose nanofibers, 1b) X-ray diffraction spectra of iron oxide nanocubes.

3.2 Scanning Electron Microscope Analysis

SEM image of the prepared Cellulose nanofibers and IronOxide nanocubes composite is shown in the figure 2. It was observed that the obtainedIron Oxide material had uniform cube like structure. The cube side had the range from 60nm to75nm. From the SEM images, we observed the nanocubes along with the celluloseNano fibers. The diameter of the nanofibers of around 22nm to 60nm and the length of 190nm to400nm were obtained.

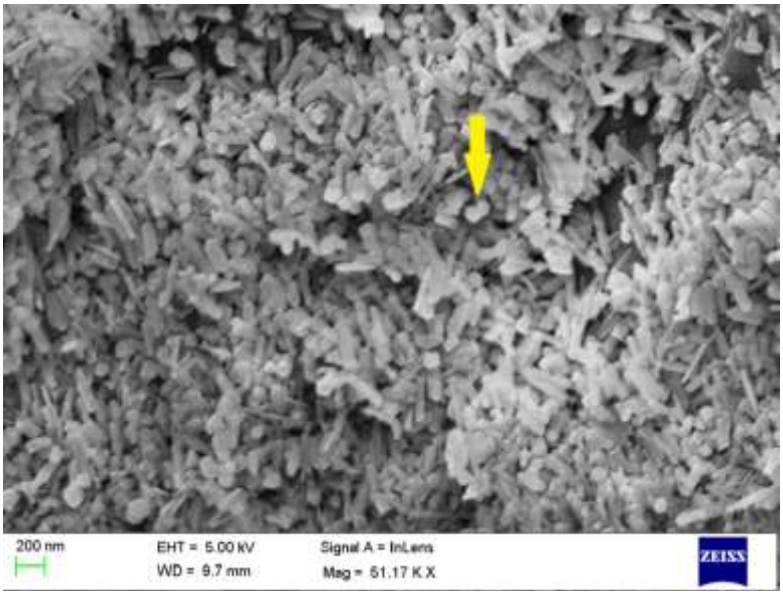

Figure 2: SEM image of cellulose nanofibers and iron oxide nanocubes

3.3. Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Figure 3a and b shows the FTIR spectra between the ranges of 4000 to 400 cm^{-1} of preparedcellulosenanofibers and iron oxide nanocubes, respectively. From the figure 3a, it is observed that there is reduction of peaks from 1736 – 1068cm^{-1} which explains the removal of much of lignin and hemicellulose contents by alkaline andbleaching

pretreatment. The absorbance peaks at 1635, 1417and 1025 cm^{-1} arenormalized assuming that a negligible amount of cellulose is removed during thebleaching process [11]. The sample residue after bleaching was more exposed to acidattack in acid treatment process since more lignin was removed. Figure 3b represents the FTIR spectrum of α-Fe_2O_3 Nanocubes, the peaks at 500 and 581 $cm^{-1}$are attributed to the Fe-O bond vibration of the Fe_2O_3. The spectrum showed the bands at 901 and 803 cm^{-1} corresponds to the out-ofplane C–H vibration caused by the remnant of triethylamine on the surface of particles
And the peaks at around 1657 cm^{-1} were tentatively assigned to the vibration of C–N bond[12].

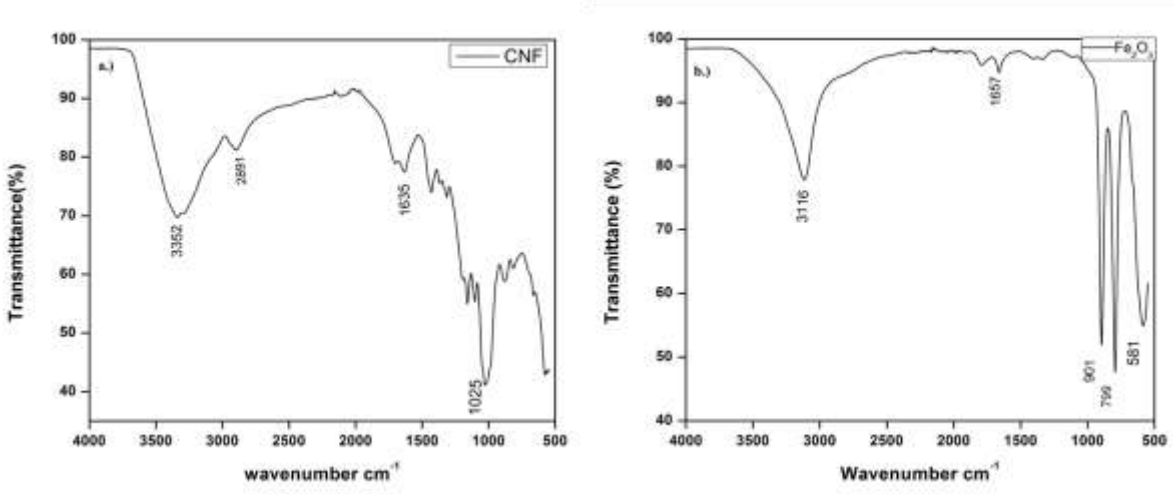

Figure 3a) FTIR spectra of cellulose nanofibers, 3b) FTIR spectra of iron oxide nanocubes.

4. Antibacterial activity

The antibacterial activities of the iron oxide nanocubes and cellulose nanofibers evaluated against the pathogenic bacteria, Staphylococcusaureus are studied. The result of antibacterial activity of Iron Oxidenanocubes showed moderate antimicrobial activity against the bacteria. Cellulosenanofibers didn't show any antibacterial activity.

5. Oil absorption activity

The Oil absorption activity of the synthesized composite of cellulose nanofibers and Iron oxidenanocubes was studied. The prepared nanocomposite was weighed and deposited on the pre-cleaned cotton fabric, then dipped in the oil water mixture. There was increment in the weight of the cotton fabric deposited with nanocomposite. To ensure the oil absorptivity, they were kept overnight on the butter paper, it confirms the absorption and desorption property of the cellulose nanofibers.

6. *Conclusion*

Cellulose nanofiberswere prepared using acid hydrolysismethod. Iron Oxide nanocubes were synthesized using hydrothermal method. The compositeswere prepared by stirring and mixing of cellulose nanofiber and iron oxide. The characterization of the prepared material was done using X-Ray Diffraction (XRD),Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and antibacterial study. X-Ray Diffraction confirmedthe formation of the desired material. SEM image showed the morphology of the composite andiron oxide nanocubes were uniformly distributed on the nanofibers.FTIR presented the bond structure of the prepared nanomaterials.Oil

absorptivity was analysed using this cellulose nanofiber and iron oxide nanocubes composite. Oil absorptivity was observed in the nanocomposite.

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