Preparation of Lignocellulosic Nanofibres by Electrospinning for Filtration

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ABSTRACT

The fabrication of nanofibres was conducted from lignocellulosic materials obtained from Pennisetum clandestinum (Kikuyu grass). Grass was fractionated in H_2SO_4 to produce lignocellulose which was then chemically modified with siloxanes. The modified lignocellulose was used to prepare composites with clinoptilolite. Solutions of modified lignocellulose and composites were prepared in PAN-DMSO for electrospinning to produce nanofibres with diameters ranging from 89 to 400 nm. FT-IR, TGA and SEM were used to characterise the products. Nanofibres were tested for nanofiltration, and dropped the turbidity of water from 63.07 to 3.06 NTU.

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INTRODUCTION

Since some decade, technology is drifting to the production of miniature devices which can only be made possible by designing new raw materials that fit within the 21st century. Therefore, preparation of materials at nanoscale is an attractive field of research by using top-down or bottom-up processes for the production of nanoparticles and different other techniques for nanofibres.

Many processing techniques enable the fabrication of nanofibres, such as: drawing, template synthesis, phase separation, self-assembly, sea-island-type conjugated melt spinning, single-orifice melt blowing, jet blowing and electrospinning are listed amongst the processing techniques [MITRI and SOTIRCHOS, 2005; VASITA and KATTI, 2006; SUZUKI and SHIMIZU, 2011; RATHINAMOORTHY, 2012]. Nanofibres have special properties and can be used for several applications, such as: medical, barrier, wipes, personal care, composites, garments, insulation, energy storage, aerospace, capacitors, transistors, drug delivery systems, battery separators, fuel cells, information technology and filtration [RATHINAMOORTHY, 2012].

Amongst the processing techniques for nanofibres fabrications, electrospinning seems to have more advantages over others, because of its potential for laboratory and industrial processing. It also can be scaled up or down and the fibre's dimension can be controlled [MITRI and SOTIRCHOS, 2005; VASITA and KATTI, 2006]. Electrospinning produces nanofibres directly from a polymer solution; suggesting that special care on the choice of an appropriate solvent is of critical importance for successful nanofiber production [MONTAÑO-LEYVAET AL., 2011]. The difficulty with using cellulosic materials is that they exhibit very low solubility in organic solvents due to their crystallinity and their large number of hydrogen bonds, which complicate the production of nanofibres by electrospinning. This is a major challenge for research on the use of cellulose and cellulose derivatives as raw material for electrospinning [YOUN-MOOK et al., 2010]. However, efforts are being made to overcome the solubility issue of this material using different solvents to allow electrospinning [MONTAÑO-LEYVA et al., 2011]. Some solvents such as DMSO/TBAF, DMSO/NMI and DMSO/LiCl have led to a substantial improvement in handling lignocellulosic materials [LU and RALPH, 2003; FASCHING et al., 2008; WANG et al., 2009].

Therefore, Montaño-Leyva et al [2011] reported successful production of nanofibres by electrospinning of cellulose isolated from wheat straw (by chemical treatment using trifluoroacetic acid as solvent). They obtained nanofibres having 270 ± 97 nm in diameter. Chiu-Yin et al. [2011] reported the alkaline treatment of corncob and wheat straw, which was successfully electrospun after blending the product obtained (soluble fibrous residues) with 6% polyvinyl alcohol (w/v). Bedford et al.[2012] succeeded in the electrospinning of cellulose acetate (purchased from Sigma-Aldrich) in acetic acid. The electrospun fibres were used for the degradation of cyanobacteria toxin microcystin-LR. Hong Dong et al. [2012] reported the electrospinning of cellulose nanocrystals (prepared from commercial grade softwood dissolving pulp) blended with poly(methyl methacrylate).

In this study, the focus is on electrospinning of lignocellulose modified with siloxanes and composites (lignocellulose-siloxane-clinoptilolite) to produce nanofibres which were used to investigate the possibility of their utilization in water nanofiltration.

MATERIAL AND METHODS

Chemicals

Polyacrylonitrile (PAN, from Aldrich) was used in a blend with

lignocellulosic materials in order to carry out electrospinning. This is because of its intrinsic viscosity in N,N-dimethyl formamide (DMF). DMF was used as solvent because of its appropriate boiling point (153°C) and excellent conductivity (conductivity ≤ 2.5 µS/cm, dipole moment= 3.82 Debye) and its capability for swelling lignocellulosic material; Dimethylsulfoxide (DMSO) also has a great swelling property which is an important factor for electrospinning [ASHTON, 1973; PARK et al., 2008].

Preparation of materials

Lignocellulosic material

Pennisetum clandestinum was pre-treated according to the procedure obtained from Ruiz and Ehrman [1996] and Palmowski & Muller [1999]. Soluble substances and hemicellulose were extracted by decoction for 30 minutes. The mixture was filtered and the residue extensively washed with water until the filtrate became "colourless". The solid residue (lignocellulose) was oven-dried to constant weight at 65°C overnight. The powder obtained was fractionated (hydrolysed) in H_2SO_4 according to the procedure obtained from Shibazaki et al. [1995], Curreli et al. [2002], Xiang [2003] and Hong & Qiu [2008], prior to chemical modification.

The chemical modification of lignocellulosic material by siloxane was adapted from the work of Matías et al. [2000] and Le Digabel et al. [2004] and carried out as follows: In a 3-neck round bottomed flask, 10 mL of 3-aminopropyl-terminated polydimethylsiloxane was added to 1.5 g of lignocellulose (from acid hydrolysis) in 30 mL of DMF and refluxed for 5 h at 130°C. The reaction was carried out under a nitrogen atmosphere, in the presence of 200 µL of dibutyltin dilaurate. The products were Soxhlet-extracted with 100 mL THF for 5 h. The obtained products (modified lignocellulose) were oven dried overnight at 65°C. The resulting modified lignocellulosic materials were designated according to the abbreviation for the particular siloxane used: LNH15D (lignocellulose modified with siloxane NH15D), LNH40D (lignocellulose modified with siloxane NH40D and LNH130D (lignocellulose modified with siloxane NH130D) while grass with H_2SO_4 was considered as the product obtained after the treatment of grass with sulfuric acid.

Lignocellulose-clinoptilolite composites were prepared according to the procedure used by Vala [2013]. The resulting composites materials were designated according to the abbreviation for the particular siloxane used: CNH15D (composite obtained with siloxane NH15D), CNH40D (composite obtained with siloxane NH40D and CNH130D (composite obtained with siloxane NH130D).

Preparation of electrospun solutions

Materials subjected to electrospinning were first ground to allow passage through a 425µm sieve. Electrospinning solutions of lignocellulose modified with siloxanes and composites were prepared according to a procedure modified from literature[(OKSMAN et al., 2006; XIE et al., 2007; BINDER and RAINES, 2009], as follows, solution ratios were:

- Solvents, DMF:DMSO = 19:1 (v/v) for PAN-modified lignocellulose (or composites) ratio of 19:1 (w/w) and
- Solvents, DMF:DMSO = 9:1 (v/v) for PAN-modified lignocellulose (or composites) ratio of 9:1 (w/w).

The solutions obtained were first stirred for 6 h at 40°C and then sonicated in an ultrasonic bath for 45 min. The viscous solution obtained was used in a simple and adapted electrospinning apparatus. A high voltage power supply was used to apply electric power. Electrospinning was carried out under the following conditions: electric power: 25 kV, manual feeding, tip-to-collector distance: 16cm.

RESULTS AND DISCUSSION

Lignocellulose modified with siloxanes and their composites were successfully electrospun in DMF/DMSO. Although nanofibres

obtained can be used for many applications, the **C≡N-** group of PAN in the structure of these materials are expected to behave as a chelating agent when the nanofibres mat is used for the removal of unwanted compounds (such as heavy metals) from air or water.

FT-IR of nanofibres

Fourier transfer infrared (FT-IR) spectra were obtained in order to study the efficiency of the PAN-modified lignocellulose and PAN-composites blending and the appearance or disappearance of new functional groups was studied. Therefore, **Figure 1** presents the FT-IR spectra of some nanofibres prepared from the blending of PAN and lignocellulose modified with siloxanes.

The spectra obtained show peaks characteristic of PAN at 2255 cm⁻¹. Observation of the nanofibres spectra reveals an insight in the blending process. First of all, the most important peak characteristic of PAN, -**C≡N** group, has been largely reduced to a very small peak. Also, the peak has shifted from 2255 cm⁻¹ to around 2291 cm⁻¹. There is also the appearance of a peak around 2071 cm⁻¹ in the spectra of all nanofibres which is not visible in PAN. Another observation is the shifting of the peak from 2976 cm⁻¹ to 3247 cm⁻¹.
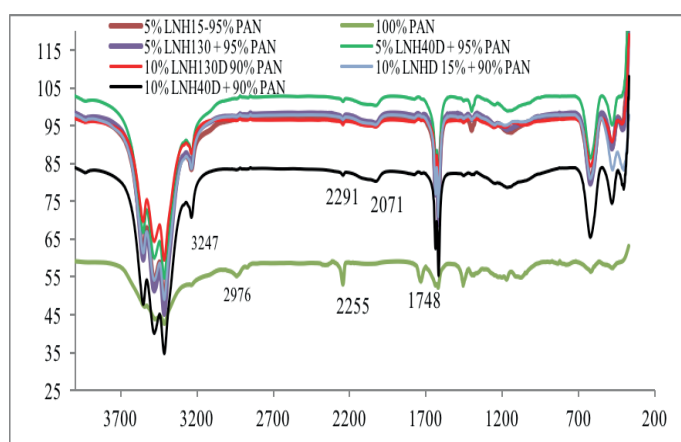

Figure 1| FT-IR of PAN and lignocellulosic nanofibres

The FT-IR spectra of composites and PAN (PAN blended with modified lignocellulose-siloxanes-clinoptilolite) are presented in **Figure 2**.
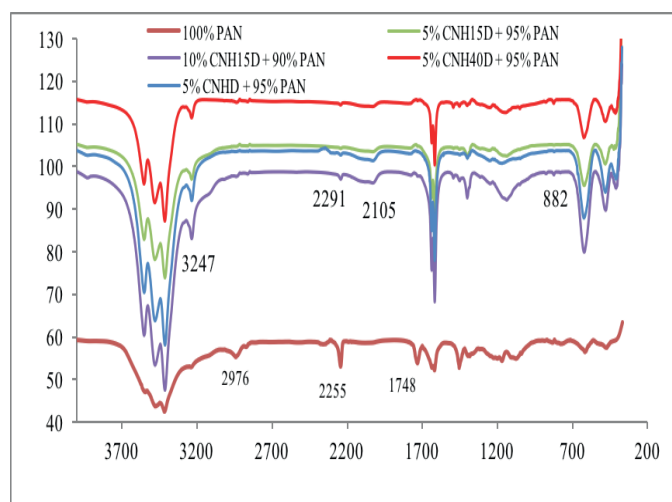

Figure 2| FT-IR of PAN and composites nanofibres

It is also possible to trace peaks of PAN nanofibres in the spectra of PAN-composites. Peaks involving Si bonds (in siloxane and clinoptilolite) are not clearly observed; probably because of their small amounts in the nanofibres. However, it is possible to observe very small peaks around 882 cm-1 (in the spectra of

composites), indicating Si-C bond because of large silicone content (from siloxane and clinoptilolite) than in lignocellulose modified with siloxane.

TGA analysis

Thermogravimetric analysis(TGA) of nanofibres was carried out in order to study their behaviour when exposed to heat from 20°C to 900°C. All results hav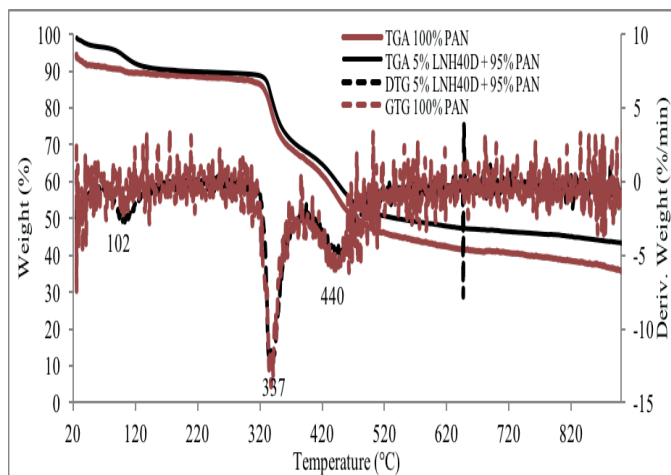e almost the same pattern as illustrated by plots displayed in **Figures 3** and **4**. It appeared that modified lignocellulose-PAN and composites-PAN nanofibres thermograms differed from those of PAN nanofibres at around 93°C and 102°C, probably because of moisture loss (since lignocellulose hydrophilicity property is well known). However, a general degradation pattern of PAN nanofibres and that of modified lignocellulose-PAN and composites-PAN nanofibres mass loss was observed at about 337°C and 440°C. This mass loss might have been due to the conversion of nanofibres to an intermediate compound which, being less stable at high temperature was then slowly converted to the residue which was more or less stable at 900°C.

Modified lignocellulose-PAN nanofibres produced more residue (43%) than PAN nanofibres (36.5%). This was likely the result of the silicone content in the composites, which made them more thermally stable.

Figure 3| TGA and DTG of lignocellulosic nanofibres
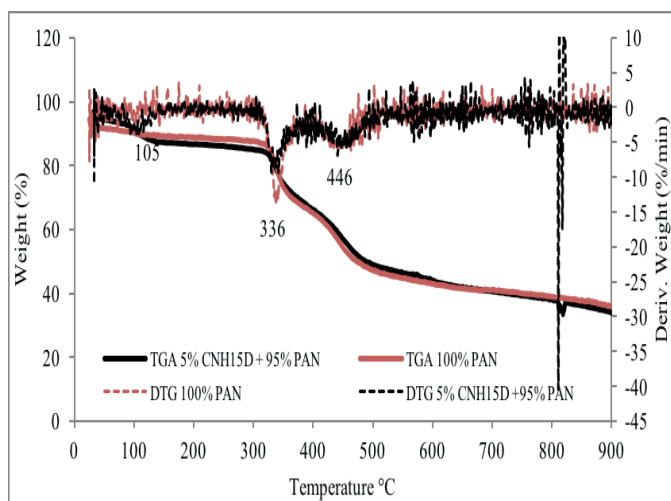
Figure 4| TGA and DTG of composites nanofibres

Table 1| Nanofibres diameters

Nanofibres	Diameter (nm)	
	Range	Average
LNH15D 5%	127.3 - 210.1	161.3
LNH15D 10%	89.0 - 237.8	145.0
LNH40D 5%	100.3 - 251.2	177.2
LNH40D 10%	111.0– 239.0	194.6
LNH130D 5%	94.2 –239.0	173.0
LNH130D 10%	205.3 - 306.3	263.8
CNH15D 5%	128.4 - 252.2	171.0
CNH15D 10%	118.9 - 326.7	203.2
CNH40D 5%	164.8 – 352.1	272.6
CNH40D 10%	114.8 – 205.0	167.8
CNH130D 5%	165.0 – 263.0	213.0
CNH130D 10%	113.0 – 426.1	210.6
PAN	212.1 - 446.8	328.6

SEM images

Scanning electron microscopy (SEM) was used to examine the surface morphology of the materials. Nanofibres meshes were obtained from the electrospinning process. Generally, the nanofibrous meshes consisted of fibres with diameters ranging from 89 to 306.3 nm, except for some infrequent nanofibres which had diameters above 400 nm. Details on the nanofibres diameters are given in **Table 1**. They appeared more aligned than entangled, with a non-woven structure, although their surfaces looked regular and relatively smooth. The regular morphology depicted the effectiveness of the conditions used during electrospinning.
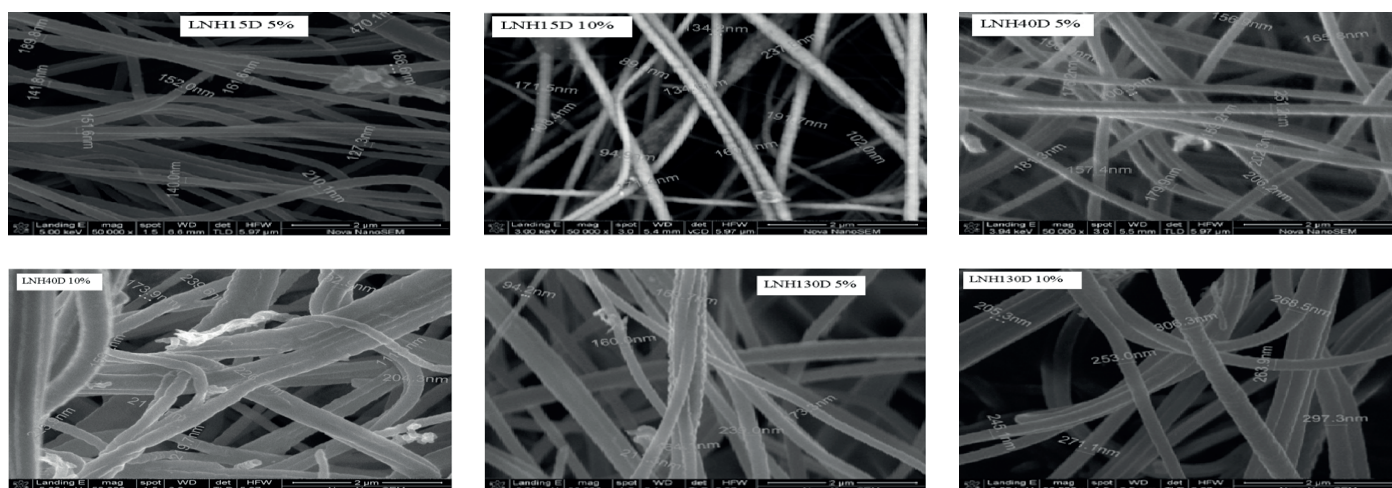

Figure 5| SEM micrographs of lignocellulose modified with siloxanes nanofibres
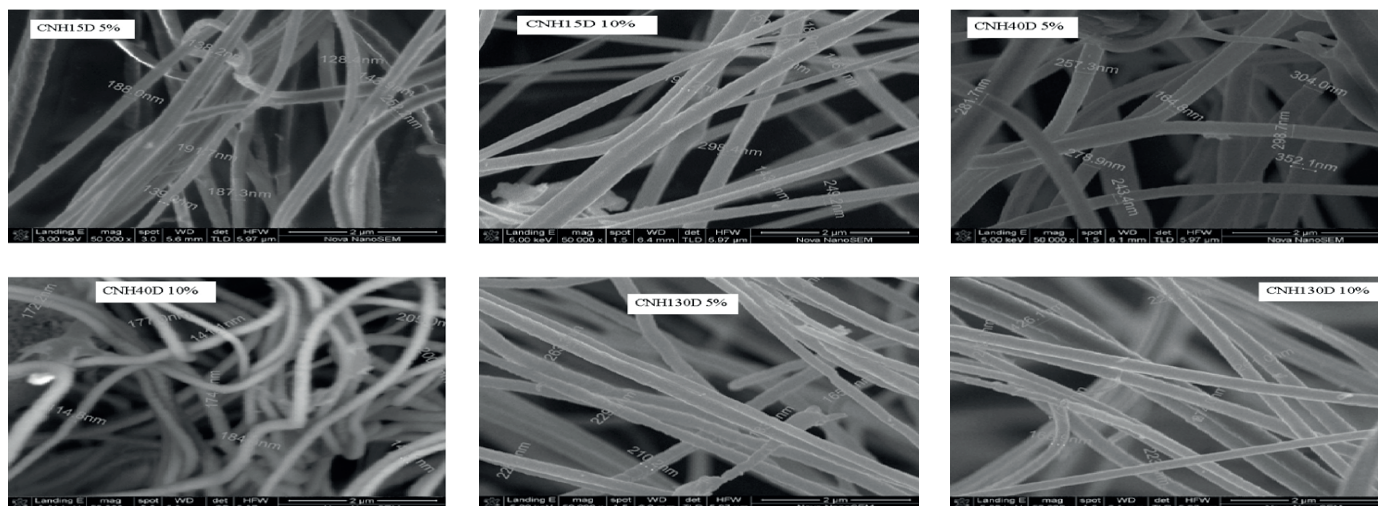
Figure 6| SEM images of composites nanofibres

Beads defects could be caused by the viscoelasticity and surface tension of the electrospun solution and the volatilization rate of the solvent [FONG et al., 1999;LIN et al., 2004; ZUO et al., 2005; SHENOY et al., 2005].

Figure 5 presents the morphology of nanofibres meshes of lignocellulose modified with siloxanes. Comparison of nanofibres of the same materials at different concentrations does not show any specific trend. Their average diameter is 185.8 nm SEM micrographs of composite nanofibres are presented in **Figure 6**. Comparison of nanofibres of the same materials of different concentrations shows that 10% of the composites blended with PAN, yielded the smallest nanofibres diameters (**Table 1**). Their average diameter was 206.4 nm.

As already mentioned, PAN was used for blending with either the modified lignocellulose or with lignocellulose-clinoptilolite composites. PAN was electrospun alone for the sake of comparison with the materials prepared. SEM image of PAN nanofibres is displayed in **Figure 7**. It appears that all measured PAN fibres had large diameters (from 212.1 to 446.8 nm) with an average of 328.6 nm than the blended sample, suggesting the tightening effect of the materials prepared on the size of nanofibres.

Nanofiltration with the prepared nanofibres

Turbidity was the parameter used to assess the filtration efficiency of the nanofibres mat in cleaning water. Turbidity is the cloudiness
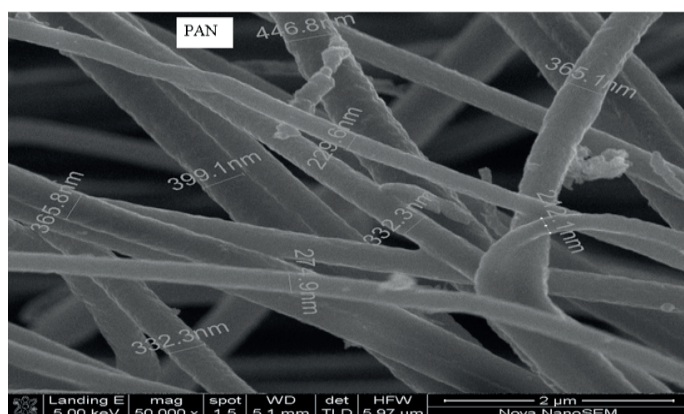

Figure 7| SEM micrograph of PAN nanofibres

of a fluid (e.g. water) caused by individual suspended solids (particles) that are generally invisible to the naked eye. The measurement of turbidity is one of the key tests of water quality.

Experimental Procedure of Filtration

The nanofibers prepared formed into a web (nanoweb) that was used without any special handling and filter pleating equipment. Efficiency of the nanofibres prepared which were to be used for filtration, was determined by assessing the turbidity of a known water sample as follows: 0.0230 gof nanofibre mats forming 0.5 cm thickness size was loaded in a Pasteur pipette. Then, water having a turbidity value of 63.07 NTU was allowed to pass from a burette through the material (nanofibres) for filtration and the filtrate was collected and a turbidity measurement obtained. Just as in conventional filtration, gravity was the force responsible for draining out water. Results of filtration presented in **Table 2** showed the efficiency of the novel materials for the removal of waterborne (pollutant).

Table 2| Turbidity of water before and after filtration through nanofibres

			Before Filtration	After Filtration
Turbidity (NTU)		**PAN nanofibres**	63.07	12.23
	Ligno-cellulose (modified with siloxanes) nanofibres	**LNH 15D 5%**	63.07	5.43
		LNH 40D 5%	63.07	3.86
		LNH 40D 10%	63.07	9.54
		LNH 130D 10%	63.07	3.26
	Compos-ites nano-fibres	**CNH 15D 5%**	63.07	7.02
		CNH 15D 10%	63.07	10.28
		CNH 40D 10%	63.07	3.06
		CNH 130D 5%	63.07	5.87

The best result showed that turbidity of raw water dropped from 63.07 NTU to 3.06 NTU, which was 21 times less the turbidity of the raw water. This is a significant improvement since the World Health Organization standard is 5.0 NTU [WHO, 2006]. When compared to PAN nanofibres, lignocellulose and composites nanofibres showed high filtration efficiency. The high turbidity values (>5.0 NTU) after filtration (of the prepared materials) could be attributed to slip flow (movement of waterborne material through the pipette without colliding with the nanofiber) in the inner surface of the pipette or to nanofibres mat flaps.

CONCLUSION

Lignocellulose modified with siloxanes and their composites (with clinoptilolite) were successfully electrospun by blending with PAN in a solvent mixture of DMF-DMSO. The blend and the solvent facilitated the production of a colloidal mixture required for electrospinning. It was possible to monitor the presence of PAN, lignocellulose and clinoptilolite in the nanofibres structure from FT–IR and TGA results.

Nanofibre mats were loaded in a Pasteur tube and dirty water was allowed to pass through for nanofiltration. Good results were obtained because turbidity of water dropped from 63 to 3.06 NTU.

RÉSUMÉ

La fabrication des nanofibres a été faite à partir de la lignocellulose obtenue de la plante *Pennisetum clandestinum* (Kikuyu, une pelouse dont le nom tire son origine du Kenya). Cette pelouse était fractionnée dans H_2SO_4 pour produire la lignocellulose qui a son tour était chimiquement modifiée avec des siloxanes. La lignocellulose modifiée était utilisée pour préparer des composites avec le clinoptilolite (zéolite). Les solutions de lignocellulose modifiée et des composites étaient préparées dans PAN-DMSO pour l'électrospinning afin de produire des nanofibres dont les diamètres varient de 89 à 400 nm. FT-IR, TGA et SEM étaient utilisés pour la caractérisation des produits obtenus. Les nanofibres étaient utilisées pour la nanofiltration, la turbidité a été baissée de 63,07 à 3,06 NTU.

Mots clés : Lignocellulose, Clinoptilolite, modification chimique, siloxanes N-terminal, Nanofibres, Nanofiltration

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