Cellulose Based Electrospun Nanofilters: Perspectives On Tannery Effluent Waste Water Treatment

Senthil Rethinam (senthilbiop@gmail.com)
Central Leather Research Institute CSIR

Sardar Batikan Kavukcu
Ege Universitesi

Thiagarajan Hemalatha
Central Leather Research Institute CSIR

A.Wilson Aruni
California University of Science and Medicine

Aylin Sendemir
Ege Universitesi

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Abstract

Development of nanofilters with the capability to remove toxic metal ions from effluent wastewater will be of immense help to the leather industry. In this study, fibrous nanofilter (FNF) was prepared using microcellulosic fiber (MCF) and tea leaves microparticles (TLM) blended in poly (vinyl) alcohol (PVA). FNF was analysed for its efficacy to remove hazardous metals from tannery effluent wastewater. The FNF had promising traits of tensile strength (19.24+0.05 Mpa), elongation at break (22.31+0.12 %), flexibility (10.88+0.05 %), water absorption (37.86+0.14 %) and desorption (32.54+0.33 %). The metal adsorption studies clearly reflected the removal of toxic Cr (VI) ions from the effluent water by FNF. The study establishes an economically feasible and highly efficient way to remove hazardous metal ions from effluent wastewater.

Introduction

Leather industries pose a severe threat to the environment owing to the discharge of effluent waste water which contains a wide range of pollutants. In one way leather industries benefit mankind by converting raw hide into leather by the process of tanning; but on the other hand, the process involved generates air, water and solid pollution (Stanislaw, 2020). The tanning industry generates 145 billion gallons of waste water annually (Sathish et al., 2016), which when discharged into the viable water sources without proper treatment becomes detrimental to all the lifeforms. Water contamination especially with heavy metals has become a major ecological issue as it creates adverse impacts on living organisms particularly by accumulating in the food chain (Bhateria and Singh, 2019). Chromium (III) salts are used as tanning chemicals in 80–90% of tanneries worldwide due to time and monetary advantages. Unused chromium salts present in tannery waste water (Orukoa et al., 2020) on oxidation gets converted to chromium (VI). Hexavalent chromium (Cr VI) causes potent health hazards, and some salts are considered to be carcinogens (Kolomaznik et al., 2008). In view of this alarming facts, it becomes essentially important to treat the effluent waste water in a cost-effective manner to remove heavy metals and other contaminants, before discharge into the environment.

Around “n” number of strategies are practised globally to combat this heavy metal polluted waste water problem viz., adsorption, membrane filtration, chemical precipitation, electrochemical treatment, activated carbon etc. But these technologies are highly expensive and time consuming which becomes a great hurdle in their implementation. In this context, nanotechnology has emerged as a definite solution to safeguard the environment and life forms. Nanotechnology is the branch of science dealing with the engineering of nanosize particles (averaging less than 100 nm in length) to fabricate various materials. Nanomaterials such as membranes, films, scaffolds, colloids and quantum dots, are created in a variety of shapes and sizes (Senthil et al., 2020) and are characterized with greater surface area, surface action and specific affinity. A variety of efficient nanomaterials based on carbon, silica, metal oxides etc. have been developed for heavy metal removal from wastewater (Singh et al., 2021).
Cellulose is the most abundant polysaccharide on earth, synthesized by a large number of living organisms ranging from bacteria to plants and trees. Cellulose is used as a natural low-cost biopolymer for the removal of heavy metal impurities owing to the presence of carboxyl and hydroxyl functional groups (Saito et al., 2007). Large surface area, high hydrophilicity, good strength and transparency are the promising traits enabling the use of nanocellulose in a wide range of applications. Poly vinyl alcohol (PVA) is a biocompatible and biodegradable film forming multi-hydroxyl polymer with superior flexibility and chemical stability used in the preparation of functional membrane materials (Huo et al. 2019). Nanomembrane materials prepared using the blend of PVA and nanocellulose possessed improved thermal and chemical stability (Peng et al., 2017). Adsorption of heavy metals in waste water using agro wastes is evolving as a cost-effective strategy to overcome the limitations of existing processes using activated carbon. Tea waste is considered a promising option due to its low cost, abundant availability and its efficiency in adsorbing heavy metals like Ni, Cr (VI), Cu, Pb etc (Nandal et al., 2014).

Electrospinning is a simple and feasible techniques to produce nanofibers with high surface area and porosity (Subbiah et al., 2005). Nanofiber membranes with high specific surface area allows for very effective adsorption of pollutants from air or water, which contributes to their high filtering effectiveness (Maneal et al., 2018). Electrospun nanofibrous membranes were proved to be efficient for the removal of chromium from contaminated water (Liu et al., 2015).

The study aims to prepare and characterize a fibrous nanofilter using a combination of cellulosic nanofibers, polymeric solution (PVA) and tea waste microparticles and to evaluate its heavy metal adsorption characteristics in tannery waste water.

**Materials And Method**

Poly (vinyl alcohol) – PVA (110000-120000 Mw) and de-ionized water were purchased from Sigma Aldrich, Turkey. Cellulosic raw boards were collected from Viking Paper and Cellulose A.S. Industry, Aliaga-Izmir, Turkey. Tea waste were obtained from teashops, Bornova-Izmir, Turkey. The chrome containing tannery waste water was collected from Bursa leather industrial area of Turkey.

**Tannery Wastewater Analysis**

Physico-chemical characteristics were analyzed according to standard methods. COD, BOD and sulfate were measured using a photometric cuvette test. Chromium content was estimated in tannery waste water according to Swarnalatha et al. (2008).

**Preparation of Micro Cellulosic Fibers (MCF)**

MCF was produced from cellulose raw board through pulverization process. In brief, raw cellulosic materials were cut into small pieces and converted into cellulosic micro fibers at room temperature for 10 min using Retsch grinder machine (Retsch GmbH 5657 HAAN WEST –GERMANY & SK1) with two stage
pulverization process. The cellulosic fiber was filtered after the pulverization process (450 micron sized filter) and stored in a container until further use.

**Tea leaves Microparticles (TLM)**

Preparation of TLM was done using waste tea powder. Waste tea powder was washed with boiling water to remove the soluble and colored components. Then it was washed with distilled water and dried using hot air oven at 80-100 °C for 2 to 5 h. Finally, the resulting powder was crushed into fine particles using mortar and pestle.

**Preparation of Fibrous Nanofilter (FNF)**

FNF was electrospun using E-Spin Nano equipment (Iseg Spezialelektronik GmbH, Germany). PVA (10 g) was dissolved in 100 mL distilled water using an agitator at 80°C for 3 h. PVA solution was then blended with 3.0 g of MCF and 0.9 wt % TLM, by vigorous stirring for 12 h. The spinning solution was carefully placed in the capillary position (New Era Pump Systems, USA) and linked to a positive electrode of high-voltage power supply after cooling to room temperature and flow rate of 0.5 mL/min. The electrospinning sample was collected, and the membranes were vacuum-sealed and stored at 65°C for 12 h and used for further experiments. All the experiments were conducted at room temperature. The preparation FNF is depicted in the schematic diagram (Fig.1).

**Cross-linking of Fibrous Nanofilter**

The residues of the electrospinning solution can still be found in the electrospun nanofibers. Themostabilization process was done in electro-thermostatic oven according to Beck et al., (2017). In brief, the electrospun scaffold was heated in a constant air flow from 50 to 260 °C at a rate of 2 °C/min, and then maintained at the set point for 1 h. The structure of fibrous nanofilter obtained by chemical crosslink is shown in Fig.2.

**Characterization of MCF and FNF**

FTIR measurements were carried out to determine the formation and changes in the functional groups of MCF and FNF. Nicolet 360 FTIR spectrometer was used to measure the spectra with a resolution of 4 cm⁻¹ in the frequency range of 4000 - 500 cm⁻¹. SEM analysis was carried out using Thermo Scientific Apreo SEM at 15 kV accelerating voltage. The samples were coated with gold ions using an ion coating unit and then micrographs were taken. TGA was done using High resolution TGA 2950 (TA Instruments). Samples weighing 10 to 20 mg were placed in a platinum pan and tested in a programed temperature range of 0-800 °C at a heating rate of 5 °C/min in a nitrogen atmosphere with a flow rate of 50 mL/min. AFM was done to have a deep understanding of the surface morphology of FNF electrospun fibers. The electrospun fibers were deposited on silicon wafers and evaluated in air at room temperature (25+1°C) using a BRUKER Dimension Edge with Scan Analysis AFM. Calibrating binding energy to C1s, X-ray photoelectron spectroscopy (XPS) analysis was performed with a PHI 5000 Versa Probe-Scanning ESCA Microprobe.
and a monochromatized A1 Kα X-ray source (h= 1486.6 eV, 15 kV, 39.3 W, diameter beam spot: 200 μm) (285.1 eV). Surface contaminants were extracted using a moderate sputtering process with Ar+ ions at 2 kV.

**Mechanical Properties**

Three dumbbell-shaped specimens, each 4 mm wide and 10 mm in length, were used to test mechanical characteristics. At a rate of 5 mm/min, tensile strength (MPa) and elongation at break (%) were evaluated using a Universal testing machine (INSTRON model 1405). The STM 129 test method was used to determine flexibility (%) utilizing a fibers board flexing (TER 74) machine. According to Senthil et al (2015), the water absorption and desorption (%) properties of PVA, PVA: MCF and PVA: MCF: TLM fibrous nanofilter were determined.

**Metal Adsorption studies**

Batch method was used to investigate the adsorption of hazardous metals on FNF. The adsorption test was performed at room temperature by mixing 50 mg of FNF with 25 mL of chrome-containing wastewater in 150 mL Erlenmeyer flasks on a shaking incubator at 120 rpm. Experiments were conducted at varied pH levels in the range of 3.0-11.0 to determine the effect of solution pH. After allowing the FNF to settle for 12 h, it was tested for physico-chemical parameters and adsorption mechanism (APHA method 1998 & APHA method 2005).

**Statistical analysis**

The results are presented as mean ± standard deviation (SD) for three individual experiments (n = 3). ANOVA (Analysis of variance) and Duncan's multiple range analysis were done to determine the significant differences among the different groups. P values of < 0.05 were considered significant.

**Results And Discussion**

Nanocellulosic fibers are typically made by a mechanical process using raw cellulosic boards containing cellulose, hemicellulose and lignin. It had an inherent physical structure with polymeric ionic surface, and it acted as a functional agent in hazardous wastewater treatment.

**Tannery Wastewater Analysis**

The pH profile of tannery waste water was 4.03. The COD and BOD results of tannery waste water, 2787±262 mg/L and 508±86 mg/L, respectively. The Cr\textsuperscript{3+} content of tannery waste water was 6,298 mg/L. The Cr\textsuperscript{6+} content of tannery waste water was 6,298mg/L.

**Preparation of Micro Cellulosic Fibers (MCF)**
MCF prepared using cellulosic raw board are shown in Fig.3a and their corresponding surface MCF are given in Fig.3b. The MCF had smooth surface fibers and they were light weight in nature.

**Tea leaves Microparticles (TLM)**

TLM had a smooth texture and it was microparticle size in nature (Fig.4a). Surface morphology of TLM (Fig.4b) was revealed by scanning electron microscopy. It was confirmed from the micrograph that microparticles. From the EDX spectrum, it was confirmed that elements viz., C and O on the TLM surfaces.

**Fourier transform infrared spectroscopy (FTIR)**

Fig.5 (a and b) shows the FTIR spectra of MCF and FNF. The significant absorption peak at 1087 cm$^{-1}$ is due to C-O stretching and O-H bending of PVA (Peresin et al., 2014). The stretching peaks at 2942 and 2908 cm$^{-1}$ are typical O-H and C-H peaks. The stretching of the O-H bond due to intermolecular and intramolecular hydrogen bonding corresponds to the broad band from 3200 to 3550 cm$^{-1}$. The C-H stretch from alkyl groups causes the vibrational band between 2840 and 3000 cm$^{-1}$, whereas the C-O and C=O stretches from the remaining acetate groups in PVA cause the peaks between 1730 and 1680 cm$^{-1}$ (Cho et al., 2000). Structural alterations of cellulose were observed in the range of 850-1500 cm$^{-1}$ (Nelson and Connor, 1964). The peak seen at 1058 cm$^{-1}$ in cellulosic nanofiber was attributed to cellulose C-OH stretching. The tea leaf characteristics band was visible on spectra between 1800 and 1300 cm$^{-1}$ (Peresin et al., 2010).

**Thermo gravimetric analysis (TGA)**

Fig. 5c Show the thermal stability of MCF and FNF as a function of temperature. MCF, had a two-step weight loss at 300 and 390 °C, while 87% remained as residue. The primary degradation of cellulosic fibers, which was related with cellulose pyrolysis, occurred in the lower temperature range of 200 to 450°C. Cellulosic fiber was degraded into carbon dioxide at temperatures exceeding 450°C, depolymerizing the lignin molecules (Mascheroni et al., 2016). The evaporation of water caused the first weight loss of 6% in cellulosic fiber at approximately 100°C. In the temperature range of 250 to 450°C, a weight loss of 87% occurred due to the dehydration of polyvinyl alcohol. FNF showed no loss of mass below 380-800°C, indicating thermal stability, which is a useful attribute for effluent wastewater treatment applications (El Miri et al., 2015). The FNF was quite stable at environmental and industrial temperatures and can be sterilized by heat. The thermal performance of FNF could be attributed to the hydrogen bond formation by PVA, which was consisted with the earlier report on PVA based scaffolds (Peresin et al., 2014). Pectin is an anionic polysaccharide present in tea leaves which forms electrostatic, steric, and covalent interactions, contributing to thermal stability (Rajaphasa and Shimizu, 2020)

**Atomic absorption spectroscopy (AFM).**
Fig. 5d shows the structure and size distribution of an FNF as studied by AFM. The scanning area was shown to be 1.2 µm to 0.1 µm. The phase and amplitude image of FNF revealed the presence of nanometer scale bundles of long cellulose fibers, as well as a particle layer. Electrospun FNF had a diameter ranging from 22.0 to 100 nm, with an average diameter of 39.0±14.5. AFM could offer enough mechanical data to guide the development of scaffolds by stretching individual fibers and monitoring parameters such as elasticity and extension capabilities under both dry and wet circumstances (Spurlin et al., 2009).

**Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)**

The SEM and EDX images of MCF and FNF are given in Fig. 6a and b respectively. MCF shows diameter of fibers around one micron. In terms of diameter range, and uniformity, the blended electrospun materials were of high quality. The combination of MCF and TLM in FNF aids in the decrease of nanofiber diameter size and distribution from 100 to 250 nm. The electrospinning of plant-derived microparticles resulted in a smoother surface with reduced shrinking (Yingngam et al., 2018). In our study, we found no distinguishable PVA micropores, and MCF-TLM exhibited smooth surface area. Excellent adhesion between the MCF-TLM and the polymeric layer was observed. This could be due to the hydroxyl groups in both cellulosic and TLM, which could contribute to the comparatively strong interfacial interaction that would result in close adhesion between the two materials (Huda et al., 2008). The SEM analysis reveals precise specific surface area and pore area, as well as specific pore volume, which is useful in analyzing the impact of surface porosity and particle size in a variety of applications.

**Mechanical Properties**

Table 1 summarizes the mechanical properties of electrospun scaffolds (PVA, PVA: MCF and PVA: MCF: TLM), including tensile strength, elongation at break, flexing index, water absorption and desorption. The results demonstrate that FNF had better values than PVA and PVA: MCF. Water filters must have appropriate mechanical qualities to carry out their intended functions. Individual nanofiber mechanical properties control deformations, dynamic and static reactions, interactions, and resistance in nanofiber channels (Fang et al., 2011). Study on PVA/cellulosic acetate composites, revealed that the tensile strength of PVA was 3.5 MPa, whereas the tensile strength of PVA and cellulosic acetate was 8 MPa. This finding supports the hypothesis that adding cellulose improves mechanical characteristics (Shunya et al., 2018).

**Table 1.** Mechanical properties of PVA, PVA:MCF, and PVA:MCF:TLM.
| Samples          | Tensile strength (MPa) | Elongation at break (%) | Flexing Index (%) | Water absorption (%) | Water desorption (%) |
|------------------|------------------------|-------------------------|-------------------|----------------------|----------------------|
| PVA              | 15.14±0.04             | 20.22±0.19              | 8.30±0.10         | 35.78±0.12           | 30.91±0.07           |
| PVA: MCF         | 18.21±0.03             | 21.25±0.09              | 9.26±0.14         | 36.36±0.30           | 31.40±0.29           |
| PVA: MCF: TLM    | 19.24±0.05             | 22.31±0.12              | 10.88±0.05        | 37.86±0.14           | 32.54±0.33           |

The data are presented as mean ±SD of three individual experiments.

* p < 0.05. as compared to PVA, using Duncan’s multiple range analysis.

**XPS analysis**

XPS analysis is particularly useful for determining the elemental composition and chemical structure on the surface of FNF. Fig.7 depicts the C1s, N1s and O1s spectra. PVA precursor fiber C1s binding energy peaked at 281.3 eV. It was made up of two components, one for the main polymer chain and other for the nitrile group. PVA/cellulose membrane had sulfur and nitrogen element, as well as an amide group (O=C-NH) present in C1s 288.2eV. Binding Al indicated that 73.50 eV oxidized aluminum in tea micro particles which may improve metal adsorption capabilities of electrospun membrane.

**Metal Adsorption studies**

The presence of phenolic compounds in electrospun membranes has a direct bearing on the materials overall performance. Fig.8a shows the hazardous metal adsorption of PVA, PVA: MCF, and PVA: MCF: TLM. FNF had a better adsorption capacity than the other two samples which could be due to the combined influence of surface structure alterations and nanomaterial size in nanofiber (Nuri et al., 2015). The presence of hydroxyl and carboxyl groups in MCF play a vital role in the removal of Cr (VI) ions. The functional groups present in TLM viz., carboxylate, aromatic carboxylate, phenolic hydroxyl and oxyl groups also contribute towards efficient heavy metal adsorption (Nandal et al. 2014). The effect of adsorption experimental factors such as solution pH, temperature and contact time on the removal of hazardous metal in a batch system were investigated in this study. Fig.8b shows the function curves of Cr (VI) adsorption capacity Qe (mg/g) and removal efficiency (%) at pH levels ranging from 3 to 11. The relationship between adsorption temperature and FNF adsorption performance is shown in Fig.8c. In Fig 8d, the results are determined as a function of adsorption time. FNF after adsorbing Cr (VI) from chrome-containing solution is shown in the SEM metal mapping image in Fig.8 (e&f). The results showed that at low pH, Cr (VI) adsorption was significant, which could be due to effective adsorption between the anionic surfaces on the cellulosic fibers and tea leaves particles (Wang and Ge, 2013). As the temperature increases, the electrospun mat adsorption capacity and removal efficiency improved as well (Li and Aiqin, 2007). In sewage treatment by adsorption, the contact time between the adsorbate and the adsorbent is essential (Chafik, 2014).
The diameter of MCF with TLM electrospun nanofibers were lower than those of pure cellulose nanofiber materials, which augmented the adsorption capacity in electrospun mat. Toxic metallic ions such as lead, copper, and cadmium, were removed by the membrane which clearly portrays the promising potential of MCF to be used in leather industry effluent wastewater treatment.

**Conclusions**

Electrospun membrane was prepared via electrospinning techniques for the removal of hazardous metal ions from leather industry effluent wastewater. The physico-chemical properties like FTIR, TGA, SEM and XPS of fabricated electrospun membrane were investigated. The mechanical properties of the electrospun membrane exhibited significant values in term of tensile strength, elongation at break, flexibility, water absorption and desorption. Electrospun membrane was able to remove Cr (VI) from chrome containing wastewater. The interactions between PVA, MCF and TLM contributed towards the adsorption of hazardous metal on the FNF layer. The results clearly reveal the development of highly efficient and cost effective nanomat for wastewater treatment.

**Declarations**

**Conflict of interest statement**

The authors of this manuscript have no conflicts of interest related to the content of the study.

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**Credit authorship contribution statement**

Senthil Rethinam – Methodology, Characterization, Formal analysis and writing original draft.

Serdar Batikan Kavukcu-Characterization

Thiagarajan Hemalatha- Validation and Formal analysis

A.Wilson Aruni -Software

Ayiln Sendimir-Statistical Analysis

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Figures

Figure 1

Preparation of Fibrous nanofilter - schematic illustration
Figure 2

Chemical crosslinking formed by hydrogen bond between PVA, nano cellulosic fiber and tea leaves microparticles.
Figure 3

(a) Raw cellulosic board (b) Micro cellulosic fibers

Figure 4

(a) Tea leaves microparticles (b) SEM & EDX
Figure 5

(a) FTIR of MCF (b) FTIR of FNF (c) TGA of MCF and FNF (d) AFM of FNF
Figure 6

(a) SEM and EDX of NCF (b) SEM and EDX of FNF

Figure 7

XPS analysis of FNF
Figure 8

(a) Hazardous metal adsorption of PVA, PVA:MCF and PVA:MCF:TLM (b) effect of pH on adsorption (c) effect of temperature on adsorption (d) effect of contact time on adsorption (e) Hazardous metal absorption SEM and EDX images of FNF and (f) Hazardous metal mapping image of FNF.