Highly Hydrophilic Electrospun Polyacrylonitrile/ Polyvinypyrrolidone Nanofibers Incorporated with Gentamicin as Filter Medium for Dam Water and Wastewater Treatment

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Abstract: The need for advancement in filtration technology has spurred attention to advanced materials, such as electrospun nanofiber membranes, for providing clean water at a low cost with minimum initial investment. Polymer nanofibers can be fabricated by using different techniques, such as template synthesis, self-assembly, drawing, phase separation, and electrospinning. Due to its distinctive properties, electrospinning has become a method of choice for fabricating nanofiber membranes quickly with minimal investment. In this study, polyacrylonitrile (PAN) was dissolved in dimethylformamide (DMF), and different weight percentages of polyvinylpyrrolidone (PVP) and gentamicin sulfate powder were added to the solution to fabricate nanomembranes via the electrospinning process. Gentamicin was added to remove bacteria and viruses and prevent fouling, while PVP was added to make the surface of the membrane hydrophilic for enhancing the filtration rate and efficiency. Two water samples were chosen for the filtration processes: dam water and city wastewater. For the dam water sample, PH, turbidity, TDS, Ca⁺⁺, Mg++, sulfates, nitrates, fluoride, chloride, alkalinity and silica were reduced to +3.64%, 89.6%, 6.52%, 10.5%, 9.96%, 5.16%, 17%, 19.5%, 6.63%, 1.43% and 63.5% respectively. The total coliforms and E. coli content were reduced to 4.1 MPN/100ml and 0 MPN/100ml, respectively with PAN containing 10 wt. % PVP and 5 wt. % Gentamicin. For wastewater sample, PH, turbidity, TDS, TSS, BODs, phosphate, ammonia, oil-greases and DO were reduced to + 3.62%, 79%, 6.33%, 84%, 68%, 1.70%, 15.8%, 0% and 6% respectively. The total coliforms and E. coli content were also lowered to 980 MPN/100ml and 1119.9 MPN/100ml, respectively with PAN containing 10 wt. % PVP and 5 wt. % Gentamicin. The morphology and dimensions of the nanofibers were observed using a scanning electron microscope (SEM). Both SEM and microscopic images of the nanomembrane before and after filtration proved that electrospun PAN nanofibers have superior water filtration performance.

Keywords: Nanotechnology, Electrospinning, Water Treatment, Total Coliform, *E. coli*, Turbidity, Total Suspended Solids (TSS).

1. INTRODUCTION

Polymeric nanofiber membranes have been receiving extensive attention worldwide for their application in nanotechnology, biotechnology, and many other fields [1-3]. Electrospinning is one of the simplest and more straight-forward techniques for generating nanosized fibers from a polymeric solution [4-6]. Nanomaterials have nanoscale dimensions that range from 1 to 100 nm, and often exhibit novel and significantly changed physical, chemical, and biological properties because of their structure, larger surface area per unit of volume, and quantum effects that occur at the nanoscale. These outstanding properties enhance the significance of polymeric nanofibers in numerous industrial applications, such as tissue engineering, wound dressing, molecular filtration, and many more [1,4, 7-11]. Electrospinning is a relatively easy process of producing fibers that range in size from

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micrometers (~100 µm) to nanometers (~3 nm) [1,12]. The advantages of electrospinning are low cost, high speed, vast material choices, fast operation, versatility, and small space requirements. In addition, this technique offers control over fiber diameter and microstructure. In the electrospinning process, a polymeric solution is initially held at the tip of a needle by the surface tension of the polymeric solution. When the applied voltage to the polymeric solution overcomes the surface tension, a charged jet initiates from the needle, follows a linear pattern for some distance, then undergoes a whipping or spiral motion, which is commonly referred to as bending instability of the electrified jet, and finally collects on a grounded screen placed at some distance from the needle [1, 4, 7, 8].

Nanotechnology has been recognized as a novel technology with the potential for playing a dominant role in water purification/treatment. Water treatment processes involve the use of several types of membranes such as microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF)

[13-16]. RO is capable of providing the purest water; however, currently an NF membrane has been considered a novel method in water treatment. It has the ability to quickly and economically remove total dissolved solids from the surface and ground water, pathogens (bacteria, virus, molds, and fungus), monovalent and multivalent anions and cations (water softening agents), salts, minerals, and other suspended nanoparticles [8,17]. The NF membrane has extensive applications in several industries such as beverage, food, textile, oil, chemical, and others. The pore size of the NF membrane can be as small as 1 nm in order to selectively remove larger molecules from smaller molecules and size the nanomaterials in different fractions [18-21].

Nanofiltration is highly effective in removing protozoa (such ascryptosporidium and giardia). Similarly, nanofiltration can remove bacteria (such ascampylobacter, salmonella, shigella, and Escherichia coli [*E. coli*]) effectively. Nanofiltration can also remove viruses (such asenteric virus, hepatitis A, norovirus, and rotavirus) effectively. However, nanofiltration is only moderately effective in removing chemicals. Membrane filtration can play a vital role in water purification, since conventional processes of water treatments such as coagulation, sedimentation, flocculation, and activated carbon, are unable to separate many pollutants to specific limits.

Hydrophilicity is an important factor relative to the wettability of membranes and development of lowpressure filters because the lower water contact angle of hydrophilic membranes will significantly reduce the capillary pressure of the filter media, and increase the flow rate of the liquid and separation ability of the suspended particles. In addition, it will greatly eliminate the biofouling and clogging of the filter media during the filtration process [7,8]. Polyacrylonitrile (PAN) can be used to produce ultra-thin and homogeneous nanofibers that exhibit a hydrophobic nature [22-28]. The wettability of the membrane surface depends on its microstructure and chemical nature; however, surface modification can be applied on the membrane to increase its hydrophilicity [29-33]. Polyvinylpyrrolidone (PVP) has outstanding wettability properties due to its high surface tension [34]. The purpose of adding PVP to a PAN polymeric solution is to make the membrane more hydrophilic in order to facilitate effective filtration. A homogeneous polymeric solution for electrospinning process can be made by dissolving PVP in an appropriate solvent, such as deionized (DI)water, dichloromethane (DCM), tetramethylammonium

chloride, and dimethylformamide (DMF) [35-39]. Several studies have mentioned the application of gentamicin as an antibiotic agent because of its capability of preventing or killing bacteria [40-42]. In this study, PVP was added indifferent weight percentages (0, 5, and 10 wt%) to PAN, and gentamicin was added in different weight percentages (0, 2.5, and 5 wt%) to the polymeric solution, and then this was electrospun to produce highly hydrophilic nanofiber membranes. The surface properties of the membranes were studied in relation to their filtration efficiency for different water suspensions.

All the latest equipments were employed in this study to measure different parameters in order to make this study a comprehensive one. Besides measuring TDS, conductivity, PH, dissolved oxygen, turbidity, TSS and COD, we also measure total alkalinity, silica, sulfates $(SO_4^{2^-})$, nitrates (NO_3^-) , fluoride (F^-) , and chloride (CI^-) , calcium (Ca^{2+}) , and magnesium (Mg^{2+}) , BOD, total coliform and *E. coli*. The nanomembrane was characterized by means of FTIR and Raman spectroscopy to determine the chemical nature before the filtration tests. SEM and microscopic images were also provided before and after the filtration.

2. EXPERIMENT

2.1. Materials

Polyacrylonitrile (PAN) with molecular weight 150,000g/mole (CAS no. 25014-41-9), Polyvinylpyrrolidone (PVP) with molecular weight 130,000 g/mole (CAS no. 9003- 39-8), Dimethylformamide (DMF) (CAS no. 68-12-2, 99.8%) and gentamicin sulfate (CAS no. 1405-41-0) were purchased from Sigma-Aldrich and used without any further purification.

2.2. Synthesis of PAN/PVP Nanofibers

Recently, electrospinning procedure has been used to produce polymer nanofibers embedded with additives such as anti-bacterial materials for water treatment and separation. Nanofibers have been gaining considerable attention due to their unique properties [43-46]. They are generally referred to as ultra fine fibers, possess some unique features, such as nanoscaled dimension in the cross-sectional area and macroscopic length on the axis of fibers. There fibers possess high surface area, flexibility and porous structure which allow much higher sites for separation processes [43-46].

In this study, PAN was dissolved in DMF at a percentage weight ratio of 10:90. Then, 0, 5, and 10

wt% of PVP and 0, 2.5, and 5 wt% of gentamicin was added into the PAN/DMF mixture. The purpose for using PVP and gentamicin was to increase the filtration rate and reduce membrane biofouling, respectively. Nine different polymeric solutions were created based on different percentages of PVP and gentamicin. All solutions were allowed to form homogeneous mixtures by stirring them on a hot plate for 1 hour at 75°C at 500 rpm. The fully mixed polymeric solution was then transferred into a 10-mL syringe having an inside diameter of 0.5 mm and placed in a KD Scientific syringe pump at a flow rate of 1 mL/hr. One end of a copper electrode with a 0.25-mm diameter was attached to a high DC supply at 25 kV, and the other end was attached to the syringe. A distance of 25 cm was maintained between the capillary tube and the collector screen, which was covered with aluminum foil. This experimental setup for the electrospinning process, as shown in Figure 1, was carried out under ambient conditions. The electrospun fibers were dried 24 hours before removing them from the aluminum foil.

2.3. Filter Setup

The filter setup used in this study, shown in Figure **2**, consisted of a porcelain Buchner funnel having an inner diameter of 90 mm, a rubber stopper with a hole to accept the Buchner funnel, and a filtering flask with a capacity of 1,000 ml. The flask was connected by a vacuum tube to the Millipore vacuum/pressure pump with two gauges. The vacuum gauge has a range from 0 to 30 in Hg, while the pressure gauge ranges from 0 to 160 psi.

2.4. Samples Selection

Two different samples—dam water and wastewater—were selected for this study. The most

important properties of dam water to be measured were pH, total dissolved solids (TDS), turbidity, conductivity, calcium (Ca²⁺), magnesium (Mg²⁺), total hardness, sulfates (SO₄²⁻), nitrates (NO₃⁻), fluoride (F⁻), chloride (Cl⁻), bromate (BrO₃⁻), total alkalinity, silica (SiO₂), total coliform bacteria, and *E. coli*. The most important properties of wastewater to be measured were pH, turbidity, TDS, conductivity, total suspended solids (TSS), chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), phosphate (PO₄³⁻), ammonia (NH₃-N), oil and grease, dissolved oxygen (DO), total coliform bacteria, and *E. coli*. The diversity in properties of the selected samples makes this study very useful and interesting.

2.4.1. Dam Water Sample

A dam is a storage structure that impounds water or underground streams. To be effective, it must remain stable during large storms and also provide water for irrigation, human consumption, industrial consumption, and hydropower. All developing countries, and especially countries in aridlocations such as Saudi Arabia, need to build dams in order to store rain water for later use [47]. Currently, almost all countries are engaged in designing wastewater treatment plants in order to reuse water in different sectors such as agriculture, landscape, industrial consumption, and human consumption [48]. A sample of dam water was taken from the Alzraib dam, which is located between the city of Tabuk and the Red Sea in Saudi Arabia. This dam is 200 m long and 7 m high. Alzraib valley is more than 45 km long and has many branches where rainwater gathers. At the onset of rain, a huge torrent of water starts to move through the valley, carrying with it a large amount of sand, mud, and rocks, which causes the dam water to become high in TDS and silica content.



Figure 1: Schematic view of electrospinning process.



Figure 2: Schematic view of filter setup.

2.4.2. Wastewater Sample

A sample of wastewater was taken from the Tabuk Sewage Treatment Plant (Tabuk STP), which is located in Tabuk. The Tabuk STP design capacity is 100,000 m³/day of raw wastewater. As can be seen in Figure **3**, Tabuk STP separates solids from the liquid in three major treatment stages: primary, secondary, and tertiary.

The primary treatment stage includes the following: a mechanical screen to trap solids and floating objects, a grit removal system to remove smaller particles such as grit and sand, and a degreasing unit to separate and remove oil and grease from the wastewater. The secondary treatment stage includes a large aeration tank with eight aerators to feed the bacteria for their own growth and reproduction, and four sedimentation tanks where more solids settle to the bottom and clean treated water is produced at the top. The tertiary treatment stage includes a sand filter, which is designed to remove most of the remaining impurities that were left during the secondary treatment. Disinfection with chlorine, the final step before



Figure 3: Wastewater treatment processes in Tabuk STP.

discharging the effluent, is a significant step because it protects the health of the people and animals. In this current study, gentamicin has been added to the nanofibers to replace the disinfection process. Lastly, the sludge treatment process includes two thickener tanks to allow the sludge to settle to the bottom and separate from the water for up to 24 hours, and a dewatering unit (belt press) for further sludge treatment to make it safer for the environment. Figure **4** and Table **1** show the water properties before and after each treatment stage in the Tabuk STP.



Figure 4: Wastewater before and after each treatment stage in Tabuk STP.

In this study, the electrospun PAN nanofibers with different wt% of PVP and gentamicin were used as the filter medium (membrane). PAN fibers were used as the membrane between the secondary and tertiary treatments. Wastewater from the sewage after the secondary treatment was allowed to pass through the PAN electrospun membrane before tertiary treatment. Results from the PAN membrane were compared to wastewater after tertiary treatment at Tabuk STP.

2.5. Analysis of Water and Wastewater Quality

Several water quality measuring devices were used in this study. The Hach sens ION5 (Hach Company, Loveland, CO, USA) was used to measure both TDS and conductivity. The Hach sens ION3™ (Cole-Parmer Instrument Company, Vernon Hills, IL, USA) was used to measure pH. The HachHQ30d (Hach Company, Loveland, CO, USA) was used to measure dissolved oxygen for wastewater samples. The Hach DR/890 colorimeter (Hach Company, Loveland, CO, USA) was used to measure turbidity, TSS, and COD. A HachDR/2010 spectrophotometer (Hach Company, Loveland, CO, USA) was used to measure ammonia (NH₃-N), total alkalinity, and silica. Ion chromatography (Metrohm AG Company, Herisau, Switzerland) was used to measure the heavy materials based on two categories: anions, and cations. Anions measured with this device included sulfates (SO_4^{2-}) , nitrates (NO_3^{-}) , fluoride (F), and chloride (CI). Cations measured by this same device were calcium (Ca²⁺), and magnesium (Mg^{2+}) . Figure **5** shows the instruments that were used to measure BOD₅: Lovibond incubator (Lovibond Water Testina Tintometer GmbH Group, Dortmund, Germany), and HachBODTrak[™] II (Hach Company, Loveland, CO, USA).

 BOD_5 is one of the most important factors to be measured in wastewater. A 460-ml quantity of the

Table 1: Water Properties before and after each Treatment Stage in Tabuk STP

Analysis	Influent Maximum Design	Influent	After Secondary Treatment	After Tertiary Treatment	Removal % (from Secondary to Tertiary Treatment)
pН	6-9	7.2	7.41	7.58	+2.29
Turbidity (NTU)	500	253	18	7	61.11
TDS (mg/l)	2500	2010	1943	1902	2.11
Conductivity (µS/cm)	5000	4112	3968	3881	2.19
TSS (mg/l)	500	251	18	4	77.78
COD (mg/l)	1000	672	30	14	53.33
BOD ₅ (mg/l)	600	265	18	6	66.67
Phosphate (PO ₄ ³⁻) (mg/l)	45	38	14	13	7.14
Ammonia (NH ₃ -N) (mg/l)	100	45	15	14	6.67
Oil-Grease (mg/l)	100	51	2	0	100
DO (mg/l)	nr	0	4	4	0

Note: average results in 2014.



Figure 5: Instruments used to measure BOD₅.

samples were prepared and cooled to 20°C, then transferred to BODTrak II bottles. A stir bar and two potassium hydroxide pellets were added to each of the bottles, which were then put on the BODTrak II chassis and transferred to inside the incubator. The incubator temperature was adjusted to 20°C, and the samples were kept in the incubator for five days, after which time the readings for each sample were taken. Bacteria in water, a common issue facing both developed and developing countries, is the most alarming source of disease in humans; therefore, its treatment and elimination is significant in water and wastewater treatment. Several techniques are commonly used to detect the existence of total coliform and E. coli in water: the "membrane filter," "multiple fermentation tube," and "most probable number" (MPN). In this study. the Quanti-Tray/2000 technique (IDEXX Laboratories Inc., Westbrook, ME, USA) was used to detect total coliform and E. coli. This technique takes advantage of other techniques that use the MPN, but it has a very high counting range (from 1 to 2,419) and 95% confidence limits. Figure 6 shows the Quanti-Tray/2000 process to detect total coliform and E. coli.

As shown in Figure **6**, the Quanti-Tray/2000 technique involves many steps. First, Colilert reagent was added to a 100 ml of water sample and shaken until completely dissolved. Then, the reagent/sample mixture was poured into a Quanti-Tray/2000 and sealed using the Quanti-Tray Sealer model 2X. The sealed tray was then placed in an incubator manufactured by Lenton Company (Hope Valley, Derbyshire, UK) at 35°C for 24 hours. Then, the number of positive yellow wells were counted, and the



Figure 6: Quanti-Tray/2000 technique: (a) Colilert reagent used to mix with 100 ml of water sample, and tray with mixture, (b) Quanti-Tray Sealer, (c) incubator used to keep sealed tray at 35°C for 24 hours, and (d) UV lamp cabinet to detect *E. coli* by counting positive fluorescence wells.

most probable number table was referred to in order to obtain the MPN for total coliform. Finally, *E. coli* was detected by placing a 365 nm UV light on the sealed tray in a dark environment and counting the positive fluorescence wells. For the last step, a UV lamp cabinet model CM-10A (Spectroline Company, Westbury, NY, USA) was used to detect *E. coli*.

3. RESULTS AND DISCUSSION

3.1. Water Contact Angle Measurement

The water contact angle values of PAN fiber samples were determined with an optical contact angle goniometer, purchased from KSV Instruments Ltd. (Model #CAM 100). This compact, video-based instrument is used to measure contact angles between 1° and 180° with an accuracy of $\pm 1^{\circ}$. Computer software provided by KSV Instruments Ltd. precisely measured and took pictures of the contact angles. Samples were dried in a vacuum overnight after removing them from the collector screen. Then they were placed on the goniometer sample holder, and a droplet of water was gently dropped on the sample from a syringe attached to the goniometer. Figure 7 of shows schematic views superhydrophobic, hydrophobic, hydrophilic, and superhydrophilic surfaces.

The contact angle measurements for the samples used in this study are shown in Figure 8. As can be seen, all samples are hydrophilic, having static water

contact angle less than 90°. The sample without PVP shows a higher water contact angle. However, the addition of PVP makes fibers hydrophilic due to the hydrophilic nature of PVP.

Hydrophobicity and hydrophilicity are terms related to the behavior of solid surfaces when placed in contact with water droplets. A hydrophobic surface is one on which a droplet of water forms a contact angle greater than 90°, whereas a hydrophilic surface is one on which a droplet of water forms a contact angle less than 90° [49-51]. Polymer surfaces with contact angles between 150° and 180° are called super-hydrophobic. This phenomenon is also known as the "lotus effect," which exhibits self-cleaning and anti-contamination features. The hydrophobicity or wettability of a membrane plays an important role in the performance of a membrane because a membrane with high wettability can wet the surface of a membrane and thereby increase the filtration efficiency [33]. Figure 8 shows that water droplets for PAN nanofibers with different percentage of PVP are spherical in shape indicating near superhydrophilic properties of nanofiber surface. As is seen in Figure 8a, the static water contact angle on the left side is 34.23° and on the right side 34.22° with a mean value of 34.22°. In Figure 8b, the static water contact angle on the left side is 23.85° and on the right side 23.12° with a mean value of 23.48°. In Figure 8c, the static water contact angle on the left side is 10.38° and on the right side 9.91° with a mean value of 10.15°. Gentamicin plays no role in



Figure 7: Schematic views of superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic surfaces (left to right).



Figure 8: Water contact angle values for electrospun nanofibers: (a) PAN + 0 wt% PVP + 5 wt% gentamicin, (b) PAN + 5 wt% PVP + 5 wt% gentamicin, and (c) PAN + 10 wt% PVP + 5 wt% gentamicin.



Figure 9: SEM images of electrospun nanofibers before filtration: (a) PAN + 0 wt% PVP + 0 wt% gentamicin, (b) PAN + 0 wt% PVP + 5 wt% gentamicin, and (c) PAN + 5 wt% PVP + 5 wt% gentamicin, and (d) PAN + 10 wt% PVP + 5 wt% gentamicin.

wettability of the PAN membrane. PVP has higher wettability characteristics since the surface tension of PVP is 68 mN/m.

3.2. SEM and Microscope Images

Figure **9** shows the SEM micrograms of a PAN nanomembrane used in this study. The average diameter of PAN fibers is around 100 nm. No significant change was observed when 5 wt% gentamicin was added, as can be seen in Figure **9b**; that is, gentamicin has no significant effect on the fiber diameter. A slight increase in fiber diameter was observed with an average fiber diameter of approximately 150 nm, after a 5wt% addition of PVP, as shown in Figure **9c**. The average diameter of the fibers increased substantially (200 nm) after a 10 wt% addition of PVP, as shown in Figure **9d**.

Figure **10** shows SEM images of nanofibers after filtration of dam water. As can be seen in all of these images, suspended particles, colloidal particles, and small metal particles are clearly visible. Figure **11** shows dam water before and after filtration. As shown,

the water after filtration does not contain any suspended particles and gases. The nanomembrane removes virtually all particles larger than 0.001 microns. Figure **12** shows SEM images of the nanofibers after wastewater filtration at various magnifications. The black arrows show some bacteria were removed after the filtration process.

These nanomembranes virtually remove all bacteria such as *E. coli*, coliform, salmonella, giardia, cryptosporidium, and other water-borne microorganisms that can cause such diseases as typhoid fever, flu, tetanus, polio, dysentery, cholera, meningitis, infectious hepatitis, and respiratory diseases. Figure **13** shows microscopic images of the nanomembrane before and after filtration.

As shown in Figures **13b** and **c**, suspended matter adheres to the surface of, or in the pores of, an absorbent filtration membrane. Filtration of contaminants depends largely on the amount of contaminant, size of contaminant particles, and degree of contaminant particle. The nanomembrane after wastewater treatment clearly shows a large amount of



Figure 10: Different SEM images of nanofibers after dam water filtrationat various magnifications.



Figure 11: Dam water before (left) and after filtration (right).

suspended particles, whereas the nanomembrane after dam water treatment clearly shows a lesser amount of suspended particles. The nanostructured membrane, preferably termed nanomembrane, can be used to reject suspended particles, bacteria, macromolecules, viruses, colloids, organic compounds, and multivalent ions. Therefore, they are mainly utilized for drinking water production (for water softening or disinfection),



Figure 12: Different SEM images of nanofibers after wastewater filtration at various magnifications (black arrows show some bacteria).



Figure 13: Microscope images: (a) electrospun nanofibers before filtration, (b) nanofibers after dam water filtration, and (c) nanofibers after wastewater filtration.

and the treatment of landfill leachate and industrial wastewater (decoloring). Other applications may be found in the dairy industry.

3.3. Fourier Transform Infrared Radiation Analysis

Fourier transform infrared radiation (FTIR) analysis is considered to be a useful tool for determining the chemical interaction of PAN. With the help of the spectra, it is possible to study the elaxation between chemical changes and strength [52]. The FTIR spectra of bulk PAN nanofibers and PAN fibers with 5 and 10 wt% of PVP are depicted in Figures **14**, **15**, and **16**, respectively.

The FTIR spectra of PAN fibers have many peaks, which relate to the existence of CH_2 , $C\equiv N$, C=O, C=O, and C-H bonds [52]. A peak is observed at 2,916 cm⁻¹, which relates to the C-H bonds in CH, CH_2 , and CH_3 [52]. Another peak observed at 2,243 cm⁻¹, which indicates the presence of nitrile (C=N) bonds, shows the existence of a nitrile group in the PAN chain [52].



Figure 14: FTIR spectra of bulk PAN nanofibers.

The intensity corresponding to 1,668 cm⁻¹ is due to the cyclic C=O peak for the methyl acrylate comonomer [53]. The peak corresponding to 1,456 cm⁻¹ is due to CH.

Figure **15** shows FTIR spectra of PAN with 5 wt% PVP. As can be seen, a peak is observed at 2,916 cm⁻¹, similar to that shown in Figure 14, which relates to the CH/CH₂ stretching vibration. Another peak is observed at 1,456 and is due to CH deformation of the cyclic CH₂ groups. A peak corresponding to 1,662 cm⁻¹ can also be seen in Figure **15**, which is a result of the contribution from C=O of the PVP film [54]. The vibrational band relating to the pyrrolidone C=O group is located at 1,662 cm⁻¹ and corresponds to C=O stretching of the PVP polymer film [54]. A peak corresponding to 534 cm⁻¹ could be attributed to the amide IV band.

Figure **16** shows FTIR spectra of PAN with 10 wt% PVP. As can be seen, the band relating to the pyrrolidone C=O group is located at 1,664 cm⁻¹. The vibrational band at 1,698 cm⁻¹ corresponds to C=O stretching of the PVP polymer film, and the absorption band located at 2,920cm⁻¹ indicates C-H asymmetric stretching of the CH₂. The band at 1,664 cm⁻¹, which is due to the vibration band of C=O, suggests that some H-bonding carbonyl groups exist in PVP [55]. The bands at 1,290 cm⁻¹ and 1,450 cm⁻¹ are attributed to C-N stretching vibration and C-H bending vibration of PVP, respectively [54].

3.4. Raman Spectra Analysis

Figure **17** depicts a typical Raman spectra of PAN fibers in the range of 160 to 3,160 cm⁻¹, showing a number of sharp peaks superimposed on a broad



Figure 15: FTIR spectra of PAN+5 wt% PVP nanofibers.



Figure 16: FTIR spectra of PAN+10 wt% PVP nanofibers.



Figure 17: Raman spectra of bulk PAN nanofibers.

feature over almost the entire region. It can be suggested that the entire spectra is due to secondorder Raman scattering, and only sharp peaks are firstorder Raman bands. The sharp peak at 2,990 cm⁻¹ is due to first-order Raman scattering, which is very sensitive to the crystalline structure and microstructure of the material. This peak indicates that the sample is highly crystalline.

No broadening in peaks were observed in the Raman spectra, either in pure PAN fibers (Figure 17) or PAN fibers with different wt% of PVP (Figures 18 and 19), which indicates that there is no breakdown of the long-range order of crystallinity in the samples. In fact, Raman spectra confirm a long-range order of crystallinity in the sample. Figures 18 and 19 show the Raman spectra of PAN with 5 and 10 wt% PVP,

respectively. As shown, the intensity of the Raman band corresponding to the C-N vibration band at 719 cm⁻¹ (Figure **18**) and 785 cm⁻¹ (Figure **19**) and C-C stretching vibration at 901 cm⁻¹(Figure **18**) and 897 cm⁻¹ (Figure **19**) is due to PVP. The bands at 1,109 cm⁻¹ (Figures **18** and **19**) are due to C-N stretching of pure PVP.

3.5. Chemical and Physical Analysis

3.5.1. Chemical and Physical Analysis of Filtered Dam Water Samples

Table **2** shows chemical and physical analysis of filtered dam water samples. The pH is the measurement of potential activity of hydrogen ions in the sample. The pH is positively correlated with electrical conductance and total conductivity. In the



Figure 18: Raman spectra of PAN+5 wt% PVP nanofibers.



Figure 19: Raman spectra of PAN+10 wt% PVP nanofibers.

present study, the average pH was found to be 7.53 after filtration of the dam water. The average turbidity of water after filtration was found to be 2.4 NTU, which is very encouraging, since many studies show that the turbidity value to be around 4 NTU after filtration. The TDS was found to be 3,150 mg/l. The electrical conductivity, or ability to conduct or transmit electricity, was found to be 6,351 µS/cm. Pure water is not a good conductor of electricity. Since the electrical current is transported by the ions in solution, the conductivity increases as the concentration of ions increases. The conductivity of drinking water is between 0.005 and 0.05 S/m. The prescribed limitation for hardness of drinking water is 300 mg/l. Results from the present study showed a hardness value of 394 mg/l. In the present investigation, it was observed that the sulfate concentration is much lower compared to IS10500. We observed a calcium concentration of 7.87 mg/l. The intake of excess fluorides causes dental, skeletal, and non-skeletal fluorosis. Fluorosis has been considered

one of the incurable diseases. Hence, prevention is its only solution. In the present study, the fluoride concentration was found to be 0.82 mg/l, which means that the sample is within the permissible limit. The acceptable limits for nitrates in drinking water is 10 mg/l, and the present study showed a nitrate concentration of 2.48 mg/l. The acceptable limit for sulfates in drinking water is 250 mg/l, and the present study showed a sulfate concentration of 77.87 mg/l. The acceptable limits for Ca⁺⁺ in drinking water is 75 mg/l, according to IS10500 standards, and the present study showed a Ca⁺⁺ concentration of 93.4 mg/l. The acceptable limits for Mg⁺⁺ in drinking water is 30 mg/l, according to IS10500 standards, and the present study showed a Mg⁺⁺ concentration of 39.3 mg/l. Silica, or silicon dioxide, is a compound of silicon and oxygen (SiO₂). This hard, glassy mineral substance occurs in a variety of forms, such as sand, quartz, sandstone, and granite. It is also found in the skeletal parts of various animals and plants. Silicon is the most abundant

Nanofibers	рН	Turbidity (NTU)	TDS (mg/l)	Cond. (µS/cm)	Ca⁺⁺ (mg/l)	Mg ⁺⁺ (mg/l)	T. Hardness (mg/l of CaCO₃)	Sulfates SO4 ²⁻ (mg/l)	Nitrates NO ₃ ⁻ (mg/l)	Fluoride F (mg/l)	Chloride Cl ⁻ (mg/l)	Total Alkalinity (mg/l)	Silica SiO₂ (mg/l)
Raw Water Before Filtration	7.27	23.1	3370	6825	104.4	43.65	440	82.109	2.989	1.024	1786.1	134.6	86.44
PAN+0 wt% PVP + 0 wt% Gent.	7.52	1.82	3112	6288	92.1	38.8	389	76.8	2.437	0.882	1647.12	132.4	30.51
PAN+0 wt% PVP + 2.5 wt% Gent.	7.59	1.66	3098	6201	94.9	40.06	401	75.65	2.401	0.913	1639.98	131	29.32
PAN+0 wt% PVP + 5 wt% Gent.	7.61	1.61	3068	6198	94.2	39.72	398	75.1	2.551	0.827	1622.68	133.4	30.8
PAN+5 wt% PVP + 0 wt% Gent.	7.54	1.92	3176	6414	88	36.9	371	77.88	2.525	0.733	1682.76	131.8	31.3
PAN+5 wt% PVP + 2.5 wt% Gent.	7.49	2.33	3161	6374	91.04	38.3	385	80.1	2.389	0.801	1673.11	134.2	31.81
PAN+5 wt% PVP + 5 wt% Gent.	7.5	2.37	3153	6355	93.33	39.4	395	79.34	2.4	0.776	1670.03	132.9	32.4
PAN+10 wt% PVP + 0 wt% Gent.	7.59	3.67	3202	6462	96.32	40.87	408	79.6	2.449	0.787	1695.02	133.6	32.05
PAN+10 wt% PVP + 2.5 wt %Gent.	7.51	2.92	3191	6433	95.1	40.3	403	79.31	2.532	0.863	1688.41	132.3	33.15
PAN+10 wt% PVP + 5 wt% Gent.	7.46	3.27	3193	6439	95.7	39.4	401	77.05	2.605	0.841	1690.2	131.7	32.9
Average	7.53	2.4	3150	6351	93.4	39.3	394	77.87	2.48	0.82	1667.7	132.6	31.58
Removal %	+ 3.64	89.62	6.52	6.94	10.5	9.96	10.33	5.16	17.14	19.46	6.63	1.49	63.46

 Table 2:
 Chemical and Physical Analysis of Filtered Dam Water Samples

element on earth after oxygen, which explains why most water supplies contain some traces of silica. All natural water supplies contain some dissolved silica, and most also contain suspended or colloidal silica. In solution, silica can exist as silicic acid or silicate ion, depending upon the pH. The silica content in natural water is commonly in the range of 5 to 25 mg/l, although concentrations over 100 mg/l occur in some areas. This study shows a silica content of 31 mg/l, which is very close to the acceptable limit.

3.5.2. Chemical and Physical Analysis of Filtered Wastewater Samples

Table **3** shows the chemical and physical analysis of filtered wastewater samples. In the present study, the average pH of the wastewater after filtration was found to be 7.70. The average turbidity of water after filtration was found to be 14.22 NTU. The TDS was found to be 1,589 mg/l. The electrical conductivity, or ability to conduct or transmit electricity, was found to be 3,219 μ S/cm. Total suspended solids, or particles larger than 2 microns, are generally found in water. Any particle smaller than 2 microns (average filter size) is considered a dissolved solid. Most suspended solids are made up of inorganic materials, although bacteria and algae can also contribute to the total solids concentration. These solids include anything floating in

the water, from sediment, silt, and sand to plankton and algae. Organic particles from decomposing materials can also contribute to the TSS concentration. As algae, plants, and animals decay, the decomposition process allows small organic particles to break away and enter the water as suspended solids. Even chemical precipitates are considered a form of suspended solids. Total suspended solids are a significant factor in observing water clarity. The higher content of TSS makes water less clear. Biochemical oxygen demand and chemical oxygen demand are two different ways to measure how much oxygen the water will consume when it enters the recipient. In both cases, the oxygenconsuming substances are mainly of organic origin. These substances should be reduced to a minimum in the wastewater treatment plant. Industries normally focus more on the removal of COD and municipalities concentrate more on the removal of BOD. The excess content of phosphorus in water leads to extensive algae growth (eutrophication). The phenomenon of eutrophication usually decreases the water quality and as a result may significantly increase the cost of water treatment at treatment plants for surface water. The load of phosphorus discharged to receiving waters comes from various sources, the main sources of which are agricultural use of fertilizers, domestic and industrial wastewater, and atmospheric deposition. The

average phosphate concentration after filtration was found to be 34.43 ml/g. Ammonia toxicity varies by temperature and by pH of water. Natural levels in ground waters are usually below 0.2 mg of ammonia per liter. Higher natural contents (up to 3 mg/l) are found in strata-rich humic substances or iron or in forests. Surface waters may contain up to 12 mg/l. Ammonia may be present in drinking-water as a result of disinfection with chloramines. The presence of ammonia at higher than geogenic levels is an important indicator of fecal pollution. Grease is hydrophobic, which means that it can float on the surface of water. Large amounts of grease in wastewater can cause pipe lines to clog, thereby restricting the flow of wastewater. No grease content was found in the filtered wastewater sample in our study. The measurement of dissolved oxygen is also very important. A concentration of 5mg/l DO is generally recommended. Our study shows a DO concentration of 5.70 mg/l.

Generally, the most important factors that must be considered for measuring the quality of filtered wastewater are turbidity, TSS, COD, and BOD. By using a PAN electrospun membrane, the turbidity, TSS, COD, and BOD were reduced by 78.57%, 83.33%, 28.44%, and 67.62%, respectively. Household kitchens and various industries such as the food industry is one of the most important sources of oil that mixes with wastewater. Oil contains toxic and harmful elements of the environment and pose a major threat to human and animal health [56]. Therefore, it is significant to remove oil through several methods such as nanofibers membranes. Oil and grease were completely removed. A similar study by Makaremi *et al.* [12] showed similar results with PAN nanofibers exhibiting superior oilwater separation.

3.6. Bacterial Analysis

3.6.1. Bacterial Analysis of Filtered Dam Water Samples

In underground and surface water, total coliform is generally very high, while *E. coli* is usually low. However, the waste of some animals and birds is a source of *E. coli* in surface water. Therefore, as shown in Table **4**, a raw dam water sample shows a low content of *E. coli* and a high content of total coliform. *E. coli* is a sub-group of the fecal coliform group. It is generally found in the intestines of warm-blooded animals (cows, chickens, and dogs). It consists of up to 1% of bacteria biomass. Sewage may contain many types of disease-causing organisms. Fecal coliform bacteria is associated with human or animal waste. It usually lives in intestinal tracts, and its presence in

Nanofibers	рН	Turbidity (NTU)	TDS (mg/l)	Cond. (µS/cm)	TSS (mg/l)	COD (mg/l)	BOD₅ (mg/l)	Phosphate PO ₄ ³⁻ (mg/l)	Ammonia NH₃-N (mg/l)	Oil-Grease (mg/l)	DO (mg/l)
Raw Water Before Filtration	7.45	42	1658	3356	36	55	21	35.3	19	2	6.2
PAN+0 wt% PVP + 0 wt% Gent.	7.52	18	1599	3238	14	33	10.1	35.1	18	0	5.52
PAN+0 wt% PVP + 2.5 wt% Gent.	7.71	17	1597	3229	12	27	9.2	34.2	17	0	5.48
PAN+0 wt% PVP + 5 wt% Gent.	7.77	15	1604	3247	11	22	8.5	34.6	17	0	5.61
PAN+5 wt% PVP + 0 wt% Gent.	7.55	18	1587	3217	9	36.9	9.4	34.9	17	0	5.78
PAN+5 wt% PVP + 2.5 wt% Gent.	7.78	15	1607	3253	8	38.3	9	33.5	16	0	6.05
PAN+5 wt% PVP + 5 wt% Gent.	7.76	11	1591	3221	8	39.4	8.1	35	17	0	5.43
PAN+10 wt% PVP + 0 wt% Gent.	7.80	14	1601	3245	8	40.87	9.6	33.8	18	0	5.66
PAN+10 wt% PVP + 2.5 wt %Gent.	7.68	11	1570	3179	8	40.3	7.3	34.1	16	0	5.92
PAN+10 wt% PVP + 5 wt% Gent.	7.72	9	1553	3148	6	39.36	6.8	34.7	16	0	5.83
Average	7.70	14.22	1589.89	3219.67	9.33	35.24	8.67	34.43	16.89	0	5.70
Removal %	+3.62	78.57	6.33	6.20	83.33	28.44	67.62	1.70	15.79	100	5.97

 Table 3:
 Chemical and Physical Analysis of Filtered Wastewater Samples

Nanofibers	Total Coliforms (MPN/100ml)	<i>E. coli</i> (MPN/100ml)
Raw Water Before Filtration	>2420	14
PAN+0 wt% PVP + 0 wt% Gent.	1120	5
PAN+0 wt% PVP + 2.5 wt% Gent.	547.5	2
PAN+0 wt% PVP + 5 wt% Gent.	8.4	0
PAN+5 wt% PVP + 0 wt% Gent.	1203.3	4
PAN+5 wt% PVP + 2.5 wt% Gent.	488.4	2
PAN+5 wt% PVP + 5 wt% Gent.	5.2	0
PAN+10 wt% PVP + 0 wt% Gent.	1046.2	4
PAN+10 wt% PVP + 2.5 wt %Gent.	456.9	1
PAN+10 wt% PVP + 5 wt% Gent.	4.1	0

Table 4: Bacterial analysis of filtered dam water samples	es.
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drinking water is a strong indication of recent sewage or animal waste contamination. E. coli is one of hundreds of strains of the bacterium E. coli. Although most strains are harmless and live in the intestines of healthy humans and animals, this strain produces a powerful toxin and can cause severe illness [57,58]. Infection often causes severe bloody diarrhea and abdominal cramps; sometimes the infection causes non-bloody diarrhea. In some people, particularly children under five years of age and the elderly, the infection can also cause a complication called hemolytic uremic syndrome, in which the red blood cells are destroyed and the kidneys fail. In this study, the Quanti-Tray/2000 technique by IDEXX was used for both total coliform and E. coli analyses. Many recent studies have used this technique because it is accurate and has a high confidence limit [59].

As can be seen in Table **4**, PAN fibers with 10 wt% PVP and 5 wt% gentamicin showed remarkable results, with total coliform concentration reduced to 4.1 MPN/100ml and *E. coli* concentration reduced to 0. However, PAN fibers with 10 wt% PVP and 2.5 wt% gentamicin also showed higher removal of total coliform and *E. coli*, while PAN fibers with 10 wt% PVP and 0 wt% gentamicin showed less bacteria removal.

3.6.2. Bacterial Analysis of Filtered Wastewater Samples

Contrary to the raw dam water sample, the raw wastewater sample had a high number of *E. coli*, since human waste is also considered to be an important source of *E. coli*. The total number of both *E. coli* and total coliform exceeded 5,000 MPN/100 ml; however, the MPN table (Table **5**) shows 2,420 MPN/100 ml as the maximum number. Table **5** also shows the bacterial

analysis of filtered wastewater samples. As can be seen, the concentration of *E. coli* and total coliform is much higher compared to filtered dam water. Many studies have been conducted on bacterial removal employing different techniques. Lev et al. [60] demonstrated an E. coli removal method in wastewater by employing electrospun polyurethane nanofibers. As shown in Table 5, PAN fibers with 10 wt% PVP and 5 wt% gentamicin showed better results, with the total coliform concentration reduced to 980.4 MPN/100ml and the E. coli concentration reduced to 1,119.9 MPN/100 ml. Fecal coliform tests were performed in order to serve as quantitative indicators of the extent of fecal contamination in dam water and wastewater. The presence of E. coli is considered to be a specific indicator of fecal contamination and reflects the possible presence of enteric pathogens. The purpose of this study was to collect quantitative data on E. coli and total coliform so that it could be used for establishing an E. coli-based wastewater standard to help in protecting public health.

4. CONCLUSIONS

The necessity of meeting the rising demand of clean drinking water has led to increased attention in advanced nanosized materials, such as electrospun nanomembranes, as a solution for providing clean drinking water at a low cost. In this study, PAN nanofiber membranes embedded with PVP and gentamicin were used to filter dam water and wastewater. PVP was added to make the membrane hydrophilic, while gentamicin was added in order to remove bacteria and other microorganisms in order to eliminate fouling. The produced nanofibers were characterized using FTIR, Raman spectroscopy and

Nanofibers	Total Coliforms (MPN/100ml)	E. coli (MPN/100ml)	
Raw Water Before Filtration	>2420	>2420	
PAN+0 wt% PVP + 0 wt% Gent.	>2420	>2420	
PAN+0 wt% PVP + 2.5 wt% Gent.	>2420	>2420	
PAN+0 wt% PVP + 5 wt% Gent.	1986.3	1732.9	
PAN+5 wt% PVP + 0 wt% Gent.	>2420	>2420	
PAN+5 wt% PVP + 2.5 wt% Gent.	1732.9	>2420	
PAN+5 wt% PVP + 5 wt% Gent.	1203.3	1553.1	
PAN+10 wt% PVP + 0 wt% Gent.	>2420	>2420	
PAN+10 wt% PVP + 2.5 wt %Gent.	1413.6	1986.3	
PAN+10 wt% PVP + 5 wt% Gent.	980.4	1119.9	

Table 5: Bacterial Analysis of Filtered Wastewater Samples

SEM in order to ascertain the chemical nature of the fibrous membrane prior to the filtration tests. Due to their nanosized pores, these nanomembranes virtually reduced bacteria such as *E. coli* and total coliform bacteria to a significant level. Generally, the most important factors that must be considered for measuring the quality of filtered water are turbidity, TSS, COD, and BOD. These nanomembranes reduced all these factors to a significant level.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Kansas NSF EPSCoR (# R51243/700333) and Wichita State University for financial and technical support of the present work.

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Received on 01-03-2016

Accepted on 06-04-2016

Published on 25-07-2016

DOI: http://dx.doi.org/10.6000/1929-6037.2016.05.02.1

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