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Development and application of electrospun modified polyvinylidene fluoride (PVDF) nanofibers membrane for biofouling control in membrane bioreactor

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ABSTRACT

Polyvinylidene fluoride (PVDF) membrane possesses the chemical property of hydrophobicity. The hydrophobic solutes are easily adsorbed and deposited on the membrane surface due to hydrophobic–hydrophobic interaction causing the membrane blocking and lead to severe biofouling and cut down the membrane's life. An innovative nano-fibrous membrane was developed by modifying the PVDF matrix with the blending of cellulose acetate and using co-electrospinning with nylon-6 in order to minimize the hydrophobic nature of the membrane. The modified and non-modified PVDF membranes were prepared and examined using the bench-scale setup for biofouling examination. The sessile drop method was used to determine the extent of reduction in water contact angle from 141° to 125°. It was found that biofouling reduced significantly in the case of the modified PVDF membrane causes an increase in water flux from 55 to 80 Lm^{-2} h.

Keywords: Electrospun nanofiber membranes; Biofouling; Membrane bioreactor; Modified polyvinylidene fluoride

1. Introduction

The industrial and municipal wastewaters not only pose a threat to public and environmental health but also contribute to the high costs of tertiary treatment by using membrane technology. Various wastewater treatment technologies are used such as aerated lagoon, activated sludge process, and advanced oxidation pond, etc. Membrane bioreactor (MBR) is considered the most important innovative technology for wastewater treatment [1]. It contributes to overcome the drawbacks of the conventional activated sludge processes [2].

Polyvinylidene fluoride (PVDF)–(CH2CF2)*n*– has been used as a membrane material for the application of wastewater treatment. In recent years, PVDF has become one of the membrane materials for wastewater treatment applications [3]. As compared to other materials such as polyethersulfone, polysulfone the PVDF possess excellent chemical resistant property, high thermal stability and high mechanical strength [4]. However, PVDF possesses a high degree of hydrophobicity and relatively low surface energy, which makes the PVDF membranes susceptible to biofouling, especially when treating aqueous influents containing protein, oil, and other types of organic foulants. Membrane biofouling is a phenomenon of attachment of biomass on membrane surface which forms a cake layer onto and into the membrane surface; thus, it reduces membrane efficiency and increases operational cost and thereby reduces its overall performance. Biofouling contributes to more than 45% of all membrane fouling [5].

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Biofouling is the Achilles heel in the MBR technology since microorganisms available in feed water can reproduce over time even if 99.9% of them are removed, yet there remain enough cells that may grow at the expense of biodegradable substances in the feed water [6]. Biofilms are the mixture of bacterial cells surrounded in an extracellular polymeric matrix/polysaccharides (EPS) made up of proteins nucleic acids and polysaccharides [7]. The high hydrophobicity of polypropylene membrane easily causes biofouling due to the biofilm formation [8]. In a MBR, EPS plays a major role in biofouling and has been divided into bound and free EPS [9]. A polysaccharide is the main cause of fouling due to the adsorption on the membrane surface by the growth of microorganisms to form a biofilm [10]. Soluble microbial products (SMPs) are the predominant foulants determining fouling extent in MBRs. The fouling behaviors of SMPs during the initial operational period of a MBR was found that, although being low content, SMPs rather than sludge particulates preferentially adhered to membrane surface to accumulate a gel layer, and moreover, specific filtration resistance of SMPs was approximately 700 times larger than that of the sludge particulates at operational day [11]. Biofouling is considered as an abiotic form of organic fouling, while fouling caused by organic matter derived from microbial cellular debris is considered as an abiotic form of biofouling [12]. The organic matter, such as proteins available in the wastewater, is easily adsorbed by the PVDF membrane due to its hydrophobic nature; and because of this phenomenon, the PVDF membrane pores are partially or completely chocked [13]. In addition, the hydrophobic nature of PVDF can cause a huge problem in wetting during the filtration process. By the addition of hydrophilic materials to the PVDF membranes, which enhance the wettability and decreases fouling potential [14].

Nanotechnology enables great potential in advancing wastewater treatment to improve treatment efficiency. Nanofibers membrane possess excellent properties such as large surface area, unique texture and porosity [15]. The application of nanotechnology in the wastewater treatment process can overcome major problems faced by existing treatment technologies as well as it also provides new treatment capabilities that could allow economical utilization of unconventional water sources to expand the water supply [16]. The blending of polymers, for the preparation of membrane, is a new trend to improve antifouling properties, polymer to polymer interaction provides information about the nature of interaction [17]. The miscibility of solvents blend are varied from solvent to solvent [18] and the mixture of polymers are considered as immiscible without any chemical interactions between them [19].

An approach is presented in the current study nanofiber PVDF membrane converted into biofouling-resistant PVDF membranes by modifying the synthesis recipe and fabricated by electrospinning. The membrane was synthesized by blending PVDF polymer with cellulose acetate polymer (CAP) and co-electrospinning of nylon-6 was carried out. The different interactions are possible between blends due to hydrogen bonds, donor-acceptor interactions between carbonyl groups and Fluorine in PVDF or co-electrospinning in nylon-6.

The blending of PVDF with cellulose acetate (CA) increased the enthalpy of mixing, decreased the thermodynamic compatibility and increase both amorphous structure and surface pore size which results in higher water flux [20].

The performance of the newly developed biofouling-resistant PVDF membrane was assessed by comparing it with a non-modified PVDF membrane. The modified membranes have higher water flux, lower water contact angle and reduction in biofouling as compared to non-modified PVDF nanofibers membrane. This study demonstrated that the membrane prepared by combining CAP and nylon-6 with PVDF polymer caused a reduction in hydrophobicity, consequently, the synthesized biofouling-resistant PVDF membrane was applied in MBR for wastewater treatment and the results are presented in the paper.

2. Materials and methods

2.1. Materials

PVDF pellets of 5 mm (MW~534000) has been purchased from Goodfellow Cambridge Ltd., (England) and its solvents such as acetone, N,N-dimethylformamide (DMF) and CAP having molecular weight 30 kDa and 39% acetyl content and nylon-6 all were purchased from Sigma-Aldrich Company, (USA).

2.2. Synthesis of electrospun non-modified PVDF and modified PVDF membrane

2.2.1. Synthesis of non-modified membrane

The non-modified membranes were made through the electrospinning method. PVDF polymer 18% (w/w) were dissolved with binary solvents of DMF and acetone at equal volume ratio through procedure reported previous literature [21] and mixed by vigorously stirrer speed at a temperature of 80°C for 5 h in an airtight glass bottle. The electrospinning conditions and polymer composition is mentioned in Tables 1 and 2. The polymers were then injected with a plastic syringe of 3 mL attached to the capillary tip which consists of an inner diameter of 0.6 mm.

Table 1
Electrospinning parameters for non-modified polyvinylidene fluoride membranes

Solution			Ambient condition	Electrospinning parameters		
Polymer	Solvents	Con. (%)	Temp. (°C)	Humidity (%)	App. voltage (KV)	Distance (cm)
Polyvinylidene fluoride	Dimethylformamide/ acetone	18	80°C	40–45	20	10

Table 2
Electrospinning parameters for modified polyvinylidene fluoride membranes

Solution		Ambient condition		Electrospinning parameters		
Polymer	Solvents	Con. (%)	Temp. (°C)	Humidity (%)	App. voltage (KV)	Distance (cm)
Polyvinylidene fluoride	Dimethylformamide/acetone	18	80°C	40–45	20	10
Cellulose acetate		18				
Nylon	Formic acid	22				

The angle of the syringe was 11° from the abscissa. The negative terminal was connected to the ground metallic collector while the positive terminal was connected to copper wire and dipped into the PVDF solution rotating at the speed of 16 rpm. A distance between tip and collector was adjusted to 10 cm and DC voltage was applied at 20 kV. The non-modified PVDF nanofibers were deposited continuously over a collector that was wrapped with aluminum foil to obtain the desired thickness of 150–160 μm. After the electrospinning, the non-modified PVDF membranes were peeled out from the collector and dried at room temperature for 24 h.

2.2.2. Synthesis of the modified membrane

Similarly modified nanofibers membrane were made by blending PVDF solution with cellulose acetate and co-electrospinning with a nylon-6 solution in a ratio of 80:20 and 70:30 by increasing the concentration of cellulose acetate to increase the hydrophilicity of membranes. The parameters of electrospinning of modified PVDF membranes are also given in Table 2.

2.3. Characterization of nanofiber membranes

To examine the morphology, the non-modified PVDF and modified PVDF nanofiber membranes were characterized using the scanning electron microscopy (SEM) technique.

The SEM images were generated with voltages of 10 kV, the working distance was kept at 4-mm and a digital micrometer having measuring efficiency up to 1 μm was used for the measurement of the average thickness of modified and non-modified PVDF membrane. Further, it was important to determine the hydrophilicity of both membranes. The sessile drop method was used for the measurement of hydrophilicity and hydrophobicity of both membranes, and it was found that due to the presence of cellulose acetate and nylon-6 in modified nanofibers membranes and larger porosity, it has a lower contact angle and higher water permeability. The apparent porosity and apparent density of modified and non-modified PVDF membrane were calculated using Eqs. (1) and (2) [22].

Furthermore, the water flux test was performed and it confirms that due to the hydrophilicity and larger porosity of the modified nanofibers membrane, it has the highest water flux as compared to non-modified PVDF nanofibers membranes. It was also found that increasing the concentration of cellulose acetate in PVDF solution caused an increase in hydrophilicity of membranes.

$$A_d\left(\frac{\text{g}}{\text{cm}^3}\right) = \frac{N_f(\text{g})}{M_t(\text{cm}) \times M_a(\text{cm}^2)} \tag{1}$$

$$M_p = 1 - \frac{A(\text{g/cm}^3) \times 100\%}{B_d\left(\frac{\text{g}}{\text{cm}^3}\right)} \tag{2}$$

where A_d is the membrane apparent density, N_f is the nanofibers membrane mass, M_t is the membrane thickness, M_a is the membrane area, M_p is the membrane porosity and B_d is the bulk density of the mixture.

2.4. Membrane permeability

The membranes piece were cut from the large sheets of non-modified PVDF and modified PVDF nanofibre membranes according to the size of the vessel, and synthetic wastewater was passed from both membranes and flux rate was calculated through dead-end filtration setup at constant pressure by using the following equation as reported [23].

$$J = \frac{V}{A \times \Delta T} \tag{3}$$

where J is a total flux, L m^{-2} h; V is permeated volume, L; A is an area, m^2 and T is the time, h.

From the above equation, it is found that modified membrane due to higher hydrophilicity and larger porosity it has the highest water flux rate as compared to non-modified PVDF membrane as shown in Fig. 6.

2.5. Membrane biofouling test

In order to determine the biofouling of non-modified PVDF and modified PVDF nanofibers membranes, a dead-end filtration experiment was performed using the system known as Amicon Cell 200 ml (Amicon USA) experimental setup as shown in Fig. 1. From the large sheet of membranes, a small piece of the membrane of 28.31 cm^2 was cut according to the size and shape of the vessel, this piece of material has the identical characteristic as it is installed in the laboratory as a lab-scale model.

The synthetic wastewater was prepared as shown recipe in Table 3 in which the humic acid of 25 mg, 20 g of sodium alginate, 25 mg of bovine serum albumin (BSA)

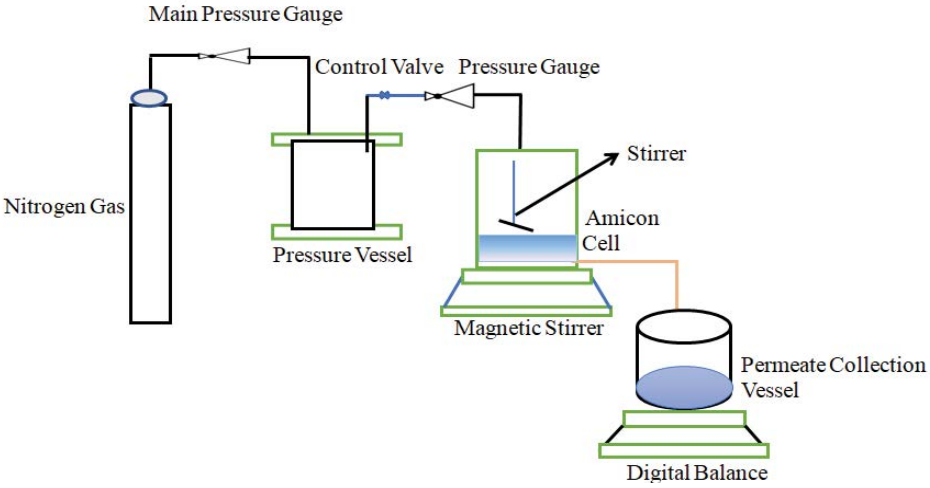

Fig. 1. Schematic showing the dead-end filtration setup.

Table 3
Synthetic wastewater prepararion and its composition for biofouling test

Material/parameter	Quantity/condition
Distilled water	800 mL
Temperature	22°C
Pressure	10 psi
Stirring speed	10 rpm
Sodium alginate	20 g
Humic acid	25 mg
Filtered sludge	20 mL
Bovine serum albumin	25 mg
Time	30 min

were used, and for filtration 1.45 µm filter paper was used. The dung sludge filtered with 1.45 µm filter paper to remove suspended solids, and all chemicals are mixed with distilled water of 800 mL and stirred for 3 h in order to get homogeneity of the mixture. After mixing, this solution was placed for 10 days in a vessel in order to increase the bacterial growth and finally, the membrane biofouling tests were performed by using non-modified and modified nanofibre membranes. The setup of the dead-end filtration system can be seen in Fig. 1. The filtration was performed using a stirred batch cell test. Nitrogen gas was introduced in the vessel to keep a constant transmembrane pressure (TMP) of 10 psi. The permeate generation was measured at the outlet using a balance. The flux decline in case of the non-modified PVDF was first then with modified PVDF membrane as shown in Fig. 1.

3. Results and discussion

3.1. Morphology of nanofibers

The surface morphology of non-modified PVDF and modified PVDF membranes was observed by using SEM. The non-modified PVDF membrane is shown in Figs. 2a and b the uniform, smooth and bead free nanofibers membranes, however in Figs. 2c and d the nanofibers roughness were observed on the modified membranes it may be due to the blending of cellulose acetate or nylon-6, the average diameter of both membrane nanofiber was calculated through image – J Software and found that modified PVDF nanofibers membrane has higher average diameter than non-modified PVDF membrane, this may be due to the blending of cellulose acetate and co-electrospinning of nylon-6 with PVDF polymers.

It is shown in Figs. 2e and f from both histograms that non-modified PVDF fibers have an average diameter of 610 nm, however, the modified PVDF fibers have a diameter of 880 nm.

The causes of the increase of the diameter of nanofibers are due to the increase of applied voltages [20]. Another literature [24] shows that the most important parameters which affect the fiber diameter are solution viscosity, higher viscosity results in higher fibers diameter.

Since the diameter of modified and non-modified PVDF Nanofibers varies, so it is crucial to know the porosity of the membranes, by calculating the apparent density of Nanofibers membrane and individual bulk densities of polymers, the porosity of modified and non-modified membranes were measured as in Table 4. It has been found that the porosity of non-modified membrane was 83.6% by addition of cellulose acetate and nylon-6 then porosity of membrane was increased to 92.5%.

3.2. Fourier-transform infrared spectra of non-modified and modified PVDF membrane

Fourier-transform infrared spectroscopy (FTIR) of the non-modified PVDF, nylon-6, cellulose acetate and modified PVDF nanofibers are shown in Fig. 3, in non-modified PVDF nanofibers. The band that appears at 642 cm^{-1} are due to the asymmetric stretching, at 1,067 and at 869 cm^{-1} are due to the CH_2 in and out of a plane in PVDF nanofibers [25]. The two absorption bands are observed in PVDF nanofibers at 1,169 and 1,400 cm^{-1} due to the CF_2 group [26].

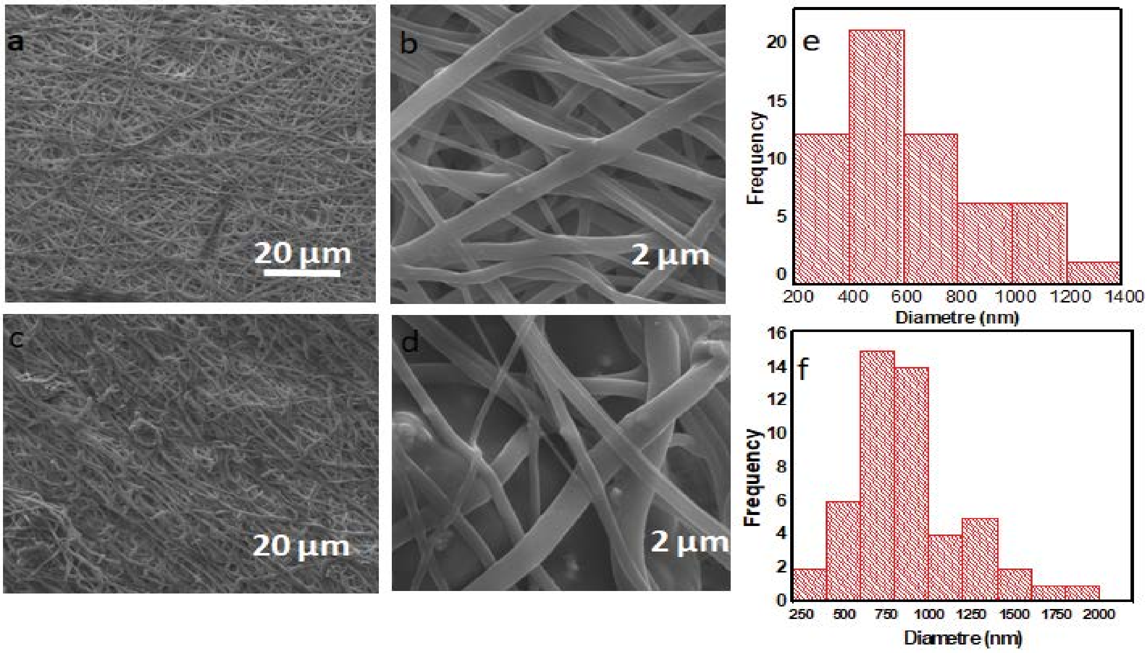

Fig. 2. (a and b) Scanning electron microscopy images for non-modified PVDF membrane, (c and d) modified membrane (PVDF/CA/nylon-6), and (e and f) shows the diameter distribution of non-modified and modified PVDF membrane.

Table 4
Porosity of modified and non-modified polyvinylidene fluoride membrane

Nanofibrous membrane	Porosity%
Modified polyvinylidene fluoride	92.5
Non-modified polyvinylidene fluoride	83.6

The bands of cellulose acetate occurring at 1,727 cm^{-1} are due to C=O symmetrical stretching of an acetyl group), 1,368 cm^{-1} (C–H deformation), 1,221 cm^{-1} (C–O stretching of ester group), 1,029 cm^{-1} (C–O–C cyclic ether bond), and 901 cm^{-1} (CH bending) in the CA [27].

However in the FTIR spectra of nylon-6, the bands at 2,931 cm^{-1} are CH$_2$ symmetric stretching, 1,645 cm^{-1} are Amide group and at 1,078 cm^{-1} C–C stretching [28]. Accordingly in case of modified PVDF the vibration band occurred due to symmetrical stretching caused by (C=O acetyl group) at 1,725 cm^{-1}, (C–H deformation) at 1,368 cm^{-1}, (C–O stretching of ester group) at 1,221 cm^{-1} is due to the presence of CA. However, the bands (N–H stretching hydrogen bond) at 3,300 cm^{-1}, (CO–NH amide group) at 1,645 cm^{-1} these bands are due to the presence of nylon-6 so it can easily be seen that the CA and nylon-6 were successfully incorporated into the modified PVDF membrane.

3.3. Water contact angle of non-modified PVDF and modified PVDF membranes

Hydrophilicity and hydrophobicity of non-modified PVDF and modified PVDF membranes have been calculated through the Sessile Drop Method as reported [29]. And contact angle was used to measure the hydrophilicity of the membrane [30]. With the help of a syringe a droplet, water was placed on to the membrane surface and the contact angle was measured, the five separate measurements of each membrane were calculated.

The decrease of contact angle value was observed in modified PVDF/CA/nylon-6 as compare to non-modified PVDF membrane attribute to CA and nylon-6 into PVDF matrix. The contact angle of the non-modified PVDF membrane is 141° was much higher as compared to modified PVDF with CA and nylon-6 having 125°. The ability of membrane for wettability is the function of surface roughness and hydrophilicity of membrane as reported in [31]. It was also observed that by addition of a higher concentration of hydrophilic polymers into the PVDF matrix can increase further its hydrophilicity. This value increases further; this may be attributed to the particle aggregation resulting in the non-uniform distribution of particles within the membrane matrix [32]. As shown in Figs. 4a and b it was also indicated that modified PVDF membrane consists of the higher concentration of hydrophilic polymer incorporated into PVDF matrix result in a decrease of contact angle hence leads to antifouling performance as compare to non-modified PVDF membrane.

3.4. Filtration analysis of electrospun non-modified and modified PVDF membranes

In order to calculate the permeability and rejection of non-modified and modified PVDF nanofibers membranes, a dead-end filtration is performed. The temperature of distilled water and synthetic water was 22°C, stirrer speed was 10 rpm and the pressure was 10 psi. Distilled water was used as clean water and synthetic water was used as

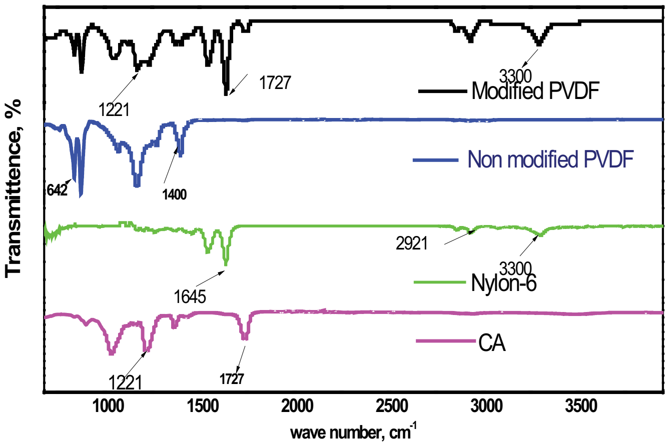

Fig. 3. Fourier-transform infrared spectroscopy results for non-modified PVDF, modified PVDF with nylon-6 and cellulose acetate.

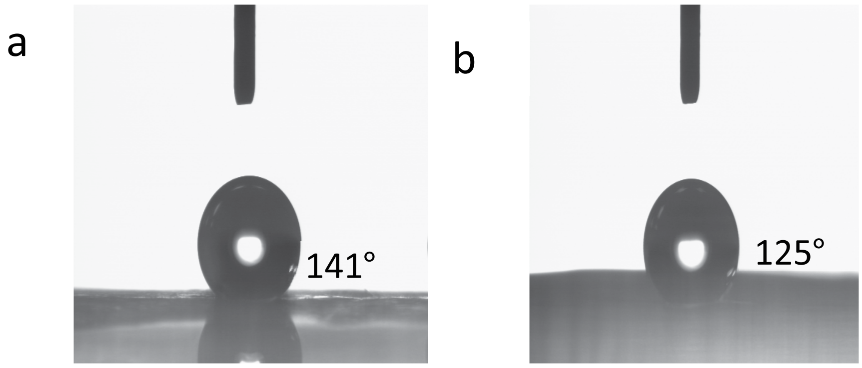

Fig. 4. Water contact angle images for (a) non-modified PVDF and (b) modified PVDF membrane with nylon-6 and cellulose acetate.

polluted water. Clean water and synthetic water flux of non-modified and modified PVDF with CA and nylon-6 as a function of TMP can be seen in Figs. 5a–d. As shown in Figs. 5a and b a modified PVDF with CA and nylon-6 had the highest clean water flux of 80 Lm^{-2} h^{-1} and synthetic water flux was 42 Lm^{-2} h^{-1} highest rejection of synthetic pollutants. This might be caused by the following reasons. The modified PVDF membrane had better hydrophilic property because of the addition of hydrophilic polymers such as CA and nylon-6 into the PVDF matrix and other reasons could be better porosity as reported [33].

However, in Figs. 5c and d, it is showed that the synthetic and clean water had greater resistance to the flux of non-modified PVDF nanofibers membrane. The clean water flux was 55 L m^{-2} h, and synthetic water flux was 22 Lm^{-2} h because due to its hydrophobic nature and less porosity it has greater resistance to flow. BSA which was taken as a model of proteins which can easily interact with non-modified PVDF membranes due to its hydrophobic–hydrophobic interaction, so the synthetic water flux was also suddenly declined. In filtration of proteins, the proteins adsorb more strongly to hydrophobic surfaces than hydrophilic ones. The use of hydrophilic membranes can help reducing membrane biofouling [34]. On the other hand, the modified PVDF membrane was found to be more hydrophilic as compare to non-modified PVDF membranes so it had higher water permeability. The proteins and bacteria's biomass were not easily interacted with modified membranes due to the hydration layer which prevents the membranes for biomass and proteins deposition, so pores were not blocked easily and higher permeate flux were seen in the modified membrane.

3.5. Anti-biofouling performance of non-modified and modified PVDF membrane

Hydrophilicity and porosity of nanofibers membrane are the major factors affecting the biofouling behavior and filtration performance applications of nanofibers membranes. Similarly, modified nanofibers were prepared by blending of PVDF solution with cellulose acetate and co-electrospinning of nylon-6 in the ratio of 80:15:5 and 70:20:10 by increasing the concentration of cellulose acetate and nylon-6 then the hydrophilicity and anti-biofouling properties of membranes were increased. It has been found from Fig. 6c that modified PVDF nanofibers membranes with 70:20:10 have the highest anti-biofouling properties as compared to Figs. 6a and b due to the presence of a higher concentration of cellulose acetate and nylon-6. Sodium alginate has been used as a model of polysaccharides to study the filtration behavior and fouling mechanisms of SMPs in many studies [35].

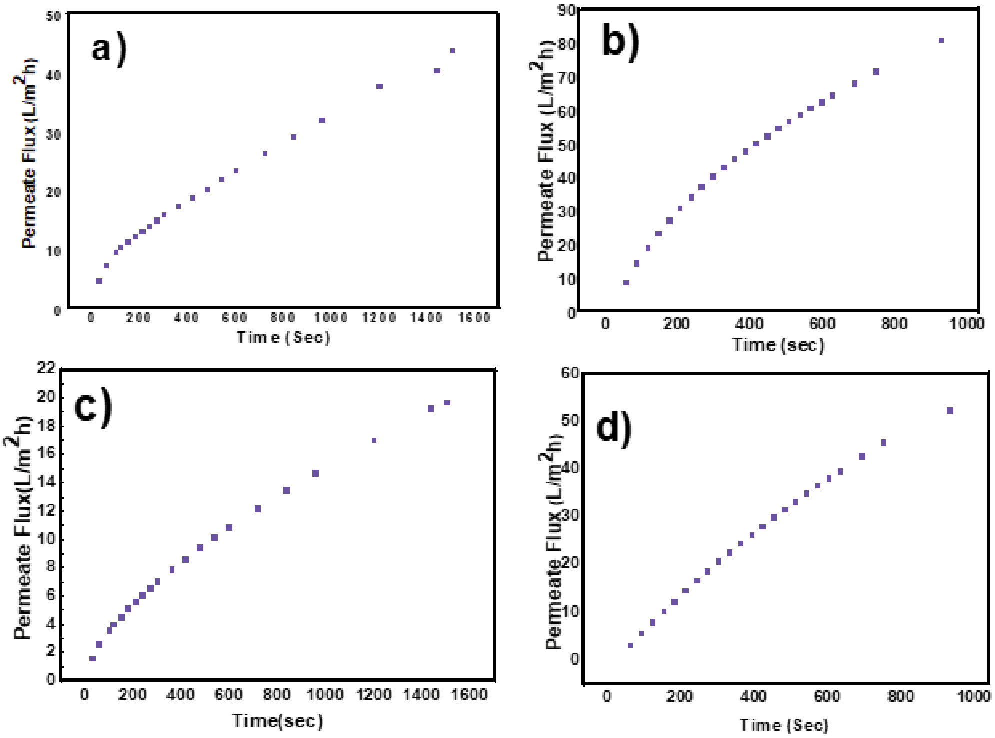

Fig. 5. Water flux data (a and b) synthetic water and clean water flux of modified PVDF membrane and (c and d) synthetic and clean water flux of non-modified PVDF membranes.

The biofouling is mainly caused by the SMP which is polysaccharides and EPS which are mainly composed of proteins, so for biofouling testing the synthetic water was used as a model of biofouling by adding BSA, sodium alginate, HA and so on as shown in Table 2. The normalized flux *J*/*J*° was used to evaluate the anti-biofouling performance of nanofibers membranes as shown in Figs. 6a–c. From Fig. 6a, in the first filtration step, the flux declined to start suddenly during 30 min to non-modified PVDF nanofibers membranes due to its highly hydrophobic nature, the deposition of bacterial biomass, BSA as proteins model and sodium alginate as a model of polysaccharide were easily deposited on the surface of membranes which completely block the membranes.

However, in the second filtration step, Figs. 6b and c the flux declined to start slowly on modified nanofibers membranes due to its hydrophilicity. In hydrophilic membranes, a layer of water is formed onto the membrane surface which consequently resists the penetration and adsorption of pollutants on and into the membrane surface and thereby the phenomenon of biofouling is reduced [36]. The hydrophobic surface of the membrane is a great cause of biofouling due to the attachment of microbial cells because of hydrophobic–hydrophobic interaction, for reducing the biofouling membrane must be modified to hydrophilic [37]. Here we compare the results of our proposed method with those of traditional methods due to the presence of cellulose acetate and nylon-6 on PVDF nanofibers membranes then the morphology of PVDF has been changed from hydrophobicity to hydrophilicity due to this bacterial biomass, bovine serum albumin, and sodium alginate are not easily deposited on membranes surface preventing it from biofouling. Hence, compared to the hydrophilic modified membranes, the non-modified PVDF membrane is more susceptible to bio-fouling caused by organic molecules. The obtained results are depicted in Figs. 6a–c.

From Fig. 6a it is seen that the non-modified PVDF nanofibers membrane due to hydrophobicity the bacterial biomass and polysaccharide are also hydrophobic in nature so hydrophobic–hydrophobic interactions take place and membranes are easily blocked and flux decline take place easily. However, Figs. 6a and b the modified PVDF membranes are hydrophilic and due to hydrophilicity, the hydration layer is formed over the surface of membranes so biomass of bacteria, proteins, and polysaccharide are not easily deposited on the membrane surface so the flux decline of modified membranes is less as compared to non-modified PVDF membrane.

4. Conclusion

In order to control the biofouling issues of PVDF nanofibers membranes in a MBR, The membrane was synthesized through electrospinning by blending of PVDF polymers with hydrophilic CAP and co-electrospinning of nylon-6 and its water contact angle decreased from 141° to 125° clean water flux increased from 55 to 80 Lm^{-2} h. Due to the hydrophilicity of membranes, the hydration layer is formed between water and modified membranes so the biomass of bacteria, sodium alginate model of polysaccharides and proteins are not easily interacting on modified PVDF membranes. Resultantly biofouling is decreased,

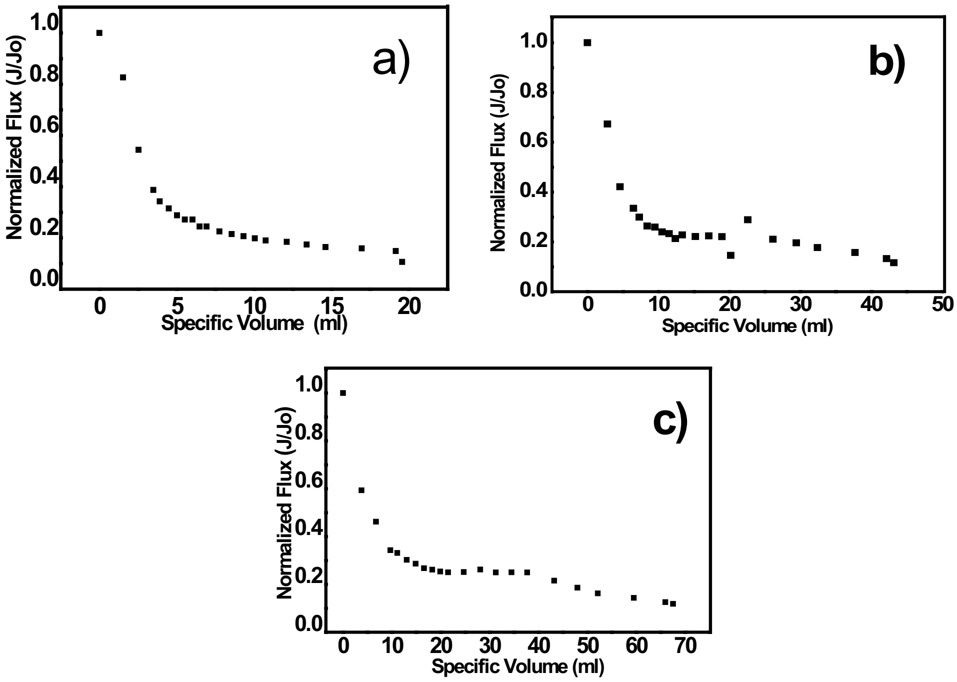

Fig. 6. Flux decline data plot (a) non-modified PVDF, (b) modified PVDF with 80%/20%, and (c) modified PVDF with 70%/30% of cellulose acetate and nylon-6

the study provides an innovative solution to control the biofouling in the membranes and can result in a wider application of MBR for wastewater treatment.

Symbols

J — Is a total flux, $Lm^{-2}\,h^{-1}$
V — Permeated volume, L
A — Area, m^2
T — Time, h
A_d — Membrane apparent density
N_f — Nanofibers membrane mass
M_t — Membrane thickness
M_a — Membrane area
M_p — Membrane porosity
B_d — Bulk density of the mixture
DMF — Dimethylformamide
CAP — Cellulose acetate polymer
PVDF — Polyvinyledene fluoride
BSA — Bovine serum albumin
SA — Sodium alginate
SMP — Soluble microbial product
EPS — Extracellular polymeric substance

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