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RESEARCH ARTICLE

Electrospun Biodegradable Bi-layered Microfiber Membranes for Aluminum Removal from Drinking Water

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ARTICLE HISTORY

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Abstract: ***Aims***: This study aimed to eliminate metallic contaminants from drinking water by using electrospun bi-layered microfiber membranes.

Background: Fast industrialization triggers environmental pollution. Heavy metals like silver, lead and aluminum are the major contaminants that are extremely toxic and accumulate in biological tissues through the food chain and cause a health hazard. Electrospinning is a promising technique among other conventional techniques of removing these metals from drinking water. Electrospun membranes possess suitable properties for microfiltration purposes. In this study, to fabricate electrospun membranes, polycaprolactone (PCL) and zeolites were used as materials. PCL polymer is biocompatible and biodegradable, and zeolite is microporous, which is good for filtration or molecular sieving application.

Method: Using the electrospinning technique, PCL, PCL/zeolite, PCL and PCL/zeolite bi-layered electrospun membranes were fabricated. The properties of the membranes were evaluated using different techniques. The performance of the membranes was tested by filtering Aluminum (Al) present in drinking water.

Results: Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses confirmed the removal of Al using the membranes. ICP-OES results showed more than 90% of Al removal using PCL and PCL/zeolite electrospun membranes.

Conclusion: These membranes are non-toxic and biodegradable and have the potential to be used for microfiltration purposes.

Keywords: Polycaprolactone, zeolite, aluminum, electrospun membrane, filtration, bi-layered.

1. INTRODUCTION

Industrial waste containing toxic heavy metals can cause water pollution. Besides, natural disasters, for example, a volcanic eruption can cause contamination of water by heavy metals. Cancer and other health hazards can be caused by the accumulation of certain heavy metals [1]. Heavy metals are metallic elements and are toxic at very low concentrations [2]. Common heavy metals that are toxic to humans and all other organisms are arsenic, lead, copper, chromium, nickel, and aluminum.

One of the heavy metals is aluminum (Al) which exists in many forms such as aluminum chloride ($AlCl_3$), aluminum hydroxide $Al(OH)_3$, aluminum oxide (Al_2O_3) and aluminum nitrate $Al(NO_3)_3$. All the forms of Al are used extensively in the industries as antiperspirant, food additive, as a structural material in aircraft and automobile industries, in cooking utensils and also as food packaging. Al is used in industries as a coagulant for water treatment. However, aluminum is toxic above certain concentrations. Besides, the pH of water can influence the toxicity of aluminum, which increases as the pH decreases. Hence, acid rain increases the toxicity of aluminum [3]. Water pollution can occur when Al salt reacts with the acid from the rain. Besides, aluminum is harmful to osseous and hemopoietin cells [4]. Moreover, aluminum has a high affinity towards DNA and RNA which eventually causes enzyme inhibition [3].

Several methods are being used to treat water pollution. One of the promising techniques in filtering polluted water is water filtration by an electrospun membrane. The electrospun membrane is a membrane that is made up of polymeric nano- or micro-sized porous fibers fabricated using the electrospinning technique. This technique uses high voltage electrical force to produce polymer fibers. The size and diameter of the fiber produced are highly dependent on the applied voltage [5]. To produce large diameter fibers, high voltage is needed to be applied. It is also important to keep the voltage constant for getting homogenous fibers. On the other hand, the flow rate also plays an important role in fabricating fibers with suitable properties. Lower flow rate is favorable as it gives adequate time for the solvent to evapo-

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rate before depositing on a grounded collector. A conductive grounded collector is crucial for getting non-beaded fibers [6]. Electrospun membranes have a high surface area and large porosity, which is beneficial for being used in microfiltration. On the other hand, by incorporating nanoparticles, the membrane can achieve the adsorption property, which can further enhance the performance of the membrane in the application of the removal of metallic contaminants. Recently, the bubble electrospinning technique has attained much attraction due to the increased production rate than the traditional electrospinning [7, 8]. Briefly, a bubble-electrospinning introduces an electrode which is placed inside a polymer solution reservoir with a gas tube to feed the reservoir from the bottom, as a result, several bubbles of different sizes are formed. Bubble electrospinning can be upscaled easily for the industrial application [7]. It was reported that the bubble electrospinning with aqueous solvent can fabricate nanofibers' diameter of less than 100 nm [8].

PCL is a synthetic hydrophobic polymer that has a chemical formula $(C_6H_{10}O_2)_n$ containing carbon, hydrogen and oxygen atoms that are linked together by hydrogen bond and ester linkage. PCL has been used widely in the biomaterial field for wound healing and as a material for scaffold and hemostats. PCL polymer is biocompatible and biodegradable. It is non-toxic to the human body and can be easily decomposed [9]. Apart from this, zeolites are natural aluminosilicate minerals that are microporous. Due to the chemical structure of the zeolite, it is innocuous in ion-exchange which makes it particularly suitable to remove heavy metal ions in polluted water [10]. The microporous characteristic of zeolite makes it a good filter [11-13]. The removal of another metallic contaminant, silver, has been reported previously in a separate study using the electrospun membrane [14]. In this study, we are reporting the application of PCL/zeolite-based electrospun membranes to remove aluminum from drinking water.

2. METHODS

2.1. Materials

Poly (caprolactone) (PCL) (MW: 70,000-90,000) polymers were purchased from Sigma and Beta zeolite powder (0.55-0.70 nm pore) (MR: 40) was purchased from ACS Material. Analytical grade (purity 99.9%) acetone was used as a solvent.

2.2. Preparation of Polymer Solution

15% w/v PCL solution was prepared by dissolving 1.50g PCL in 10ml acetone, at 50°C. To prepare a PCL/zeolite solution, 20% w/v (0.3g) zeolite powder was added to the as-prepared PCL solution. PCL/zeolite solution was stirred using a magnetic stirrer for 1 hour at room temperature and homogenized for 3 minutes.

2.3. Preparation of Al Contaminated Water

An amount of 0.005g aluminum powder was mixed with 100ml distilled water to prepare a model of contaminated water. It was homogenized using a homogenizer for 3 minutes to ensure it was perfectly mixed. 15ml of aluminum-containing water was taken in a centrifuge tube to measure the initial concentration using an Agilent technology 700 Series inductively coupled plasma optical emission spectrometry (ICP-OES).

2.4. Fabrication of Composite Membrane

Na Bond Nanofiber Electrospinning Unit, China was used for the electrospinning. 3 types of electrospun membranes were fabricated: PCL electrospun membrane, PCL/zeolite electrospun membrane as well as PCL and PCL/zeolite layer by layer electrospun membrane. The PCL solution was loaded to a syringe and placed on a syringe pump (NE-300, New Era Pump Systems, Inc.) and connected to high voltage. Fibers were deposited to a grounded collector. The same parameters were used for the fabrication of the PCL/zeolite electrospun membrane. For PCL and PCL/zeolite layer by layer electrospun membrane, the PCL solution was spun for 1 hour and the solution was replaced with PCL/zeolite solution and spun for another 1 hour. Parameters used for all the electrospinning processes were the same. Tip-to-collector distance was set at 10 cm, humidity 54%, flow rate 3 ml/h, voltage 20 kV, electrospinning duration for 1 hour and syringe size of 21G.

2.5. Characterization

2.5.1. Morphology

Electrospun membranes were sputter-coated and the morphology was viewed under Hitachi TM3000 Tabletop scanning electron microscope (SEM) at magnification 500x and 1000x. Pore size and fiber diameter were measured using Image J software. 40 readings of diameter were taken.

2.5.2. Elemental Analysis of Membranes

Energy Dispersive X-ray (EDX) was used for elemental analysis of the electrospun membrane by using Swift-ED3000. It enlightened the elements that exist inside the membrane in the spectrum. Another function of EDX mapping was to find out the position of specific elements emitting characteristic x-rays and they were interpreted in different colors.

2.5.3. Wettability Analysis

Water Contact Angle (WCA) measuring system, VCA Optima, AST Products, Inc. was used for determining the contact angle of PCL, PCL/zeolite and PCL/zeolite layer by layer membranes. 3 different measurements were taken for each membrane. Measurements were obtained within 3 seconds after the droplet of water contacted with the membrane surface.

2.6. Water Filtration Testing

Fabricated membranes were cut into a cone shape with a diameter of about 80mm each. The membranes were folded like a filter paper, put into a filter funnel and connected to a vacuum pump. 25ml of water containing a fixed amount of Al was passed through the electrospun membranes.

2.7. Post Characterization

Filtered solutions were analyzed using ICP-OES to record the amount of aluminum element passed through the electrospun membranes. After the filtration process, all electrospun membranes were dried and viewed under SEM for the trapped aluminum on the membrane pores.

3. RESULTS AND DISCUSSION

3.1. Surface Characterization of As-fabricated PCL, PCL/zeolite as well as PCL and PCL/zeolite Layer by Layer Electrospun Membrane

The SEM micrographs for as-fabricated PCL, PCL /zeolite as well as PCL and PCL/zeolite layer by layer membrane are shown in (Fig. **1**). From the SEM results, the average fiber diameter range for pure PCL, PCL/zeolite as well as PCL and PCL/zeolite layer by layer membrane was between 1µm - 3µm. The morphology did not change much after adding zeolite in the PCL solution. No agglomeration of zeolites was noticed in PCL/zeolite or the bi-layered membrane. (Fig. **2**) shows the average pore sizes of different membranes. The average pore size was decreased in PCL/zeolite bi-layered electrospun membrane than only PCL and PCL/zeolite membranes.

Pores are the spaces between fibers. Smaller pores provide more effective filtration properties. Therefore, the smaller the pore size, the greater the amount of aluminum trapped on the membrane. Control of pore size and pore distribution is also necessary to determine the effectiveness of microfiltration [6]. The electrospinning technique is a promising technique to obtain a membrane with high porosity above 90% and a large surface area to volume ratio [15, 16].

The water contact angles of PCL, PCL/zeolite as well as PCL and PCL/zeolite bi-layered electrospun membrane are shown in (Table **1** and Fig. **3**). Fig. (**3**) shows that the wettability decreased for the PCL/Zeolite membrane than that of the PCL membrane.

Wettability of an electrospun membrane surface is affected by chemical bonding, surface roughness and surface morphology [16]. Materials with a higher value of contact angle indicate lower wetting tendency. Wettability is one of the most important properties of the electrospun membrane. Characteristics that affect membrane wetting are the distribution and geometry of fibers, pore size, hydrophobicity and surface energy of the membrane [17]. Different characteristics of the electrospun membrane result in a different function. For instance, polyvinylidene fluoride (PVDF) electrospun membrane has hydrophilic properties which make it not suitable to be used for water filtration as PVDF is a polymer which is soluble in water. However, the electrospun membrane which is fabricated with polycaprolactone (PCL) polymer is hydrophobic (Table **1**, Fig. **3**). A study reported that a hydrophobic membrane with small porous (<10 µm) characteristics demonstrated good filtering function [18].

3.2. Surface Characterization of PCL, PCL/zeolite as well as PCL and PCL/zeolite Layer by Layer Electrospun Membrane After Filtration

Electrospun membranes of PCL, PCL/zeolite as well as PCL and PCL/zeolite layer by layer membranes were collected after filtration of Al-containing water to determine the effectiveness of the electrospun membrane's filtration efficiency. Morphology of the electrospun membranes was examined under an SEM at a magnification of 500x and 1000x as shown in (Fig. **4**). As these electrospun membranes had smaller pore sizes, Al particles were expected to be trapped on the membrane. A comparison was also done by checking the SEM micrographs before and after the filtration of the electrospun membranes (Fig. **1** and Fig. **4**). After the filtration process, white agglomerated particles were observed at different locations of the membranes. The size range of the agglomerated particles was 10-30 µm. These particles did not affect the original fiber morphology. These particles were further analyzed using an EDX to confirm the elemental composition.

Fig. (**5**) compares the EDX elemental analysis for as-fabricated and post-filtration membranes. The presence of elements such as carbon and oxygen in pure PCL was expected (Fig. **5a**). Carbon has the highest atomic percentage compared to oxygen. The presence of both carbon and oxygen revealed that they are predominant components in the PCL membrane with carbon as the major element. Fig. (**5b**) illustrates the presence of Si which is a constituent of zeolite in the PCL/zeolite membrane. Zeolite is defined as an aluminosilicate mineral that is made up of silicon and aluminum. The term 'aluminosilicate' refers to the composition of aluminum, silicon, oxygen. The EDX spectrum in (Fig. **5c**) shows the presence of small peaks of aluminum and silicon and confirms the successful incorporation of zeolites in the PCL/zeolite membrane. (Fig. **5e**) shows the EDX spectra of PCL and PCL/zeolite layer by layer electrospun membrane. Based on the result, the presence of aluminum and silicon was detected in the membrane. After the filtration process, all the membranes exhibited high peaks of aluminum (Fig. **5b**, **d**, **f**) which confirms the ability of the membranes to filter Al from the model contaminated water.

To identify the distribution of Al, EDX mapping was conducted by emitting characteristic x-rays within an inspection field which can be interpreted by a particular color (Fig. **6**). The presence of the aluminum element on the membrane is shown in purple. (Fig. **6b, d, f**) shows the distribution of aluminum on the electrospun membrane after filtration.

Filtrated water was analyzed using ICP-OES to determine the amount of aluminum present in the filtered water. From the ICP-OES analysis, the initial concentration of aluminum in water was found as (7.59 ± 0.11) ppm. Water filtered by PCL, PCL/zeolite and Bi-layered electrospun membrane showed(0.76± 0.02)ppm of aluminum concentration. It also gives evidence that allaluminum was filtered by the electrospun membranes.

The efficiency of the electrospun membrane was calculated using the following formula:

$$\text{Efficiency} = \frac{initial - Final}{initial} \text{ x } 100\%$$

Thus, filtering efficiency for the electrospun membranes was found to be above 90%. From these results, we can conclude that as the lab-scale electrospun membranes have shown more than 90% efficiency, therefore, these membranes can be used as a micro-filter to remove metallic components from drinking water.

The mechanism of the bi-layered electrospun membrane to remove metallic contaminants from drinking water

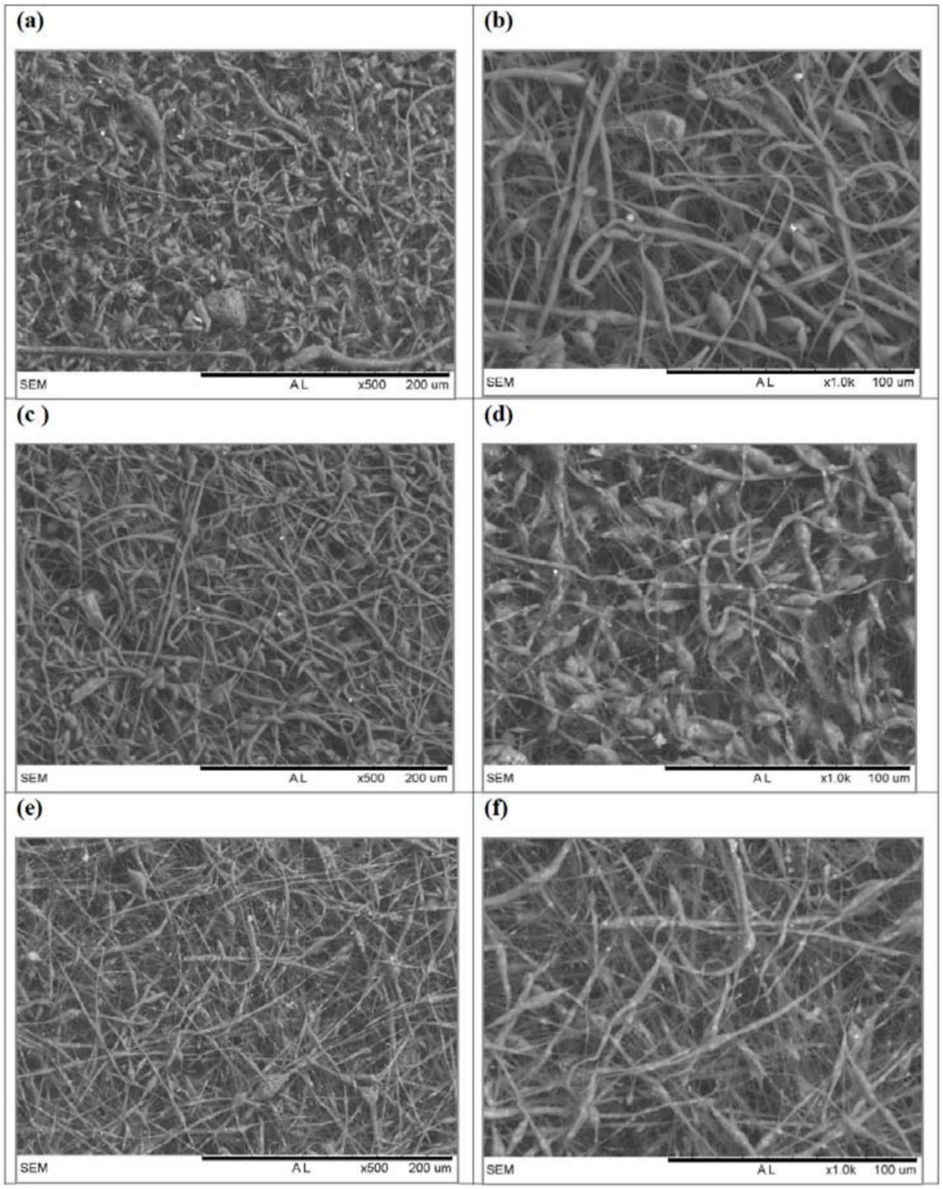

Fig. (1). SEM micrographs of PCL (**a**,**b**), PCL/zeolite (**c**,**d**), PCL and PCL/zeolite bi-layered (**e**,**f**) electrospun membranes.

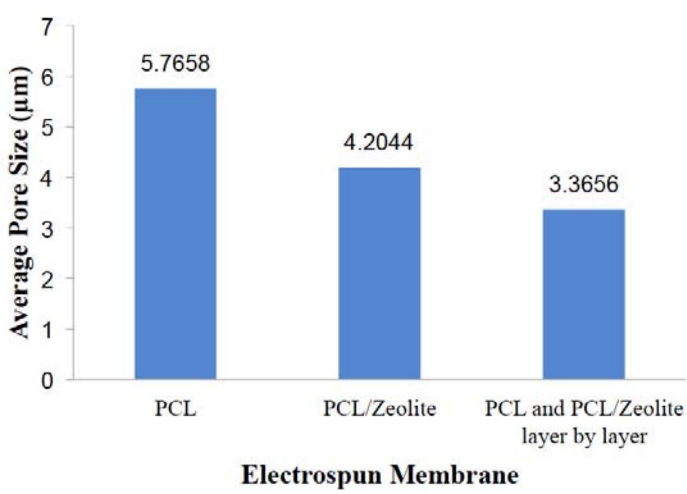

Fig. (2). Average pore sizes of PCL, PCL/zeolite and PCL and PCL/zeolite layer by layer electrospun membrane. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

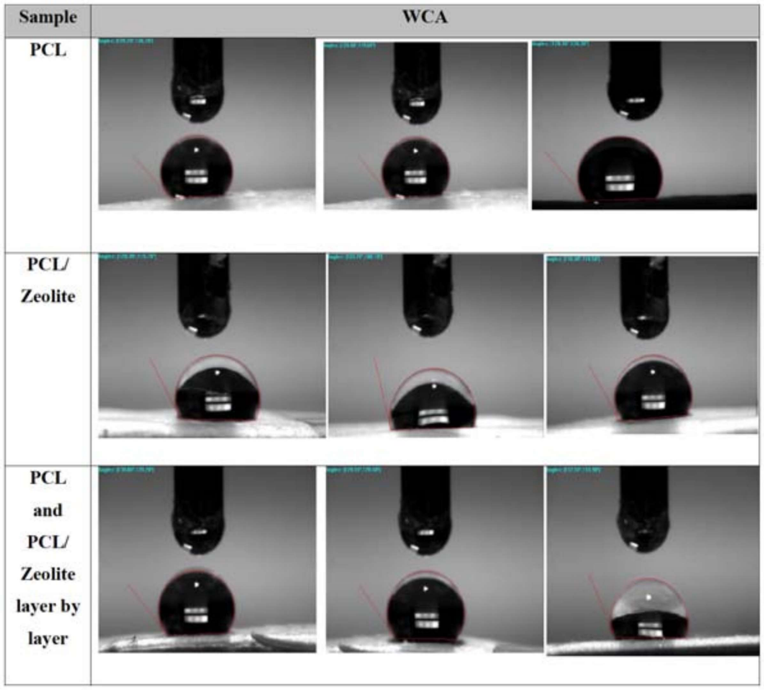

Fig. (3). Contact angle of PCL, PCL/zeolite as well as PCL and PCL/zeolite bi-layered electrospun membrane. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

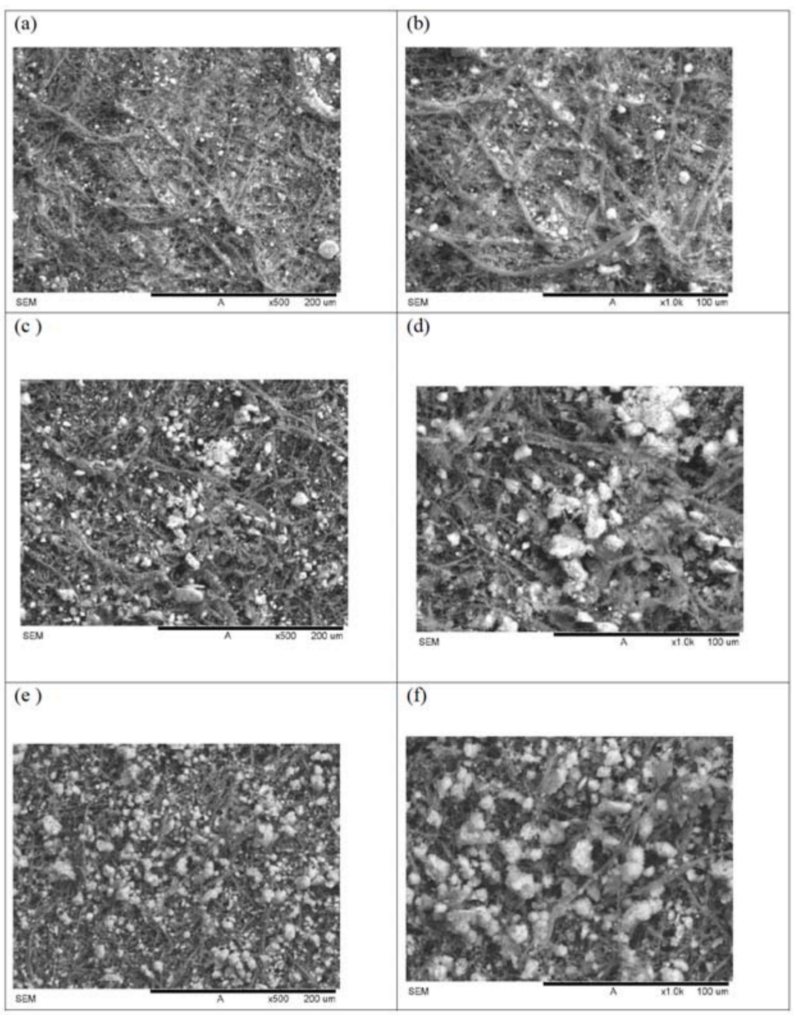

Fig. (4). SEM micrographs of PCL (**a**,**b**), PCL/zeolite (**c**,**d**) and bi-layered membranes (**e**,**f**) after filtration.

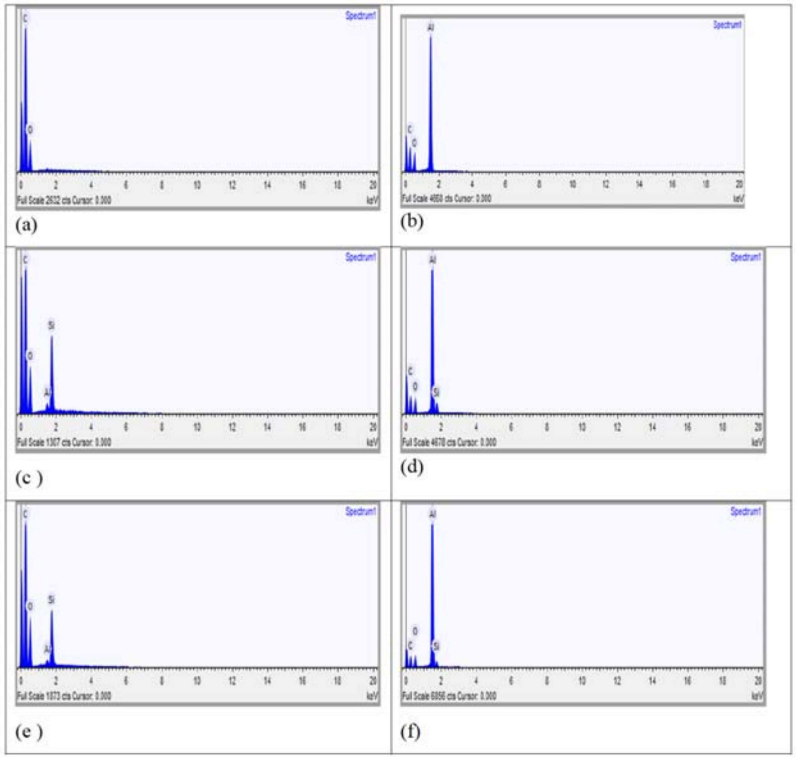

Fig. (5). EDX spectra of as-fabricated (**a**, **c**, **e**) and post filtered (**b**, **d**, **f**) PCL, PCL/zeolite and bi-layered membranes, respectively. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

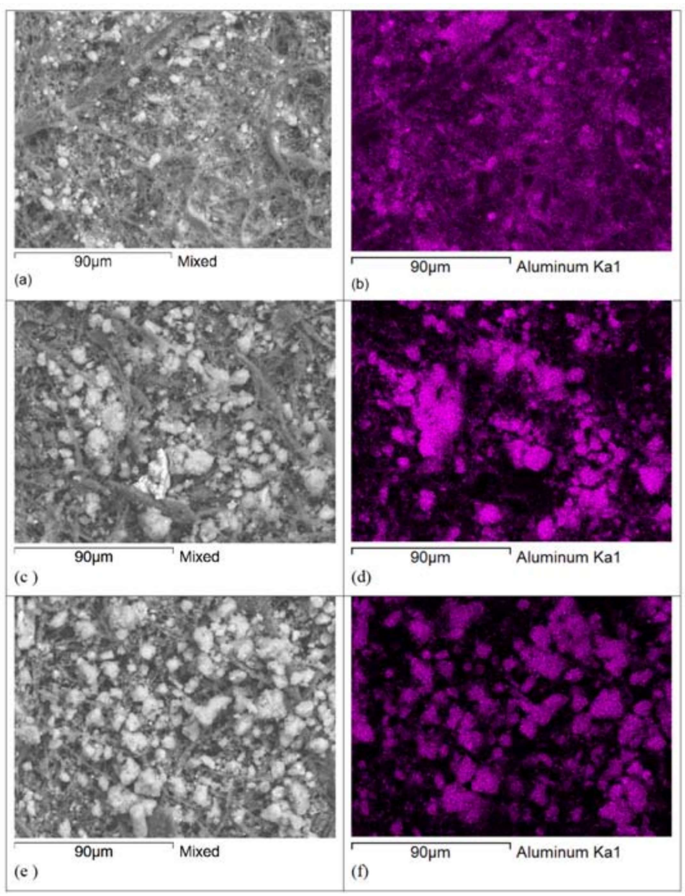

Fig. (6). EDX mapping of PCL (**a**,**b**); PCL/Zeolite (**c**,**d**) and Bi-layered (**e**,**f**) membranes. (*A higher resolution / colour version of this figure is available in the electronic copy of the article*).

Table 1. Contact angles of PCL, PCL/zeolite as well as PCL and PCL/zeolite layer by layer electrospun membrane.

Samples	Average Contact Angle (°)	Properties
PCL	128.87°	Hydrophobic
PCL/zeolite	113.6°	Hydrophobic
PCL and PCL/zeolite layer by layer	125.67°	Hydrophobic

involves both adsorption and filtration. It was reported that electrospun membranes showed enhanced micro /nanofiltration ability [19-21]. It was also reported that the bi-layered membranes had higher transport properties for filtration applications [21]. Furthermore, the incorporation of well-known adsorbent zeolite nanoparticles can significantly enhance the adsorption capacity of the electrospun membranes. Water contamination, specifically with aluminum, is a very serious problem as it causes many deleterious effects on people such as brain function degradation, breast cancer, *etc*. As water is the main source of life, frequent intake of contaminated water will expose people to a high risk of many diseases. Water filtration using the non-toxic electrospun membrane is one of the potential methods to have safe drinking water.

CONCLUSION

PCL, PCL/zeolite, PCL and PCL/zeolite layer by layer electrospun membranes were successfully fabricated by electrospinning technique. Zeolites were distributed homogeneously in the electrospun membranes. Water contact angle results showed that all of these electrospun membranes were hydrophobic. After the filtration, SEM and EDX analyses proved that the membranes entrapped 90% of aluminum from the contaminated water. EDX mapping showed the distribution of Al in all the membranes. Based on the results of EDX, SEM, and ICP-OES analyses, it was proved that most of the contaminants were successfully filtered by using these electrospun membranes. The development of these membranes could be very useful to ensure pure water supply.

CONSENT FOR PUBLICATION

The author gives the consent for publication.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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