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Zeolite Incorporated Polycaprolactone/Zeolite Nanocomposite Membranes for Silver Removal

N. Sultana*, M. S. I. Rusli, M. I. Hassan

Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

ABSTRACT

The presence of heavy metals in drinking water leads to several health problems. Nano and micro fiber membranes can be used to overcome this through nano or microfiltration process. In this study, polycaprolactone (PCL)/zeolite electrospun composite membranes were fabricated and characterized. PCL is one of the synthetic polymers used in biomedical applications. It has several advantages, including biocompatibility, biodegradability and mechanical flexibility. On the other hand, zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. Electrospinning is a promising technique to produce membranes by applying high voltage electricity. In this research, an electrospinning technique was used to fabricate the electrospun membrane based on PCL and zeolite. In order to produce electrospun membrane, 15% (w/v) of PCL polymer solution was dissolved in acetone and 20% (w/v) zeolite nanoparticles were incorporated into the PCL polymer solution. The diameter range of fiber was 2-6 µm. Zeolite nanoparticles were distributed homogenously into the fibers. EDX spectrum confirmed the presence of zeolite throughout the membrane. From the performance testing, it was revealed that the membrane can be potentially used as microfiltration to entrap silver contaminants in drinking water. Apart of that, the membranes are prepared with biocompatible, non-toxic materials which can be eco-friendly.

Keywords: Electrospinning, nanocomposite membrane, polycaprolactone, Zeolite; characterization

1.0 INTRODUCTION

All sources of drinking water contain some naturally occurring contaminants. As water flows in streams sits in lakes and filters through layers of soil and rock it dissolves or absorbs the substances that it touches. Water such as mineral water or ingredient of a wide range of commodities, can be the end products in the food industry. In addition, different types of water sources used for the production of drinking water used in the food industry such as bottled water, tap water, ice cubes. In each of these cases, potential hazards inside the water could affect the consumers' health, either it was from the water sources itself or indirectly as an ingredient of any food commodity that is consumed without further processing.

Meanwhile, enormous usage of colloidal silver and silver nanoparticles (AgNPs) in coal water filters has elevated the potential of silver absorption by the human organism. Indeed, ingestion is the predominant way through which humans are bare to toxic elements like metals, and this exposure can abort in health crisis [1]. Grey-blue discoloration of the skin (argyria), harm to the liver and kidney in severe cases [2] and disruption to the circulatory, central nervous,

* Corresponding to: N. Sultana (email: naznin@biomedical.utm.my)

hepatic, and dermal systems [3] are some of the chronic effects happen on the excessive amount of silver toxicity inside the human body.

Hence, the World Health Organization (WHO) and the US Environmental Protection Agency (EPA) set a guideline of maximum contaminant level at 0.1 mg/L or 100ppb over a lifetime of exposure in drinking water for silver particles as soluble silver ions have been classified as hazardous substances in water by WHO and EPA [1].

Therefore, researches on filtering silver molecules are encouraged in order to improving the health care level into a standard. Despite that, layer by layer electrospun membrane of polycaprolactone (PCL) and zeolite were constructed by using electrospinning technique.

The consolidation of the electrospraying phenomenon which is based on a physical and electrical mechanism known as electrospinning technique [4-7] is one of the methods of production of layer membranes. It is a simple and applicable technique used for the fabrication of multilevel ultrafine fibers by applying a high voltage to create electricity charged jet of polymer solution from the syringe [8]. PCL is one of the popular synthetic aliphatic polymers [9] that is used for tissue regeneration either hard or soft tissue which massive benefits.

On the other hand, zeolites are microporous, aluminosilicate minerals that suitable to be used in advance application, for instance, molecular sieves, adsorbents, catalysts and etc. Several researchers reported the synthesis of zeolites from a wide variety of starting materials containing high amounts of Si and Al, e.g., kaolin, high-silica bauxite, halloysite, interstratified illitesmectite, montmorillonite, bentonite, and incinerated ash [10].

2.0 METHODS

2.1 Materials

Poly (caprolactone) (PCL) (MW: 70,000-90,000) were purchased from Sigma, Beta Zeolite Powder (0.55-0.70 nm pore) (MR: 40) was purchased from ACS Material. Acetone was analytical grade which was used as solvents. Silver nanopowder, <100nm particle size, contains PVP (MW: 107.87) purchased from Sigma was used to mimic the silver contaminated by silver.

2.2 Preparation of Polymer Solution

In order to produce a 15% w/v of Poly (caprolactone) solution, 1.50 g of PCL was dissolved in 10 mL of acetone, at 50°C for about an hour. Meanwhile, 20% w/v 0.30g of zeolite powder was added up into the PCL solution and magnetically stirred at room temperature for another hour to produce PCL/zeolite solution. After that, PCL/zeolite solution was homogenized at the speed of 16-20 1/min x 1000 for about 3 min.

2.3 Fabrication of Composite Membrane

In order to fabricate PCL nanofiber membrane, PCL solution was filled into syringe and placed on the syringe pump. The process was repeated with zeolite solution to form zeolite nanofiber membrane. The process of electrospinning took an hour each. Meanwhile, for the fabrication of PCL and PCL/Zeolite layer by layer nanofibers, all the steps involved in the electrospinning process of PCL or zeolite were repeated including the parameters remain constant. However, the same collector was used which means that the PCL/Zeolite nanofibers were collected on top of the PCL nanofibers. The successful fabricated membranes were removed from the aluminium foils right after the electrospinning process.

2.4 Characterization

A Hitachi TM3000 Scanning Electron Microscope (SEM) was used to observe the morphologies of the fabricated membranes. Then, the diameters of the fibers were calculated by using ImageJ software where 40 reading were taken out and the average value was calculated.

EDX was used for the elemental analysis or chemical characterization. Also, EDX mapping had been conducted as this technique introduced the position of specific elements emitting characteristic x-rays within an inspection field can be interpreted by unique color.

ATR-FTIR was used to determine the chemical bonding of the electrospun membranes produced. The analysis was performed using an ATR-FTIR spectroscopy (Perkin-Elmer Series, USA Model and Thermo Scientific Nicolet iS5) in the range of 4000-350 cm^{-1}. Omnic software was used to analyse the graph obtained.

Water contact angle measuring system, VCA Optima, AST Products, Inc. was used to determine the hydrophilicities of PCL, PCL/zeolite as well as PCL and PCL/zeolite layer by layer. In this process, 3 different measurements for each of the membranes were taken. In order to test the performance of the membrane, silver contaminated water was prepared in-house by dispersing silver nanoparticles in water. After the filtration process using the membrane as filter, EDX was conducted to identify the presence of silver in the membrane.

3.0 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM)

Samples collected on the aluminium foil were peeled off and then a double-tape was used to fix the nanofiber on the SEM's sample holder or stage. These samples were visualized at various magnifications for example 400x, 500x, 1000x, 1500x and 2000x at the same time.

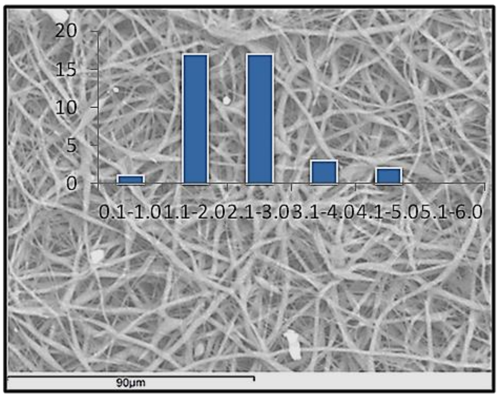
Regulating the voltage applied plays the crucial rules in order to obtain the clear morphological images. Although the electrospinning process was not technically complex with the ease of adaptability, numbers of processing variables needed to be optimized in order to generate nanofibers instead of droplets or beaded morphologies. After several trials, 15% w/v of PCL and 20% w/v of zeolite were used to produce the membranes. Significantly, the presence of large amount of zeolite was highly recommended for molecular sieve as zeolites are commonly established in water treatment application [11].

In terms of molecular sieve, zeolites forms purified oxygen from air using its ability to seize impurities, in a process involving the adsorption of nitrogen, leaving highly purified oxygen and up to 5% argon.

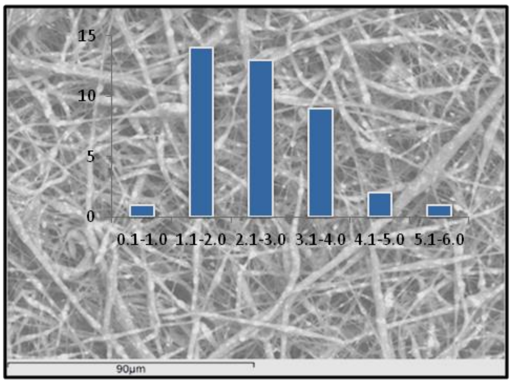
As the electrospinning is able to produce very thin fiber diameters [12], results of the fabricated fiber diameter membranes were targeted to vary between the ranges of the 2 µm- 6 µm. These values generally indicate that the membranes are applicable to use as microfiltration unit [13] and reduce the needle blockage during the electrospinning. From the obtained results, PCL membrane achieved the average diameter of 2.29 µm.

On the other hand, PCL/zeolite membrane's average fiber diameter was slightly increased to 2.62µm.

Apart from that, fiber diameter of PCL and PCL/zeolite later by layer membrane was recorded as 2.45µm. Figure 1 shows the SEM micrograph and the fiber distribution of 15% (w/v) PCL and PCL/zeolite membranes. The fiber diameter then analyzed by using ImageJ regarding to the scale information state on the SEM image.



(a)



(b)

Figure 1 SEM micrograph of (a) 15% (w/v) PCL and (b) PCL/zeolite membranes with fiber diameter distribution in µm

3.2 Contact Angle Measurement

Table 1 describes about the average contact angle of the PCL and PCL/zeolite electrospun nanofiber. The water contact angle of PCL/zeolite membrane was almost same as pure PCL membrane. Contact angle measurement for pure PCL electrospun fibrous membrane was 109° [14]. The lifespan of membrane can be described as same as PCL which was favorable in biomedical application [9].

For the membrane A (PCL membrane), the average contact angle was 107.73°±8.54° and membrane B (PCL/zeolite membrane) was 119.53°±5.24°. For the PCL and PCL/Zeolite layer by layer, reading was taken twice which was on top and bottom of layer of the membrane. By combining PCL and PCL/zeolite layer by layer, the hydrophobicity of the membrane was increased. On the top layer of the membrane, the contact angle was 123.02°±2.60°, while reading of 120.08°±4.73° was taken from the bottom layer of the membrane.

It was observed that the membranes were hydrophobic. However, due to the reason that application (microfiltration) was more preferred to hydrophilic surface, further improvement is recommended in order to reduce the hydrophobicity of samples. It can save the time when dealing with large amount or quantity of waste water.

Table 1 Contact angle measurement

Membrane	Contact Angle (°)	Properties
A	107.73±8.54	Hydrophobic
B	119.53±5.24	Hydrophobic
C (top)	123.02±2.60	Hydrophobic
C (bottom)	120.08±4.73	Hydrophobic

If the hydrophilicity of samples is improved, this can ensure that the water filtration could be done more effectively and encourage the application to be more marketable, also

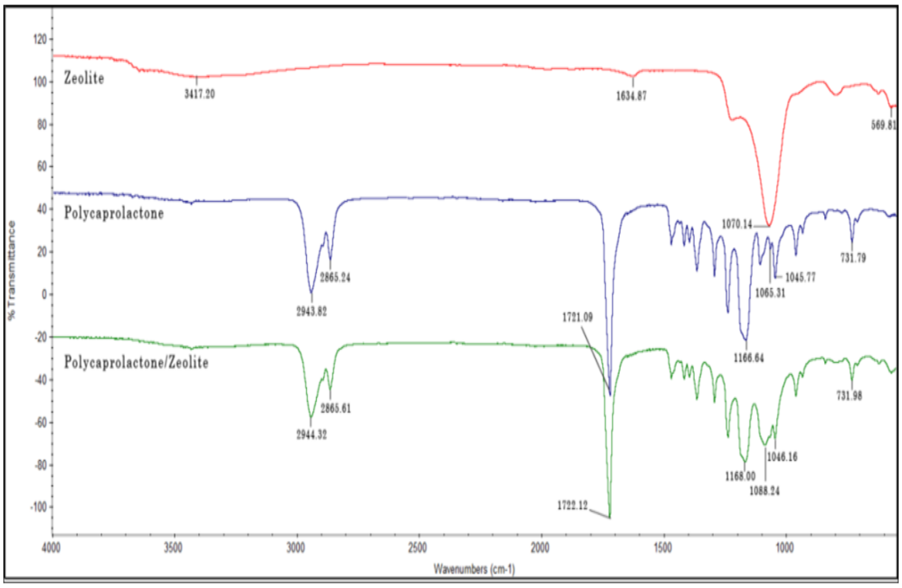


Figure 2 ATR-FTIR Spectrums for zeolite powder, PCL membrane and PCL/Zeolite membrane

reliable to use in various forms of applications.

3.2 ATR-FTIR

Figure 2 shows the FTIR patterns for the pure PCL, pure zeolite and PCL/zeolite membrane. Peak 1070.14 cm^{-1} on zeolite spectrum indicates the T-O-T (T=Al or Si) asymmetric stretching vibration [15]. Meanwhile, at peak 569.8 cm-1 shows the presence of the double 4 ring (DR4) and peaks were found in 1070.14 cm-1 can be described as an impact on PCL when combining with zeolite [15, 16].

The peak at that value on PCL/zeolite shortens due to the presences of zeolite increases the T-O-T asymmetric stretching vibration of PCL membrane. It also shows the presence of the ester group in PCL spectra at peak 1721.09 cm-1 which was due to stretching of carbonyl group. The peaks that exist at peak 2943.82 cm-1 and peak 2865.24 cm-1, defined the existence of C–H hydroxyl group asymmetric stretching and C hydroxyl groups symmetric stretching respectively [17].

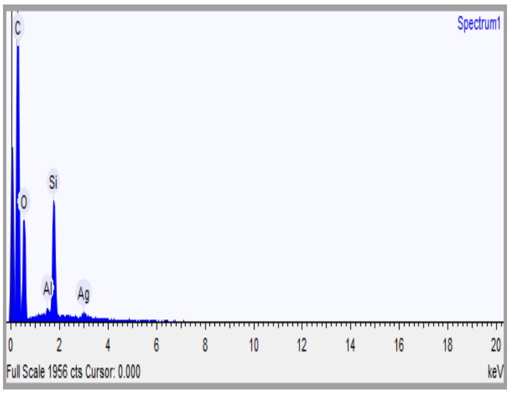


Figure 3 EDX spectrum and elemental analysis of the membrane after filtration

3.3 Performance Testing

A vacuum pump was used to test the performance of the membrane filtration. The filtration time could be reduced by applying the vacuum pump attached to the filter. Varying the speed of the vacuum pump would increase the rate of time of sieving process. After the filtration was performed using silver in water, the membrane was tested using an EDX to confirm the presence of silver in the membrane (Figure 3 and Table 2).

Table 2 EDX survey on membrane surface

Element	Weight %	Weight % σ	Atomic %
Carbon	57.589	0.651	65.999
Oxygen	36.477	0.661	31.384
Aluminum	0.289	0.049	0.147
Silicon	4.827	0.116	2.366
Silver	0.819	0.158	0.104

4.0 CONCLUSIONS

The membrane based on PCL and zeolite was successfully fabricated using electrospinning technique. PCL membrane achieved the average diameter of 2.29 μm. and PCL/zeolite membrane's average fiber diameter was slightly increased to 2.62 μm. Zeolite nanoparticles were homogeneously distributed on the PCL matrix. Contact angle results showed that the membranes were hydrophobic. Performance testing results showed that the membrane could efficiently filter the silver nanoparticles from water. As the PCL and zeolite electrospun nanofibers possessed desired characteristics, it is potentially great to be further deployed in molecular sieving application.

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