J. Applied Membrane Science & Technology, Vol. 23, No. 3, December 2019, 76–83

Electrospun Bi-layered Composite Membrane for the Removal of Metallic Contaminants in Drinking Water

N. Sultana*, D. E. Daniels

Medical Academy, Prairie View A&M University, TX 77446, Texas, USA

Submitted: 7/9/2019. Revised edition: 2/10/2019. Accepted: 3/10/2019. Available online: 10/10/2019

ABSTRACT

Using biodegradable polymer polycaprolactone (PCL) and zeolite, the present experiment was conducted with the aim of using biodegradable PCL and zeolite based composite membrane to remove silver in drinking water. After optimizing the electrospinning parameters, a double-layered PCL and PCL/zeolite electrospun composite membranes were manufactured. The membranes were then characterized using a scanning electron microscope (SEM) and an energy dispersive X-ray (EDX) and the filtration phenomenon was conducted by dispersing silver nanoparticles in water. After comparing the filtration results using an inductively coupled plasma optical emission spectrometry (ICP-OES), it was observed that the bi-layered membrane filtered 90% of silver present in the water. The present work shows that the new PCL/zeolite based double-layered membrane can be promising to remove contaminants in drinking water.

Keywords: Biodegradable, membrane, PCL, zeolite, electrospinning

1.0 INTRODUCTION

Heavy metals have been defined as any metallic element that has a relatively high density and hazardous or poisonous even at a low concentration [1]. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, silver, and arsenic. Although some of them generate bio-importance as a trace element, the biotoxic effects of most of them in human biochemistry are of greater concern. Since heavy metals have been consumed by the human for a long time, several detrimental health effects of heavy metals have been known. For instance, low-level exposure of Aluminium (Al) inside the human body is reported to not think to be harmful, but long-term intake has linked to impaired brain function, including Alzheimer's disease [2,3]. Several studies reported that Al was one of the contributors to breast cancer [4, 5]. On the other hand, lead (Pb) is particularly dangerous to children. Lead in the body attacks the nervous system and can cause brain and kidney damage [6]. In the meantime, enormous usage of colloidal silver and silver nanoparticles (AgNPs) in coal water filters has elevated the potential of silver absorption by the human. Indeed, ingestion is the predominant way through which humans are bare to toxic elements like metals, and this exposure can abort in health crisis [7]. Grey-blue discoloration of the skin (argyria), harm to the liver and kidney in severe cases and disruption to the circulatory, central nervous, hepatic, and dermal systems are some of the chronic effects happen on the excessive amount of silver toxic inside the human body [8, 9]. Despite the fact that cell membranes can engage

* Corresponding to: N. Sultana (email: nasultana@pvamu.edu)
DOI: https://doi.org/10.11113/amst.v23n3.171

directly with AgNPs, AgNPs toxicity to most organisms has been predominantly associated with Ag+ ions release [10]. 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 100 ppb over a lifetime of exposure in drinking water for silver particles. In addition, soluble silver ions have been classified as hazardous substances in water by WHO and EPA [7].

Commercial methods that are currently available for the removal of metallic contaminants are costly as well as energy-consuming. The efficiency is not high too. Electrospun biopolymer based-membranes could be promising to overcome the problem using a microfiltration mechanism without leaving any toxic waste. Adsorption processes can also be applied to remove metallic contaminants. However, the exposure to heavy metals continues, and reported in increasing patterns in some parts of the world, in particular in less developed countries, though emissions have declined in most developed countries over the last 100 years. Hence, the appropriate understanding of its conditions such as the concentrations states, which cause morbidity, is extremely needed.

Polycaprolactone (PCL) is known as a nontoxic, biocompatible and biodegradable synthetic polymer [11, 12] and has been approved for biomedical application by the Food and Drug Administration (FDA) [13]. PCL has various advantages, including mechanical flexibility, easy processability, and low degrees of chronic persistence. On the other hand, Zeolite has been widely explored especially in drug delivery, petrochemical, and plastic industry. Zeolite is microporous, aluminosilicate minerals which are also commonly used as commercial adsorbents. Zeolites can be used in various applications as molecular sieves, adsorbents, and catalyst regarding specific pore sizes and large surface areas. 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 illite-smectite, montmorillonite, bentonite, and incinerated ash [14].

The electrospinning technique is a promising technique to fabricate electrospun nanofibrous membranes. Recent trends in the preparation and characterization of electrospun nanofibers membranes and their potential applications in water treatment were reported [15]. Electrospinning technique is considered as the potential technique [16] of fabricating the polymer and ceramic nanofibers with different diameter up to nanoscale [17, 18], by applying the electro-field theory. It is conducted by applying high voltage electricity charges [19]. Solution viscosity, applied voltage range, humidity, tip to the collector distance are some of the dominant parameters that govern the formation of nanofibers. Controlling the above-mentioned parameter will result in the formation of thin to thick membranes and smooth to corrugated surfaces.

The hypothesis of the experiment was that layer by layer electrospun membrane based on biodegradable polycaprolactione (PCL) and PCL/Zeolite membrane through electrospinning technique will be able to filter metal contaminant Silver (Ag) in drinking water. Meanwhile, the effectiveness of the fabricated membranes will be investigated to achieve the maximum set level of silver contamination allowed which is has been set up by WHO and EPA at 0.1 mg/L [7]. As a result, it can improve the quality of consumer health. Although many studies have been conducted in improving the adsorption application, the utilization of PCL based in this project will be introduced its benefits and advantages to be used in the molecular sieve application. Adding the zeolite can boost the membrane properties [20].

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, LLC. Acetone was of analytical grade which was used as solvents. Silver nanopowder, <100 nm particle size, contains PVP (MW: 107.87) purchased from Sigma.

2.2 Preparation of Electrospun Composite Membrane

1.5 g of PCL polymer and 10 ml of acetone were used in order to prepare a 15% w/v PCL solution. The mixtures were then magnetically stirred at 50°C for an hour. PCL polymer gradually dissolved in acetone. In order to prepare the PCL/Zeolite solution, 20 % w/w zeolite powder was incorporated into the 15 % w/v PCL solution and magnetically stirred at room temperature for an hour. After that, the solution of PCL and Zeolite was homogenized using a hand-held homogenizer at a speed of 16~20 x 1000 rpm/min for 5 minutes to make sure the perfectly dispersed zeolite in PCL solution.

Firstly, 15 % w/v of PCL polymer solution was transferred into a 6 ml syringe. The syringe was placed on a syringe pump that was placed inside the electrospinning chamber. A collector of an aluminum foil 10x10cm was placed to collect the membrane. A high voltage power supply (20 kV) was connected to the needles of the syringe to produce high electrostatic force towards the polymer solution with a flow rate of 3 ml/h to produce the membrane. The positive terminal was attached to the needle of the syringe, while the negative terminal was placed behind the collector plate. The operation of electrospinning continued for about an hour to produce the membrane using PCL polymer.

The duration of the electrospinning process was 2 hours to produce PCL and PCL/Zeolite layer by layer membrane. Firstly, by following the parameters used in the fabrication of the PCL membrane, the PCL/Zeolite solution was injected on the same collector, which means that the PCL/Zeolite nanofiber was collected on top of the PCL nanofibers. The fabricated membrane was stored in sealed plastic bags.

2.3 Characterization of Composite Membrane

Scanning electron microscopy (SEM) (Hitachi-made model TM 3000) was used to observe the morphology of the as-fabricated membrane. An "Image J" software was utilized to measure the fiber diameters and pores. At least, 40 diameters and pores were measured and the average was calculated. SEM analysis was also conducted for the membranes after the filtration. EDX analyses and EDX mapping were carried out to confirm the presence of silver on the membrane.

2.4 Filtration

Filtration process using the membrane filter was aided by using a vacuum pump. In order to investigate the effectiveness of the fabricated membrane, 0.005 g of silver (Ag) nanoparticles were dispersed in 100 ml of distilled water to prepare a silver-containing water for the testing purpose. By using the homogenizer, the solution was homogenized. After that, 15 ml of water containing Ag nanoparticles was taken in a centrifuge tube, the initial concentration was 110 µg/L measured by using an inductively coupled plasma optical emission spectrometry (ICP-OES). Fabricated membranes were cut in a circular shape of diameter (80 mm). The membrane was placed inside the glass filter funnel. With the aid of a vacuum pump, the process was conducted with 25 ml of Ag containing water.

Filtered water was then further analyzed using (ICP-OES) to record the amount of silver element passes through the membranes. The amount of Ag in the filtrate water was compared with the initial value. The analysis was carried out for at least 3 times to check the reproducibility.

3.0 RESULTS AND DISCUSSION

Figure 1a shows the SEM micrograph of the electrospun PCL/Zeolite bilayered membrane. The average fiber diameter of the membrane was 1.1 µm with a diameter range of 0.1-5.1 µm. The pores were interconnected, the densely compacted fibers produced micro size pores. Although the electrospinning technique is well known for the ease of adaptability, still various processing variables need to be controlled in order to fabricate a membrane with micro or nanofibers. One of the challenges of the electrospinning process was to optimize the parameters in order to achieve desired morphology and properties. These processing parameters are the applied voltage, flow-rate, polymer concentration, solution viscosity, nature of the solvent, solution conductivity, and the distance between the capillary and collector [21].

Dispersing nanoparticles in polymer membranes is another challenge. The maximum amount of incorporated zeolite was 10 % w/v. More than this concentration, agglomeration of zeolite nanoparticles was observed on the membrane. Zeolites are commonly used in water treatment applications [22]. EDX analysis confirmed the presence of Si and Al (the main constituents of zeolites) on the resulting spectrum in PCL/Zeolite (Figure 1b). Figure 1c represents the cross-section of the bi-layered membrane. The distribution of Al, C, and Si on the membrane was validated by using EDX mapping (Figure 1 d,e,f).

ICP-OES analyses results showed that the presence of Ag in filtered water after the filtration process using PCL/Zeolite bilayered membrane was only 0.01±0.001 µg/L in comparison to an initial amount 110±0.01 µg/L. The efficiency of the membrane filter was above 99%. It should be noted that World Health Organization (WHO) and the US Environmental Protection Agency (EPA) have set a guideline of maximum contaminant level at 0.1 mg/L or 100 ppb over a lifetime of exposure in drinking water for silver particles [7].

The membranes were further examined using EDX after the sieving process with Ag containing water. EDX spectrum and mapping proved the presence of Ag nanoparticles on the PCL/Zeolite membrane (Figure 2). EDX analyses compared the as-fabricated membrane and the membrane after the filtration process, the presence of Ag further proved the suitability of the membrane.

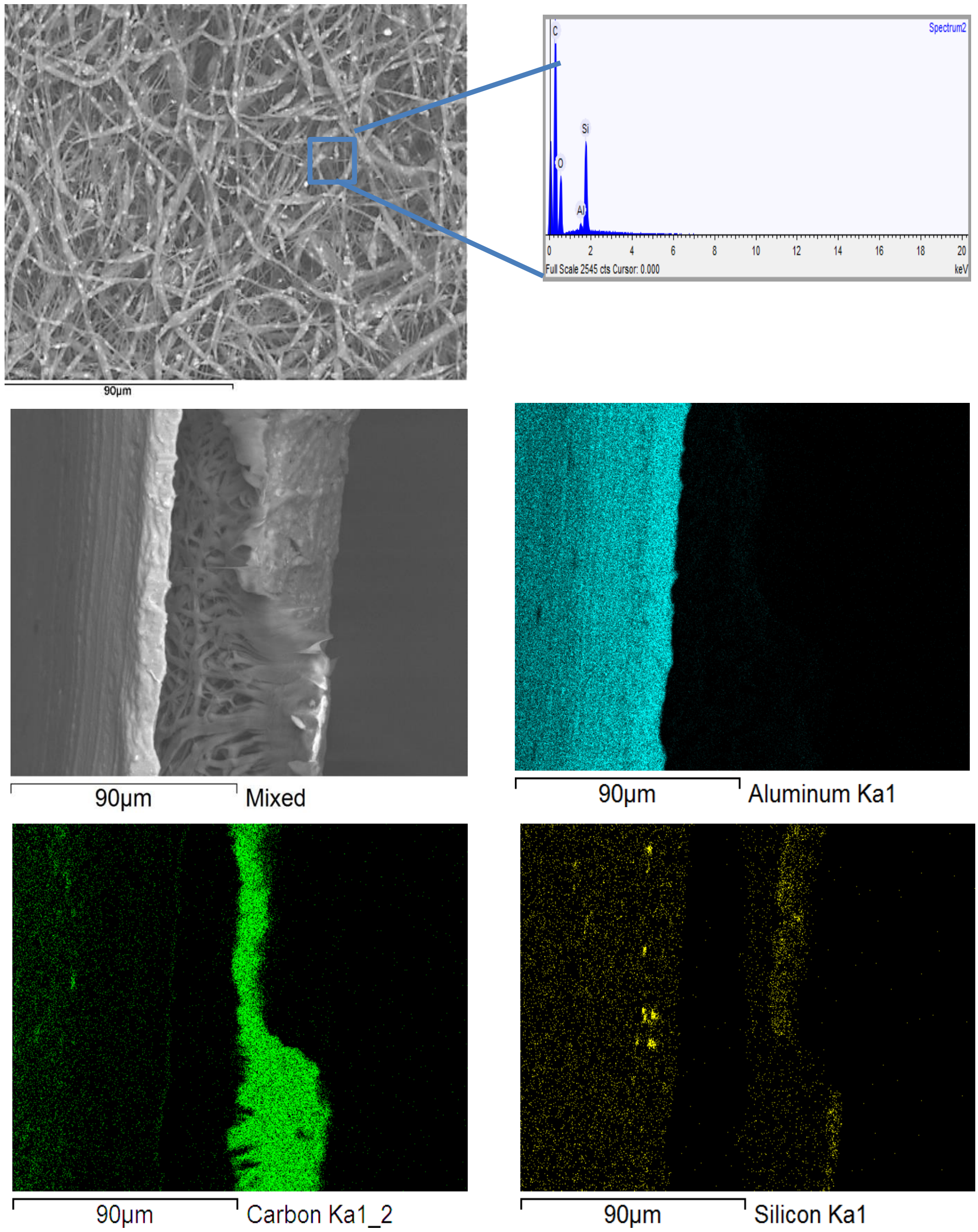

Figure 1 (a) SEM micrograph of bi-layered PCL/Zeolite membrane; (b) EDX spectrum of PCL/Zeolite membrane; (c) SEM micrograph of the cross-section of bi-layered membrane; (d, e, f) EDX elemental mapping for aluminium, carbon, and silicon

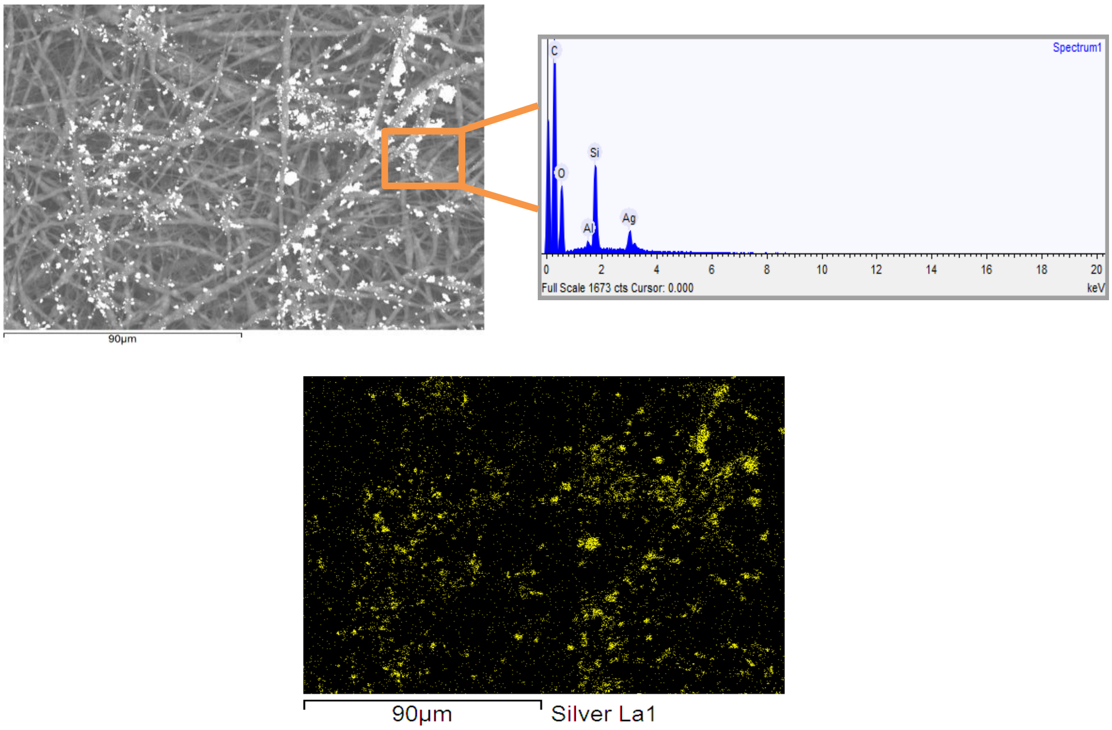

Figure 2 (a) SEM micrograph of PCL/Zeolite membrane after the filtration of Ag in water; (b) EDX spectrum confirming the presence of Ag in the membrane after the filtration; (c) EDX elemental mapping for Ag in the membrane

The mechanism of the bi-layered electrospun membrane to remove metallic contaminants from drinking water is both adsorption and filtration. It was reported that electrospun membranes showed enhanced micro/nanofiltration ability [23-25]. It was also reported that the bi-layered membranes had higher transport properties for filtration applications [23]. Furthermore, the incorporation of well-known adsorbant zeolite nanoparticles can significantly enhance the adsorption capacity of the electrospun membranes.

4.0 CONCLUSION

In this paper, we report the application of an electrospun fibrous membrane based on biodegradable polymer PCL and Zeolites to remove metallic contaminants in drinking water. The characterization analyses of the membrane and the performance testing were performed. SEM results suggested that the membranes had microfiber morphology and nanosized pores. EDX results confirmed the presence of Zeolites in the PCL fibers for as-fabricated membranes. Performance testing confirmed that the membranes can efficiently remove 90% silver contaminants in drinking water. EDX analyses further confirmed the presence of silver in the membrane suggesting the application of PCL/Zeolite membrane in water filtration application.

ACKNOWLEDGEMENT

The author would like to thank Mohd. Syhamiel Rusli, A. F. Ismail, FBME, AMTEC UTM for the support.

REFERENCES

[1] J. O. Duruibe, M. O. C. Ogwuegbu, and J. N. Egwurugwu. 2007. Heavy Metal Pollution and Human Biotoxic Effects. *Int. J. Physic. Sci.* 2(5): 112-118.

[2] S. C. Bondy. 2010. The Neurotoxicity of Environmental Aluminum is Still an Issue. *Neurotoxicology*. 31(5): 575-581.

[3] S. Brenner. 2013. Aluminum May Mediate Alzheimer's Disease through Liver Toxicity, with an Aberrant Hepatic Synthesis of Ceruloplasmin and Atpase7b, the Resultant Excess Free Copper Causing Brain Oxidation, Beta-amyloid Aggregation and Alzheimer Disease. *Medic. Hypoth*. 80(3): 326.

[4] A. Pineau, B. Fauconneau, A. P. Sappino, R. Deloncle, and O. Guillard. 2014. If Exposure to Aluminium in Antiperspirants Presents Health Risks, Its Content Should Be Reduced. *J. Trace Elem. Med. Biol.* 28(2): 147-150.

[5] P. D. Darbre. 2016. Aluminium and the Human Breast. *Morphologie*. 100(329): 65-74

[6] L. Farzin, M. Amiri, H. Shams, M. A. A. Faghih, M. E. Moassesi. 2008. Blood Levels of Lead, Cadmium, and Mercury in Residents of Tehran. *Biolog. Tra. Elem. Res.* 123(1-3): 14-26.

[7] L. R. Rosa, R. D. Rosa, M. A. M. S. da Veiga. 2016. Colloidal Silver and Silver Nanoparticles Bioaccessibility in Drinking Water Filters. *J. Env. Chem. Eng.* 4(3): 3451-3458.

[8] K. M. Stepien, R. Morris, S. Brown, A. Taylor, L. Morgan. 2009. Unintentional Silver Intoxication Following Self-medication: An Unusual Case of Corticobasal Degeneration. Annals Clinic. *Biochem.* 46(6): 520-522.

[9] M. C. Stensberg, Q. Wei, E. S. McLamore, D. M. Porterfield, A. Wei, M. S. Sepúlveda. 2011. Toxicological Studies on Silver Nanoparticles: Challenges and Opportunities in Assessment, Monitoring, and Imaging. *Nanomedicine*. 6(5): 879-898.

[10] N. Cruz, S. M. Rodrigues, D. Tavares, R. J. R. Monteiro, L. Carvalho, T. Trindade, A. C. Duarte, E. Pereira, E., P. F. Römkens. 2015. Testing Single Extraction Methods and in Vitro Tests to Assess the Geochemical Reactivity and Human Bioaccessibility of Silver in Urban Soils Amended with Silver Nanoparticles. *Chemosphere*. 135: 304-311.

[11] N. Sultana, T. H. Khan. 2013. Polycaprolactone Scaffolds and Hydroxyapatite/Polycaprolactone Composite Scaffolds for Bone Tissue Engineering. *J. Bionanosci.*7(2): 169-173.

[12] J. Song, H. Gao, G. Zhu, X. Cao, X. Shi, Y. Wang. 2015. The Preparation and Characterization of Polycaprolactone/Graphene Oxide Biocomposite Nanofiber Scaffolds and Their Application for Directing Cell Behaviors. Carbon. 95: 1039-1050.

[13] M. M. Lim. 2013. Electrospun Membranes for Drug Delivery and Tissue Engineering Applications. Doctoral Dissertation. Universiti Teknologi Malaysia.

[14] V. P. Mallapur, J. U. K. Oubagaranadin, S. S. Lature. 2013. Synthesis of Zeolite from Inorgranic Wastes. *IJRET*. 431-433.

[15] R. Balamurugan, S. Sundarrajan, S. Ramakrishna. 2011. Recent

Trends in Nanofibrous Membranes and Their Suitability for Air and Water Filtrations. *Membranes*. 1(3): 232-248.

[16] M. I. Hassan, T. Sun, N. Sultana. 2014. Fabrication of Nanohydroxyapatite/poly (caprolactone) Composite Microfibers Using Electrospinning Technique for Tissue Engineering Applications. *J. Nanomater*. 2014: 1-10.

[17] S. Wanjale, M. Birajdar, J. Jog, R. Neppalli, V. Causin, J. Karger-Kocsis, J. Lee, P. Panzade. 2016. Surface Tailored PS/TiO 2 Composite Nanofiber Membrane for Copper Removal from Water. *J. Colloid Interf. Sci*. 469: 31-37.

[18] S. A. A. N. Nasreen, S. Sundarrajan, S. A. S. Nizar, R. Balamurugan, S. Ramakrishna. 2013. Advancement in Electrospun Nanofibrous Membranes Modification and Their Application in Water Treatment. *Membranes.* 3(4): 266-284.

[19] S. Nagamine, T. Matsumoto, Y. Hikima, M. Ohshima. 2016, Fabrication of Porous Carbon Nanofibers by Phosphate-Assisted Carbonization of Electrospun Poly (Vinyl Alcohol) Nanofibers. *Mater. Res. Bulletin.* 79: 8-13.

[20] A. Huang, H. Bux, F. Steinbach, J. Caro. 2010, Molecular-sieve Membrane with Hydrogen Permselectivity: ZIF-22 in LTA Topology Prepared with 3-Aminopropyltriethoxysilane as a Covalent Linker. *Angewandte Chemie.* 122(29): 5078-508.

[21] V. Pillay, C. Dott, Y. E. Choonara, C. Tyagi, L. Tomar, P. Kumar, L. C. du Toit, V. M. Ndesendo. 2013. A Review of the Effect of Processing Variables on the Fabrication of Electrospun Nanofibers for Drug Delivery Applications. *J. Nanomater*. 2013: 1-10.

[22] K. Margeta, A. Farkas, M. Šiljeg, N. Z. Logar. 2013. Natural Zeolites in Water Treatment-How Effective is Their Use. Intech Open Access Publisher. 81-106.

[23] M. Makaremi, C. X. Lim, P. Pasbakhsh, S. M. Lee, K. L. Goh, H. Chang. 2016. Electrospun Functionalized Polyacrylonitrile–chitosan Bi-layer Membranes for Water Filtration Applications. *RSC Adv*. 6: 53882-53893.

[24] V. Sencadas, D. M. Correia, C. Ribeiro, S. Moreira, G. Botelho, J. G. Ribelles. 2012. Physical-chemical Properties of Cross-linked Chitosan Electrospun Fiber Mats. *Polym. Test*. 31: 1062-1069.

[25] K. Govindasamy, C. Fernandopulle, P. Pasbakhsh, and K. Goh. 2014. Synthesis and Characterisation of Electrospun Chitosan Membranes Reinforced by Halloysite Nanotubes. J. Mecha. *Med. Biol.* 14: 1450058.