Research article

Preparation, characterization, and desalination study of polystyrene membrane integrated with zeolite using the electrospinning method

Yuan Alfinsyah Sihombing a,*, M. Zulham Efendi Sinaga b,c, Rini Hardiyanti b, Susilawati a, Indah Revita Saragi b, Rangga a

a Department of Physics, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Jl. Bioteknologi No.1, Medan 20155, Indonesia
b Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Jl. Bioteknologi No.1, Medan 20155, Indonesia
c Center of Excellence Chitosan and Advanced Materials, Universitas Sumatera Utara Medan 20155, Indonesia

ARTICLE INFO

Keywords:
Styrofoam
Zeolite
Electrospinning
Membrane
Desalination

ABSTRACT

The novel composite membranes of Styrofoam (polystyrene) integrated with natural zeolite particles were produced using the electrospinning method for desalination purposes. The product was then characterized using FTIR, XRD, and TGA. Subsequently, the effect of different zeolite concentrations, namely 0, 5, 10, 15, 20, and 30 wt.% on its morphological structure and effectiveness was determined. Desalination of artificial seawater was carried out using the gravitational filtration principle to confirm the membrane's capabilities, after which its performance was evaluated using 4 wt.% NaCl solution. The morphological analysis showed that the composite membrane obtained has a smooth surface with microdomains on a few parts, which indicates the presence of zeolite. The result showed that the product integrated with 30 wt.% zeolites had the best performance in the desalination of artificial seawater. This was determined by comparing the conductivity value of the seawater before and after the process. The conductivity led to an 82.63% decrease using 30 wt.% zeolites. The developed polystyrene membrane embedded with zeolite has good thermal stability, hence, it can be used for desalination.

1. Introduction

Water pollution is a serious problem faced by all populations in the world, specifically people who live in big cities. This has led to the development of various water treatment technologies, such as reverse osmosis, thermal vapor, and distillation. However, a suitable method with low energy consumption, environmentally friendly, and cost-effective is needed for long-term treatment [1]. Desalination is a process that can be used to prepare clean water from seawater. It is often carried out with the reverse osmosis (RO) method, which involves the use of a membrane.

A high-performance membrane is often produced by embedding a filler that has a nanoscale [2]. This helps to enhance its functional properties in separating and purifying water [3, 4, 5, 6]. Zeolite is one of the materials that has been extensively used as a filler for various purposes, but not limited to membrane production [7]. It can be modified through mechanical treatment to reduce the particle size into nano. The presence of a unique pore structure on its surface can also inhibit the transport of salt ions due to the sieving effect. Several studies have been carried out on zeolite integrated membrane. For example, high salt rejection of brackish water using desalination led to a 98% enhancement after it was integrated into the polyamide membrane. Another study revealed that its presence increased hydrophilicity, water flux, and salt rejection. The important aspect that must be considered when preparing a membrane with zeolite as a nanofiller is the filler dispersion quality [8, 9, 10, 11, 12].

Styrofoam is one of the waste products that can easily be obtained and is often used for food and electronic packaging [13, 14, 15]. It is also known as polystyrene, a polymer that consists of styrene as the monomer. Polystyrene has several characteristics, including low cost, non-degradable, and superior mechanical strength [15, 16], but the hydrophobic properties limit its application as a membrane for water treatment [6, 17, 18, 19, 20, 21]. However, this limitation still offers an advantage, because water molecules can pass through the membrane when the breakthrough pressure is attained. The product obtained is often used a low surface tension solvent and for the filtration of gas.

Several studies reported that the use of zeolite as a nanofiller can enhance the hydrophilicity of polystyrene membranes, and they were suitable for water filtration [22, 23]. There are no studies on the...
production of these materials using polystyrene and natural zeolite as well as their effectiveness for desalination. This study aims to use the composite membrane of polystyrene/zeolite to obtain superior desalination performance and mechanical properties. The zeolite particles were prepared from the natural form, which was obtained from the Pahae region, North Tapanuli, North Sumatera, Indonesia. Previous studies explored its potential for separation purposes, including gas and desalination. The presence of nanopores in the zeolite structure inhibits the passage of hydrated salt ions.

Therefore, this study aims to investigate the performance of polystyrene membrane integrated with different zeolite concentrations, namely 5, 10, 15, 20, and 30 wt.% using XRD, FTIR, SEM-EDX, mechanical testing, TGA, and desalination process.

2. Experimental

2.1. Material

Styrofoam (polystyrene) was obtained from a used electronic package, while dimethylformamide, sulphuric acid (98 wt.%), sodium hydroxide, and sodium chloride were purchased from Merck. Furthermore, natural zeolite was collected from Pahae region, North Tapanuli, North Sumatera, Indonesia. All chemicals were used without any further treatment.

2.2. Sample preparation

Pahae Natural Zeolite (PNZ) microparticles were prepared using the milling and sieving processes. The powder obtained was then dispersed in 6 wt.% sulphuric acid and stirred at a speed of 350 rpm. The temperature of the solution was set at 70 °C, and the stirring was carried out for 4 h. Subsequently, the residue obtained was washed until the neutral pH was reached, and the drying process was performed at 105 °C for 1 h.

Table 1. Composition of polystyrene/zeolite membrane.

| PNZ (wt. %) | Polystyrene – DMF (g) |
|------------|-----------------------|
| 5          | 0.115 g               | 2.189 g               |
| 10         | 0.226 g               | 2.031 g               |
| 15         | 0.365 g               | 2.066 g               |
| 20         | 0.530 g               | 2.120 g               |
| 30         | 0.927 g               | 2.163 g               |

The membrane was prepared by dissolving 4.7 g of polystyrene in 20 mL of 99.8 wt.% dimethylformamide, followed by stirring at 350 rpm. The temperature of the solution was set at 80 °C, and the stirring was carried out for 30 min [13, 24, 25]. After the solution reached room temperature, the zeolite microparticles were added with the compositions presented in Table 1.

The electrospinning device was set, as shown in Figure 1. The polystyrene-DMF solution was placed in a syringe with 0.8 mm needle size. The distance between the needle and collector was 10 cm. The flow rate of the solution was then set at 13 μL/min along with a voltage of 15 kV. This procedure was then repeated for the mixture of polystyrene and zeolite.

2.3. Characterization

XRD analysis was used to determine the crystalline phase of the samples. Furthermore, the process was carried out using Panalytical Empyrean Model. The analysis of the functional group present in each sample was determined using FTIR - Agilent Technologies-Cary 630 at a range of 650–4000 cm⁻¹ and 16 cm⁻¹ resolution. The thermal stability of
each sample was evaluated using Thermogravimetric Analysis (TGA) at a range of 30–450 °C, and the heat rate was set at 5 °C/min. The mechanical properties, such as tensile strength and elongation at break were measured using UTM - Tensilon RTF equipped with a 5-kN load cell at a speed of 10 mm/min. The morphology of each sample was observed using Scanning Electron Microscopy - Zeiss with 1500x magnification. The instrument was equipped with Energy Dispersive X-Ray (EDX) to evaluate the element composition. The capability of the membrane for desalination was determined by filtering artificial seawater. The solution was prepared by dissolving 4 g of NaCl in deionized water until the concentration was 4 wt.% [26, 27, 28, 29]. The conductivity of the solution was measured before and after desalination with the prepared membrane using a digital conductivity meter – EZDO 6022. The ion exchange capacity of the product obtained was determined by immersing the membranes in 1 M NaCl solution for 24 h. Immersion was performed in a shaker at room temperature. Subsequently, 3 drops of phenolphthalein were added to the solution, and titrated using 0.01 M NaOH. The ion exchange capacity was calculated by multiplying the concentration and volume of NaOH, followed by division by the weight of the dry membrane. The final unit of ion exchange capacity was mmol/g [30].

3. Result and discussions

Figure 2 shows the diffractogram of zeolite, polystyrene, and polystyrene/PNZ composites. The XRD results of zeolite, polystyrene, and polystyrene/PNZ composites showed the characteristic peaks of zeolite at 20 10.24, 25.6, and 27.4°. The diffractogram of polystyrene fiber showed the presence of an amorphous pattern. Similar results were also obtained by a previous study at 20 9.23°, 16.85°, and 22.23° [31, 32]. The occurrence of a crystalline pattern was due to the presence of the additive. The type of polystyrene used in this study was the expanded form, which is often produced with the incorporation of different additives. The diffractogram of composites was dominated by zeolite, which indicates that its particles were homogeneously distributed in the polystyrene matrix, as shown in Figure 2. It also indicated that there was no strong specific interaction between the matrix and zeolite. However, additional interaction, such as non-specific interaction can occur between the hydroxyl group on zeolite surface and polystyrene. The increase of diffractogram intensities has a linear correlation with the amount of additive in the composite, which confirmed that it was incorporated into the matrix. The amorphous structure of zeolite was due to the impact of mechanical treatment, namely ball milling, which enhanced lattice structure disorder [11, 13, 33].

This finding is consistent with the FTIR spectra as shown in Figure 3. The spectra of neat polystyrene and the composites have a similar shape and number of degradation steps to neat polystyrene. The TG curve of the composites has a similar shape and number of degradation steps to neat polystyrene. The TG curve of the composites has a similar shape and number of degradation steps to neat polystyrene. The TG curve of the composites has a similar shape and number of degradation steps to neat polystyrene.
The degradation temperature and weight loss of all samples are presented in Table 3. The early weight loss phenomenon, which occurred at a range of 30–300 °C, indicated the evaporation of small molecules, such as water and organic solvent. The loss of weight caused by this process in all samples was between the range of 1–8 wt.%. The maximal temperature for the depolymerization step of polystyrene (Tdmax) occurred at 342–438 °C, and this step was known as the first degradation step. The composites experienced a weight loss of 23–87% at Tdmax. Comparing the second degradation step of neat polystyrene and polystyrene/PNZ, the presence of zeolite in the matrix provided more thermal stability to the composites. However, a decrease occurred after its addition at a concentration of 20 and 30 wt.% due to the catalytic effect. Several studies reported the use of zeolite in polymer pyrolysis. These effects were caused by its natural properties, including acidity, pore structure, and size [36].

Desalination using gravitational filtration was used to evaluate the polystyrene/PNZ membrane's performance in reducing the number of salt and ions present in the sample. A digital conductivity meter was used to measure the conductivity of the seawater model sample, namely NaCl 4 wt.%, before and after desalination. Before the process, the initial conductivity was 1474 S cm⁻¹. Table 4 shows the value obtained for each solution after desalination as well as the ion exchange capacity of the membranes.

Table 4 shows data on the electrical conductivity value of artificial seawater, namely NaCl 4 wt.%. The incorporation of zeolite into the polystyrene matrix enhanced ion removal, which increased linearly with the amount added. The highest ion removal was observed after the addition of 30 wt.% zeolites. The electrical conductivity value of artificial seawater reduced up to 86.30% after using 30% polystyrene/PNZ as the membrane. This finding indicates that polystyrene/PNZ has the potential to be used for desalination. The results also showed that zeolite plays an important role in the process, and it is often used as an adsorbent due to the presence of micropores on its surface. Apart from the adsorption mechanism, it can also be assumed that the ion exchange occurred during desalination. However, ion exchange plays a minor role during the process, as shown in Table 4. This is because there was no linear correlation between the percentage of conductivity reduction and ion exchange capacity when it was assumed to be the main mechanism during desalination.

| Sample          | C O Si Al |
|-----------------|-----------|
| Polystyrene     | 98.17 1.69 | - - |
| Polystyrene/PNZ | 96.77 2.32 | 0.73 0.18 |
| Polystyrene/PNZ | 91.63 3.01 | 1.05 0.26 |
| Polystyrene/PNZ | 94.53 3.92 | 1.27 0.26 |
| Polystyrene/PNZ | 91.51 6.04 | 2.03 0.42 |
| Polystyrene/PNZ | 88.52 7.98 | 3.07 0.70 |

Table 3. Thermal properties of polystyrene and polystyrene/PNZ.

| Sample       | Tdmax (°C) | Weight loss (%) |
|--------------|------------|-----------------|
| Polystyrene  | 408        | 87              |
| Polystyrene/PNZ 5% | 411        | 48              |
| Polystyrene/PNZ 10% | 424        | 56              |
| Polystyrene/PNZ 15% | 438        | 52              |
| Polystyrene/PNZ 20% | 428        | 45              |
| Polystyrene/PNZ 30% | 342        | 23              |

Figure 5. Morphology of (a) polystyrene and polystyrene/PNZ fibers (b) 5 wt.%, (c) 10 wt.%, (d) 15 wt.%, (e) 20 wt.%, and (f) 30 wt.%.

Figure 6. TGA curve of polystyrene and polystyrene/PNZ composites.
Table 4. The electrical conductivities after the desalination process and the ion exchange capacity of polystyrene and polystyrene/PNZ composites.

| Sample        | Electrical Conductivity (S·cm⁻¹) | Percentage of reduction (%) | Ion Exchange Capacity (mmol/g) |
|---------------|----------------------------------|-----------------------------|--------------------------------|
| Polystyrene   | 848                              | 42.47                       | 1.38                           |
| Polystyrene/PNZ 5% | 623                              | 57.73                       | 1.79                           |
| Polystyrene/PNZ 10% | 478                              | 67.57                       | 0.87                           |
| Polystyrene/PNZ 15% | 314                              | 78.70                       | 0.67                           |
| Polystyrene/PNZ 20% | 210                              | 85.75                       | 0.56                           |
| Polystyrene/PNZ 30% | 202                              | 86.30                       | 1.17                           |

4. Conclusion

The combination of zeolite and polystyrene produced composites, which have the potential to be used for desalination. The diffractogram and morphology of the products indicated that the zeolite has an amorphous structure and was evenly distributed in the polystyrene matrix. Microdomains were also observed in some parts of the fiber. The tensile strength showed that the composites are more mechanically resistant. The result further showed that composites incorporated with 15 wt.% zeolites had higher thermal stability, while lower values were obtained from others with 30 wt.% This finding indicates that the zeolite filler acted as a pyrolysis catalyst. The desalination process confirmed that polystyrene/PNZ has the potential to be used as membrane in the future. The electrical conductivity value of artificial seawater linearly decreased with the amount of zeolite in the polystyrene matrix.

Declarations

Author contribution statement

Yuan Alfinsyah Sihombing: Conceived and designed the experiments; Wrote the paper.
M. Zulham Efendi Sinaga, Rangga: Performed the experiments.
Rini Hardiyanti, Susilawati: Contributed reagents, materials, analysis tools or data.
Indah Revita Saragi: Analyzed and interpreted the data; Wrote the paper.

Funding statement

This work was supported by Universitas Sumatera Utara through grant research under the title of Penelitian Profesional Dosen Muda/Pemula with contract no. 412/UN5.1.R/PPM/2020 (April 27, 2020).

Data availability statement

Data included in article supplementary material referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

[1] F.E. Ahmed, B.S. Lalia, R. Hashaileh, A review on electrospinning for membrane fabrication: challenges and applications, Desalination 326 (2013) 15–30.
[2] N. Arahman, Swaya Wallah Munnah, T. Amin, M.M.R. Bilad, Fabrication of polyethersulfone membranes using nanocarbon as additive, Int. J. GEOMETE 15 (50) (2018) 51–57.
[3] H. Zheng, Chapter 1 - General Problems in Seawater Desalination, Solar Energy Desalination Technology, 2017, pp. 1–46.
[4] S. Homaeighob, M. Elshahi, Graphene membranes for water desalination, NPG Asia Mater. 9 (8) (2017) 427.
[5] K.C. Khutie, T. Matsura, Art to use electropun nanofibers/nanofiber based membrane in waste water treatment, chiral separation and desalination, J. Membr. Sci. Res. 5 (2019) 100–125.
[6] I. Tili, T.A. Alkanhal, Nanotechnology for water purification: electropun nanofibrous membrane in water and wastewater treatment, J. Water Reuse Desalination 9 (3) (2019) 232–247.
[7] N. Rosita, T. Erawati, M. Moegiherjo, Pengaruh perbedaan metode aktivasi terhadap efektivitas zeolit sebagai adsorbent, Majalah Farmasi Airlangga (Airlangga Journal of Pharmacy) 4 (1) (2004) 20.
[8] A. Gisting, D. Anggranin, S. Indarayti, R. dan Kriswanti, Karakterisasi komposisi kimia, luas permukaan pori dan sifat temal dari zeolit bayah, taksimalaya, dan alumin. Jurnal Teknologi Bahan Nuklir 3 (1) (2007) 38–48.
[9] Susilawati, M.N. Nasrudin, K. Chandra, I. Nainggolan, Y.A. Sihombing, Ethanol filtration membranes for water purification using natural active zeolite as adsorption distillation method, Journal of Physics: Conference Series 1116 (2018), 32037.
[10] Susilawati, T.I. Nasution, F. Zebua, H. Nainggolan, Hydrogen purification using natural zeolite Na zeolit and coccus rind based filter, Int. J. Appl. Eng. Res. 12 (13) (2017) 3914–3918.
[11] Nasruddin M.N. Susilawati, Y.A. Sihombing, S.N.Y. Pakpahan, B. Ferdiansyah, Preparation of Pahae natural zeolite nanoparticles using high energy milling and its potential for bioethanol purification, Rasayan J. Chem. 14 (2) (2021) 1265–1272.
[12] Y.A. Sihombing, S.U. Susilawati Rahayu, A. Siahaan, Fabrication of chitosan/natural zeolite composite-based polymer electrolyte membranes, Rasayan J. Chem. 13 (4) (2020) 2181–2187.
[13] A. Rajak, D.A. Hapedin, F. Iskandar, M.M. Munir, K. Khairurrijal, Controlled morphology of electropun nanofibers from waste expanded polystyrene for aerosol filtration, Nanotechnology 30 (42) (2019), 425602.
[14] T. Maharan, Y.S. Negi, B. Mohanty, Review article: recycling of polystyrene, Polym.-Plast. Technol. Eng. 46 (7) (2007) 729–735.
[15] C. Shin, G.G. Chase, D.H. Reneker, Recycled expanded polystyrene nanofibers applied in filter media, Colloids Surf. A Physicochem. Eng. Asp. 262 (1-3) (2005) 211–215.
[16] M. Khoshki, A. Hassan, S.A. Sadiq, S. Abdelbaqi, A dynamic thermal response on thermal conductivity at different temperature and moisture levels of EPS insulation, Case Stud. Therm. Eng. 14 (2019), 100481.
[17] A. Listiyarini, Pemanfaatan limbah Stryfoom sebagai fikulan dalam proses penjerihan air melalui proses sulfonasi, Jurnal Kimia dan Kemasan 27 (2) (2005) 14–20.
[18] P.S. Saja, C.R. Reshmi, P. Sagitha, A. Sojith, Electropun nanofibrous membranes for water purification, Polym. Rev. 57 (3) (2017) 467–504.
[19] Z. Yang, Y. Zhou, Z. Feng, X. Rui, T. Zhang, Z. Zhang, A review on reverse osmosis and nanofiltration membranes for water purification, Polymers 11 (8) (2019) 1252.
[20] M.M.A. Shirazi, S. Bazgir, F. Meshkani, Electropun nanofibrous membranes for water treatment, Advanc. Membr. Technol. (2020).
[21] V.E. Krisanndika, Produksi Nano Fiber Dari Aplikasinya Dalam Pengolahkan Air. Zemodo, 2017, pp. 1–7.
[22] A. Malara, P. Frontera, L. Bonaccorsi, P.L. Antonucci, Hybrid zeolite SAPO-34 fibres made by electrospinning, Materials 11 (12) (2018) 2555.
[23] A.M. Piras, F. Chiellini, E. Chiellini, L. Nikkola, N. Ashamakhki, New multicomponent bioerodible electropun nanofibers for dual-controlled drug release, J. Biomat. Sci. Polym. 23 (5) (2008) 423–443.
[24] S. Huan, G. Liu, G. Han, W. Chong, Z. Fu, Q. Wu, Q. Wang, Effect of experimental parameters on morphological, mechanical and hydrophobic properties of electropun polystyrene fibers, Materials 8 (5) (2015) 2718–2734.
[25] T. Noguchi, M. Miyashita, Y. Inagaki, H. Watanabe, A new recycling system for expanded polystyrene using a natural solvent. Part 1. A new recycling technique, Polymer. Technol. Sci. 11 (1) (1998) 19–27, 199802.
[26] P.W. Goetz, The New Encyclopaedia Britannica, fifteenth ed., 3, Encyclopaedia Britannica Inc., Chicago, 1986, p. 937.
[27] R. Budiyono, Pengaruh Salinitas Terhadap Pertumbuhan Ikan Sidat Fase Glass Eel Sebagai Alternatif Teknologi Budidaya Ikan Sidat (Anguilla Bicolor Bicolor). Undergraduate Thesis, FMIPA UNS, 2013.
[28] M. Fatoni, C. Muryni, S. Nograh, Studi agihan salinitas air tanah daging dki Kecamatan puring kabupaten kebumen tahun 2016, J. Geoloo 4 (1) (2018) 77–87.
[29] L.D. Talley, Salinity Patterns in the ocean in the earth system: Physical and chemical Dimensions of global environmental change, encyclopedia of global environmental change, in: Michael C MacCracken and John S Perry, John Wiley & Sons, Chichester, 2002.
[30] V. Vijayakdevi, D. Kisharg, Eco-friendly methanesulfonic acid and sodium salt of dodcylbenzene sulfonic acid soped cross-linked chitosan based polymer electrolyte membranes for fuel cell applications, J. Membr. Sci. 525 (2017) 45–59.
N. Wu, X. She, D. Yang, X. Wu, F. Su, Y. Chen, Synthesis of network reduced graphene oxide in polystyrene matrix by a two-step reduction method for superior conductivity of the composite, J. Mater. Chem. 22 (2012) 17254–17261.

M.J.A. Sales, S.C.L. Dias, J.A. Dias, T.A.P.F. Fimentel, Stability studies of ZSM-5/polystyrene and V/polystyrene composites, Polym. Degrad. Stabl. 87 (1) (2005) 153–160.

A. Rahma, M.M. Munir, A. Khairurrijal Praetoyo, V. Suendo, H. Rachmawati, Intermolecular interactions and the release pattern of electrospun curcumin-polyvinyl (pyrrolidone) fiber, Biol. Pharm. Bull. 39 (2) (2016) 163–173.

A.A. Bhutto, D. Vesely, B.J. Gabrys, Miscibility and interactions in polystyrene and sodium sulfonated polystyrene with poly(vinyl methyl ether) PVME blends. Part II. FTIR, Polymer 44 (21) (2003) 6627–6631.

C.W. Purnomo, B. Lenora, W. Budhijanto, H. Hinode, Sorption and ion exchange behaviour of natural zeolite packing, Makara J. Tech. 21 (1) (2017) 33–36.

M. Fires, M. Murariu, A.M. Cardoso, L. Bonnard, P. Dubois, Thermal degradation of poly(lactic acid)-zeolite composites produced by melt-blending, Polym. Bull. 77 (2020) 2111–2137.