ISSN: 0974-5823 Vol. 7 No. 7 July, 2022

International Journal of Mechanical Engineering

Fabrication and Characterization of Mixed Matrix Membrane for Aroma Recovery

Dhivya Arikrishnan

Department of Chemical Engineering, National Institute of Technology Raipur, India

Amit Keshav

Department of Chemical Engineering, National Institute of Technology Raipur, India.

***Abstract* -** Mixed matrix membranes have gained a lot of interest in recent years for its wide variety of applications, aroma recovery in the food industry being the one. A mixed matrix composite membrane was developed by overlaying polyvinyl alcohol (PVA) – zeolite solution on a low-cost ceramic substrate via the spin coating technique. The prepared mixed matrix membrane was characterized using Fourier Transform Infrared Spectroscopy (FTIR), scanning electron microscope (SEM), Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD), and contact angle (CA) measurement. The FTIR quantities revealed the surface functional group in zeolites. The homogeneous dispersion of zeolite particles is depicted in this SEM image. The existence of zeolite particles is disclosed by XRD peaks, the thermal stability of the membranes is demonstrated by TGA, and the membrane is obtained to be hydrophilic in nature by CA measurement. The developed membrane survived the gas permeability course successfully. Thus the prepared mixed matrix membranes can be employed in pervaporation-based aroma recovery of waste streams.

Index Terms – *Food industry, aroma recovery, pervaporation, membranes, characterization*

INTRODUCTION

Membrane clarification of fruit juices especially the one involving ceramic membrane offers significant advantages such as, being heat resistant, a clean method of recovery, and potentially lower aroma losses [1-3]. In this regard, mixed matrix membrane (MMM) is a novel type of membrane material that has the potential to significantly advance existing membrane-based separation technology. MMM, being an appealing material with excellent separation qualities, has been the topic of several academic investigations undertaken by various academics worldwide. Traditionally, these developing materials for separation were created by integrating typical inorganic fillers into a polymer matrix, such as zeolite, carbon molecular sieve, and silica nanoparticles [4]. A mixed matrix pervaporation membrane made of multiwall carbon nanotubes (MWCNTs) and polydimethylsiloxane (PDMS) was successfully produced and characterized with a dipping quantity of 2% by Li, Liao, Sun, Li, Zhu, Zhong and found the recovery rates of linalool, MetSa, and Ionone to be 85.80%, 90.84%, and 83.40%, respectively from brewed black tea [5]. Rao, Ni, Sun, Zhu, Zhou, Yao [6] fabricated ZIF-8/PDMS hybrid membranes which were utilized to extract volatile aromatic compounds (VACs) from natural blackberry juice. At a temperature of 50 °C, the maximum recovery rates for linalool, benzaldehyde, and ethyl acetate were 93.8%, 92.1%, and 75.2%, respectively, demonstrating the outstanding performance of the ZIF-8/PDMS hybrid membrane.

A critical review of the above kinds of literature conveys that the organic polymer matrix loaded with inorganic fillers is successful in volatile organic compounds recovery. This integration of the excellent selectivity of zeolite molecular sieves and the structural stability and cheap ease of processing of polymeric materials, improve membrane separation performance far beyond the inherent characteristics of the polymer matrix [7]. In the present work, the preparation of PVA- LTA zeolite mixed matrix membrane for aroma recovery was presented. Inexpensive ceramic support was prepared using kaolin (50%) and titanium dioxide (50%) in the uniaxial compaction method, followed by the preparation of PVA -LTA zeolite solution. Subsequently, the PVA-LTA zeolite is coated on the ceramic support with the help of a spin coater. Running time, and volume required for coating are studied. To determine the general membrane properties, a morphological examination of the membrane was undertaken by Field emission scanning electron microscopy (FESEM), thermal stability was studied using TGA, functional group identification was done using FTIR, and phase transition was determined by XRD. The contact angle analysis was also performed to determine the hydrophilicity nature of the composite membrane prepared.

MATERIAL AND METHODS

I. Materials

Kaolin, titanium dioxide, polyvinyl alcohol, sodium aluminate, sodium metasilicate, and sodium hydroxide were supplied by Loba Chemie, Ltd. India. The precursors used in this work, have their specific roles to play, for instance, kaolin was used as a base material that offers refractory properties to the membranes and titanium dioxide improves the membrane’s thermal stability.

II. Synthesis of ceramic membrane support

The inexpensive clay reserves are utilized for making ceramic flat membranes. The kaolin and titanium dioxide are mixed in equal proportions (50:50 wt %) with 4 mL of 2% of polyvinyl alcohol (PVA) in the pestle and mortar. The flat ceramic membrane support was prepared from the above composition in a circular form. The required amount of powder was then compressed using a hydraulic press (Guru Ramdas Machine Works, Raipur, India) with stainless steel mould at a higher pressure (50 MPa) to have a disc type of membrane (51 mm diameter and 5 mm thickness). The resulting disc membrane was then dried in a hot air oven at 100 ^{o}C for 24 h to eliminate the moisture existing in the membrane. The membrane was then sintered for 6 h at 1000 ^{o}C in a muffle furnace (Nanotec, Chennai, India) at a heating rate of 2 ^{o}C per minute. The cooling of the membrane was accomplished through a natural cooling process that involved turning off the muffle furnace. After sintering, the membrane was cleaned on both sides with an abrasive sheet (No. 220) and washed with an ultrasonicator (PCI Analytics, India) to remove any loose particles in the pore route. Finally, the membrane was dried for 24 h at 100 ^{o}C.

III. Synthesis of LTA zeolite

To proceed, sodium aluminate (NaO_2 Al_2O_3 $3H_2O$) and sodium metasilicate (Na_2SiO_3 $5H_2O$) solutions were made by dissolving sodium aluminate (NaO_2 Al_2O_3 $3H_2O$) and sodium metasilicate (Na_2SiO_3 $5H_2O$) in sodium hydroxide solution. To accomplish so, 0.723 g of sodium hydroxide was dissolved in 80 mL of Millipore water to make a sodium hydroxide solution. The concentration of NaOH solution obtained was 0.226 M. Finally, the NaOH solution was split into 2 parts. Aluminate solution was generated by adding an assumed amount of sodium aluminate to one portion of the NaOH solution. To make the silicate solution, 15.48 g of sodium metasilicate was added to the remaining NaOH solution. Finally, the silicate solution was carefully mixed with the aluminate solution to form a homogeneous solution. The resulting solution's molar composition was 3.165 M Na_2O Al_2O_3 1.926 M SiO_2 128 H_2O. The solution mix was then introduced to a Teflon-lined autoclave reactor with a capacity of 250 mL. The crystallization was carried out for 4 h at a temperature of 100 ^{o}C. The zeolite particles were retrieved and dried at 100 ^{o}C for 24 h and calcined at 600 °C for 6 h [9].

IV. Synthesis of the composite membrane

Granular PVA powder with MW = 1,15,000 g/mol of 5 wt % was dissolved in Millipore water at 90 ^{o}C with constant agitation until a full solution was obtained. LTA – Zeolite of 0.1% was then combined with PVA solution and agitated for 3 h at 70 ^{o}C. The PVA- Zeolite suspension was spin-coated (Nano tech, Chennai, India) on ceramic membrane support at 500 rpm, for 3 cycles. For each cycle, 1 mL of PVA zeolite solution was used for coating. The membranes were then dried in an oven at 40 ^{o}C for 24 h before being heated at 120 ^{o}C for 1 h to allow PVA cross-linking [10].

V. Characterization techniques

Membrane characterization approaches include porosity, pore size, and water permeability. The methods used for membrane characterization have been described elsewhere [11]. Fourier Transform Infrared Spectroscopy (FTIR), (Alpha Bruker, Germany) was utilized to determine their functional group from PVA, LTA-Zeolite, and the composite membrane. Scanning electron microscope (SEM), (ZEISS EVO18, Germany) was conducted to analyse the morphology of the synthesized LTA-Zeolite and composite membrane. Thermogravimetric analysis (TGA), was used to determine the thermal stability of the composite membrane. X-Ray Diffraction (XRD), (Karlsruhe, Bruker AXS instrument, Germany) was used to determine phase transition in PVA and the composite membrane. Contact angle (CA) measurement, (Surface Electro-Optics, Korea) was performed to determine the composite membrane's hydrophilicity. Finally, gas permeability tests were performed for the composite membrane using nitrogen with the same setup used for water permeability by changing the feed tank to a nitrogen cylinder.

VI. Gas permeation test

The gas permeation test was conducted for the prepared composite membrane using a spin coater. The membrane was encased in a stainless-steel casing with a rubber seal into the membrane assembly. The output of the membrane assembly was connected to a bubble flow meter for air permeation studies, which measures the gas flow rate for varied trans-membrane pressure drops of air. The membranes' hydraulic permeability and related pore diameter are also determined. At a temperature of 25 oC, (room temperature) all permeation experiments were carried out [11].

RESULTS AND DISCUSSION

I. Characterization of the ceramic support

The ceramic membrane support was prepared using inexpensive raw materials by the uniaxial compaction method. The prepared support is found to have good chemical stability as it showed trivial weight loss in acid, alkali, and chlorine solutions. Moreover, the support withstands high pressure (up to 414 kPa), which indicates the membrane is suitable for high-pressure operation, particularly in the food industry. From the morphological investigation by SEM analysis, it is obverted that the membrane support is free of pinholes and cracks. In general, the membrane characteristics such as porosity, average pore size, and water permeability determines the general performance of any membrane. In this work, the prepared membrane support had porosity, average pore size, and water permeability of 48%, 0.56 µm, and 1.07×10^{-6} m^3/m^2s, respectively. These results showed that the prepared had better support character.

II. Characterization of LTA zeolite

In this study, the LTA zeolite was synthesized via hydrothermal crystallization. Fig. 1 depicts the SEM images of the prepared zeolite. It is apparent that the zeolite particles are crystal in nature and cubic in shape.

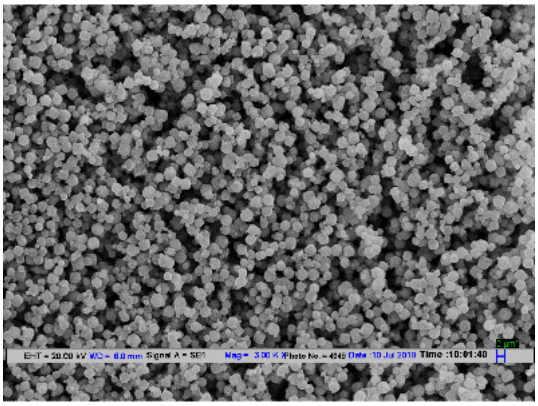


Fig. 1 SEM image of the prepared LTA zeolite

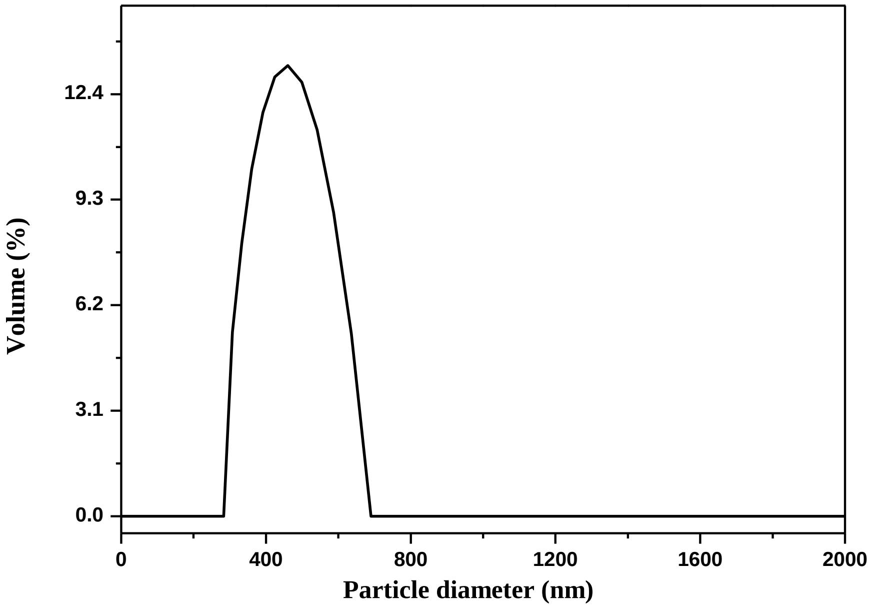


Fig.2. Particle size distribution of synthesized zeolite particles

Also, the figure indicates that the crystals are completely grown. A similar kind of image is reported for LTA zeolite synthesized by hydrothermal crystallization [9]. Fig 2 illustrates the particle size distribution of the zeolites. The particle size varies from 280 nm to 689 nm and the average particle size was 460 nm. The particle size concordance with the particle size reported in the literature [12].

III. Characterization of Composite Membrane

The FTIR spectrum of a pure PVA, LTA zeolite, and the composite membrane is presented in Fig. 3. It vividly addresses the main peaks connected with poly (vinyl alcohol). For example, there is a C–H broad alkyl stretching band (2850–3000 cm^{-1}) and characteristic strong hydroxyl bands for free alcohol (3600 – 3650 cm^{-1}), as well as a hydrogen-bonded band (3200 – 3570 cm^{-1}) [10]. The FTIR spectrum of the synthesized LTA zeolite is also shown in Fig. 3. FTIR spectroscopy in the mid-infrared region confirmed the synthesis of LTA zeolite. The bands 968, 666 and 460 cm^{-1} are like those attributed to the asymmetric stretching vibration of internal tetrahedra, the symmetric stretching vibration [13]. The 599 cm$^{−1}$ band is due to D4R which is the major secondary building unit in LTA zeolite and the band at 967 cm$^{−1}$ is attributed to the flexion vibration of the OH group in adsorbed water. Eventually, around 3361 cm^{-1}, a characteristic stretched broadband of water is present. The composite PVA-zeolite membrane showed both PVA and LTA zeolite spectra. The peak at 3400 cm^{-1} confirmed the presence of PVA which can be noted in the figure, whereas the LTA zeolite peak was observed at 967 cm^{-1}. With the above peaks, we confirm the presence of zeolite in the polymer layer.

Fig. 4 shows an SEM image of a mixed matrix membrane that has been prepared. The membrane has a smooth and dense morphological structure, as can be seen. Furthermore, it shows the uniform distribution of zeolites in the polymer matrix. A similar kind of SEM image is produced elsewhere [9].

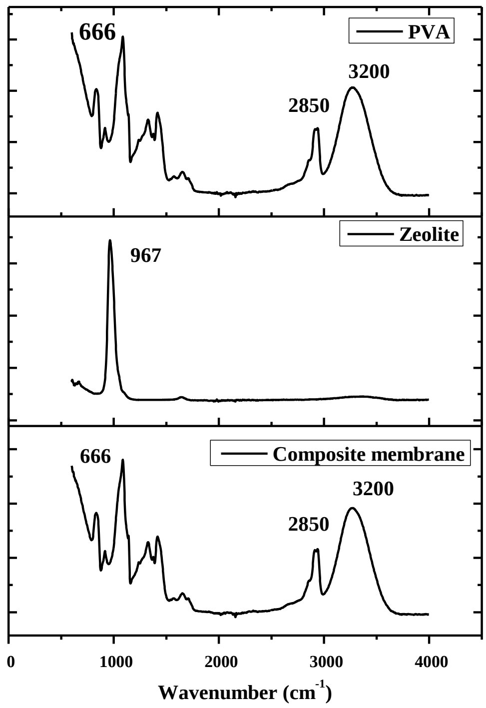


Fig 3. FTIR analysis of the PVA, Zeolite, and composite membrane

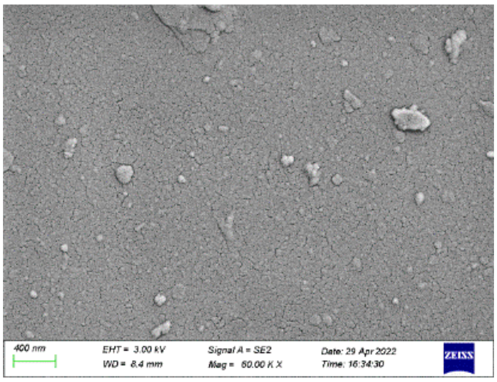


Fig 4. SEM image of the composite membrane

The TGA curve for the mixed matrix membrane is shown in Fig 5. For PVA, in the temperature range of 90–220 ºC, and moisture is released slowly. As seen in the image, there is a significant fall in weight. This is due to the degradation of the polymer in the membrane and the moisture being removed. Another weight loss of the membrane is found from 250 – 600 ºC. The sample's total weight reduction is estimated to be 7%. This proves that the zeolite is thermally stable at calcination conditions (600 ºC), allowing the zeolite membrane to be employed in gas separation with processing flow temperatures of up to 200 °C. The zeolite membrane has a similar TGA profile, according to the literature [9].

Fig. 6 shows the XRD pattern of the produced mixed matrix membrane. The XRD profile of the membrane is typical of highly crystalline materials. The main reflections are shown at 7.2^{o}, 16.2^{o} minor peaks, and could observe a significant peak at 21.7^{o}, corresponding to LTA zeolite. According to the literature, it has been compared to the values of the literature elsewhere [9,13].

Fig.7 reveals that the PVA-zeolite membrane's contact angle with water was 44^{o}. A compact structure created between the nanoparticles and the polymer matrix was linked to an increase in contact angles. Furthermore, nanoparticles on the film's surface boosted the rigidity and durability of PVA membranes and prevented water droplets from penetrating the composite film.

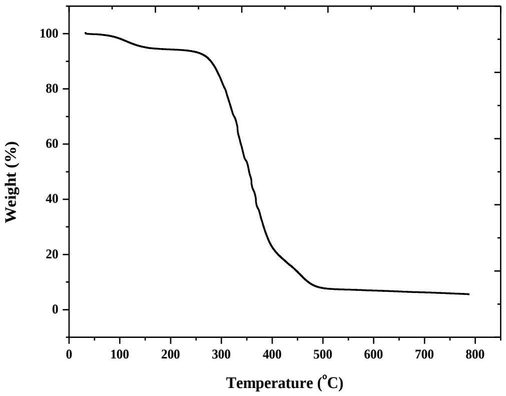


Fig. 5. TGA profile of PVA-zeolite composite membrane

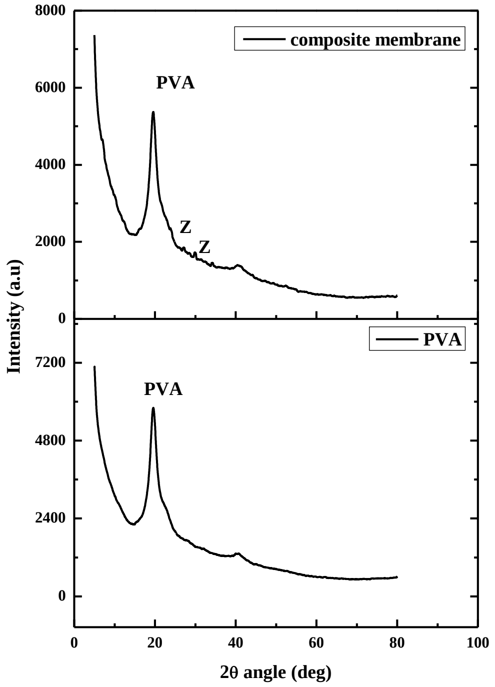
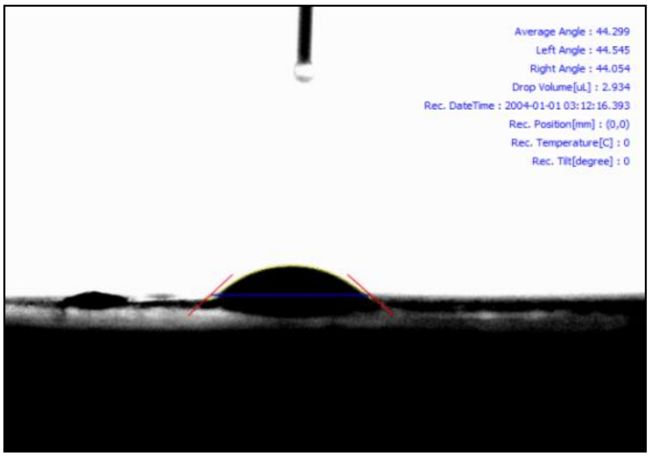


Fig. 6. XRD pattern of PVA-zeolite composite membrane and pure PVA

This was like the results obtained in literature elsewhere [14].

IV. Gas permeation

In general, gas permeation is used to identify the performance of the mixed matrix polymeric membranes as they are nonporous. In this study, a PVA-zeolite mixed matrix membrane was prepared and subjected to a nitrogen gas permeation experiment. The gas permeability was found to be 0.052 L/m^2 h kPa.



```
Average Angle : 44.299
Left Angle : 44.545
Right Angle : 44.054
Drop Volume[uL] : 2.934
Rec. DateTime : 2004-01-01 03:12:16.393
Rec. Position[mm] : (0,0)
Rec. Temperature[C] : 0
Rec. Tilt[degree] : 0
```

Fig. 7. Contact angle measurement of PVA-zeolite composite membrane

The result indicates that the membrane is suitable for pervaporation application to recover the aroma. Similar kinds of results are also reported in various literature [11].

CONCLUSION

The PVA-zeolite thin film was coated on the low-cost ceramic support, which was prepared using inexpensive raw materials by spin coating. The coating was found to be stable with the required thickness for pervaporation application. The composite membrane had better chemical stability with nitrogen gas permeation of 0.052 L/m^{2}hkPa, which indicates that the membrane has sufficient gas permeability and will be used for aroma recovery by pervaporation application.

REFERENCES

[1] Selvamuthukumaran, M., 2020, Applications of Membrane Technology for Food Processing Industries, CRC Press.

[2] Silvestre, W. P., Livinalli, N. F., Baldasso, C., and Tessaro, I. C., 2019, “Pervaporation in the separation of essential oil components: A review,” Trends Food Sci. Technol., 93, pp. 42-52.

[3] Emani, S., Uppaluri, R., and Purkait, M.K., 2013, “Preparation and characterization of low cost ceramic membranes for mosambi juice clarification,” Desalination., 317, pp. 32-40.

[4] Goh, P.S., Ismail, A.F., Sanip, S.M., Ng, B.C., and Aziz, M., 2011, “Recent advances of inorganic fillers in mixed matrix membrane for gas separation,” Sep. Purif. Technol., 81, pp. 243-64.

[5] Li, J., Liao, H., Sun, Y., Li, R., Zhu, B., Zhong, Z., and Yao, Z., 2021, “Fabrication of MWCNTs/PDMS mixed matrix membranes for recovery of volatile aromatic compounds from brewed black tea,” Sep. Purif. Technol., 259, pp.118101.

[6] Rao, Y., Ni, F., Sun, Y., Zhu, B., Zhou, Z., and Yao, Z., 2020, “Efficient recovery of the volatile aroma components from blackberry juice using a ZIF-8/PDMS hybrid membrane,” Sep. Purif. Technol., 230, pp.115844.

[7] Bastani, D., Esmaeili, N., and Asadollahi, M., 2013, “Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: A review,” J Ind Eng Chem., 19, pp. 375-93.

[8] Achari, D.D., Hegde, S.N., Pattanashetti, N.A., Kamble, R.R., and Kariduraganavar, M.Y., 2021, “Development of zeolite-A incorporated PVA/CS nanofibrous composite membranes using the electrospinning technique for pervaporation dehydration of water/tert-butanol,” New J. Chem., 45, pp. 3981-96.

[9] Vasanth, D., Pugazhenthi, G., and Uppaluri, R., 2017, “Preparation, characterization, and performance evaluation of LTA zeolite–ceramic composite membrane by separation of BSA from aqueous solution,” Sep Sci Technol., 52(4), pp.767-77.

[10] Khoonsap, S., Khansawai, P., and Amnuaypanich, S., 2010, “Mixed matrix membranes from crosslinked poly (vinyl alcohol)(PVA) composited with zeolite 4A grafted with poly (2-hydroxyethyl methacrylate)(zeolite-g-PHEMA),” InAdvanced Materials Research Trans Tech Publications Ltd, 93, pp. 137-140.

[11] Nandi, B.K., Uppaluri, R., and Purkait, M.K., 2008, “Preparation and characterization of low cost ceramic membranes for micro-filtration applications,” Appl Clay Sci., 42(1-2), pp. 102-10.

[12] Kannangara, I., Jayawardhana, Y., Munasinghe, E., Rajapakse, A., Bandara, A., Weerasooriya, R., and Jayarathna, L., 2020, “Synthesis and characterization of nano zeolite-A with aid of sodium dodecyl sulfate (SDS) as particle size-controlling agent,” Colloids Surf. A Physicochem. Eng. Asp., 589, pp.124427.

[13] Belaabed, R., Elabed, S., Addaou, A., Laajab, A., Rodríguez, M.A., and Lahsini, A., 2016, “Synthesis of LTA zeolite for bacterial adhesion,” Bol. Soc. Esp. Ceram. Vidr., 55(4), pp. 152-8.

[14] Zhang, Y., Li, H., Li, H., Li, R., and Xiao, C., 2006, “Preparation and characterization of modified polyvinyl alcohol ultrafiltration membranes,” Desalination., 192(1-3), pp. 214-23.