Fabrication of ZIF-300 membrane and its application for efficient removal of heavy metal ions from wastewater

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A B S T R A C T

Membrane technology is an energy-efficient approach for purification of wastewater. In this work, for the first time, a novel pure zeolite imidazolate framework-300 (ZIF-300) MOF membrane was fabricated and applied for removing heavy metal ions from wastewater. The fine structure of ZIF-300 layer was characterized by positron annihilation spectroscopy technique. Cross-flow and long-term operation test was also carried out to investigate the membrane stability. The obtained ZIF-300 membrane exhibited a high and stable performance with the water permeance of 39.2 L/m\textsuperscript{2} h bar and rejection rate of 99.21% for CuSO\textsubscript{4}. This high separation performance combined the extraordinary stability demonstrated that the as-prepared pure ZIF-300 MOF membrane could be a potential candidate for the water treatment.

1. Introduction

Due to the rapid development of industries, such as metal plating, mining operations, battery, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, etc., heavy metal contaminants were directly or indirectly discharged into the environment. Unlike other organic contaminants, heavy metal ions are non-biodegradable and do harmful to mankind health, causing various diseases and disorders, therefore they must be removed from the wastewater and collected before discharge. This will require better water treatment and collection systems. In this work, for the first time, a novel pure ZIF-300 MOF membrane was fabricated and applied for removing heavy metal ions from wastewater. The fine structure of ZIF-300 layer was characterized by positron annihilation spectroscopy technique. Cross-flow and long-term operation test was also carried out to investigate the membrane stability. The obtained ZIF-300 membrane exhibited a high and stable performance with the water permeance of 39.2 L/m\textsuperscript{2} h bar and rejection rate of 99.21% for CuSO\textsubscript{4}. This high separation performance combined the extraordinary stability demonstrated that the as-prepared pure ZIF-300 MOF membrane could be a potential candidate for the water treatment.

Zeolite imidazolate framework-300 (ZIF-300, Zn(2-mim)\textsubscript{0.86}(bbIm)\textsubscript{1.14}) \cite{28} is a new kind of water-stable ZIF with cha-bazite (CHA) topology, which was facilely prepared by the reaction of Zn(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O and 2-methylimidazolate with the link of 5(6)-bromobenzimidazole in the mixed solution of N,N-dimethylformamide (DMF) and water (Fig. 1). According to the BET characterization of ZIF-300 crystals, the aperture size of ZIF-300 is about 7.9 Å \cite{28}, and it is larger than the kinetic diameter of water (H\textsubscript{2}O, ∼2.8 Å), but smaller than the hydrated diameter of heavy metal ions that need to be removed (Table S1) \cite{32}. Moreover, crystal structure and sorption performance of ZIF-300 were remained under humid conditions. With the size discrimination as well as the water-stable property, ZIF-300 crystals will be employed as a novel membrane material to be applied in removal of heavy metal ions from water if ZIF-300 membrane can be fabricated.
This work, for the first time, reports the design and fabrication of pure ZIF-300 membrane via second-growth method [33–37]. The synthesis conditions of ZIF-300 membrane were investigated in order to optimize the membrane quality, which includes metal concentration of synthesis temperature, concentration of mother solution and synthesis duration. Additionally, the positron annihilation spectroscopy (PAS) technique was carried out to non-destructively characterize the hierarchical structure of the ZIF-300 membranes. Membrane stability was studied by the cross-flow long-term operation test. The obtained membrane shows outstanding operational stability, there is no degradation of membrane performance observed after nearly 12 h rejection test. Thus, the as-prepared ZIF-300 membrane exhibited good potential in the application of wastewater treatment.

2. Experimental section

2.1. Materials

5(6)-bromobenzimidazole (bbImH), 2-methylimidazole (2-mImH), N, N-dimethylformamide (DMF) and alumina powders (particle size of ~ 400 nm) were purchased from Sigma Aldrich (USA). Anhydrous methanol was obtained from Acros Organics. Zinc nitrate hexahydrate were purchased from Merck Chemical Co. rhodamine B (RhB, C28H31ClN2O3, MW: 479.02 g/mol), methyl orange (MO, C14H14N3NaO3S, MW: 327.33 g/mol), cupric sulfate (CuSO4), cadmium sulfate (CdSO4), cobalt sulfate (CoSO4) were obtained from Sigma Aldrich (USA). All of these chemicals were used without further purification.

2.2. Alumina substrate preparation

A certain amount of α-Al2O3 powders were pressed at 20 MPa to prepare the disks. The α-Al2O3 porous substrates are an average pore size of 150 nm and porosity of about 35%. The final α-Al2O3 support is 2 mm thick and 28 mm in diameter. Before the growing of the ZIF-300 membranes, one side of the sintered and flinty support was polished by 1200-mesh SiC sand paper, washed in deionized water to get rid of powders, and then dried in an oven at 120 °C for 24 h.

2.3. Synthesis of ZIF-300 crystals

ZIF-300 MOFs were synthesized following to the procedures in recent work [28]. Zn(NO3)2·4H2O (29.8 mg, 0.114 mmol), 2-mImH (11.7 mg, 0.143 mmol), and (bbImH, 28.2 mg, 0.143 mmol) were dissolved in a solvent mixture of DMF (4.75 mL) and water (0.25 mL) in a 10 mL PTFE reaction still. Then the still was heated at 120 °C for about 72 h. The ZIF-300 MOFs powder was achieved by centrifugation at the speed of 10000 rpm for 10 min and washed by DMF three times. After the initial washing, the ZIF-300 MOFs were immersed in methanol for three days for solvent exchange at ambient temperature. Finally, at the end of the third day, the ZIF-300 MOFs were evacuated at 10 mTorr for 24 h at the room temperature, followed by subsequent heating at 180 °C for 24 h.

2.4. ZIF-300 seeding layer deposition

The dried home-made Al2O3 substrate polished by 1200-mesh SiC sand paper was seeded with ZIF-300 seed by dip-coating. The hydrothermally synthesized ZIF-300 crystals was removed from the PTFE reaction followed by subsequent centrifugation to wipe off the bulky particles. Then, the mother solution with ZIF-300 nanoparticles was poured into a culture dish used as seeding solution. The polished side of alumina substrate was immersed into the ZIF-300 MOFs suspension for 1 min and then heated in the vacuum oven at 50 °C for 2 h.

2.5. ZIF-300 membrane preparation

The ZIF-300 membrane was fabricated on α-Al2O3 substrate by the second-growth method (Fig. 2). The second-growth process, prepared by mixing 2-mImH (23.4 mg, 0.286 mmol), bbImH (56.4 mg, 0.286 mmol), and Zn(NO3)2·4H2O (59.6 mg, 0.228 mmol) with 25 mL DMF and 5 mL DI water. Then, ZIF-300 seeded alumina substrate was placed vertically in a Teflon lined stainless steel autoclave with the mixed solution. After that, the autoclave was moved to the oven and heated at 120 °C for 72 h. Finally, the membrane was washed with DMF for several times and immersed into methanol solution for solvent exchange for 3 days, and then followed by subsequent heating at 100 °C for 24 h.

2.6. ZIF-300 MOF crystal stability test

ZIF-300 MOF crystals stability tests were carried out by immersing it to different feed solutions (CuSO4, 10 mM; CdSO4, 10 mM; CoSO4, 10 mM, Al2(SO4)3, 10 mM; CuSO4·CdSO4, (1:1)). After nearly 30 days, the samples were filtrated and washed with deionized water thoroughly. Finally, the samples were evacuated at 10 mTorr at room temperature for 24 h, followed by subsequent heating at 180 °C for 24 h.
2.7. Characterizations

The crystalline structure of ZIF-300 membrane and the stability of the ZIF-300 MOFs particles immersed in the ion and dye solutions were measured by X-ray diffraction (XRD, D8-advance, Bruker, Germany) using Cu Kα radiation in the range of 0–50° with an increment of 0.05° at ambient temperature. The morphology and energy dispersive spectroscopy (EDS) characterization of the as-prepared ZIF-300 membranes were characterized by field emission scanning electronic microscope (FESEM, S4800, Hitachi, Japan). All the samples were treated by gold under vacuum. The pore size distribution of the porous alumina circular disk was analyzed by automatic mercury porosimeter (Poremaster GT-60, AUANTACHROME, USA). The concentration of feed side and permeate side of dyes were characterized by UV–Visible Spectrophotometer (UV–Vis, Perkin Elmer, Lambda 950, USA). Inductively coupled plasma atomic emission spectrometry was carried out to measure the concentration of ion aqueous solutions (ICP-AES, Optima 2000 DV).

2.8. Positron annihilation lifetime spectroscopy

The positron annihilation spectroscopy including positron annihilation lifetime spectroscopy (PALS) and Doppler broadening energy spectroscopy (DBES) was carried out to non-destructively characterize the pore structure of supported ZIF-300 membrane. This experiment was investigated in the R&D Center for Membrane Technology at Chung Yuan University in Taiwan [38–40]. The surface of the ZIF-300 membrane with different synthesis temperature was subjected to positron irradiation. The pore size and the distribution were examined by PALS at a certain depth nearly 9 µm, while the DBES qualitatively examines the pore profiles as a function of depth from the membrane surface. All these achieved PALS spectra were analyzed by a finite-term lifetime analysis method using PATFIT program. It provides the details about the average lifetime for the pick-off ortho-positronium (o-Ps) (τ) and its intensity (I). The mean pore radius is followed by the semi-empirical Eq. (1):

\[
\tau = \frac{1}{2} \left[ 1 - \left( \frac{R}{R + \Delta R} \right)^2 + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R + \Delta R} \right) \right]^{-1}
\]

where R is the pore radius and ΔR is an empirical parameter. In this work, ΔR is 1.656 Å. [41]

The DBES was investigated at different positron incident energies in the range of 0.1–25 keV and recorded by a HP Ge solid-state detector for a sample membrane. The incident energy of the slow positron beam (E+) is followed by the Eq. (2):

\[
Z = \frac{40 E_+^{1.6}}{\rho}
\]

where Z is nm, E+ is in keV and ρ refers to the density of the membrane. In this work, ρ is 1 g/cm³. The obtained parameters, S and R were collected form DBES [38].

2.9. Separation performance measurement

A self-designed dead-end membrane cell and cross-flow cell filtration equipment were established to evaluate the filtration performance of ZIF-300 membrane. (Fig. 5). All feed ion aqueous solutions (CuSO₄, CoSO₄, CdSO₄) were with the concentration of 10 mM, and all dye aqueous solutions (RhB, MB, MO) were with the concentration of 50 ppm. In order to avoid of the influence of the adsorbing of ion and dye, the data collection was started after nearly 3 h stability test [42]. Additionally, each rejection performance is the average of at least three membranes synthesized at the same condition. The water permeance was calculated according to the Eq. (3)

\[
J = \frac{V}{A \times t \times P}
\]

where V (L) is the volume of the collected water in the permeate side, A is effective area of the membrane (m²), t (h) is the operation time and p (bar) is the transmembrane pressure, respectively.

The concentrations of heavy ion solutions (CuSO₄, CoSO₄, CdSO₄) were characterized by inductively coupled plasma atomic emission spectrometry (ICP-AES), and UV–Vis spectra was carried out to measure the concentration of dye retentions (RhB, MB, MO). The rejection ratios can be expressed by Eq. (4)

\[
R = \left( 1 - \frac{c_p}{c_f} \right) \times 100\% 
\]

where \(c_p\) and \(c_f\) id the concentration of permeate and feed side, respectively.

![Schematic illustration of ZIF-300 membrane preparation process.](image)
3. Results and discussion

3.1. Optimization of membrane synthesis conditions

The membrane quality was checked by morphology from SEM, crystal structure from XRD and separation performance. It was found that the synthesis temperature played the most significant influence on the formation of ZIF-300 membrane on the Al2O3 substrate. As revealed by the surface and cross-sectional SEM images in Fig. S1, the ZIF-300 layer is not completely continuous until the synthesis temperature is increased up to 120 °C, while it was destroyed if the temperature is too high (140, 160 °C). The XRD patterns further confirmed this membrane structural variation with the synthesis temperature (Fig. 3a). The ZIF-300 characteristic peaks appear in the membrane samples synthesized at low temperatures (80, 100 °C), although they are weaker than that of the membranes synthesized at 120 °C due to the imperfect membrane layer. However, when the synthesis temperature is higher than 120 °C, which is undesirable for nucleation and growth of the ZIF-300 crystals. As a result, these characteristic peaks can be hardly detected in the high-temperature synthesized ZIF-300 membranes, indicating the damage of ZIF-300 layer or structure. When the synthesis temperature is increased to 120 °C, the CuSO4 rejection rate of ZIF-300 membrane is gradually improved to 99.87%, suggesting an integrated ZIF-300 separation layer (Fig. 3b). However, the rejection rate sharply drops to ~ 25% when the temperature is higher than 120 °C, which is attributed to a highly defective membrane structure. The separation performance agrees well with the XRD results (Fig. 3a) and SEM (Fig. S1).

In order to confirm the formation and filtration mechanism of ZIF-300 membranes, we took the PAS techniques again to characterize the pore structure of the ZIF-300 membranes with different synthesis temperatures. As shown in Fig. 3c-d, the lifetime distribution curves were obtained by MELT program at a fixed incident energy of 2 keV and 5 keV, respectively. The results show that free-volume are different for the ZIF-300 membranes synthesized under different temperatures (Tables 1, 2). When synthesis temperature increased from 80 to 120 °C, the free-volume radius (at positron energy of 2 keV) of the membranes became smaller (from 3.553 Å to 3.117 Å, indicating that higher temperature is beneficial for the inter-growth of ZIF-300 crystals). However, synthesis temperature higher than 120 °C would have destructive effect on the growth of ZIF-300 crystal structure, as revealed by XRD characterizations (Fig. 3a). Additionally, free-volume radius of the membranes suddenly increased to 4.179 Å when the synthesis temperature reached 140 °C, which also proves that the structural change of the membrane layer. Thus, it can be expected the membrane synthesized at 120 °C exhibited better separation performance due to the

![Fig. 3.](a)XRD patterns of ZIF-300 membrane supported on alumina circular disk with different synthesis temperature (80 °C, 100 °C, 120 °C, 140 °C and 160 °C); (b) Separation performance (CuSO4) of ZIF-300 membranes with different synthesis temperature, the feed solution is CuSO4 with the concentration of 10 mM, operating conditions: pressure 1 bar at 25 °C; (c) 2 keV (44 nm) and (d) 5 keV (450 nm) distribution curves of o-Ps with lifetime in the range of 0-6 ns representing all the micropores in the membranes with different synthesis temperature.

Table 1

<table>
<thead>
<tr>
<th>sample</th>
<th>Temperature (°C)</th>
<th>τ3 (ns)</th>
<th>Δτ3 (ns)</th>
<th>I3 (%)</th>
<th>R (Å)</th>
<th>ffv (%)</th>
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<td>2.878</td>
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<td>4.930</td>
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<td>0.046</td>
<td>13.394</td>
<td>3.215</td>
<td>3.355</td>
</tr>
<tr>
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<td>120</td>
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<td>0.042</td>
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<td>3.117</td>
<td>2.521</td>
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<tr>
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smaller size of the free-volume in the ZIF-300 membrane. Furthermore, identical tendency can be clearly observed under the positron energy of 5 keV (Table 2). This again indicates that free-volume size decreased with the increase of synthesis temperature, which offers the feasibility of the fabrication of defect-free MOF membrane.

The formation of ZIF-300 membrane can also be controlled by the concentration of mother solution [Zn(NO\(_3\)]\(_2\cdot4\)H\(_2\)O] or synthesis duration which mainly determines the membrane thickness ranging from 3 to 40 \(\mu\)m, as indicated from the SEM images shown in Figs. S2 and S3. Meanwhile, the XRD peak intensity of ZIF-300 membrane is increased gradually with the lift of Zn(NO\(_3\)]\(_2\cdot4\)H\(_2\)O concentration or synthesis duration (Figs. S4a and S5a). Once a continuous ZIF-300 layer is formed, the resulting thicker membranes with higher transport resistance exhibit reduced water permeance with nearly constant separation which mainly determines the membrane thickness ranging from 3 to 40 \(\mu\)m, as indicated from the SEM images shown in Figs. S2 and S3.

### Table 2

<table>
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<tr>
<th>sample</th>
<th>Temperature (°C)</th>
<th>(\tau_f) (ns)</th>
<th>(\Delta\tau_f) (ns)</th>
<th>(I_s) (%)</th>
<th>(R) (Å)</th>
<th>(\psi) (%)</th>
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<td>0.047</td>
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<td>4.670</td>
</tr>
<tr>
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<td>120</td>
<td>3.903</td>
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<td>7.317</td>
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<tr>
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<td>9.413</td>
<td>4.624</td>
<td>7.019</td>
</tr>
</tbody>
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3.2. Characteristics of ZIF-300 membrane

Fig. 4e-f present the morphology of optimized ZIF-300 membrane supported on Al\(_2\)O\(_3\) disk. A well inter-grown ZIF-300 layer is formed on top of the porous substrate with the thickness of \(\sim 10\ \mu\)m. The membrane surface is dense without cracks or defects. EDX mapping was used to further confirm chemical property of the separation layer and support layer. As displayed in Fig. 4e-d and S6, a distinct boundary exists between the ZIF-300 layer (Zn mapping) and Al\(_2\)O\(_3\) layer (Al mapping), indicating a good combination and no interfacial defects of the supported MOF membrane. Fig. S7 gives the typical XRD patterns of defective and defect-free ZIF-300 membranes. Apparently, the defect-free membrane exhibited the strongest characteristic peaks and best crystallinity compared with the defective membrane and seeding layer.

PAS techniques including PALS and DBES were carried out to characterize the microstructure of the ZIF-300 layer. As shown in Fig. 5a, the surface of the ZIF-300 membrane was subjected to positron irradiation. According to the demonstration of DBES in reported literature [38,39,43], the parameter \(S\) is associated with the positronium (Ps) pick-off annihilation in free volumes (Å to nm). From the DBES, parameter \(S\) was achieved to analyze the pore structure. Interestingly, it was found that the ZIF-300 separation layer is asymmetric in the case of its free volume distribution (Fig. 5a). As shown in Fig. 5b, the \(S\) parameter is as a function of the positron incident energy. From the plot of \(S-E\), three major regions of the ZIF-300 membrane can be identified- (I) near the top surface and dense skin ZIF-300 layer (region I), (II) transition layer (ZIF-300 + seed layer, region II), and (III) seed layer (region III). Due to back diffusion of the positron from the surface, the \(S\) parameter initially shows a relative lower value (In region I). When the positron penetrates into the window of the MOFs, the majority of the positron will be trapped in the cage. Then, this positron was annihilated, leading to the sharp increase of \(S\) parameter with the mean depth. As the positron penetrated deeper into the transition layer (In region II), the \(S\) parameter decreased at a relatively low rate. This phenomenon was mainly result from the steady increase of the free volume (lower density relative to dense skin layer). When the positron continues penetrating into the seed layer, the \(S\) parameter decreased sharply with the increase of mean depth (In region III). Due to the low growth density of the seed layer, the positron may penetrate through the seed layer without resistance and inhibit the formation of positronium.

3.3. Separation performance

The heavy metal ion rejection test of ZIF-300 membrane with optimal synthesis parameters was carried out by filtration under transmembrane pressure of 1 bar at 25 °C (Fig. S8). The ion concentration...
was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). ZIF-300 membranes exhibited excellent rejection for all the tested pure and mixed ions (Fig. 6a, rejection rate for CuSO4: 99.87%, CoSO4: 99.63%, CdSO4: 99.32%, Al₂(SO₄)₃: 99.52%, CuSO₄:CoSO₄ (1:1): 98.95%). Additionally, it showed higher water permeance for the CuSO₄ rejection than other ions, which might be due to the lower sorption of Cu²⁺ on the membrane surface leading lower transport resistance for water[44]. Each rejection performance is the average of at least three membranes synthesized at the same condition, which can all maintain good reproducibility. Furthermore, we chose three different dyes with different charge properties to identify whether electrostatic interaction would contribute to the rejection: rhodamine B (RhB) is an electroneutral molecule, methylene blue (MB) is positively charged and methyl orange (MO) is negatively charged. The concentration of organic dye was determined by UV–Vis spectra. As shown in Fig. 6b, it exhibits improved rejections for all the tested dyes (rejection rate for RhB: 99.91%, MB: 99.64%, MO: 98.89%). These results indicate that the achieved enhanced rejection of metal ions and dyes in this novel ZIF-300 membrane is on the basis of size-exclusion mechanism. Meanwhile, they further demonstrate that the successful formation of a continuous ZIF-300 membrane with high separation performance.

A continuous cross-flow nanofiltration test (Fig. S9) with feed of CuSO₄ solution was carried out to study the stability of the ZIF-300 membrane. During 12 h of continuous operation, the CuSO₄ rejection performance is kept high and stable, showing an average water permeance of 39.2 L/m²h bar and rejection rate of 99.21% (Fig. 7). This indicates our as-prepared ZIF-300 membranes are potential in the...
application of the wastewater treatment.

XRD characterization of the ZIF-300 membrane (Fig. 8a) was carried out after the separation tests. Results show that all membranes maintained the original crystal structure of ZIF-300, indicating a good stability of ZIF-300 membrane in aqueous environment. Moreover, after the ZIF-300 crystals were immersed in various kinds of water solutions (CuSO₄, 10 mM; CdSO₄, 10 mM; CoSO₄, 10 mM; Al₂(SO₄)₃, 10 mM; CuSO₄·CdSO₄ (1:1), respectively) for nearly 30 days, the crystallinity of ZIF-300 was still well maintained without peak shifts as shown in Fig. 8b. Additionally, as shown in Fig. 9, the crystal morphology is also preserved after the immersion. There is a minor morphology variation among these images in Fig. 9a-f, which could be mainly due to the non-uniform morphology of the as-synthesized ZIF-300 crystals used for the stability test. Indeed, we found that the as-synthesized ZIF-300 crystals before immersing in the feed solution, also showed a similar morphology variation under SEM characterization.

As compared in Fig. 10 and Table S2, our ZIF-300 membrane exhibited extraordinarily high water permeance, which is nearly 1.5–49 times higher than that of commercial membranes, inorganic membranes and organic membranes. Meanwhile, the preserved high rejection during the continuous filtration of CuSO₄ solution suggests the size discrimination effect of ZIF-300 contributing to the excellent separation performance.
4. Conclusions

As desired, for the first time, an integrated pure ZIF-300 membrane was successfully fabricated on Al2O3 substrate by second-growth method. The effect of synthesis temperature, duration and concentration of mother solution were systematically investigated. Additionally, PAS technique was carried out to non-destructively characterize the hierarchical structure of the ZIF-300 membranes. Owning to the good size discrimination property as well as water stability, the ZIF-300 membrane is a potential candidate for the wastewater treatment.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jmemsc.2018.10.080.

References