

# A mini-review and recent outlooks on the synthesis and applications of zeolite imidazolate framework-8 (ZIF-8) membranes on polymeric substrate

Putu Doddy Sutrisna,<sup>a\*</sup>  Nicholaus Prasetya,<sup>b</sup> Nurul Faiqotul Himma<sup>c</sup> and I Gede Wenten<sup>d</sup> 

## Abstract

Zeolite imidazolate framework (ZIF) is one of the subclasses of metal–organic frameworks (MOFs) that has been widely investigated in the last decade. Among the ZIF members, a particular interest has been devoted to ZIF-8 due to various factors, such as mild and fast synthesis conditions, framework stability and the right pore aperture to perform various separations. Recently, there has also been growing interest in developing ZIF-8 as a thin layer membrane on polymeric substrates as they are considerably cheaper than the inorganic ones. This review then discusses recent advances in this field, focusing on various fabrication strategies and promising future applications. The challenges and future perspectives are also discussed with an emphasis on employing this approach in industrial scale.

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**Keywords:** mini-review; ZIF-8 membrane; polymeric substrate; synthesis; applications

## INTRODUCTION

Metal–organic framework (MOF) is an inorganic–organic hybrid material that has gained considerable interest in the last two decades. This is because it offers numerous benefits, such as high surface area and tailorability, making it suitable for various applications including gas adsorption and catalysis. Among the subclasses of MOFs, the zeolitic imidazolate framework (ZIF) has been widely investigated.<sup>1</sup> This material has a similar topology to zeolite and it is constructed from tetrahedral transition metal cations such as  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ , which are linked to imidazole-based ligands. Although their coordination bonds are not as stable as those found in zeolite, several ZIFs, such as ZIF-8, ZIF-11 and ZIF-69, can maintain their framework stability in boiling solvents.<sup>2</sup> Among ZIF material, ZIF-8, which is constructed from  $\text{Zn}^{2+}$  and 2-methylimidazole with sodalite (SOD) topology, is the most extensively studied.<sup>3</sup> This might be due to various factors, such as its relatively mild reaction conditions, considerably fast reaction time, framework flexibility and stability, and molecular sieving potential ability based on its pore aperture.<sup>4</sup>

Recently, there has also been a growing interest in turning ZIF-8 into a membrane. Figure 1 shows the trends in publications on ZIF-8-based membranes and applications. In general, the synthesis of ZIF-8-based membranes could be accomplished by two different methods. In the first method, ZIF-8 particles are dispersed in a polymer matrix, which is then cast into a membrane. This approach is known as mixed matrix membranes (MMMs).<sup>5</sup> In the second method, ZIF-8 is fabricated as a selective thin layer, which is grown on a porous substrate.<sup>6</sup> Both inorganic and polymeric

substrates have been applied to synthesize ZIF-8 membranes. However, compared with inorganic materials, polymeric materials could offer more benefits, particularly since they are more easily processed and considerably cheaper than inorganic substrates, such as alumina, which could hamper the industrial implementation of ZIF-8 membrane.<sup>7</sup> Growing a defect-free ZIF-8 membrane on a polymeric substrate could then produce a low-cost membrane that is more scalable and more industrially attractive.<sup>7</sup> Therefore, this review focuses on the development of ZIF-8 membrane on polymeric substrates. The review is divided into three main sections: fabrication strategies, various promising applications, and challenges and future perspectives.

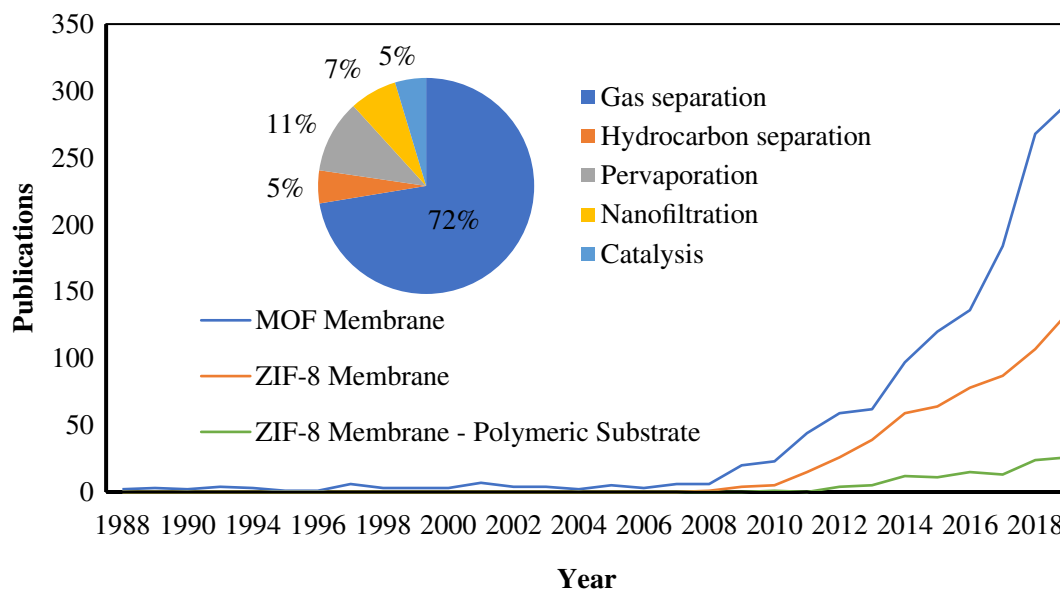
\* Correspondence to: PD Sutrisna, Department of Chemical Engineering, University of Surabaya, Jalan Raya Kalirungkut, Surabaya 60293, Indonesia. E-mail: pudod@staff.ubaya.ac.id

a Department of Chemical Engineering, University of Surabaya, Surabaya, Indonesia

b Barrer Centre, Department of Chemical Engineering, Imperial College London, London, UK

c Department of Chemical Engineering, Universitas Brawijaya, Malang, Indonesia

d Department of Chemical Engineering, Institut Teknologi Bandung, Bandung, Indonesia



**Figure 1.** Number of published papers related to ZIF-8-based membrane, indexed by Scopus. The inserted pie chart illustrates the distribution of ZIF-8 membrane applications.

## FABRICATION STRATEGIES OF ZIF-8 MEMBRANES ON POLYMERIC SUBSTRATES

The techniques employed to fabricate ZIF membranes on polymeric substrate can be classified into two techniques: *in situ* growth and secondary growth techniques. The processes are depicted in Fig. 2(A) and (B), respectively. There are also other fabrication techniques that could be used, such as counter-diffusion. These strategies are discussed below.

### *In situ* growing method

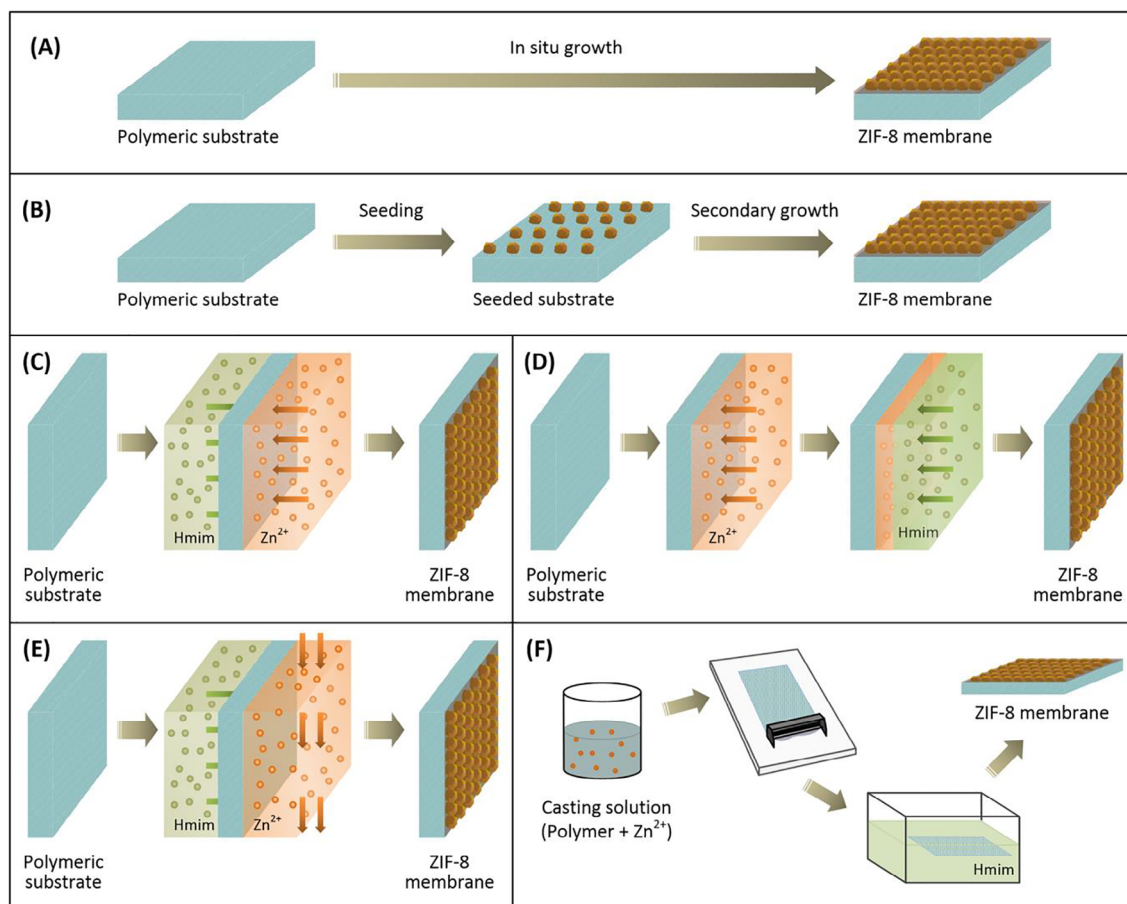
*In situ* growing is one method to fabricate a ZIF-based membrane without a particle seeding step. During the synthesis, a porous support is soaked or immersed in ZIF precursor solutions at a controlled temperature.<sup>8,9</sup> Both nucleation and crystal growing steps occur simultaneously since no crystal seed is provided during the membrane fabrication, resulting in a defect-free ZIF membrane layer on the polymeric substrates. Both flat-sheet and hollow fibre membrane configurations have been utilized to grow defect-free ZIF membranes using this strategy.

The simplest strategy to grow ZIF-8 membrane based on this method is to directly immerse the polymeric substrate into MOF precursor solutions. Various polymers have been investigated using this approach, such as polysulfone (PSF),<sup>10</sup> polyphenylsulfone (PPSU)<sup>11</sup> and polyimide (PI).<sup>12</sup> In this approach, controlling the synthesis condition is important since it will affect both the particle size of the ZIF-8 and the final membrane structure.<sup>10,12</sup> Apart from direct immersion, *in situ* growing could also be accomplished by first depositing a metal precursor on a polymeric substrate, followed by crystal growing. ZnO has been investigated for use as a metal precursor deposited on polyacrylonitrile (PAN) polymeric substrate.<sup>13</sup> The layer was then converted into a ZIF-8 membrane once the substrates underwent a solvothermal reaction. A similar approach has also been used by depositing Zn-based gel on various polymeric substrates, such as polyether sulfones (PES), polyvinylidene fluoride (PVDF), PAN and PSF.<sup>14</sup> *In situ* growing technique can also be combined with other approaches, such as layer-by-layer deposition method as

depicted in Fig. 2(D).<sup>11,15</sup> When using this technique, the polymeric substrate was first immersed in a precursor solution containing the metal ions. It was then subsequently immersed in a ligand precursor solution, followed by washing and drying. This procedure was repeated several times to obtain a few ZIF-8 layers on the polymeric substrate.

Although relatively simple, one of the main challenges for fabricating using unmodified polymers is relatively weak interaction between the particle and the substrate. Another challenge is the tendency of the particles to self-aggregate on the surface or inside the pores of polymeric support. The presence of aggregates will form defects that can reduce the selectivity and/or rejection capacity of the membranes. The aggregation of particles can be alleviated by modifying the surface of the particles, such as surface functionalization to adjust the hydrophilicity/hydrophobicity of the particles or to add additional functional groups, thus enhancing particle–polymer interaction.<sup>16–24</sup> Efforts to create either more hydrophilic or hydrophobic surface can be achieved by various techniques, including the application of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxydisilane (FAS-17) or 5,6-dimethylbenzimidazole (DMBIM) to decrease the particle's surface energy,<sup>19,25</sup> postsynthetic covalent modification,<sup>26,27</sup> dip coating or spray coating in hydrophobic solution.<sup>21,28</sup> In addition, the surface of polymeric substrate can be modified to provide a superhydrophobic surface that can enhance its interaction with the particles.<sup>18</sup> Furthermore, it was also observed that more than one step synthesis is required to obtain a defect-free ZIF membrane.<sup>10</sup> This can then be addressed, for example, by slightly modifying the synthesis process by gradually removing the solvent during ZIF-8 membrane synthesis. This step contributes to increasing reactant concentration during membrane synthesis and thus enhances ZIF-8 crystallization on PAN substrate, resulting in a defect-free membrane.<sup>29</sup>

Another way to address the polymer–particle interaction issue is to modify the polymeric substrates. Introducing a heterogeneous nucleation site on top of the polymeric substrate is one way to address the issue. This could be accomplished, for instance, by depositing a non-activated ZnO layer.<sup>30</sup> Differing from ZnO as the metal source for membrane growing, the non-activated state of ZnO will limit the involvement of Zn<sup>2+</sup> ion from ZnO to form



**Figure 2.** Various techniques to synthesize ZIF-8 membrane on polymeric substrates: (A) *in situ* growth; (B) secondary growth; (C) counter-diffusion; (D) layer-by-layer; (E) interfacial; and (F) phase transformation interfacial growth; Note: Hmim = 2-methylimidazole.

ZIF-8 during membrane formation. Therefore, ZnO will act as a heterogeneous nucleation site that could establish a stronger anchor between the PVDF substrate and the particle. A TiO<sub>2</sub> layer coated on an 3-aminopropyl)triethoxysilane-functionalized PVDF substrate has also been shown to be able to act as a heterogenous nucleation site where a defect-free ZIF-8 membrane could be directly grown by immersing in the MOF precursor solutions without further pre-seeding.<sup>16,31,32</sup>

Another way to address the interaction issue is to introduce new functional groups on to the polymeric substrate that could establish a stronger bond with the ZIF-8 particles. Modification of PVDF through ammoniation has been reported for enabling the fabrication of an ultrathin ZIF-8 membrane through vapor phase conversion of deposited ZnO.<sup>33</sup> The structural integrity of the ultrathin membrane showed enhanced polymer–particle interaction. Ethylenediamine (EDA) has also been employed to introduce amine groups on to a bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide (BPPO) polymeric substrate by reaction with its bromine (–CH<sub>2</sub>Br) group. EDA contributes in various ways to obtaining a defect-free ZIF-8 membrane, such as by providing heterogeneous nucleation sites and covalently binding the Zn<sup>2+</sup>.<sup>34</sup> Polymeric substrate modification could also be accomplished by hydrolysis. This has been investigated on a PAN support, which was modified by NaOH solution. The process successfully hydrolysed the CN group to be carboxyl group, hence establishing a stronger bond with the metal ion during growth of the ZIF-8 layer.<sup>35</sup>

### Secondary growing method

Although relatively simple, the *in situ* growing technique of ZIF-8 membranes faces some challenges particularly in controlling the growing of particles on the substrate surface. To enhance the performance of ZIF membranes, several studies have employed a secondary growing technique to produce defect-free ZIF membranes. In the secondary growing technique, the nucleation and crystal growing steps are separated and thus offer better control on the microstructure of the membranes.

Seeding the polymeric substrate is the first step in accomplishing this method. This step is also crucial since a homogeneous particle seeding across the substrate surface is highly required to obtain a homogeneous ZIF-8 membrane. Once the seeding process is complete, the substrate is subjected to secondary growing to obtain ZIF-8 membranes through various methods such as solvothermal and microwave-assisted techniques.<sup>36</sup>

There are various techniques to coat the substrate surface with ZIF-8 particles. Rubbing could be used to introduce the seed on to the polymeric substrate. This strategy has been used to grow a thin film of ZIF-8 on the surface of PES by first rubbing the support surface with ZIF-8 seed particles, followed by immersing the substrate in the ZIF-8 synthesis solution for secondary growing.<sup>37</sup> Dip coating is also another simple strategy to introduce ZIF seeds on to a polymeric substrate.<sup>38</sup> In this case, the polymeric substrate is dipped in a suspension containing ZIF-8 particles, followed by

drying. Another method that could be used is spin coating. This technique has been used to introduce a mixed seed containing ZIF-8 and 2D graphene oxide (GO) on a Nylon substrate.<sup>39</sup> Spin coating can offer better control coating through parameter adjustment.

Particle seed can also be generated *in situ* on the polymeric substrate. In this scenario, the ZIF-8 seed is generated on the polymeric substrate rather than prepared in advance. This has been investigated using Matrimid hollow fibre as a polymeric substrate.<sup>40</sup> The metal solution was first pumped into the bore side of the hollow fibre, followed by pumping the ligand solution. While the ligand solution is still being pumped, the hollow fibre is placed in a microwave to induce crystallization process. The microwave-assisted seeding process is believed to improve the interaction of both physical and chemical bonding between the seeds and the substrate. The seeded hollow fibre is then further subjected to secondary growing by pumping a ZIF-8 synthesis solution into the bore side. Another technique is to introduce a metal source that could be converted into ZIF-8 seeds. This technique has been used to deposit a composite layer consisting of gelatin and zinc hydroxide nanostrands (ZHN) on a PVDF hollow fibre substrate through filtration.<sup>41</sup> The layer could be deposited either inside or outside the hollow fibre. The ZHN in the layer was then converted into ZIF-8 seeds once immersed in the ZIF-8 precursor solution in the first step, which was then followed by secondary growing to form the ZIF-8 membrane.

As in *in situ* growing, polymeric support modification could also be employed to enhance the adhesion of ZIF-8 membranes on the support. This has been investigated using vapour phase modification to add amine functional groups and reduce the pore size of the support. This technique could produce a ZIF-8 membrane with a relatively continuous structure.<sup>34</sup> Two-step polymeric support modification could also be conducted to further enhance the adhesion of ZIF-8 membrane on a PI support layer.<sup>38</sup> The first step involved modifying the PI support with EDA to introduce an amine functional group. The amine functional group was then further covalently bonded with imidazole-2-carboxaldehyde (ICA) to produce homogeneous seeds. The modified support was then immersed in ZIF-8 solution for particle seeding, followed by secondary growing.

Another approach to modify the polymeric substrate is to turn it into a mixed matrix support. Using ZnO as the nanofiller in polyetherimide (PEI) polymer matrix, a continuous and defect-free ZIF-8 membrane has been successfully fabricated. The substrate was first seeded with ZIF-8 particles through a combination of rubbing and dip coating method, followed by secondary growing. ZnO is assumed to act as a secondary source of metal ion to enhance ZIF-8 adhesion to the support.<sup>42</sup> ZIF-8 seed could also be directly embedded into a polymer, resulting in a mixed matrix membrane support.<sup>43</sup> Upon secondary growing, a continuous ZIF-8 membrane could be uniformly grown on the mixed matrix support.

### Other approaches

In addition to *in situ* and secondary growing methods, several studies offer new and innovative techniques to grow ZIFs layer on the surface of polymeric substrate. One strategy is through a counter-diffusion technique, which is depicted in Fig. 2(C). In this strategy, the polymeric substrate acts as a barrier between the metal and ligand precursor solution.<sup>44</sup> The reaction then occurs at the interface, resulting in ZIF membranes that could be grown on either side of the membrane depending upon the synthesis

conditions and configuration. This technique has been shown to grow a ZIF-8 membrane on a Nylon<sup>44</sup> and poly-thiosemicarbazide polymeric substrate.<sup>45</sup>

One of the key challenges in this approach is to control the diffusion process of both metal and ligand. Uncontrolled diffusion leads to the formation of membrane defects.<sup>46</sup> This could then be addressed using various approaches such as substrate modification. BPPO covalently bonded to EDA has been proven to address this issue. EDA can act as an anchor for the metal precursor to control its diffusion, so that its concentration is higher on the metal side of the substrate, resulting in a well-controlled condition for ZIF-8 membrane growth.<sup>47</sup> A polymeric substrate with narrower pore size than in a microfiltration range could also be employed to control the diffusion process, since it offers better control for the transport of both metal and ligand. This has been shown by using a composite substrate of polydopamine and single-wall carbon nanotube (PD/SWCNT) to fabricate a ZIF-8 membrane.<sup>46</sup> Another strategy is to utilize a 2D material that could act as a confined space and barrier between the two reactants. This has been investigated by using a mixed-seed of ZIF-8 and 2D GO coated on a Nylon substrate. The presence of the 2D layer offers better crystallization control during the counter-diffusion process and thus can produce an ultra-thin ZIF-8 membrane.<sup>39</sup>

Interfacial synthesis (Fig. 2E) can also be employed to produce a defect-free ZIF-8 membrane on a polymeric substrate. This strategy is inspired by the interfacial polymerization technique, which has been widely investigated to fabricate a thin-film composite membrane. Differing from counter-diffusion, the main idea of interfacial synthesis is to use two immiscible liquids as solvents for metal and ligand precursors. The reaction occurs at the interface between the two liquids. Using this strategy, a defect-free ZIF-8 membrane can be fabricated using PES as the substrate.<sup>48,49</sup> The substrate was first immersed in the aqueous metal precursor solution, followed by immersion in ligand precursor in an organic solvent. A longer reaction time with higher ligand:metal ratio fabricated on a denser polymeric substrate was found to be beneficial in producing a defect-free ZIF-8 membrane.<sup>48,49</sup>

Another innovative method to grow a ZIF-8 membrane on a polymeric substrate is through microfluidic continuous processing. There are two possible scenarios in this case. The first option is to continuously flow both metal and ligand solutions on one side of the substrate. They could be flowed simultaneously<sup>50</sup> or in sequence.<sup>51</sup> In this scenario, the ZIF-8 membrane will grow on the side where the reagent solution is flowed, and controlling the flow rate is important to obtain a defect-free membrane.<sup>50</sup> Another scenario is to flow both metal and ligand solutions separately, with the polymeric substrate acting as a barrier separating both solutions.<sup>52-54</sup> Differing from the first scenario, the second scenario offers more flexibility to grow the membrane on either side of the membrane, depending on the location of the metal reagent.<sup>52,53</sup> Various processing parameters can then affect the resulting ZIF-8 membrane formation in this scenario, such as solvent selection to dissolve the reagents, flow rate of the reagent solution, polymeric substrate porosity and heat pretreatment of polymeric substrate before membrane formation.<sup>53,54</sup>

Another strategy that could be employed is by integrating the ZIF particle synthesis with conventional membrane fabrication. Li and coworkers described this strategy as phase transformation interfacial growth (PTIG), as depicted in Fig. 2(F).<sup>55</sup> This was started by first dissolving the PES as the polymeric substrate with Zn metal precursor in a solvent. After casting the first precursor

solution, it was then immersed in a coagulation bath containing 2-methylimidazole and poly(sodium 4-styrenesulfonate) (PSS) to induce non-solvent-induced phase separation to form a continuous layer of ZIF-8 membrane on the polymer substrate. The role of the PSS is to heal the intercrystalline defects of the ZIF-8.

## APPLICATIONS OF ZIF-8 MEMBRANES ON POLYMERIC SUBSTRATES

Once successfully turned into a membrane on a polymeric substrate, ZIF-8 membranes can be used for various applications, which will be discussed below.

### Gas and hydrocarbon separation

Gas separation is one of the most widely investigated fields for ZIF-8-based membranes grown on a polymeric substrate. This is due to the pore aperture of ZIF-8 (0.34 nm), which is suitable for performing molecular sieving once a defect-free membrane could be fabricated, particularly for H<sub>2</sub> (kinetic diameter 0.29 nm) and CO<sub>2</sub> (kinetic diameter 0.33 nm) separation against other gases. The membrane could then be applied, for example, in the field of both pre- and post-combustion CO<sub>2</sub> separation.

Apart from gas separation, ZIF-8 has also been widely investigated for hydrocarbon separation. Particular attention has been given to olefin/paraffin separation, since performing this separation using a membrane could significantly improve the current process in terms of energy consumption.<sup>56</sup> This application has also been investigated with a ZIF-8 membrane grown on a polymeric substrate with emphasis on propylene/propane separation, which is currently performed using cryogenic distillation, since the molecular structure of ZIF-8 is suitable for performing this separation.<sup>45</sup> A defect-free ZIF-8 membrane thus exhibits high propylene permeance while maintaining a satisfactory separation factor.<sup>7</sup>

Compared with ZIF-8 grown on an inorganic substrate, ZIF-8 membrane on a polymeric substrate might suffer both lower permeance and separation factor. This could be for several reasons, such as polymeric chain rigidification during high-temperature synthesis conditions<sup>40</sup> and membrane cracking during handling because of the flexibility of the polymer.<sup>13</sup> Despite this, membranes with satisfactory gas separation performance could still be obtained in the absence of ZIF-8 intercrystalline defects. Certain strategies could then be employed, such as growing nanosized rather than micro-sized crystals<sup>10</sup> and coating with other polymers such as PDMS on top of the ZIF-8 layer.<sup>10</sup> A summary of gas and hydrocarbon separation performance of various ZIF-8 membranes grown on polymeric substrates is given in Table 1.

### Pervaporation

Pervaporation is a membrane-based separation process where a liquid mixture is separated based on the vaporization of one of its constituents. The vaporization occurs because the permeate side of the membrane is operated under vacuum. Since the vapor phase is involved in pervaporation, the ZIF-8 membrane could be suitable for carrying out the process because of its hydrophobic properties.<sup>58</sup> This application has then been investigated either by using ZIF-8 as a porous filler to form a mixed matrix membrane or as free-standing membrane.<sup>59,60</sup>

This objective could also be then carried out using ZIF-8 membrane grown on a polymeric substrate. Zhao and coworkers have shown this by growing ZIF-8 on a modified PI substrate for dehydration of isopropanol.<sup>38</sup> This is based on the kinetic diameter of

the water molecule (0.265 nm), which is able to pass through the ZIF-8 pore aperture. It was observed that introducing ZIF-8 membrane on to the substrate could enhance the separation factor compared with only modified PI. The separation factor could be further improved with a thicker ZIF-8 layer and additional polymer coating (PDA or PDMS) since, as in gas separation, the additional coating could contribute in healing the defects although with the sacrifice of membrane flux.

### Nanofiltration

Nanofiltration is another application field employing a ZIF-8 membrane that has been grown on a polymeric substrate. The pore aperture of ZIF-8 is suitable for filtering Red Bengal (RB) dye dissolved in water and ethanol.<sup>48,49</sup> The rejection rate was observed to be more than 90% and, although the solvents used have a larger molecular size than the pore aperture of ZIF-8, they could still permeate through because of the framework flexibility of ZIF-8. This satisfactory performance, however, could only be obtained under optimized ZIF-8 membrane synthesis conditions. This could be achieved by using a less porous polymeric substrate, for example, since it could contribute in increasing the ligand:metal ratio during the ZIF-8 membrane fabrication, resulting in a defect-free membrane with higher rejection rate.<sup>48</sup>

Rhodamine-B (RhB) is another dye molecule that could be filtered by ZIF-8 membrane grown on PVDF substrate.<sup>41</sup> Since RhB diameter (1.1 nm) is larger than the ZIF-8 pore aperture, it could be exclusively rejected, while the water could permeate easily through the membrane. It was observed that more than 90% rejection could be obtained with water permeance reaching around 137 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>.

### Catalysis

Apart from separation, the ZIF-8 membrane also has the potential to be employed in catalysing several reactions. It has been previously observed that ZIF-8 particles could be used as a catalyst for transesterification of vegetable oil<sup>61</sup> and in the Knoevenagel condensation reaction.<sup>62</sup> This ability could then be translated once it is turned into a membrane. ZIF-8 membrane grown on PI substrate has been observed also to catalyse the Knoevenagel condensation reaction.<sup>12</sup> Reactions of various aromatic aldehydes and malononitrile could be carried out with the membrane, and a comparable yield was obtained with a reaction catalysed by 2-methylimidazole, indicating their role as a weak base for the reaction. Compared with using particles, utilizing the ZIF-8 in a membrane form is more beneficial since the catalyst separation process is not required once the reaction finishes.

## CHALLENGES AND FUTURE PERSPECTIVES

Efforts to improve the separation performance and application of ZIF-8 membrane have been made recently and can be distinguished by synthesis and application points of views. In terms of membrane synthesis, there are various challenges in fabricating a ZIF-8 membrane on a polymeric substrate that need to be addressed in future research. From membrane formation, reducing the ZIF-8 membrane thickness is important since this could significantly improve membrane productivity by increasing its permeance. In microfluidic continuous processing, one of the strategies is to limit the diffusion process of the reactants and thus inhibit over-growing of the ZIF-8 membrane.<sup>54,63</sup> This could be done, for example, by initially heating the polymeric substrate

**Table 1.** Gas separation performance of ZIF-8 membranes grown on various polymeric substrates

| Support                | Membrane fabrication method                               | Thickness ( $\mu\text{m}$ ) | $\text{H}_2$ permeance <sup>a</sup>                | Selectivity   |  | Ref. |
|------------------------|---|-----------------------------|--|---|--|------|
|                        |   |                             |  | $\text{H}_2/\text{CO}_2$  | $\text{H}_2/\text{N}_2$                              |      |
| Poly-thiosemicarbazide | Counter-diffusion   | 0.68                        | $2.1 \times 10^{-7}$                               | 1737 ( $\text{H}_2/\text{C}_3\text{H}_8$ )                            | 25.5 ( $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ ) | 45   |
| PEI/ZnO                | Mixed matrix substrate                                    | 1.5                         | $1.6 \times 10^{-6}$                               | 22.4 ( $\text{H}_2/\text{C}_3\text{H}_8$ )                            |  | 42   |
| PSF                    | None  | 35                          | $2 \times 10^{-7}$                                 | 10.5 ( $\text{H}_2/\text{CH}_4$ )                                     | 12.4   | 10   |
| PD/SWCNT               | Counter-diffusion   | ~0.55                       | 6.31   | 43  | NA   | 46   |
| PES                    | <i>In situ</i> growth using Zn-based gel deposition       | 20                          | $1.11 \times 10^{-7}$                              | NA  | 22.7   | 14   |
| PPSU                   | Layer-by-layer <i>in situ</i> growing directed with PEBAX | 32                          | $76 \times 10^{-8}$                                | 6.4 ( $\text{CO}_2/\text{CH}_4$ )<br>5.7 ( $\text{CO}_2/\text{N}_2$ ) | 12.5   | 11   |
|                        | <i>In situ</i> growing directed with PEBAX                | 30                          | $46 \times 10^{-8}$                                | 7.3 ( $\text{CO}_2/\text{CH}_4$ )<br>6.9 ( $\text{CO}_2/\text{N}_2$ ) | 14.4   |      |
| PSF                    | Continuous processing                                     | 3.6                         | $4.7 \times 10^{-9}$                               | 2.6   | 18.3   | 50   |
| ZIF-8/PES composite    | Secondary growing   | 6.5–8                       | $7.3 \times 10^{-9}$ ( $\text{CO}_2$ )             | 14.6 ( $\text{CO}_2/\text{CH}_4$ )                                    |  | 43   |
| PVDF                   | Non-activated ZnO coating                                 | ~50                         | $20.1 \times 10^{-7}$                              | 16.3  | 18.1   | 30   |
| PVDF hollow fibre      | $\text{TiO}_2$ functionalized                             | ~1                          | 201  | 7   | 7.8  | 16   |
| PVDF hollow fibre      | Ammoniation   | ~40                         | 24.43  | 12.18   | 14.31  | 57   |
| PAN hollow fibre       | Dehydrogenation   | <1                          | 3.05   | 6.85  | N/A  | 35   |
| Nylon hollow fibre     | Counter-diffusion   | ~16                         | 126.2  | N/A   | 3.7  | 44   |
| Porous PSF             | Micro-nanosized growth                                    | ~50                         | 2.0  | N/A   | 12.4   | 10   |
| BPPO                   | Chemical modification                                     | 0.2                         | 20.5   | 12.8  | 9.7  | 34   |
| BPPO flat sheet        | Counter-diffusion   | ~2                          | 7.5  | 5.1   | 8.3  | 47   |
| Torlon HF              | Continuous processing                                     | 8.5                         | 22 GPU   | 22 ( $\text{CO}_2/\text{N}_2$ )                                       |  | 53   |
| Matrimid               | Secondary growing   | 0.8                         | $183.2 \times 10^{-10}$ ( $\text{C}_3\text{H}_6$ ) | 45.5 ( $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ )                  |  | 40   |

<sup>a</sup> Permeance units are  $\times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ .

during the first step of membrane formation. This step will induce faster crystallization and create a thin, dense crystal layer which acts as an additional resistance for the transport of reactants and thus inhibit ZIF-8 membrane formation, resulting in a thinner membrane.<sup>54</sup> Another way to create a thinner membrane is by reducing the ZIF-8 particle size and enhancing interaction between the ZIF layer and porous support. The reduction in particle size can potentially provide better crystal packing during ZIF-8 growth on the polymeric substrate. This reduction can be prepared by controlling the crystal growth to produce smaller-size crystals with narrow crystal size distribution (CSD).<sup>8</sup> Improved interaction between the support and ZIF-8 layer can be achieved by functionalization of the support and ZIF-8, as well as improving the membrane intergrowth through chemical, physical, thermal and improved seeding techniques.<sup>8,64</sup>

There are also several challenges from the application point of view. Although usually exhibiting sharp molecular sieving between  $\text{H}_2$  and other larger gases, ZIF-8 membrane grown on a polymeric substrate is rarely investigated for other promising gas separation applications such as for  $\text{CO}_2$  separation ( $\text{CO}_2/\text{N}_2$  or  $\text{CO}_2/\text{CH}_4$ ). Although the kinetic diameter of  $\text{CO}_2$  is just below the pore aperture of ZIF-8, the kinetic diameter similarities of the gas pairs could make the separation process more challenging, which could be exacerbated by the ZIF-8 framework flexibility.<sup>7</sup> Testing the ZIF-8 membrane under real conditions for gas separation is also necessary, since ZIF-8 is a weak base and thus

prone to framework destruction, particularly in the presence of contaminants and acid gases such as  $\text{H}_2\text{S}$ .<sup>7</sup>

Another application challenge is related to the stability of the ZIF-8 membrane for liquid-based separation. A previous report has shown the issue of ZIF-8 framework stability under hydrothermal conditions both as particles or in membrane form.<sup>65,66</sup> This issue must then be considered if the membrane is to be applied in liquid-based applications, so the performance will not be compromised. This issue could be addressed, for example, by modifying and functionalizing the ZIF-8 membrane so that its hydrothermal resistance could be improved.

In addition, to realize the industrial application of ZIF-8 membrane, it is very important to consider using a more environmentally benign solvent during ZIF-8 membrane development and fabricating the ZIF-8 membrane using low-energy techniques to reduce production costs and to ensure the sustainability of our environment.<sup>4,5</sup>

## CONCLUSIONS

This review has successfully illustrated recent advances in the fabrication of ZIF-8 membrane on a polymeric substrate. Various strategies can be employed to grow a defect-free ZIF-8 membrane, the simplest being through *in situ* growing. Although relatively simple, this approach usually suffers from poor particle-polymer substrate interaction. This could then be improved by

modifying the substrate or through secondary growing to build a stronger anchor between the particle and the substrate. Apart from these methods, various innovative approaches could also be used to grow ZIF-8 on a polymeric substrate. One of the most widely investigated is through counter-diffusion and microfluidic continuous processing.

Once a defect-free ZIF-8 membrane is obtained, it could then be employed for various applications. One of the most widely investigated is for H<sub>2</sub> separation and propylene/propane separation, since its pore aperture is ideal to perform these separations. However, there is also a possibility to extend this to other gas separations, although some modifications are required. In addition, various liquid-based separations such as nanofiltration and pervaporation have been investigated. However, this should be treated cautiously as some investigations have also shown ZIF-8 framework instability under hydrothermal conditions.

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## Sequential extraction of lutein and $\beta$ -carotene from wet microalgal biomass

Fabrizio Di Caprio, Pietro Altimari, Francesca Pagnanelli

Pages: 3024-3033 | First Published: 07 May 2020

[Abstract](#) | [Full text](#) | [PDF](#) | [References](#) | [Request permissions](#)

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## Productivity and scale-up of poly(3-hydroxybutyrate) production under different oxygen transfer conditions in cultures of *Azotobacter vinelandii*

Claudio Padilla-Córdova, Beatrice Mongili, Pablo Contreras, Debora Fino, Tonia Tommasi, Alvaro Díaz-Barrera

Pages: 3034-3040 | First Published: 09 May 2020

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## Biological cyanide removal from industrial wastewater by applying membrane bioreactors

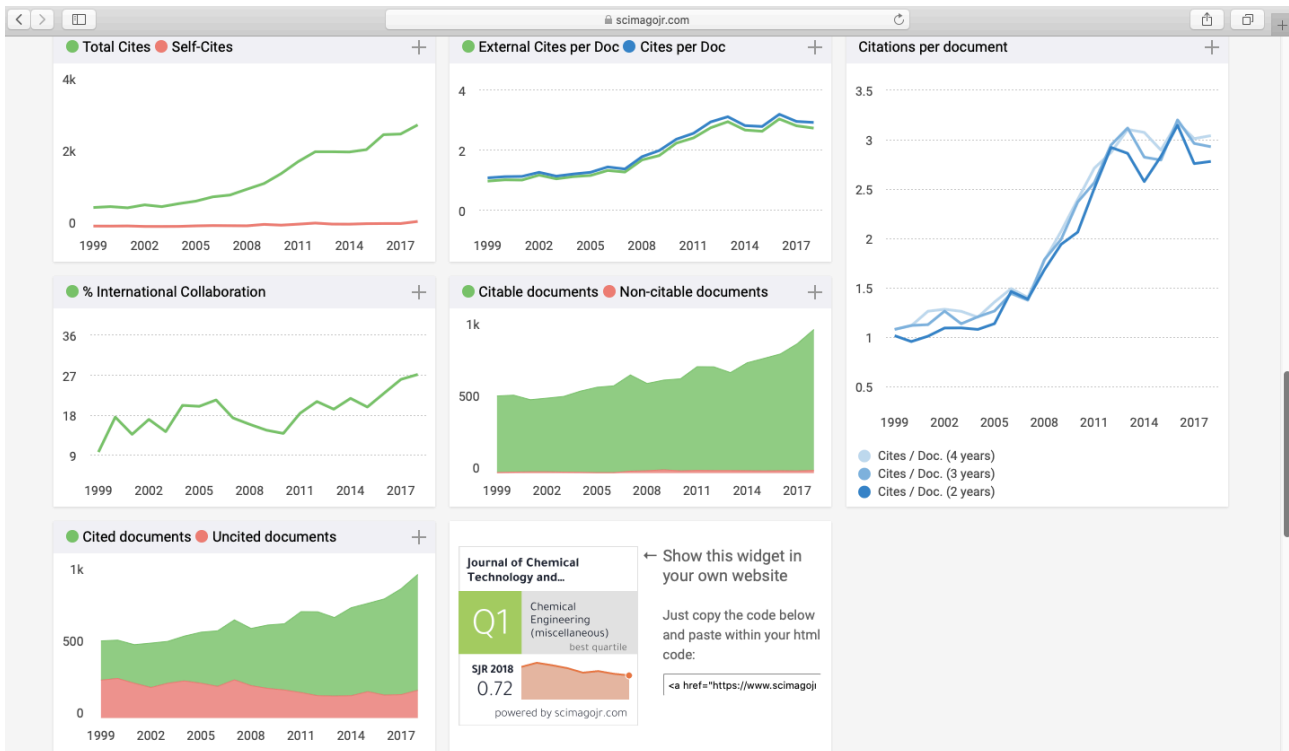
Loukas Lintzos, Elena Koumaki, Panagiota Mendrinou, Kostas Chatzikonstantinou, Nikolaos Tzamtzis, Simos Malamis

Pages: 3041-3050 | First Published: 09 May 2020

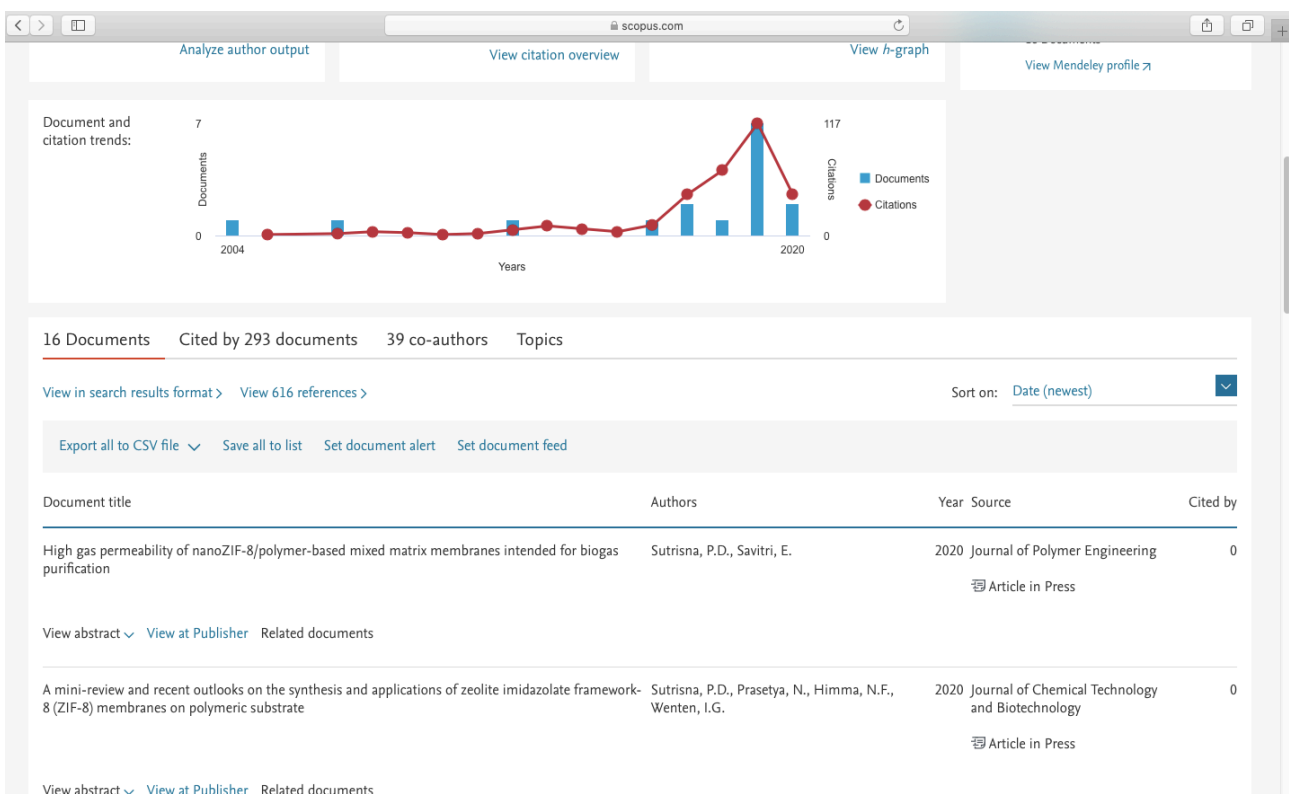
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## 1. Bukti Journal Scopus Q1 dalam halaman website Scimagojr.com



## 2. Bukti artikel dalam halaman Scopus penulis:



### 3. Bukti artikel dalam halaman Sinta penulis:

The screenshot shows the Sinta website for author Putu Doddy Sutrisna. The author's profile includes his name, affiliation (Universitas Surabaya), SINTA ID (6016571), and subjects/areas (Membrane technology, Metal organic frameworks (MOFs), Material science and engineering, Polymer science and engineering). Performance metrics are displayed: Overall Score 22.47, Overall Score V2 2071, 3 Years Score 6.89, 3 Years Score V2 1047, Rank in National 1382, 3 Years National Rank 629, Rank in Affiliation 3, and 3 Years Affiliation Rank 2. A list of publications is shown with columns for Quartile, Publications, and Citation.

| Quartile | Publications  | Citation |
|----------|---|----------|
| Q4       | Impact of instant-controlled pressure drop treatment on thermal properties and microbial decontamina<br>AIP Conference Proceedings   vol: 2114   issue :   2019-06-26   Conference Proceedin                              | 1        |
| Q1       | A review on emerging organic-containing microporous material membranes for carbon capture and separa<br>Chemical Engineering Journal   vol:   issue :   2019-01-01   Journal  | 1        |
| Q3       | Organic-inorganic nanocomposite membranes for molecular separation and bioapplications<br>IOP Conference Series: Materials Science and Engineering   vol: 703   issue :   2019-12-05   Conference Proceedin               | 1        |
| Q3       | Microfiltration of Oily Waste Water: A Study of Flux Decline and Feed Types<br>IOP Conference Series: Materials Science and Engineering   vol: 543   issue :   2019-01-01   Conference Proceedin                          | 0        |
| Q3       | Current Perspectives and Mini Review on Zeolitic Imidazolate Framework-8 (ZIF-8) Membranes on Organi<br>IOP Conference Series: Materials Science and Engineering   vol: 703   issue :   2019-12-05   Conference Proceedin | 0        |
| Q3       | High gas permeability of nanoZIF-8/polymer-based mixed matrix membranes intended for biogas purifica<br>Journal of Polymer Engineering   vol:   issue :   2020-01-01   Journal  | 0        |
| Q1       | A mini-review and recent outlooks on the synthesis and applications of zeolite imidazolate framework<br>Journal of Chemical Technology and Biotechnology   vol:   issue :   2020-01-01   Journal                          | 0        |

### 4. Bukti email penerimaan dari Editor Journal

The screenshot shows an email from the JCTB Editorial Office to Putu Doddy Sutrisna. The subject is "Accept - Journal of Chemical Technology & Biotechnology - Manuscript JCTB-19-1226.R1". The email text states that the manuscript, titled "A Mini Review and Recent Outlooks on The Synthesis and Applications of Zeolite Imidazolate Framework-8 (ZIF-8) Membranes on Polymeric Substrate", has been accepted for publication in the Journal of Chemical Technology & Biotechnology. It provides information about the publication process, including the timeline for receiving proofs and the option to publish online open access.

Accept - Journal of Chemical Technology & Biotechnology - Manuscript JCTB-19-1226.R1

JCTB Editorial Office <onbehalf@manuscriptcentral.com>  
to me, nicholaus.prasetya14, nfhimma, igw, bart.vanderbruggen

23-Mar-2020

JCTB-19-1226.R1

Dear Dr Sutrisna,

I am very pleased to inform you that your manuscript, entitled "A Mini Review and Recent Outlooks on The Synthesis and Applications of Zeolite Imidazolate Framework-8 (ZIF-8) Membranes on Polymeric Substrate", has been accepted for publication in the **Journal of Chemical Technology & Biotechnology**. Please do inform your co-authors of this decision.

Your article cannot be published until the publisher has received the appropriate signed license agreement. Within the next few days the corresponding author will receive an email from Wiley's Author Services system which will ask them to log in and will present them with the appropriate license for completion.

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Please do not hesitate to contact me should you have any questions about this process.

Many thanks for your contribution to **Journal of Chemical Technology & Biotechnology**, we look forward to seeing more of your work in the future.

Best wishes,

## 5. Copy halaman website yang memuat paper

The screenshot shows a web browser displaying the Wiley Online Library page for a mini-review. The browser's address bar shows [onlinelibrary.wiley.com](http://onlinelibrary.wiley.com). A dark blue banner at the top contains the text "COVID-19 campus closures: see options for Remote Access to subscribed content." Below this is the "Wiley Online Library" header with a search bar and a "Login / Register" link. A large advertisement banner features the text "The latest COVID-19 resources for the research community" and "VISIT THE WILEY NETWORK".


The main article content includes the journal title "Journal of Chemical Technology and Biotechnology" with the "SCI" logo. The article is identified as a "Mini-review" with the title "A mini-review and recent outlooks on the synthesis and applications of zeolite imidazolate framework-8 (ZIF-8) membranes on polymeric substrate". The authors listed are Putu Doddy Sutrisna, Nicholaus Prasetya, Nurul Faiqotul Himma, and I Gede Wenten. The publication date is "First published: 05 April 2020" and the DOI is <https://doi.org/10.1002/jctb.6433>. Below the title and authors are icons for "Read the full text", "PDF", "TOOLS", and "SHARE".

The "Abstract" section begins with the text: "Zeolite imidazolate framework (ZIF) is one of the subclasses of metal-organic frameworks (MOFs) that has been widely investigated in the last decade. Among the ZIF members, a particular interest has been devoted to ZIF-8 due to various factors, such as mild and fast synthesis conditions, framework stability and the right pore aperture to perform various separations. Recently, there has also been growing interest in developing ZIF-8 as a thin layer membrane on polymeric substrates as they are considerably cheaper than the inorganic ones. This review then discusses recent advances in this field, focusing on".

On the right side of the page, there are several promotional elements: an "Early View" notice stating "Online Version of Record before inclusion in an issue" with a thumbnail image; an advertisement for "ADVANCED SCIENCE" journal, a "Premium Open Access Journal" with an "Impact Factor 15.804" and a "Submit now" button; and a "Metrics" section with "Related" and "Information" links.



## Journal of Chemical Technology and Biotechnology

| COUNTRY  | SUBJECT AREA AND CATEGORY  | PUBLISHER                               | H-INDEX    |
|--|--|---|------------|
| <a href="#">United Kingdom</a><br> Universities and research institutions in United Kingdom | <a href="#">Biochemistry, Genetics and Molecular Biology</a><br><a href="#">Biotechnology</a><br><a href="#">Chemical Engineering</a><br><a href="#">Chemical Engineering (miscellaneous)</a><br><a href="#">Chemistry</a><br><a href="#">Inorganic Chemistry</a><br><a href="#">Organic Chemistry</a><br><a href="#">Energy</a><br><a href="#">Fuel Technology</a><br><a href="#">Renewable Energy, Sustainability and the Environment</a><br><a href="#">Environmental Science</a><br><a href="#">Pollution</a><br><a href="#">Waste Management and Disposal</a> | <a href="#">John Wiley and Sons Ltd</a> | <b>117</b> |

| PUBLICATION TYPE         | ISSN               | COVERAGE             | INFORMATION  |
|--------------------------|--------------------|----------------------|--|
| <a href="#">Journals</a> | 02682575, 10974660 | 1979-1981, 1983-2020 | <a href="#">Homepage</a><br><a href="#">How to publish in this journal</a><br><a href="mailto:jctb@wiley.com">jctb@wiley.com</a> |

## SCOPE

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B **ben lakhdar** 1 year ago

good morning, please I don't understand what Q1, Q2, Q3 and Q4 mean, can you give me a clearer idea of its meaning.

thanks in advance, my greetings.

reply



**Melanie Ortiz** 1 year ago

SCImago Team

Dear Ben,

Thank you for contacting us.

The set of journals have been ranked according to their SJR and divided into four equal groups, four quartiles. Q1 (green) comprises the quarter of the journals with the highest values, Q2 (yellow) the second highest values, Q3 (orange) the third highest values and Q4 (red) the lowest values.

Best Regards, SCImago Team

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Scopus coverage years: from 1979 to 1981, from 1983 to Present

Publisher: Wiley-Blackwell

ISSN: 0268-2575 E-ISSN: 1097-4660

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