

Alia Aqilah Ghazali, Sunarti Abd Rahman\* and Rozaimi Abu Samah

# Potential of adsorbents from agricultural wastes as alternative fillers in mixed matrix membrane for gas separation: A review

<https://doi.org/10.1515/gps-2020-0023>

Received July 17, 2019; accepted January 07, 2020.

**Abstract:** Mixed matrix membrane (MMM), formed by dispersing fillers in polymer matrix, has attracted researchers' attention due to its outstanding performance compared to polymeric membrane. However, its widespread use is limited due to high cost of the commercial filler which leads to the studies on alternative low-cost fillers. Recent works have focused on utilizing agricultural wastes as potential fillers in fabricating MMM. A membrane with good permeability and selectivity was able to be prepared at low cost. The objective of this review article is to compile all the available information on the potential agricultural wastes as fillers in fabricating MMM for gas separation application. The gas permeation mechanisms through polymeric and MMM as well as the chemical and physical properties of the agricultural waste fillers were also reviewed. Additionally, the economic study and future direction of MMM development especially in gas separation field were discussed.

**Keywords:** adsorbent; gas separation; agricultural waste; low-cost filler; mixed matrix membrane

## 1 Introduction

Separation of gases is crucial especially in chemical and petrochemical plants such as landfill gas purification, biogas upgrading, and natural gas sweetening [1]. Natural gas carries a large amount of energy that can be used as a source of cooking, heating, and electricity, as well as fuel for vehicles and as a chemical feedstock. However, crude natural gas contains acid gases such

as carbon dioxide ( $\text{CO}_2$ ) and hydrogen sulfide ( $\text{H}_2\text{S}$ ) [2]. These acidic gases are very corrosive, toxic, and flammable which can cause corrosion problems in gas transportation system. Therefore, it is necessary to remove these impurities from natural gas to meet the pipeline quality standard specifications, which only allows  $\text{CO}_2$  of less than 2 mol% [3].

Conventional industrial methods employed for gas separation include cryogenic distillation [4], physical adsorption [5] and chemical absorption [6]. Although the processes are widely known and established, they have their own inherent problems which include sensitive operating conditions, less effective, and high energy consumption [7]. Concerning these deficiencies, numerous methods have been introduced to find an alternative process for gas separation application. Membrane-based gas separation technology is growing fast and has gained a great interest by the researchers due to its promising features, such as its simplicity, easy operation, low energy consumption, and its compact structure [8].

Polymeric membrane is the commonly used membrane due to its superior gas separation properties [9]. However, the inherent trade-off between the gas permeability and selectivity deters the application of polymeric membranes [10]. A considerable effort has been put into investigations to overcome the limitation of polymeric membranes. Mixed matrix membrane (MMM), a new type of membrane formed by introducing fillers into a polymer matrix, has been identified to solve the aforementioned issues [11]. The most widely used fillers employed in the literature of adsorptive MMM are inorganic materials such as zeolite, carbon nanotube, and metal organic framework [12]. This type of membrane has the probability to achieve higher permeability and enhance selectivity, or both simultaneously [13]. However, the high cost of the existing inorganic material restricts its application [14]. This issue creates demand for new filler materials for MMM.

Recently, attention has been given towards new and novel materials which is agricultural wastes to replace the costly commercial inorganic fillers. The utilization

\* **Corresponding author: Sunarti Abd Rahman**, Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia, email: sunarti@ump.edu.my, tel.: +609-5492822, fax: +609-5492889

**Alia Aqilah Ghazali and Rozaimi Abu Samah**, Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

of agricultural wastes as a potential adsorbent has been explored by many researchers for various applications as listed in Table 1.

The literature shows that adsorbents prepared from agricultural wastes have been extensively used due to their excellent performances and low cost. There is minimal information on agricultural waste adsorbent used for gas separation. However, the number of studies in the field is increasing due to its promising features and excellent performances. On top of that, this paper will arrange all the available information on the progress of that has already been made and elaborate more on

agricultural waste as potential filler in MMM used for gas separation application.

## 2 Gas permeation mechanism

The morphology and performance of the MMM mainly depend on the choice of polymer, filler, and the amount of filler loaded in the polymer matrix. To identify the right type of polymer and dispersed filler, the transport mechanisms through the membrane should be first taken into consideration. All the gas permeation

**Table 1:** Adsorbent from agricultural wastes for various applications.

No	Agricultural wastes	Applications	References
1.	Almond shells	• CO <sub>2</sub> adsorption	Plaza et al. [15]
2.	Argan fruit shells	• CO <sub>2</sub> capture	Boujibar et al. [16]
3.	Avocado peel	• Removal of dyes	Palma et al. [17]
4.	Bagasse fly ash	• Removal of Orange G and methyl violet	Mall et al. [18]
5.	Banana peel	• Adsorption of dyes from aqueous solution	Annadurai et al. [19]
6.	<i>Caesalpinia bonducella</i> seed	• Removal of Ni(II)	Goh et al. [20]
7.	Cherry stone	• CO <sub>2</sub> /CH <sub>4</sub> separation	Álvarez-Gutiérrez et al. [21]
8.	Coconut shell	• SO <sub>2</sub> adsorption and thermal regeneration • Phenol adsorption from aqueous solution	Tseng and Wey [22] Karri et al. [23] Karri et al. [24]
9.	Coffee	• CO <sub>2</sub> capture	Querejeta et al. [25]
10.	Corn cob	• Carbon adsorbents	Kaźmierczak et al. [26]
11.	Eggshell	• CO <sub>2</sub> adsorption	Witoon [27]
12.	<i>Eucalyptus camaldulensis</i> wood	• CO <sub>2</sub> adsorption	Heidari et al. [28]
13.	Fir bark	• CO <sub>2</sub> adsorption	Luo et al. [29]
14.	Hazelnut shell	• Adsorption of Cr(VI)	Kobyia [30]
15.	Kernell shell	• CO <sub>2</sub> adsorption	Nasri et al. [31]
16.	Longan shells	• CO <sub>2</sub> capture	Wei et al. [32]
17.	Lotus stem	• CO <sub>2</sub> capture	Wu et al. [33]
18.	Macadamia nut shell	• CO <sub>2</sub> capture	Bae and Su [34]
19.	Oil palm frond	• Adsorption of bentazon from aqueous solution	Salman and Hameed [35]
20.	Oil palm shell	• Removal of H <sub>2</sub> S	Guo et al. [36]
21.	Olive stone	• CO <sub>2</sub> adsorption	Plaza et al. [37]
22.	Orange peel powder	• Water purification	Bhatnagar et al. [38]
23.	Palm oil kernel shell	• Disposal of Zn(II) from aqueous environment	Karri and Sahu [39] Karri and Sahu [40] Sumathi et al. [41]
24.	Palm shell	• Removal of SO <sub>2</sub> and NO	Zhu et al. [42]
25.	Paulownia sawdust	• CO <sub>2</sub> adsorbent	Nowrouzi et al. [43]
26.	Persian ironwood	• CO <sub>2</sub> capture	Hameed et al. [44]
27.	Pineapple stem waste	• Removal of dyes from wastewater	Lua and Yang [45]
28.	Pistachio nut shell	• SO <sub>2</sub> adsorption	Serafin et al. [46]
29.	Pomegranate peels	• CO <sub>2</sub> capture	Li et al. [47]
30.	Rice husk	• CO <sub>2</sub> adsorption	Rana et al. [48]
31.	Soya chunk	• O <sub>2</sub> reduction and CO <sub>2</sub> capture	Manyà et al. [49]
32.	Vine shoot	• CO <sub>2</sub> separation	Rouzitlab et al. [50]
33.	Walnut shell	• CO <sub>2</sub> adsorption and separation	Liu and Fan [51]
34.	Wheat straw	• Removal of Cd in aqueous solution	Nguyen-Thanh and Bandosz [52]
35.	Wood	• H <sub>2</sub> S removal • SO <sub>2</sub> retention	Macías-Pérez et al. [53]

mechanisms in polymeric membrane and MMM are explained in this section.

### 2.1 Gas permeation mechanism through polymeric membranes

Membrane transport mechanisms are very much dependent on membrane morphology or microscopic structure. Membranes can be broadly classified into two classes; porous and nonporous (dense) [54]. The mechanism of gas separation by nonporous membranes is different to that of porous membranes.

A porous membrane consists of a rigid matrix with highly voided structure that are interconnected and randomly distributed [55]. The separation of particles occurs in porous membranes mainly depends on the molecular size and membrane pore size distribution. Generally, only molecules that differ in sizes can be separated efficiently by porous membranes. Another class of membrane which provides good separation of particular gas from their mixtures but with low transport rates of the gases is called nonporous or dense membrane. The separation of solutes in nonporous membrane may be achieved if the solubility and diffusivity differ significantly.

For gas separation across the membrane, various mechanisms have been discovered which include viscous flow, Knudsen diffusion, molecular sieve effect, and solution–diffusion mechanism [56]. Figure 1 represents the schematic diagram of the mechanisms for the permeation of gases through porous and nonporous membranes.

Separation using porous membrane is usually described by Knudsen diffusion and molecular sieve effect [57]. Gas molecules tend to interact more with the pore walls compared with other gas molecules. Each molecule moves independently as there are less collisions among molecules. Thus, the separation occurs successfully due to different gas species moving at different speeds. Next, molecular sieving is basically depends on the precise pore size and shape distribution among various gas molecules by micropores of less than 7 Å in diameter [58].

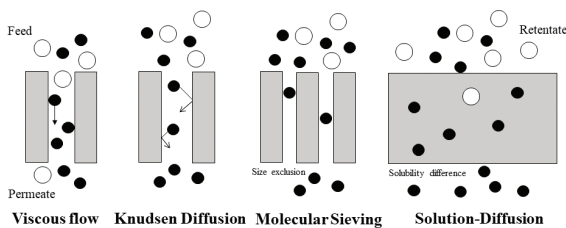


Figure 1: Mechanisms for permeation of gases through membranes.

According to Bernardo et al. [59], commercial membrane modules employed for gas separation are nonporous. It obeys the solution–diffusion mechanism which involves a three-step process (schematically illustrated in Figure 2) [58]: (1) the absorption or adsorption at the surface of the membrane (upstream side), (2) activated diffusion (solubility) through the membrane, and (3) desorption at the downstream side. The permeation of molecules across the membranes is based on two major factors, which are diffusivity coefficient ( $D$ ) and solubility coefficient ( $S$ ) [12,60]. Diffusivity measures the capability of a molecule to pass through the membrane. Meanwhile, solubility is the ratio of the dissolved penetrant concentration in the upstream side of the polymer to the upstream penetrant partial pressure. Therefore, the permeability ( $P$ ) can be defined as shown in Eq. 1 [61].

$$P = DS \tag{1}$$

The diffusion and solubility coefficients are expressed in  $\text{cm}^2/\text{s}$  and  $\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ polymer atm})$  or  $\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ polymer cm Hg})$ , respectively. The ability of a membrane to separate two different gas molecules (A and B), is the ratio of their permeabilities, or also known as ideal selectivity as shown in Eq. 2 [62].

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{2}$$

The gas transport in composite membranes is strongly dependent on the selective layer structure, characteristics of gas molecules and the interaction between the gas molecules and the membrane material.

A few approaches have been adopted by researchers to modify and optimize the structure of the polymer

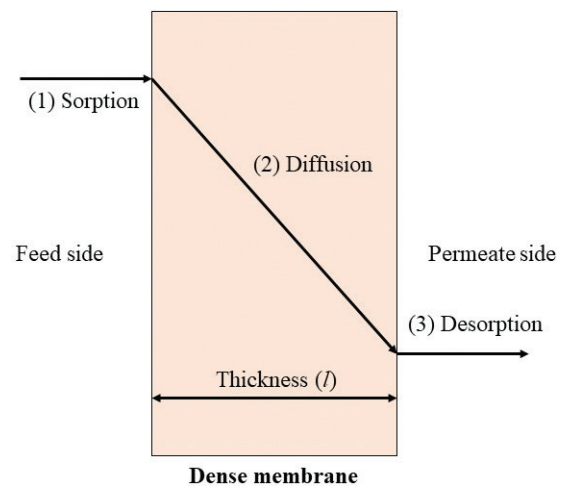


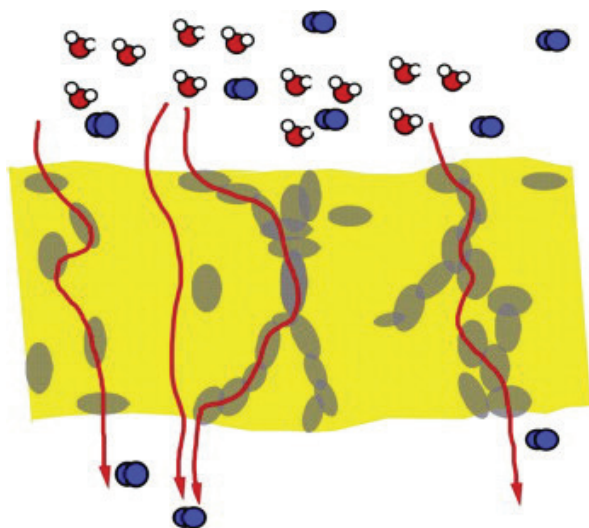
Figure 2: Illustration of the three steps involved in the solution diffusion theory.

membrane to overcome the trade-off problems. Attempts have been made where inorganic fillers are embedded in a polymer matrix producing MMM to improve the solubility of permeate molecules [20]. The mechanism of gas permeation through MMM is covered in the next section.

## 2.2 Gas permeation mechanism through mixed matrix membrane (MMM)

MMM is one of the latest kind of composite membranes which consists of two phases; organic polymer and inorganic filler as the dispersed phase [63]. Figure 3 shows a typical separation mechanism of a gas pair using MMM. The dominant mechanism in MMM is the combination of solution-diffusion and Knudsen diffusion [64].

Mainly, the adsorption process occurs in the MMM comes from the dispersed filler particles. The fillers incorporated into the polymer matrix can be classified into porous (zeolite [65], graphene oxide [66], carbon molecular sieve (CMS) [67], metal organic framework (MOF) [68] and carbon nanotubes (CNTs) [69]) and nonporous (silica [70] and titanium oxide ( $\text{TiO}_2$ ) [71]) fillers [72]. For porous filler, the transportation of gas molecules through the filler follows the effects of molecular sieve and surface diffusion [73]. The term molecular sieve defines a class of material that separates different gases in a mixture by their molecular size or shape [15]. The addition of filler with molecular sieving properties in the MMM is expected to enhance the permeability of the membrane. Adsorption and selective surface flow mechanism need to be considered if the pore size is significantly bigger



**Figure 3:** Schematic diagram of a typical separation mechanism of gases in MMM [64]. Copyright 2019. Reproduced with permission from Elsevier Science Ltd.

than the size of particle [7]. Nonporous fillers reduce the diffusion of larger molecules. Therefore, the application of nonporous filler in industrial applications is very limited due to its low permeability and expensive price.

The success of an MMM largely depends on the type of polymer matrix and inorganic filler as well as the relationship between both phases [74]. The presence of filler particles in polymer matrix could modify the membrane properties and alter the morphologies of the membrane. Besides, the size of the inorganic fillers also plays a big role in the MMM performance. The presence of nanosized inorganic fillers (<100 nm) may increase free-volume of membranes by altering the polymer chains leading to a higher gas diffusion [75,76].

## 3 Role of agricultural waste adsorbent in mixed matrix membrane (MMM)

For the past few decades, MMM attracted a great attention by the industry and academia for gas separation [77]. However, the current available fillers are significantly pricier and less economical which restricts its application. Recently, researchers have particularly concentrated on the adsorbents produced from agricultural wastes due to their favorable circumstances of low cost, availability, and eco friendliness. The attractive features offered by this technology have stimulated the interest to discover the performance of agricultural waste fillers in the fabrication of MMM for gas separation applications. In 2016, a new concept of MMM with the incorporation of agricultural waste filler into the polymer matrix was introduced.

Waheed et al. [78] studied the effects induced by the incorporation of agricultural waste filler in the separation properties of the MMM for gas separation application. They fabricated an MMM based on PSF and mesoporous silica filler extracted from rice husk ash for the separation of  $\text{CO}_2$ . In the study, the rice husk silica (RHS) underwent surface modification with 4-aminophenazone (4-AMP) to enhance the  $\text{CO}_2$  adsorption. The performance of the MMM containing various amounts (10, 20, 30 and 40 wt% based on polymer weight) of RHS and RHS functionalized with 4-AMP were compared with a pristine polymeric membrane of PSF. The prepared MMMs showed a better membrane permeability (85%) compared to that of the plain PSF membrane (55%). The most ideal MMM with the best performance was recorded with functionalized RHS loading of up to 40%. The authors stated that the existence of large mesopores in the filler offered a broad



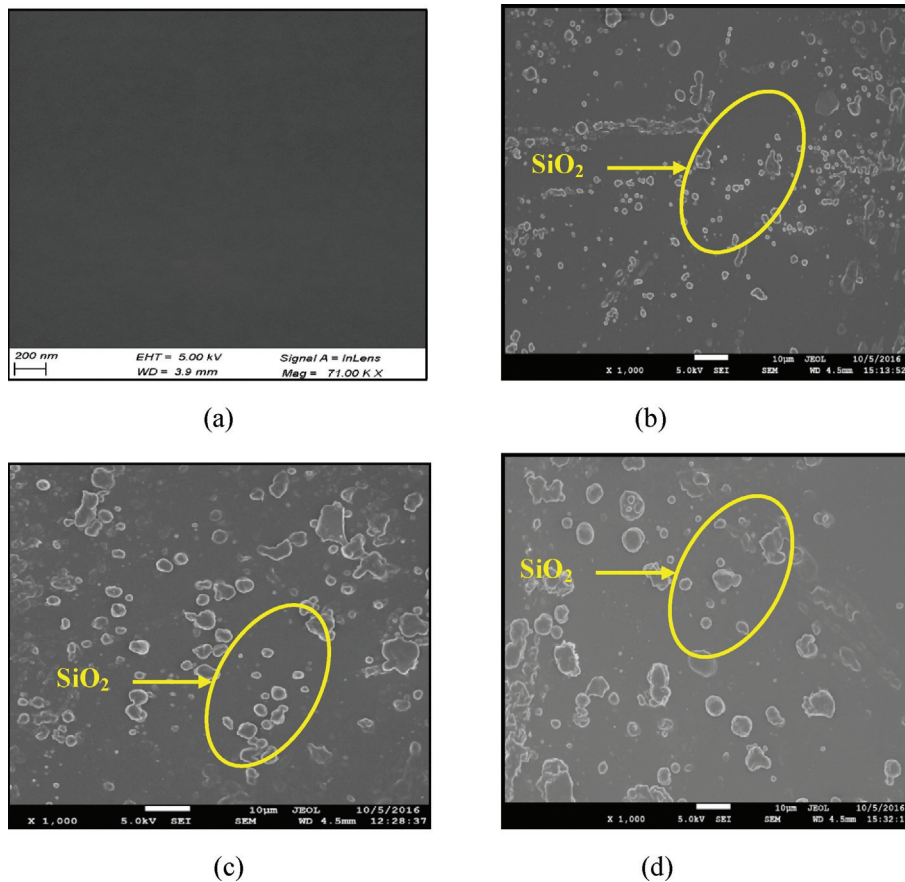
passage for the transportation of gases through the membranes, which increased the membrane permeability. Besides, the functionalized RHS showed significantly better gas selectivity compared to the nonfunctionalized RHS. The possible reason to this behavior is due to surface modification decreased the surface area, pore volume and pore size of the RHS which resulted in reduced permeability of the undesired and bigger gas molecules ( $\text{CH}_4$  and  $\text{N}_2$ ) but did not significantly affect the smaller species ( $\text{CO}_2$ ). Table 2 summarized the Brunauer, Emmett and Teller (BET) analysis data for the silica extracted from agricultural wastes and commercial silica. The slight difference in the surface areas and pore characteristics

of these agricultural waste fillers compared to the commercial silica indicates that agricultural wastes are possible to be an alternative low-cost filler.

Bhattacharya and Mandal [79] reported the performance of nano sized silica extracted from rice straw as filler in polyether-polyamide block copolymer (PEBA) for  $\text{CO}_2$  separation application. The nanosilica/PEBA membrane was prepared by solution casting method with different nanosilica concentrations (0.5, 1, and 2 wt%) added into the PEBA matrix. From the field emission scanning electron microscopy (FESEM) images as shown in Figure 4, it is observed that the surface morphology of all the membranes are dense in structure. The bright spots

**Table 2:** BET analysis of silica extracted from rice husk and rice straw as well as the commercial silica fillers.

Sample type	BET surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)	References
RHS	295.02	0.146	15.35	Waheed et al. [78]
RHS-AMP	257.29	0.095	11.33	
Silica from rice straw	404.3	0.571	5.0	Bhattacharya and Mandal [79]
Commercial silica	326.9	0.220	2.6	Lu and Hsieh [80]



**Figure 4:** FESEM images of dense (a) pure PEBA and nanocomposite PEBA membranes, (b) 0.5 wt%, (c) 1wt%, and (d) 2 wt% bio-nano-SiO<sub>2</sub> particles [79]. Copyright 2019. Reproduced with permission from Elsevier Science Ltd.

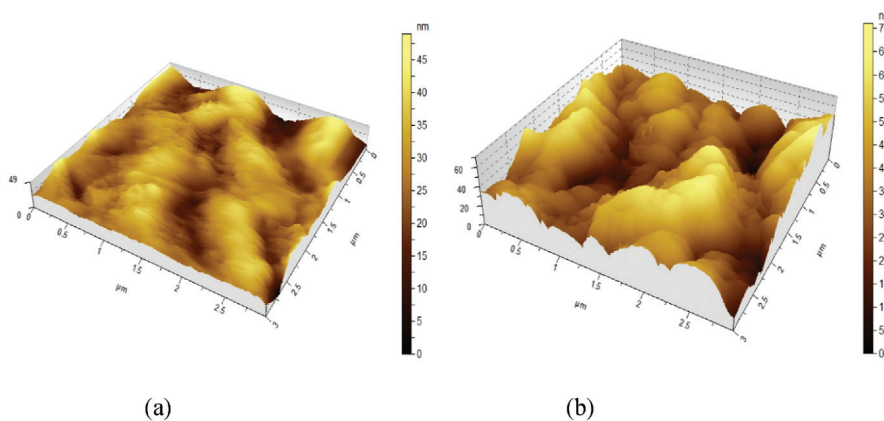
on the surface of the membranes represent the presence of nanosilica distributed homogeneously throughout the PEBA matrix indicating that the nanofiller and polymer were in good interface compatibility. However, at higher nanosilica loadings, the size of the nano-silica increased which could be ascribed to excess nanosilica particles aggregate exposed on the outer surface of the PEBA membrane. Similarly as reported in Sanaeepur et al. [74] recent study where agglomeration occurred at 2 wt% of copper nanoparticles loadings. The accumulation tendency of nanofillers in polymer matrix is due to the strong attractive energy between these nanoparticles (bonded by Van der Waals interactions) [81].

Meanwhile, the atomic force microscopy (AFM) results revealed that there are variation in surface roughness of pure PEBA and MMM. Figure 5 displays the plane and three-dimensional (3D) views of the membrane surface topography with and without the nanofillers. Based on the results obtained, the introduction of nanosilica significantly effects the surface roughness of the membrane. The surface roughness parameter of the nanocomposite membrane enhanced as compared to the pure PEBA membrane. The surface of the membrane

becomes rougher with an addition of nanosilica resulting in an enlarged surface area which may leads to a better gas permeation through the membrane [82]. The gas permeation results show significant improvement in the permeability of CO<sub>2</sub> for 2 wt% nanosilica/PEBA membrane compared to pure PEBA membrane, from 22.0 up to 270.0 Barrer, respectively. Similarly as reported by Zhao et al. [83] in the preparation of graphene oxide nanocomposite membrane.

The use of this filler significantly impacts the surface chemistry and separation efficiency of the membrane. Subsequently, the incorporation of this filler into the polymer matrix influence the physical and chemical properties such as porosity, surface roughness and surface charge. Table 3 summarized the permeability and selectivity results of MMMs incorporated with fillers from wastes compared to the commercial fillers reported in the recent years.

Generally, the addition of a small weight fraction of agricultural waste filler into polymer matrix can give a substantial improvement in the overall membrane separation performance. The filler production from agricultural waste is considered to be both economical



**Figure 5:** Atomic force microscopy (AFM) image of surface roughness of (a) pure PEBA membrane and (b) silica/PEBA MMM (PS-2) [79]. Copyright 2019. Reproduced with permission from Elsevier Science Ltd.

**Table 3:** Comparison of the gas performances of the agricultural wastes and commercial fillers.

Filler	Polymer matrix	Test conditions	Gas pair	CO <sub>2</sub> permeability (Barrer)	Selectivity	References
Nano-silica extracted from rice straw	Polyether block amide (Pebax)	P = 7 bar T = 30°C	CO <sub>2</sub> /CH <sub>4</sub> CO <sub>2</sub> /Air	270	5.3 4.1	Bhattacharya and Mandal [79]
Silica extracted from rice husk	Polysulfone (PSF)	P = 10 bar T = 25°C	CO <sub>2</sub> /CH <sub>4</sub> CO <sub>2</sub> /N <sub>2</sub>	8.46	33.31 32.79	Waheed et al. [78]
Commercial silica	Pebax-1074	P = 15 bar T = 25°C	CO <sub>2</sub> /CH <sub>4</sub>	105.94	26.09	Azizi et al. [84]
Nano-silica	Polyimide	P = 15 bar T = 25°C	CO <sub>2</sub> /CH <sub>4</sub>	265	32	Chen et al. [85]
Nano-zeolite	Matrimid	P = 35 bar T = 25°C	CO <sub>2</sub> /CH <sub>4</sub>	17.52	43.3	Ebadi Amooghin et al. [86]
Fumed silica	Pebax	P = 8 bar T = 25°C	CO <sub>2</sub> /CH <sub>4</sub>	60.15	26.15	Aghaei et al. [87]

and environmentally beneficial. Sumathi et al. [41] stated that specific properties of the agricultural wastes such as large specific area, porous structure, and enriched surface functional groups make it to be promising adsorbents for various applications including gas separation. The slight difference in the permeability and selectivity of these agricultural waste fillers compared to the commercial fillers indicates that agricultural wastes are possible to be an alternative low-cost filler. According to these results, the application of adsorbents prepared from agricultural wastes is promising to replace the costly commercial adsorbent for gas separation. However, the number of research on MMM containing agricultural wastes particles for gas separation is still low compared to that for wastewater treatment.

All in all, the utilization of agricultural waste material as low-cost filler in MMM is proven to enhance the membrane performance. Compared to conventional filler, this low-cost filler will bring a new pathway for green synthesis of MMM, making the process environmentally and cost effective.

## 4 Economic potential

Like other developing countries, Malaysia also faces the issues of waste generation and disposal [88]. Roughly 30,000 tons of municipal solid wastes are produced daily, covering 83% of the country's waste generation, including agricultural wastes. Worldwide, the amount of agricultural waste generated is around 998 million tons annually and in Malaysia, 1.2 million tons of agricultural waste is dumped and buried in landfills per year [89]. Clearly, recycling or reusing these wastes would greatly reduce waste disposal and its resultant impact on the environment. Some agricultural wastes such as coconut shells and orange peels are both nonhazardous and nontoxic in nature. Therefore, they have high potential to be converted into useful products at low cost especially adsorbent or as filler in MMM.

Cost of filler is one of the important matters that must be considered when choosing a filler. The prices of fillers from agricultural wastes need to be compared with the conventional fillers available in the market to identify the cost effectiveness. However, the prices of fillers listed in the previous section are very limited and some are not available. According to Mashhor, pineapple peel waste can be obtained at RM0.10/kg in Malaysian Pineapple Industry Board (personal communication, February 8, 2019). Meanwhile, the estimated market price of fillers such as nano graphene oxide is approximately RM 4,380 to 7,140/kg (depends on its grade) (personal communication,

Feb 13, 2018). It is obvious that agricultural waste is way cheaper than the commercial filler. Generally, it is widely known that agricultural wastes can be acquired at a lower cost value due to its abundant availability.

According to Waheed et al. [78], chemically modified agricultural wastes exhibit better adsorption performances than their unmodified forms. Although it requires extra cost, the improvement of the adsorption capacities may cover the overall cost. Moreover, the superior adsorption capacity of the filler from agricultural waste indicates that the filler is potentially marketable.

Despite the positive trend of the development worldwide, no MMM incorporated with agricultural waste filler has been available for commercialization so far. This suggests that more research and development work on the mass production of the MMM containing agricultural waste filler with enhanced performance need to be effectively evaluated and investigated prior to commercialization.

## 5 Future work

MMM has attracted a great attention from the researchers due to the outstanding performance of high permeability and better selectivity. Despite the excellent performance, MMM still has its limitation. The main problem faced in the formation of a defect-free MMM is mainly due to the poor contact between the polymer and fillers because of the difference in properties between these two phases, coupled with the strong aggregation tendency of fillers. These polymer-particle interface defects can affect the overall membrane separation performances. Regarding the issues, the following defects should be avoided for the formation of an ideal MMM: (1) interface voids formation, (2) polymer layer around the particles, and (3) filler particles pore blockage.

Voids formation at the surface of the membrane provides the path for the gas molecules to pass through them causing a higher permeability compared to that of the neat polymer. Depending on the size of the voids, the selectivity can be higher than, closely equal to or lower than the neat polymer. Furthermore, polymer layer formed around the particles can cause immobilization of polymer chains at the polymer-particle interface, which lowers gas sorption and permeation in semi-crystalline structure. Although filler particles pore blockage did not change the selectivity due to the effect of partial pore blockage of particle and polymer chain rigidification, but, it will decrease the permeability of the membrane. Improper material selection will form the undesirable morphologies at the polymer-filler interface [90].

MMMs for application in gas separation are normally comprised of different inorganic/organic fillers embedded into the polymer matrix. However, the most severe challenges in MMM preparation are the agglomeration and sedimentations of particles in the polymer matrix caused by poor dispersion of inorganic fillers. Difference in physico-chemical properties such as the density and polarity of the filler and polymer results in particle accumulation which leads to solid sedimentation or migration to the surface. Successful MMMs are essential to improve multiple functions with appropriate pore structure and surface area of the filler, so that they will give an impact on real commercial applications. Therefore, using a proper filler, altering the interfacial morphology of the filler-polymer, controlling the MMM preparation condition as well as suppressing the formation of undesired defects are the important aspects should be considered for development of high performance MMMs [91].

Even though the agricultural waste fillers have significant effects on the MMM performance, the number of research that can be found in the literature on the production and application of agricultural waste filler particles incorporated into MMM for purification and separation of gases are still minimal compared to those pure polymeric membranes. Subsequently, it shows that MMM still requires a long journey to completely explore and utilize its potential.

**Acknowledgments:** The authors would like to express their gratitude to Universiti Malaysia Pahang for supporting this work under Fundamental Research Grant Scheme (FRGS/1/2018/TK02/UMP/02/8).

## References

- [1] Bernardo P., Drioli E., Membrane gas separation progresses for process intensification strategy in the petrochemical industry. *Petrol. Chem.*, 2010, 50, 271-282.
- [2] Mozafari M., Abedini R., Rahimpour A., Zr-MOFs-incorporated thin film nanocomposite Pebax 1657 membranes dip-coated on polymethylpentylene layer for efficient separation of CO<sub>2</sub>/CH<sub>4</sub>. *J. Mater. Chem. A*, 2018, 6, 12380-12392.
- [3] Zhang Y., Sunarso J., Liu S., Wang R., Current status and development of membranes for CO<sub>2</sub>/CH<sub>4</sub> separation: A review. *Int. J. Greenh. Gas Con.*, 2013, 12, 84-107.
- [4] Xu J., Lin W., A CO<sub>2</sub> cryogenic capture system for flue gas of an LNG-fired power plant. *Int. J. Hydrog. Ener.*, 2017, 42, 18674-18680.
- [5] Ramírez-Santos Á.A., Castel C., Favre E., A review of gas separation technologies within emission reduction programs in the iron and steel sector: Current application and development perspectives. *Sep. Purif. Technol.*, 2018, 194, 425-442.
- [6] Wang M., Lawal A., Stephenson P., Sidders J., Ramshaw C., Post-combustion CO<sub>2</sub> capture with chemical absorption: A state-of-the-art review. *Chem. Eng. Res. Des.*, 2011, 89, 1609-1624.
- [7] Alqaheem Y., Alomair A., Vinoba M., Pérez A., Polymeric Gas-Separation Membranes for Petroleum Refining. *Int. J. Polym. Sci.*, 2017, 2017, 1-19.
- [8] Park S., Jang E., An H., Choi W., Kim J.-H., Lee J.-H., et al., The Lifshitz-van der Waals acid-base theory assisted fabrication of MFI-containing mixed matrix membranes for gas separations. *Micropor. Mesopor. Mat.*, 2018, 264, 60-69.
- [9] Karimi M.B., Khanbabaee G., Sadeghi G.M.M., Vegetable oil-based polyurethane membrane for gas separation. *J. Membrane Sci.*, 2017, 527, 198-206.
- [10] Zhang C., Dai Y., Johnson J.R., Karvan O., Koros W.J., High performance ZIF-8/6FDA-DAM mixed matrix membrane for propylene/propane separations. *J. Membrane Sci.*, 2012, 389, 34-42.
- [11] Bastani D., Esmaeili N., Asadollahi M., Polymeric mixed matrix membranes containing zeolites as a filler for gas separation applications: A review. *J. Ind. Eng. Chem.*, 2013, 19, 375-393.
- [12] Zhang Y., Sunarso J., Liud S., Wanga R., Current status and development of membranes for CO<sub>2</sub>/CH<sub>4</sub> separation: A review. *Int. J. Greenh. Gas. Con.*, 2013, 12, 84-107.
- [13] Sanip S.M., Ismail A.F., Goh P.S., Soga T., Tanemura M., Yasuhiko H., Gas separation properties of functionalized carbon nanotubes mixed matrix membranes. *Sep. Purif. Technol.*, 2011, 78, 208-213.
- [14] Adams R., Carson C., Ward J., Tannenbaum R., Koros W., Metal organic framework mixed matrix membranes for gas separations. *Micropor. Mesopor. Mat.*, 2010, 131, 13-20.
- [15] Plaza M.G., Pevida C., Martín C.F., Feroso J., Pis J.J., Rubiera F., Developing almond shell-derived activated carbons as CO<sub>2</sub> adsorbents. *Sep. Purif. Technol.*, 2010, 71, 102-106.
- [16] Boujibar O., Souikny A., Ghamouss F., Achak O., Dahbi M., Chafik T., CO<sub>2</sub> capture using N-containing nanoporous activated carbon obtained from argan fruit shells. *J. Environ. Chem. Eng.*, 2018, 6, 1995-2002.
- [17] Palma C., Lloret L., Puen A., Tobar M., Contreras E., Production of carbonaceous material from avocado peel for its application as alternative adsorbent for dyes removal. *Chinese J. Chem. Eng.*, 2016, 24, 521-528.
- [18] Mall I.D., Srivastava V.C., Agarwal N.K., Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash-kinetic study and equilibrium isotherm analyses. *Dyes and Pigments*, 2006, 69, 210-223.
- [19] Annadurai G., Juang R.-S., Lee D.-J., Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. *J. Hazard. Mater.*, 2002, 92, 263-274.



- [20] Goh P.S., Ismail A.F., Sanip S.M., Ng B.C., Aziz M., Recent advances of inorganic fillers in mixed matrix membrane for gas separation. *Sep. Purif. Technol.*, 2011, 81, 243-264.
- [21] Álvarez-Gutiérrez N., Gil M.V., Rubiera F., Pevida C., Adsorption performance indicators for the CO<sub>2</sub>/CH<sub>4</sub> separation: Application to biomass-based activated carbons. *Fuel Process. Tech.*, 2016, 142, 361-369.
- [22] Tseng H.-H., Wey M.-Y., Study of SO<sub>2</sub> adsorption and thermal regeneration over activated carbon-supported copper oxide catalysts. *Carbon*, 2004, 42, 2269-2278.
- [23] Karri R.R., Sahu J.N., Jayakumar N.S., Optimal isotherm parameters for phenol adsorption from aqueous solutions onto coconut shell based activated carbon: Error analysis of linear and non-linear methods. *J. Taiwan Inst. Chem. E.*, 2017, 80, 472-487.
- [24] Karri R.R., Jayakumar N.S., Sahu J.N., Modelling of fluidised-bed reactor by differential evolution optimization for phenol removal using coconut shells based activated carbon. *J. Molecul. Liq.*, 2017, 231, 249-262.
- [25] Querejeta N., Gil M.V., Pevida C., Centeno T.A., Standing out the key role of ultramicroporosity to tailor biomass-derived carbons for CO<sub>2</sub> capture. *J. CO<sub>2</sub> Util.*, 2018, 26, 1-7.
- [26] Kaźmierczak J., Nowicki P., Pietrzak R., Sorption properties of activated carbons obtained from corn cobs by chemical and physical activation. *Adsorption*, 2012, 19, 273-281.
- [27] Witoon T., Characterization of calcium oxide derived from waste eggshell and its application as CO<sub>2</sub> sorbent. *Ceram. Int.* 2011, 37, 3291-3298.
- [28] Heidari A., Younesi H., Rashidi A., Ghoreyshi A., Adsorptive removal of CO<sub>2</sub> on highly microporous activated carbons prepared from Eucalyptus camaldulensis wood: Effect of chemical activation. *J. Taiwan Inst. Chem. E.*, 2014, 45, 579-588.
- [29] Luo L., Chen T., Li Z., Zhang Z., Zhao W., Fan M., Heteroatom self-doped activated biocarbons from fir bark and their excellent performance for carbon dioxide adsorption. *J. CO<sub>2</sub> Util.*, 2018, 25, 89-98.
- [30] Kobya M., Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies. *Bioresource Technol.*, 2004, 91, 317-321.
- [31] Nasri N.S., Hamza U.D., Ismail S.N., Ahmed M.M., Mohsin R., Assessment of porous carbons derived from sustainable palm solid waste for carbon dioxide capture. *J. Clean. Prod.*, 2014, 71, 148-157.
- [32] Wei H., Chen H., Fu N., Chen J., Lan G., Qian W., et al., Excellent electrochemical properties and large CO<sub>2</sub> capture of nitrogen-doped activated porous carbon synthesised from waste longan shells. *Electrochim. Acta*, 2017, 231, 403-411.
- [33] Wu X.-X., Zhang C.-Y., Tian Z.-W., Cai J.-J., Large-surface-area carbons derived from lotus stem waste for efficient CO<sub>2</sub> capture. *New Carbon Materials*, 2018, 33, 252-261.
- [34] Bae J.-S., Su S., Macadamia nut shell-derived carbon composites for post combustion CO<sub>2</sub> capture. *Int. J. Greenh. Gas Con.*, 2013, 19, 174-182.
- [35] Salman J.M., Hameed B.H., Effect of preparation conditions of oil palm fronds activated carbon on adsorption of bentazon from aqueous solutions. *J. Hazard. Mater.*, 2010, 175, 133-137.
- [36] Guo J., Luo Y., Lua A.C., Chi R.-A., Chen Y.-L., Bao X.-T., et al., Adsorption of hydrogen sulphide (H<sub>2</sub>S) by activated carbons derived from oil-palm shell. *Carbon*, 2007, 45, 330-336.
- [37] Plaza M.G., García S., Rubiera F., Pis J.J., Pevida C., Evaluation of ammonia modified and conventionally activated biomass based carbons as CO<sub>2</sub> adsorbents in postcombustion conditions. *Sep. Purif. Technol.*, 2011, 80, 96-104.
- [38] Bhatnagar A., Sillanpää M., Witek-Krowiak A., Agricultural waste peels as versatile biomass for water purification – A review. *Chem. Eng.*, 2015, 270, 244-271.
- [39] Karri R.R., Sahu J.N., Process optimization and adsorption modeling using activated carbon derived from palm oil kernel shell for Zn (II) disposal from the aqueous environment using differential evolution embedded neural network. *J. Molecul. Liq.*, 2018, 265, 592-602.
- [40] Karri R.R., Sahu J.N., Modeling and optimization by particle swarm embedded neural network for adsorption of zinc (II) by palm kernel shell based activated carbon from aqueous environment. *J. Environ. Manage.*, 2018, 206, 178-191.
- [41] Sumathi S., Bhatia S., Lee K.T., Mohamed A.R., Cerium impregnated palm shell activated carbon (Ce/PSAC) sorbent for simultaneous removal of SO<sub>2</sub> and NO - Process study. *Chem. Eng.*, 2010, 162, 51-57.
- [42] Zhu X.-L., Wang P.-Y., Peng C., Yang J., Yan X.-B., Activated carbon produced from paulownia sawdust for high-performance CO<sub>2</sub> sorbents. *Chinese Chem. Lett.*, 2014, 25, 929-932.
- [43] Nowrouzi M., Younesi H., Bahramifar N., Superior CO<sub>2</sub> capture performance on biomass-derived carbon/metal oxides nanocomposites from Persian ironwood by H<sub>3</sub>PO<sub>4</sub> activation. *Fuel*, 2018, 223, 99-114.
- [44] Hameed B.H., Krishni R.R., Sata S.A., A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions. *J. Hazard. Mater.*, 2009, 162, 305-311.
- [45] Lua A.C., Yang T., Theoretical and experimental SO<sub>2</sub> adsorption onto pistachio-nut-shell activated carbon for a fixed-bed column. *Chem. Eng.*, 2009, 155, 175-183.
- [46] Serafin J., Narkiewicz U., Morawski A.W., Wróbel R.J., Michalkiewicz B., Highly microporous activated carbons from biomass for CO<sub>2</sub> capture and effective micropores at different conditions. *J. CO<sub>2</sub> Util.*, 2017, 18, 73-79.
- [47] Li D., Ma T., Zhang R., Tian Y., Qiao Y., Preparation of porous carbons with high low-pressure CO<sub>2</sub> uptake by KOH activation of rice husk char. *Fuel*, 2015, 139, 68-70.
- [48] Rana M., Subramani K., Sathish M., Gautam U.K., Soya derived heteroatom doped carbon as a promising platform for oxygen

- reduction, supercapacitor and CO<sub>2</sub> capture. *Carbon*, 2017, 114, 679-689.
- [49] Manyà J.J., González B., Azuara M., Arner G., Ultra-microporous adsorbents prepared from vine shoots-derived biochar with high CO<sub>2</sub> uptake and CO<sub>2</sub>/N<sub>2</sub> selectivity. *Chem. Eng.*, 2018, 345, 631-639.
- [50] Rouzitalab Z., Mohammady Maklavany D., Rashidi A., Jafarnejad S., Synthesis of N-doped nanoporous carbon from walnut shell for enhancing CO<sub>2</sub> adsorption capacity and separation. *J. Environ. Chem. Eng.*, 2018, 6, 6653-6663.
- [51] Liu L., Fan S., Removal of cadmium in aqueous solution using wheat straw biochar: effect of minerals and mechanism. *Environ. Sci. Pollut. Res. Int.*, 2018, 25, 8688-8700.
- [52] Nguyen-Thanh D., Badosz T.J., Activated carbons with metal containing bentonite binders as adsorbents of hydrogen sulfide. *Carbon*, 2005, 43, 359-367.
- [53] Macías-Pérez M.C., Bueno-López A., Lillo-Ródenas M.A., Salinas-Martínez de Lecea C., Linares-Solano A., SO<sub>2</sub> retention on CaO/activated carbon sorbents. Part I: Importance of calcium loading and dispersion. *Fuel*, 2007, 86, 677-683.
- [54] Gutha Y., Munagapati V.S., Alla S.R., Abburi K., Biosorptive Removal of Ni(II) from Aqueous Solution by *Caesalpinia bonducella* Seed Powder. *Separ. Sci. Technol.*, 2011, 46, 2291-2297.
- [55] Muntha S.T., Kausar A., Siddiq M., A Review Featuring Fabrication, Properties, and Application of Polymeric Mixed Matrix Membrane Reinforced with Different Fillers. *Polym.-Plast. Technol.*, 2017, 56, 2043-2064.
- [56] Ismail A.F., Khulbe K.C., Matsuura T., Fundamentals of Gas Permeation Through Membranes. *Gas Separation Membranes*, 2015.
- [57] Pandey P., Chauhan R.S., Membranes for gas separation. *Prog. Polym. Sci.*, 2001, 26, 853-893.
- [58] Sridhar S., Bhargava S., Bee S., Membrane-based Gas Separation: Principle, Applications and Future Potential. *Chem. Eng. Digest*, 2014.
- [59] Bernardo P., Drioli E., Golemme G., Membrane Gas Separation: A Review/State of the Art. *Ind. Eng. Chem. Res.*, 2009, 48, 4638-4663.
- [60] Chung T.-S., Jiang L.Y., Li Y., Kulprathipanja S., Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Prog. Polym. Sci.*, 2007, 32, 483-507.
- [61] Sanders D.F., Smith Z.P., Guo R., Robeson L.M., McGrath J.E., Paul D.R., et al., Energy-efficient polymeric gas separation membranes for a sustainable future: A review. *Polymer*, 2013, 54, 4729-4761.
- [62] Sutrisna P.D., Hou J., Li H., Zhang Y., Chen V., Improved operational stability of Pebax-based gas separation membranes with ZIF-8: A comparative study of flat sheet and composite hollow fibre membranes. *J. Membrane Sci.*, 2017, 524, 266-279.
- [63] Aroon M.A., Ismail A.F., Matsuura T., Montazer-Rahmati M.M., Performance studies of mixed matrix membranes for gas separation: A review. *Sep. Purif. Technol.*, 2010, 75, 229-242.
- [64] Rezakazemi M., Ebadi Amooghin A., Montazer-Rahmati M.M., Ismail A.F., Matsuura T., State-of-the-art membrane based CO<sub>2</sub> separation using mixed matrix membranes (MMMs): An overview on current status and future directions. *Prog. Polym. Sci.*, 2014, 39, 817-861.
- [65] Zarshenas K., Raisi A., Aroujalian A., Mixed matrix membrane of nano-zeolite NaX/poly(ether-block-amide) for gas separation applications. *J. Membrane Sci.*, 2016, 510, 270-283.
- [66] Zhao D., Ren J., Qiu Y., Li H., Hua K., Li X., et al., Effect of graphene oxide on the behavior of poly(amide-6-b-ethylene oxide)/graphene oxide mixed-matrix membranes in the permeation process. *J. Appl. Polym. Sci.*, 2015, 132.
- [67] Nasir R., Mukhtar H., Man Z., Shaharun M.S., Abu Bakar M.Z., Effect of fixed carbon molecular sieve (CMS) loading and various di-ethanolamine (DEA) concentrations on the performance of a mixed matrix membrane for CO<sub>2</sub>/CH<sub>4</sub> separation. *RSC Adv.*, 2015, 5, 60814-60822.
- [68] Friebe S., Diestel L., Knebel A., Wollbrink A., Caro J., MOF-Based Mixed-Matrix Membranes in Gas Separation - Mystery and Reality. *Chem.-Ing.-Tech.*, 2016, 88, 1788-1797.
- [69] Wang D., Yao D., Wang Y., Wang F., Xin Y., Song S., et al., Carbon nanotubes and graphene oxide-based solvent-free hybrid nanofluids functionalized mixed-matrix membranes for efficient CO<sub>2</sub>/N<sub>2</sub> separation. *Sep. Purif. Technol.*, 2019, 221, 421-432.
- [70] Hu C.-C., Cheng P.-H., Chou S.-C., Lai C.-L., Huang S.-H., Tsai H.-A., et al., Separation behavior of amorphous amino-modified silica nanoparticle/polyimide mixed matrix membranes for gas separation. *J. Membrane Sci.*, 2019.
- [71] Ahmadpour E., Sarfaraz M.V., Behbahani R.M., Shamsabadi A.A., Aghajani M., Fabrication of mixed matrix membranes containing TiO<sub>2</sub> nanoparticles in Pebax 1657 as a copolymer on an ultra-porous PVC support. *J. Nat. Gas Sci. Eng.*, 2016, 35, 33-41.
- [72] Nuhnen A., Dietrich D., Millan S., Janiak C., Role of Filler Porosity and Filler/Polymer Interface Volume in Metal-Organic Framework/Polymer Mixed-Matrix Membranes for Gas Separation. *ACS Appl. Mater. Inter.*, 2018, 10, 33589-33600.
- [73] Han Y., Ho W.S.W., Recent advances in polymeric membranes for CO<sub>2</sub> capture. *Chinese J. Chem. Eng.*, 2018, 26, 2238-2254.
- [74] Sanaeepur H., Ahmadi R., Ebadi Amooghin A., Ghanbari D., A novel ternary mixed matrix membrane containing glycerol-modified poly(ether-block-amide) (Pebax 1657)/copper nanoparticles for CO<sub>2</sub> separation. *J. Membrane Sci.*, 2019, 573, 234-246.
- [75] Sheikh M., Asghari M., Afsari M., Effect of nano Zinc Oxide on gas permeation through mixed matrix Poly (Amide-6-b-Ethylene Oxide)-based membranes. *Int. J. Nano. Dimens.*, 2017, 8, 31-39.
- [76] Ahn J., Chung W.-J., Pinnau I., Guiver M.D., Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation. *J. Membrane Sci.*, 2008, 314, 123-133.

- [77] Nik O.G., Chen X.Y., Kaliaguine S., Functionalized metal organic framework-polyimide mixed matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation. *J. Membrane Sci.*, 2012, 413-414, 48-61.
- [78] Waheed N., Mushtaq A., Tabassum S., Gilani M.A., Ilyas A., Ashraf F., et al., Mixed matrix membranes based on polysulfone and rice husk extracted silica for CO<sub>2</sub> separation. *Sep. Purif. Technol.*, 2016, 170, 122-129.
- [79] Bhattacharya M., Mandal M.K., Synthesis of rice straw extracted nano-silica-composite membrane for CO<sub>2</sub> separation. *J. Clean. Prod.*, 2018, 186, 241-252.
- [80] Lu P., Hsieh Y.-L., Highly pure amorphous silica nano-disks from rice straw. *Powder Technol.*, 2012, 225, 149-155.
- [81] Ebadi Amooghin A., Omidkhan M., Kargari A., The effects of aminosilane grafting on NaY zeolite–Matrimid®5218 mixed matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation. *J. Membrane Sci.*, 2015, 490, 364-379.
- [82] Vicinanza N., Svenum I.H., Peters T., Bredesen R., Venvik H., New Insight to the Effects of Heat Treatment in Air on the Permeation Properties of Thin Pd77%Ag23% Membranes. *Membranes (Basel)*, 2018, 8.
- [83] Zhao W., Liu H., Meng N., Jian M., Wang H., Zhang X., Graphene oxide incorporated thin film nanocomposite membrane at low concentration monomers. *J. Membrane Sci.*, 2018, 565, 380-389.
- [84] Azizi S., Azizi N., Homayoon R., Experimental Study of CO<sub>2</sub> and CH<sub>4</sub> Permeability Values Through Pebax®-1074/Silica Mixed Matrix Membranes. *Silicon*, 2018, 11, 2045-2057.
- [85] Chen X.Y., Vinh-Thang H., Rodrigue D., Kaliaguine S., Effect of macrovoids in nano-silica/polyimide mixed matrix membranes for high flux CO<sub>2</sub>/CH<sub>4</sub> gas separation. *RSC Adv.*, 2014, 4.
- [86] Ebadi Amooghin A., Omidkhan M., Kargari A., Enhanced CO<sub>2</sub> transport properties of membranes by embedding nano-porous zeolite particles into Matrimid®5218 matrix. *RSC Adv.*, 2015, 5, 8552-8565.
- [87] Aghaei Z., Naji L., Hadadi Asl V., Khanbabaie G., Dezhagah F., The influence of fumed silica content and particle size in poly (amide 6-b-ethylene oxide) mixed matrix membranes for gas separation. *Sep. Purif. Technol.*, 2018, 199, 47-56.
- [88] Budhiarta I., Siwar C., Basri H., Current Status of Municipal Solid Waste Generation in Malaysia. *Int. J. Advan. Sci. Eng. Inform. Tech.*, 2012, 2.
- [89] Tahir T.A., Hamid F.S., Vermicomposting of two types of coconut wastes employing *Eudrilus eugeniae*: a comparative study. *Int. J. Recycl. Organic Waste Agr.*, 2012, 1.
- [90] Ghasemi Estahbanati E., Omidkhan M., Ebadi Amooghin A., Interfacial Design of Ternary Mixed Matrix Membranes Containing Pebax 1657/Silver-Nanopowder/[BMIM][BF<sub>4</sub>] for Improved CO<sub>2</sub> Separation Performance. *ACS Appl. Mater. Inter.*, 2017, 9, 10094-10105.
- [91] Ebadi Amooghin A., Mashhadikhan S., Sanaeepur H., Moghadassi A., Matsuura T., Ramakrishna S., Substantial breakthroughs on function-led design of advanced materials used in mixed matrix membranes (MMMs): A new horizon for efficient CO<sub>2</sub> separation. *Prog. Mater. Sci.*, 2019, 102, 222-295.