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

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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 (CO_2) and hydrogen sulfide (H_2S) [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 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

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

$$P = DS \quad (1)$$

The diffusion and solubility coefficients are expressed in cm^2/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].

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (2)$$

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 (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 CO_2 . In the study, the rice husk silica (RHS) underwent surface modification with 4-aminophenazone (4-AMP) to enhance the 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 (CH_4 and N_2) but did not significantly affect the smaller species (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 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 (m^2/g)	Pore volume (cm^3/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) 1 wt%, and (d) 2 wt% bio-nano-SiO₂ particles [79]. Copyright 2019. Reproduced with permission from Elsevier Science Ltd.

on the surface of the membranes represent the presence of nanosilica distributed homogenously 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_2 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_2 permeability (Barrer)	Selectivity	References
Nano-silica extracted from rice straw	Polyether block amide (Pebax)	P = 7 bar T = 30°C	CO_2/CH_4	270	5.3	Bhattacharya and Mandal [79]
Silica extracted from rice husk	Polysulfone (PSF)	P = 10 bar T = 25°C	CO_2/Air		4.1	
Commercial silica	Pebax-1074	P = 15 bar T = 25°C	CO_2/CH_4	8.46	33.31	Waheed et al. [78]
Nano-silica	Polyimide	P = 10 bar T = 25°C	CO_2/N_2		32.79	
Nano-zeolite	Matrimid	P = 15 bar T = 25°C	CO_2/CH_4	105.94	26.09	Azizi et al. [84]
		P = 35 bar T = 25°C	CO_2/CH_4	265	32	Chen et al. [85]
			CO_2/CH_4	17.52	43.3	Ebadi Amooghin et al. [86]
Fumed silica	Pebax	P = 8 bar T = 25°C	CO_2/CH_4	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.

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