

Application of Graphene-Based Derived Rice Husk Waste for Membrane Gas Separation Technologies: A Comprehensive Review

M. S. Ismail^{a,b}, N. Yusof^{a,b,*}, M. Z. M. Yusop^{b,c}

^aFaculty of Chemical & Energy Engineering, Universiti Teknologi Malaysia,
81310 UTM Johor Bahru, Johor, Malaysia

^bAdvanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi
Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^cFaculty of Mechanical Engineering, Universiti Teknologi Malaysia,
81310 UTM Johor Bahru, Johor, Malaysia

Submitted: 8/10/2023. Revised edition: 14/11/2023. Accepted: 29/11/2023. Available online: 28/3/2024

ABSTRACT

This study intends to comprehensively evaluate the application of graphene-based nanofillers obtained from rice husk waste in the field of membrane gas separation technologies. Graphene, owing to its distinctive structural characteristics, has emerged as a highly promising filler material for membrane fabrication in gas separation applications. This comprehensive review provides an in-depth evaluation of the diverse synthesis methods employed and the resulting properties of graphene obtained from rice husk waste materials, with an inclusive chemical mechanism of graphene formation from rice husk waste. Furthermore, this study reveals the inherent capabilities of graphene in enhancing the performance of membranes while also examining the influence of nanofillers on solubility selectivity. In conclusion, it is imperative to underline the need for additional research and development activities aimed at expanding the efficiency and scalability of the membrane fabrication process through the utilization of graphene nanofillers derived from rice husk waste.

Keywords: Graphene-based nanofillers, membrane, gas separation, rice husk waste

1.0 INTRODUCTION

The field of nanotechnology has emerged as a significant advancement, presenting numerous possibilities across diverse domains of study. Particularly, the nanofillers embedded within membrane formation for gas separation application are usually utilized to improve gas solubility selectivity and gas affinity towards the penetrant's gas compound (surface adsorption) on the nanofillers surface [1]. Depending on the specific interaction between the nanofillers and the polymer matrix, these membranes can be categorized as either Mixed Matrix Membranes (MMMs) or

Nanocomposite Membranes (NCMs). Furthermore, nanofiller can dislocate polymer chain packing and modify gas transport pathways via yielding appropriate transport channels at the interface connecting the polymer matrix and nanofiller [2].

As reviewed by Norahim *et al.* (2018), they have acknowledged that the principal function of the incorporating nanofiller is usually either to behave as a barrier for the unwanted molecule or to behave as a fast-track channel for the target gas [3]. In some instances, nanofillers often improve the polymeric membrane's mechanical and chemical stability [1]. Nanofillers could be categorised as

porous or nonporous [2], [4]. The permeability of porous nanofiller is higher and its selectivity is lower compared to nonporous nanofiller. On the other hand, nonporous nanofiller decreases the diffusion of bigger gas molecules, resulting in lower permeability [5].

The industrial application of nonporous nanofillers, including palladium, nickel, and zirconia, in membrane technology is currently limited due to their inherent characteristics of low permeability and high cost [4], [5]. Therefore, up to now, porous nanofiller is more favoured to be utilized due to their superior separation capabilities [6]. In the case of porous nanofiller, membrane's gas transport properties can be modified by nanofiller's intrinsic separation properties [2]. In most cases, the nanofillers' pore structure and design are modified prior to their integration into the membrane matrix.

In comparison to nonporous alternatives, porous nanofillers are more intriguing because of their remarkable gas uptake capacities and establish secondary transport pathways when incorporated into the membrane matrix of a particular membrane design [6]. The limitless potential for optimising the architecture of these porous nanofillers frequently encourages the concurrent enhancement of the membrane's permeability, selectivity, and stability characteristics, thereby facilitating progress towards industrial application [6].

2.0 GRAPHENE-FAMILY NANOFILLERS FOR MEMBRANE GAS SEPARATION APPLICATIONS

The most commonly utilized nanofiller by the adsorptive membrane for gas separation application are zeolite

nanoparticles [7], silica nanoparticle [8], TiO₂ nanoparticles [9], MOF (like MOF-801, ZIF-7, ZIF-8, UiO-66, MIL-101, and ZIF-7/8) [10]–[14], and graphene-family materials (like GO, rGO, CNT, and Graphene nanoparticles) [11], [15]–[19].

The above design of the nanofillers has the possibility to attain optimal permeability and improved selectivity, or both, respectively. Nevertheless, the massive prices of the current nanofiller materials limit their implementations for industrial applications [5]. Such a problem generates demand for new nanofiller materials for membrane fabrications.

When materials technology progresses, several novel materials containing diverse functionalities and dimensionalities appear. Now, there is considerable interest in 2D graphene-family materials (GFMs) on account of their exceptional structural characteristics [20]. Therefore, among the extensively researched nanofiller materials, GFMs nanofillers can be economically synthesised due to their ability to be produced from renewable resources, such as agricultural wastes, thereby serving as an economical alternative to the expensive commercial nanofiller materials [5], [21].

Although, research on agricultural waste based GFMs utilized as nanofillers for gas separation applications appears limited, it represents a promising avenue due to its potential for cost-effectiveness and sustainability. Despite this, there is a growing body of research on the subject as a result of its promising characteristics and outstanding outcomes [5]. This trend highlights the need for further exploration and development of agricultural waste-based GFMs, alongside continued research on established sources like graphite, carbide precursors, and chemical vapor deposition (CVD).

Further research and development studies on manufacturing the membrane containing both agricultural waste-based GFMs and other established graphene materials as nanofillers must be effectively evaluated and examined to optimize their performance and unlock their full potential in gas separation applications.

GFMs are recognized as emerging nanofiller with various qualified features as a membrane material for gas separation application [18], [22]. Generally, GFMs consist of multiple graphitic carbon materials such as fullerenes, carbon nanotube (CNT), graphene nanoparticles (GNPs), graphite, and other graphene derivatives (like graphene oxide (GO) and reduced graphene oxide (rGO)). Graphene is a substance consisting of pure carbon, with atoms structured in a typical hexagonal lattice like graphite [23].

However, defining these GFMs has created misunderstandings in the scientific literature. The term “graphene” was first mentioned by Boehm *et al.* (1986), which indicates only to single-layer carbon; later, it was then formalized by the International Union for Pure and Applied Chemistry (IUPAC) [24], [25]. In 2013, Bianco *et al.* (2013) had proposed the first nomenclature for 2D carbon with the motive of achieving graphene study easier for other researchers where the term “graphene” is represented by the prefix “graph” from graphite and the suffix “ene” from the carbon-carbon double bonds [24], [26].

According to Bianco *et al.* (2013), graphene is defined as a single-atom-thick layer of hexagonally structured, sp^2 -bonded carbon atoms, which is not an integral component of a carbon substance but is freely suspended or adhered to a foreign substrate [26]. Consider this description, other representatives of GFMs of 2D

materials cannot be called solely as “graphene.” However, it should be identified using a unique multi-word expression that separates them from the isolated monolayer [26].

Therefore, the numerous type and terms of “graphene” can be subjoined depend on resulted graphene by “monolayer,” “bilayer,” “trilayer,” “layer,” “few-layer,” “multi-layer,” “nanosheet,” “microsheet,” “nanoribbon,” “quantum dots,” “reduced graphene oxide,” or “graphene oxide” [24], [26]. These classifications were established based on the electronic properties, carbon material properties (size, orientation, and degree of perfection), stacking structures arrangement, crystallography, and lateral dimensions (width) of fabricated carbon materials [26]–[28].

However, the free-standing graphene was reported to exist where the fabricated graphene exhibits massless Dirac fermions and high carrier mobilities. The observation of the electric field effect in graphene fabricated via mechanical exfoliation of a small amount of highly oriented pyrolytic graphite [27]. These groundbreaking experiments on 2D graphene material have secured Novoselov and Geim to be awarded the Nobel Prize in Physics 2010 [23], [28]–[30].

As indicated previously, graphene is a mother of all graphitic forms, where in other words, graphene is a fundamental constructional unit, and it is considered the starting point for recognition of other dimensionalities graphitic allotropes [28], [29], [31]–[34]. The graphene plane can be wrapped up into zero-dimensional (0D) fullerenes or known as buckyballs, rolled into one-dimensional (1D) carbon nanotubes (CNT), or stacked up a number of graphene layers into three-dimensional (3D) graphite [2], [23],

[27], [28], [32], [35].

The utilization of graphene – a single layer of carbon atom – which corresponds to its 2D atomic crystal structures has drawn significant interest in membrane preparation due to distinct possibilities, such as high specific surface area which up to 2630 m²/g [36]; exceptional mechanical properties, specifically, a high Young's modulus around 0.5 -1.0 Tpa [37], [38], large aspect ratio, high tensile strength of 130 Gpa [39], and flexibility, that meet the requirements strengthening the physicochemical properties of neat polymer; excellent thermal conductivity in the range of 4840 – 5300 W/mK at room temperature [40], hence, it appeared as among the efficient heat dissipater materials; tremendously large charge carrier mobility in the range of 2000-5000 cm²/V⁻¹s⁻¹ [41], allow graphene favorable as a filler to impart conductivity to the insulating polymer material; relative inertness; and better adsorption properties to all standard gases [1], [2], [23], [29], [42]–[44]. Therefore, graphene is held as a promising nanofiller intended for membrane gas separation applications and remained at the core of scientific research [44], [45].

Concerning the impermeability characteristic of graphene, some researchers propose the creation of pore within the graphene's basal plane to create a sieving effect by exclude larger gas molecules but allow smaller gas molecules to pass through [1], [2], [23], [31]. While research by Janakiram *et al.* (2018) and Ebadi Amooghin *et al.* (2019) demonstrates the potential of manipulating interlayer spacing in graphene to create size-selective membranes for gas separation [1], [31], the benefits of incorporating graphene extend beyond this specific effect. Researchers exploit various properties of graphene to enhance different

aspects of membrane performance.

For example, graphene's high surface area and intrinsic porosity can create more pathways for desired gas molecules while hindering the passage of larger or less desirable ones. For instance, Zhao *et al.* (2013) used graphene oxide to increase water permeability and improve salt ion rejection in a polymer membrane [32]. Apart from that, Graphene's exceptional mechanical strength and chemical resistance can enhance membrane durability. Yu *et al.* (2015) incorporated reduced graphene oxide into a polyamide membrane, resulting in improved mechanical strength, chemical stability, and resistance to chlorine degradation compared to the pure membrane [33].

Apart from that, graphene can undergo surface functional modification to establish efficient gas transport pathways and to provide them with new characteristics [46]. Keep in mind that different functional group on functionalized graphene exhibits various kinds of characteristics [47].

3.0 AGRICULTURAL WASTE-BASED GRAPHENE FOR MEMBRANE GAS SEPARATION APPLICATIONS

The unconventional, economical, sustainable, and eco-friendly agricultural waste as a highly appropriate alternative start-up material for graphene preparation has pursued considerable interest among researchers to investigate more on discovering graphene performance derived from agricultural waste materials [48]–[53].

Agricultural waste is an organic material that generally comes from plants, an unwanted residue from agricultural activities, including crop residues, weeds, trunks, leaf litter, husks, or extracted forms like lignin [51], [54]. Agricultural waste materials

are currently popular due to their abundance, need for recycling, and great carbon source. Agricultural wastes primarily consist of carbohydrates, fiber, and proteins [55].

Apart from that, Safian *et al.* (2020) have stated that agricultural waste can be categorized as lignocellulosic biomass, which is also identified as plant dry matter [51]. Lignocellulosic biomass comprises three main natural polymers components: cellulose, hemicellulose, and lignin, along with minor components, including pectins, proteins, and minerals [51], [55], [56]. However, the amount of each component differs amongst different types of plant species and between other parts from the same plant type [51], [56].

The global agricultural waste generated is 998 million tonnes per year, and particularly in Malaysia, the agricultural waste disposed into landfills is 1.2 million tonnes per year [57]. The projected amount of agricultural waste will continue to increase as data provided by Ali (2020) that agricultural waste generation in Malaysia was 0.122 (kg/cap/day) in 2009, and the estimated amount by 2025 to reach 0.210(kg/cap/day) [57]. Agricultural wastes are worth revealing as the generated amount keeps increasing year by year at predictable locations, and policies concerning agricultural waste recycling have been established. However, agricultural waste generation still far outstrips the recycling capacity [51].

Agricultural waste such as rice husk, rice straw, hemp fiber, tea leaves, coconut shells, sugarcane bagasse, orange peel, mango peel, dead camphor leaves, oil palm fiber, oil palm leaves, oil palm kernel shell, wheat straw, nutshells, palm oil empty fruit branch, and pulp waste (black liquor) have been utilized as a precursor for graphene synthesis [49]–[51], [58].

The appropriate graphene synthesis derived from agricultural waste varies on chemical composition and properties; however, its carbon content and morphology characteristics are critical factors for synthesizing proper graphene [51], [58]. According to Xie & Goodell (2014), all agricultural waste materials encompass long chains of carbon, hydrogen, and oxygen compounds, and their carbon content is as high as 55 wt% [59]. Therefore, various types of agricultural waste have its own specific techniques of synthesis that are appropriate for them.

4.0 AGRICULTURAL WASTE-BASED GRAPHENE SYNTHESIS METHOD

Generally, most of the synthesis procedures for graphene derived from agricultural waste preparation are divided into three typical processes: pre-treatment, graphene conversion treatment, and post-treatment [51]. The pre-treatment process is set for the agricultural waste materials, where its need to be physically treated through chopping, shredding, washing with water, filtered, drying, and grinding [51]. This undertaken process step was set to ensure there are no impurities exist in the sample.

For graphene conversion treatment, generally, the process of agricultural waste conversion to graphene involves concentrating the carbon content by removing other components through thermal treatment [51]. It is worth mentioning that the thermal treatment process of consolidating the carbon content within the agricultural waste materials by eliminating other light molecular weight compounds is called carbonization [51]. Carbonization is the thermal treatment process that consolidates carbon content within agricultural waste materials by eliminating other light molecular

weight compounds. The required temperature range for effective carbonization varies depending on the type of agricultural waste, the desired product, and the chosen carbonization method. The carbonization process typically occurs within a temperature range of 400°C to 900°C, according to studies conducted by researchers. However, the carbonization process frequently generates amorphous carbon instead of a graphitic-like structure [51].

According to Xie and Goodell (2014), carbon from agricultural waste materials after undergoing the carbonization process is usually amorphous; however, it can be altered from non-graphitic into graphitic carbon by undergoing a graphitization process [59]. Graphitization is the process of organizing carbon structures to create a graphitic-like structure [51].

There are two types of commonly utilized technologies in the graphitization process: catalytic graphitization and non-catalytic graphitization [59]. The catalytic graphitization of amorphous carbon has utilized transition metal as catalysts to stimulate the transformation of carbon-derived agricultural waste from a non-graphitic structure to a graphitic ordered structure at a particular carbonization temperature [51]. This catalytic method utilizes transition metals to facilitate graphitization at lower temperatures, it can be more expensive compared to the non-catalytic method due to the cost of the catalyst. However, the catalytic method offers benefits such as improved control over the process and energy savings due to lower operating temperatures.

Hence, it is worth noting that transition metal as a catalyst is the most critical component that impacts the catalytic graphitization process of numerous amorphous carbon [60]. Xie

& Goodell (2014) have stated that the graphitization is relatively localized, where only the amorphous carbon that in contact with a transition metal catalyst will be transformed into graphitic ordered carbon throughout the catalytic graphitization process [59].

For more than 50 years, the researchers studied catalytic graphitization of solid carbon and developing the catalytic graphitization method due to numerous carbon precursors and catalysts [60]–[62]. Hence, it has been well established that certain transition metals, in particular iron (Fe), cobalt (Co), and nickel (Ni), have an apparent catalytic impact on graphitization of the product structure by the active phase and reaction conditions [60], [62]. Two mechanisms have been recommended for catalyzing the graphitization process of the amorphous carbon over transition metal catalyst: (i) the dissolution-precipitation method, (ii) metal carbide formation and decomposition method [59]–[62].

In the case of the dissolution-precipitation method, the amorphous carbon and transition metal catalyst were mixed and undergoing thermal treatment at a particular temperature. It has been described that the amorphous carbons tend to diffuse and dissolve into the transition metal until saturated carbon solubility reaches equilibrium condition during thermal treatment. Then, throughout thermal treatment completion at decreasing temperature, the transition metal will be supersaturated with carbon and precipitates in a graphitic-like structure since it has the lowest Gibbs free energy [59], [62].

Whereas for the second method, as the mix of amorphous carbon and transition metal catalyst undergo thermal treatment, a transition metal might initially react with amorphous carbon to form metal carbides, and

subsequently, it decomposes into metal and graphite [59], [61], [62].

Throughout both recommended catalytic graphitization mechanisms, the reactivity of the transition metal catalyst with the amorphous carbon can be categorized into three groups, which is (i) metal that has low carbon solubility, (ii) metals can dissolve a substantial carbon; and (iii) metals that can form strong chemical bonds with carbon to form in the metal carbides [62].

On the other hand, non-catalytic technologies have been established to generate carbon with a graphite-like structure without a catalyst. Generally, the non-catalytic technologies involve thermal treatment in the absence of oxygen, known as pyrolysis [51]. Pyrolysis is a recognized thermal treatment process where the product depends on several parameter settings during the pyrolysis process, such as temperature, heating rate, and holding time [51].

Agricultural waste materials, as Safian *et al.* (2020) point out, decompose around 300°C during the initial stage of a multi-step process for transforming them into graphene [51]. However, the exact decomposition temperature can vary depending on the specific type of agricultural waste used. KOH activation, often employed as part of this process, is a popular choice among researchers due to its flexibility in adapting to different materials and its ability to minimize the formation of unwanted oxidized carbon structures by maintaining an oxygen-free environment [55].

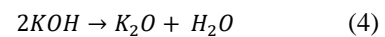
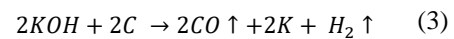
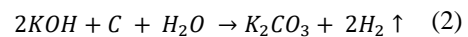
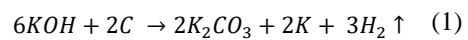
While this method offers advantages like flexibility and controlled oxygen exposure, it is crucial to consider potential drawbacks. The high temperature required for pyrolysis can significantly increase energy consumption, potentially leading to higher operating costs. The overall cost-

effectiveness of KOH activation, therefore, depends on several factors, including the chosen energy source and the scale of production.

Exploring alternative methods that utilize different catalysts or activation agents and require lower processing temperatures could be a valuable avenue for future research. Such alternatives could potentially offer a more balanced approach, optimizing both cost and operational efficiency in the quest for sustainable and cost-effective graphene production from agricultural waste.

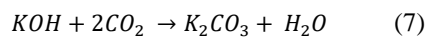
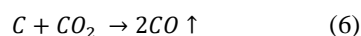
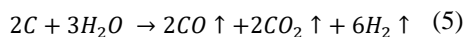
5.0 MECHANISM REACTION FORMATION

When the reaction of KOH and RHC at high temperature occur, it is believed that carbon undergo oxidation process by producing carbon dioxide, hydrogen, metallic potassium, water, and potassium carbonate, whereas water-soluble KOH undergo reduction process by producing potassium carbonate, evolved hydrogen, and carbon monoxide [63]. This reaction is believed to bring significant effects on the pore formation of resultant GRHC and it is better explained via redox mechanism reaction as follows:

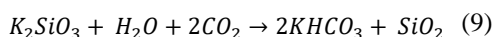
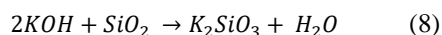


Apart from that, it is believed that the carbon is also undergo reductions for secondary redox mechanism reaction by reacting with water and carbon dioxide into volatile substance in the presence of KOH, that contribute to producing pore structures as they vaporized from carbon structure [63]. While the KOH undergoes oxidation

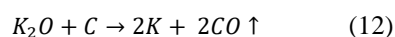
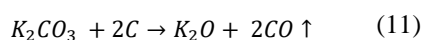
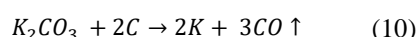
process by reacting with carbon dioxide and producing potassium carbonate and water.



According to Seitzhanova *et al.* (2018), RHC is believed to contain silica composite and serves as a template for pore formation while undergo redox reaction with KOH, where KOH undergo reduction process producing potassium silicates and water (Seitzhanova *et al.*, 2018). For secondary redox mechanism reactions, potassium silicates undergo reduction process when react with water and carbon dioxide, resulting in potassium bicarbonate and silica. Hence, at the end of the chemical activation process, there is some white solid on top of the resultant sample but after washing treatment with hydrochloric acid and water, this white compound (potassium bicarbonate) will dissolve with water and remove from the resultant sample.



At the end of chemical activation process, during washing with hydrochloric acid and water, the intercalated potassium compounds within the carbon structure such as potassium carbonate, metallic potassium, potassium oxide, and potassium silicates, become the simplest potassium compounds and were removed from the resultant material.



6.0 EXPLORING THE POTENTIAL OF GRHC

A straightforward, economical, and scalable approach was demonstrated by Hiroyuki Muramatsu *et al.* in 2014 to produce graphene from rice husk waste that possessed consistent and smooth surfaces. This was accomplished by activating 5g of rice husk char (RHC) to 25g of potassium hydroxide (KOH) in an impregnation ratio of 1:5, operating at 850 °C for two hours in the presence of air [52]. According to the authors, their product comprised edge-enriched graphene and monolayer corrugated graphene featuring nanoscale pores and topological defects the size of a few nanometers, as determined by HRTEM images. [52].

Apart from Hiroyuki Muramatsu study, there are several comprehensive studies also have concluded that since the chemical activation has been utilized towards the rice husk char (obtain from carbonization process of raw material, which is rice husk waste) at higher temperature (850°C) is held to obtain porous materials [63], [64].

As to be correlated to Raman spectroscopy, based on Muramatsu *et al.* (2014) study, their Raman spectrum displayed the 2D peak at 2692 cm⁻¹ with a half-width at half-maximum of 39.3 cm⁻¹ and intensity ratio I_{2d}/I_g at 1.57 that suggest the growth of monolayer graphene and agree to HRTEM observation [52]. They also have observed the decrease of the I_d/I_g ratio of graphene sample compared with rice husk char sample, which signifies an effective removal of amorphous carbons [52]. They also have confirmed the high specific surface area of 2220 m²g⁻¹ [52].

Hence, they have stated that the KOH has two main functions for the method in preparing graphene materials from rice husk waste materials, which is: (i) efficiently etching amorphous

carbon and (ii) assists in the graphene formation consists of stable and clean edges and induce porosity in carbon materials due to the gaseous/molten KOH penetrating behaviour [52].

Two years later, Rhee *et al.* (2016) have had adopted the KOH activation process toward the graphene preparation method; however, Rhee and his co-workers have slightly improvised and stated a more detailed preparation route than Muramatsu *et al.* (2014). Rhee *et al.* (2016) have demonstrated a detailed pre-treatment process, which is the carbonization process at various temperatures varying from 400 to 600°C with a heating rate of 10°C/min to obtain rice husk char (RHC) [53].

They have improvised activation method using different impregnation ratio of 1:4, which is 2.5 g of RHC was then mixed with 10 g of KOH and heated at the same activation temperature (850 °C) and activation time (2 hours) with a heating rate of 10°C/min in air environment [53]. They have observed their graphene sample via TEM that comprises a corrugated-paper-like structure with large-sized pores [53] as displayed in Figure 1.

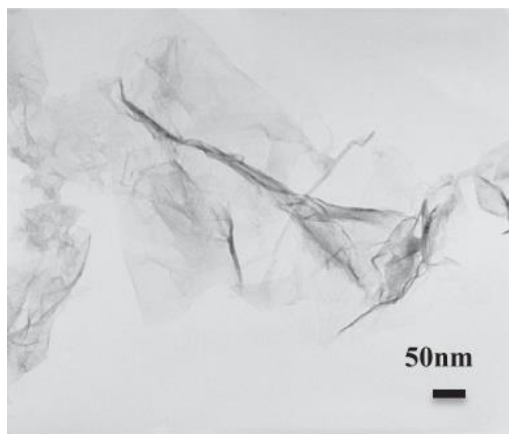


Figure 1 TEM images of a corrugated-paper-like structure of rice husk-derived graphenes [53]

They also have evaluated their graphene sample via Raman

spectroscopy, which showed a strong G peak at 1583 cm^{-1} , a comparatively broad D peak at 1353 cm^{-1} , and a relatively sharp 2D peak at 2702 cm^{-1} [53]. Hence, their intensity ratio of I_{2d}/I_g at 1.21 suggests the growth of bilayer graphene.

Compared to Muramatsu *et al.* (2014), the graphene sample prepared by Rhee groups has an intensity ratio I_d/I_g of 0.66, which signifies their graphene sample has a lower amount of amorphous and disordered carbon within their graphene structure. They also have evaluated the specific surface area of their graphene product and found out that it is around 2943.3 m^2g^{-1} [53]. Therefore, they have concluded, on the basis of their findings, that the impregnation quantity of KOH has an effect on the morphology of resultant graphene by means of its penetrating behaviour, which exposes the carbon structure and increases the specific surface area of the graphene [53].

In 2017, two groups had further adopted the KOH activation process toward the graphene preparation method. They improvised the activation temperature at 700 °C [65] and 900 °C [66]. Sangkar *et al.* (2017) had mentioned that they have first undergone the carbonization process at 600 °C for 2 hours in air. They have then proceeded for a similar activation process using 3g RHA to 12g KOH at an impregnation ratio of 1:4 at 700 °C for 2 hours in air [65]. The results demonstrated few-layer graphene with an ultra-thin crumpled-silk-veil-wave, sheet-like structure along with a specific surface area around 1225 m^2g^{-1} [65].

However, there is no analysis regarding Raman spectroscopy by Sangkar groups. While Singh *et al.* (2017) just generally stated that they had synthesized graphene by undertaken a carbonization process followed by an activation process using

3g RHA to 15g KOH with an impregnation ratio of 1:5 at 900 °C for 2 hours in air [66]. They have observed that the produced graphene has few layers with an agglomeration of silica particles [66]. While their intensity ratio of I_{2d} / I_g on the Raman spectrum, around 0.67, confirmed the trilayer's growth to a few layers of graphene [66].

In 2018, another group adopted the KOH activation process toward the graphene preparation method. Seitzhanova *et al.* (2018) have included the desilication process before undergoing the activation process towards rice husk in order to remove silica impurities [67]. It is known that the rice husk consists of 17-20% of carbon, and over 80% are silica impurities, with the remainder of other metallic impurities [58]. However, this information appears to contradict Xie & Goodell's (2014) statement that all agricultural waste materials, including rice husk, have a carbon content as high as 55 wt% [59]. Further investigation is needed to reconcile these conflicting statements and determine the accurate carbon content of rice husk.

Hence, Seitzhanova *et al.* (2018) have taken inventive steps by includes the desilication process using one molar of sodium hydroxide (NaOH) and further heated at 110°C for 3 hours. Then, the prepared sample was washed 5-7 times with distilled water to reach the equilibrium of pH ~7 and dried in a hot air oven for at least 2 hours at 110°C [67]. After that, the prepared sample was further activated using 1g RHA to 5g KOH with an impregnation ratio of 1:5 at 850 °C for 2 hours [67]. Compared to the KOH activation method's typical route, Seitzhanova and her co-workers had utilized argon instead of air as the medium for activation towards the prepared sample.

Moreover, they also include the exfoliation process toward the prepared sample after activation process using

hydrogen peroxide solution (H_2O_2 , 37%) for 48 hours in order to further remove amorphous carbon [67]. However, they have demonstrated a lower specific surface area of the produced graphene around $350 \text{ m}^2\text{g}^{-1}$ [67]. As shown in Figure 2, TEM image revealed the edge structures of the fabricated graphene.

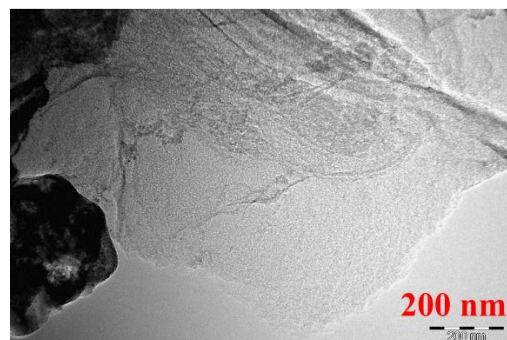


Figure 2 TEM image of the fabricated graphene with edge structures [67]

Besides, their produced graphene has an edge structure with several nanometers. The produced graphene also had topological defects and nanoscale pores. These undertaken results can be correlated with the intensity ratio of I_{2d} / I_g on the Raman spectrum around 1.56 confirmed the monolayer's growth of graphene, and their intensity ratio I_d / I_g of 0.87, which signifies their graphene sample still has an amount of amorphous and disordered carbon within their graphene structure even after exfoliation process using hydrogen peroxide solution for 48 hours [67].

In the year of 2020, Yeleuov *et al.* (2020) had adopted the KOH activation process toward the graphene preparation method and try to remodel it a bit on activation setup by utilizing a vertical tubular furnace with argon flow as a gas medium [68]. Moreover, they also improvise the carbonization process by utilizing the rotating tubular furnace with argon flow as a gas

medium [68]. The resulting graphene product showed few-layer graphene with clean-edges layers containing defected and corrugated graphene structures via TEM observation [68].

These undertaken TEM observations can be correlated with the intensity ratio of I_{2d}/I_g on the Raman spectrum, which is around 0.63, confirmed the graphene growth of trilayer to a few-layer. Their intensity ratio I_d/I_g of 0.45 signifies their graphene sample has a small amount of amorphous and disordered carbon within their graphene structure [68]. Nevertheless, their intensity ratio I_d/I_g is among the lowest value throughout the literature on the KOH activation process. Apart from that, they have obtained a surprisingly larger specific surface area around $3292\text{ m}^2\text{g}^{-1}$ of the graphene product [68].

7.0 CONCLUSION

This comprehensive review has provided a more in-depth insight into agricultural waste materials as a precursor for graphene preparation, including its synthesis method, formation mechanism, and the properties of resulted graphene materials. Thus far, this paper reviewed several studies utilizing the KOH activation process on rice husk waste toward the graphene preparation method by discussing the progress made throughout the years.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

ACKNOWLEDGEMENT

The authors also would like to acknowledge the financial support from

Ministry of Higher Education (MOHE) Malaysia and Universiti Teknologi Malaysia (UTM) under Fundamental Research Grant Scheme (FRGS/1/2022/STG05/UTM/02/10) and UTM Fundamental Research (Q.J130000.3846.23H37).

REFERENCES

- [1] S. Janakiram, M. Ahmadi, Z. Dai, L. Ansaloni, and L. Deng. (2018). Performance of nanocomposite membranes containing 0D to 2D nanofillers for CO₂ separation: A review. *Membranes (Basel)*, 8, 2.
- [2] P. S. Goh and A. F. Ismail. (2020). *Nanocomposite membrane materials for gas separation*. Elsevier. 21-99.
- [3] N. Norahim, P. Yaisanga, K. Faungnawakij, T. Charinpanitkul, and C. Klaysom. (2018). Recent membrane developments for CO₂ separation and capture. *Chem Eng Technol.*, 41(2), 211-223.
- [4] N. N. Rosyadah Ahmad, H. Mukhtar, D. F. Mohshim, R. Nasir, and Z. Man. (2016). Surface modification in inorganic filler of mixed matrix membrane for enhancing the gas separation performance. *Reviews in Chemical Engineering*, 32(2), 181-200.
- [5] A. A. Ghazali, S. Abd Rahman, and R. Abu Samah. (2020,). Potential of adsorbents from agricultural wastes as alternative fillers in mixed matrix membrane for gas separation: A review. *Green Processing and Synthesis*, 9(1), 219-229.
- [6] M. Ahmadi, S. Janakiram, Z. Dai, L. Ansaloni, and L. Deng, (2018). Performance of mixed matrix membranes containing

- porous two-dimensional (2D) and three-dimensional (3D) fillers for CO₂ separation: A review. *Membranes (Basel)*, 8(3).
- [7] K. Zarshenas, A. Raisi, and A. Aroujalian. (2016). Mixed matrix membrane of nano-zeolite NaX/poly (ether-block-amide) for gas separation applications. *J Memb Sci*, 510, 270-283.
- [8] I. Khalilinejad, A. Kargari, and H. Sanaeepur. (2017). Preparation and characterization of (Pebax-1657 + silica nanoparticle)/PVC mixed matrix composite membrane for CO₂/N₂ separation. *Chemical Papers*, 71(4), 803-818.
- [9] E. Ahmadpour, M. V. Sarfaraz, R. M. Behbahani, A. A. Shamsabadi, and M. Aghajani. (2016). Fabrication of mixed matrix membranes containing TiO₂ nanoparticles in Pebax 1657 as a copolymer on an ultra-porous PVC support. *J Nat Gas Sci Eng.*, 35, 33-41.
- [10] T. Li, Y. Pan, K.-V. Peinemann, and Z. Lai. (2013). Carbon dioxide selective mixed matrix composite membrane containing ZIF-7 nano-fillers. *J Memb Sci.*, 425-426, 235-242.
- [11] J. Sánchez-Laínez, I. Gracia-Guillén, B. Zornoza, C. Téllez, and J. Coronas. (2019). Thin supported MOF based mixed matrix membranes of Pebax-1657 for biogas upgrade. *New Journal of Chemistry*, 43(1), 312-319.
- [12] A. Jomekian, R. M. Behbahani, T. Mohammadi, and A. Kargari. (2017). High speed spin coating in fabrication of Pebax 1657 based mixed matrix membrane filled with ultra-porous ZIF-8 particles for CO₂/CH₄ separation. *Korean Journal of Chemical Engineering*, 34(2), 440-453.
- [13] J. Sun, Q. Li, G. Chen, J. Duan, G. Liu, and W. Jin. (2019). MOF-801 incorporated PEBA mixed-matrix composite membranes for CO₂ capture. *Sep Purif Technol.*, 217(January), 229-239.
- [14] M. Mozafari, R. Abedini, and A. Rahimpour. (2018). Zr-MOFs-incorporated thin film nanocomposite Pebax 1657 membranes dip-coated on polymethylpentylene layer for efficient separation of CO₂/CH₄. *J Mater Chem A Mater*, 6(26), 12380-12392.
- [15] S. A. Mohammed *et al.* (2019). CO₂/N₂ selectivity enhancement of PEBAX-1657/Aminated partially reduced graphene oxide mixed matrix composite membrane. *Sep Purif Technol.*, 223, 142-153.
- [16] N. Norahim, K. Faungnawakij, A. T. Quitain, and C. Klaysom. (2019). Composite membranes of graphene oxide for CO₂/CH₄ separation. *Journal of Chemical Technology and Biotechnology*, 94(9), 2783-2791.
- [17] S. A. Habibiannejad, A. Aroujalian, and A. Raisi. (2016). Pebax-1657 mixed matrix membrane containing surface modified multi-walled carbon nanotubes for gas separation. *RSC Adv.*, 6(83), 79563-79577.
- [18] F. Pazani and A. Aroujalian. (2020). High-performance gas separation using mixed-matrix composite membranes containing graphene nanoplatelets. *Polymer Bulletin*, 0123456789.
- [19] G. Huang *et al.* (2018). Pebax/ionic liquid modified graphene oxide mixed matrix

- membranes for enhanced CO₂ capture. *J Memb Sci*, 565, 370-379.
- [20] C. Y. Chuah *et al.* (2018). Harnessing filler materials for enhancing biogas separation membranes. *Chem Rev.*, 118(18), 8655-8769.
- [21] K. C. Wong, P. S. Goh, T. Taniguchi, A. F. Ismail, and K. Zahri. (2019). The role of geometrically different carbon-based fillers on the formation and gas separation performance of nanocomposite membrane. *Carbon N Y*, 149, 33-44.
- [22] H. W. Yoon, Y. H. Cho, and H. B. Park. (2015). Graphene-based membranes: Status and prospects subject areas. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 24(374), 1-23.
- [23] A. F. Ismail, K. C. Khulbe, and T. Matsuura. (2015). *Gas separation membranes: Polymeric and inorganic*. Springer International Publishing. 331.
- [24] K. A. Madurani, S. Suprpto, N. I. Machrita, S. L. Bahar, W. Illiya, and F. Kurniawan. (2020). Progress in graphene synthesis and its application: history, challenge and the future outlook for research and industry. *ECS Journal of Solid State Science and Technology*, 9(9), 093013.
- [25] H. P. Boehm, R. Setton, and E. Stumpp. (1986). Nomenclature and terminology of graphite intercalation compounds. *Carbon N Y*, 24(2), 241-245.
- [26] A. Bianco *et al.* (2013). All in the graphene family - A recommended nomenclature for two-dimensional carbon materials. *Carbon N Y*. 65, 1-6.
- [27] K. S. Novoselov *et al.* (2004). Electric field effect in atomically thin carbon films. *Science*, 306, 666-669.
- [28] Y. Bleu, F. Bourquard, T. Tite, A. Loir, and C. Maddi. (2018). Review of graphene growth from a solid carbon source by pulsed laser deposition (PLD). *Front Chem.*, 6(572).
- [29] A. Boretti, S. Al-Zubaidy, M. Vaclavikova, M. Al-Abri, S. Castelletto, and S. Mikhalovsky. (2018). Outlook for graphene-based desalination membranes. *NPJ Clean Water*, 1(1), 1-11.
- [30] T. J. M. Fraga, M. N. Carvalho, M. G. Ghislandi, and M. A. Da Motta Sobrinho. (2019). Functionalized graphene-based materials as innovative adsorbents of organic pollutants: A concise overview. 36(1).
- [31] A. Ebadi Amooghin, S. Mashhadikhan, H. Sanaeepur, A. Moghadassi, T. Matsuura, and S. Ramakrishna. (2019). Substantial breakthroughs on function-led design of advanced materials used in mixed matrix membranes (MMMs): A new horizon for efficient CO₂ separation. *Prog Mater Sci.*, 102, 222-295.
- [32] Y. Xu, H. Cao, Y. Xue, B. Li, and W. Cai. (2018). Liquid-phase exfoliation of graphene: an overview on exfoliation media, techniques, and challenges. *Nanomaterials*, 8, 942-974.
- [33] A. K. Geim. (2012). Graphene prehistory. *Phys Scr.*, T146.
- [34] P. R. Wallace. (1974). The band theory of Graphite. *Physical Review*, 71(9), 622-634.
- [35] A. K. Geim and K. S. Novoselov. (2007). The rise of graphene. *Nat Mater*, 6, 183-191.

- [36] Y. Zhu *et al.* (2010). Graphene and graphene oxide: Synthesis, properties, and applications. *Advanced Materials*, 22(35), 3906-3924.
- [37] I. W. Frank, D. M. Tanenbaum, A. M. van der Zande, and P. L. McEuen. (2007). Mechanical properties of suspended graphene sheets. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, 25(6), 2558.
- [38] C. Lee, X. Wei, J. W. Kysar, and J. Hone. (2008). Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 321(5887), 385-388.
- [39] A. Amiri, M. Naraghi, G. Ahmadi, M. Soleymaniha, and M. Shanbedi. (2018). A review on liquid-phase exfoliation for scalable production of pure graphene, wrinkled, crumpled and functionalized graphene and challenges. *FlatChem*, 8, 40-71.
- [40] A. A. Balandin *et al.* (2008). Superior thermal conductivity of single-layer graphene. *Nano Lett.*, 8(3), 902-907.
- [41] K. S. Novoselov *et al.* (2005). Two-dimensional atomic crystals. *Phys Today*, 102(30), 10451-10453.
- [42] S. Gadipelli and Z. X. Guo. (2015). Graphene-based materials: Synthesis and gas sorption, storage and separation. *Prog Mater Sci.*, 69, 1-60.
- [43] S. Chhetri, T. Kuila, and N. Chandra Murmu. (2016). Graphene composites. *Graphene Technology: From Laboratory to Fabrication*, 63-111.
- [44] M. Liu, D. Song, X. Wang, C. Sun, and D. Jing. (2020). Asymmetric two-layer porous membrane for gas separation. *Journal of Physical Chemistry Letters*, 11(15), 6359-6363.
- [45] N. Song, X. Gao, Z. Ma, X. Wang, Y. Wei, and C. Gao. (2018). A review of graphene-based separation membrane: Materials, characteristics, preparation and applications. *Desalination*, 437(February), 59-72.
- [46] G. Dong, J. Hou, J. Wang, Y. Zhang, V. Chen, and J. Liu. (2016). Enhanced CO₂/N₂ separation by porous reduced graphene oxide/Pebax mixed matrix membranes. *J Memb Sci.*, 520, 860-868.
- [47] W. Yu, L. Sisi, Y. Haiyan, and L. Jie. (2020). Progress in the functional modification of graphene/graphene oxide: A review. *RSC Adv.*, 10(26), 15328-15345.
- [48] S. Goswami, P. Banerjee, S. Datta, A. Mukhopadhyay, and P. Das. (2017). Graphene oxide nanoplatelets synthesized with carbonized agro-waste biomass as green precursor and its application for the treatment of dye rich wastewater. *Process Safety and Environmental Protection*, 106, 163-172.
- [49] N. F. Tajul Arifin, N. Yusof, A. F. Ismail, J. Jaafar, F. Aziz, and W. N. Wan Salleh. (2020). Graphene from waste and bioprecursors synthesis method and its application: A review. *Malaysian Journal of Fundamental and Applied Sciences*, 16(3), 342-350.
- [50] N. Raghavan, S. Thangavel, and G. Venugopal. (2017). A short review on preparation of graphene from waste and bioprecursors. *Appl Mater Today*, 7, 246-254.
- [51] M. T. Safian, U. S. Haron, and M. N. Mohammad Ibrahim.

- (2020). A Review on bio-based graphene derived from biomass wastes. *Bioresources*, 15(4), 9756-9785.
- [52] H. Muramatsu *et al.* (2014). Rice Husk-derived graphene with nano-sized domains and clean edges. *Small*, 1-5.
- [53] I. Rhee, J. Seok, Y. Ahm, J. Hee, and J. Hoon. (2016). Electrically conductive cement mortar: Incorporating rice husk-derived high-surface-area graphene. *Constr Build Mater*, 125, 632-642.
- [54] K. Sharma and V. K. Garg. (2019). *Vermicomposting of waste: A zero-waste approach for waste management*. Elsevier B.V.
- [55] T. Purkait, G. Singh, M. Singh, D. Kumar, and R. S. Dey. (2017). Large area few-layer graphene with scalable preparation from waste biomass for high-performance supercapacitor. *Sci Rep*, 7(1), 1-14.
- [56] X. Zhou, L. J. Broadbelt, and R. Vinu. (2016). *Mechanistic understanding of thermochemical conversion of polymers and lignocellulosic biomass*. 1st ed. Elsevier Inc. 49.
- [57] N. E. Ali. (2020). Agricultural Waste Management System (AWMS) in Malaysian. *Open Access Journal of Waste Management & Xenobiotics*, 3(2), 1-2.
- [58] Y. Yan *et al.* (2020). Synthesis of graphene: Potential carbon precursors and approaches. *Nanotechnol Rev*, 9(1), 1284-1314.
- [59] X. Xie and B. Goodell. (2014). Thermal degradation and conversion of plant biomass into high value carbon products. *ACS Symposium Series*, 1158, 147-158.
- [60] H. Li, H. Zhang, K. Li, J. Zhang, M. Sun, and B. Su. (2020). Catalytic graphitization of coke carbon by iron: Understanding the evolution of carbon Structure, morphology and lattice fringes. *Fuel*, 279(March), 118531.
- [61] A. Oya, R. Yamashita, and S. Otani. (1979). Catalytic graphitization of carbons by borons. *Carbon N Y*, 17, 131-137.
- [62] Q. Yan *et al.* (2018). Catalytic graphitization of kraft lignin to graphene-based structures with four different transitional metals. *Journal of Nanoparticle Research*, 20(9).
- [63] R. Nandi, M. K. Jha, S. K. Guchhait, D. Sutradhar, and S. Yadav. (2023). Impact of KOH activation on rice husk derived porous activated carbon for carbon capture at flue gas alike temperatures with high CO₂/N₂ selectivity. *ACS Omega*, 8(5), 4802-4812.
- [64] M. Seitzhanova, D. Chenchik, M. Yeleuov, Z. Mansurov, R. Di Capua, and N. Elibaeva. (2018). Synthesis and characterization of graphene layers from rice husks. *Chemical Bulletin of Kazakh National University*, 2, 12-18.
- [65] S. Sankar *et al.* (2017). Ultrathin graphene nanosheets derived from rice husks for sustainable supercapacitor electrodes. *New Journal of Chemistry*, 41, 13792-13797.
- [66] P. Singh, J. Bahadur, and K. Pal. (2017). One-step one chemical synthesis process of graphene from rice husk for energy storage applications. *Graphene*, 6, 61-71.
- [67] M. Seitzhanova, M. Yeleuov, and Z. A. Mansurov. (2018). Synthesis and characterization of

- graphene layers from rice husks. *Chemical Bulletin of Kazakh National University*, 2(89), 12-18.
- [68] M. Yeleuov *et al.* (2020). Modified activated graphene-based carbon electrodes from rice husk for supercapacitor applications. *Energies (Basel)*. 13(18), 1-10.