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## Microwave-assisted Hydrothermal Synthesis of Zeolite Particle from Malaysia's Low-grade Kaolin to Improve Membrane Properties and Performance

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### ABSTRACT

Modification of membrane through additives have been widely implemented to improve membrane properties. With integration of hydrophobic particles, it does not only improve water flux permeation but also able to enhance antifouling properties of polymer membrane. This study presents a remarkable synthesis of LTA type zeolite from a locally available kaolin found in peninsula Malaysia. The effect of the synthesis protocol on the phase purity of the synthesized zeolite was evaluate by qualitative and quantitative XRD analysis using the Xpert highscore plus software. The prepared zeolite was characterized by FTIR, SEM and BET. The microwave synthesis has shown the capability of reducing the synthesis time by 4-8 times and the product shows a smaller particle size distribution for a better surface area as compared to the clinoptilolite natural zeolite. The surface area, pore size and the size distribution of the synthesized zeolite portrayed its potentials for use as an additive in membrane technology.

#### Keywords:

Microwave-assisted; hydrothermal; synthesis; zeolite; membrane

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## 1. Introduction

Membrane technology has developed over the past few years to becoming a widely held separation technology that is used in many industrial processes domestic purification and environmental separation purposes. The quick and wide acceptability of the membrane technology can be connected to its enormous advantages and perceived future assurances such as; not requiring chemical additives, simplicity of operation, potential future expansion and the operation has a quite

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low energy consumption [1]. These and many features credited to membrane technology made it to be widely applied into various areas of application as itemized by Shao *et al.*, [2] to include “gas purification, environmental protection, water treatment, pharmaceutical industry, and food processing.” Since the early stage of membrane technology expansion, classification of membrane on the account of the membrane materials include: polymeric membranes, inorganic membranes, liquid membranes and mixed matrix membranes (MMM). Research shows that, large amount of the membranes used were produced with organic polymer or inorganic materials. Additionally, Warsinger *et al.*, [3] indicated that the membrane market is saturated by organic polymers. Reasons for such a wider market domination by the polymeric membranes was highlighted by Kang and Cao [5] to include its accomplished processability, tuneability, and economic attractiveness. Among the classified membrane types, the polymeric and liquid membranes have been reported by researchers to have a number of challenges and drawbacks i.e. poor thermal strength, low chemical and a prevalence imbalance between selectivity and permeability [4-6].

In an attempt to alleviate the challenges attached with the polymeric membrane, researchers have studied the inorganic materials for the preparation of membrane body. Jamalludin *et al.*, [4] found that the inorganic materials are the motivating materials which show increased stabilities against temperature and chemical effects. Therefore, the inorganic membranes may tolerate working at high pressure and temperature. Similarly, Harun *et al.*, [7] considered the inorganic membranes to have better chemical stability and the advantage of high selectivity in comparison with the organic polymer membranes. However, Tul Muntha *et al.*, [8] cautioned that the industrial application of the inorganic membrane is subject to achieving “high membrane permeability and selectivity, availability of large-area membrane modules, high reproducibility, cost effective fabrication and long-term stability and possibility of repeated membrane regeneration.” An appreciable achievement was recorded towards attaining to success in inorganic membrane, but they exhibit challenges of low sensitivity or permeability by poisoning the dense membrane and also high cost of the materials [9].

Contemporary approach aiming at developing membrane that can overcome the challenges of organic and inorganic membranes lead to the discovery of MMM [10]. The concept combines the organic polymer as matrix with the inorganic filler material. Here, the inherent fragility of the inorganic materials is circumvented by employing organic polymer as matrix. While, inorganic filler particles were added to solve the fouling and hydrophobicity problem of polymer membrane. MMM are capable to realize better permeability and high selectivity as compared with the polymeric membranes [10-11]. But, the improvement in properties of the MMM is mostly ascribed to the in-built special separation ability of the inorganic particles. Therefore, large portion of the MMM success heavily relies on the unique properties of the dispersed particles otherwise called the additives. Additives addition in membrane fabrication has been extensively employed to develop a MMM that can offer better hydrophilicity, wettability, pore structure, surface roughness and to aid in reducing the fouling problem of polymer membrane.

Various inorganic particles have been used to solve the fouling and hydrophobicity problem such as Zinc Oxide, Silver, Titanium Dioxide and zeolite [8]. These inorganic particles offer unique properties which include molecular sieving, high toxicity to a broad spectrum of microorganism and good performance as anti-bacterial agents. Among many inorganic materials that were used as a polymer filler in MMM, zeolite is well known to have a good microporous structure, anti-wear and high strength, good chemical inactivity, thermal stability and low cost as well as its availability. Accordingly, researchers have studied the fabrication of MMM using zeolite as a filler, and have achieved remarkable outcome in its application such as drinking water purification, water desalination, bacteria removal, gas separation, and wastewater treatment [12-15].

The main feature of zeolite reinforced polymeric membrane is the ability to perform both adsorption and separation as well as able to tolerate working at high pressure and temperature. However, for a better adsorptive performance, the zeolite must possess a high surface area and higher molecular sieving capability. Several studies on zeolite/polymer MMM utilized natural zeolite whose particles size is in micron range [16]. But the addition of natural zeolite as a filler was also reported to have some shortcomings such as: non-uniform pore size, inadequate supply, impurities and low ion exchange capacities [17]. Synthetic zeolites are developed and used in MMM because of high purity and uniform pore size. However, it has some challenges too, such as: application of toxic organic templates, emission of harmful greenhouse gases during processing, coupled with the use of expensive sources of silica and alumina. Thus, making the process expensive and un-sustainable.

Ecological raw materials proved to be economical, greener and more sustainable for the synthesis of zeolite over standard synthetic chemicals [18-19]. Among the many ecological materials studied, kaolin has proved to be more suitable and sustainable for the production of zeolite than rice husk, fly ash and red mud. Thus, this study presents a remarkable synthesis of zeolite-A from a locally available kaolin found in peninsula Malaysia. The effect of microwave-assisted heating process as a modification of the conventional hydrothermal synthesis because of the advantage it offered for higher and uniform heating rates, which is more suitable over the conventional facile method [20]. The inexpensive pure phase zeolite will eventually be used in producing a MMM with a good adsorption and molecular sieving properties.

## 2. Methodology

This study utilized a low grade kaolin obtained around Sedeli Forest, Kota Tinggi, Johor state, Malaysia. Prior to the microwave-assisted synthesis, the raw kaolin was calcined at 700 °C for 2 h holding time. After a successful calcination, the product of the calcination operation called metakaolin, was evaluated using XRD, FTIR and SEM.

The reaction mixture for the synthesis was prepared by adding 3g of the metakaolin into a 70mL 2 M alkaline solution, after which ageing is done for 12 h at 40 °C. The mixture is then transferred into the reaction vessel, and the microwave irradiation was performed for 1, 2 and 3 hours respectively. The sample is then centrifuged at 1500 rpm for 20 minutes and the reclaimed solid is washed with deionized water to control the alkalinity. Finally, the obtained product was dried in a furnace at 90 °C and packaged for further operations. The XRD analysis of the produced zeolite powder was done with a Philips X-ray diffractometer (Model Bruker D8, Germany) which operated at 40 mA and 40 kV at  $2\theta$  range of 5° and 90° and a step increment rate of 0.02 °/min. The morphological investigation was done using JSM-6380LA; Joel SEM machine.

## 3. Results

Figure 1(A) shows a SEM micrograph of the kaolin clay material with a dominant presence of kaolinite indicating a layered crystalline morphology with an irregular platelet. While Figure 1(B) illustrates the effect of the calcination on the kaolinite structure of the raw kaolin.

The intention of calcination is to transform the raw kaolin into a metakaolin, a material that is highly disordered and amorphous [21]. Thus, the calcination causes the disintegration of the kaolin clay structures thereby forming a structure that is characterized with leaf-like morphology as shown in Figure 1(B), which is conforming to the result of Chandrasekhar [22]. Figure 2(A) and (B) is the FTIR spectra which further illustrates the transformation of the kaolinite structure into a metakaolin.

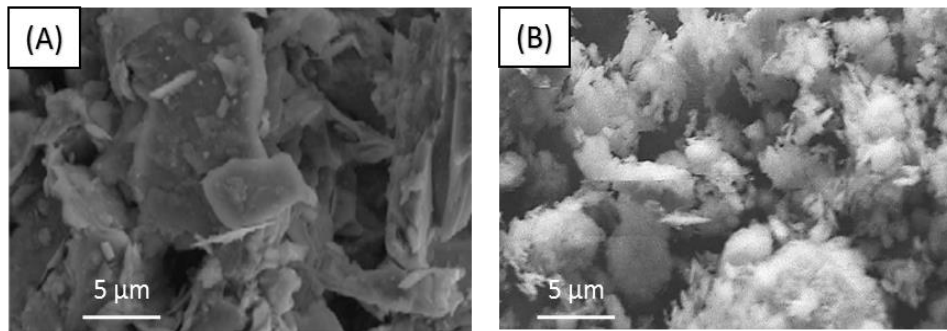


Fig. 1. SEM micrographs of (A) the raw kaolin and (B) calcined kaolin

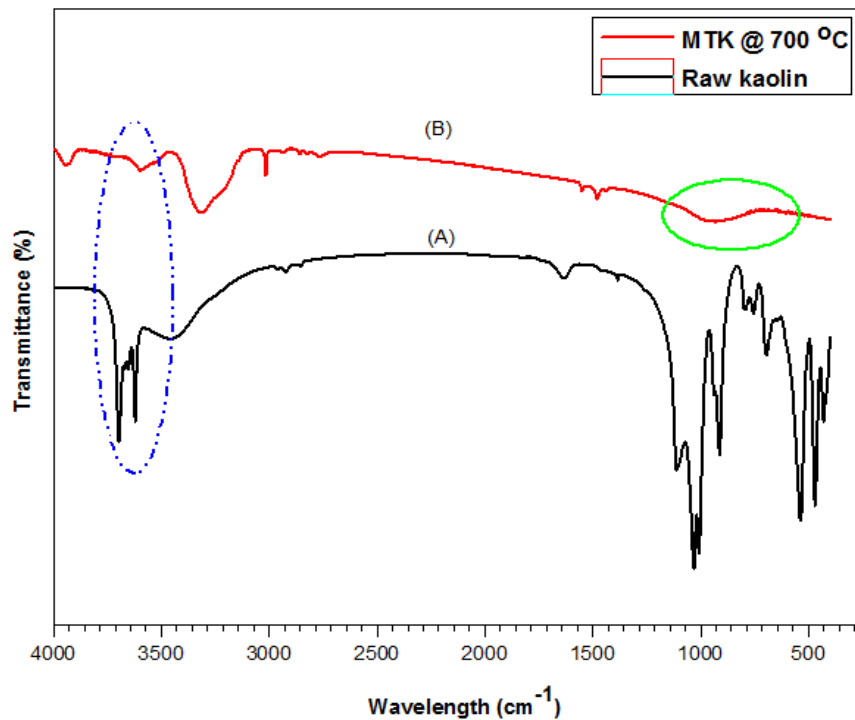


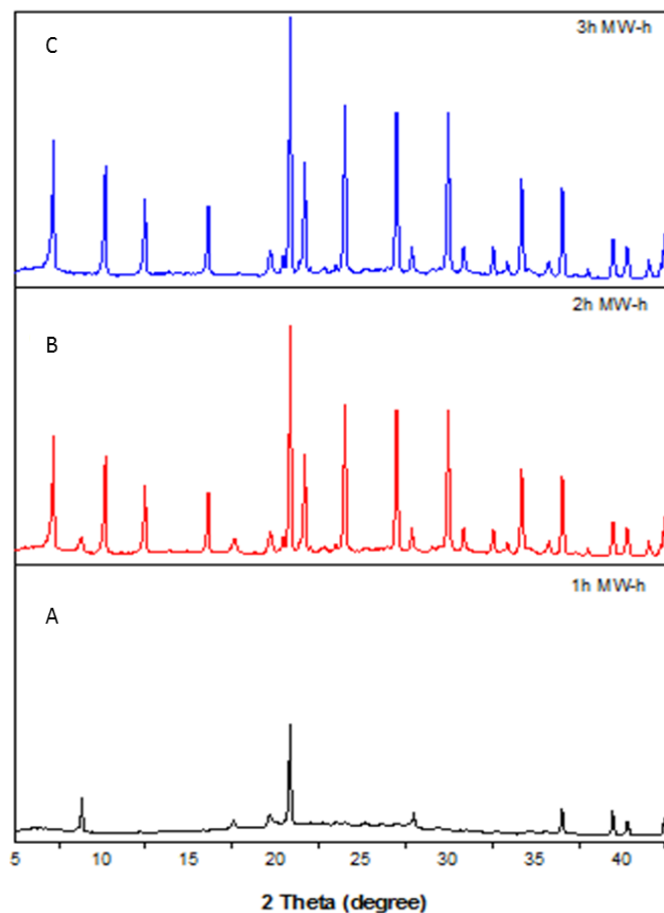
Fig. 2. FTIR spectra for (A) the raw kaolin (B) metakaolin after calcination at 700 °C

From Figure 2, the complete elimination of the kaolinite visible peaks at  $1092.11\text{cm}^{-1}$  and  $458.72\text{cm}^{-1}$  that represents the asymmetric stretching and bending vibrations of the Al-O and Si-O bonds of the kaolin structure was evident. Thus, indicating that it has actively participated in the transformation from kaolin to metakaolin as already observed by Chandrasekhar [22].

In addition, Figure 3 describes the XRD diffractograms obtained after treatment of three samples at 1, 2 and 3 hours microwave irradiation. From the XRD result, the obvious decrease of time for crystallization has become very pronounced as compared to the previous studies where crystallization occurred at 9 and 12 hours by conventional facile synthesis [19, 23].

The result indicated that at 1 hour microwave irradiation, the reaction gel has undergone a tremendous transformation to the extent that the powder product obtained was no longer amorphous, but a poorly crystalline material. Further qualitative analysis of the XRD pattern indicated that hydroxysodalite (SOD) and a relict crystal of NaX type zeolite were produced at 1 hour microwave heating, along with some unreacted amorphous aluminosilicate and quartz, which is similar to the result obtained in the previous studies [24]. However, the crystallinity is better than

the result obtained after 9 hour crystallization via conventional hydrothermal synthesis as presented in the previous work of Abdullahi *et al.*, [18, 19].



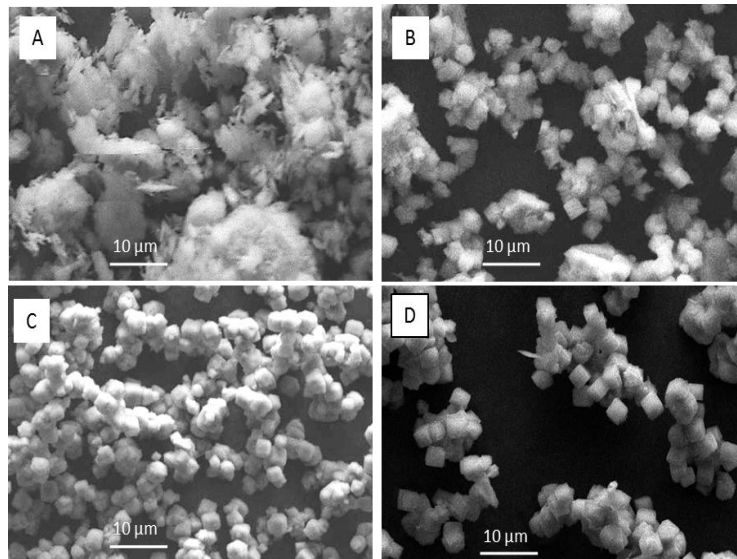
**Fig. 3.** X-ray diffractograms of crude kaolin samples

When the reaction proceeded for 2 hours microwave heating (MW-h), a product with a moderate crystallinity and a better cubic crystal morphology was obtained. But, the accompanied hydroxysodalite peaks are still visible. After crystallization for 3 hours using microwave heating, a maximum crystalline zeolite A is produced. This is demonstrated by the high peak intensity of the (1 1 0) reflection plane in the XRD pattern of the powder product after 3 hours crystallization.

The SEM images illustrated in Figure 4, provides a supporting description to the discussions on the effect of microwave heating on type A zeolite synthesis process.

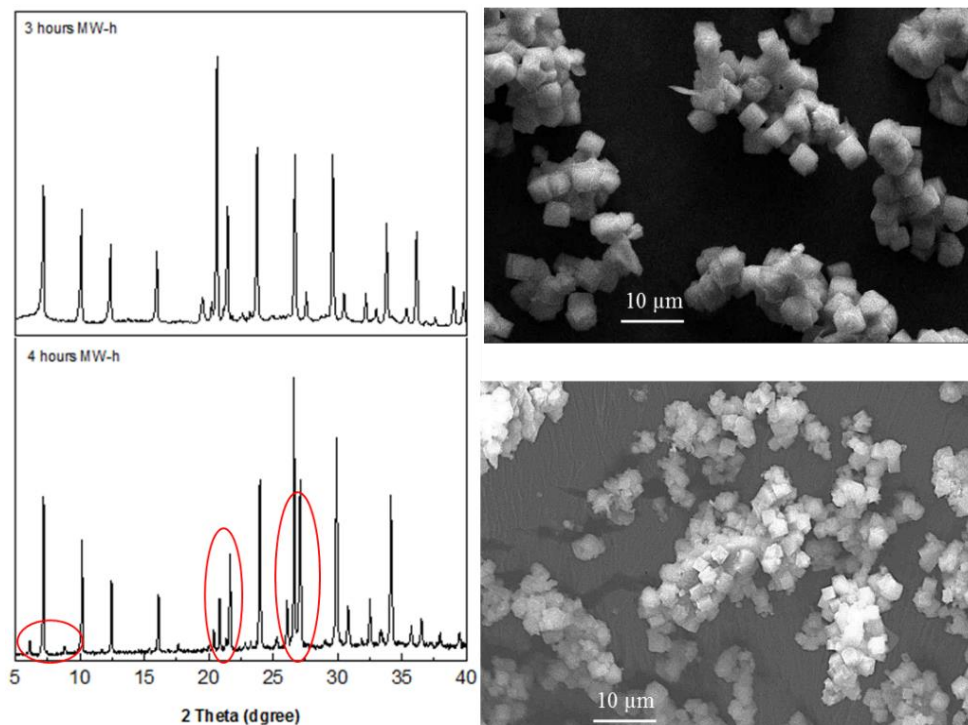
Figure 4(A) illustrates the morphology of the calcined kaolin before the crystallization treatment, Figure 4(B) is dominated by a poorly crystalline SOD particle with very few scattered cubic-like crystals of NaA zeolite, that are formed due to the insufficient energy of crystallization in the solution, which failed to initiate the required crystal growth to achieve full transformation at 1 hour microwave irradiation [25]. Figure 4(C) illustrates the dominance of type A zeolite crystal and very few spherical shaped SOD crystals. However, a well crystalline zeolite A was the product of 3 hours microwave heating as illustrated in Figure 4(D).





**Fig. 4.** SEM micrographs of (A) calcined kaolin (B) 1 hour MW-h (C) 2 hour MW-h and (D) 3 hour MW-h

It became clear, that the 3 hours microwave heating time produces a pure phase and a well crystalline zeolite-A product. Thus, making it the most suitable heating time for the conversion of the Malaysia's low grade kaolin to zeolite. This result significantly differed with the work of Youssef *et al.*, [25] where they reported 4 hour microwave heating time for the synthesis of zeolite A using kaolin from Georgia, USA. An attempt was made to validate the suitability of 3 hours microwave heating for the synthesis process, by prolonging the time to 4 hours. The results obtained is shown in Figure 5.



**Fig. 5.** Comparison of zeolite obtained from microwave heating synthesis at 3 hour MW-h and 4 hours MW-h

The results obtained after 4 hours microwave heating shows a smaller size cubic crystal of the synthesized powder. However, the product purity and crystallinity was apologetic, due to the

formations of NaX phases. This finding was in agreement with Youssef *et al.*, [25] that, prolonged crystallization will lead to the formation of zeolite X. This result therefore, has affirmed the suitability and superiority of 3 hour microwave heating for the synthesis of type A zeolite, especially using the low grade kaolin. On the account of crystallization time, the microwave assisted synthesis route was able to produce the targeted zeolite at a very low crystallization time of 3 hours. Thus, the process has proved to be very suitable, economical and sustainable.

The surface area measurement of the synthesized zeolite-A was performed via multipoint N<sub>2</sub> BET method, at liquid nitrogen temperature. The surface area of the synthesized zeolite-A is established to be around 350 m<sup>2</sup>/g. The result further revealed that the synthesized zeolite-A demonstrates a narrow average pore size. The synthesized zeolite A is compared to the clinoptilolite (natural zeolite powder), which was obtained from Shijiazhuang Mining Trade Co. Ltd, from Liaoning Province, China, with the same average particle size as the synthesized zeolite A. The results of the evaluation as summarized in Table 1 which shows that the synthesized zeolite obtained in this study has a larger surface area than the clinoptilolite (natural zeolite powder), and that makes it a better candidate for adsorption and other related application which found the larger zeolite surface area as added advantage.

**Table 1**

Comparison of surface area and pore size distribution of the synthesized zeolite A and clinoptilolite (Natural zeolite)

Description	Natural zeolite (clinoptilolite)	Synthesized zeolite A
BET surface area	27.69 m <sup>2</sup> /g	57.48 m <sup>2</sup> /g
Langmuir surface area	37.07 m <sup>2</sup> /g	76.14 m <sup>2</sup> /g
BJH Adsorption cumulative pore volume	0.085 m <sup>3</sup> /g	0.04 m <sup>3</sup> /g
BJH Adsorption average pore width	16.74 nm	11.36 nm

The twin roles of adsorption and separation has been confirmed to be achieved in Zeolite MMM [2]. Nonetheless, it is equally known that, the surface of the adsorbent (zeolite filler/support material) has the largest concentration of the adsorption sites. This implies that, the superior adsorption performance of the zeolite based MMM typically relates to the surface area of the adsorbent. In accordance with this stance [3-4] cautions that to accomplish a better adsorption performance with zeolite based mixed matrix membrane, the zeolite reinforcement must have a high surface area. The authors further stated that finest material particles are more suitable to achieve a larger surface area per volume compared to that of bigger material particles. Therefore, the larger BET surface area achieved by the synthesized zeolite as reported in this study is a pointer to the fact that if it is used as a filler in preparing MMM, a pleasant result with improved performance is assured.

#### 4. Conclusions

The calcination of the raw kaolin as 700 °C suggested that the water of crystallization in the kaolin was sufficiently removed to form metakaolin. Due to the breaking down of the clay structure, thereby improving the reactivity of the precursor material. The morphological analysis of the synthesized zeolite shows that, no considerable amount of amorphous materials is detected at the end of the synthesis process. The phase purity and good crystallinity of the synthesized product is an indication that the low grade Malaysia's kaolin can be successfully transformed to zeolite-A through the microwave-assisted hydrothermal process, by adopting the novel methodology and parameters as

presented in this study. The synthesized zeolite obtained in this study has a larger surface area than the clinoptilolite (natural zeolite powder). Thus, it is recommended for use in zeolite based MMM.

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