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Sustainable Red Mud Conversion to ZSM-5

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Abstract

Red mud (RM), a highly alkaline industrial byproduct of alumina production, poses significant environmental challenges due to its massive accumulation and hazardous composition. This study addresses these issues by developing a sustainable method to convert RM into high-performance mesoporous ZSM-5 zeolite. A dual-hydrothermal synthesis approach was employed, combining alkali fusion and hydrothermal treatment with cetyltrimethylammonium bromide (CTAB) as a structure-directing agent to enhance mesoporosity. Comprehensive characterization was performed to confirm the structural and textural properties of the synthesized ZSM-5. X-ray diffraction (XRD) analysis confirmed the successful formation of the highly crystalline MFI zeolite framework, while Fourier-transform infrared spectroscopy (FTIR) validated the incorporation of aluminosilicate species. Nitrogen adsorption-desorption analysis revealed a significant enhancement in surface area (734 m^2/g) and dual porosity, with micropores (1.18 nm) and mesopores (2.79 nm) present. Scanning electron microscopy (SEM) highlighted the morphological transformation from aggregated particles in RM to well-defined cubic structures characteristic of ZSM-5. The synthesized material exhibited promising properties for adsorption applications, particularly in addressing environmental challenges such as wastewater treatment. This study demonstrates a scalable and eco-friendly approach to valorizing industrial waste, contributing to sustainable material development and the circular economy.

Keywords: Red mud, ZSM-5 zeolite, Dual-hydrothermal synthesis, Mesoporous materials, Waste valorization, Adsorbent characterization, Sustainable material development

Introduction

Red mud (RM) is a highly alkaline by product generated during the Bayer process for alumina extraction, with an estimated production of 1 to 1.8 tons of RM for every ton of alumina. This has resulted in an annual accumulation of over 150 million tons globally, posing significant environmental and economic challenges [1]. The improper disposal of RM leads to soil and water contamination, hazardous dust

generation, and extensive land usage, all of which have long-term environmental and societal impacts [2]. Given its complex chemical composition, predominantly comprising oxides of iron, aluminum, silicon, titanium, and calcium. RM represents both an environmental liability and a potential resource for material valorization. Addressing this dual challenge requires innovative strategies that align with sustainability principles [3].

One promising avenue for RM utilization is its conversion into zeolites, crystalline aluminosilicate materials with unique structural features such as high surface area, tunable porosity, and exceptional thermal and chemical stability [4,5]. Among zeolites, ZSM-5 is particularly valued for its well-defined MFI framework, combining microporous and mesoporous characteristics. These properties make ZSM-5 a versatile material for applications including adsorption, catalysis, and gas separation. However, conventional synthesis of ZSM-5 is hindered by the reliance on expensive and non-renewable raw materials, as well as energy-intensive processes. Transforming RM into ZSM-5 offers a sustainable and cost-effective alternative, reducing industrial waste while producing high-performance materials [6].

Despite its potential, the synthesis of ZSM-5 from RM is challenging due to its heterogeneous composition and high impurity levels, particularly iron oxides, which can interfere with zeolite crystallization [7]. Previous studies have explored various methods for RM-derived zeolite synthesis, including alkali fusion and hydrothermal treatments [8,9]. However, many of these approaches focus on microporous zeolites, which may limit their effectiveness in adsorption applications requiring larger pore sizes. Enhancing the mesoporosity of ZSM-5 is critical to improving its adsorption efficiency for bulky organic molecules, such as dyes, and for expanding its industrial applicability.

Therefore, this study presents a dual-hydrothermal synthesis method to convert RM into mesoporous ZSM-5, leveraging alkali fusion and structure-directing agents to achieve superior structural and textural properties. The synthesis process involves the removal of impurities, mobilization of silica and alumina, and controlled crystallization to produce a material with both micropores and mesopores. The dual hydrothermal method developed in this study is an innovation in the synthesis of mesoporous ZSM-5 from red mud, with higher adsorption effectiveness than conventional methods. This research not only contributes to the utilization of industrial waste but also has a wide environmental and economic impact on wastewater management and other industrial applications.

Cetyltrimethylammonium bromide (CTAB) was employed as a structure-directing agent to enhance mesoporosity, while tetra-propylammonium hydroxide (TPAOH) was used to guide the formation of the MFI zeolite framework. Comprehensive characterization techniques, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption analysis, and scanning electron microscopy (SEM), were employed to evaluate the structure, crystalline, and morphology of the synthesized ZSM-5. By transforming RM into high-performance ZSM-5, this study addresses 2 critical environmental challenges: mitigating the disposal of hazardous industrial waste and developing sustainable materials for environmental remediation. The findings highlight the scalability and eco-friendliness of the dual-hydrothermal synthesis method, contributing to the advancement of sustainable material science and circular economy practices.

Materials and methods

Materials

The materials used in this study included sodium hydroxide (NaOH, 99 %, Merck), colloidal silica (Ludox 30 %, Aldrich), tetra propylammonium hydroxide (TPAOH, 40 wt.% solution in water, Merck), cetyltrimethylammonium bromide (CTABr, $C_{19}H_{42}NBr$, Aldrich), and methylene blue (MB $C_{16}H_{18}ClN_3S$, Merck Millipore). Deionized water was used for all solution preparations and washing steps to maintain consistency in experimental conditions. The red mud (RM) used as the primary raw material for synthesis was sourced from Bintan Island, Indonesia, in moist, brown chunks. The material underwent an initial drying process at 105 °C for 24 h to remove excess moisture. The dried chunks were then crushed using a mortar, further ground with a blender, and sieved through a 325-mesh sieve to achieve uniform fine grains. The refined RM was subjected to an additional drying step at 105 °C in an oven to ensure complete removal of residual moisture.

Synthesis of mesoporous ZSM-5

The preparation of ZSM-5 from RM followed a method based on our previous work Tehubijuluw *et al.* [10], with modifications to enhance the material's composition and performance. Initially, the high Fe_2O_3 content in RM was reduced to increase the relative concentration of Al_2O_3 and SiO_2. A total of 10 g of RM was mixed with 10 g of NaOH and subjected to thermal treatment at 450 °C for 2 h. After cooling, the resulting solid was combined with 127.5 mL of deionized water and stirred continuously for 24 h. The mixture was filtered, and the solid phase was dried at 105 °C for 24 h, yielding sodium aluminosilicate.

The dried sodium aluminosilicate (0.663 g) was dissolved in 24.67 mL of deionized water and mixed with 39.55 g of colloidal silica (LUDOX) under constant stirring for 8 h. To this mixture, 20.34 g of TPAOH solution was added, and the solution was heated in a Teflon-lined autoclave at 80 °C for 9 h. After cooling to room temperature, 18.93 g of CTAB was introduced to the mixture and stirred for 1 h to enhance mesoporosity. The resulting mixture was reheated at 150 °C for 24 h. The final product had a pH of 13. To neutralize the material, it was washed repeatedly until the supernatant reached a neutral pH of 7. The solid was then dried at 105 °C for 16 h, producing the mesoporous ZSM-5 ready for further characterization and application.

Characterization of mesoporous ZSM-5

The synthesized ZSM-5 samples were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption analysis, and scanning electron microscopy (SEM) to determine their structural, textural, and morphological properties. XRD analysis was conducted using a Phillips Expert Diffractometer with Cu Kα radiation (λ = 1.54056 Å). The diffractometer operated in the 2θ range of 5 - 50 °, allowing for phase identification and the determination of relative crystallinity. FTIR spectra were recorded using KBr pellet techniques on a Shimadzu FTIR spectrometer within the range of 1,800 to 400 cm^{-1}. This analysis identified the functional groups and structural features of the samples. Nitrogen adsorption-desorption isotherms were obtained using a Quanta Chrome Corporation (Nova-1200) instrument. Before analysis, approximately 0.05 g of each sample was degassed under vacuum at 300 °C for 3 h. The specific surface area (S_{BET}) was estimated using the Brunauer-Emmett-Teller (BET) equation, and the pore size distribution was determined using the non-local density functional theory (NLDFT) method. The surface morphology and particle distribution of the samples were examined using a ZEISS EVO MA 10 scanning electron microscope (SEM). This technique provided detailed insights into the structural features of the synthesized materials.

Results and discussion

Sample characterization

The XRD patterns of RM and ZSM-5 (**Figure 1(a)**) revealed distinct differences, underscoring the structural transformation of RM during synthesis. RM exhibited broad peaks corresponding to various mineral phases, including gibbsite (18.28, 20.31, 20.54, 36.59, 37.64 °), boehmite (38.38, 49.93, 49.21 °), hematite (24.14, 33.15, 35.61, 40.86, 49.48, 54.90 °), magnetite (30.91, 35.42, 43.04 °), quartz (20.86, 26.64, 36.54, 39.47 °), and TiO_2 anatase (25.28, 37.80, 48.05 °). Peaks associated with tsaregorodtsevite (19.84, 24.88 °) and SiO_2 polymorph (12.29 °) further illustrated the complex composition of RM. These peaks reflect RM's heterogeneous nature, dominated by iron oxides, silicates, and aluminum-containing minerals, which contribute to its low adsorption performance in its raw state. In contrast, the synthesized ZSM-5 displayed sharp and well-defined peaks at 2θ = 7.9, 8.8, 23.1, 23.9, and 24.3 °, characteristic of the MFI zeolite framework. The disappearance of peaks associated with RM's mineral impurities, particularly those of hematite and quartz, indicates the successful removal of impurities during synthesis. This transformation was facilitated by the alkali fusion step, which increased the SiO_2 and Al_2O_3 content in the precursor material. The relative crystallinity of ZSM-5, confirmed by the intensity of its diffraction peaks, demonstrated the formation of a highly ordered microporous structure. These findings are consistent with previous studies that reported similar transformations during the synthesis of zeolites from industrial waste. Therefore, the XRD results establish that the dual-hydrothermal synthesis method effectively converts RM into ZSM-5, yielding a material with a highly crystalline and ordered structure. The absence of characteristic RM peaks, combined with the emergence

of well-defined ZSM-5 peaks, underscores the material's potential for adsorption and catalytic applications.

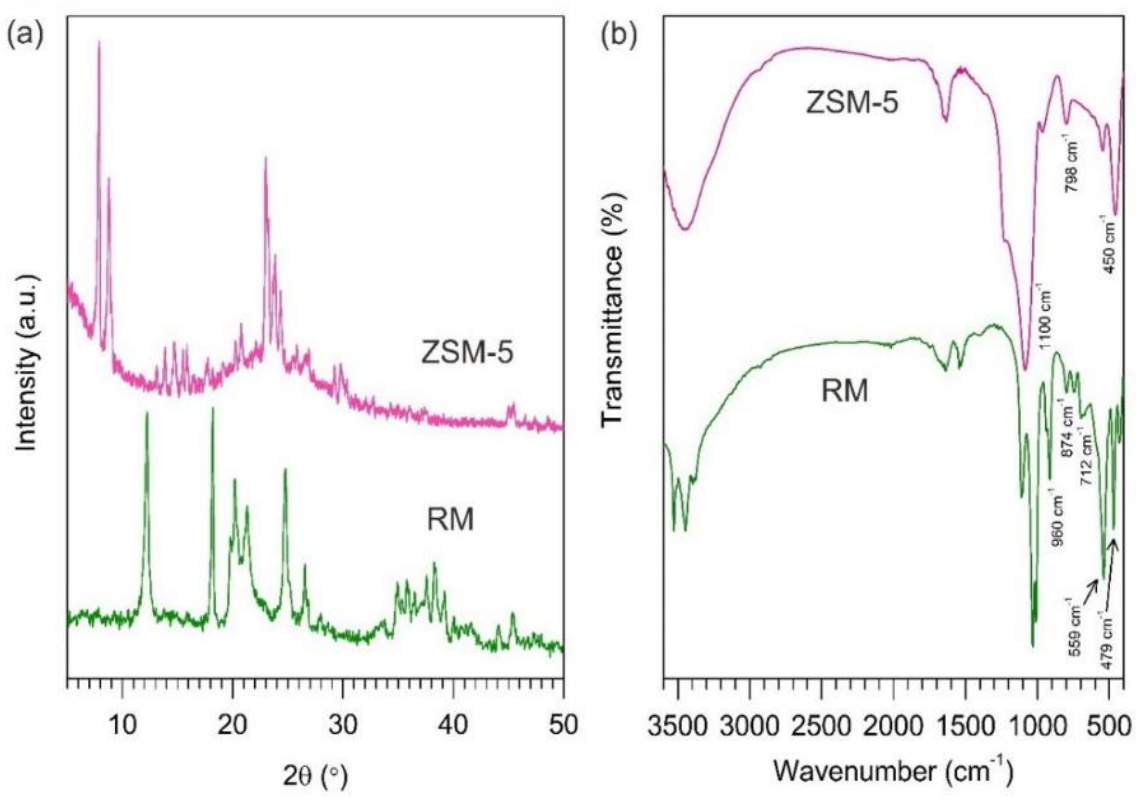

Figure 1 The diffraction pattern (a) and FTIR spectra (b) of RM and ZSM-5.

FTIR spectroscopy (**Figure 1(b)**) further confirmed the structural transformation of RM into ZSM-5 by identifying the functional groups associated with each material. The FTIR spectrum of RM exhibited broad absorption bands at 3,550 - 3,300 cm^{-1}, corresponding to hydroxyl groups in gibbsite. Peaks at 559 and 479 cm^{-1} were attributed to hematite, while the vibrational mode of Si–O at 960 cm^{-1} confirmed the presence of quartz. Additional peaks at 874, 712, and 628 cm^{-1} were associated with Al^{3+}–O^{2-} bonds, highlighting the aluminum content in RM. After synthesis, the FTIR spectrum of ZSM-5 revealed significant changes. The disappearance of peaks associated with hematite and hydroxyl groups in gibbsite indicated the removal of RM impurities. New peaks corresponding to the bending vibrations of T-O-T (T = Si or Al) bonds at 450 cm^{-1} and the symmetric (798 cm^{-1}) and asymmetric stretching vibrations (1,100 cm^{-1}) of TO_4 tetrahedral were observed. These features are characteristic of the ZSM-5 framework and confirm the successful incorporation of Si and Al into the zeolite structure. These results align with earlier studies, which reported similar vibrational modes in ZSM-5 synthesized from waste materials. The FTIR results provide strong evidence of the structural changes that occurred during the transformation of RM into ZSM-5. The formation of a well-defined zeolite framework, combined with the removal of RM impurities, highlights the effectiveness of the dual-hydrothermal synthesis method.

The nitrogen adsorption-desorption isotherms of RM and ZSM-5 (**Figure 2(a)**) demonstrate significant improvements in the textural properties of the synthesized material. RM exhibited a type II isotherm, typical of non-porous or macroporous materials. The slow initial adsorption rate, followed by a sharp increase at higher relative pressures, indicates weak adsorbent-adsorbate interactions. A low H3-type hysteresis loop was observed, suggesting the presence of slit-shaped mesopores formed by particle aggregation. The pore size distribution (**Figure 2(b)**) revealed an average pore diameter of 42.789 nm, consistent with macroporous

characteristics. The low BET surface area of RM (33.781 m^2/g, **Table 1**) further confirmed its limited porosity and poor suitability as an adsorbent. In contrast, ZSM-5 exhibited a combination of type I and type IV isotherms, characteristic of materials with both microporous and mesoporous structures. Rapid nitrogen adsorption at low relative pressures indicated micropore filling, while adsorption at higher relative pressures confirmed the presence of mesopores. NLDFT analysis revealed micropores and mesopores with diameters of 1.18 and 2.79 nm, respectively. The BET surface area increased significantly to 734 m^2/g, and the hysteresis loop formation was attributed to capillary condensation within mesopores.

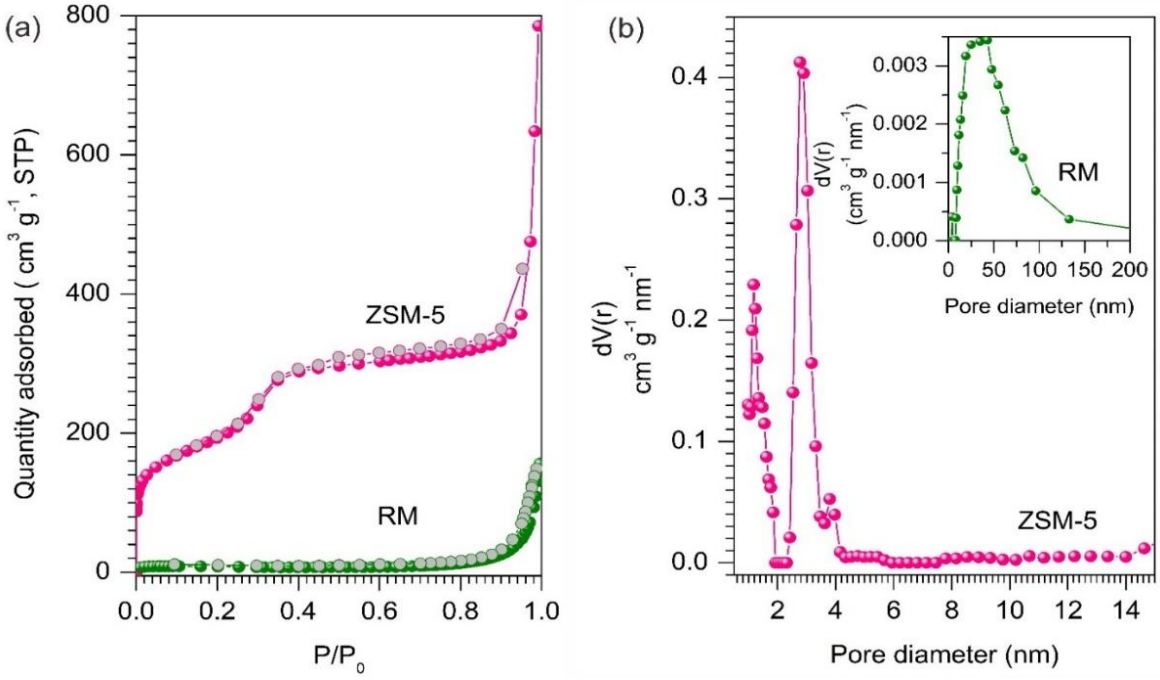

Figure 2 N_2 adsorption- desorption isotherm (a) and NLDFT pore size distribution (b) as synthesized samples (the dashed line at 2 nm shows the separation of micropore and mesopore).

The addition of CTAB as a structure-directing agent during synthesis played a crucial role in generating mesoporosity, while the calcination step removed the CTAB template, leaving behind a mesoporous structure. These results align with previous studies that highlighted the benefits of combining micropores and mesopores for the adsorption of larger organic molecules. The dual porosity of ZSM-5, characterized by its micropores for high surface area and mesopores for enhanced accessibility, makes it highly effective for adsorption applications. The significant improvements in surface area, pore size distribution, and porosity underscore the success of the synthesis process.

Table 1 Textural properties of the red mud samples from the N2 physisorption analyses.

Material	S_{BET} ($m^2\ g^{-1}$)	Smeso [a] ($m^2\ g^{-1}$)	Smicro [b] ($m^2\ g^{-1}$)	*V*meso ($cm^3\ g^{-1}$)	*V*micro ($cm^3\ g^{-1}$)	*d*meso (nm)	*d*micro (nm)
ZSM-5	734	252	233	0.58	0.25	2.79	1.18
RM	33.781	25.287	9.368	0.242	0.018	42.789	1.61

[a]Calculated by the NLDFT method at a relative pressure range of 0.9 - 1.0

[b]Calculated by the t-plot method

The SEM images (**Figure 3**) revealed substantial morphological differences between RM and ZSM-5. RM exhibited irregular morphologies, including rods, spheres, and aggregated particles. This non-uniform structure, combined with low surface area, limits RM's adsorption performance in its raw state. In contrast, ZSM-5 showed a well-defined micro-cubic morphology, characteristic of the MFI zeolite framework. The high degree of particle uniformity and internal porosity of ZSM-5 enhances its adsorption potential for organic pollutants like methylene blue. Some particle aggregation was observed in ZSM-5, likely due to incomplete crystallization, but this did not significantly affect its overall performance. EDX analysis (**Figure 4**) confirmed the elemental composition of RM and ZSM-5. RM contained elements such as Si, Al, O, Na, Ca, Fe, and Ti, reflecting its diverse mineral composition. Following synthesis, ZSM-5 retained most of these elements, but the Fe content was significantly reduced due to the alkali fusion step. The reduction in Fe content enhances the purity and crystallinity of the ZSM-5 framework, making it more suitable for adsorption and catalytic applications.

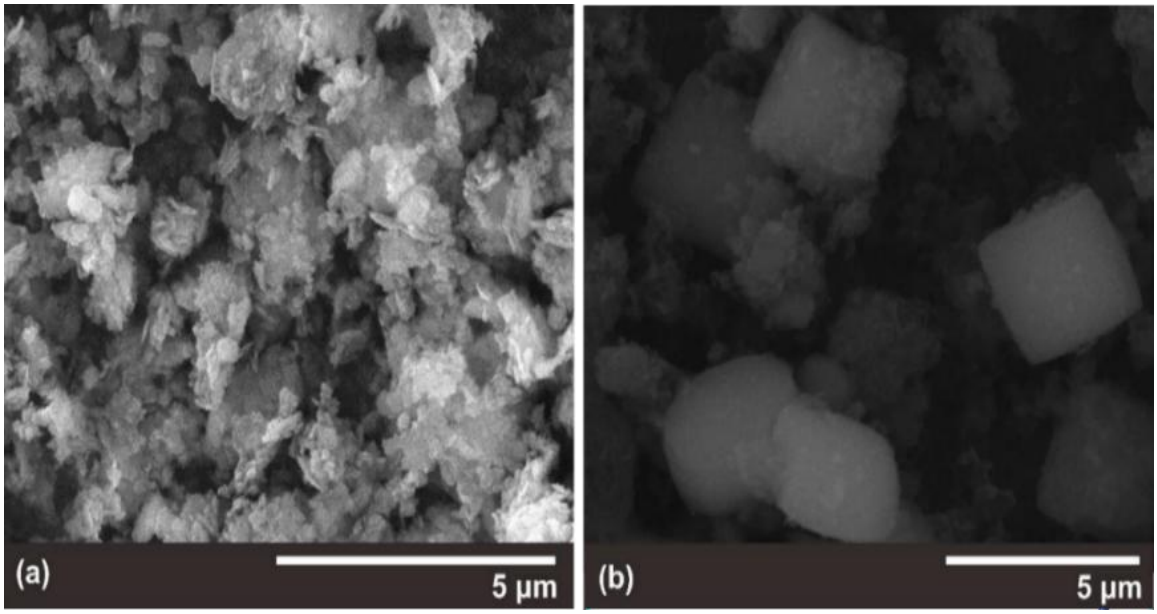

Figure 3 SEM image of (a) RM and (b) ZSM-5.

The gathered characterization results confirm the successful transformation of RM into mesoporous ZSM-5 with significantly enhanced structural, textural, and morphological properties. These improvements, including higher surface area, dual porosity, and improved crystallinity, highlight the potential of ZSM-5 for adsorption applications. The synthesis process not only addresses the environmental challenges associated with RM waste but also provides a scalable and sustainable pathway for producing high-performance materials for environmental remediation.

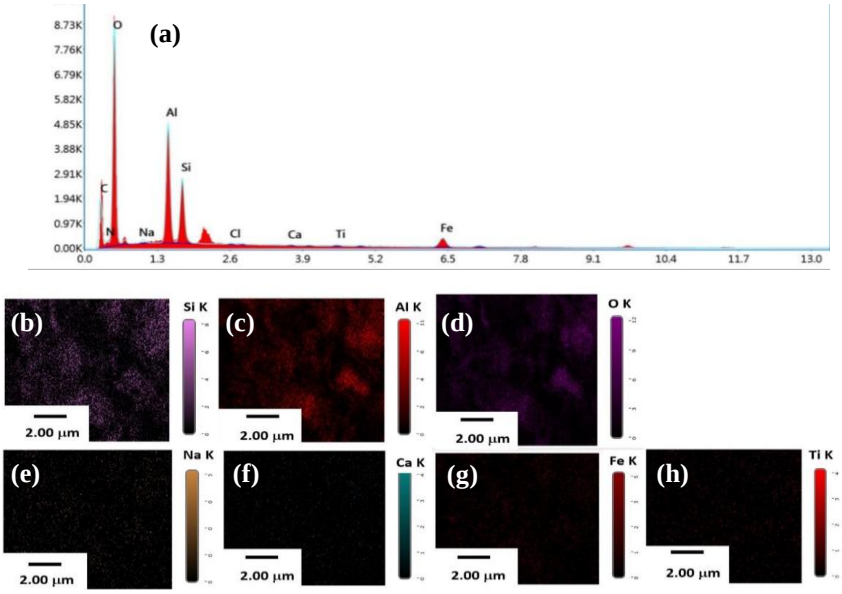

Figure 4 EDX (a) and mapping (b) - (h) images of RM.

The combination of the characterization results confirms that the dual hydrothermal method successfully produces mesoporous ZSM-5 from red mud with better crystal structure, higher surface area, and increased adsorption capacity. The results of this study were compared to the previous study conducted by Cheng *et al.* [11], NaP1 zeolite, using red mud (RM) as raw material, was successfully prepared via alkali fusion and hydrothermal method, the surface area of methylene blue was 79.3 m^2/g and the adsorption capacity was 48.7 mg/g, respectively. The result of the method used is lower porosity and no significant mesopores. Meanwhile, the results of the research conducted by Taher *et al.* [12] using the batch method, methylene blue adsorption, surface area and adsorption capacity are 77.42 mg/g and adsorption capacity is 171 mg/g. It shows low surface area, smaller adsorption capacity. In this study, the dual-hydrothermal method with CTAB surfactant obtained a surface area of 734 m^2/g and an adsorption capacity of 208 mg/g. The advantages of this method increase adsorption efficiency and show effectiveness in removing organic pollutants. Then it is more environmentally friendly than acid activation, because it does not produce excess acid waste.

Conclusions

This study proved that red mud can be modified into mesoporous ZSM-5 with improved pore structure, which significantly enhanced the adsorption capacity towards methylene blue. Transformation of RM via dual-hydrothermal method using CTABr as a template was shown to increase the surface area and pore volume, which enabled the improvement of MB removal efficiency from water. ZSM-5 showed significantly better performance than RM, both under laboratory conditions and when tested using real seawater. Adsorption isotherms and kinetics showed that the process was controlled by chemical adsorption with a heterogeneous mechanism. These results open opportunities for the utilization of red mud as a base material for the synthesis of ZSM-5 in wastewater treatment applications, particularly in the removal of hazardous dyes such as methylene blue.

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