



Co-pyrolysis of microalgae and sewage sludge over ZnO/MgO/CeO₂/HZSM-5 catalyst for energy and water treatment application

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ABSTRACT

The growing demand for sustainable energy and efficient waste management has fueled demand in producing bioenergy from biomass. This study delves into the co-pyrolysis of microalgae and sewage sludge using a novel ZnO/MgO/CeO₂/HZSM-5 catalyst, aiming to enhance biofuel production and contribute to environmental remediation through water treatment applications. The metal oxides loaded HZSM-5 hybrid catalyst was prepared by applying the impregnation technique for incipient wetness. The synthesized catalyst was characterized using different analytical techniques. The co-pyrolysis process was conducted at a temperature of 500 °C, biomass blend ratio of 1:1 and biomass to catalyst ratio of 2:1. The findings established that the co-pyrolysis of microalgae and sewage sludge using ZnO/MgO/CeO₂/HZSM-5 catalyst significantly enhanced the production quality of bio-oil relative to the pyrolysis of individual feedstocks. Benzene and its derivatives are the predominant aromatic compounds present in the pyrolytic bio-oils. The removal efficiency of methylene blue (MB) from an aqueous solution onto biochar obtained from the co-pyrolysis of microalgae and sewage sludge modified with catalyst (CMS biochar) was assessed through batch adsorption experiments. The optimum MB dye removal (93.2 %) was obtained using a 50 minute contact time, a 60 mg/L initial MB dye concentration, and a 40 mg CMS biochar dosage. The biochar demonstrated strong potential for reuse, with only a slight decline of approximately 5 % in its removal efficiency after six regeneration cycles. This study highlights the dual benefits of the co-pyrolysis process, demonstrating its viability not only for bioenergy generation but also for addressing water treatment challenges. The findings offer new perspectives on the application of advanced catalytic systems in biomass conversion, offering a sustainable approach to managing waste and producing valuable resources.

1. Introduction

Biomass conversion into bioenergy has gained significant attention due to the rising global insistent for sustainable energy and the urgent need for effective waste management [1,2]. Among various biomass resources, microalgae and sewage sludge have emerged as promising feedstocks. Specifically, sewage sludge is abundant as a by-product of wastewater treatment and poses disposal challenges, making its valorization highly beneficial [3]. Microalgae, on the other hand, are fast-growing and have a high lipid and volatile content, which supports efficient biofuel production [4,5]. Both feedstocks are renewable and allow for the recycling of waste products, making them attractive options for sustainable biofuel generation and environmental remediation. The global production of microalgae has seen remarkable growth, with estimates indicating that over 100 million metric tons of biomass are produced annually, largely for biofuels, nutraceuticals, and other

high-value products [6]. This growth reflects a significant increase from earlier decades, driven primarily by advancements in cultivation techniques and rising demand for microalgae in various industries. Despite this promise, the high cost of feedstock remains a significant challenge for large-scale commercial production of microalgae-based biofuels [3]. However, cultivating microalgae in wastewater has shown great potential as a cost-effective method for reducing feedstock expenses while contributing to wastewater treatment [7,8]. On the other hand, sewage sludge, a byproduct of wastewater treatment processes, presents both an opportunity and a challenge. Globally, around 45–53 million dry metric tons of sewage sludge are produced each year, with this number projected to increase due to urbanization and improved wastewater treatment facilities [9,10]. This high organic content material poses environmental risks when disposed of improperly, making energy recovery a promising approach for both waste management and bioenergy production [11]. Sewage sludge is an almost cost-free by-product of

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wastewater treatment, making it economically attractive for pyrolysis applications [12,13]. However, on its own, sewage sludge faces challenges such as low heating value and high ash content, which reduce its energy efficiency [14,15]. By combining it with microalgae, which has a high lipid and volatile content, the overall energy yield can be enhanced. This co-pyrolysis approach leverages the complementary properties of both feedstocks, offering a promising solution to improve both the quality and yield of bio-oil, while also reducing overall production costs through the use of inexpensive feedstock [16].

Co-pyrolysis which refers to the concurrent thermal breakdown of two or more feedstocks, has been identified to be a viable approach for enhancing both the quality and yield of biofuels. The combined pyrolysis of microalgae with various types of biomass has shown significant potential to better both the quality and yield of bio-oil. Research indicates that combining microalgae with lignocellulosic biomass, organic waste or manure digestate leads to notable synergistic effects [17–20]. This method can improve thermal decomposition rates, lower activation energy and boost gas and bio-oil yields [18]. For instance, co-pyrolysis of microalgae with bamboo has been noticed to improve bio-oil yield to as much as 66.63 wt% while increasing the concentration of long-chain fatty acids and minimizing unwanted by-products like acetic acid and nitrogenous compounds [19]. Additionally, employing catalysts such as copper doped HZSM-5 and CaO can further upgrade the quality of the microalgae-derived biofuel by boosting the aromatic content and reducing the presence of nitrogenous and oxygenated compounds [4,17]. Kumar et al. [21] demonstrated that co-pyrolysis of lipid extracted algae with waste tires can significantly increase the yield of bio-oil to as much as 48.96 wt%, while also enhancing the quality of the resulting bio-oils and biochar. In another study, the co-pyrolysis of swine manure digestate and microalgae shows synergistic effects, as evidenced by enhanced reaction kinetics, increased gas yields, and greater thermal degradation compared to the individual feedstocks [20]. However, a combined pyrolysis of sewage sludge with other biomass also presents a promising avenue for enhancing energy recovery from waste materials. This process not only improves oil yield but also optimizes the thermal efficiency of the biomass conversion. Co-pyrolysis of sewage sludge with waste polypropylene was studied by Chen and Huang [22], revealing positive synergy in activation energy and improved oil quality. It was also observed that optimal ratio of petrochemical product component was achieved with HZSM-5 catalyst. Liu et al. [23] discovered that in the combined pyrolysis of sewage sludge and corn stalk, the inclusion of corn stalk reduced the yield of char while significantly increasing yield of bio-oil.

While co-pyrolysis of sewage sludge with microalgae holds significant potential for both energy production and waste management [3], fully realizing its benefits requires further investigation. Previous studies have largely focused on the pyrolysis of sewage sludge and microalgae independently, leaving the combined pyrolysis of these two feedstocks underexplored. Co-pyrolysis leverages the unique properties of each biomass, microalgae with its high lipid and volatile content and sewage sludge as an abundant, cost-effective material can potentially overcome limitations such as low heating value and high ash content associated with sewage sludge alone. However, achieving optimal product yield and quality from this combination is challenging and requires innovative catalytic approaches.

Zaker et al. [24] studied the impact of HZSM-5 and activated char derived from sludge as catalysts on the thermal decomposition process of sewage sludge. Both catalysts were observed to enhance the reaction rates and reduced gas emissions during the sewage sludge pyrolysis. HZSM-5 has demonstrated strong catalytic performance in enhancing aromatization and deoxygenation in pyrolytic bio-oils, though it has limited effectiveness in reducing nitrogen content [4]. In contrast, metal oxides such as ZnO, MgO, and CeO₂ are effective in selective cracking and in lowering nitrogen and oxygenated compounds, which improves the quality of bio-oil [25]. Developing catalysts that combine these multifunctional qualities could lead to significant progress in optimizing

bio-oil quality and achieving more sustainable and efficient biomass thermal conversion. When combined with suitable catalysts, co-pyrolysis can actively reduce contaminants through catalytic cracking and adsorption, leading to cleaner fuel production and biochar by-products that are beneficial for water treatment. This study introduces a novel catalyst blend of ZnO/MgO/CeO₂ supported on HZSM-5, distinguishing it from conventional studies that focus on standard catalysts. This unique combination is expected to enhance co-pyrolysis efficiency by promoting selective cracking, reducing undesirable compounds in bio-oil, and increasing the adsorption capacity of the resulting biochar. Additionally, while co-pyrolysis is well-regarded for bioenergy production, its application in environmental remediation, particularly in wastewater treatment, remains underexplored. Methylene blue (MB) is a widely used synthetic dye and a prevalent pollutant in wastewater, particularly from the textile, printing, paper, leather and food industries [26]. It is persistent in aquatic environments and poses significant environmental and health risks due to its toxicity and potential for bioaccumulation [27]. Biochar, particularly from pyrolysis processes, has demonstrated promising adsorption capabilities for removing MB due to its high surface area, porous structure, and functional groups that can readily bind with dye molecules [28]. Biochar derived from co-pyrolysis process, modified by novel catalysts, could offer enhanced pollutant adsorption and water quality improvements, providing dual benefits of energy recovery and environmental remediation. This approach not only aims to improve product quality and yield but also introduces new functional applications for biochar, enhancing the overall economic and environmental viability of the process.

The novelty of this research lies in the simultaneous utilization of microalgae and sewage sludge as co-feedstocks in a co-pyrolysis process catalyzed by a ZnO/MgO/CeO₂/HZSM-5 system. The study focuses on the synergistic effects of these feedstocks and evaluates the catalytic performance of the proposed catalyst. It aims to enhance biofuel production while also addressing water treatment issues, specifically wastewater treatment to remove methylene blue dye. By examining both energy generation and environmental remediation, this research promotes a more sustainable and integrated method for biomass conversion.

2. Materials and methods

2.1. Raw materials

Microalgae *Scenedesmus obliquus* was cultivated in a 2000-liter open raceway pond, utilizing using BG 11 growth media. The harvested samples were sun-dried for one week, after which the dried microalgae biomass flakes were ground into a fine powder using a 5MT industrial blender. The resulting powder was then sieved to achieve a particle that is < 125 µm and kept in storage for further application. The sewage sludge was provided by a wastewater treatment plant in Johannesburg, South Africa. It was obtained after the digestion stage, representing digested sludge. The samples were oven dried at 105 °C for 24 hours and crushed into fine particles (<125 µm). In Table 1, the proximate, ultimate, and biochemical compositions of both samples are presented. By following the procedure provided by Mustapha et al. [29], the biochemical composition of the microalgae was determined. The ultimate analysis was conducted using an elemental analyzer (Vario EL-II Elementar Analysensysteme GmbH, Hanau, Germany). The higher heating value (HHV) of the biomass was then estimated using the Dulong correlation (Eq. 1), in corresponding to the elemental composition of the samples [30].

$$HHV \left(\frac{MJ}{kg} \right) = 0.338C + 1.428 \left(H - \frac{O}{8} \right) + 0.095S \quad (1)$$

The percentages of weight of carbon, hydrogen, oxygen, and sulfur in

Table 1
Properties of microalgae and sewage sludge samples.

	Microalgae	Sewage sludge
Moisture (%)	2.09	3.11
Ash (%)	17.59	40.93
Volatile matter (%)	78.61	54.96
Fixed carbon (%) ^a	1.71	1.00
C (%)	42.36	32.96
H (%)	6.01	4.82
N (%)	7.32	2.95
S (%)	0.00	0.00
O (%) ^a	44.31	59.27
Lipid (%)	15.35	-
Protein (%)	44.26	-
Carbohydrate (%)	22.54	-
Heating value, HHV (MJ/kg)	14.99	7.44

^a Fixed carbon content and oxygen content were calculated by mass balance method

the biomass are represented by C, H, O, and S, respectively.

The pyrolysis process used nitrogen gas obtained from Afrox® with a purity of 99.995 %. Ammonium-ZSM-5 powder (CBV 2314), with a SiO₂/Al₂O₃ molar ratio of 23:1, Na₂O content of 0.05 %, and a surface area of 425 m²/g, was supplied by Zeolyst International. All chemicals utilized in the study were of analytical grade and required no further purification.

2.2. Synthesis of catalyst and characterization

HZSM-5 was prepared by calcining ammonium ZSM-5 (NH₄-ZSM-5) at 550 °C for 5 hours [4]. The metal oxide-supported catalyst was synthesized by employing the incipient wetness impregnation (IWI) method as described by Yadav and Das [31]. To prepare the metal oxide-supported catalysts (M/HZSM-5), various metals (Zn, Mg, and Ce) were impregnated onto the HZSM-5 support. Metal nitrates [Zn (NO₃)₂·6 H₂O, Mg (NO₃)₂·6 H₂O, and Ce (NO₃)₃·6 H₂O] with 10 wt% loadings each were mixed with 20 g of HZSM-5 support. A stoichiometric amount of each metal nitrate was dissolved in deionized water to form an aqueous solution, which was added dropwise to the HZSM-5 support and thoroughly mixed to form a paste. The mixture was placed in a desiccator for the entire night, dried for 12 hours at 100 °C in an oven, crushed with a mortar and pestle, and then calcined for 5 hours at 550 °C.

Energy dispersive spectroscopy (EDS) was utilized for examining the elemental content of the produced catalyst, while field emission scanning electron microscopy (FESEM) was employed to examine its morphology. The crystalline structure was determined by X-ray diffraction (XRD) using a Bruker AXS D8-Advance diffractometer (Germany) with a Cu K α radiation source (λ = 0.1541 nm) at a scanning speed of 2° per minute. Under atmospheric pressure, data were collected in the 5–90° range of 2 θ angles. Using a TA Instrument (SDT Q600), thermogravimetric analysis (TGA) was conducted with the catalyst heated under nitrogen environment from 20 to 990 °C at a rate of 10 °C per minute.

2.3. Pyrolysis experiments and product characterization

Pyrolysis experiments were performed in a fixed-bed reactor for both individual and combined biomass samples, with and without the addition of a catalyst. Details and specifications of the reactor setup are available in our previous studies [4,29]. The reactor was heated at a rate of 20 °C/min to a target temperature of 500 °C after the reactor system was purged with pure nitrogen gas at a flow rate of 30 mL/min to maintain an inert atmosphere [4]. Non-catalytic experiments used 10 g of each biomass, while catalytic tests utilized a mixture of biomass and catalyst in a 2:1 ratio (g/g). The microalgae powder and sewage sludge powder were thoroughly mixed with the catalyst prior to being

introduced into the reactor. The reaction temperature was kept at a constant value for 1 hour throughout each pyrolysis run, and the resulting vapors were rapidly removed from the reaction zone with nitrogen at 30 mL/min. The condensable volatiles were obtained as bio-oil, while the solid residues were recovered as biochar after the reactor was naturally cooled to ambient temperature. The yields of bio-oil and biochar were calculated as a percentage of the biomass weight, with the catalyst weight subtracted from the total solid recovered. The yield of non-condensable gases and any other losses were determined through mass balance. Each pyrolysis experiment was conducted twice, and the average results were reported.

The elemental composition of the bio-oils generated by co-pyrolyzing microalgae and sewage sludge, both with and without the ZnO/MgO/CeO₂/HZSM-5 catalyst, was resolute utilizing an elemental analyzer (Vario EL-II Elementar Analysensysteme GmbH, Hanau, Germany). The Agilent 7890–5975 C gas chromatography/mass spectrometry (GC-MS) equipment was employed to evaluate the chemical components of the pyrolytic bio-oils, with detailed measurement conditions as outlined in our previous research [4]. The functional groups within the bio-oil and biochar samples were identified using a Fourier-transform infrared (FTIR) spectrophotometer (Bruker Vertex 70, Bruker Optics, Billerica, MA, USA), with spectra recorded over a range of 450–4000 cm^{−1} at a resolution of 4 cm^{−1}. The surface morphology of the biochars was examined through field emission scanning electron microscopy (FESEM) coupled with an Energy Dispersive X-ray Spectrometer (EDS). Additionally, the surface area of the biochars was measured with a BET surface area analyzer (Nova 800 BET, Anton Paar). The biochar was first degassed at 180 °C for 1080 min and the Brunauer-Emmett-Teller (BET) technique was used to determine the surface area [32].

2.4. Adsorption of methylene blue (MB) onto CMS biochar and reusability study

For this study, CMS biochar refers to the catalyst modified biochar obtained from the catalytic co-pyrolysis of microalgae and sewage sludge. Catalyst recovery or separation from the biochar was not the focus of this study. Due to the challenges associated with separating the catalyst post-pyrolysis, our approach involved utilizing the catalyst-modified biochar directly for methylene blue (MB) removal in wastewater treatment. This approach provides a practical application for the catalyst-modified biochar, eliminating the need for catalyst separation and regeneration steps. The solid product, with embedded catalyst particles, was thus repurposed as an adsorbent for MB treatment, addressing the challenge of catalyst recovery while adding value to the by-product.

The efficiency of methylene blue (MB) removal from an aqueous solution employing CMS biochar was assessed through batch adsorption experiments. The one-factor-at-a-time (OFAT) technique was adopted to investigate the effects of contact time, initial dye concentration, and adsorbent dosage on the adsorption efficiency of CMS biochar. The contact time was varied between 20 and 120 minutes, the initial MB concentration ranged from 20 to 100 mg/L, and the adsorbent dosage was adjusted from 10 to 60 mg. Each experiment was run at a constant agitation speed of 150 rpm and a temperature of 303 K, following the approach described by Jabar et al. [33]. For the batch adsorption tests, 50 mL of the MB dye solution at a predetermined concentration (mg/L) was mixed with a pre-weighed amount of biochar (mg) and agitated under the aforementioned conditions for a specific duration. Following each experiment, the biochar was separated from the solution by centrifuging for 10 minutes at 4000 rpm. The final absorbance of the supernatant was measured using a UV-Vis double-beam spectrophotometer (Perkin Elmer LAMBDA 365) at 665 nm. Each of the absorption tests was repeated twice and the average value of final absorbance recorded. The concentration of the MB in the supernatant was calculated using a calibration curve created from the absorbance of serially diluted

MB solutions (ranging from 20 to 140 mg/L) [34]. The percentage of dye removed and the adsorption capacity were determined through using the following equations:

$$\text{Percentage removal(\%)} = \left(\frac{C_o - C_f}{C_o} \right) * 100 \quad (2)$$

$$\text{Adsorption capacity, } Q_e \text{ (mg/g)} = \frac{(C_o - C_f) * V}{W} \quad (3)$$

where C_o and C_f represent the initial and final MB dye concentrations (mg/L), V is the volume of the dye solution (L), and W is the mass of the adsorbent used (g).

The regeneration of CMS biochar following adsorption test was performed using the method outlined by Jabar et al. [33]. The CMS-biochar loaded MB (300 mg/L) was added to a beaker containing 50 mL of 0.1 M NaOH solution. The mixture was stirred continuously for 8 hours to facilitate desorption. Afterward, the CMS-biochar-MB was separated from the solution by centrifuging for 10 minutes at 4000 rpm. The desorbed CMS-biochar was then thoroughly rinsed with water, dried in an oven at 105°C. The regenerated CMS biochar was then reused in up to six consecutive adsorption-desorption cycles.

3. Results and discussion

3.1. Catalysts characterization

The XRD patterns of the ZnO/MgO/CeO₂/HZSM-5 catalyst were compared with those of pure HZSM-5, as shown in Fig. 1. The characteristic X-ray diffraction (XRD) peaks for HZSM-5, a zeolite with an MFI framework, are observed at 2θ angles of 7.8° to 8.0° (associated with the [011] plane), 8.8° to 8.9° (associated with [020] plane), and 23.0° to 24.5° (corresponding to [051], [033], and [151] planes). The peaks between 7.8° - 8.8° and 23.0° - 24.5° are particularly notable and serve as the fingerprint region for HZSM-5, confirming its typical crystalline MFI framework structure [4,35,36]. From the figure, it is clear that the XRD pattern of the ZnO/MgO/CeO₂/HZSM-5 catalyst in comparison with HZSM-5 exhibits additional peaks at $2\theta = 28.5^\circ$ (111 plane) and 47.5° (220 plane), which are characteristic of CeO₂ and confirm its presence and crystallinity [37]. Peaks at 31.7° (100 plane), and 34.4° (002 plane) indicate the presence of ZnO, consistent with its hexagonal wurtzite crystal structure [38]. Additionally, the peak at $2\theta = 36.9^\circ$ (111 plane) was attributed to the presence of MgO, which typically exhibits diffraction peaks at 36.9° (111 plane), 42.9° (200 plane), 62.3° (220 plane), 74.7° (311 plane), and 78.6° (222 plane), confirming its face-centered cubic (FCC) crystalline structure [39]. Furthermore, a

reduction in the intensity of the hybrid catalyst was observed, likely due to the doping effect of metal oxides on the HZSM-5 structure. This aligns with findings by Roustaie et al. [40], who reported a similar decrease in intensity when ZnO was supported on the surface of ZSM-5.

The TGA/DTG analysis of the synthesized ZnO/MgO/CeO₂/HZSM-5 catalyst (Fig. 2) was performed to assess its thermal stability and decomposition characteristics. The DTG curve illustrates the weight loss rate (the derivative of the TGA curve) throughout the same temperature range as the TGA curve, which depicts the weight loss of catalyst as a function of temperature. As illustrated in Fig. 2, the TGA plot shows a weight loss between 1 % and 8 % from room temperature up to approximately 200°C. This initial weight loss is most likely as a result of evaporation of physically adsorbed water and the removal of volatile impurities present within the catalyst matrix [4]. The corresponding peak in the DTG curve confirms this endothermic process, indicating the desorption of moisture and volatile impurities from the catalyst surface. Beyond 200°C and up to 800°C, the catalyst exhibits significant thermal stability, suggesting it is well-suited for high-temperature applications such as pyrolysis or gasification. The slight weight loss observed between 200°C and 800°C in Fig. 2 is likely due to the gradual release of surface-bound or chemisorbed moisture, along with the removal of residual organics or weakly bonded impurities on the catalyst surface. The lack of substantial weight loss above 800°C further indicates that the catalyst structure remains stable under operational conditions, which is crucial for maintaining its catalytic activity and durability. The slight weight loss occurring above 800°C may indicate small structural adjustments rather than any substantial degradation. This could result from trace impurities, residual precursors, thermal sintering of metal oxides, or minor structural changes like dealumination in HZSM-5 zeolites.

Fig. 3(a-b) displays the morphology of both HZSM-5 and the ZnO/MgO/CeO₂/HZSM-5 catalyst. The HZSM-5 morphology reveals slight particle aggregates with an elongated prismatic shape, as previously reported by Roustaie et al. [40]. In contrast, the FESEM images of the ZnO/MgO/CeO₂/HZSM-5 catalyst show reduced gaps between particles, forming woolly, cloud-like aggregations. These morphological changes may be due to the agglomeration of new phases consisting of surface metal oxides. The elemental composition of the synthesized catalyst, analyzed by EDS, confirms the presence of Al (2.20 %), Mg (3.9 %), Zn (6.3 %), C (6.6 %), Ce (6.9 %), Si (23.8 %), and O (50.3 %), with no other impurities detected (Fig. 3c). This result indicates the successful synthesis of the ZnO/MgO/CeO₂/HZSM-5 catalyst and confirms the incorporation of ZnO, MgO, and CeO₂ nanoparticles within the HZSM-5 framework.

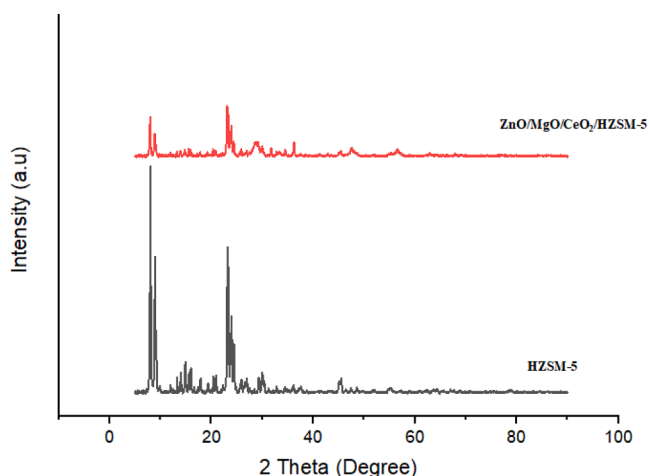


Fig. 1. XRD patterns of HZSM-5 and ZnO/MgO/CeO₂/HZSM-5 catalyst.

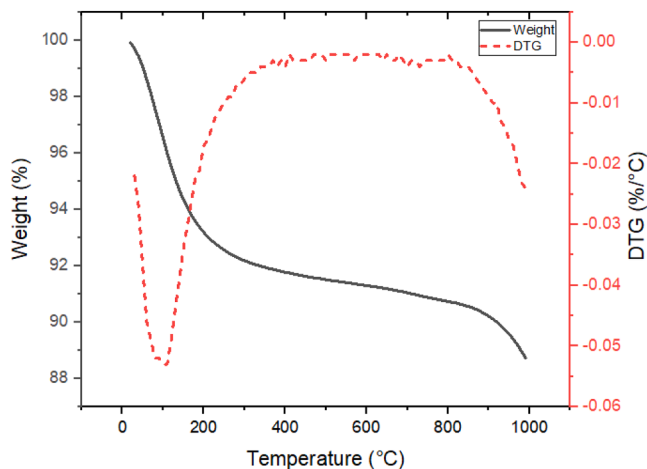


Fig. 2. TGA and DTG Plots of the synthesized ZnO/MgO/CeO₂/HZSM-5 catalyst.

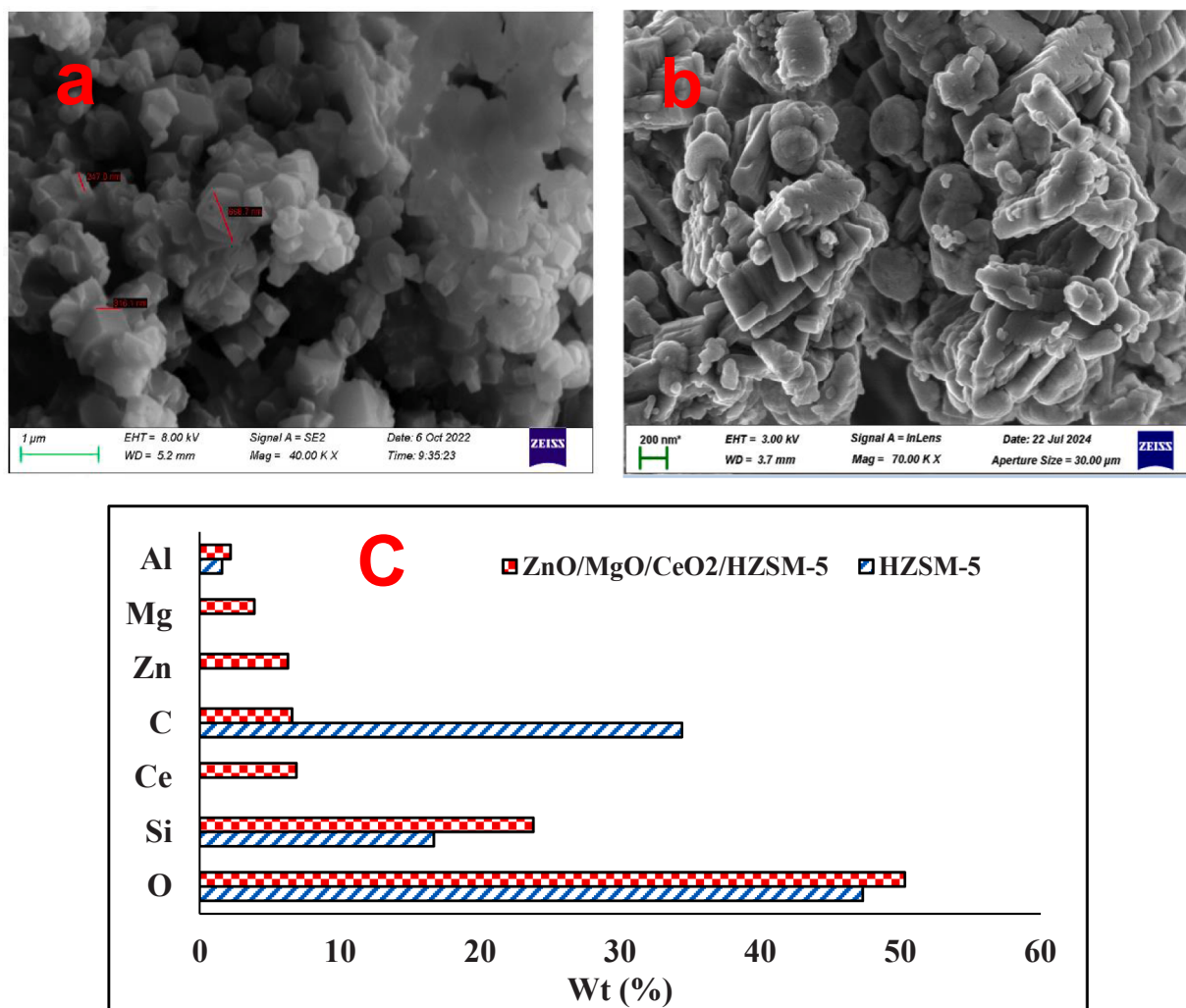


Fig. 3. SEM Image of (a) HZSM-5 (b) ZnO/MgO/CeO₂/HZSM-5 (c) EDS Analysis.

3.2. Pyrolysis product yield

The pyrolysis and co-pyrolysis of microalgae and sewage sludge were investigated at 500 °C to determine their potential for bio-oil

production. The effect of the ZnO/MgO/CeO₂/HZSM-5 catalyst on the co-pyrolysis process was also studied, with the yields of the pyrolysis products presented in Fig. 4a. The pyrolysis of microalgae (M) alone resulted in the highest bio-oil yield at 29.2 wt%, while sewage sludge (S)

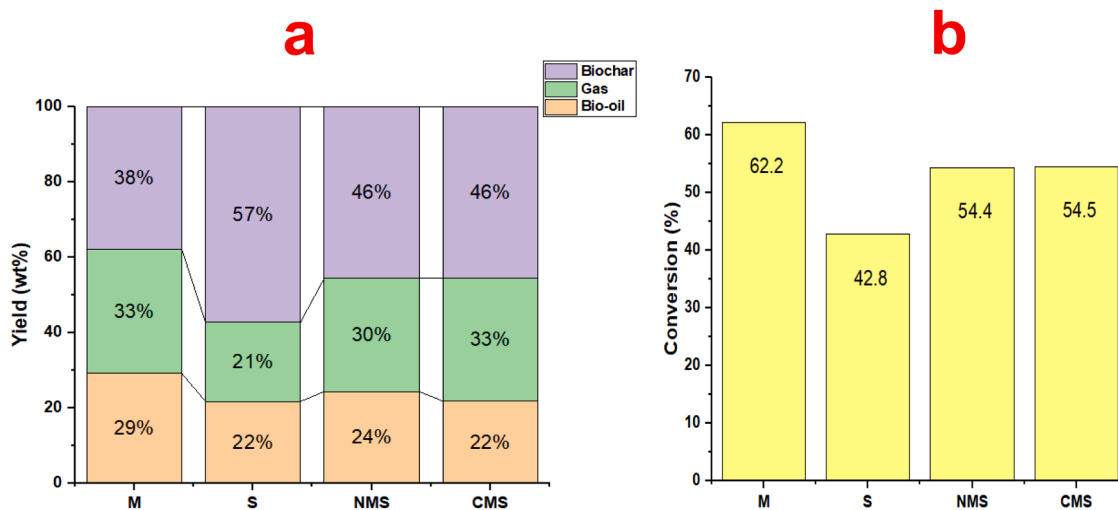


Fig. 4. (a) Product yield and (b) conversion for the individual and co-pyrolysis process (M- microalgae alone, S- sewage sludge alone, NMS- non-catalytic microalgae-sewage sludge, CMS- catalytic microalgae-sewage sludge).

yielded 21.8 wt%. The greater bio-oil yield from microalgae is primarily due to its higher volatile matter and lower ash content, as noted in Table 1. The composition of the feedstock has a major impact on both the yield and the composition of the products generated through pyrolysis, as different materials with varying characteristics can significantly affect the outcomes of the pyrolysis process [5]. While microalgae demonstrated a potential for high bio-oil yield and heating value, challenges remain in terms of high cultivation costs and the elevated nitrogen content in the bio-oil, which pose obstacles to large-scale commercial production [29]. On the other hand, the high ash content in sewage sludge results in reduced bio-oil yield and lower heating value, affecting the stability of the pyrolysis process. Co-pyrolyzing sewage sludge with microalgae offers a promising solution by leveraging the synergistic properties of both materials, which could reduce production costs and improve product quality. When microalgae and sewage sludge were co-pyrolyzed in a 1:1 biomass ratio, the bio-oil yield was 24.4 wt% for the non-catalytic co-pyrolysis process (NMS), which slightly decreased to 21.9 wt% in the presence of the ZnO/MgO/CeO₂/HZSM-5 catalyst (CMS). Combining the two biomass types in the specified ratio creates a new feedstock composition, which influences the product yield from the co-pyrolysis process. The variation in product yield observed during co-pyrolysis confirms that the composition of the feedstock strongly affects the pyrolytic product output. Rathnayake et al. [41] also showed that ash content and volatile matter have a substantial impact on the yields of biochar, bio-oil, and gases during the co-pyrolysis of biosolids with lignocellulosic biomass.

As shown in Fig. 4b, microalgae exhibited the highest conversion rate of 62.2 %, while sewage sludge had the lowest at 42.8 %. When comparing the catalytic and non-catalytic co-pyrolysis processes, there was no significant difference in conversion rates for the co-pyrolysis of microalgae and sewage sludge with or without the catalyst. However, the product distribution differed. For example, the use of a catalyst during the co-pyrolysis process was found to enhance gas production, while simultaneously decreasing the yield of bio-oil. While the yield of bio-oil reduced from 24.4 wt% to 21.9 wt%, the yield of gas increased slightly from 30 wt% to 32.6 wt%. This reduction in bio-oil yield is likely due to the intense cracking activity at the active sites of the catalyst [42]. The surface acid sites of the catalyst can stimulate a number of pyrolysis-related processes, including dehydration, decarbonylation, decarboxylation, and deamination, which speed up a breakdown process and produce additional gaseous products [43].

3.3. Bio-oil analysis

The elemental composition of bio-oil consists of the percentages of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O), is vital for assessing its fuel quality and environmental impact. Generally, a higher carbon and hydrogen content in bio-oil signifies a greater energy content, while increased oxygen content tends to lower both the stability and heating value. Table 2 summarizes the elemental composition of the generated bio-oils from the co-pyrolysis of microalgae and sewage sludge, both with and without the ZnO/MgO/CeO₂/HZSM-5 catalyst.

The data from the Table 2 shows that the bio-oil obtained from co-

pyrolysis had significantly higher carbon and hydrogen content, and a substantially lower oxygen content compared to the individual feedstocks. Specifically, the carbon content increased from a range of 32.96–42.36 % in the original feedstocks to 71.53 % in the co-pyrolysis bio-oil, while the hydrogen content rose from 4.82–6.01–9.42 %. In contrast, the oxygen content dramatically decreased from 44.31–59.27–11.57 %. The co-pyrolysis process had minimal effect on the nitrogen content, which remained similar to that of the original feedstocks. Further, the inclusion of the ZnO/MgO/CeO₂/HZSM-5 catalyst in the co-pyrolysis process, compared to the non-catalytic system, resulted in additional increases in the carbon and hydrogen content from 71.53 % to 74.81 % and 9.42–9.77 %, respectively. Concurrently, the nitrogen content decreased from 7.48 % to 7.11 %, and the oxygen content significantly dropped from 11.57 % to 6.57 %.

The atomic ratios, such as hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C), provide further insights into the chemical nature and quality of the bio-oil. A higher H/C ratio, indicating more aliphatic and less aromatic content, generally correlates with better combustion characteristics and a higher heating value (HHV). A lower O/C ratio suggests a reduced presence of oxygenated compounds, which are typically less stable and have lower energy content. When the bio-oil was produced with the ZnO/MgO/CeO₂/HZSM-5 catalyst, it exhibited a higher H/C ratio and lower O/C and N/C ratios which suggests that the bio-oil produced is of better quality.

The incorporation of a catalyst into the co-pyrolysis process resulted in a reduction of oxygen content and an increase in the higher heating value (HHV) of the bio-oil, likely due to enhanced cracking and deoxygenation reactions [4]. Additionally, the catalyst may have facilitated the release of nitrogen-containing compounds into the gas phase, resulting in a reduction in nitrogen content [4]. Bio-oil derived from microalgae typically has a higher nitrogen content due to the protein-rich nature of the biomass, which can impact its suitability as a fuel [29]. Similarly, the higher oxygen content often found in sewage sludge-derived bio-oil can negatively affect its stability and storage life [3]. The outcome of this investigation show that the synthesized ZnO/MgO/CeO₂/HZSM-5 catalyst is effective in upgrading the quality of bio-oil generated from the co-pyrolysis of microalgae and sewage sludge, enhancing its fuel properties and overall performance.

The bio-oil FTIR analysis results that were obtained from individual and co-pyrolysis processes are presented in Fig. 5a. The FTIR spectrum provides valuable insights into the functional groups identified in the bio-oils produced by pyrolysis, which directly relate to their chemical composition and potential applications. The figure shows that while most of the functional groups that have been identified are common across the different bio-oils analyzed, the intensities of the peaks may slightly vary. Absorption peaks observed around 2850–2950 cm⁻¹ indicate aliphatic C-H stretching vibrations, which are associated with alkanes contributing to the energy content and combustibility of the bio-oil [45]. Peaks between 1450 and 1600 cm⁻¹ indicate the possibility of aromatic compounds, while oxygenated compounds are indicated by various peaks corresponding to C=O, C-O, and O-H stretching. For example, the peaks around 1700 cm⁻¹ are characteristic of carbonyl groups (C=O), signifying the presence of ketones, aldehydes, esters, and

Table 2
Comparison of elemental composition of co-pyrolysis bio-oil and raw feedstock.

Condition	Elemental analysis					Atomic ratios			HHV ^a (MJ/kg)	HHV ^b (MJ/kg)
	C (%)	H (%)	N (%)	S (%)	O (%)	H/C	N/C	O/C		
NMS	71.53	9.42	7.48	0.00	11.57	1.58	0.09	0.12	35.56	34.82
CMS	74.81	9.77	7.11	0.75	6.57	1.57	0.08	0.08	37.96	36.46
Raw Microalgae	42.36	6.01	7.32	0.00	44.31	1.70	0.15	0.78	14.99	-
Raw Sewage Sludge	32.96	4.82	2.95	0.00	59.27	1.75	0.08	1.35	7.44	-

^a HHV calculated using Dulong correlation [30]; NMS, CMS-bio-oils from non-catalytic and catalytic co-pyrolysis of microalgae-sewage sludge)

^b HHV calculated using correlation valid for liquid fuels by Boie [44] $HHV(MJ/kg) = 0.3517C + 1.1626H + 0.1047S - 0.111O$

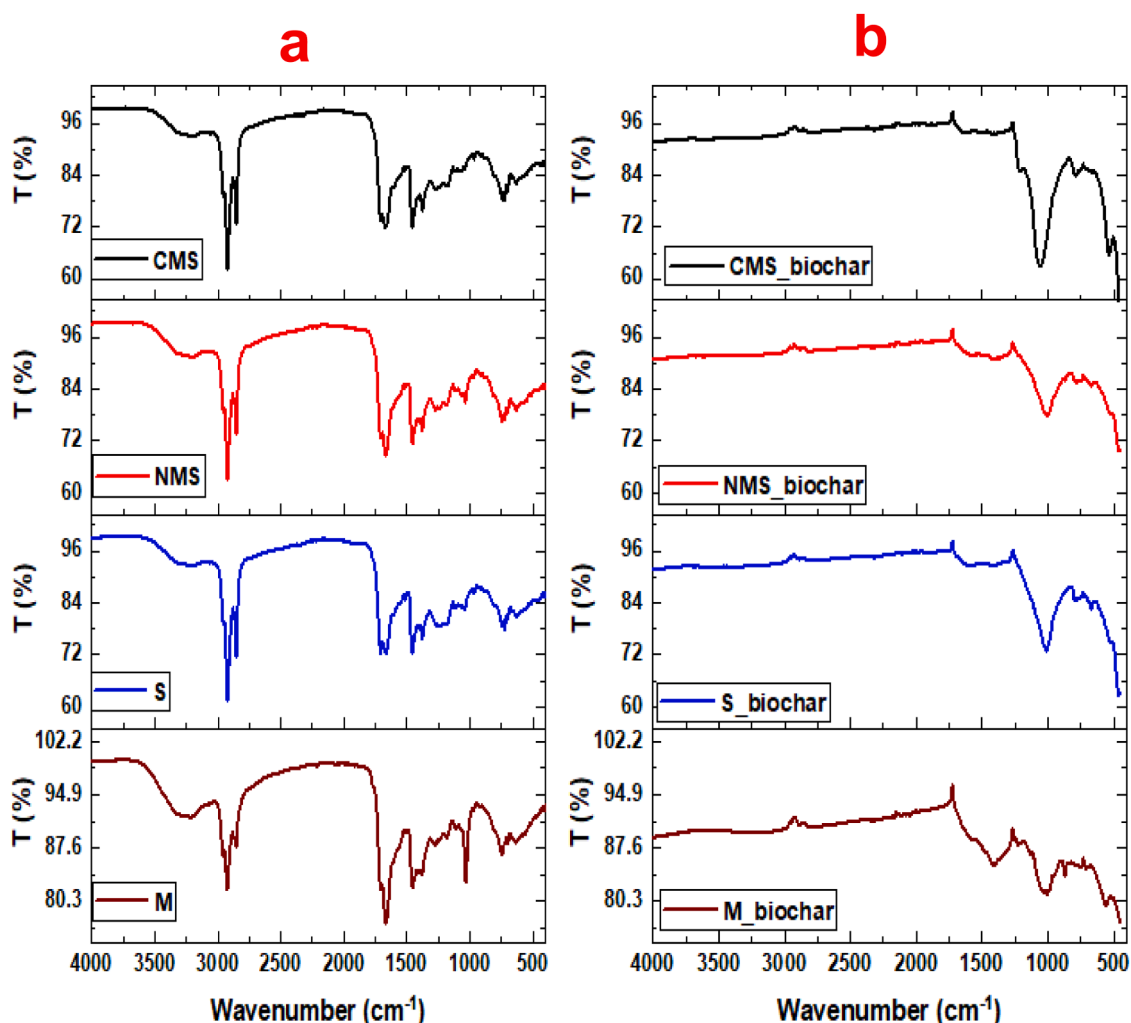


Fig. 5. FTIR Analysis result (a) bio-oils and (b) biochars obtained from the individual and co-pyrolysis process (M- microalgae alone, S- sewage sludge alone, NMS- non-catalytic microalgae-sewage sludge, CMS- catalytic microalgae-sewage sludge).

carboxylic acids, that contribute to the acidity and corrosiveness of the bio-oil [46]. Peaks between $1000\text{--}1300\text{ cm}^{-1}$ correspond to C-O stretching vibrations, indicating alcohols, esters, and ethers [47]. Broad peaks around $3200\text{--}3600\text{ cm}^{-1}$ are associated with O-H stretching vibrations, suggesting the presence of hydroxyl groups from alcohols and phenols [45].

The presence of the $\text{ZnO/MgO/CeO}_2/\text{HZSM-5}$ catalyst during pyrolysis resulted in a reduction in the intensity of peaks corresponding to oxygenated functional groups, particularly C=O and O-H. This indicates that catalytic pyrolysis enhances deoxygenation, producing a bio-oil with reduced oxygen content and higher hydrocarbon content. The differences observed between the catalytic and non-catalytic bio-oils highlight the effectiveness of catalysts like $\text{ZnO/MgO/CeO}_2/\text{HZSM-5}$ in promoting deoxygenation and improving the overall quality of the bio-oil.

With gas chromatography-mass spectrometry (GC-MS), the chemical composition of the bio-oils generated from the separate and co-pyrolysis of microalgae and sewage sludge was analyzed, and the distribution of the main compounds is illustrated in Fig. 6. The compounds involved in the bio-oils are categorized into the following groups: acids, aldehydes, alcohols, ethers, nitrogen-containing aliphatics, nitrogen-containing aromatics, and aliphatic hydrocarbons. Detailed relative abundances for each chemical compound are provided in Tables S1 to S4. The bio-oil obtained from the pyrolysis of microalgae alone exhibited the highest content of aliphatic hydrocarbons (16.64 %), compared to just 1.83 % in

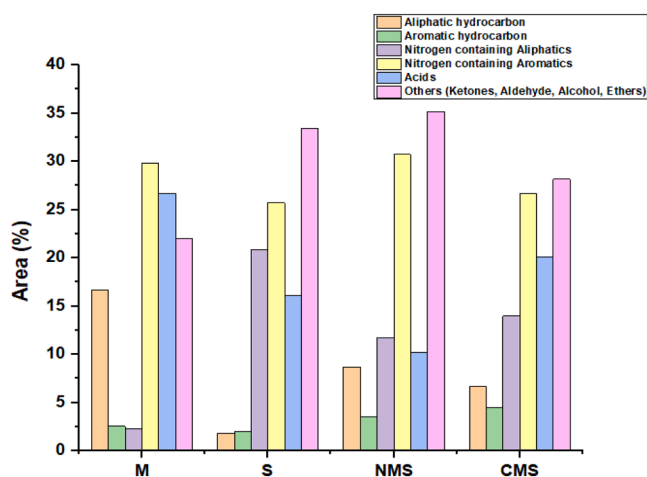


Fig. 6. Component distribution of bio-oils obtained from the individual and co-pyrolysis process (M- microalgae alone, S- sewage sludge alone, NMS- non-catalytic microalgae-sewage sludge, CMS- catalytic microalgae-sewage sludge).

the bio-oil derived from sewage sludge. These aliphatic compounds, typically characterized by their long carbon chains, are mainly derived from the lipid content of the biomass. Due to their high hydrogen-to-

carbon ratio, aliphatic hydrocarbons significantly enhance the energy content and combustion properties of bio-oil.

In contrast, the catalytic co-pyrolysis of microalgae and sewage sludge yielded the highest proportion of aromatic compounds compared to individual and non-catalytic pyrolysis processes. The presence of the ZnO/MgO/CeO₂/HZSM-5 catalyst in the co-pyrolysis process favored the formation of aromatic compounds while reducing the proportion of aliphatic hydrocarbons. This increase in aromatic content is likely due to the catalyst's ability to promote deoxygenation of oxygenated aromatic compounds and secondary reactions involving the Diels-Alder mechanism [48]. The catalyst effectively cracks larger molecules into smaller, more useful hydrocarbons while minimizing the formation of undesirable by-products, such as nitrogen and oxygenates. A potential reaction mechanism for transforming microalgae into aromatic and polyaromatic compounds was previously reported in our earlier work [3]. Previous research has shown that HZSM-5-based catalysts can improve the formation of aromatic compounds while lowering the oxygen content in bio-oils [49,50]. As indicated in Tables S1 to S4, benzene and its derivatives are the primary aromatic compounds found in the pyrolytic bio-oils. The co-pyrolysis of sewage sludge and microalgae using the ZnO/MgO/CeO₂/HZSM-5 catalyst creates a more balanced composition of hydrocarbons and oxygenated compounds, suggesting a synergistic effect that boosts the quality of the generated bio-oil. The observed

reduction in nitrogen-containing and oxygenated compounds in the catalytic co-pyrolyzed bio-oil, compared to non-catalytic co-pyrolysis, further indicates that the ZnO/MgO/CeO₂/HZSM-5 catalyst enhances the bio-oil's fuel properties.

3.4. Biochar characterization

The chemical structure and functional groups in biochars produced from the pyrolysis of microalgae, sewage sludge, and their co-pyrolysis were analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra revealed various absorption bands corresponding to distinct functional groups. Broad peaks in the 3200–3600 cm⁻¹ range indicate O-H stretching vibrations, which are characteristic of hydroxyl groups found in alcohols or phenols [1]. These groups can enhance the hydrophilicity of biochar and increase its capacity to adsorb polar contaminants. Peaks identified between 2850 and 2950 cm⁻¹ correspond to C-H stretching vibrations of aliphatic hydrocarbons, typically associated with residual organic matter that has not been fully pyrolyzed [33]. Peaks around 1600 cm⁻¹ correspond to stretching vibrations of the C=C bond, indicating the existence of aromatic structures, which contribute to the biochar's stability and resistance to degradation. The presence of these aromatic structures suggests a high degree of carbonization, enhancing thermal stability and long-term persistence in

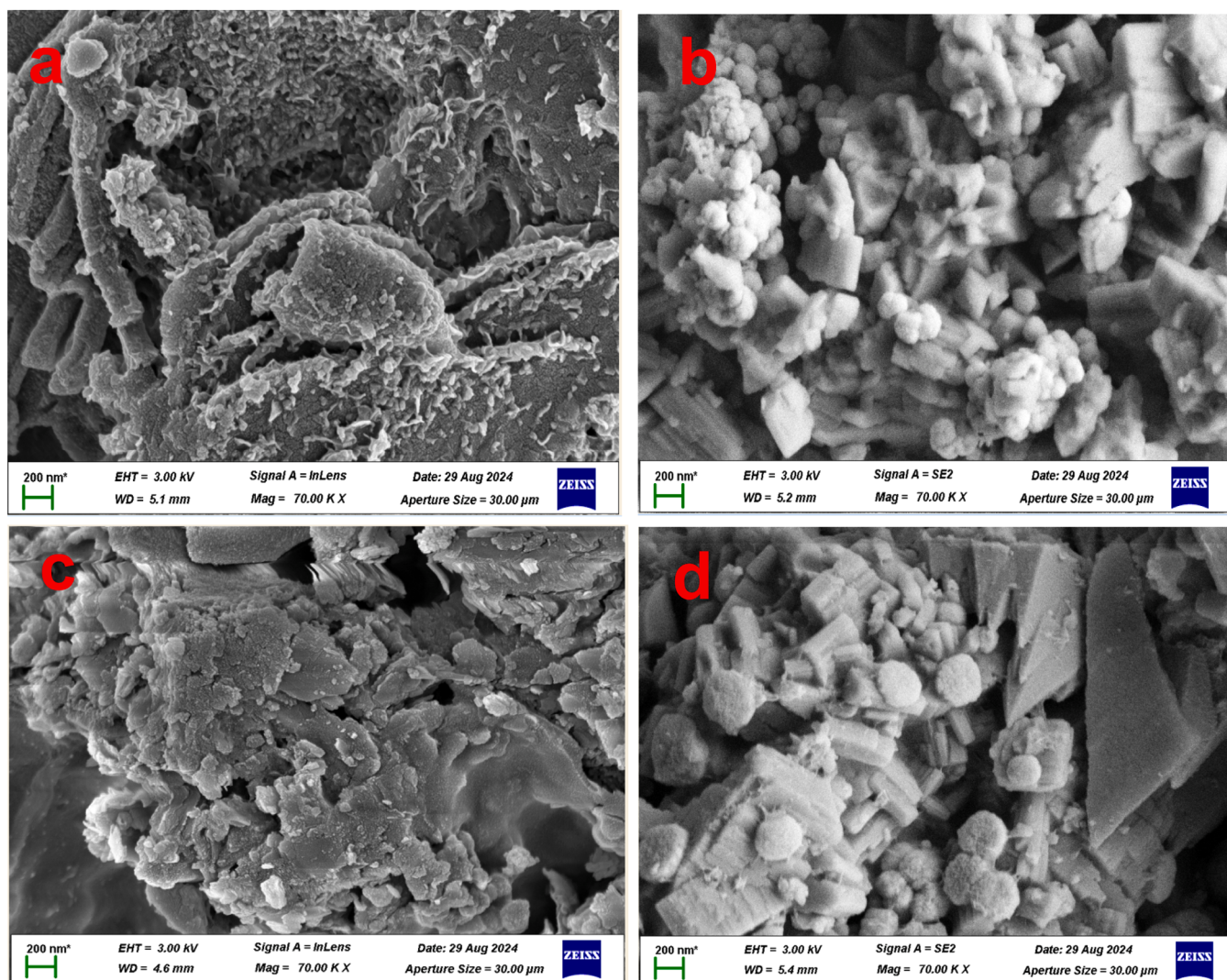


Fig. 7. SEM Image of biochars obtained from the individual and co-pyrolysis process (a) M- microalgae alone, (b) S- sewage sludge alone, (c) NMS- non-catalytic microalgae-sewage sludge, (d) CMS- catalytic microalgae-sewage sludge.

the environment. Peaks near 1700 cm^{-1} correspond to $\text{C}=\text{O}$ stretching vibrations, indicating the presence of carbonyl groups, such as those found in ketones, aldehydes, or carboxylic acids, which can affect the reactivity of biochar, especially in its interactions with other substances. Peaks around $1400\text{--}1300\text{ cm}^{-1}$ may be associated with phenol or tertiary amine groups, while those between 1100 and 1200 cm^{-1} correspond to $\text{C}-\text{O}$ stretching bonds, indicating the existence of alcohol and hydroxyl groups [1]. Additional aromatic out-of-plane $\text{C}-\text{H}$ bending groups are evident from peaks between 600 and 900 cm^{-1} . Lower frequency peaks, observed below 600 cm^{-1} , suggest the presence of ash content in the biochar. Notably, biochar produced with the $\text{ZnO}/\text{MgO}/\text{CeO}_2/\text{HZSM-5}$ catalyst showed a reduction in the intensity of oxygen-containing functional groups, such as $\text{C}=\text{O}$ and $\text{O}-\text{H}$, likely due to the catalyst's enhanced deoxygenation effects.

The Scanning Electron Microscopy (SEM) images of biochars produced from the individual and co-pyrolysis processes reveal notable morphological differences among the samples, as shown in Fig. 7(a-d). The biochar derived from microalgae (M) exhibits a porous surface which is typical due to its high volatile matter content. In contrast, the biochar from sewage sludge (S) shows an irregular surface with fewer pores, likely due to its higher ash content and the presence of inorganic minerals. The biochar generated by co-pyrolyzing sewage sludge and microalgae (NMS) in the absence of catalyst displays a combination of both microalgae and sewage sludge characteristics, resulting in a mixed morphology. In comparison, the biochar from the catalytic co-pyrolysis process (CMS) demonstrates a more complex surface morphology with distinct pores and cracks. This is likely due to the catalytic activity that promotes enhanced cracking and deoxygenation reactions. The catalyst particles appear to be well-dispersed on the surface of the CMS biochar, indicating effective interaction during the pyrolysis process.

Energy Dispersive X-ray Spectroscopy (EDS) analysis shown in Figure S1(d) further confirms the presence of elements associated with the $\text{ZnO}/\text{MgO}/\text{CeO}_2/\text{HZSM-5}$ catalyst in the CMS biochar, such as zinc (Zn), magnesium (Mg), cerium (Ce), aluminum (Al), silicon (Si), carbon (C), and oxygen (O). This suggests that catalyst residues are effectively embedded within the biochar matrix, contributing to its modified surface properties. Additionally, the EDS analysis of biochars from microalgae (M), sewage sludge (S), and the non-catalytic co-pyrolysis (NMS) (shown in Figure S1 (a – c)) also detects some of these elements, albeit at lower concentrations. This could be due to trace amounts of similar elements naturally occurring in the feedstocks or minor contamination during the pyrolysis process. The presence of microalgae and the $\text{ZnO}/\text{MgO}/\text{CeO}_2/\text{HZSM-5}$ catalyst in the co-pyrolysis process may indeed influence the heavy metal content of the biochar. However, this study primarily explores the biochar's adsorption properties for MB removal,

and further work is needed to fully assess the effect of co-pyrolysis and catalyst usage on heavy metal reduction.

The isotherms for nitrogen adsorption-desorption and the associated average pore size distribution of the biochars produced from the co-pyrolysis process, both with and without the catalyst, are illustrated in Fig. 8 and Figure S2, respectively. As seen in Fig. 8, the isotherms for both non-catalytic (NMS) and catalytic (CMS) biochars correspond to type III isotherms [32]. This suggests that these biochars contain a limited number of micropores and mesopores, resulting in weak adsorption characteristics. The CMS biochar exhibits a significantly richer pore structure compared to the NMS biochar, likely due to the presence of the $\text{ZnO}/\text{MgO}/\text{CeO}_2/\text{HZSM-5}$ catalyst. Across the entire range of relative pressure (P/P_0), the amount of N_2 adsorbed by the CMS biochar continuously exceeded that of the NMS biochar, indicating a more porous nature. The pore size distribution, as illustrated in Figure S2, further highlights these differences. While both biochars have pores centered around $5\text{--}6\text{ nm}$, the pore volume of the CMS biochar is notably greater.

The mesoporosity of the biochars is further supported by the pore width and volume data presented in Table 3. The biochar produced from the non-catalytic system (NMS) exhibits a lower surface area and pore volume in comparison with the biochar derived from the catalytic system (CMS). The higher BET surface area of CMS biochar ($63.16\text{ m}^2/\text{g}$) compared to NMS biochar ($16.22\text{ m}^2/\text{g}$) is attributed to the incorporation of the $\text{ZnO}/\text{MgO}/\text{CeO}_2/\text{HZSM-5}$ catalyst on the surface and within the pores of the CMS biochar (Fig. 7d). When compared to some pyrolytic biochars established in the literature, it is evident that an additional activation step after pyrolysis can result in significantly higher surface areas. For instance, Wang et al. [32] investigated the catalytic pyrolysis of lignin and reported an increase in the BET surface area of the resulting biochar, which rose from $76.71\text{ m}^2/\text{g}$ to $307.96\text{ m}^2/\text{g}$ following further activation with FeCl_3 . This suggests that pyrolytic biochars may require further activation to enhance their surface area, particularly if they are

Table 3

BET surface area, pore width and pore volume of raw feedstock and biochar products.

Samples	BET surface area, S_{BET} (m^2/g)	Pore width (nm)	Pore volume (cm^3/g)
Raw microalgae	18.85	6.08	0.007
Raw sewage sludge	10.71	5.88	0.02
NMC biochar	16.22	6.08	0.03
CMC biochar	63.16	5.09	0.05

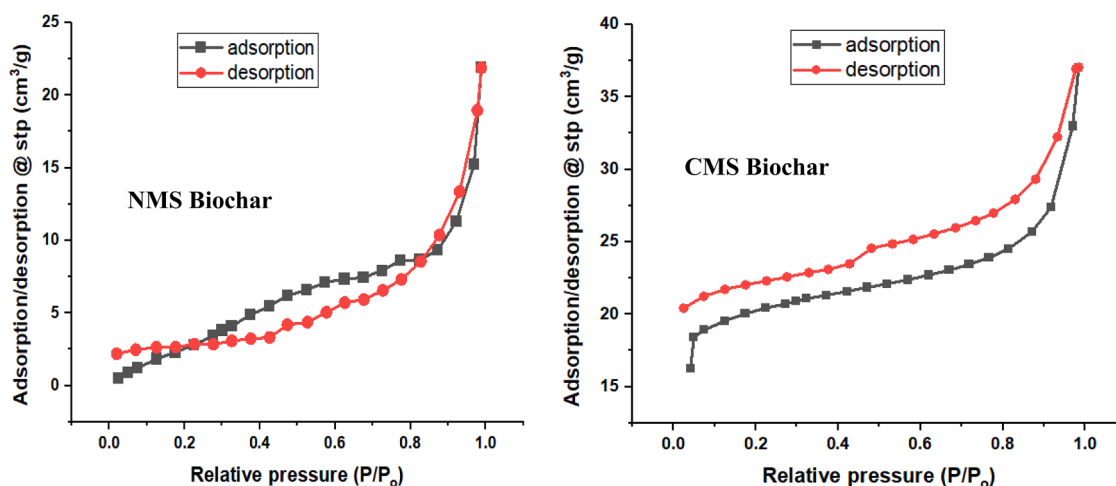


Fig. 8. Adsorption-desorption isotherm of biochars derived from the co-pyrolysis process. (a) NMS- non-catalytic microalgae-sewage sludge, (b) CMS- catalytic microalgae-sewage sludge.

intended for adsorption applications.

3.5. Adsorption of methylene Blue (MB) onto CMS biochar

Before the adsorption process, the zeta potential of CMS biochar was determined using a Zetasizer Nano 90 (Malvern Instruments, UK). The biochar exhibited a zeta potential of -28 ± 0.55 mV, indicating a negatively charged surface. Through the electrostatic attraction of the negatively charged biochar with the positively charged MB molecules, this negative charge enhances the adsorption of methylene blue (MB) [51]. This observation is consistent with literature reports, which suggest that a near-neutral pH range is optimal in order to adsorb MB dye from wastewater [33,52].

By varying the adsorption time from 20 to 120 min whilst keeping the initial dye concentration (60 mg/L) and adsorbent dosage (40 mg) constant, the effect of contact time on the adsorption of MB dye was investigated. The experimental results of the percentage removal (%) and adsorption capacity (mg/g) at varying contact time is presented in Fig. 9a. As shown in the figure, more than 82 % dye removal was achieved in the first 20 min and after 30 minutes, equilibrium was reached. The optimal percentage removal (93.2 %) and adsorption capacity (69.88 mg/g) was achieved after 50 min. The rapid removal of dye

molecules and high adsorption capacity observed within the first 20 minutes can be attributed to the availability of lot of vacant active sites on the CMS biochar surface and the rapid diffusion rate of MB dye molecules toward the biochar. Once equilibrium was reached, there was minimal or no significant change in adsorption capacity or percentage dye removal. This stabilization is likely due to a reduction in the diffusion rate of the dye molecules and the depletion of active sites on the biochar surface [53].

The impact of initial methylene blue (MB) concentration on the adsorption process was determined by varying the dye concentration between 20 and 100 mg/L at room temperature (303 K), with 150 rpm stirring speed, 40 mg/L of adsorbent dosage, and 50 minutes of optimal contact time. As illustrated in Fig. 9b, the experimental results demonstrated 97.5 % removal of MB at an initial concentration of 20 mg/L from an aqueous solution. Beyond this, a slight reduction in dye removal efficiency was observed for concentrations between 20 and 60 mg/L, with a more pronounced decline occurring at concentrations between 60 and 100 mg/L. The high dye removal recorded at lower concentration of 20 mg/L is likely attributed to the relatively small quantity of dye molecules on the CMS biochar surface in relation to the number of available active sites. Conversely, the dye adsorption capacity increased as the initial MB concentration rose from 20 to 100 mg/L, likely due to a

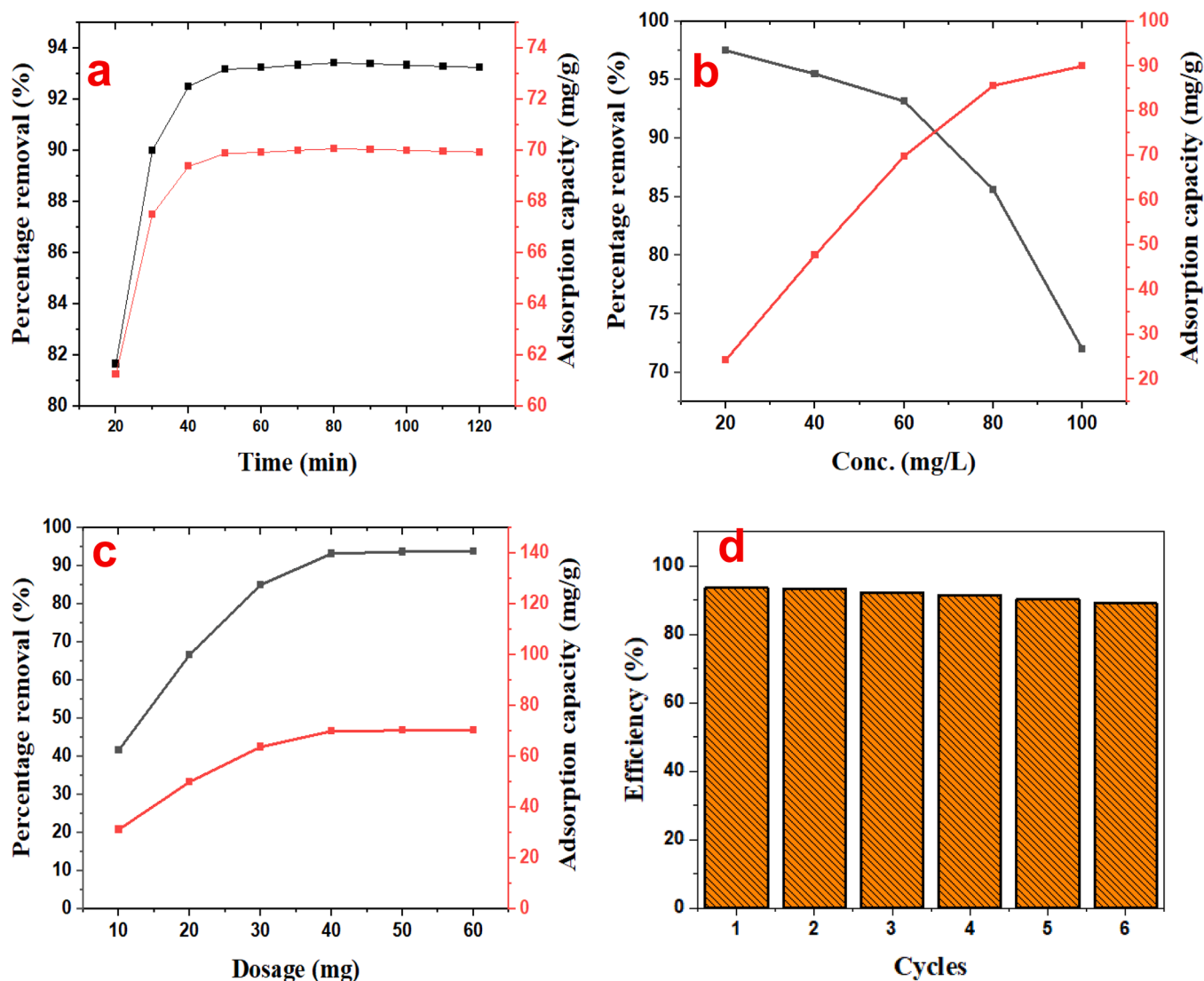


Fig. 9. Percentage removal and adsorption capacity of CMS biochar dose at different (a) contact time (b) initial MB dye concentration (c) dosage (d) reusability of CMS biochar as adsorbent.

higher diffusion rate at greater dye concentrations. These results align with the findings of Jabar et al. [33]. The noticeable reduction in dye removal efficiency at concentrations between 60 and 100 mg/L suggests that 60 mg/L is the optimal initial concentration for effective MB removal using CMS biochar as the adsorbent.

By varying the dose between 10 and 60 mg, at room temperature (303 K), with a stirring speed of 150 rpm, an initial dye concentration of 60 mg/L, and an optimal contact time of 50 minutes, the effect of adsorbent dosage on the adsorption process (Fig. 9c) was assessed. Fig. 9c illustrates that when the dosage of adsorbent increased from 10 to 40 mg, the % removal of methylene blue (MB) increased gradually. This improvement in MB removal can be attributed to the greater number of active sites available on the CMS biochar surface as the dosage increased. However, beyond a dosage of 40 mg, there was little to no further augmentation in MB removal efficiency, likely due to the agglomeration of biochar particles. This agglomeration may have hindered the accessibility of some active sites, preventing them from adsorbing the dye [54]. These findings confirm that 40 mg is the optimal dosage of CMS biochar for the effective removal of MB from aqueous solution. Table 4 presents a comparison of the maximum adsorption capacities of CMS biochar to other biochars derived from thermal conversion of various biomass sources for methylene blue (MB) removal. The CMS biochar demonstrated a maximum adsorption capacity of 90 mg/g, which is higher than that of most biochars derived from different biomass sources reported in the literature for MB removal from aqueous solutions. This suggests that biochar from the co-pyrolysis of sewage sludge and microalgae, modified with the ZnO/MgO/CeO₂/HZSM-5 catalyst (CMS biochar), could be a highly effective adsorbent for MB removal from wastewater.

The regeneration and reusability of CMS biochar were evaluated over six adsorption cycles as shown in Fig. 9d. the regeneration of the CMS biochar was conducted using 0.1 M NaOH as a desorbing medium [33]. The biochar demonstrated strong potential for reuse, with only a slight decline in its removal efficiency. After six regeneration cycles, there was approximately a 5 % reduction in removal efficiency. This minimal loss suggests that the CMS biochar maintains its adsorption capability over multiple uses, highlighting its robustness and cost-effectiveness for wastewater treatment applications. However, further optimization of the regeneration process could help minimize performance degradation and enhance long-term sustainability.

4. Conclusion

The ZnO/MgO/CeO₂/HZSM-5 catalyst was successfully synthesized, and various characterization techniques confirmed the incorporation of ZnO, MgO, and CeO₂ nanoparticles within the HZSM-5 framework. Pyrolysis of microalgae achieved the highest conversion rate at 62.2 %, while sewage sludge biomass had the lowest at 42.8 %. During co-pyrolysis, the catalyst favored the production of gases over bio-oil, increasing the gas yield slightly from 30 wt% to 32.6 %, while the bio-oil yield decreased from 24.4 wt% to 21.9 wt%. The co-pyrolysis of sewage sludge and microalgae over the ZnO/MgO/CeO₂/HZSM-5 catalyst (CMS) resulted in a more balanced composition of hydrocarbons and oxygenated compounds, indicating a synergistic effect that enhanced the quality of the bio-oil. Additionally, this study demonstrated the effectiveness of CMS biochar as an adsorbent for methylene blue removal from wastewater, achieving a maximum adsorption capacity of 90 mg/g. The biochar also exhibited strong regeneration and reusability, with only a slight decrease in removal efficiency after six cycles, making it a promising solution for sustainable and cost-effective wastewater treatment.

CRediT authorship contribution statement

Sherif Ishola Mustapha: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis,

Table 4

Maximum adsorption capacity of different biochars for methylene blue (MB) removal.

Biochar Source	Preparation condition	Adsorption capacity (mg/g)	Reference
<i>Phyllostachys edulis</i>	Pyrolysis at 700 °C, 3 h	67.71	[55]
<i>L. Digitata</i>	Pyrolysis at (400 °C, 60 min)	112.30	[56]
Petung bamboo	Microwave-assisted pyrolysis at 500 °C, 1.5 h, 960 W	45.28	[57]
Sewage-sludge	Pyrolysis (550 °C, 2 h)	29.85	[58]
Corn cob biomass	Pyrolysis at 700 °C, 2 h	20.42	[59]
Tea waste and sewage sludge	Co-pyrolysis Pyrolysis (300 °C, 2 h)	8.94	[60]
Mandarin peel (MP) and Algae (AG)	Microwave irradiation at 800 W for 15 min in conjunction with H ₃ PO ₄	48.50	[61]
Microalgae	Microwave at 2450 MHz, 800 W	113	[62]
Pig manure	Pyrolysis (500 °C, 2 h)	466.95	[63]
Reeds	Pyrolysis (500 °C, 2 h)	48.84	[64]
Banana peel extract	Pyrolysis (600 °C, 60 min)	40.19	[65]
Jerusalem artichokes straw	Pyrolysis at 800° C, modified with zinc carbonate	477.13	[66]
Mixed municipal discarded material (MMDM)	Pyrolysis (300 °C, 12 h)	7.25	[67]
<i>Lantana camara</i> Stem	Pyrolysis at 600 °C,	15.39	[68]
sludge-rice husk biochar	pyrolysis at 500 °C, for 2 h	22.59	[69]
Magnolia grandiflora L. leaf	Pyrolysis at 500 °C	78.60	[70]
Rabbit faeces	Pyrolysis (500 °C, 2 h)	86.85	[63]
Municipal solid waste	Pyrolysis (400–500 °C, 15 min)	21.83	[71]
Microalgae and sewage sludge (CMS)	Co-pyrolysis (500 °C, 1 h) modified with ZnO/MgO/CeO ₂ /HZSM-5 catalyst	90.00	This study

Conceptualization. **Yusuf Makarfi Isa:** Writing – review & editing, Validation, Supervision, Resources, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2024.114955](https://doi.org/10.1016/j.jece.2024.114955).

Data availability

No data was used for the research described in the article.

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