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Characterization of Bio-Sorbent from the Pyrolysis of Patchouli Dregs to Remove Methylene Blue Dyes

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Abstract. Increasing textile production leads to a corresponding rise in dye waste, including substances such as methylene blue. Methylene blue poses a significant environmental challenge due to its non-biodegradable nature and high toxicity, which can adversely affect both human health and ecosystems. To address this issue, various methodologies have been explored, with adsorption emerging as a promising technique. This study focuses on employing adsorption utilizing an adsorbent derived from patchouli dregs and activated using hydrochloric acid (HCl). The research commenced with the pyrolysis of patchouli dregs at different temperatures: 300°C, 340°C, and 380°C for 1.5 hours. Subsequently, chemical activation was carried out using HCl solutions with concentrations of 0.3 M, 0.5 M, and 0.7 M. The resulting activated adsorbent underwent characterization to assess its morphological structure, functional groups, and crystalline composition. The scanning electron microscopy (SEM) analysis revealed prominent pores in the patchouli dregs adsorbent post-activation, with a size of 14.699 μm. X-ray diffraction (XRD) analysis demonstrated an irregular microcrystalline structure and amorphous nature of the activated patchouli dregs adsorbent. Additionally, Fourier transform infrared (FTIR) analysis identified active functional groups including O-H, C=O, C=C, C≡C, and C=H, which facilitate methylene blue adsorption. Characterization of the various iterations of the patchouli dregs adsorbent confirmed its suitability for methylene blue adsorption, meeting the quality standards outlined in SNI 06-3730-1995. These standards include a water content of 1.935%, ash content of 7.568%, and iodine adsorption capacity of 1,270.41 mg/g. In summary, this study elucidates the potential of patchouli dregs-derived adsorbents activated with hydrochloric acid for effective methylene blue removal, providing insights into their morphological, structural, and functional characteristics crucial for addressing the challenges associated with textile dye waste management.

Introduction

Methylene blue, a non-biodegradable synthetic dye, poses a significant threat when released into surface and underground water due to its inherent toxicity to nervous tissue, reproductive systems, and skin. Conventional biological processes are ineffective in breaking down such non-biodegradable dyes, exacerbating the environmental and health risks associated with their uncontrolled emissions. Compounding the issue, methylene blue contains active ingredients like azo compounds (monoazo, diazo, triazo) known for their carcinogenic properties. Given its organic origin, methylene blue proves challenging to decompose [1], with permissible concentrations in water typically ranging from 5-10 mg/L [2]. To address this, adsorption emerges as a promising method for removing methylene blue from liquid waste [3].

Several studies have addressed the removal of methylene blue from liquid waste. Maryudi et al. [4] investigated the impact of activated carbon size variations on methylene blue adsorption, considering concentration and contact time. Their findings revealed that smaller activated carbon sizes, particularly those below 100 mesh, exhibited higher adsorption capacities, reaching up to 9.8%. Optimal conditions for a low concentration of 15 ppm methylene blue were observed at 30 minutes, achieving full adsorption. In addition to activated carbon, Misran et al. [5] explored the potential of natural waste materials for real-world applications, specifically focusing on methylene blue dye waste adsorption. Their research utilized banana stem waste as a source of active carbon, demonstrating its effectiveness as raw material for adsorbent production and yielding promising results.

Mariana et al. [6] employed activated carbon derived from coconut fiber, modified with SiO_2, to create adsorbents for ammonia and methylene blue adsorption. Additionally, Mariana et al. [7] utilized activated carbon sourced from coconut shells and fly ash for methylene blue adsorption. This composite achieved an impressive methylene blue adsorption capacity of up to 45.36 mg/g, with a coconut shell to fly ash ratio of 30:70 and an adsorption equilibrium time of 120 minutes. The process of utilizing biomass for adsorption is termed biosorption, and the adsorbent derived from it is referred to as a biosorbent.

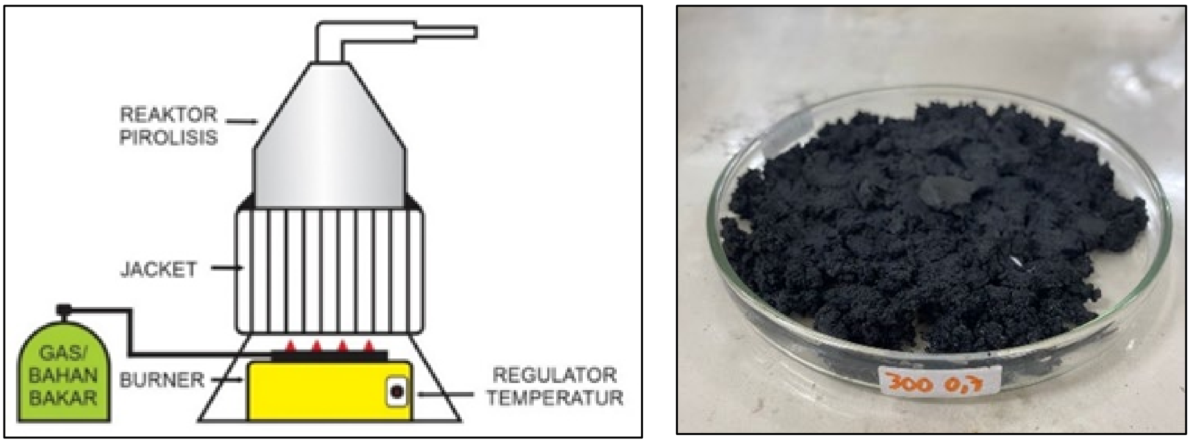
Conversely, Indonesia stands as the world's foremost supplier of patchouli, contributing between 70% to 90% of the global market demand [8]. According to the Indonesian Directorate General of Plantations, by 2022, Indonesia's patchouli oil production is projected to reach 2,404 tons, cultivated across 18,076 hectares. This staggering output underscores Indonesia's role in satisfying approximately 90% of the world's patchouli requirements. However, this substantial production also generates a significant amount of biomass waste. Therefore, there exists a compelling opportunity to optimize the utilization of patchouli oil production waste, aiming to mitigate the impact of other natural wastes, notably methylene blue.

Traditionally, the processing of patchouli dregs as sorbent involves carbonization process in furnaces. However, this approach raises environmental concerns due to its high energy consumption, typically reaching around 800°C. To address this issue, this research adopts a pyrolysis method, which consumes less energy compared to furnaces and yields a valuable by-product in the form of liquid smoke, offering further utilization opportunities. Moreover, this study specifically investigates the influence of pyrolysis temperature and acid concentration on the characteristics of the patchouli dregs adsorbent.

Experiment

Materials. The materials utilized in this study comprise patchouli dregs sourced from local farmers in Aceh province, Indonesia, serving as the carbon source for producing adsorbents. Deionized water, obtained from the Environmental Laboratory of Chemical Engineering at USK, was used as a solvent. Additionally, HCl 37%, procured from Merck, Germany, served as the acid activator in the experiment.

Patchouli Dregs Adsorbent Production. The preparation of raw patchouli dregs before the activation process is crucial to eliminate impurities originating from their source. This involves washing the patchouli dregs thoroughly with clean, running water to prevent contaminants from reappearing. Subsequently, the patchouli dregs are dried in an oven at 70°C until a constant weight is achieved, effectively removing any residual moisture from the previous step. For the pyrolysis process, the equipment configuration depicted in Fig. 1(a) is utilized. Petroleum gas serves as the fuel to heat the pyrolysis reactor, with a temperature regulator situated on the burner to maintain the operating temperature. A jacket is employed to stabilize the operating temperature, minimizing heat loss during the process. Pyrolysis is conducted for a duration of 1.5 hours, with temperature variations set at 300, 340, and 380°C. The outcomes of the pyrolysis process on the patchouli dregs are illustrated in Fig. 1(b).



(a) (b)

Fig. 1. Pyrolysis equipment scheme (a) and Patchouli dregs adsorbent after pyrolysis (b)

Acid Activation of Patchouli Dregs Adsorbent. The pyrolysis process yielded activated charcoal, tar, and liquid smoke as its primary products. The charcoal was subsequently ground and sieved through a 100 mesh size, resulting in a 12-gram portion selected for activation with 250 mL of HCl solution at concentrations of 0.3, 0.5, and 0.7 M [9,10]. Following thorough stirring for 1 hour, each mixture was left to stand for 24 hours [11]. Subsequently, the mixtures underwent filtration, followed by washing with distilled water until reaching a neutral pH (pH = 7). The activated charcoal was then dried in an oven at 105°C for 3 hours. Once dried, the resulting activated carbon was cooled in a desiccator at room temperature until completely dry. A comprehensive overview of the entire process is depicted in Fig. 2.

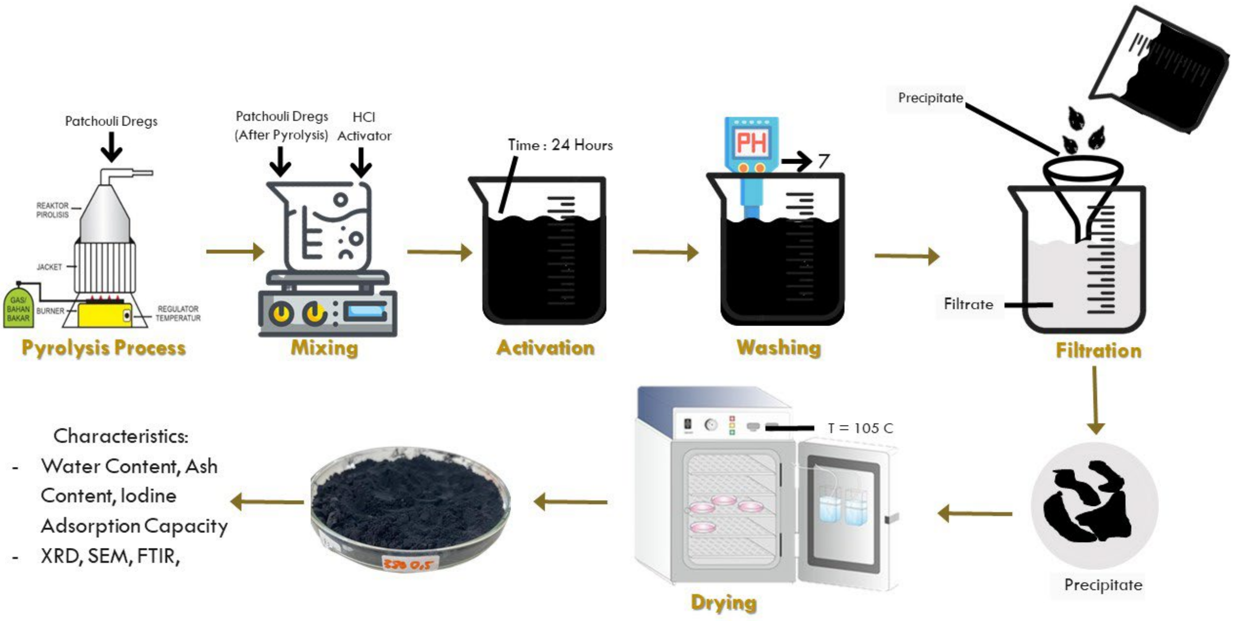


Fig. 2. Chemical activation process of patchouli dregs sorbent using HCl

Water Content Analysis. A total of 2 grams of adsorbent was placed into a pre-weighed porcelain cup. The cup was then subjected to an oven temperature of 105°C for 24 hours, followed by cooling in a desiccator before being reweighed. The water content of the adsorbent was determined using Eq. (1) [12], where 'a' represents the initial weight of the adsorbent (in grams), and 'b' represents the final weight of the adsorbent (in grams).

$$Water\ content(\%) = \frac{a-b}{a} x100\% \tag{1}$$

Ash Content Analysis. Two grams of the adsorbent were placed into a previously weighed porcelain cup. The cup was then placed in a muffle furnace at 600°C for a duration of 3 hours. Afterward, it was allowed to cool in a desiccator before being reweighed. The ash content was determined using Eq. (2) [12], where 'a' represents the weight of the ash (in grams), and 'b' represents the initial weight of the adsorbent (in grams)..

$$Ash\ content(\%) = \frac{a}{b} x100\% \tag{2}$$

Iodine Adsorption Analysis. 0.15 grams of the adsorbent was placed in a dark, enclosed container. Subsequently, 25 mL of 0.1 N iodine solution was added and stirred using a magnetic stirrer for 15 minutes before being filtered. A portion of 10 mL of the filtrate was then titrated with 0.1 N sodium thiosulfate solution. Upon nearing the disappearance of the yellow color in the solution, 1% starch was introduced as an indicator, resulting in a color change to dark blue. The titration continued until the dark blue color faded away. The iodine adsorption number was determined using Eq. (3), where 'V' represents the volume of sodium thiosulfate (in mL), and 'N' denotes the concentration of sodium thiosulfate.

$$Iodine\ Adsorption\left(\frac{mg}{g}\right) = \frac{\left\{10-\left(\frac{NxV}{0.1}\right)\right\}}{S} x12.69x2.5 \tag{3}$$

Adsorbent Functional Group Analysis. Fourier-Transform Infrared Spectroscopy (FTIR) analysis which conducted using a SHIMADZU P-21 instrument was aimed to identify the functional groups present in the adsorbent. This characterization sought to pinpoint active groups crucial for methylene blue adsorption. The FTIR analysis was performed on patchouli dregs at various stages: before pyrolysis, after pyrolysis, after activation, and after adsorption. The infrared spectrum measurements employed the potassium bromide (KBr) pellet method, wherein patchouli dregs biosorbent were mixed with KBr in specified proportions and pressed using a hydraulic press to create a thin film. The FTIR spectrum was recorded across the range of 400-4000 cm^{-1}.

Adsorbent Morphology. Scanning Electron Microscopy (SEM) analysis, conducted using a HITACHI TM 3000 instrument, was aimed to examine the surface morphology of the adsorbent material, including pores and surface area characteristics. For this analysis, 2 grams of patchouli dregs biosorbent were coated with gold or platinum and then placed onto the surface to be tested. The sample was then subjected to SEM imaging at a magnification of 2,000x.

XRD Analysis. X-ray diffraction (XRD) analysis, performed with a D-6000 instrument by SHIMADZU, aimed to ascertain the molecular shape and crystal structure of the adsorbent, crucial factors influencing the adsorption process. To conduct this analysis, 2 grams of patchouli dregs biosorbent powder were placed into an aluminum cuvette. Subsequently, the surface of the biosorbent powder was compacted and leveled using a glass piece. This process involved pressing the glass while moving it over the surface of the cuvette, ensuring a solid and flat surface parallel to the cuvette's surface. Finally, the sample was irradiated with X-rays for analysis.

Results and Disscussion

Water Content. Assessing the water content of a biosorbent is crucial for understanding its hygroscopic characteristics. A lower water content enhances adsorption efficiency as it allows more sites within the pores to be available for adsorbate binding [13]. The relationship between temperature, HCl activator concentration, and the water content of the biosorbent derived from patchouli dregs is depicted in Fig. 3.

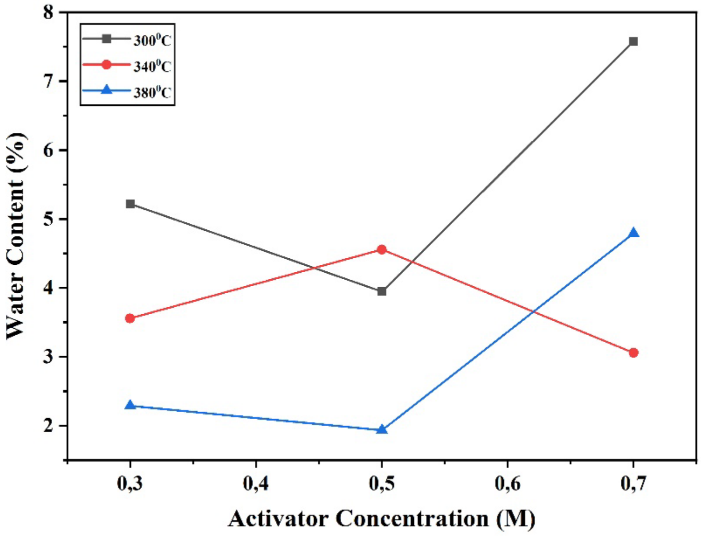


Fig. 3. Interconnection of biosorbent water contents with activator concentration and temperature

According to the findings presented in Fig. 3, the water content analysis of the patchouli dregs biosorbent aligns with the quality standards stipulated in SNI No. 06-3730-1995, wherein the water content within the adsorbent remains below 15%. Notably, the research reveals that the water content in activated carbon falls within the range of 2-8%. The biosorbent exhibiting the lowest water content is derived from a 0.5 M HCl-activated adsorbent subjected to pyrolysis at 380°C, registering a water content of 1.935%. Conversely, the biosorbent with the highest water content originates from a 0.7 M HCl-activated adsorbent processed at 300°C, demonstrating a water content of 7.576%. These results underscore the favorable adsorbent quality across all variations due to their low water content, facilitating the presence of large pores and an expansive adsorbent surface area [14].

Furthermore, the concentration of HCl activator and pyrolysis temperature exert notable influences on the water content in activated carbon, corroborating established theories and prior research [15]. Specifically, the water content tends to decrease with escalating concentrations of HCl activator and pyrolysis temperature in activated carbon. This phenomenon stems from the behavior of water molecules at temperatures exceeding 100°C and under 1 atm pressure, wherein they undergo a phase transition into gas. Consequently, water molecules dissociate from their carbon bonds, transitioning into a gaseous state. Utilizing HCl as a hygroscopic activator proves instrumental in optimizing the reduction of water content within the produced activated carbon. The diminished water content in activated carbon lowers the barrier for other molecules to access the pores, thereby enhancing adsorption efficiency [16].

Ash Content. The ash content parameter test serves the purpose of identifying the residual mineral content retained throughout the pyrolysis and activation processes. This residual content has the potential to obstruct the pores of activated charcoal, consequently diminishing its adsorption efficiency [15]. The interplay between temperature and the concentration of HCl activator in relation to the ash content of the biosorbent derived from patchouli dregs is illustrated in Fig. 4.

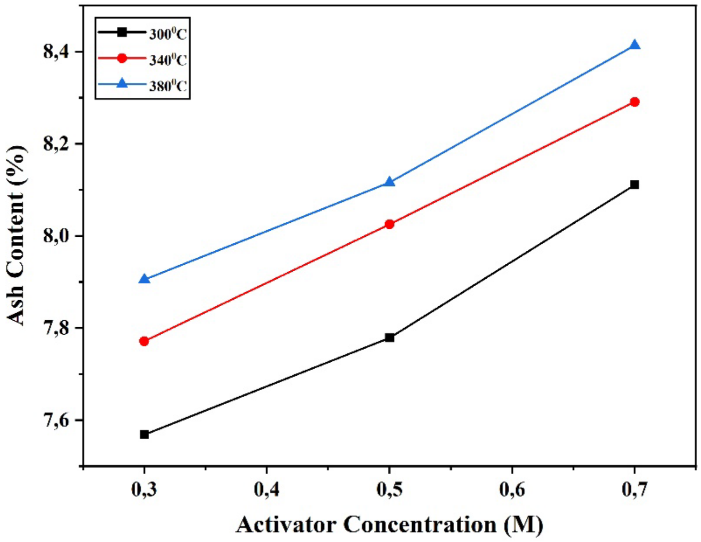


Fig. 4. Ash content on patchouli dregs adsorbent

As depicted in Fig. 4, the average ash content analysis results for the patchouli dregs adsorbent fall within the range of 7-8%, meeting the adsorbent standards outlined in SNI No. 06-3730-1995, which stipulates a maximum ash content limit of 10%. The biosorbent exhibiting the lowest ash content originates from a 0.3 M HCl-activated adsorbent subjected to a pyrolysis process temperature of 300°C, registering an ash content of 7.568%. Conversely, the biosorbent with the highest ash content stems from a 0.7 M HCl-activated adsorbent processed at a pyrolysis temperature of 380°C, demonstrating an ash content of 8.413%. These test results affirm the favorable adsorbent quality across all variations due to their low ash content, indicative of minimal blockage from mineral residues on the adsorbent surface [17].

The ash content test results depicted in Fig. 4 indicate a notable increase with escalating pyrolysis temperature and HCl activator concentration. Elevating the pyrolysis temperature correlates with higher ash content in activated carbon, attributable to the oxidation of inorganic elements forming ash compounds that adhere to the activated carbon surface [18]. Similarly, greater HCl activator concentrations result in higher ash content within the adsorbent. This trend arises from the heightened HCl concentration reducing water content, leading to the formation of mineral salts, some of which are insoluble and adhere to the pores of activated carbon [19].

Iodine Adsorption Capacity. The evaluation of iodine adsorption capacity aims to evaluate the ability of activated carbon to adsorb iodine, with higher iodine adsorption values indicating greater adsorption capacity of the adsorbent [20]. The relationship between temperature and HCl activator concentration with the iodine adsorption capacity of the biosorbent derived from patchouli dregs is illustrated in Fig. 5.

From Fig. 5, it is evident that the biosorbent exhibiting the highest iodine adsorption value originates from a 0.3 M HCl-activated adsorbent subjected to a pyrolysis process temperature of 300°C, registering an iodine adsorption value of 1,270.41 mg/g. Conversely, the biosorbent with the lowest iodine adsorption value is derived from a 0.7 M HCl-activated adsorbent processed at a pyrolysis temperature of 380°C, demonstrating an iodine adsorption value of 824.568 mg/g. Notably, the analysis results of the iodine adsorption capacity for each variation comply with the standards outlined in SNI 06-3730-1995, specifying a minimum iodine adsorption value of 750 mg/g.

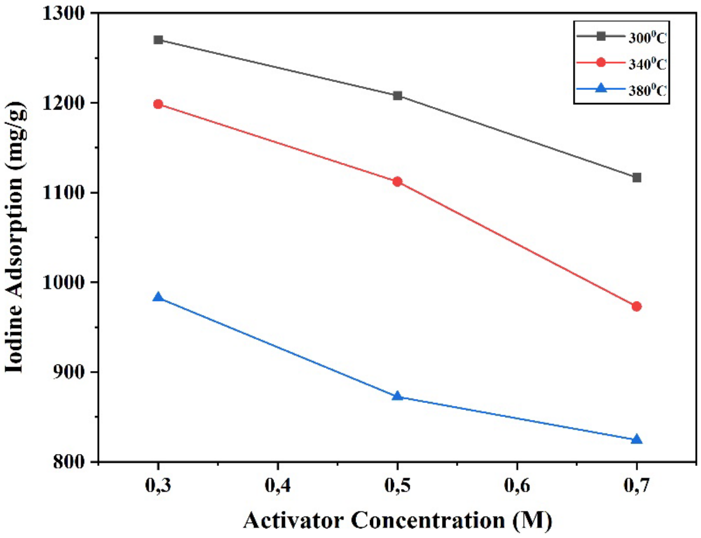


Fig. 5. The iodine adsorption capacity of patchouli dregs adsorbent

As depicted in Fig. 5, there is a notable decrease observed with increasing pyrolysis process temperature and HCl activator concentration. Elevated pyrolysis temperatures correlate with lower iodine adsorption, attributed to surface damage of the carbon caused by the high temperatures, leading to a brittle carbon structure [21]. Contrary to expectations, higher concentrations of the HCl activator tend to yield higher iodine adsorption capacity. However, in this study, the inverse relationship is observed due to excessively high HCl concentrations causing damage to the carbon pores formed [16]. Furthermore, the iodine adsorption capacity is influenced by the results of the ash content analysis. A lower ash content contributes to higher iodine adsorption capacity, as ash can potentially obstruct the pores of activated carbon, thereby reducing the surface area available for iodine adsorption [22].

The crystallinity of Patchouli Dregs Adsorbent. The XRD characterization was conducted to elucidate the crystalline structure of the patchouli dregs adsorbent before, after pyrolysis, and after chemical activation. Fig. 6 illustrates a comparison of the XRD analysis of the patchouli dregs adsorbent across these stages, characterized by peaks at 2θ temperature.

The X-ray diffraction results depicted in Fig. 6 unveil the crystalline structure evolution of the patchouli dregs adsorbent throughout the stages of pyrolysis and chemical activation. The diffraction patterns of the three samples closely align with the JCPDS standard (No. 41-1487), affirming the formation of a carbon crystal structure. Sharp peaks observed around 21-260, 440, and 640 for all samples solidify the presence of a crystalline carbon structure [23]. Notably, the XRD results post-pyrolysis exhibit shallower peaks, suggesting that the pre-activation phase was not yet amorphous. This characteristic is evidenced by the absence of prominent peaks in the pre-activation samples. However, after activation, a distinct high peak emerges at an angle of 2θ: 25-30, indicative of a planar structure resembling the graphite hexagon observed in carbon-based materials. This structure indicates the presence of a semicrystalline phase in the activated carbon [24]. Moreover, the peaks observed in the XRD results post-pyrolysis demonstrate a regular structure with closely spaced peaks lacking sharpness, signifying the formation of amorphous activated carbon. This phenomenon suggests the involvement of OH groups from various organic materials in producing regular crystal structures within the activated carbon [25].

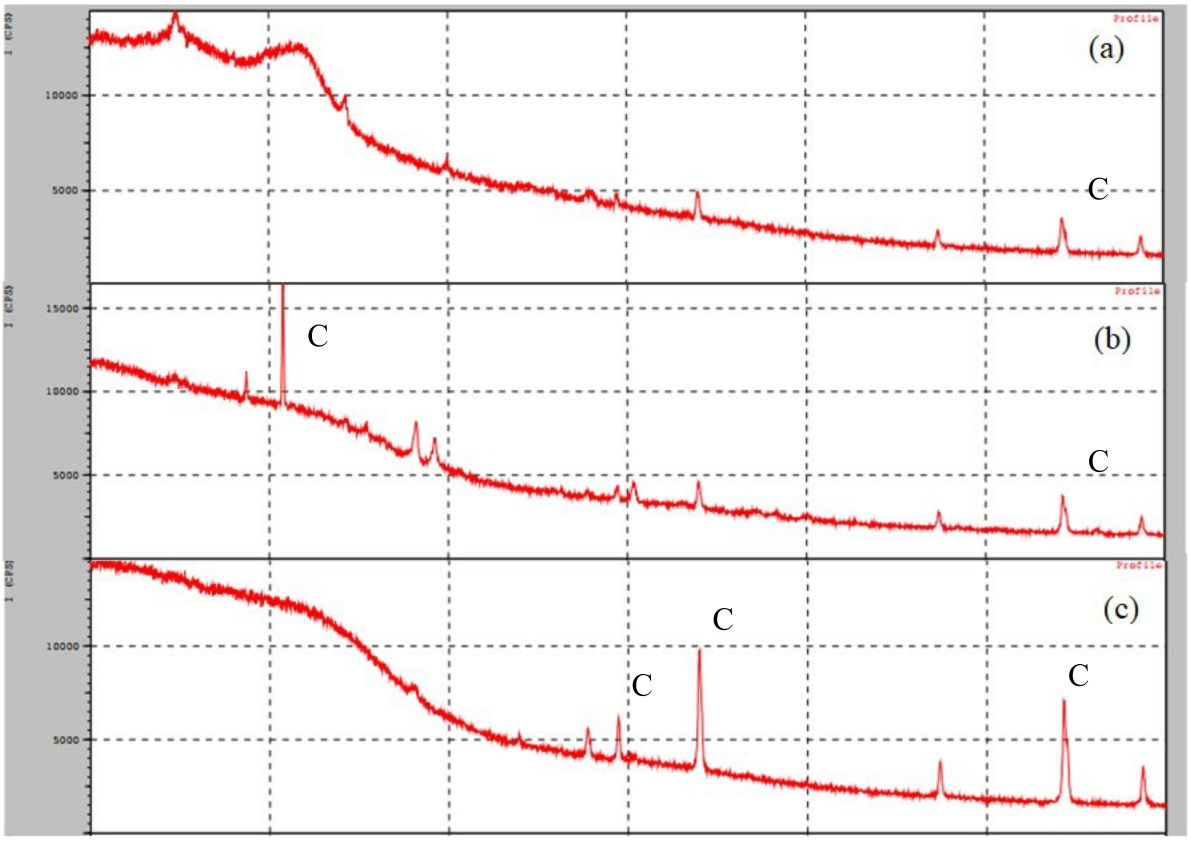
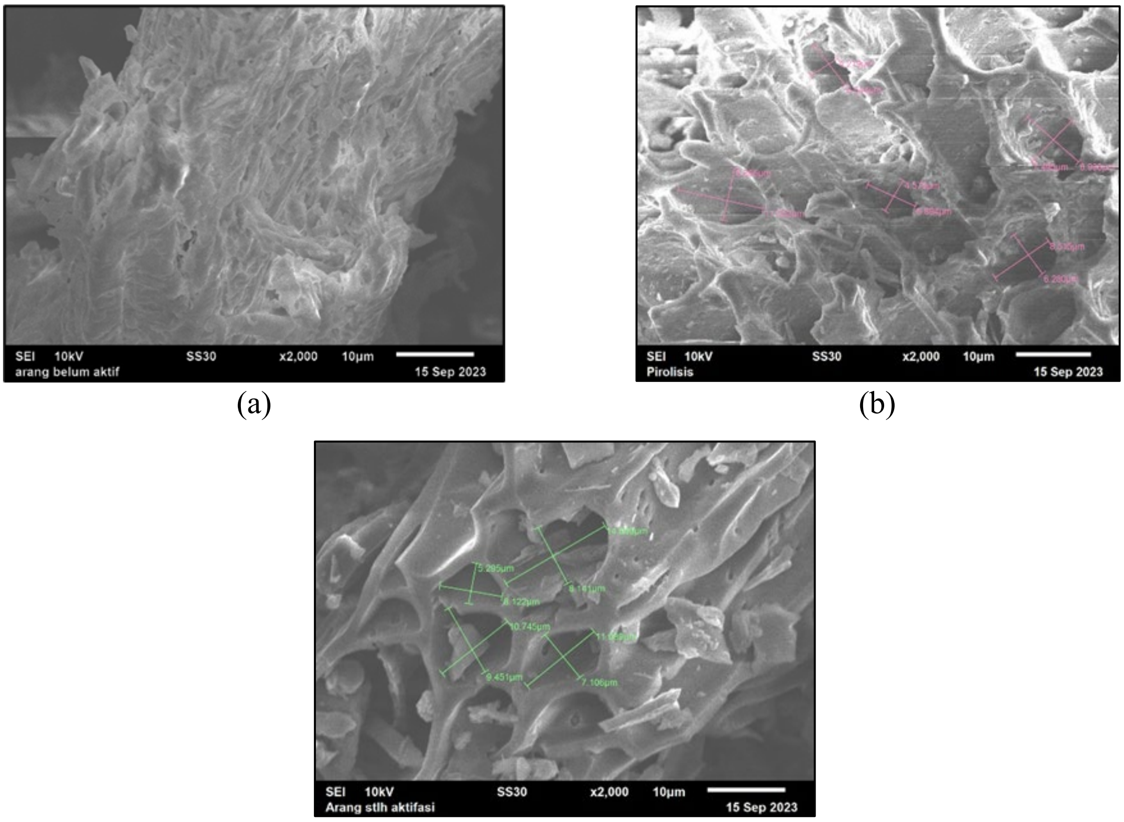


Fig. 6. XRD pattern of patchouli dregs adsorbent (a) before pyrolysis, (b) after pyrolysis, and (c) after acid activation

Morphology of Patchouli Dregs Adsorbent. The characterization of the adsorbent through Scanning Electron Microscopy (SEM) aimed to examine the morphological structure and pore size on the surface of the adsorbent. The SEM analysis results for the patchouli dregs waste adsorbent, both before and after pyrolysis and after chemical activation, are presented in Fig. 7.

Fig. 7 depicts the SEM findings on the patchouli dregs adsorbent treated before, after pyrolysis, and after chemical activation at a magnification of 2000 times. Image (a) illustrates the morphology of dried patchouli dregs before pyrolysis, exhibiting an absence of pores, necessitating the carbonization process for subsequent use as an adsorbent. Conversely, images (b) and (c) showcase the morphology of patchouli charcoal post-pyrolysis and after chemical activation, demonstrating suitable spaces for adsorbates to adhere. The activation of patchouli dregs charcoal using HCl aimed to enhance the adsorbent's dye adsorption capacity. Chemical activation was conducted using HCl at concentrations of 0.3, 0.5, and 0.7 M to enlarge the pores by breaking hydrocarbon bonds or oxidizing surface molecules, thereby increasing the surface area and affecting adsorption efficiency [26].

Based on Fig. 7, the morphology of the three adsorbents exhibits a rough and hollow texture, except for the patchouli material before pyrolysis, which lacks pores. The patchouli dregs waste adsorbent before chemical activation displayed the smallest pore size at 4,219 µm and the largest pore size at 11,552 µm. Conversely, after chemical activation, the patchouli dregs waste adsorbent demonstrated the smallest pore size at 5,295 µm and the largest pore size at 14,699 µm. Comparing the pore sizes of these two adsorbents reveals that the patchouli dregs adsorbent after chemical activation has larger pores, indicating enhanced adsorption capability compared to its precursor. Furthermore, the patchouli dregs waste adsorbent before and after chemical activation belongs to the microporous material class, characterized by pore sizes of <2 nm [27]. The pore size significantly influences the adsorbent's adsorption capacity, with larger pores exhibiting higher adsorbate adsorption tendencies [28].



(a) (b)

(c)

Fig. 7. Patchouli dregs adsorbent morphology (a) before pyrolysis, (b) after pyrolysis, and (c) after acid activation

Adsorbent Functional Group. Fig. 8 and Table 1 show that the spectra obtained have slightly different analysis results between patchouli dregs before and after pyrolysis and after activation. The difference can be seen in the spectrum of patchouli dregs before pyrolysis. O-H stretching can be seen as evidenced by a characteristic adsorption peak that is quite sharp and broad at wave number 3311 cm^{-1}. In the FTIR wave spectrum before pyrolysis, an adsorption peak also appears at 1641 cm^{-1} to 1525 cm^{-1}, indicating the presence of C=O and C=C groups, typical groups found in activated carbon.

Table 1. Functional groups found in the adsorbent samples

Functional Group	**Wave number (cm^{-1})**			
	References	**Before Pyrolysis**	**After Pyrolysis**	**After Activation**
O-H (Hydroxyl)	4000-3400	-	3631	3612
O-H stretching	3500-3200	3311	-	-
C=H	3000-2800	2920	2947	2953
C=C	2450-2345	-	2351	2953
C-O	1470-1000	1334	1386	1282
C=O Keton C=C Lignin	1700-1500	1641, 1622, 1525	1585	1697, 1606
C-O Carboxylic Acid	1250-1000	1249, 1047	1056	1064
C-C	1000-500	601	842, 638	823, 609

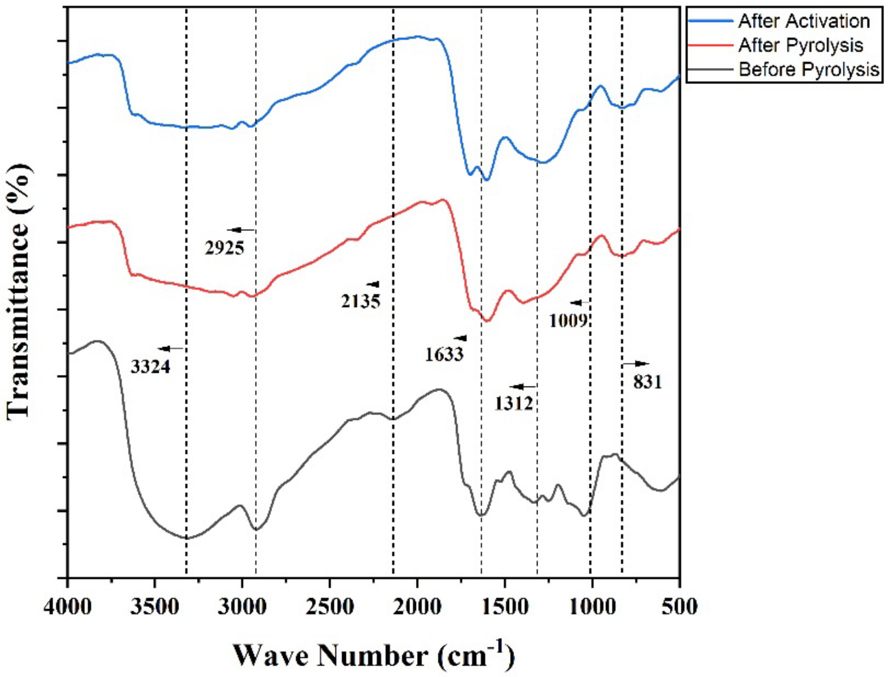


Fig. 8. IR spectrum of patchouli dregs adsorbents

The O-H group (stretching) no longer exists in the patchouli dregs spectrum after pyrolysis and after activation due to the pyrolysis process, which evaporates the water content in the patchouli dregs. Other research also states that the lower hydrogen and oxygen content in biochar after pyrolysis may be caused by dehydration, carbonization during activation, or due to the pyrolysis process [29].

Summary

This work concludes that the patchouli dregs-based adsorbents especially after activated chemically demonstrates their compliance with quality standards set forth in SNI No. 06-3730-1995. Through XRD analysis, an amorphous structure with characteristic diffraction peaks, consistent with the JCPDS standard (No. 41-1487), was observed, indicating the presence of a carbon crystal structure. SEM analysis further elucidated the augmentation of surface area and pore structure due to chemical activation. Moreover, FTIR analysis identified key functional groups—O-H, C=O, C=C, C≡C, and C=H—within the adsorbent, serving as active sites for methylene blue adsorption. This comprehensive characterization underscores not only the fulfillment of quality criteria but also provides valuable insights into the structural and chemical attributes enhancing adsorption capabilities. These findings underscore the potential of HCl-activated patchouli dregs as effective adsorbents, offering promise for diverse applications in wastewater treatment and environmental remediation. Further research could delve into the adsorption performance, optimizing activation methods and exploring the adsorption mechanisms to harness the full potential of these biosorbents.

Acknowledgments

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