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Utilization of thermally treated cocoa pod husk residues as a sustainable bioadsorbent for methylene blue removal

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ABSTRACT

Cocoa pod husk (CPH), an abundant agricultural waste, represents a promising lignocellulosic resource for sustainable material development. In this study, solid residues (dregs) obtained after extraction of soluble components from CPH were valorized as a novel bioadsorbent for methylene blue (MB) removal from aqueous solutions. The material was prepared via thermal treatment with and without citric acid modification, followed by physicochemical characterization using FTIR, SEM, and BET analyses. The results revealed that the prepared adsorbents possess a predominantly microporous structure with surface areas ranging from 200 to 624 m^2/g, depending on the treatment conditions. Adsorption experiments demonstrated high removal efficiency of MB, exceeding 95% under optimal conditions. The enhanced adsorption performance is attributed to the combined effects of surface functional groups and developed porosity. These findings demonstrate that CPH dregs can serve as an effective, low-cost, and sustainable bioadsorbent for wastewater treatment, enabling the direct valorization of agricultural waste within a circular economy framework.

Keywords: bioadsorbent, batch adsorption, cocoa pod husk, methylene blue.

INTRODUCTION

The cocoa plant (*Theobroma cacao* L.) is a major agricultural commodity cultivated in tropical regions, with approximately 70% of global production concentrated in West Africa and largely driven by smallholder farmers (Asante et al., 2025). Indonesia is among the leading cocoa-producing countries, with a reported production of 728,046 tons of dry cocoa beans, most of which originates from smallholder plantations in Sulawesi (Ditjenbun, 2021; Masitah and Hasbiadi, 2022). The large-scale production and processing of cocoa generate substantial quantities of agricultural residues, particularly cocoa pod husk (CPH), which accounts for approximately 70–75% of the total fruit mass (Lu et al., 2018; Zambrano-Mite et al., 2023). Given the global scale of cocoa production, this corresponds to several million tons of CPH generated annually. Despite its abundance and lignocellulosic nature, this biomass remains largely underutilized and is often treated as waste (Perkebunan, 2021).

Theobroma cacao L. species, cultivated worldwide for its valuable beans, generates up to 72% weight of the fruit as waste. Cocoa by-products consist of cocoa pod husk, cocoa shell, pulp, and primary residue (70%) from cocoa industrialization is cocoa pod husk (Lu et al., 2018; Zambrano-Mite et al., 2023). Cocoa pod husk which

accounts for ~70% of fresh weight is considered a waste product and creates environmental issues. The environmental impact of cocoa pod waste is related to methane and carbon dioxide generation by bacterial degradation; moreover, disposed of by-products can propagate diseases (black pod rot) causing significant crop losses (Puig et al., 2022). However, cocoa pod husk waste can be a potential source of high - value products to increase its economic value while reducing waste aligned with the circular economy (Barrios-Rodríguez et al., 2022; Mariatti et al., 2021; Sotelo-Coronado et al., 2025).

CPH, the main by-product of cocoa processing, is rich in lignocellulosic components including cellulose (35%), lignin (14.6%), hemicellulose (11%), pectin (6.67%), and proteins (5.9%), as well as minerals and ash (Jarrín-Chacón et al., 2023; Yaya Ouattara et al., 2021). In addition, CPH contains a variety of extractable bioactive compounds such as phenolic compounds, anthocyanidins, pigments, methylxanthines, and phytosterols (Campos-Vega et al., 2018; Nguyen et al., 2022). These compounds have been exploited in the production of cellulose nanocrystals, nutraceuticals, and cosmetic ingredients (Herrera-Barrios et al., 2022; Ramos-Escudero et al., 2023; Vargas-Arana et al., 2022). Importantly, after extraction of pectin and other bioactive compounds, the remaining CPH dregs are still rich in lignocellulosic materials and functional groups (Belwal et al., 2022; Dewi et al., 2022, 2025). Despite this potential, the use of CPH dregs as bioadsorbents for the removal of dyes such as methylene blue has not been systematically studied. Tea waste residue is characterized by a high content of insoluble fibers and functional groups, such as hydroxyl and carbonyl, which facilitate the binding of dye molecules (Sylvia et al., 2023). Research indicates that the monolayer adsorption capacity of tea waste for methylene blue ranges from 28.99 mg/g to 85.16 mg/g (Choi and Yu, 2019; Hussain et al., 2018). Similarly, sugarcane bagasse, as a waste product rich in cellulose and lignin, exhibits MB adsorption capacities that vary significantly depending on the treatment method, ranging from 6.73 mg/g to a theoretical prediction of 1.000 mg/g under specific optimal conditions (Sharma and Kaur, 2011). Furthermore, residues from the coffee industry are abundant in cellulose and hemicellulose (Sukhbaatar et al., 2021). The adsorption capacity for MB using filter coffee waste has been reported to reach 312.515 mg/g (Savcı and Karadağ, 2020).

The availability of CPH as a renewable and abundant biomass, rich in modifiable functional groups, makes it an attractive candidate for wastewater treatment applications. Previous studies have shown that surface modification of CPH, for example through reaction with cationic polymers or alkaline treatment, can enhance adsorption performance toward phosphate, nitrate, and other contaminants (Aini et al., 2023; Hernández et al., 2024). Water pollution from industrial and domestic sources is a growing global concern, particularly due to persistent synthetic dyes, which can cause severe environmental and health problems (Enaime et al., 2020; Strokal and Kroeze, 2020; Yerima et al., 2024). Methylene blue (MB) is widely used in textiles, leather, paper, and food industries, and is commonly employed as a model pollutant in adsorption studies due to its stability and cationic nature (Ozturk et al., 2009). However, the widespread application of conventional adsorbents, such as commercial activated carbon, is often constrained by high production and processing costs (Chahal et al., 2024). Furthermore, many existing treatment methods involve complex chemical activation procedures that can be energy-intensive and environmentally taxing (Hussain et al., 2018). Another critical limitation is the difficulty in regeneration; many adsorbents exhibit a significant decline in adsorption capacity after repeated cycles, which limits their long-term economic viability and sustainability in industrial-scale wastewater treatment (Chahal et al., 2024; Sukhbaatar et al., 2021).

Adsorption is a widely applied and effective method for dye removal from aqueous solutions (Agarwala and Mulky, 2023; Sonawane et al., 2025). Various biomass-derived adsorbents, such as activated carbon from corn biomass, sodium humate-modified biochar, polymeric resins, and bentonite clay, have demonstrated high adsorption capacities for MB and other dyes (Karami et al., 2022; Dou and Jiang, 2019). However, most existing adsorbents face challenges in terms of cost, regeneration, and preparation complexity. This motivates the development of low-cost, high-capacity, and reusable adsorbents from abundant agricultural residues. Adsorption is a widely applied and effective method for dye removal from aqueous solutions (Agarwala and Mulky, 2023; Sonawane et al., 2025). Various biomass-derived adsorbents, such as activated carbon from corn biomass, sodium humate-modified biochar, polymeric resins, and bentonite clay,

have demonstrated high adsorption capacities for MB and other dyes (Karami et al., 2022; Dou and Jiang, 2019). However, most existing adsorbents face challenges in terms of cost, regeneration, and preparation complexity (Belay et al., 2025; Yerima et al., 2024). This motivates the development of low-cost, high-capacity, and reusable adsorbents from abundant agricultural residues. Although CPH has been extensively studied for extraction of bioactive compounds, the potential of CPH dregs the solid residues remaining after extraction as bioadsorbents remains largely unexplored. Specifically, there is no systematic evaluation of how thermal pretreatment and chemical modification affect the structural properties and adsorption efficiency of these dregs.

Recent investigations into CPH dregs indicate that thermal-acid pretreatment can yield an exceptional adsorption capacity of approximately 497.1 mg/g, achieving a removal efficiency of over 95% for methylene blue. This quantitative benchmark significantly exceeds the capacities reported for other common agricultural residues, such as tea waste (85.16 mg/g) and rice husk (40.59 mg/g), thereby highlighting the superior potential of post-extraction CPH residues as high-performance bioadsorbents (Choi and Yu, 2019; Hussain et al., 2018). The objective of this study is to develop and characterize CPH dregs obtained after pectin extraction as bioadsorbents for methylene blue removal from aqueous solutions to fill the knowledge gap regarding the valorization of post-extraction CPH residues and provide insight into their applicability as low-cost, sustainable bioadsorbents. The work investigates the effects of thermal pretreatment with citric acid on the structural and surface properties of CPH dregs, and evaluates their adsorption performance under different conditions of pH, contact time, and dye concentration. This research hypothesizes that the residual lignocellulosic matrix and functional groups of CPH dregs can be effectively tuned through thermal pretreatment to enhance their adsorption capacity for cationic dyes.

MATERIAL AND METHODS

Materials

Cocoa pod husk (CPH) waste was collected from smallholder cocoa farmers in Enrekang District, South Sulawesi, Indonesia. The samples were carefully cleaned of visible impurities, cut into pieces of approximately 2 cm in length, and sun-dried until the moisture content reached ~5% (ASTM, 2002). The dried CPH was ground using a mill to obtain a uniform powder of 60 mesh (0.25 mm) particle size and stored in airtight containers at room temperature until use. Analytical grade reagents were used: hydrochloric acid (37%), sodium hydroxide (NaOH), both obtained from Merck (Darmstadt, Germany), and methylene blue (MB) dye from Rofa Lab Center, Bandung, Indonesia.

Preparation of CPH dregs

For each experiment, 500 g of CPH powder was mixed with citric acid (2%) and nanopure water (0.05 L). The mixture was subjected to autoclave treatment at 121°C and a pressure of <1 atm for 10 minutes (Valladares-Diestra et al., 2022). After treatment, the solid residue was separated from the supernatant by filtration. The residue was washed with deionized water until neutral pH was reached using pH meter, then oven-dried at 105 °C for 24 hours until the moisture content reached ~3.5% (ASTM D2867-09). Dried samples were weighed and stored in airtight containers, labeled CPHAS and CPHAQ. An untreated sample (CPHK) was prepared as a control.

CPH characterization

Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was conducted using a Shimadzu FTIR spectrometer (Japan). CPH powder (CPHAS, CPHAQ, CPHK) was mixed with potassium bromide (KBr) and pressed into pellets. Spectra were recorded over the range 4000–400 cm^{-1}, with 32 scans at a resolution of 4 cm^{-1}.

Scanning electron microscopy (SEM)

Surface morphology was observed using a Hitachi FlexSEM 1000II (Tokyo, Japan) at an accelerating voltage of 3 kV. Samples were sputter-coated with gold using an SPI-Module sputter coater for 50 s. Images were captured at multiple magnifications ranging from 50,000× to 500,000.

Surface area and pore analysis

Nitrogen adsorption-desorption isotherms were measured at 77 K using a Quantachrome NOVAtouch LX2 analyzer. Approximately 0.10 g of sample was degassed at 300 °C for 4 h under

vacuum (<10^{-2} Torr) with a heating rate of 5 °C/min. Adsorption-desorption isotherms were recorded over relative pressure (P/P_0) 0.01–0.99.

Specific surface area (S BET) was calculated using the BET method in the range $P/P_0 = 0.05–0.30$ ($R^2 \geq 0.998$), and total pore volume at $P/P_0 \approx 0.99$. Pore size distribution and average pore diameter were obtained from the desorption branch using the BJH method, following Rouquerol consistency criteria

Adsorption studies

Preparation of MB solutions

A stock solution of MB at 1000 mg/L was prepared in deionized water and diluted to working concentrations of 5, 10, 15, and 20 mg/L. For adsorption experiments, 0.25 g or 0.5 g of adsorbent (CPHAS, CPHAQ, or CPHK) was added to 50 mL of MB solution in Erlenmeyer flasks.

Adsorption experiments

Adsorption was performed at 25 °C for varying contact times (15, 30, 45, 60, 90, 120, 130, 150 min). After adsorption, samples were filtered, and the absorbance of the supernatant was measured at 665 nm using a Shimadzu UV mini-1240 UV–VIS spectrophotometer. MB concentrations were determined using a calibration curve prepared from 5–20 mg/L solutions.

Effect of pH

The effect of pH (3–10) measured using a pH meter on adsorption was evaluated by adjusting the solution using 0.1 N NaOH or HCl. MB solution concentrations ranged from 250 to 2300 mg/L.

Calculation of adsorption capacity

The adsorption efficiency (% removal) and equilibrium adsorption capacity (q_e, mg/g) were calculated as follows:

From the data obtained from the adsorption experiments, level of dye removal and adsorption capacity was calculated using the following Equation 1 and Equation 2:

$$\%A = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where: C_i – the initial concentration, C_f – the final concentration in the solution.

$$q_e = \frac{(C_o - C_e)V}{M} \quad (2)$$

where: q_e – the equilibrium uptake capacity (mg/g), C_e – the equilibrium concentration (mg/L), V – volume of MB solution (L), M – the bioadsorbents dosage (g).

RESULTS AND DISCUSSION

Pretreated CPH to solid residue (dregs) as an adsorbents

The preparation of CPH solid residue is based on the pectin extraction method with solvent under thermal and pressure conditions Jarrín-Chacón et al. (2023) as shown in Figure 1. The process begins with CPH sample pretreatment (drying and size reduction followed solvent extraction proceeds in a heated and pressured autoclave. Under pretreatment conditions, a solid fraction of 68% (CPHAS) and 76% (CPHAQ) was produced. Previous research reported that optimal pretreatment produced a solid residues of 66.7% and extractables fraction. Structural composition of the solid fraction showed enrichment in cellulose, hemicellulose and lignin fractions. The solid CPH residues has a high lignocellulose content, which is very suitable for fermentation process to produce bioethanol and biochar adsorbents by thermochemical process (Dewi et al., 2025; Jarrín-Chacón et al., 2023).

CPH characterization

Fourier-transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy is a valuable tool in the study of biomass components and their derivatives. The FTIR technique was used to identify functional groups of bioadsorbents that play a role in dye adsorption. Cocoa Pod Husks biomass, is composed mainly of cellulose, hemicellulose, lignin and pectin. Each of these polysaccharide components exhibits characteristic absorption bands (signals) in the Fourier Transform Infrared spectrum due to its specific functional groups (Santiago-Gómez et al., 2025). Changes in chemical structure of components before and after thermal treatments of CPH were analyzed by FTIR spectroscopy (Figure 2). A number of absorption bands are in the form of broad, sharp and weak peaks in the wave number

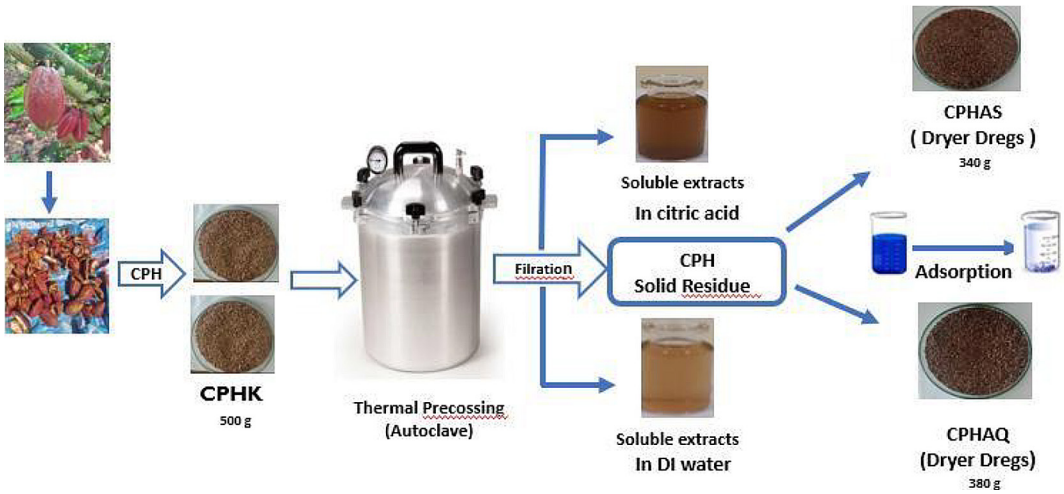

Figure 1. Diagram of the preparation process of CPH dregs

region between 4000–400 cm^{-1}. The samples CPHAS, CPHAQ and the CPHK showed similar absorption bands, broad peak types with different intensities (%T) in the wavenumber region between 3600–3200 cm^{-1}. Absorption bands with broad peaks were identified at around 3429.55 cm^{-1} (CPHAS), 3427.62 cm^{-1}(CPHAQ), 3427.62 $cm^{-1}$and a narrow absorption band at around 3533.71 cm^{-1} (CPHK). The existence of absorption bands at similar wave numbers is associated with the stretching of the OH functional groups in the structure of the cellulose, hemicellulose, lignin and pectin (Adjin-Tetteh et al., 2018; Holguín Posso et al., 2024; Santiago-Gómez et al., 2025). The absorption band above 3500 cm^{-1} (CPHK) is the O-H stretching vibrations for free OH groups of biomass-based adsorbents (Bedia et al., 2018).

Similarly, the absorption band in Figure 2 around 3000–2800 cm^{-1} is related to the C-H stretching vibration of the methyl group (CH3) of the methyl ester, absorption bands were detected around 2924.18 cm^{-1}, CPHAS (2922.25 cm^{-1}), CPHAQ (2918.40 cm^{-1}), and CPHK with different absorption intensities (% T). For the CPHK, there is also an absorption band with a wave number around 2852.81 cm^{-1} which is not found in the CPHAS and CPHAQ. The FTIR spectrum in the range between 1750–1730 cm^{-1} (Figure 2), there is an absorption band (1734.06 cm^{-1}) in CPHAS and CPHAQ with a lower intensity (%T) compared to CPHK (1741.78 cm^{-1}), absorption band (signals) corelated to the C=O stretching of the carbonyl ester group (C=O) found in the galacturonic acid chain which is a characteristic of the pectin backbone, acetyl (acetyl C=O) and esters found in hemicellulose (Andrade et al., 2023; Holguín Posso et al., 2024; Hozman-Manrique et al., 2023). This result is strengthened by the presence of the CPH pectin absorption band at 1732 cm^{-1} (Santiago-Gómez et al., 2025). The shift in wave number (cm^{-1}) and decrease in intensity (%T) of the absorption bands of the CPHAS and CPHAQ samples are strongly suspected to be due to the release of pectin and acetylation compounds during thermal pre-treatment of CPH in citric acid and DI water solvents. Extraction with citric acid and DI water solvents under thermal conditions effectively releases soluble polysaccharides, and pectin components from cocoa pod husk (Jarrín-Chacón et al., 2023; Santiago-Gómez et al., 2025).

Absorption bands were also detected at around 1639.55 cm^{-1} (CPHAS), 1641.48 cm^{-1} (CPHAQ), and 1635.69 cm^{-1} with high intensity (CPHK), indicating the presence of C=C alkenes (conjugated and nonconjugated C=C stretch vibrations) or water absorbed in polysaccharide) from the CPH sample (Holguín Posso et al., 2024). Similar absorption bands with high intensity (% T) in Figure 2, detected at around 1514.17 cm^{-1} (CPHK), 1512.24 cm^{-1} (CPHAS), 1512.24 cm^{-1} (CPHAQ), are related to aromatic ring stretching (C=C stretching aromatic ring) and C-H bonds of lignin. When compared to the CPHK comparison sample, the wave number and intensity (%T) of the absorption bands of the CPHAS and CPHAQ samples were lower, indicating a partial reduction in the lignin component in the adsorbent due to thermal pre-treatment in an acidic environment (Santiago-Gómez et al., 2025).

FTIR absorption band (Signal) that appears between 1065–1255 cm^{-1} is an indication of the

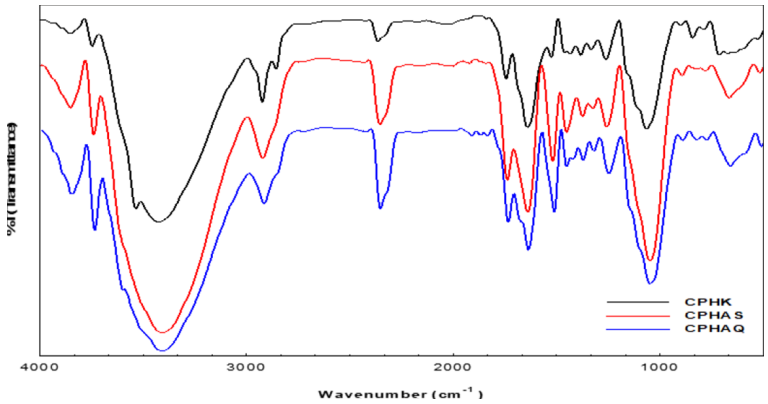

Figure 2. FTIR spectra of CPH before (CPHK) and after pre-treatment thermal (CPHAS, and CPHAQ)

type of C=O stretching vibration such as the glycosidic bonds of polysaccharides in CPH. Additional absorption bands around 1253.77 cm^{-1} (CPHAS), 1253.77 cm^{-1} (CPHAQ) and 1249.91 cm^{-1} (CPHK), are C-O stretching of ether/aromatic bonds of lignin molecules or C-O stretching of esters and C-O-C bonds of hemicellulose and pectin (Adjin-Tetteh et al., 2018; Santiago-Gómez et al., 2025). There are absorption bands around 1055.1 cm^{-1} (CPHAS), 1055.1 cm^{-1} (CPHAQ), 1151.54 cm^{-1} and 1060.88 cm^{-1} (CPHK). This indicates the presence of C-O-C or C–O stretch groups of cellulose and lignin polysaccharide structures, stretching which is a characteristic of alcohol or ester (C−O ester) (Adjin-Tetteh et al., 2018; Holguín Posso et al., 2024). In addition, the two absorption bands (1060.88 cm^{-1} or 1055.1 cm^{-1}) are also thought to be related to the stretch vibrations of C-O bonds of carboxyls, alcohols, and phenols groups Ruiz-Velducea et al., (2024) or also related to keto-conjugated carbonyls, C=O groups with benzene rings (lignin) and H–O–H bending vibrations of absorbed water molecules. The thermal pre-treatment process of CPH in citric acid and DI water solutions can change the structure of lignocellulosic biomass, indicated by changes in the absorption band of the FTIR spectrum.

Scanning electron microscopy (SEM) analysis

The surface morphology of cocoa pod husk samples before and after pre-treatment with citric acid and water under thermal conditions was determined using a Scanning electron microscopy (SEM) analyzer. SEM was also used to examine the surface morphology of bioadsorbents after adsorption of methylene blue in solution (Figure 3 and Figure 4). SEM of CPHK sample shows a texture with a coarse and dense fibrous surface with an amorphous structure with little porosity, similar to that reported by previous researchers (Abou Alfa et al., 2024; Aini et al., 2023; Dewi et al., 2025). The coarse fibrous texture can also be explained by the fact that cocoa pod husk contains macromolecules such as cellulose, hemicellulose, lignin and pectin (Akinjokun et al., 2021; Mekuiko et al., 2023). The morphological appearance of the CPHAS and CPHAQ dregs samples changed significantly, marked by damage to the fiber structure, resulting in a hollow and textured surface (Figure 4). Both adsorbent samples (CPHAS and CPHAQ) were found to have different morphologies with porous and irregular surfaces between them compared to the comparison sample (CPHK).

The CPHAQ sample experienced swelling of the soluble pectin fiber and produced a different texture appearance than CPHAS and CPHK. However, in the CPHAS sample, a more obvious morphological change was seen due to the release of the soluble pectin fiber component and other soluble compounds with citric acid solution. The changes in adsorbent morphology are supported by the results of FTIR spectrum analysis which show changes in absorption bands between 3600–3200 cm^{-1}, 3000–2800 cm^{-1}, and 1740–1730 cm^{-1}. The phenomenon of changes in the morphology of CPH residues after soluble components extraction has also been reported by previous researchers (Dewi et al., 2025). Physical and chemical treatment of biomass waste significantly affects the surface morphology of the adsorbent with a more porous structure (Alfa et al., 2024; Aini et al., 2023). The presence of pores on the surface of the biosorbent helps in increasing the adsorption or diffusion capacity of pollutant substances into the adsorbent. SEM images (Figure 5) show

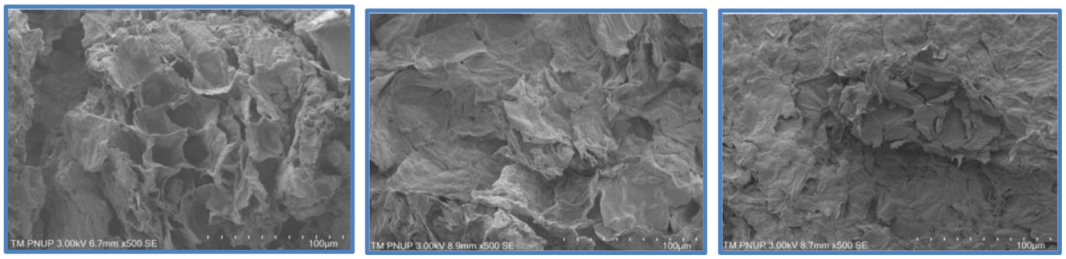

Figure 3. Scanning electron micrograph of CPHAS (a), CPHAQ (b), and CPHK (c) (500x magnification)

significant changes in the surface morphology of the CPHAS, CPHAQ, and CPHK adsorbents after the adsorption of methylene blue and present a homogeneous surface with small porosity and a smooth texture compared to the initial structure before the adsorption of methylene blue.

It appears that the surface of the adsorbent is partially covered, after the interaction between the adsorption side of the surface area and the methylene blue dye which results in a reduction in the number of active pores. The appearance of these changes mainly occurs in the CPHK and CPHAQ sample. Thus, CPHK as cocoa husk waste, CPHAS and CPHAQ dregs have the potential to be adsorbents that can be used to remove industrial waste, especially methylene blue dye. This observation is in line with the research on the characteristics of agave angustifolia bagasse adsorbent and bean shell post- adsorption of methylene blue (Ruiz-Velducea et al., 2024). The CPH dregs, produced after pectin extraction, is very promising as a adsorbent or as a precursor for biochar production because it has many functional groups in its structure to adsorb methylene blue dye as a model pollutant.

Surface area and pore analysis

The surface characteristics of bioadsorbent samples; CPHAS, CPHAQ, and CPHK were analyzed by N_2 adsorption - desorption method using Quanturmcrome NOVA LX2 instrument. The textural properties of bioadsorbents were calculated by BET and BJH methods. The performance of bioadsorbents is influenced by their textural and chemical properties. The pore surface area (SBET – SBJH), pore volume (VBJH), pore diameter and the presence of groups are important parameters that determine the adsorption of molecules (Mak et al., 2009). In Table 1, the specific surface area (SBET) and adsorption surface area (SBJH) of the CPHAS sample were 200.876 m^2/g and 244.161 m^2/g), for the CPHAQ sample, SBET (594.794m^2/g and SBJH (706.347 m^2/g) and for the (CPHK) comparison sample, SBET (624.03 m^2/g) and SBJH (744.257 m^2/g). The CPHAS sample experienced a significant decrease in SBET and SBJH and was suspected to be related to the release of the pectin component after thermal pretreatment in citric acid solution. The presence of pectin fiber components influences the texture characteristics including the specific surface area (SBET and SBJH) of biomass – based adsorbents. Another research report mentioned the low specific surface area (SSR) of the solid residue (dregs) of CPH (~1.0 m^2/g) after extraction of phenol compounds. The removal of dissolved components in CPH has an impact on morphology and porosity which causes a decrease in the SSR (Dewi et al., 2025). The samples (CPHAS and CPHAQ) and CPHK have average pore radius characteristics ranging from 1.6682 nm to 1.7006 nm. The average pore radius of the CPHAS adsorbent is (1.7006 nm), followed by CPHK (1.6725 nm) and CPHAQ (1.6682 nm). According to the International Union of Pure and Applied Chemistry (IUPAC) standards, the three adsorbent samples are included in the micropore category (Micropores have a radius of less than 2 nm).

Besides surface area, pore volume (cc/g) is another critical aspect in assessing the ability of an adsorbent to adsorb a pollutant. The pore volume of the CPHAS sample was (0.1708 cc/g), lower than the CPHAQ bioadsorbents samples (0.49628 cc/g) and CPHK (0.52198 cc/g). A large pore volume value allows the material to accommodate more adsorbate so that the adsorption capacity becomes large. The surface area and the presence of surface carboxyl functional groups that chemically interact with the dye greatly determine the adsorption performance of the bioadsorbent (Soroush et al., 2024). Adsorbent with low surface area characteristics (<10 m^2/g) is effective in removing toxic metal Cd from solution (Melia et al., 2018).

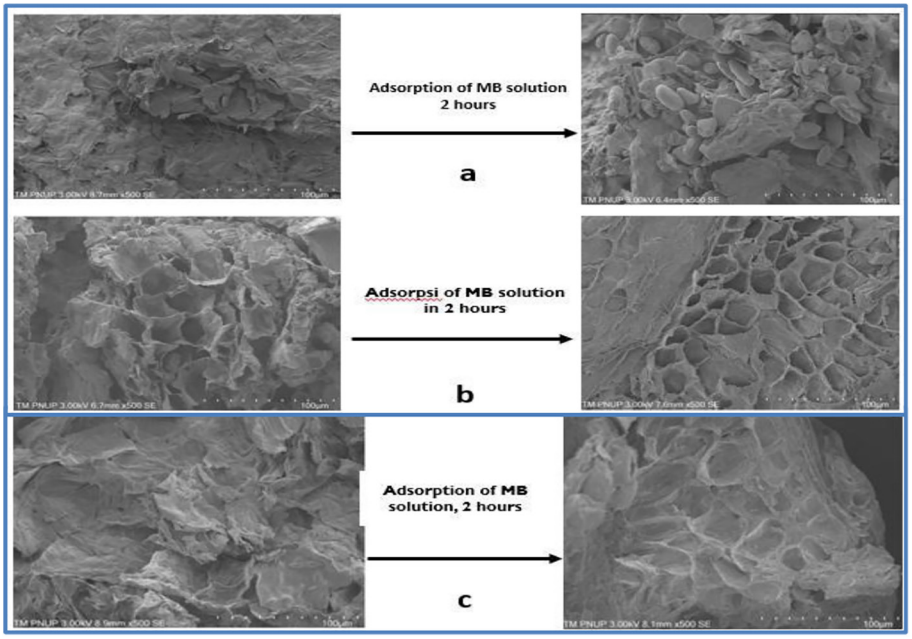

Figure 4. SEM of CPHK (a), CPHAS (b)and CPHAQ (c) sampel after adsorption of MB

Table 1. Characterization of the surface area, pore volume and pore radius of CPHAS, CPHAQ and CPHK by BET analysis using Quantachrome Instruments Nova LX2

Parameter	CPHAS Sample	CPHAQ Sample	CPHK
Surface area (BET) (m^2/g)	200.876	594.974	624.203
Pore volume (cc/g)	0.1708	0.49628	0.52198
Avarage pore radius (nm)	1.7006	1.6682	1.6725
BJH adsorption surface area) (m^2/g)	244.161	706.374	744.257
BJH pore volume (cc/g)	0.2491	0.7189	0.7482

Based on the parameters of surface area, pore volume, and average pore radius, cocoa pod husk - based biomass has adsorption performance as a asorbent to remove methylene blue dye in solution. The present work shows that the solid residues or dregs sample obtained after extraction of pectin from CPH are very promising for use as adsorben or carbon precursors for bio-oil and biochar production. Pyrolysis is known to increase the surface area of the material (Tsai et al., 2020). The development of biomass waste pre-treatment protocols affects the surface area, pore volume, and pore diameter of the adsorbent as well as the adsorbent capacity (Priyanka et al., 2023).

Adsorption study

Effect of pH on the adsorption performance

Bath adsorption study was conducted to determine the effect of pH, contact time, and MB concentration on the MB adsorption capacity of CPHAS, CPAQ, and CPHK samples. pH is an important factor in the adsorption process, especially for dye removal. The adsorption performance of CPH adsorbents samples in the pH range of 3.0–10 (with the addition of 0.1 M HCl or 0.1 M NaOH is shown in Figure 5. The maximum adsorption capacity and removal rate of MB dye of the three adsorbent samples (CPHAS, CPHAQ) and CPHK were achieved at different pH. At pH variations from acidic to neutral around alkaline, the removal rate and adsorption capacity increase. For CPHAS sample, the adsorption capacity increased from 99.667 mg/g at pH 3 to 99.896 mg/g at pH 7 and decreased to 99.332 mg/g (pH 10). CPHAQ sample, from 99.861 mg/g at pH 3 to 99.890 mg/g at pH 5 and decreased to 99.759 mg/g (pH 10). The removal rate of CPHAS and CPHAQ dregs adsorbent towards MB dye increased with increasing pH and decreased after the adsorption equilibrium achieved with different

optimum pH. At the specified pH range, the maximum dye removal rate of dregs adsorbents was above 95%. The release of pectin components via thermal pre-treatment affects the abundance of functional groups COOH and OH as charge contributors on the surface of the adsorbent.

In the current study, we obtained maximum adsorption performance at pH 7 for CPHAS and pH 5 for CPHAQ. In contrast, for CPHK, the optimum adsorption performance was achieved at pH 3, and decreased with increasing pH of medium (Figure 5). In highly acidic solutions (pH 3), the high concentration of hydrogen ions (H^+) protonates the functional groups. This reduces the negative charge on the biosorbent surface, weakening the electrostatic attraction with the cationic dye molecules and decreasing adsorption efficiency. The presence of hydrogen ions in solution competes with MB in the adsorption process (Rozi et al., 2022; Sukmana et al., 2025). Studies show that the greatest adsorbed amounts of cationic MB dyes are typically observed at around pH 5, or 7 pH levels (neutral to slightly basic). Above the optimum pH, competition occurs between the adsorbents and the hydroxyl ions (OH–) of the cationic MB dye, consequently the adsorption of the dye tends to decrease at high pH. Most studies reported similar pH characteristics for MB adsorption with lignocellulose-based adsorbents. Pre-treatment of CPH biomass material causes changes in the physicochemical properties of the adsorbent, including the pH of dye adsorption (Murthy and Gowrishankar, 2020; Olakunle et al., 2018).

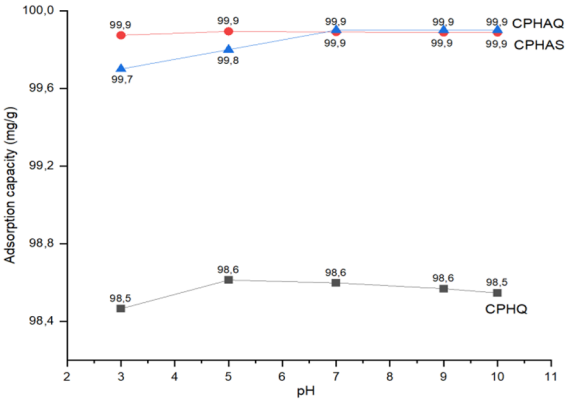

Figure 5. Effect of pH on methylene blue removal by CPHK, CVPHAQ, and CPHAS (adsorbent dose: 0.6 g, initial concentration of dyes: 60 mg/L, room temperature, time: 60 min)

Effect of contact time on the adsorption performance

Contact time is an important parameter required to achieve maximum MB dye removal efficiency. During the contact duration, organic molecules in water diffuse and are physicochemically adsorbed on the surface of the adsorbent. The effect of contact time on MB adsorption by CPH dregs adsorbent was investigated in the range of 15–150 min at initial conditions. In Figure 6, the optimal equilibrium time of CPHAS sample was achieved at 90 minutes with an adsorption capacity value of 99.877 mg/g and a removal rate above 98%. For the CPHAQ adsorbent sample achieved at 60 minutes, the adsorption capacity value was 49.898 mg/g, with a removal rate above 98%. For the CPHK as comparison sample, the contact time achieved was longer (120 min) with a removal rate above 95 % and an adsorption capacity value of 14,723 mg/g.

The removal rate of methylene blue occurred faster in the CPHAQ sample followed by CPHAS and CPHK with a longer time. As the contact time increases, the functional active sites on the surface of the adsorbent become completely saturated by the adsorbate, and further adsorption slows down and eventually does not occur, resulting in the adsorption capacity becoming constant and even decreasing (Negarestani et al., 2023). The adsorption of MB dye in Figure 6 takes place as follows: occurs quickly on the outer surface of the adsorbent and subsequent adsorption occurs on the inner surface slowly and with a relatively small total amount of dye adsorbed. Therefore, it takes a long time for the adsorption process to take place optimally (Olakunle et al., 2018).

Effect of MB concentration on the adsorption performance

This study examined the adsorption performance of the developed CPH dregs adsorbent with higher concentrations of methylene blue (1000–2300 mg/l), and the results are illustrated in Figure 7. Previously, adsorption performance tests were carried out at lower MB concentrations (< 1000 mg/l). The adsorption capacity increased with increasing MB concentration in the solution. At an MB concentration of 1000 mg/L, the adsorption capacity of CPHAQ was 199.62 mg/g, becoming 457 mg/g at an MB concentration of 2300 mg/L. but the MB removal rate decreased from 99.81% to 99.35%. This test was carried out

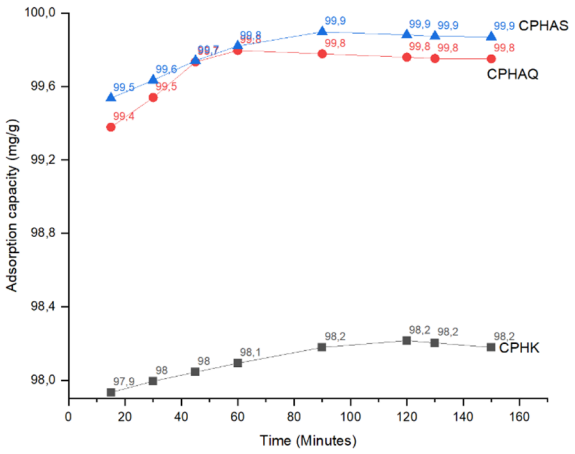

Figure 6. Effect of contact time on methylene blue removal by CPHK, CVPHAQ, and CPHAS adsorbents at optimum condition, constant MB concentration (500 mg/L and room temperature)

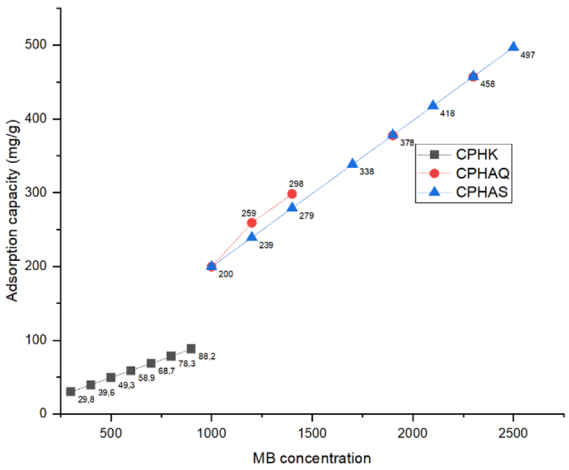

Figure 7. Effect of methylene blue concentration on methylene blue removal by CPHK, CVPHAQ, and CPHAS at optimum condition

at optimum conditions of pH 7, contact time of 90 minutes, and dose of 0.25 g/50 ml.

For the CPHAS sample, the adsorption capacity was 199.69 mg/G to 497 mg/g, the MB removal rate was from 99.85% to 99.40%. Also this test took place at optimum conditions of pH 7, contact time 90 minutes and dose 0.25 g/ml. For the CPHK, the removal rate decreased with increasing MB concentration from 98.95% to 98.50% under the test conditions. The adsorption capacity of CPHK adsorbent increased from 29.68 mg/g to 88.65 mg/g. The MB removal efficiency with CPHK and CPHAQ samples was comparable to that of CPHAS, although the surface area of both was higher than that of CPHAS according to BET results, as reported in Table 1. Both adsorbent samples (CPHAQ and CPHAS) had adequate surface active sites, without significant surface saturation at the final MB concentration of 2300 mg/L. As shown in Figure 7, the MB removal percentage decreased with increasing MB concentration, which may be due to the saturation of adsorption sites on the surface of the adsorbents. Higher dye concentrations result in saturation of the available active adsorption sites, thus reducing the amount of dye removal (Dawood et al., 2016).

CONCLUSIONS

This research successfully demonstrates that cocoa pod husk dregs secondary residues typically discarded after pectin extraction can be transformed into an exceptionally high-performance bioadsorbent. The study confirms that thermal acid modification (121 °C, 1 atm with citric acid) effectively tunes the lignocellulosic matrix, enabling the CPHAS sample to achieve a maximum adsorption capacity of 497.1 mg/g for Methylene Blue, with removal efficiencies consistently ranging between 95.49 and 99.85%. These results signify that the technical goal of valorizing post extraction residues was fully achieved, providing a sustainable and high-capacity alternative for wastewater remediation. Adsorption performance of the modified CPH dregs significantly surpasses reported values for other established biomass derived adsorbents, such as corncob (417.12 mg/g), tea waste (28.99–85.16 mg/g), and raw sugarcane bagasse (starting at 6.73 mg/g). This discovery fills a critical knowledge gap regarding the technical utility of secondary agro-industrial waste, proving that the structural properties and functional groups of such residues are highly responsive to simple, low-energy thermal tuning. Furthermore, this study opens new prospects for a "waste from waste" circular economy model in the cocoa and pectin industries. By proving that secondary waste can be repurposed into a superior material for industrial-scale pollutant capture, this research provides a robust foundation for economically viable and environmentally friendly dye removal systems. These findings offer a scalable pathway to mitigate the environmental impact of synthetic dyes while simultaneously reducing the volume of industrial solid waste generated by agro-processing facilities.

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