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Palm kernel shell based hydrothermal carbon for methylene blue removal in wastewater treatment: application of dual adsorption isothermal models

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ABSTRACT

The application of hydrothermal carbonization (HTC) in biomass waste conversion has increased especially in preparation of adsorbent for waste water treatment. This study focuses on (*i*) the preparation of hydrothermal carbon (HC) from palm kernel shell (PKS), (*ii*) assessment of material quality by application of HC PKS on the removal of Methylene Blue (MB) and (*iii*) determination of maximum adsorption capacity (q_m) based on adsorption isotherm. Four isothermal adsorptions (Langmuir, Freundlich, Dubinin-Raduskevich (D-R) and Temkin) were used to analyze the results of adsorption experiment. The HC PKS tends to follow two isotherms simultaneously in MB adsorption. At low MB concentrations (10–50 ppm), HC PKS follows the Freundlich isothermal, while at high concentrations (75–130 ppm) HC PKS can also follow the Langmuir isothermal besides Freundlich. We introduce and discuss Dual Adsorption Isothermal Model for interaction between adsorbent – adsorbate at certain initial concentration. Isothermal D-R was used to determine the q_m of HC PKS where it was found that HC PKS with chemical activation treatment after HTC (KCS-2) had the largest q_m (54.01 mg/g). The surface area of KCS-2 is 32.21 m³/g which is the largest among HC PKS. The surface area supports the adsorption capacity value of KCS-2. The results of FTIR analysis show that the functional groups for all HC PKS are almost similar.

Keywords: palm kernel shell, hydrothermal carbon, water treatment, dual adsorption isothermal model.

INTRODUCTION

Palm kernel shell is a byproduct of palm oil production, specifically the outermost part of the palm seed that shields the kernel (Baffour-Awuah et al., 2021). After the oil is extracted from the palm kernel, the shell is often left as waste (Ameen et al., 2022). Based on data from the Indonesian Central Bureau of Statistics, the production volume of palm kernel shell (PKS) reached 3,168,848 tonnes (Directorate of Food Crops, 2022). Most of this huge amount of biomass waste has not been utilized properly by the Indonesian farmers. Of course, the accumulation of this biomass waste will be a serious problem if it is not processed properly (Bampenrat et al., 2023; Hakim et al., 2025). The direct use of waste biomass without special treatment also still causes problems (Ma et al., 2022; Monedero et al., 2024; Remon et al. 2017). One potential method dealing with these difficulties is hydrothermal carbonization (HTC) (Mannarino et al., 2022).

The HTC process requires the transformation of biomass feedstock into carbon-rich materials under elevated temperature and pressure conditions, normally spanning from 150 to $350 \,^{\circ}$ C and 2 to 10 MPa, respectively (Wang et al., 2022; Yu et al., 2023). The HTC product, or hydrochar, exhibits a porous structure, high surface area, and various functional groups, making it a suitable adsorbent for the removal of organic pollutants, such as methylene blue, from aqueous solutions (Owsianiak et al., 2016; Pecchi et al., 2022) and the potential utilization as water filter (John et al., 2022).

Water contamination due to the release of dye-containing effluents has become a remarkable environmental concern, especially in the textile and paper industries (Menyaa et al., 2023; Petrovich et al., 2024). Amongst the miscellaneous synthetic dyes, methylene blue is one of the most extensively used cationic dyes, with applications in printing, dyeing, and as a biological stain (Tabassum et al., 2024). However, the existence of methylene blue in water environment can have unfavorable effects on aquatic life and human health, focusing the need for successful wastewater treatment approach (Soffian et al., 2022).

Adsorption is a broadly identified method for the disposal of dyes from aqueous solutions due to its simplicity, efficiency, and cost-effectiveness (Zaini et al., 2023). Different adsorbent materials, including clay minerals, activated carbon and agricultural waste, have been examined for the removal of methylene blue (Fahmi et al., 2019). Palm kernel shell, a by-product of the palm oil industry, has become as a favorable precursor for the production of hydrothermal carbon, a versatile adsorbent material with high surface area and adsorption capacity (Mahdi et al., 2024; Mahmud et al., 2022).

Many research have been carried out regarding the use of PKS as a carbon source for several applications (Ameen et al., 2022). PKS was modified with sulfuric acid which gives PKS-sulfo, and eventually utilized for the handling of heavy metal-contaminated water (Baby et al., 2023). PKS based activated carbon has been prepared using CO₂ activation for adsorption of methane (Zaini et al., 2023; Sevilla et al., 2011). Preparation and characterization of activated carbon from PKS through pyrolysis for Methylene Blue (MB) adsorption has also been conducted (Fahmi et al., 2019; Rashidi et al., 2019). HTC of oil palm kernel shell has been prepared as well (Ameen et al., 2022). In addition, PKS was converted to activated carbon by pyrolysis and activation (physical and chemical) for application as electrode material for high performance supercapacitors (Misnon et al., 2015).

In this research, we convert PKS into hydrothermal carbon (HC) through three treatments. In the first treatment, PKS is added with water and then treated with hydrothermal carbonization. In the second treatment, the results of the first treatment are chemically activated (with KOH) then put in the oven for 24 hours. In the third treatment, PKS is directly mixed with KOH solution and then the mixture is treated hydrothermally. These three carbons are used to adsorb methylene blue. At this stage of the research, we wanted to evaluate the adsorption capacity of MB by HC PKS as well as to test the quality of the HC and determine the adsorption capacity of the carbon.

We also examine the isothermal adsorption of HC PKS on MB and discuss the data obtained within the framework of, what we call, "dual adsorption isothermal models". In the literature, there are many terminologies related to dual adsorption isotherm models, i.e. single gas dual process Langmuir (DPL) model (Ritter et al, 2011), dual site Langmuir isotherm (Brandani, 2024), dual Langmuir-Freundlich (LF) model and linearized Dubinin-Radiskovich (DR) model (Zheng et al., 2024), dual site adsorption model (Lin et al., 2008), etc. Many theoretical studies have been provided regarding that model, but experimental evidence provided is still lacking. In this research, we show that a material can experience two isothermal adsorption models at once, of course under certain conditions. We introduce and discuss dual adsorption isothermal model for interaction between adsorbent - adsorbate at certain initial concentration based on experimental data.

EXPERIMENTAL

Preparation of palm kernel shell based hydrothermal carbon

The palm kernel shells were collected from a local palm oil mill in Bontang area, East Kalimantan Province, Indonesia. The samples were washed, and dried in an oven at 75 C for 3 days. The dried shells were then subjected to hydrothermal carbonization at 220 °C for 2 hours under autogenous pressure (Ameen et al., 2022). The resulting hydrochar was further washed, dried, and characterized using



Figure 1. Source and overall preparation procedure of KCS 1(a), KCS 2(b), KCS 3 (c) and palm kernel shell (d)

nitrogen adsorption-desorption analysis and Fourier-transform infrared spectroscopy. The carbon was labelled with KCS-1, KCS-2 and KCS-3. The complete preparation procedure of KCS from PKS is given in Figure 1.

Adsorption experiment

Batch adsorption experiments were conducted to evaluate the performance of the palm kernel shell-based hydrothermal carbon for the removal of methylene blue from aqueous solutions. Detail of adsoption experiments are referred to Tabassum et al. (2024).

The effects of various parameters, including initial dye concentration, contact time, and solution pH, on the adsorption capacity were investigated. The percentage of removal of MB dye was calculated by the following formula:

% Removal =
$$\left(\frac{c_0 - c_e}{c_0}\right) \times 100\%$$
 (1)

where:
$$C_o$$
 and C_e are concentration (mg/L) at initial and equilibrium states, respectively.

The number of adsorbed MB per amount of adsorbent in gram (q_e) was determined using the following equation:

$$q_e = \left(\frac{(C_0 - C_e)V}{w}\right) \tag{2}$$

where: V and w are the dye solution volume and adsorbent amount (mg), respectively.

Adsorption isotherm modeling

The experimental adsorption data were fitted to four widely used isotherm models: Langmuir model, Freundlich models, Dubinin-Raduskevich model and Temkin model to gain insight into the adsorption mechanism and surface heterogeneity of the adsorbent. All formulas of Langmuir model, Freundlich models, Dubinin-Raduskevich model and Temkin model that are used in the calculation of this study can be found in Tabassum et al. (2024).

RESULTS AND DISCUSSION

Calibration curve of MB solution

The absobance of the MB standard solution can be seen in Figure 2. The regression equation obtained is y = 0.161x + 0.004 with a good correlation coefficient, namely $R^2 = 0.9989$; where x and y are respectively MB concentration and absorbance of MB solution. This calibration curve was then used to determine the concentration of MB in solution or the amount of MB that was not adsorbed by KCS in all adsorption experiments carried out in this study.

Adsorption study of MB dye

The influence of pH, contact time between adsorbent and adsorbate and amount of adsorbents are important parameters in adsorption experiments. Before varying the initial concentration, the optimum values for these parameters were determined for all existing adsorbents: KCS-1, KCS-2 and KCS-3. The optimum pH value for the three adsorbents is 8, while the optimum value for contact time and the amount of adsorbents are respectively 30 minutes and 0.1 gram. Thus, all adsorption experiments in this study were carried out at pH 8 for 30 minutes with 0.1 gram adsorbents.

The experimental isotherm data

In this research stage, the initial concentration of MB was varied at constant pH, contact time and amount of adsorbent (8, 30 minutes and 0.1 gram, respectively). The concentration of MB at equilibrium (C_e) was determined by measuring the absorbance of MB in solution after filtration of the mixture of adsorbent and MB solution after 30 min of experiment. C_e was then calculated using the calibration curve in Figure 2. To calculate the adsorption capacity (q_e) of KCS, Equation 2 was employed by using the initial concentration applied in this experiment and the C_e value was taken from the previous calculation results.

Four sets of adsorption isotherms were utilized to determine what isotherm is suitable. As shown in Table 1, these adsorption data were gained experimentally through a series of batch experiments from three adsorbents: KCS-1, KCS-2 and KCS-3 for adsorption of MB in solutions with various initial concentration (Co = 10, 20, 25, 30, 50, 75, 90, 110, 120, 130 mg/L).

Adsorption trend using Langmuir model for KCS-1, KCS-2 and KCS-3

Before evaluating the data with four adsorption isotherms available (Langmuir, Freundlich, Dubinin-Radushkevich and Temkin), a data trend analysis was carried out. At this stage the Langmuir model is used in linear form. The C_e value is plotted entirely against the C_e/q_e value for all initial concentrations used. Regression analysis was also performed. The results obtained for KCS-1, KCS-2 and KCS-3 are described in Figure 3.

It is clearly seen that, there are two tendency groups for all adsorption data obtained. We arrive at an opinion that for all adsorbents, the initial concentration can be divided into two categories, i.e. low and high. The low concentration category is started from 10 to 50 mg/L of MB, while the high concentration group range is 75–130 mg/L.



Figure 2. Calibration curve of MB solution

Co (mg/L) / samples	KCS 1		KCS 2		KCS 3	
	Ce	qe	Ce	qe	Ce	qe
10	0.224	2.444	0.182	2.454	0.185	2.454
20	0.267	4.933	0.193	4.952	0.208	4.948
25	0.286	6.179	0.195	6.201	0.238	6.190
30	0.290	7.428	0.195	7.451	0.248	7.438
50	0.304	12.424	0.197	12.451	0.257	12.436
75	0.315	18.671	0.197	18.701	0.288	18.678
90	0.427	22.393	0.290	22.428	0.341	22.415
110	0.913	27.272	0.313	27.422	0.488	27.378
120	1.337	29.666	0.350	29.913	0.574	29.856
130	1.596	32.101	0.381	32.405	1.246	32.188

Table 1. Adsorption data of three adsorbents (KCS 1, KCS 2 and KCS 3) for MB removal in solution with different initial concentrations (experiment at pH = 8, contact time = 30 min and adsorbent amount = 0.1 g)

Based on the data in Figure 3, it is shown that for all initial concentrations (Co = 10, 20, 25, 30, 50, 75, 90, 110, 120, 130 mg/L), they do not follow one isothermal model, if they are used simultaneously. For example, with the Langmuir model used recently, all the R^2 values obtained are very low (see Figures 3b, 3d and 3f), meaning that the relationship between the x and y axes is not linear if all data are used at once (10–130 mg/L) (Tabassum et al., 2024). If the data is partitioned



Figure 3. Linear plot ($C_e vs C_e/q_e$) of Langmuir adsorption isotherm for KCS-1with scatter (a), KCS-1 with regression line (b), KCS-2 with scatter (c), KCS-2 with regression line (d), KCS-3 with scatter (e), and KCS-3 with regression line (f). Dashed line at scatter curve is a guide for eyes.

into two groups, the low concentration group (10–50 mg/L) will have a linear trend. However, it is impossible for this data group to follow the Langmuir model, because the slope of the line is negative, meaning that the adsorption capacity value is negative, which is impossible (Al Awadi et al., 2022). For the high group (75–130 mg/L) it also looks linear, and most likely follows the Langmuir model because the slope of the line is positive or in other words the adsorption capacity is positive (Jasri et al., 2023).

The phenomenon is clarified as follows. The whole sequences of MB adsorption onto the active site (or sites) of the pore surface of KCS can be simply explained by an adsorption model that the process is divided into three steps as shown in Figure 4. The first step is mass transfer of MB molecule from the bulk solution down into the external surface of the KCS adsorbent. Then, the *next* is diffusion of MB molecule from the pore mouth down into the area that is close to the active site, and the last one is adsorption of MB molecules onto the active site (or sites) of the internal pore surface (Lin et al., 2008). To complete the explanation for the existence of two tendency groups, the single gas DPL (Dual-Process Langmuir) model can also be applied (Ritter et al., 2011). The model describes that the amount adsorbed of a single gas or a single adsorbate on a heterogeneous adsorbent that is consisted of two homogeneous but energetically different sites depends only on the saturation capacity and affinity parameter of each sites (Do et al., 1999). The adsorption will take place until a pore is saturated, and the process will move to other site (or sites) (Garcia-Zubiri et al., 2009). The process depends strongly on the saturation capacity and affinity parameter. It is possible that adsorption mechanism in pore 1 will be different in pore 2 (Fig. 4). In this study we only want to show the possibility of these two groups of tendencies can occur, and discuss the data obtained with the selected isothermal model.

Complete data analysis using four adsorption isotherms (Langmuir, Freundlich, Dubinin-Radushkevich and Temkin) for the KCS-1 adsorbent is given in Figures 5–8. Data analysis for the remaining adsorbents (KCS-2 dan KCS-3) is given in the Supplementary Data section.

In Figure 5(a), as explained previously, a linear line with R^2 is quite large (0.9871), which means the relationship between the x and y axes is indeed linear. However, the gradient of the line obtained is negative, which means that the maximum adsorption capacity (q_m) is also negative, which is impossible (Tabassum et al., 2024). Therefore, we conclude that in the low concentration range (10–50 mg/L), KCS-1 does not follow the Langmuir adsorption model, but follows one of the others, whether Freundlich, Dubinin-Radushkevich or Temkin.

In the high concentration range (75-130 mg/L), the R² coefficient of the line obtained is very large (0.9959). The gradient of the line obtained is positive, so the adsorption capacity will be positive too. Thus, in the high concentration range, KCS-1 follows the Langmuir isothermal adsorption model. This is what we call "the dual adsorption isothermal model"; where an adsorbent experiences two adsorption models if it interacts with an adsorbate at a certain concentration (Ritter et al., 2011).

For Figure 6, these two concentration ranges can be categorized as following the Freundlich adsorption model because the R² values are large (0.9337 and 0.9766). However, it is necessary to calculate the values of K_F (Freundlich's constant) and n. As n is a function of the strength of adsorption, adsorption becomes more beneficial with the



Figure 4. Model for sequences of MB adsorption on KCS adsorbent from aqueous solution



Figure 5. Linear Langmuir plot for KCS-1 at initial MB concentration range of 10–50 mg/L (a), and 75–130 mg/L (b)

increasing value of n (Dasgupta et al., 2016). The classification for n value is 2–10: good adsorption; 1–2: good adsorption; and less than 1: very poor adsorption (Iqbal et al., 2017).

It's theoretically possible for an adsorbent to exhibit Freundlich-like behavior at both low and high concentration ranges, but with different equation parameters. K_f and n can vary depending on the surface characteristics and adsorption mechanism (Tabassum et al., 2024).

At low concentrations, multilayer adsorption on a heterogeneous surface can lead to Freundlich behavior. At high concentrations, even if the surface becomes saturated and monolayer adsorption dominates, the heterogeneity of the surface can still result in a Freundlich-type isotherm, but with different K_f and n values. The change in parameters reflects the shift in adsorption mechanism and the varying influence of surface heterogeneity at different concentration ranges (Lin et al., 2008). This discusses the empirical nature of the Freundlich equation and its applicability to heterogeneous surfaces (Zheng at al., 2024). Freundlich isotherm might fail at high pressures, which can be related to the limitations of the model at high concentrations (Lin et al., 2008). Theoretical interpretation of the Freundlich isotherm is linking it to molecular size and equilibrium constants. These sources highlight the flexibility of the Freundlich isotherm and its potential to describe adsorption behavior across different concentration ranges, even with varying parameters.

Determination of the maximum adsorption capacity (q_m) can be obtained through a linear D-R plot, in addition to the Langmuir model, depending on the R² value and the trend of the line obtained. The R² values obtained for both concentration ranges are quite good, so this D-R plot can be used to calculate the q_m value of the adsrobent.

The value of R^2 at low concentration range is also low means the Temkin isotherm is not suitable at low concentration, while at high concentration the trend is good.

The Temkin isotherm model is used to describe the adsorption processes where the heat of adsorption of all molecules in the layer decreases linearly



Figure 6. Linear Freundlich plot for KCS-1 at initial MB concentration range of 10–50 mg/L (a), and 75–130 mg/L (b)



Figure 7. Linear D-R plot for KCS-1 at initial MB concentration of 10-50 mg/L (a), and 75-130 mg/L



Figure 8. Linear Temkin plot for KCS-1 at initial MB concentration of 10–50 mg/L (a), and 75–130 mg/L (b)

with coverage due to adsorbent-adsorbate interactions (Tabassum et al., 2024). It can be elaborated on the statistical and mechanical aspects of this model, highlighting its consideration of both lateral interaction between adsorbed molecules and energetic surface heterogeneity. Unlike the Langmuir isotherm, which assumes a constant heat of adsorption, the Temkin isotherm accounts for the decrease in heat of adsorption as more molecules are adsorbed. This makes it more suitable for systems where adsorbate-adsorbate interactions are significant. It's often applied in gas-phase adsorption studies, particularly on heterogeneous surfaces (Fahmi et al., 2019). In a broader context, including its use in thermodynamics and moisture sorption. However, the Temkin isotherm specifically addresses adsorption phenomena.

The data of all Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isothermal linear plot for KCS-1, KCS-2 and KCS -3 are then tabulated or summarized in the Table 2.

From the data in Table 2, it can be concluded that at low concentrations (10–50 ppm) the KCS-1, KCS-2 and KCS-3 materials tend to follow the Freundlich isothermal based on the R² values obtained. Meanwhile, at high concentrations, KCS-1 and KCS-3 follow the Langmuir pattern, while KCS-2 still follows the Freundlich pattern. This is what we call a discovery which states that a material can experience two adsorption models at once.

Freundlich adsorption at low initial concentration followed by Langmuir adsorption at high initial concentration is less common than the reverse (Lin et al., 2008). It's theoretically possible for a material to exhibit Freundlich isotherm behavior at lower concentrations followed by Langmuir isotherm behavior at higher concentrations, although this scenario is unusual (Ritter et al., 2011; Rashidi et al., 2019).

It could be happen, as below:

 Cooperative adsorption – if the adsorption process involves cooperative binding, where the binding of one adsorbate molecule facilitates the binding of subsequent molecules, you might initially observe Freundlich behavior. As more molecules adsorb, the cooperative effect could lead to the formation of a more ordered, monolayer-like structure, resembling Langmuir behavior at higher concentrations. This would require specific interactions between adsorbate molecules (Tabassum et al., 2024).

Initial MB concentration (mg/L)	Isothermal model	Parameter	Value for KCS1	Value for KCS2	Value for KCS3
		q _{max} (mg/g)	-1.252	-0.2605	-1.5972
	Langmuir	K (L/mg)	-2.957	-4.954	-3.401
		R ²	0.9871	0.9781	0.8618
10–50 ppm	Freundlich	K _f (mg/g)	2947	1 x 10 ¹⁴	2705
		n	0.21	0.055	0.243
		R ²	0.9337	0.8653	0.9080
	D-R	β_{DR}	3 × 10 ⁻⁷	1 × 10 ⁻⁶	2 × 10 ⁻⁷
		q _{max} (mg/g)	528.16	8.16 x 10 ¹⁰	385.6
		R ²	0.921	0.7673	0.9059
	Temkin	A (unitless)	26.478	97.121	23.523
		K _τ (L/mg)	4.7215	5.5783	5.8964
		b (kJ/mol)	93.526	25.4979	105.275
		R ²	0.7329	0.6356	0.7639
	Langmuir	q _{max} (mg/g)	37.59	178.57	39.37
		K (L/mg)	3.167	0.5657	4.305
		R ²	0.9959	0.2110	0.9705
		K _f (mg/g)	28	71	34
	Freundlich	n	3.3	1.2	2.8
		R ²	0.9766	0.9241	0.7468
75–130 ppm	D-R	β_{DR}	4 × 10 ⁻⁸	5 × 10 ⁻⁸	5 × 10 ⁻⁸
		q _{max} (mg/g)	32.87	54.01	39.04
		R ²	0,9814	0.8958	0.9162
		A (unitless)	7.6322	20.626	8.8672
	Tomkin	K _T (L/mg)	39.5452	11.91	37.273
	Iemkin	b (kJ/mol)	324.4648	120.061	279.27
		R ²	0.9863	0.8963	0.8463

Table 2. Linear isotherm constant and regression coefficient values for Langmuir, Freundlich, D-R and Temkin

- Surface reconstruction in some cases, the surface of the material might undergo structural changes upon adsorption. At low concentrations, the surface could be heterogeneous, leading to Freundlich behavior. As the surface coverage increases, the adsorbate might induce a rearrangement of surface atoms, creating a more homogeneous surface that favors Langmuir-type adsorption at higher concentrations (Lin et al., 2008).
- Pore filling if the material has a complex pore structure with a wide range of pore sizes, the smaller pores might fill first at lower concentrations, exhibiting Freundlich behavior due to the variety of adsorption sites. As the concentration increases, the larger pores, which might have more uniform surfaces, begin to fill, leading to a transition to Langmuir behavior (Ritter et al., 2011).

It's important to note that these scenarios are less common than the typical transition from Langmuir to Freundlich behavior. Observing such a phenomenon would require careful experimental investigation and analysis to confirm the underlying mechanisms. The specific adsorbateadsorbent interactions and the nature of the material's surface play a crucial role in determining the observed adsorption behavior (Lin et al., 2008).

To compare the maximum adsorption capacity (q_m) in the low MB concentration range (10–50 ppm) D-R isothermal data is used. The respective values for KCS-1 and KCS-3 are 529.16, 385.6 mg/g. The q_m value for KCS-2 is very high. In the high concentration range (75–130 ppm), the q_m values for KCS-1, KCS-2 and KCS-3 are 32.87, 54.01 and 39.04, respectively.

In general, it can be said that additional treatment on the result of the HTC method can

improve carbon quality. In this research, it was found that chemically activated HTC products would produce maximum adsorption capacity with the greatest value.

Surface textural properties of HTC

Spesicific surface area analysis

The surface area and porosity of KCS adsorbent have an important effect on adsorption perfromance (Tabassum et al., 2024). Table 3 presents the achieved BET surface area, pore volume and average pore size diameter of KCS.

BET surface area, pore size diameter and pore volume of the KCS material is shown in Table 3. The classification of KCS pores is confirmed with regulation established by IUPAC (International Union of Pure and Applied Chemistry). Pores with diameter < 2 nm, 2–50 nm and > 50 nm are assigned as micropores, mesopores and macropores, respectively. Nanoporous materials show pore diameters that are most appropriately quantified using units of nanometers. The diameter of pores in nanoporous materials is thus typically less than 100 nanometers, thus our KCS materials are classified as nanopore size materials with average pore diameter 5.23– 13.73 nm (Jasri et al., 2023).

The specific surface area of the KCS shows an average surface area of 9.08–32.21 m²/g, which is beneficial for the adsorption of MB molecules. The KCS's pore volume is between 0.02-0.04 cm³/g, while the average pore diameter of 5.23-13.73 nm demonstrate that the structure is mesoporous, which provides to the diffusion of MB molecules into the KCS pores as described in Figure 4. Importantly, the molecular size of MB is 0.7 nm (Tabassum et al., 2024). Accordingly, it is appropriate into the pores of KCS during adsorption and can make the KCS an acceptable material for adsorption applications. Although the surface area is not specifically high, research by Chaukura et al. and El Badawi et al. shows that porous materials with similar surface areas can carry out well in dye adsorption due to the availability of pores (Chaukura et al., 2017; Badawi et al., 2014).

Based on the results of the BET analysis in Table 3, it can be seen that KCS-2 has the largest surface area. This supports the result of this research that the maximum adsorption capacity is possessed by KCS-2.

Fourier transform infra red analysis

An infrared absorption peak of KCS-1 adsorbent (Figure 9) at 2355 cm⁻¹ typically corresponds to the stretching vibration of carbon dioxide (CO₂). The presence of IR spectra with peaks around 1701 cm⁻¹ and 1512 cm⁻¹ related to C=O bonds and carboxylate anions. Since the source of KCS-1 is palm kernel shell-based carbon through HTC, the presence of CO₂ could indicate there is residual gas trapped within the porous structure of the material or adsorbed on its surface. Further analysis and comparison with reference spectra would be necessary to confirm the identity of the peak. Peak at 3381 cm⁻¹ in an infrared spectrum typically indicates the presence of O-H stretching vibrations, often associated with hydroxyl groups in alcohols or phenols. It could also arise from N-H stretching in amines or amides. The presence of hydroxyl groups on the carbon surface is preferable for MB adsorption. An infrared absorption peak of KCS-1 at 2912 cm⁻¹ typically corresponds to C-H stretching vibrations, specifically those associated with aliphatic (straight-chain) CH₂ groups. Since KCS-1 is derived from organic material, the presence of aliphatic CH₂ groups is expected. These groups are common in the cellulose and lignin components of plant biomass.

Peak at 2355 cm⁻¹ in KCS-2 spectrum is disappeared. This might be because the chemical activation with KOH after HTC of PKS. Activation with KOH will remove CO_2 gas which exists in the pore. The peak at 3423 cm⁻¹ in an infrared spectrum most likely corresponds to the O-H stretching vibration of hydroxyl groups. These groups can be present

Table 3. BET surface area, pore volume and average pore size diameter of the KCS

Adsorbent	Specific surface area (m³/g)	Pore volume (cm ³ /g)	Average pore diameter (nm)					
KCS-1	11.75	0.04	13.73					
KCS-2	32.21	0.04	5.23					
KCS-3	9.08	0.02	7.66					



Figure 9. Results of FTIR analysis

in various forms, including alcohols, phenols, and adsorbed water. There is no N-H stretching in amines or amides for KCS-2 material compared to KCS-1. The infrared peak at 2902 cm⁻¹ is likely due to C-H stretching vibrations, specifically from aliphatic CH₂ groups; just like peak at 2912 cm⁻¹ for KCS-1.

A peak at 3421 cm⁻¹ in an infrared spectrum of KCS-3 is highly characteristic of O-H stretching vibrations, typically associated with hydroxyl groups. These hydroxyl groups can be present in various forms, including alcohols, phenols, or even adsorbed water molecules. This peak is almost the same with KCS-2, therefor the chemical properties of KCS-2 and KCS-3 is almost the same. The maksimum adsorption capacity (qm) of KCS-2 and KCS-3 is almost the same higher than KCS-1. The peak at 2899 cm⁻¹ in an infrared spectrum is likely attributed to C-H stretching vibrations, specifically those associated with aliphatic (straight-chain) CH₂ groups. This peak is similar to KCS-1 and KCS-2. A peak at 1610 cm⁻¹ in an infrared spectrum often indicates the presence of C=C stretching vibrations, typically associated with aromatic rings or conjugated double bonds. Peak at finger print area for all KCS-1, KCS-2 and KCS-3 is almost the same (Mozhiarasi et al., 2024).

The results of FTIR analysis show that the functional groups of the three HC PKS are all almost the same, so it is likely that the adsorption capacity is only influenced by the surface area of the carbon (Mozhiarasi et al., 2024; Musa et al., 2024).

CONCLUSIONS

Hydrothermal carbon from palm kernel shell has been prepared from palm kernel shell and we employed the carbon on the removal of MB in the water treatment. Maximum adsorption capacity was determined based on adsorption isotherm. Four adsorption isotherms (Langmuir, Freundlich, Dubinin-Raduskevich and Temkin) were used to analyze the adsorption experiment results. The HC PKS can follow two isotherms simultaneously in MB adsorption. At low MB concentrations (10-50 ppm), HC PKS follows the Freundlich isothermal, while at high concentrations (75-130 ppm) HC PKS can also follow the Langmuir isothermal besides Freundlich. Isothermal D-R was used to determine the qm of HC PKS where it was found that HC PKS with chemical activation treatment after HTC (KCS-2) had the largest qm (54.01 mg/g). The surface area of KCS-2 is 32.21 m³/g, the largest among HC PKS. This indicates that activation treatment after HTC is important to improve the carbon quality of KCS. The results of FTIR analysis show that the functional groups for all HC PKS are almost similar.

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REFERENCES

- Al Awadi, A.S., Harbawi, M.E., Algarawi, A., Alalawi, A., Elblidi, L., Alrashed, M.M., Yin, C.Y. (2022). Synthesis of carbon microspheres via hydrothermal carbonization of Sabal palms (Sabal palmetto) biomass for adsorption of methylene blue. *Biomass Conversion and Biorefinery*, 13, 16942–16953. https://doi.org/10.1007/s13399-021-02212-3
- Ameen, M., Zamri, N.M., May, S.T., Azizan, M.T., Aqsha, A., Sabzoi, N., Sher, F. (2022). Effect of acid catalysts on hydrothermal carbonization of Malaysian oil palm residues (leaves, fronds, and shells) for hydrochar production. *Biomass Conversion and Biorefinery*, 12, 103–114. https://doi.org/10.1007/ s13399-020-01201-2
- Baby, R., Hussein, M.Z., Zainal, Z., Abdullah, A.H. (2023). Preparation of Functionalized Palm Kernel Shell Bio-adsorbent for the treatment of

heavy metal-contaminated water. *Journal of Haz-ardous Materials Advances*, 10, 100253. https://doi.org/10.1016/j.hazadv.2023.100253

- Baffour-Awuah, E., Akinlabi, S.A., Jen, T.C., Hassan, S., Okokpujie, I.P., Ishola, F. (2021). Characteristics of Palm Kernel Shell and Palm Kernel Shell-Polymer Composites: A Review. *IOP Conference Series: Materials Science and Engineering*, 1107, 012090. https://doi.org/10.1088/1757-899X/1107/1/012090
- Badawi NE, Ramadan AR, Esawi AMK, Morsi ME (2014) Novel carbon nanotube– cellulose acetate nanocomposite membranes for water filtration applications. *Desalination*, 344, 79–85. https://doi. org/10.1016/j.desal.2014.03.005
- Bampenrat, A., Sukkathanyawat, H., Jarunglumlert, T. (2023). Agro-industrial waste upgrading via torrefaction process – a case study on sugarcane bagasse and palm kernel shell in Thailand. *Journal of Ecological Engineering*, 24(3), 64–75. https://doi. org/10.12911/22998993/157423
- Brandani, S. (2024) On adsorption azeotropy and a classification based on the dual site Langmuir isotherm. *Adsorption*, 30, 1593 – 1601. https://doi. org/10.1007/s10450-023-00430-x
- Chaukura, N., Murimba, E.C., Gwenzi, W. (2017). Synthesis, characterisation and methyl orange adsorption capacity of ferric oxide–biochar nanocomposites derived from pulp and paper sludge. *Applied Water Science*, 7, 2175–2186. https://doi. org/10.1007/s13201-016-0392-5
- Dasgupta, J., Kumar, A., Mandal, D.D., Mandal, T., Datta, S. (2016). Removal of phenol from aqueous solutions using adsorbents derived from low-cost agro-residues. *Desalination and Water Treatment*, 57, 14188–14212. https://doi.org/10.1080/194439 94.2015.1061455
- 10. Directorate of Food Crops, (2022), Indonesian Oil Palm Statistics 2022, ISSN 1978-9947, BPS-Statistics Indonesia. https://www.bps.go.id/en/pub lication/2023/11/30/160f211bfc4f91e1b77974e1/ indonesian-oil-palm-statistics-2022.html
- Do, D., Do, H. (1999). On the Azeotropic Behaviour of Adsorption Systems. *Adsorption*, 5, 319–329. https://doi.org/10.1023/A:1008944329330
- Fahmi, A.G., Abidin, Z., Kusmana, C., Kharisma, D., Prajaputra, V., Rahmawati, W.R. (2019) Preparation and Characterization of Activated Carbon from Palm Kernel Shell at Low Temperature as an Adsorbent for Methylene Blue. *IOP Conference Series: Earth and Environmental Science*, 399, 012015. https://doi.org/10.1088/1755-1315/399/1/012015
- García-Zubiri, I.X., González-Gaitano, G., Isasi, J.R. (2009). Sorption models in cyclodextrin polymers: Langmuir, Freundlich, and a dual-mode approach. *Journal of Colloid and Interface Science*, 337(1), 11–18. https://doi.org/10.1016/j.jcis.2009.04.071

- 14. Hakim, L., Rahayu, A., Jamilatun, S., Sisca, V., Fajri, J.A. (2025). Integrating ammonium-based polymer with phytoremediation for phosphate and chemical oxygen demand reduction in palm oil mill effluent. *Journal of Ecological Engineering*, 26(1), 46–58. https://doi.org/10.12911/22998993/195213
- Iqbal, M.Z., Shoaib, P.M., Abdala, A. (2017). Efficient removal of different basic dyes using graphene. *Desalination and Water Treatment*, 68, 226–235. https://doi.org/10.5004/dwt.2017.20213
- 16. Jasri, K., Abdulhameed, A.S., Jawada, A.H., Al Othmand, Z.A., Yousef, T.A., Duaji, O.K.A. (2023) Mesoporous activated carbon produced from mixed wastes of oil palm frond and palm kernel shell using microwave radiation-assisted K₂CO₃ activation for methylene blue dye removal: Optimization by response surface methodology. *Diamond & Related Materials*, 131, 109581. https://doi.org/10.1016/j. diamond.2022.109581
- John, J.F., Jagannathan, M., Rajendran, A.R. Mohanapriya, P., Natarajan, T.S., Dhinasekarana, D. (2022). Sustainable multilayer biomass carbon and polymer hybrid column as potential antibacterial water filter. *Chemosphere*, 286, 131691. https://doi.org/10.1016/j.chemosphere.2021.131691
- 18. Li, T., Remón, J., Shuttleworth, P.S., Jiang, Z., Fan, J., Clark, J.H., Budarin, V.L. (2017). Controllable production of liquid and solid biofuels by dopingfree, microwave-assisted, pressurised pyrolysis of hemicellulose. *Energy Conversion and Management*, 144, 104–113. https://doi.org/10.1016/j. enconman.2017.04.055
- Lin, C.I., Wang, L.H. (2008). Rate equations and isotherms for two adsorption models. *Journal of the Chinese Institute of Chemical Engineers*, 39, 579– 585. https://doi.org/10.1016/j.jcice.2008.04.003
- 20. Ma, L., Wei., W., Sun, F., Shi, Y. (2022). Research on formation mechanism of typical low-temperature fouling layers in biomass-fired boilers. *Case Studies in Thermal Engineering*, 35, 102076. https://doi. org/10.1016/j.csite.2022.102076
- 21. Mahdi, H.H., Saleh, A.M., Alias, A.B., Jawad, A.H., Salman, S.D., Qarizada, D., Mostafa, M.M., Saleh, N.M., Abdulqader, M.A. (2024). Synthesis and characterization of xerogel derived from palm kernel shell biochar and comparison with commercial activated carbon. *Journal of Ecological Engineering*, 25(6), 1–11. https://doi.org/10.12911/22998993/183719
- 22. Mahmud, M., Hossain, M.S., Mobarak, M.B., Quddus, S., Bashar, M.S., Akhter, U.S., Jahan, S.A., Islam, D., Ahmed, S. (2022). Engineering GO@Zn– Hap@CA porous heterostructure for ultra-fast and ultra-high adsorption efficacy: investigation towards the remediation of chromium and lead. *Environmental Sciences: Advances*, 1(5), 827–848. https://doi. org/10.1039/D2VA00142J

- 23. Mannarino, G., Sarrion, A., Diaz, E., Gori, R., Rubia, M.A.D., Mohedano, A.F. (2022). Improved energy recovery from food waste through hydrothermal carbonization and anaerobic digestion. *Waste Management*, 142, 9–18. https://doi.org/10.1016/j. wasman.2022.02.003
- 24. Menyaa, E., Jjagweb, J., Kalibbalac, H.M., Storzd, H., Olupotb, P.W. (2023). Progress in deployment of biomass-based activated carbon in point-of-use filters for removal of emerging contaminants from water: A review. *Chemical Engineering Research and Design*, 192, 412–440. https://doi.org/10.1016/j. cherd.2023.02.045
- 25. Misnon, I.I., Zain, N.K.M., Aziz, R.A., Vidyadharan, B., Jose, R. (2015). Electrochemical properties of carbon from oil palm kernel shell for high performance supercapacitors. *Electrochimica Acta*, 174, 78–85. http://dx.doi.org/10.1016/j.electacta.2015.05.163
- 26. Monedero, E., Pazo, A., Collado, R., Oscar J. Dura, O.J., Herna ndez, J.J. (2024). Analysis of fouling in domestic boilers fueled with non-woody biomass. *Renewable Energy*, 226, 120459. https://doi. org/10.1016/j.renene.2024.120459
- 27. Mozhiarasi, V., Natarajan, T.S. (2024). Bael fruit shell-derived activated carbon adsorbent: effect of surface charge of activated carbon and type of pollutants for improved adsorption capacity. *Biomass Conversion Biorefinery*, 14, 8761–8774. https://doi. org/10.1007/s13399-022-03211-8
- 28. Musa, S.A., Abdulhameed, A.S., Baharin, S.N.A., ALOthman, Z.A., Selvasembian, R., Jawad, A.H. (2024). Pyrolyzed coal base high surface area and mesoporous activated carbon for methyl violet 2B dye removal: Optimization of preparation conditions and adsorption key parameters. *Chemical Engineering Research and Design*, 205, 67–78. https:// doi.org/10.1016/j.cherd.2024.03.015.
- 29. Owsianiak, M., Ryberg, M.W., Renz, M., Hitzl, M., Hauschild, M.Z. (2016). Environmental performance of hydrothermal carbonization of four wet biomass waste streams at industry-relevant scales. ACS: Sustainable Chemistry & Engineering, 4, 6783–6791. https://doi.org/10.1021/ acssuschemeng.6b01732
- 30. Pecchi, M., Marco Baratieri, M., Goldfar, J.L., Maag, A.R. (2022). Effect of solvent and feedstock selection on primary and secondary chars produced via hydrothermal carbonization of food wastes. *Bioresource Technology*, 348, 126799. https://doi. org/10.1016/j.biortech.2022.126799
- Petrovich, J., Ercegovic, M., Simic, M., Kovrivica, M., Dimitrijevic, J., Jovanovic, A., Pantic, J.J. (2024). Hydrothermal carbonization of waste biomass: A review of hydrochar preparation and environmental application. *Processes*, 12, 207. https://

doi.org/10.3390/pr12010207

- 32. Rashidi, N.A., Yusup, S. (2019). Production of palm kernel shell-based activated carbon by direct physical activation for carbon dioxide adsorption. *Environmental Science and Pollution Research*, 26, 33732–33746. https://doi.org/10.1007/ s11356-018-1903-8
- 33. Ritter, J.A., Bhadra, S.J., Ebner, A.D. (2011). On the use of the dual-process langmuir model for correlating unary equilibria and predicting mixed-gas adsorption equilibria. *Langmuir*, 27, 4700–4712. https://doi.org/10.1021/la104965w
- 34. Sevilla, M., Fuertes, A.B. (2011). Sustainable porous carbons with a superior performance for CO₂ capture. *Energy & Environmental Science*, 4, 1765–1771. https://doi.org/10.1039/C0EE00784F
- 35. Soffian, M.S., Halim, F.Z.A, Aziz, F., Rahman, M.A., Amin, M.A.M., Chee, D.N.A. (2022). Carbon-based material derived from biomass waste for wastewater treatment. *Environmental Advances*, 9, 100259. https://doi.org/10.1016/j.envadv.2022.100259
- 36. Tabassum, N., Anjum, R., Haque, P., Hossain, M.S., Mobarak, M.B., Quddus, M.S., Chowdury, F., Rahman, L., Islam, D., Ahmed, S., Mahmud, M. (2024). Ag–Co ferrite-based magnetic polymeric composite film: a breakthrough in cationic dye remediation for

sustainable environment. *RSC Advances*, 14, 36557. https://doi.org/10.1039/d4ra06315e

- 37. Wang, Q., Wu, S., Cui, D., Pan, S., Xu, F., Xu, F., Wang, Z., Li, G. (2022). Co-hydrothermal carbonization of corn stover and food waste: Characterization of hydrochar, synergistic effects, and combustion characteristic analysis. *Journal of Environmental Chemical Engineering*, 10, 108716. https://doi.org/10.1016/j.jece.2022.108716
- Yu, S., Yang, X., Li, Q., Zhang, Y., Zhou, H. (2023). Breaking the temperature limit of hydrothermal carbonization of lignocellulosic biomass by decoupling temperature and pressure. *Green Energy & Environment*, 8, 1216 – 1227.
- 39. Zaini, M.S.M.Z., Arshad, M., Hassan, S.H.A.S. (2023). Adsorption Isotherm and Kinetic Study of Methane on Palm Kernel Shell-Derived Activated Carbon. *Journal of Bioresources and Bioproducts*, 8, 66–77. https://doi.org/10.1016/j.jobab.2022.11.002
- 40. Zheng, C.Z., Niu, Y., Wang, C., Hu, J., Kang, K., Song, H., Bai, S. (2024). Modeling of multitemperature Type I and II benzene/ammonia adsorption isotherms: Dual LF model and linearized DR model. *Separation and Purification Technology*, 338, 126246. https://doi.org/10.1016/j. seppur.2023.126246