Mechanistic insights into the adsorption of methylene blue by particulate durian peel waste in water

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ABSTRACT

This study aims to investigate the adsorption of methylene blue (MB) over particulate durian peel waste, which is chemically activated with hydrogen peroxide. The equilibrium data are well described by the Freundlich isotherm model, which indicates that the MB adsorption takes place predominantly on multilayers and heterogeneous surfaces of the biosorbent. The Freundlich adsorption constants, K F and n, are 11.06 L/g and 2.94, respectively. Thermodynamic data suggest that the MB adsorption occurs spontaneously and endothermically. The enthalpy and entropy for the MB adsorption are obtained as 10.26 kJ/mol and 0.058 kJ/mol K, respectively, in the temperature range of 303–323 K. Based on the stepwise desorption method, the adsorption of MB is dominated by physical interactions, particularly hydrogen bonding.

Key words: adsorption isotherms, adsorption mechanism, durian peel, hydrogen bonding, methylene blue

HIGHLIGHTS

• Durian peel waste is utilized as a biomass-derived sorbent for the removal of methylene blue in water.
• Chemical activation with hydrogen peroxide increases the removal efficiency.
• Surface carboxyl group plays a key role in the adsorption process.
• The adsorption process is primarily governed by physical interactions including hydrogen bonding and electrostatic interaction.
INDRODUCTION

Industrial activities show an important role in advancing the economy of a country. However, in addition to the benefits procured, industrial activities also have a negative impact on the environment if the waste is not handled properly (Yacout & Hassouna 2016). One type of waste that is mostly produced from industrial activities is liquid waste containing synthetic dyes, which are widely used in the textile, paper, rubber, plastic, food and other industries that involve coloring processes (Yacout & Hassouna 2016; Javaid & Qazi 2019; Lum et al. 2020; Nagajyothi et al. 2020). In developing countries, the color parameters of liquid wastes are mostly not specifically regulated (Nimkar 2018). Wastes still containing dyes cause environmental problems (Mostafa 2015). These consequences, in turn, affect the balance of the aquatic ecosystem. Therefore, an effective method for dye removal is required in order to minimize the contamination of liquid wastes containing dyes (Crini & Lichtfouse 2019).

One potential method for dye removal in the aqueous environment is biosorption (Asgher 2012; Kandisa et al. 2016). This process essentially contacts the dye contaminant with an adsorbent from lignocellulosic materials (biosorbents). The spent biosorbent can be degraded through a solid substrate fermentation. The fermented biomass, which is rich in protein due to the presence of fungi and various other microorganisms, can then be used as a soil conditioner. Compared to techniques such as membrane separation, oxidation, and irradiation, adsorption processes have been known as the most economically favorable technique for eliminating recalcitrant organic contaminants in water environment (Tran et al. 2017c).

Although the production cost is relatively low when compared to commercial adsorbents, biosorbents still have a fundamental drawback. Their adsorption capacity is not as good as that of commercial adsorbents. One way to increase the
adsorption ability of a biosorbent is to modify it (often termed an activation process) through physicochemical treatments, so that it changes the material properties that are related to its capability to adsorb an adsorbate (Gautam et al. 2014).

Several wastes or biomasses of agricultural by-products have been used as biosorbents either directly or through the activation processes prior to use (Benis et al. 2020). Rice husks (Bazargan et al. 2014), corn cobs (Peña-Fiel et al. 2020), peanut shells (Liu et al. 2018) and jackfruit skin (Akpomie & Conradie 2020) are some of the biomasses studied for water decontamination through the adsorption process. Several reviews on the utilization of agricultural by-products to remove recalcitrant compounds in the water environment are available for closer inspection (de Freitas et al. 2019; Akpomie & Conradie 2020; Bagotia et al. 2020). Other biobased materials such as fungi and algae have also been used as efficient sorbents removing contaminants from water. For instance, the usability of nonliving lichen Pseudevernia furfuracea (L.) Zopf. has been evaluated for the removal of methylene blue from water. Even without any modifications, the biomass can remove up to 60% of dye within 140 min at pH 10 (Koyuncu & Kul 2020). In fact, another class of adsorbent materials, which are inorganic sorbents such as zeolite, has long been known to be applicable for removing refractory organic contaminants from water with appreciable efficiency. The removal efficiency is typically close to 100% at the optimum operating conditions (Majid et al. 2019).

Another agricultural waste that can potentially be used as a biosorbent is durian (Durio zibethinus Murray) peel. Most of the durian fruit has the part that readily becomes waste. To increase the added value of the generated waste, one alternative is to use it as a biosorbent. Utilization of durian peel waste as a biosorbent will overcome two problems at once: (i) reducing the volume of durian peel waste itself, and (ii) eliminating the water contaminant when being used as an adsorbent. Durian peel has been reported to show promising performance for removing a number of contaminants, including metal cations such as Zn\(^{2+}\) (Ngabura et al. 2018) and Cd\(^{2+}\) (Kaewsarn 2010), as well as synthetic dyes such as methyl violet (Dahri et al. 2015a) and brilliant green (Dahri et al. 2015b).

Based on the rationale mentioned above, this study investigates the use of durian peel as a biosorbent. After preparation and chemical activation with an oxidizing agent, namely hydrogen peroxide (H\(_2\)O\(_2\)), the chemically activated durian peel is used as an adsorbent for removing the textile dye methylene blue (from this point forwards abbreviated as MB) in water. MB is chosen as a model water contaminant since it has been being largely used in the textile industry, a typical industry in developing countries (Moorthy et al. 2021). MB has been found to cause detrimental effects to the central nervous system (Vutskits et al. 2008; Gillman 2011). The contamination of MB and other dye molecules is visually easy to observe in water bodies, despite being present at low concentrations. Apart from being aesthetically unfavorable, the presence of MB in the water environment also negatively affects the aquatic life, such as a reduced level of visibility that inhibits the penetration of sunlight into water bodies and interferes with the photosynthetic activities of various biota (Contreras et al. 2019). In addition, MB is commonly used as a model contaminant when evaluating newly developed sorbent materials, and therefore, enables straightforward performance comparisons.

One of the novelties in the present study is the proposed stepwise desorption method. This simple method is potentially applicable to a diverse range of adsorption systems, which involve adsorption of molecular adsorbates onto biomass-derived adsorbents, for elucidating the individual contribution of adsorbate-adsorbent interactions. Once the primary interaction between the adsorbate and the adsorbent is known, enrichment of certain functional groups at the adsorbent surface can then be properly performed to increase the affinity of the adsorbent towards a specific adsorbate.

**MATERIALS AND METHODS**

For preparing the biosorbent, durian peel was first washed with tap water to remove dirt particles, cut into small pieces (± 1 cm), and washed again using distilled water. The cut peels were ground into powder and sieved with a size of -20 + 50 mesh (279 μm < Ø < 864 μm), unless specified otherwise. Furthermore, 50 g of the peel powder was soaked in 600 mL of distilled water at its boiling point for 30 min, rinsed with running distilled water, and then dried in an oven at 80 °C for 24 h. Activation with an oxidizing agent, which is H\(_2\)O\(_2\) (Merck), was performed. The peel powder (5 g) was put into a closed glass vessel together with 200 mL of H\(_2\)O\(_2\) 1 M. The vessel was shaken in a shaking water bath at 90 rpm at 60 °C for 4 h. The soaked powder was filtered, washed with distilled water, and dried in an oven at 80 °C for 24 h. The final products were stored in desiccator for further uses. Details of the surface chemistry characterization, isotherm modeling, and the determination adsorption mechanism are provided in the Supplementary Information.
RESULTS AND DISCUSSION

Surface chemistry

In this study, the Boehm titration method (Ben-Ali et al. 2017; Ren et al. 2019) is used to determine the number of acidic and basic functional groups present on the surface of the pristine durian peel biosorbent (DPB) and the chemically activated durian peel biosorbent (act-DPB). The results are summarized in Table 1. There is an increase in the quantity of acidic groups after chemical activation with H₂O₂. The increased quantity of acidic groups is presumably caused by an increase in the quantity of carboxylic, carboxylic and lactonic groups, because the quantity of phenolic groups decreases (Tran et al. 2017a, 2017c). The decrease in the quantity of phenolic groups, including basic groups, may be caused by oxidation of these functional groups to form carbonyl and carboxyl groups upon treatment with H₂O₂.

When the composition of the surface functional groups is altered, the electronic properties of the biosorbent surface is also changed (El Atouani et al. 2019). To clarify this supposition, pH at the zero-point charge (pH_{zpc}) is determined. pH_{zpc} is the pH when the surface of the active site is net uncharged (Silva et al. 2017). At pH_{zpc}, the total negative charge is proportional to the total positive charge. The pH_{zpc} can be determined by the pH drift method (Nasiruddin Khan & Sarwar 2007). The results are shown in Figure 1.

Figure 1 shows that the pH_{zpc} of act-DPB is lower than that of DPB, which means the basic groups' quantity decreases relative to the quantity of acidic groups. Note that the quantity of both basic and acidic groups could actually increase. After chemically activated, the quantity of carboxylic groups at the surface increases. At pH < 5.6, the surface of act-DPB is net positively charged. Meanwhile, at pH > 5.6, the surface is net negatively charged. Assuming that the electrostatic interaction-based mechanism plays a role in the adsorption process, MB as a cationic molecule is more easily adsorbed at pH > 5.6. Based on the pH_{zpc}, acidic groups dominate the surface of the active site. This finding is in agreement with the data shown in Table 1 that are based on the Boehm titration.

Moreover, it is found that the pristine biosorbent, DPB, shows much lower efficiency for the MB removal, which is 24% compared to 66% for act-DPB at identical experimental conditions. Therefore, only act-DPB is subjected to further evaluations. The enhancement mechanisms of MB removal efficiency following the chemical activation is discussed in the last part of this paper.

Table 1 | The quantity of functional groups on the surface of DPB and act-DPB (mEq/g)

| Sample   | Acidic functional groups | Acidic (total) | Basic |
|----------|--------------------------|----------------|-------|
|          | Carbonylic | Carboxylic | Lactonic | Phenolic | | |
| DPB      | 0.24        | 3.82      | 1.17     | 1.63     | 6.86 | 1.95 |
| act-DPB  | 0.39        | 5.73      | 1.21     | 1.45     | 8.78 | 1.74 |

Figure 1 | The pH drift curves of (●) DPB dan (○) act-DPB.
Effects of operating parameters

Contact time

The MB adsorption capacity was determined as a function of contact time to know the adsorption time and adsorption capacity when equilibrium is reached. The graph of the effect of contact time on the adsorption capacity of MB for the activated biosorbent is presented in Figure 2. Upon close inspection on the pattern of adsorption kinetics, it is indicated that the adsorption process takes place in several stages. In the first 25 min, adsorption is rapid, wherein the MB begins to leave the solvent; it diffuses through the solvent–solid interface, and is then bound to the active site on the outer surface of the sorbent particles. At this stage, MB also begins to enter the internal structure (macropores), and is bound to active sites on the outer surface. The fast adsorption process in this time span is due to the availability of active sites for binding (Tran et al. 2017b). Meanwhile, the appearance of a curve that is less smooth and continuous indicates a high degree of active site heterogeneity (Singh et al. 2018). This is not unexpected considering that particulate biomass contains various types of functional groups on the surface.

Furthermore, at the contact time between 25 min and 60 min, the adsorption took place more slowly, because the available active sites were decreasing and it was more difficult to be occupied by the MB molecules due to the steric hindrance of the previously bound MB molecules (Dhaouadi et al. 2020). In this time span, MB molecules also began to enter the mesoporous and microporous structures, in the interior of the cell wall of the biosorbent. In the next stage, due to the steric effect, the adsorption would proceed more slowly until it reaches equilibrium.

In general, equilibrium conditions are reached in a relatively short time (contact time ∼120 min). Possibly, this is because more adsorption takes place on the outer surface of the cell wall (Weber et al. 2013), after the mass transfer of MB through macropore structure (the middle lamella) rather than through the mesopores and micropores. Thus, it will not require a long process to reach equilibrium. On the one hand, a fast adsorption process is more advantageous. However, on the other hand, an adsorbent that possesses low porosity, which generally shows short equilibrium times, is less advantageous in terms of the large adsorption capacity factor. This is because the level of porosity is almost always directly proportional to the capacity of the adsorbent (Dhaouadi et al. 2020).

It is also seen that the appearance of the curve is not very smooth and continuous, indicating that the MB does not completely form a single layer on the surface of the active site. This is possible, as the sulfur atom of MB that carries a positive charge can not only interact with the active groups of the biosorbent, but can also interact with other partially negatively charged MB aromatic ring structures, forming a cation–aromatic π electron interaction. Although the steric barrier between MB molecules and the presence of the cation–π interaction are two contradictory factors, the possibility of the formation of these interactions still exists. This is understandable since the experimental findings observed are actually the net result of a combination of various factors that influence each other, which are often contradictory and competitive.

pH

In the adsorption system, the pH of the solution affects the charge of the active site and the level of ionization of the adsorbate (Anagnostopoulos & Symeopoulos 2013). H⁺ and OH⁻ ions can interact with the active site of the adsorbent, so that the
adsorption process of an adsorbate in the form of ions will be influenced by the solution pH. Furthermore, the dissociation of functional groups on the surface of the active site due to changes in pH will also affect the adsorption process (Mahmoodi et al. 2011). Therefore, it is very important to know the effect of pH on the adsorption ability of MB with act-DPB.

Figure 3 shows the effect of pH on the adsorption capacity of MB with act-DPB. The adsorption capacity increases with increasing pH. At low pH, the concentration of H⁺ in the solution is high. A high concentration of H⁺ results in competition between H⁺ and MB, which is also positively charged, to bind to the functional group at the active site. This high concentration of H⁺ also causes the functional groups at the active site to become positively charged, because the negatively charged and/or partially negatively charged ligand atoms in these functional groups are protonated. In addition, the nitrogen atoms in MB can also be protonated, so that the net positive charge of MB increases. These factors cause a repulsion effect when the MB begins to interact with the active site. Furthermore, as the pH increases, the concentration of H⁺ becomes smaller, so that the contribution of these effects also decreases. At a higher pH, the presence of OH⁻ with a greater concentration causes the active site to deprotonate and become negatively charged. The result is that the positively charged MB molecules will be more easily attracted to the functional groups on the deprotonated active sites.

At pH 3–5, the increase in the adsorption capacity appears quite significant, which then increases significantly until pH 7. This finding shows that in this pH range, a large H⁺ concentration greatly affects the chemical state of both the active site and MB, which in turn also affects the MB adsorption process, so that the decreased concentration of H⁺ can increase the adsorption capacity significantly. Noticeably, pHzpc is around 5.5, which is in agreement with the result of pHzpc using the pH drift method (Figure 1). Moreover, after pH 7, the increase in adsorption capacity is relatively small to nearly constant. Possibly this is due to the presence of OH⁻, which interacts with the sulfur atom in the positively charged MB molecule, so that the positive charge of the sulfur atom is reduced, thereby neutralizing the MB molecule. Due to the decrease in the net positive charge of MB, the affinity of MB for functional groups also reduces, which has implications for the reduced ability of the active site to bind to MB.

Temperature

To a certain extent, depending on the structural characteristics (type of functional group), temperature will affect the ability of the sorbent to adsorb MB (Kankılıç et al. 2016; Budnyak et al. 2020). This is because the type of functional group will determine the type of interaction, while the type of interaction will determine the adsorption ability. Each type of interaction will be affected by temperature in a different way, depending on its physicochemical properties. Therefore, in the adsorption system, there may be a linear relationship between the type of functional group, interaction type, adsorption ability and temperature. From the graph of the effect of temperature on the adsorption capacity of MB (Figure 4), it is seen that the adsorption capacity increases with increasing temperature.

The greater the adsorption capacity along with the increasing temperature, the more endothermic the adsorption process (Budnyak et al. 2020). In this case, the MB adsorption is dominated by relatively strong physical interactions (such as

![Figure 3](http://iwaponline.com/wst/article-pdf/84/7/1774/948475/wst084071774.pdf)
hydrogen bonds) with chemical interactions. It is also recognized that the higher the temperature, the more insignificant the adsorption capacity. This is because the higher the temperature, the greater the solubility of the MB and hence the stronger the interaction between the MB and the solvent molecule (H₂O) (Senthil Kumar et al. 2014). As a result, MB becomes more difficult to be adsorbed (although the collision frequency is greater).

**Particle size**

The relationship of the particle size effect on the adsorption capacity is shown in Figure 5. The adsorption capacity decreases as the particle size increases. This indicates that the external surface of the biosorbent plays a role in the adsorption process, which of course is closely related to its external surface area. For the same weight, the smaller the size of the biosorbent, the larger the external surface area. The larger the external surface area, the higher the number of active sites available for binding the adsorbates, so that the adsorption capacity is greater (Wong et al. 2008). However, in the present study, this effect did not appear to have a significant consequence, which means that the external surface of the biosorbent did not greatly contribute to the ability of the biosorbent to adsorb MB.

**Stirring speed**

The effect of stirring speed on the adsorption capacity of MB is shown in Figure 6. The adsorption capacity increases as the stirring speed increases. This is because the increase in stirring speed increases the frequency of collisions between MB and the biosorbent (Dotto & Pinto 2011), so that the possibility of MB being bound on the active site becomes greater. In addition,
stirring can also reduce the mass transfer resistance due to increased turbulence, so that it becomes easier for MB to diffuse into the internal structure of the biosorbent, which has smaller pores. However, the effect of increased stirring speed on the increase in adsorption capacity seems insignificant, because the stirring speed range is not too large in the present study.

**Biosorbent dosage**

The effect of biosorbent dosage on the adsorption capacity of MB is presented in Figure 7. The adsorption capacity decreases as the biosorbent dose increases. However, the actual amount of MB adsorbed increases (almost reaching 90% of the initial concentration). The increase in the amount of MB adsorbed along with the increasing amount of biosorbent added is probably due to the larger total surface area of the biosorbent, so that more active sites are available for binding MB (Hamzezadeh et al. 2020). Meanwhile, the decreased adsorption capacity could be attributed to the effectiveness of the active site in binding MB. The more biosorbent added, the more active sites are that are not used to bind MB. As a consequence, the number of MB bound per unit area (or per certain mass) becomes smaller. It can be said that the more biosorbent added, the lower the quantity of MB bound per unit area of the active site available for binding (Jawad & Abdulhameed 2020).

**Initial concentration of MB**

Figure 8 shows the effect of the initial concentration of MB on the adsorption capacity. The adsorption capacity becomes larger, but with the increasing initial concentration of MB, the percentage of MB removed becomes smaller. The larger
adsorption capacity, along with the increasing initial concentration of MB, provides a greater driving force for the MB adsorption (Liu et al. 2015).

However, the concentration effect shows the opposite effect on the adsorption efficiency, in which the percentage of MB removed is smaller as the initial concentration of MB increases. This is because the number of available active sites remains constant, while the number of MB molecules competing for the active sites is increasing (Ibupoto et al. 2018). The results are detrimental repulsions between MB molecules. The active site becomes saturated and the number of active sites for binding MB becomes increasingly limited, causing more MB to be left unadsorbed.

Adsorption equilibrium

Here, adsorption equilibrium data (the experimental data on the effect of initial MB concentration) are evaluated mainly using the Langmuir model and the Freundlich model, the two most commonly used isotherm models. Upon evaluating the adsorption equilibrium data, the equilibrium parameters can be obtained to describe the equilibrium conditions. Insights into the equilibrium conditions are necessary for process design.

Parameters in the Langmuir model, \( q_m \) and \( K_L \), are obtained by plotting \( C_e/q_e \) versus \( C_e \), as described in detail in the Supplementary Information. The value of \( q_e \) is calculated according to the experimental data on the effect of initial MB concentration (Figure 8). From the relationship of \( C_e/q_e \) versus \( C_e \) in Figure 9(a), the slope and the point of intersection with the y-axis can be taken to determine the Langmuir isotherm parameters, which are shown in Table 2. Compared to

Figure 8 | Effect of initial MB concentration on MB adsorption capacity of act-DPB (t = 80 min; W = 0.1 g; V = 0.1 L; T = 30 °C; \( v_{ag} = 90 \) rpm; pH = 7; \( \Theta = 381–447 \) µm).

Figure 9 | Linearized (a) Langmuir and (b) Freundlich isotherm equations.
other previously reported biosorbents that remove MB in water (Table 3), the maximum single layer adsorption capacity \( (q_m) \) of act-DPB exhibits a relatively large value, which is 90.9 mg/g.

Furthermore, the parameters in the Freundlich model, namely \( n \) and \( K_F \), are obtained by plotting log \( q_e \) versus log \( C_e \) (described in the Supplementary Information). From the plot of log \( q_e \) versus log \( C_e \) in Figure 9(b), the slope and the point of intersection with the y-axis are taken to obtain the Freundlich isotherm parameters, as presented in Table 2. The value of \( K_F \) is an indicator of adsorption capacity and \( n \) indicates the level of heterogeneity of the system. The \( K_F \) value of act-DPB is sufficiently large, up to 11.06 mg/g. Meanwhile, the large value of \( n \) (2.94) indicates that the act-DPB surface is heterogeneous (Aboua et al. 2015). When considering the correlation coefficient and the curve matching between the Langmuir model and the Freundlich model, including several other adsorption isotherms (Figure 10 and Table 4), it shows that the adsorption isotherm data are more suitable for the Freundlich model.

Let us compare the Langmuir model with the Freundlich model. The Langmuir model assumes (Duff et al. 1988; Liu 2006; Guo & Wang 2019): (i) homogeneous surface, (ii) only one adsorbate can be adsorbed, (iii) adsorption is limited to a single layer, (iv) adsorption is localized, and (v) the adsorption energy is the same on each side and does not depend on the surface characteristics. For the adsorption systems involving adsorbents with less uniform highly heterogeneous surfaces, and with many complex and irregular structural units, such as lignocellulosic-based adsorbents, the Langmuir model could be less suitable compared to the Freundlich model. The Freundlich model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinity on heterogeneous surfaces. The weakness of the Freundlich model is its assumption that there is no maximum (saturation) capacity limit. As the values of \( n \) are above 1 for most systems, the Freundlich isotherm equation becomes

\[
q_e = \frac{K_F C_e^n}{1 + C_e}
\]

This means that \( q_e \) reaches its maximum value. From Figure 10, it is actually recognized that the shape of the experimental curve is more similar to that of the Langmuir model compared with that of the Freundlich model.

Overall, it is suggested that the Langmuir model is more suitable for adsorption systems with adsorbates in the form of inorganic ions rather than molecular ions, for example, cations of second row transition metals, such as Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\). This is probably because the adsorption system can meet the assumptions of the Langmuir model, in which theoretically this type of adsorbate would not form multiple layers on the surface of the active site. In aqueous solution systems, the cations of these metals are in solvated metal ions surrounded by H\(_2\)O molecules, and are hard Lewis acids, which certainly would repel each other if they are close together, making it somewhat difficult to form multiple layers of adsorbate. The Langmuir model that assumes single layer adsorption is more suitable for this case. Conversely, the Freundlich model is more suitable for adsorbates in the form of organic molecules, which are large in size with many parts of the aromatic ring on one side, particularly Lewis bases and on the other side are cations (Lewis acids) like the cationic MB molecule. The Lewis acid moiety can interact with the Lewis base part of another molecule to form an interaction identical to the Lewis acid–base interaction. Thus, it is possible to form multiple layers on the surface of the active site. The Freundlich model also appears more suitable for multi-component adsorption systems with different types of adsorbates. Different types of adsorbates possess different characteristics; hence, they can interact with each other and form multiple layers.

### Adsorption thermodynamics

Thermodynamic studies of the adsorption process need to be carried out to confirm whether the process can occur spontaneously (De Mattos et al. 2019). The change in the Gibbs free energy, \( \Delta G \), is an indication of the process spontaneity,
while the change in the enthalpy, $\Delta H$, can roughly be used as an indicator of the adsorption type: chemical adsorption or physical adsorption.

In this study, the $\Delta G$ is determined using Equation (9) which relates the Langmuir equilibrium constant ($K_L$) to $\Delta G$ and Equation (10) which relates the Freundlich characteristic constant ($n$) to the $\Delta G$. The Supplementary Information shows and describes the mentioned equations. The $K_L$ value was obtained by plotting $C_e/q_e$ as a function of $C_e$, while the $n$ value was obtained by plotting $\log q_e$ with respect to $\log C_e$, both of which are determined at three different temperatures, 30 °C, 40 °C, and 50 °C. The results are presented in Figure 11.

### Table 3 | Maximum adsorption capacity for MB removal onto various pristine or modified biosorbents

| Biosorbent                        | $q_m$ (mg/g) | Ref.                        |
|-----------------------------------|--------------|-----------------------------|
| Waste apricot                     | 102          | Rafatullah et al. (2010)    |
| Palm kernel fiber                 | 95           | El-Sayed et al. (2014)      |
| Sunflower oil cake                | 16           | Rafatullah et al. (2010)    |
| White pine sawdust                | 102          | Salazar-Rabago et al. (2017)|
| Rice straw                        | 40           | Zhang et al. (2016)         |
| Tea waste                          | 85           | Uddin et al. (2009)         |
| Dehydrated peanut hull            | 109          | Özer et al. (2007)          |
| Coconut husk                      | 99           | Low & Lee (1990)            |
| Banana peel                       | 21           | de Carvalho et al. (2015)   |
| Coffee husk                       | 90           | Oliveira et al. (2008)      |
| Garlic peel                       | 83           | Hameed & Ahmad (2009)       |
| Gulmohar plant leaf powder        | 120          | Dogan (2007)                |
| Orange peel                       | 19           | Annamadurai et al. (2002)   |
| Rice husk                         | 41           | Vadivelan & Kumar (2005)    |
| Rubber seed shell                 | 83           | Oladoja et al. (2008)       |
| *Paspalum maritimum* Tr. weed     | 56           | Silva et al. (2019)         |
| *Cyanthilium cineereum* weed      | 76           | Silva et al. (2019)         |
| Phoenix tree’s leaves             | 81           | Han et al. (2007)           |
| Wood apple shell                  | 95           | Sulochana (2008)            |
| Peanut hull                        | 68           | Gong et al. (2005)          |
| Hazelnut shell                     | 77           | Ferrero (2007)              |
| Walnut sawdust                     | 59           | Ferrero (2007)              |
| *Luffa cylindrica* fibers         | 47           | Demir et al. (2008)         |
| Yellow passion fruit waste        | 45           | Pavan et al. (2008)         |
| Cherry sawdust                     | 40           | Ferrero (2007)              |
| Wheat shells                       | 17           | Bulut & Aydin (2006)        |
| Hen feathers                       | 135          | Chowdhury & Saha (2012)     |
| Coconut coir                       | 16           | Sharma & Upadhay (2009)     |
| Natural chaff                      | 20           | Han et al. (2006)           |
| Egg shell                          | 16           | Tsai et al. (2006)          |
| Rosewood sawdust                   | 12           | Garg et al. (2004)          |
| Meranti sawdust                    | 120          | Ahmad et al. (2009)         |
| Pineapple stem                     | 119          | Hameed et al. (2009)        |
| Tamarind fruit shell               | 2            | Saha (2010)                 |
| Neem leaf powder                   | 4            | Bhattacharyya & Sharma (2005)|
| Durian peel                        | 91           | This work                   |
As shown in Table 5, the $\Delta G$ is always negative and becomes more negative with increasing temperature. The adsorption of MB takes place spontaneously and is more likely to occur spontaneously at higher temperatures. Subsequently, $\Delta S$ and $\Delta H$ are determined by plotting $\Delta G$ as a function of $T$. From the plot of $\Delta G$ versus $T$ in Figure 12, as well as the value of the slope and the point of intersection with the $y$-axis, $\Delta S$ and $\Delta H$ can be obtained. The positive $\Delta H$ indicates that MB adsorption occurs more at higher temperatures, because the process is endothermic. When considering the adsorption nature based on the magnitude of $\Delta H$ alone, it indicates that the adsorption process is physical adsorption ($\Delta H < 25 \text{ kJ/mol}$) instead of chemical adsorption ($25 < \Delta H < 800 \text{ kJ/mol}$) (Gupta & Rastogi 2008), or alternatively it is dominated by physical adsorption that involves chemical interactions with moderate strengths.

**Table 4 | Fitted parameters for some adsorption isotherm model**

| Model               | Parameter                      | Value       | R²           |
|---------------------|--------------------------------|-------------|--------------|
| Temkin              | $q_e$                          | $RT \ln A_T + \frac{RT}{b_T} \ln C_e$ | 14.64        | 0.952        |
|                     | $b_T$ (L/mol)                  | 14.64       |              |
|                     | $K_T$ (L/mg)                   | 0.583       |              |
|                     | $R^2$                          | 0.952       |              |
| Jovanovic           | $\ln q_e = \ln q_m + KTC_e$   |             |              |
|                     | $q_m$ (mg/g)                   | 83.27       |              |
|                     | $K_T$ (L/g)                    | -0.045      |              |
|                     | $R^2$                          | 0.916       |              |
| Dubinin-Radushkevich| $\ln q_e = \ln q_m - K_{DR} \left( RT \ln \left( 1 + \frac{1}{C_e} \right) \right)^2$ | 59.65       | 0.701        |
|                     | $q_m$ (mg/g)                   | 59.65       |              |
|                     | $K_{DR}$ (kJ²/mol²)            | 3.66        |              |
|                     | $R^2$                          | 0.701       |              |
| Brunauer-Emmett-Teller| $\frac{C_e}{(C_e - C_m)q_e} = \frac{1}{q_mK_{BET}} + \left( \frac{K_{BET} - 1}{q_mK_{BET}} \right) \left( \frac{C_e}{C_T} \right)$ | 90.82       | 0.977        |
|                     | $q_m$ (mg/g)                   | 90.82       |              |
|                     | $K_{BET}$ (L/mg)               | 1101        |              |
|                     | $R^2$                          | 0.977       |              |
| Hurkins-Jura        | $\frac{1}{q_e} = \left( \frac{B_{HJ}}{A_{HJ}} \right) - \left( \frac{1}{A_{HJ}} \right) \log C_e$ | 1.000       | 0.641        |
|                     | $A_{HJ}$                       | 1000        |              |
|                     | $B_{HJ}$                       | 3           |              |
|                     | $R^2$                          | 0.641       |              |
| Halsey              | $\ln q_e = \left( \frac{1}{n_H} \right) \ln K_H - \left( \frac{1}{n_H} \right) \ln C_e$ | -2.93       | 0.990        |
|                     | $n_H$                          | -2.93       |              |
|                     | $K_H$ (L/g)                    | 8.65 × 10⁻⁴ |              |
|                     | $R^2$                          | 0.990       |              |
Conclusion is supported by the findings obtained from the adsorption mechanism study, which concludes that both physical adsorption and chemical adsorption take place simultaneously and the type of adsorption that dominates the process is physical adsorption, predominantly hydrogen bonding.

Table 5 | Thermodynamic parameters of MB adsorption determined using the Langmuir equilibrium constant ($K_L$) and Freundlich constant ($n$)

| Isotherm  | Temperature (K) | $\Delta G$ (kJ/mol) | $\Delta H$ (kJ/mol) | $\Delta S$ (kJ/(mol K)) |
|-----------|-----------------|---------------------|---------------------|------------------------|
| Langmuir  | 303             | $-22.30$            | 9.87                | 0.106                  |
|           | 313             | $-23.18$            |                     |                        |
|           | 323             | $-24.42$            |                     |                        |
| Freundlich| 303             | $-7.35$             | 10.26               | 0.058                  |
|           | 313             | $-7.81$             |                     |                        |
|           | 323             | $-8.51$             |                     |                        |

Figure 11 | Linearized (a) Langmuir and (b) Freundlich isotherm equations at three different temperatures.

Figure 12 | The relationship of $\Delta G$ (which is determined by (a) $K_L$ and (b) $n$) versus $T$. 
A positive $\Delta S$ indicates an increase in irregularity or randomness in the solid–solvent interface during the adsorption process (Tran et al. 2017c). This is probably due to the $\text{H}_2\text{O}$ molecules that are previously adsorbed on the surface and then replaced by MB molecules. The $\text{H}_2\text{O}$ molecules that previously cover the MB cations are also released (due to the damaged solvation structure of cation) after MB begins to interact with the active site. As a result, the degree of freedom of the $\text{H}_2\text{O}$ molecules in the solution system increases. The entropy of the system after MB adsorption is greater than its initial state. Hence, the entropy change becomes positive. However, the low value of $\Delta S$ indicates that there is no significant change in entropy (Tran et al. 2017a, 2017c; De Mattos et al. 2019), since there is no significant structural change in the solid–solvent interface during the adsorption process.

It is clear that the adsorption of MB onto act-DPB does not occur through physical adsorption alone. The adsorption process is accompanied by chemical interactions between MB and the active site. In other words, there is a combination of physical adsorption with chemical adsorption to a lesser extent. This is supported by the fact that the adsorption takes place better at higher temperatures (endothermic). As is known, the physical adsorption is weakened by the increase in temperature, because the physical interactions between molecules, such as van der Waals interactions, are weakened due to the increase in the kinetic energy of the molecules. Therefore, without chemical interactions, the adsorption capacity would decrease with increasing temperature.

### Adsorption mechanism

Quantitative determination of adsorption mechanism is subsequently carried out by the newly developed stepwise desorption method with water, NaCl, NaOH, and Na$_2$EDTA. The results from each desorption stage are shown in Table 6.

The amount of MB that can be desorbed with $\text{H}_2\text{O}$ is 8.89 mg/L or 20.93%. MB molecules that can be desorbed with $\text{H}_2\text{O}$ are the ones that physically interact (besides hydrogen bonding) with the active groups of act-DPB since they can be solvated easily by $\text{H}_2\text{O}$ molecules. Meanwhile, MB molecules that can be desorbed with NaCl are only 5.64 mg/L or 13.28%, and are the MB molecules that interact with the active groups, especially the carboxyl group, through a cation exchange mechanism, because they can be exchanged with Na$^+$ cations upon the desorption process. The results of MB desorption with NaOH solution show that the dominant mechanism in the MB adsorption onto act-DPB is through hydrogen bonding, with a contribution of 51.38%. Meanwhile, the desorption process with the Na$_2$EDTA solution indicates that the mechanism with the smallest contribution is through coordination interactions (chelation and/or complexation), with a portion of only 9.11%.

Upon chemical activation of pristine DPB with $\text{H}_2\text{O}_2$, the adsorption efficiency increases, and so does the quantity of the acidic groups. These findings suggest that acidic groups are responsible for the improved adsorption efficiency. Table 1 shows that among the acidic groups, carboxylic groups play the most important role in the adsorption of MB because the increase of the quantity is the highest. When considering Table 6, it is evident that the carboxylic groups interact with the MB molecule primarily through hydrogen bonding (51.38%) and physical interactions (20.93%), such as electrostatic interaction (van der Waals interaction). The proposed adsorption mechanisms for the MB removal by act-DPB are shown in Figure 13. Here, the MB adsorption takes place at pH 7. In this neutral pH, the sulfur atom of MB molecule is positively charged (Figure S1; Supplementary Information). Hydrogen bonding takes place between the hydrogen atoms of the carboxyl group and the nitrogen atoms (dipole–dipole hydrogen bonding) or the aromatic ring of the MB molecule (Yoshida hydrogen bonding) (Tran et al. 2017a). As for the physical interactions other than hydrogen bonding that involves the carboxyl group, they include electrostatic attraction and $n$–$\pi$ electron donor–acceptor interaction (Mattson et al. 1969).

| Interaction mechanism | MB desorbed (mg/L) | Contribution (%) |
|-----------------------|--------------------|------------------|
| Physical (other than hydrogen bonding) | 8.89 | 20.93 |
| Cation exchange | 5.64 | 13.28 |
| Hydrogen bonding | 21.82 | 51.38 |
| Coordination (chelation and/or complexation) | 3.87 | 9.11 |
| Others | 2.25 | 5.30 |
| **Total** | **42.47** | **100.00** |
It should be noted that due to the increased quantity of the acidic groups, the cation exchange process is supposed to increase; however, it is seen in Table 6 that the contribution of cation exchange is only 13.28%. Cation exchange with the carboxyl group appears to play a minor role in the adsorption of MB with act-DPB. In fact, identical conclusions are also reported for the removal of methylene green, a cationic dye, with golden shower pod, coconut shell and orange peel (Tran et al. 2017c) as well as activated carbon (Tran et al. 2017a). In these biomass-derived sorbents, the carboxyl group is the one that is responsible for the dye removal.

**CONCLUSIONS**

In this study, durian peel waste is utilized as the biosorbent for the adsorption of MB in water. Based on the findings obtained, the following conclusions can be drawn:

(i) Chemical activation of DPB with H₂O₂ increases the efficiency for adsorbing MB, nearly three times higher than that of pristine counterpart.

(ii) The primary functional group involved in the adsorption of MB is carboxyl group. The increased adsorption efficiency upon the chemical activation is due to the increased quantity of the carboxyl group.

(iii) The most important parameter governing the MB adsorption is the solution pH, in which the maximum adsorption is achieved under alkaline conditions. These findings suggest that the chemical state of the carboxyl group is sensitive to the solution pH and determines the extent and efficiency of the interaction between the biosorbent surface and MB.

(iv) The Freundlich model yields good fits with the equilibrium data, revealing that the MB adsorption may occur predominantly on multilayers and heterogeneous surfaces of the biosorbent.

(v) The negative value of Gibbs free energy changes indicates the spontaneous nature of the adsorption, while the positive value of enthalpy suggests an endothermic process.

**Figure 13** | Interactions between MB and the act-DPB surface: (a) dipole–dipole hydrogen bonding, (b) Yoshida hydrogen bonding, (c) n–π electron donor–acceptor, and (d) electrostatic.
(vi) The adsorption mechanisms mainly occur through hydrogen bonding (dipole–dipole hydrogen bonding and Yoshida hydrogen bonding) and physical interactions other than hydrogen bonding (electrostatic attraction and n–π electron donor–acceptor interaction), while the interactions through ion exchange and complexation are minor.

(vii) Because the monolayer adsorption capacity is relatively large (91 mg/g) compared to the previously reported biomass-derived adsorbents (other than activated carbons), the durian peel waste is thus potentially useful for the efficient removal of organic contaminants in a water environment.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Aboua, K. N., Yobouet, Y. A., Yao, K. B., Gone, D. L. & Trokourey, A. 2015 Investigation of dye adsorption onto activated carbon from the shells of Macaré fruit. Journal of Environmental Management 156, 10–14.

Ahmad, A., Rafatullah, M., Sulaiman, O., Ibrahim, M. & Hashim, R. 2009 Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution. Journal of Hazardous Materials 170 (1), 357–365.

Akpmie, K. G. & Conradie, J. 2020 Banana peel as a biosorbent for the decontamination of water pollutants. A review. Environmental Chemistry Letters 18 (4), 1085–1112.

Anagnostopoulos, V. & Symeopoulos, B. 2013 Sorption of europium by malt spent rootlets, a low cost biosorbent: effect of pH, kinetics and equilibrium studies. Journal of Radioanalytical and Nuclear Chemistry 295 (1), 7–13.

Annadurai, G., Juang, R.-S. & Lee, D.-J. 2002 Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. Journal of Hazardous Materials 92 (5), 263–274.

Asgher, M. 2012 Biosorption of reactive dyes: a review. Water, Air, & Soil Pollution 223 (5), 2417–2435.

Bagotia, N., Sharma, A. K. & Kumar, S. 2020 A review on modified sugarcane bagasse biosorbent for removal of dyes. Chemosphere 268, 129309.

Bazargan, A., Hui, C. W. & Mckay, G. 2014 Marine residual fuel sorption and desorption kinetics by alkali treated rice husks. Cellulose 21 (5), 1997–2006.

Ben-Ali, S., Jaouali, I., Souissi-Najar, S. & Ouederni, A. 2017 Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. Journal of Cleaner Production 142, 3809–3821.

Benis, K. Z., Damuchali, A. M., McPhedran, K. N. & Soltan, J. 2020 Treatment of aqueous arsenic—a review of biosorbent preparation methods. Journal of Environmental Management 273, 111126.

Bhattacharyya, K. G. & Sharma, A. 2005 Kinetics and thermodynamics of methylene blue adsorption on neem (Azadirachta indica) leaf powder. Dyes and Pigments 65 (1), 51–59.

Budnyak, T. M., Blachnio, M., Slabon, A., Jaworski, A., Tertykh, V. A., Deryholo-Marczewska, A. & Marczewski, A. W. 2020 Chitosan deposited onto fumed silica surface as sustainable hybrid biosorbent for Acid Orange 8 dye capture: effect of temperature in adsorption equilibrium and kinetics. The Journal of Physical Chemistry C 124 (28), 15312–15323.

Bulut, Y. & Aydin, H. 2006 A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. Desalination 194 (1–3), 259–267.

Chowdhury, S. & Saha, P. D. 2012 Biosorption of methylene blue from aqueous solutions by a waste biomaterial: hen feathers. Applied Water Science 2 (3), 209–219.

Contreras, M., Grande-Tovar, C. D., Vallejo, W. & Chaves-López, C. 2019 Bio-removal of methylene blue from aqueous solution by Galactomyces geotrichum KL20A. Water 11 (2), 282.

Crini, G. & Lichtfouse, E. 2019 Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters 17 (1), 145–155.

Dahri, M. K., Chieng, H. I., Lim, L. B., Priyantha, N. & Mei, C. C. 2015a Cempedak durian (Artocarpus sp.) peel as a biosorbent for the removal of toxic methyl violet 2B from aqueous solution. Korean Chemical Engineering Research 53 (5), 576–583.

Dahri, M. K., Lim, L. B. & Mei, C. C. 2015b Cempedak durian as a potential biosorbent for the removal of Brilliant Green dye from aqueous solution: equilibrium, thermodynamics and kinetics studies. Environmental Monitoring and Assessment 187 (8), 1–13.

de Carvalho, H. P., Huang, J., Zhao, M., Liu, G., Dong, L. & Liu, X. 2015 Improvement of Methylene Blue removal by electrocoagulation/banana peel adsorption coupling in a batch system. Alexandria Engineering Journal 54 (3), 777–786.

de Freitas, G. R., da Silva, M. G. C. & Vieira, M. G. A. 2019 Biosorption technology for removal of toxic metals: a review of commercial biosorbents and patents. Environmental Science and Pollution Research 26 (19), 19097–19118.
De Mattos, N. R., De Oliveira, C. R., Camargo, L. G. B., da Silva, R. S. R. & Lavall, R. L. 2019 Azo dye adsorption on anthracite: a view of thermodynamics, kinetics and cosmotropic effects. *Separation and Purification Technology* 209, 806–814.

Demir, H., Top, A., Balköse, D. & Ülkü, S. 2008 Dye adsorption behavior of *Luffa cylindrica* fibers. *Journal of Hazardous Materials* 153 (1–2), 389–394.

Dhaouadi, F., Selloumi, L., Dotto, G. L., Bonilla-Petricioleta, A., Ero, A. & Lamine, A. B. 2020 Adsorption of methylene blue on comminuted raw avocado seeds: interpretation of the effect of salts via physical monolayer model. *Journal of Molecular Liquids* 305, 112815.

Doğan, M., Özdemir, Y. & Alkan, M. 2007 Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. *Dyes and Pigments* 75 (3), 701–713.

Dotto, G. & Pinto, I. 2011 Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: stirring rate effect in kinetics and mechanism. *Journal of Hazardous Materials* 187 (1–3), 164–170.

Duff, D. G., Ross, S. M. & Vaughan, D. H. 1988 Adsorption from solution: an experiment to illustrate the Langmuir adsorption isotherm. *Journal of Chemical Education* 65 (9), 815.

El Atouani, S., Belattmania, Z., Reani, A., Tahiri, S., Aarfane, A., Bentiss, F., Jama, C., Zrid, R. & Sabour, B. 2019 Brown seaweed *Sargassum muticum* as low-cost biosorbent of methylene blue. *International Journal of Environmental Research* 13 (1), 131–142.

El-Sayed, G. O., Yehia, M. M. & Assaad, A. A. 2014 Assessment of activated carbon prepared from corn cob by chemical activation with phosphoric acid. *Water Resources and Industry* 7, 66–75.

Ferrero, F. 2007 Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust. *Journal of Hazardous Materials* 142 (1–2), 144–152.

Garg, V. K., Amita, M., Kumar, R. & Gupta, R. 2004 Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a industry waste. *Dyes and Pigments* 63 (3), 245–250.

Gautam, R. K., Mudhoo, A., Lofrano, G. & Chattopadhyaya, M. C. 2014 Biomass-derived biosorbents for metal ions sequestration: adsorbent modification and activation methods and adsorbent regeneration. *Journal of Environmental Chemical Engineering* 2 (1), 239–259.

Gillman, P. K. 2011 CNS toxicity involving methylene blue: the exemplar for understanding and predicting drug interactions that precipitate serotonin toxicity. *Journal of Psychopharmacology* 25 (3), 429–436.

Gong, R., Li, M., Yang, C., Sun, Y. & Chen, J. 2005 Removal of cationic dyes from aqueous solution by adsorption on peanut hull. *Journal of Hazardous Materials* 121 (1–3), 247–250.

Guo, X. & Wang, J. 2019 Comparison of linearization methods for modeling the Langmuir adsorption isotherm. *Journal of Molecular Liquids* 296, 111850.

Gupta, V. K. & Rastogi, A. 2008 Equilibrium and kinetic modelling of cadmium (II) biosorption by nonliving algal biomass of *Oedogonium* sp. from aqueous phase. *Journal of Hazardous Materials* 153, 759–766.

Hameed, B. & Ahmad, A. 2009 Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. *Journal of Hazardous Materials* 164 (2–3), 870–875.

Hameed, B., Krishni, R. & Sata, S. 2009 A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions. *Journal of Hazardous Materials* 162 (1), 305–311.

Hamzadeh, A., Rashbani, Y., Ashin, S., Morovati, M. & Vosoughi, M. 2020 Application of low-cost material for adsorption of dye from aqueous solution. *International Journal of Environmental Analytical Chemistry*, 1–16. In Press. DOI: 10.1080/03067319.2020.1720011

Han, R., Wang, Y., Han, P., Shi, J., Yang, J. & Lu, Y. 2006 Removal of methylene blue from aqueous solution by chaf in batch mode. *Journal of Hazardous Materials* 137 (1), 550–557.

Han, R., Zou, W., Yu, W., Cheng, S., Wang, Y. & Shi, J. 2007 Biosorption of methylene blue from aqueous solution by fallen phoenix tree’s leaves. *Journal of Hazardous Materials* 141 (1), 156–162.

Ibupoto, A. S., Qureshi, U. A., Ahmed, F., Khatri, Z., Khatri, M., Maisood, M., Brohi, R. Z. & Kim, I. S. 2018 Reusable carbon nanofibers for efficient removal of methylene blue from aqueous solution. *Chemical Engineering Research and Design* 136, 744–752.

Javaid, R. & Qazi, U. 2019 Catalytic oxidation process for the degradation of synthetic dyes: an overview. *International Journal of Environmental Research and Public Health* 16 (11), 2066.

Jawad, A. H. & Abdulhameed, A. S. 2020 Mesoporous Iraqi red kaolinit clay as an efficient adsorbent for methylene blue dye: adsorption kinetic, isotherm and mechanism study. *Surfaces and Interfaces* 18, 100422.

Kawmar, S. W. a. P. 2010 Durian peel as biosorbent for removal of cadmium ions from aqueous solution. *Applied Environmental Research* 32 (1), 17–30.

Kandisa, R. V., Saibaba, K. N., Shaik, K. B. & Gopinath, R. 2016 Dye removal by adsorption: a review. *Journal of Bioremediation and Biodegradation* 7, 6.

Kankulč, G. B., Metin, A. Ü. & Tüzün, I. 2016 *Phragmites australis*: an alternative biosorbent for basic dye removal. *Ecological Engineering* 86, 85–94.

Koyuncu, H. & Kul, A. R. 2020 Removal of methylene blue dye from aqueous solution by nonliving lichen (*Pseudocyphella furfuracea* (L.) Zopf.), as a novel biosorbent. *Applied Water Science* 10 (2), 1–14.

Liu, Y. 2006 Some consideration on the Langmuir isotherm equation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 274 (1–3), 34–36.

Liu, L., Gao, Z. Y., Su, X. P., Chen, X., Jiang, L. & Yao, J. M. 2015 Adsorption removal of dyes from single and binary solutions using a cellulose-based bioadsorbent. *ACS Sustainable Chemistry & Engineering* 5 (3), 432–442.
Liu, J., Wang, Z., Li, H., Hu, C., Raymer, P. & Huang, Q. 2018 Effect of solid state fermentation of peanut shell on its dye adsorption performance. Bioresource Technology 249, 307–314.

Low, K. & Lee, C. 1990 The removal of cationic dyes using coconut husk as an adsorbent. Pertanika 15 (2), 221–228.

Lum, P., Foo, K., Zakaria, N. & Palaniandy, P. 2020 Ash based nanocomposites for photocatalytic degradation of textile dye pollutants: a review. Materials Chemistry and Physics 241, 122405.

Mahmoodi, N. M., Arami, M., Bahrami, H. & Khorramfar, S. 2011 The effect of pH on the removal of anionic dyes from colored textile wastewater using a biosorbent. Journal of Applied Polymer Science 120 (5), 2996–3003.

Majid, Z., AbdulRazak, A. A. & Noori, W. A. H. 2019 Modification of Zeolite by magnetic nanoparticles for organic dye removal. Arabian Journal for Science & Engineering (Springer Science & Business Media BV) 44 (6), 5457–5474.

Mattson, J. A., Mark Jr., H. B., Malbin, M. D., Weber Jr., W. J. & Crittenden, J. C. 1969 Surface chemistry of active carbon: specific adsorption of phenols. Journal of Colloid and Interface Science 31 (1), 116–130.

Moorthy, A. K., Rathi, B. G., Shukla, S. P., Kumar, K. & Bharti, V. S. 2021 Acute toxicity of textile dye Methylene blue on growth and metabolism of selected freshwater microalgae. Environmental Toxicology and Pharmacology 82, 103552.

Mostafa, M. 2015 Waste water treatment in textile industries-the concept and current removal technologies. Journal of Biodiversity and Environmental Sciences 7 (1), 501–525.

Nagaiyothi, P., Prabhakar Vattikuti, S., Devarayapalli, K., Yoo, K., Shim, J. & Sreekantan, T. 2020 Green synthesis: photocatalytic degradation of textile dyes using metal and metal oxide nanoparticles-latest trends and advancements. Critical Reviews in Environmental Science and Technology 50 (24), 2617–2723.

Nasiruddin Khan, M. & Sarwar, A. 2007 Determination of points of zero charge of natural and treated adsorbents. Surface Review and Letters 14 (3), 461–469.

Ngabura, M., Hussain, S. A., Ghani, W. A. W., Jami, M. S. & Tan, Y. P. 2018 Utilization of renewable durian peels for biosorption of zinc from wastewater. Journal of Environmental Chemical Engineering 6 (2), 2528–2539.

Nimkar, U. 2018 Sustainable chemistry: a solution to the textile industry in a developing world. Current Opinion in Green and Sustainable Chemistry 9, 13–17.

Oladajo, N., Asla, I., Abolowo, C., Oladimeji, Y. & Ashogbon, A. 2008 Studies on the sorption of basic dye by rubber (Hevea brasiliensis) seed shell. Turkish Journal of Journal of Environmental Engineering 32 (3), 143–152.

Oliveira, L. S., Franca, A. S., Alves, T. M. & Rocha, S. D. 2008 Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters. Journal of Hazardous Materials 155 (3), 507–512.

Özer, D., Dursun, G. & Özer, A. 2007 Methylene blue adsorption from aqueous solution by dehydrated peanut hull. Journal of Hazardous Materials 144 (1–2), 171–179.

Pavan, F. A., Lima, E. C., Dias, S. L. & Mazzocato, A. C. 2008 Methylene blue biosorption from aqueous solutions by yellow passion fruit waste. Journal of Hazardous Materials 150 (3), 705–712.

Peñafiel, M., Matasanz, J., Vanegas, E., Bermejo, D. & Ormaz, M. 2020 Corncobs as a potentially low-cost biosorbent for sulfamethoxazole removal from aqueous solution. Separation Science and Technology 55 (17), 3060–3071.

Rafatullah, M., Sulaiman, O., Hashim, R. & Ahmad, A. 2010 Adsorption of methylene blue on low-cost adsorbents: a review. Journal of Hazardous Materials 177 (1–3), 70–80.

Ren, H., Cunha, E., Sun, Q., Li, Z., Kinloch, I. A., Young, R. J. & Fan, Z. 2019 Surface functionality analysis by Boehm titration of graphene nanoplatelets functionalized via a solvent-free cycloaddition reaction. Nanoscale Advances 1 (4), 1432–1441.

Saha, P. 2010 Assessment on the removal of methylene blue dye using tamarind fruit shell as biosorbent. Water, Air, & Soil Pollution 213 (1), 287–299.

Salazar-Rabago, J. L., Leyva-Ramos, R., Rivera-Utrilla, J., Ocampo-Perez, R. & Cerino-Cordova, F. J. 2017 Biosorption mechanism of Methylene Blue from aqueous solution onto White Pine (Pinus durangensis) sawdust: effect of operating conditions. Sustainable Environment Research 27 (1), 32–40.

Senthil Kumar, P., Fernando, P. S. A., Ahmed, R. T., Srinath, R., Priyadharshini, M., Vignesh, A. & Thanjiappan, A. 2014 Effect of temperature on the adsorption of methylene blue dye onto sulfuric acid-treated orange peel. Chemical Engineering Communications 201 (11), 1526–1547.

Sharma, Y. C. & Upadhyay, S. N. 2009 Removal of a cationic dye from wastewaters by adsorption on activated carbon developed from coconut coir. Energy & Fuels 23 (6), 2983–2988.

Silva, B., Tuuguu, E., Costa, F., Rocha, V., Lago, A. & Tavares, T. 2017 Permeable biosorbotic barrier for wastewater remediation. Environmental Processes 4 (1), 195–206.

Silva, F., Nascimento, L., Brito, M., da Silva, K., Paschoal Jr., W. & Fujiyama, R. 2019 Biosorption of methylene blue dye using natural biosorbents made from woods. Materials 12, 2486.

Singh, S., Parveen, N. & Gupta, H. 2018 Adsorptive decontamination of rhodamine-B from water using banana peel powder: a biosorbent. Environmental Technology & Innovation 18, 412–195.

Sulochana, R. M. a. N. 2008 Sorption isotherm and kinetic studies of methylene blue uptake onto activated carbon prepared from wood apple shell. Journal of Environmental Protection Science 2, 40–46.

Tran, H. N., You, S.-J. & Chao, H.-P. 2017a Fast and efficient adsorption of methylene Green 5 on activated carbon prepared from new chemical activation method. Journal of Environmental Management 188, 322–336.
Tran, H. N., You, S.-J., Hosseini-Bandegharaei, A. & Chao, H.-P. 2017b Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. *Water Research* **120**, 88–116.

Tran, H. N., You, S.-J., Nguyen, T. V. & Chao, H.-P. 2017c Insight into the adsorption mechanism of cationic dye onto biosorbents derived from agricultural wastes. *Chemical Engineering Communications* **204** (9), 1020–1036.

Tsai, W., Yang, J., Lai, C., Cheng, Y., Lin, C. & Yeh, C. 2006 Characterization and adsorption properties of eggshells and eggshell membrane. *Bioresource Technology* **97** (3), 488–493.

Uddin, M. T., Islam, M. A., Mahmud, S. & Rukanuzzaman, M. 2009 Adsorptive removal of methylene blue by tea waste. *Journal of Hazardous Materials* **164** (1), 53–60.

Vadivelan, V. & Kumar, K. V. 2005 Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *Journal of Colloid and Interface Science* **286** (1), 90–100.

Vutskits, L., Briner, A., Klauser, P., Gascon, E., Dayer, A. G., Kiss, J. Z., Muller, D., Licker, M. J. & Morel, D. R. 2008 Adverse effects of methylene blue on the central nervous system. *The Journal of the American Society of Anesthesiologists* **108** (4), 684–692.

Weber, C. T., Foletto, E. L. & Meili, L. 2013 Removal of tannery dye from aqueous solution using papaya seed as an efficient natural biosorbent. *Water, Air, & Soil Pollution* **224** (2), 1–11.

Wong, Y., Szeto, Y., Cheung, W. & McKay, G. 2008 Effect of temperature, particle size and percentage deacetylation on the adsorption of acid dyes on chitosan. *Adsorption* **14** (1), 11–20.

Yacout, D. M. & Hassouna, M. 2016 Identifying potential environmental impacts of waste handling strategies in textile industry. *Environmental Monitoring and Assessment* **188** (8), 1–13.

Zhang, S., Wang, Z., Zhang, Y., Pan, H. & Tao, L. 2016 Adsorption of methylene blue on organosolv lignin from rice straw. *Procedia Environmental Sciences* **31**, 3–11.

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