

Computational and Analytical Investigation of Date Trunk Biomass as a Bio-adsorbent for Sustainable Removal of Methylene Blue Dye from Wastewater

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Abstract

The Industrial release of synthetic dyes, such as methylene blue (MB), into water has created significant environmental concerns. The use of date trunk as a bio-adsorbent was investigated for the removal of MB dye from wastewater. The effects of several experimental parameters, such as MB dye concentration, contact time, and adsorbent dosage, were studied using a batch-laboratory operational setup. Fourier Transform Infrared (FTIR) spectroscopy was performed to reveal the presence of functional groups in the bio-adsorbent. This study evaluated the adsorption capacity of a green bio-adsorbent for the removal of MB dye from wastewater. The maximum adsorption of MB was obtained for the bio-adsorbent dosage of 0.4 gram for 50 min, achieving a maximum removal efficiency of 92.4%. The Gaussian 09 software package was used for Density Functional Theory (DFT) to optimize the molecular structures of guaiacol and methylene blue (MB) dye, , with the calculated adsorption energy ($E_{ads} = -1.43$ Hartree) confirming a thermodynamically favorable interaction. The results revealed that date trunks have great potential as efficient bio-adsorbents for the removal of MB dye from wastewater.

Keywords: Methylene Blue; Wastewater Treatment; Bio-adsorbent; Date Trunk; Bio waste

1. Introduction:

Population growth has led to the expansion of different industries, especially the textile industry, to improve human living standards [1-3]. Although these industries have many benefits for the population, they also have potentially harmful effects, including the release of different metals and dyes. In the textile industry, washing processes of dyed fabrics release different dyes in discharge water, mostly in millions of tons, which are released into water bodies without treatment [4]. The United States Environmental Protection Agency (USEPA) and the European Union (EU) have strict regulations for the discharge water of textile industries, aiming to reduce pollutants such as dyes [5, 6]. However, many industries discharge polluted water

directly into water bodies without treatment, owing to insufficient water treatment technologies[7].

Many synthetic dyes, such as methylene blue (MB), malachite green (MG), and Congo red (CR) [8, 9], are extensively used in the textile industry and are found in the harmful range of textile effluents. These dyes are harmful to aquatic life and lead to various serious health concerns in humans, including allergenicity, teratogenicity, mutagenicity and carcinogenicity [10]. Subsequently, aquatic life is affected, and the ecosystem is at risk of degradation. The textile industries are one of the principal sources of water pollution globally, primarily owing to the release of untreated or inadequately treated wastewater holding various synthetic dyes into natural water bodies [11]. These dyes, which are characterized by their high

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stability and resistance to degradation, persist in the environment for extended periods, thereby posing severe ecological and health risks [12].

Among the vast array of dyes employed in textile production, Methylene Blue (MB) has gained particular attention because of its wide usage and potential harmful effects. MB is classified as a cationic dye and has been identified as a carcinogen, mutagen, and potential cause of allergies. MB is a triarylmethane dye that is widely used in multiple industries, including the textile, paper, and cosmetic industries. However, MB is also a known environmental pollutant, and its discharge into wastewater can negatively impact aquatic life. MB dye is non-biodegradable[13], so it remains in water during conventional water treatment processes and requires special treatment methodologies to be eliminated. Many conventional techniques, such as chlorination and activated sludge processing, along with emerging technologies, such as advanced oxidation processes, reverse osmosis, membrane filtration, and have been used to treat wastewater, especially in the textile industry. These technologies improve the removal efficiency of dyes from wastewater, but each has various limitations, such as extreme costs and energy[14, 15]. Therefore, there is a pressing need to explore alternative strategies that are environmentally friendly and economically viable.

Adsorption is a particularly attractive option because it is simple, efficient, and cost-effective. Several different bio-adsorbents, including clay minerals, activated carbon, and metal oxides, were investigated for the elimination of MB dyes from wastewater[16, 17]. The date trunk is a natural material that has been shown to be an effective bio adsorbent for MB. Owing to the increased demand for synthetic dyes, particularly in the textile and apparel industries, production is increasing. Thousands of tons of these chemicals (dyes) are manufactured worldwide each year. Date trunks have been utilized for the elimination of MB dye from synthetic wastewater because of their extraordinary surface characteristics and adsorption capacity. The date trunk powder is a natural material that is readily available and inexpensive. Date trunk, a fibrous waste generated from the pruning and trimming of date palm trees, has immense potential as a bio-adsorbent owing to its porous structure and abundant availability in regions where date cultivation is prevalent[18, 19]. The

adsorption process was also found to be reversible, as MB was desorbed from the date trunk bio-adsorbent. The use of a date trunk for the elimination of MB dye from wastewater is a promising new technology that could help minimize the environmental impact of this pollutant [20].

This study contributes with ongoing current research on the elimination of MB dye from wastewater by utilizing untreated bio-waste without any chemical treatment of the synthesized bio-adsorbent-date trunks. This study aimed to eliminate MB dye from wastewater. The interaction of the synthesized bio-adsorbent and MB dye was studied by considering different factors in terms of MB concentration, time, bio-adsorbent dosage, and using a UV-Vis spectrophotometer. Moreover, FTIR and DFT confirmed the removal of MB dye using a bio-adsorbent. Current research has focused on the development of an emerging technique using date trunks as bio-adsorbents.

2. Experimentals:

2.1. Synthesizing Bio-adsorbent Material:

The date trunk was first cleaned with tap water and then twice with distilled water to remove impurities. To remove moisture, the raw bio-adsorbent material was dried in oven at 100°C for 1 hour. The dried date trunks were ground into fine particles by using a grinder, mortar, and pestle. The date trunk particles were sieved using a 50-mesh sieve to obtain a uniform particle size.

2.2. Synthetic solution of MB:

Methylene blue was procured from Sigma Aldrich (purity $\geq 99\%$). An MB dye solution of 50 PPM concentration was prepared in the laboratory, and all the MB sample solutions were taken from the stock solution and diluted.

2.3. Batch Experimentation:

Multiple batch adsorption experiments were performed to study the effects of contact time, bio-adsorbent dosage, and dye concentration on the removal efficiency of MB dye using the date trunk bio-adsorbent. The adsorption technique-based experiments were conducted in 100 mL Erlenmeyer flasks containing 50 mL of 50 ppm MB dye solution. The MB dye solution samples were agitated at 150 rpm at room temperature. The effect of bio-adsorbent dosage was investigated by adding different amounts of date trunk to the methylene blue dye solution (0.1- 0.4 g/50 mL). The time factor was examined by changing the contact time among the bio-adsorbent and dye solution (5-60 minutes). After

adsorption, Whatman filter paper 42 was used to filter the solution.

An experimental path adopted to show the synthesis of bio-adsorbent along with its practical application to eliminate MB dye and the characterization techniques adopted are shown in figure 1.

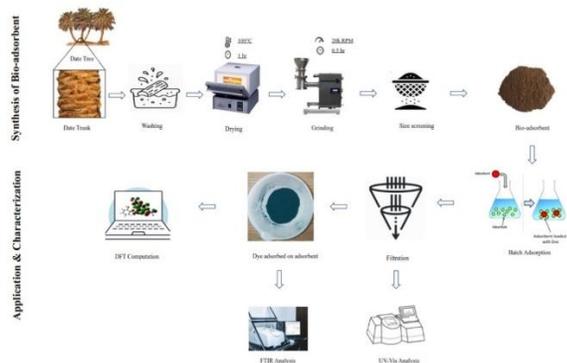


Figure 1: Experimental route for synthesis of bio-adsorbent and the removal of methylene blue dye from wastewater

3. Characterization of Materials:

3.1. UV-Vis Spectrophotometric Analysis:

UV-Vis Analysis was conducted at the MNS University of Engineering and Technology, Multan. Several samples were placed in a UV-Vis spectrophotometer to verify the MB concentration in the solution before and after the adsorption of the MB dye at the surface of the date trunk. Absorbance of the dye solution was observed at a wavelength of 665 nm. The adsorption of MB was calculated using equation 1 [21]:

$$Q_t = (C_0 - C_t) * V/M \dots\dots\dots (1)$$

$$\% \text{ Removal} = (C_0 - C_t)/C_0 * 100$$

Where Q_t = amount of sorption at time t , C_0 = initial concentration, C_t = concentration at the time t , V = volume of solution, M = mass of bio-adsorbent.

3.2. Fourier Transform Infrared Analysis:

FTIR analysis was performed to identify the functional groups of the MB dye at the surface of the adsorbent. FTIR Spectrophotometric results of the date trunk before and after the adsorption of MB were compared to observe any alterations at the surface functional groups and to verify the characteristics of the interface between DT and MB.

The FTIR spectrum of the date trunks showed the occurrence of hydroxyl, carboxylic acid, and carbonyl groups. After the MB dye was adsorbed on the date trunk, the hydroxyl peak decreased, demonstrating that

the hydroxyl groups participated in the adsorption process. The carbonyl peak shifted to a lower wavenumber, suggesting that carbonyl groups participated in the formation of complexes with MB. The carboxylic acid peak also shifted to a lower wavenumber, indicating that carboxylic acid groups played a role in the adsorption technique.

3.3. Density Functional Theory (DFT) Analysis:

The Gaussian 09 software package was used to perform the quantum chemical calculations. DFT with the B3LYP hybrid functional and the 6-31G basis set was used to optimize the molecular structures of guaiacol and methylene blue (MB) dye because date trunk biomass and guaiacol are chemically related through functional groups. Frequency calculations were performed to check the stability of the optimized geometries and confirm that no imaginary frequencies were present.

The interaction between MB and guaiacol was determined by calculating the adsorption energy using the following formula:

$$E_{ads} = E_{MBGuaiacol} - (E_{MB} + E_{Guaiacol})$$

To examine the electronic properties of the charge-transfer behavior, the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and corresponding energy gaps were studied. The Mulliken charge distribution methodology was used to observe the electrostatic interactions and electron-rich or electron-deficient regions of the molecules.

4. Results and Discussion:

4.1. Effect of Bio-adsorbent Dosage:

Figure 2 confirms that the removal efficiency of MB dye increases with increasing amounts of bio-adsorbent. The highest removal efficiency (92.4 %) was obtained with 0.4 g/50mL of bio-adsorbent. This can be recognized as a rise in the available surface area of the bio-adsorbent material, which provides supplementary sites for the adsorption of MB dye molecules.

Different dosages of the bio-adsorbent were used in contaminated synthetic water to observe dye removal efficiency. The results confirmed that the removal of MB was meaningfully improved with an increase in bio-adsorbent dosage, but after a certain limit, the removal efficiency started decreasing owing to the limited available surface area for the adherence of MB dye on the surface of the bio-adsorbent. However, 0.4g/50mL is the optimum catalyst loading rate.

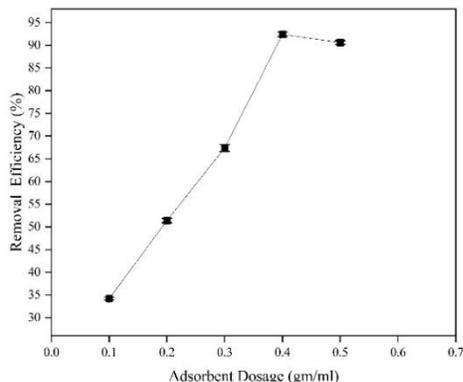


Figure 2: Bio-adsorbent Dosage on removal efficiency of MB dye

4.2. Effect of Contact Time:

Figure 3 confirms that the removal efficiency of MB dye was enhanced by increasing the contact time, reaching equilibrium after 50 min. Initially, fast adsorption was due to more available adsorption sites at the surface of the bio-adsorbent material. The gradual decrease in the rate of adsorption can be attributed to the desorption of MB dye from the surface of the bio-adsorbent. However, maximum removal efficiency was observed when stirring was performed for 50 min.

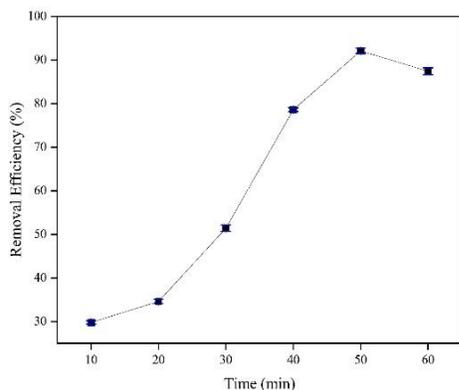


Figure 3: Contact Time on removal efficiency of MB dye

4.3. Effect of MB dye Concentration:

Figure 4 demonstrates that the use of the date trunk for the elimination of MB dye depends on different factors, comprising the concentration of MB and the concentration of the bio-adsorbent. Usually, a higher concentration of MB dye demands a higher concentration of the bio-adsorbent to achieve effective removal. This study reveals that increasing the concentration of MB dye in solutions can lead to a

decline in the removal efficiency because a higher concentration of methylene blue can lead to saturation of the bio-adsorbent surface, reducing the available binding sites for the adsorption process. However, the MB dye with a 50-ppm concentration showed the maximum removal efficiency.

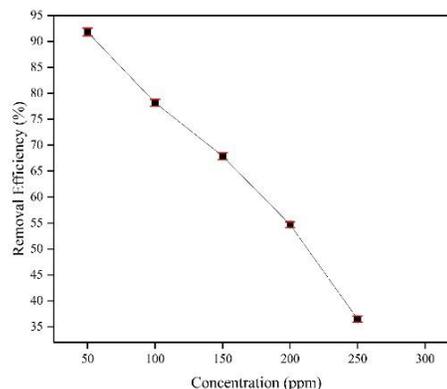


Figure 4: MB dye concentration on removal efficiency

4.4. Functional Group Detection:

Figure 5 shows the spectroscopic analysis of the date trunk, the bio-adsorbent, in both raw and treated forms after the adsorption of MB dye at the surface of the date trunk. FTIR analysis confirmed the occurrence of functional groups of the MB dye in the bio-adsorbent sample. Different peaks were observed in the spectra of the raw and treated date trunk samples. FTIR analysis revealed the presence of various functional groups on the surface of the bio-adsorbent, including phenolic, carboxyl, and hydroxyl groups.

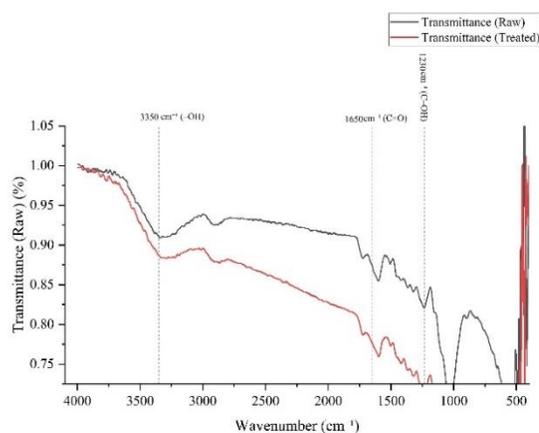


Figure 5: FTIR Analysis of Date Trunks

A wide change in the transmittance behavior was observed in the spectrum of both the raw date trunk sample and the adsorbed MB date trunk bio-adsorbent

sample. The FTIR spectra showed the existence of different functional groups, such as 860–475 cm^{-1} (Si-H group), 1090 cm^{-1} (Si-O-Si group), 1230 cm^{-1} (CHOH group), 1150–1300 cm^{-1} (CO group), 1375 cm^{-1} (aromatic CH stretching and carboxyl-carbonate structures), 1460 cm^{-1} (CH₂ and CH₃ groups), 1550–1650 cm^{-1} (C = C groups), (1650–1750) cm^{-1} (C = O group), 2900 cm^{-1} (C-H groups), and 3350 cm^{-1} (-O-H groups). Since the DFT shows strong chemical binding (chemisorption), it explains why you see shifts in the FTIR peaks after adsorption—the functional groups are literally forming new chemical environments with the dye.

4.5. Computational Methodology:

4.5.1. Charge Transfer and Electrostatic Interaction Between Guaiacol and MB:

Figure 6 clearly indicates that the charge distribution analysis confirms a clear tendency for electrostatic interactions and charge transfer between guaiacol (used as a model for the date trunk bio-adsorbent) and methylene blue (MB). The guaiacol molecule exhibits a net positive partial charge of +0.65, with significant negative charge localization on the hydroxyl oxygen (−0.591) and methoxy oxygen (−0.554), while the aromatic carbon atoms maintain moderate positive charges ranging from +0.13 to +0.31. In contrast, MB carries a net negative partial charge of −0.63, with pronounced negativity for the nitrogen atoms (−0.662) and moderately positive regions on adjacent carbons.

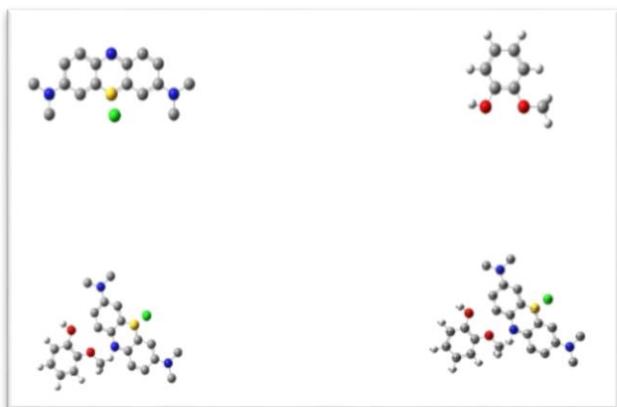


Figure 6: Optimized structures of guaiacol and MB with charge distribution. Electron-rich and deficient regions highlight electrostatic and π – π interaction sites (Image generated by Gaussian 09).

These charge characteristics support the likelihood of electron density shifting from MB to guaiacol, forming a

stable complex through electrostatic attraction. The difference in the electron density distribution enables partial charge transfer, which, alongside possible hydrogen bonding and π – π interactions, enhances the adsorption performance. Table 1 shows that the charge-based interaction mechanism reinforces the potential of lignin-rich biomass-like date trunks in effective dye removal.

Table 1: Mulliken partial charges of key atoms in guaiacol and methylene blue, indicating functional roles in electrostatic and π – π interactions.

Molecule	Atom/Group	Partial Charge (e)	Functional Role in Interaction
Guaiacol	Hydroxyl oxygen (O)	−0.591	Hydrogen bonding, electron-rich site
	Methoxy oxygen (O)	−0.554	Electron-donating site
	Aromatic carbons (C)	+0.130 to +0.310	π – π stacking with MB aromatic rings
	Net Molecular Charge	+0.65	Acts as electron acceptor
Methylene Blue	Central nitrogen (N)	−0.662	Electron-donating site
	Sulfur (S)	+0.109	Minor electron-deficient site
	Adjacent carbons (C)	+0.200 to +0.300	Site for electrostatic attraction
	Net Molecular Charge	−0.63	Acts as electron donor

4.5.2. Thermodynamic Favorability of MB Dye Adsorption onto Guaiacol:

The adsorption of MB dye onto guaiacol for dye removal is thermodynamically favorable, as indicated in Table 2,

by the calculated adsorption energy of -0.2043 Hartree (approximately -5.5592 eV). This negative adsorption energy suggests that the interaction between MB and Guaiacol is exothermic, implying that the total energy of the system decreases when MB adsorbs onto Guaiacol, resulting in a stable and spontaneous process. The energy values are as follows: the energy of MB is -1630.3912 Hartree (-44364.5749 eV), the energy of Guaiacol is -421.8644 Hartree (-11479.35219 eV), and the energy of complex (MB + Guaiacol) is -2052.4599 Hartree (-55849.4863 eV). The exothermic nature of this interaction makes it favorable for practical applications, such as dye removal, where MB can effectively adsorb onto guaiacol, offering a potential solution for water purification and environmental remediation.

The computational analysis yielded an adsorption energy E_{ads} of -5.5592 eV for the interaction between the Methylene Blue (MB) molecule and the Guaiacol model surface. In the context of adsorption thermodynamics, physisorption is generally characterized by energies less than -0.4 eV, whereas values exceeding this threshold indicate chemisorption involving the sharing or transfer of electrons. The calculated value of -5.5592 eV suggests a strong chemisorption mechanism, likely driven by robust electrostatic interactions and hydrogen bonding between the cationic nitrogen of the MB dye and the oxygen-containing functional groups (methoxy and hydroxyl) of the biomass. This high negative energy value confirms the thermodynamic favorability and spontaneous nature of the adsorption process, supporting the high removal efficiency observed in the experimental trials.

Table 2: Electronic energies (in Hartree) of guaiacol, methylene blue, and their combined complex. The adsorption energy reflects thermodynamic favorability.

Molecule	Adsorption Energy (Hartree)	Adsorption Energy (eV)
Methylene Blue (MB)	-1630.3912	-44364.5749
Guaiacol	-421.8644	-11479.3521
Complex (Methylene Blue + Guaiacol)	-2052.4599	-55849.4863
E_{ads}	-0.2043	-5.5592

4.5.3. Molecular Orbital Energies:

The adsorption of Methylene Blue (MB) on guaiacol can be understood by examining the changes in its electronic structure, specifically the HOMO-LUMO gap (HLG) and electron density distribution. Methylene Blue (MB) has a comparatively small HOMO-LUMO gap (0.58 eV, demonstrating that it has a small electronic band gap, which facilitates easier electron transfer and higher reactivity. In contrast, guaiacol has a larger HLG (5.34 eV, indicating a less reactive structure with a significant energy gap. After adsorption, the overall system's HLG decreases to 0.93 eV, resulting in the interaction between MB and Guaiacol decreasing the overall energy gap, which makes the system more reactive and increases the charge transfer. Table 3 denotes the HOMO-LUMO energies of MB dye and guaiacol.

Table 3: HOMO-LUMO energies and energy gaps of guaiacol, methylene blue, and their complex before and after adsorption.

Molecule	HOMO (Hartree)	LUMO (Hartree)	HOMO (eV)	LUMO (eV)
Methylene Blue (MB)	-0.23396	-0.21290	-6.37	-5.79
Guaiacol	-0.20476	-0.00828	-5.57	-0.23
Methylene Blue + Guaiacol	-0.18536	-0.15130	-5.04	-4.11

Molecular orbitals also showed that the electron density from the MB dye was delocalized and distributed onto guaiacol, demonstrating a significant interaction between the two molecules. This visualization is shown in Figure 7. This increased electronic interaction makes the adsorption process thermodynamically beneficial because it improves the effectiveness of the MB dye elimination process. The change in electron density of MB dye-guaiacol and reduction of HLG upon the adsorption process showed that MB dye was more efficiently adsorbed onto guaiacol, enabling better charge transfer and dye removal applications.

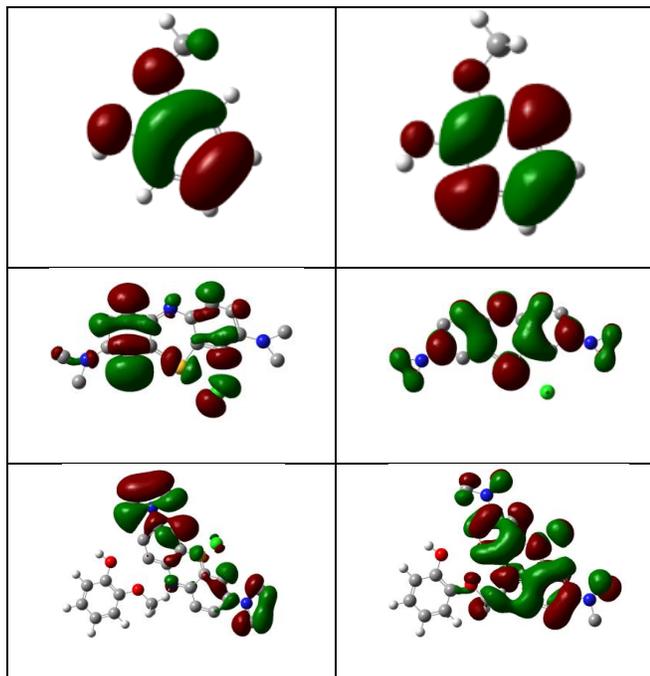


Figure 7: Visualization of HOMO and LUMO orbitals of guaiacol, MB, and their complex, highlighting orbital interaction and charge delocalization upon adsorption (Image generated by Gaussian 09).

Table 4: Comparative analysis of Bio based adsorbent-Date Trunk for the removal of MB Dye

Sr. No	Bio-adsorbent Name	Bio-adsorbent Dosage (g)	Contact Time(min)	pH	%age Removal	Reference
1	Papaya peels	0.2	85	5	88.2	[22]
2	Corn stigmata fibers	0.03	50	6	99.1	[23]
3	spathodea campanulata	0.2	110	10	99.8	[21]
4	Seaweed	0.1	70	4	98.7	[24]
5	Ackee Apple Pods	0.08	80	6	97.3	[25]
6	Coriandrum sativum	0.9	100	9	96.2	[26]
7	Sweet Potato Peels	1	50	-	72	[27]
8	Date trunks	0.4	50	-	92.4	Current work

6. Conclusion:

The findings demonstrated that date trunk is an exceptionally effective bio-adsorbent material for the elimination of MB dye from water-based solutions. The adsorbent material exhibited excellent characteristics, including diverse surface properties, porous regimes, and good surface area. Methylene blue was strongly adsorbed on the surface of the date trunks. UV Vis was used to determine the adsorption of the MB dye from the solution to the surface of the bio-adsorbents. The adsorption efficiency was influenced by several factors, including the quantity of 0.4g/50 ml bio-adsorbent, 50 min contact time, 150 rpm stirring rate, and 50 ppm dye. FTIR analysis confirmed the occurrence of MB functional groups of methylene blue on the surface of

5. A Comparative Study of Removal Efficiencies of Bio-adsorbents in Current Research:

Removal of MB dye by using the DT bio-adsorbent from wastewater is presented in Table 4 and compared to a few other bio-based adsorbents. This comparison shows that the DT bio-adsorbent significantly removed MB dye from the synthetic wastewater under optimum conditions.

the bio-adsorbent. DFT analysis measured the negative adsorption energy, which confirmed favorable thermodynamic interactions among the bio-adsorbent and methylene blue dye by establishing electrostatic interactions. The bio-adsorbent showed excellent charge transfer with the ability to share electron density by creating weak van der Waals force interactions. The results indicate that the adsorption energy showed a reduction in the HOMO and LUMO gaps. The results suggest that the use of date trunk as a bio-adsorbent material is a favorable and environmentally friendly approach for the treatment of wastewater.

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