Evaluation of carbon nanotubes/modified empty fruit bunch for adsorptive removal of methylene blue

Alena Naalini Rajoo[1], and *Noor Izzati* Md Rosli[2*]

[1]Chemical Engineering Department, Mila University, 71800 Nilai, Malaysia
[2]Chemical Engineering Department, Mila University, 71800 Nilai, Malaysia

Abstract. Dyes pose a significant risk to water pollution due to their toxic components which endangers both the environment and human health. The present research is to investigate the effectiveness of carbon nanotubes (CNTs) that were mixed with modified empty fruit bunch (MEFB) for the elimination of Methylene Blue (MB) dye. The CNTs/MEFB was prepared using a simple reflux method. The findings indicated that 0.25g of adsorbent dosage has the high removal rate and 30 mg/l is the ideal initial concentration. The pH of 8 shows the excellent methylene uptake along with ideal temperature of 40 °C.The Langmuir and Freundlich adsorption isotherm model were studied, and the equilibrium data was best discussed by the Langmuir isotherm model. Through the results obtained, CNTs/MEFB adsorbent shows an excellent result in Methylene Blue uptake.

1 Introduction

Water pollution, a critical global issue, has worsen due to the contamination of water sources with harmful substances like dyes, heavy metals, and pesticides. Methylene blue ($C_{16}H_{18}N_3ClS$), is widely used in industries like wood, linen, and silk. Its complex, heat-resistant structure makes it difficult to degrade. Exposure to methylene blue poses serious health risks, including eye damage, respiratory issues, nausea, vomiting, and a burning sensation in the mouth and throat. [1]. Due to its limited biodegradability, developing efficient and eco-friendly methods for MB removal from environmental samples is crucial to protect both ecosystems and public health. Different methods including chemical precipitation, membrane filtration, reverse osmosis, and electrochemical treatment were used to remove MB in the wastewater [2]. Among these, adsorption is often favoured for its simplicity, cheap, ease of operation, and high performance [3].

Malaysia is the world's second-largest producer of palm oil, following Indonesia. Modified empty fruit bunches (MEFBs) from palm oil production contain carboxyl groups, oxygen-containing functional groups that can bind to carbon nanotubes (CNTs) [4]. CNTs have been shown to be effective adsorbents for organic pollutants due to their unique properties, high surface area, thermochemical stability, and modifiable surfaces [5]. The

---

* Corresponding author: izzati.rosli@mila.edu.my

aim of the study is to assess the efficiency of CNTs/MEFB in adsorbing methylene blue (MB) from aqueous solutions [6]. To achieve this, various experimental factors were examined, including solution pH, adsorbent dosage, initial dye concentration, and temperature [10]. The adsorption capacity and rate of the CNTs/MEFB composite were assessed using adsorption equilibrium isotherms

2 Materials and method

2.1 Materials

Empty Fruit Bunches (EFBs) were obtained from Szetech Engineering Sdn. Bhd., located in Selangor, Malaysia. Carbon nanotubes, Methylene Blue, Nitric Acid (HNO_3), Sulfuric Acid (H_2SO_4), Sodium Hydroxide, and Hydrochloric Acid were obtained from Mila University.

2.2 Preparation of modified empty fruit bunch (MEFB)

Palm oil empty fruit bunches (EFB) were converted into biochar through a gasification process using oxygen with an airflow rate of 1 m^3/s. The resulting biochar was dried in an oven at 70°C for 24 hours, ground and sieved to a size of 200 mm using an ASTM-standard sieve [1].

2.3 Functionalization of CNTs and preparation of CNTs/MEFB adsorbent

The functionalized-CNTs was prepared by an acid treatment. In a typical procedure, 10 g of CNTs were mixed with a mixture consisting 4.0 M of nitric acid (HNO_3) and sulfuric acid (H_2SO_4) in a 1:3 volumetric ratio. Next, the suspension was refluxed at 80°C for 5 hours [7,1]. The resultant mixture was then washed with distilled water until the pH reached neutral, filtered, and dried in an oven at 50°C for 24 hours to obtain functionalized CNT. The CNTs/MEFB composite was synthesized by dispersing an amount of functionalized CNTs from 0.05g to 0.2g in 100 mL of deionized water. Then, 10g of MEFB was added into the suspension and stirred at 200 rpm for 3 hours [8]. The CNTs/MEFB mixture was subsequently centrifuged, washed with deionized water, and dried in an oven at 60°C for 12 hours. The obtained samples were stored for further used

2.4 Batch adsorption experiment

Batch adsorption studies were conducted by dispersing 1 g/L of CNTs/MEFB in a 100 mL of 10 mg/L methylene blue solution in a volumetric flask. The adsorption process was conducted in a water bath shacker for 2 hours at room temperature, and at 100 rpm. At interval of time, 3 mL of the suspension were withdrawn and filtered to remove suspended particles. The concentration of the MB was monitored using a UV-Vis spectrophotometer at a wavelength of 665 nm. The adsorptive performance of prepared adsorbent was investigated through the effects of adsorbent dosage, initial MB concentration, temperature, and solution pH on the adsorption performance.

3 Materials and method

3.1 Batch adsorption study

The influence of various parameters on the adsorption of MB by CNTs/MEFB were assessed through One-factor-at-time (OFAT) method.

3.1.1 Effect of adsorbent dosage

Figure 1 illustrates the percentage removal of MB was increased with increasing adsorbent loading from 0.10 to 0.25 g/L. Notably, a removal efficiency exceeding 90% was achieved with 0.25 g of adsorbent dosage [9]. This improvement was due to the increased availability of adsorption sites on the adsorbent's surface, as a higher adsorbent dosage exposes a larger overall surface area of CNTs/MEFB, facilitating greater dye adsorption [10].

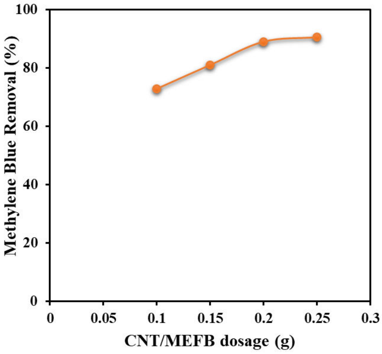

Fig. 1. The effect of CNTs/MEFB dosage (g) on removal percentage of MB.

3.1.2 Effect of concentration of methylene blue

Figure 2 shows the effect of initial concentration of MB significantly affected the adsorption capacity of MB (Fig.2). The highest adsorption capacity was attained at 30 mg/l. Under saturation conditions, CNTs/MEFB exhibits its maximum adsorption capacity [11]. This occurs because all available active sites on the CNTs/MEFB surface are completely occupied by adsorbate molecules, resulting in the highest possible mass of adsorbate per unit mass of adsorbent [12].

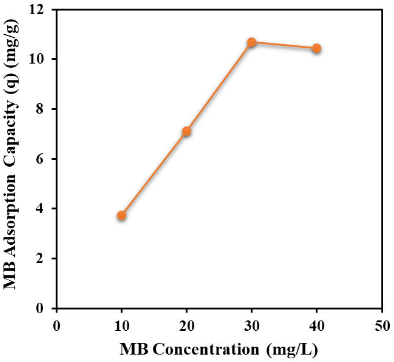

Fig. 2. The effect of initial MB Concentration (mg/L) on MB uptake (q) (mg/g).

3.1.3 Effect of solution pH

Figure 3 demonstrates a significant increase in adsorption capacity of MB as pH increases from 2 to 8. The maximum adsorption capacity of 3.845 mg/g was achieved at an initial pH of 8. This enhancement is attributed to the increased electrostatic attraction between the cationic MB dye molecules and the negatively charged surface of the CNTs/MEFB adsorbent at higher pH values. This favourable electrostatic interaction promotes greater dye uptake [13].

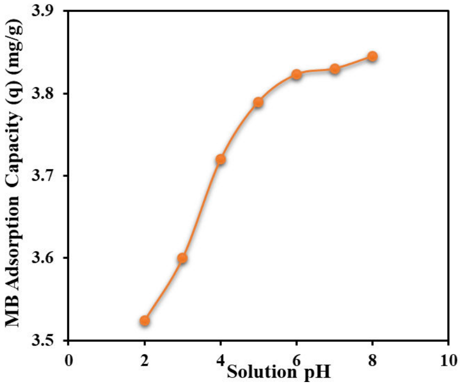

Fig. 3. The effect of solution pH on MB uptake (q) (mg/g).

3.1.4 Effect of methylene blue temperature

Figure 4 displays the effect of adsorption temperature on the percentage of MB removed. The adsorption capacity for the dye increased with temperature from 25°C to a maximum of 4.126 mg/g at 40°C, subsequently decreasing to 60°C. This temperature-dependent behaviour suggests an initial enhancement in dye uptake likely due to increased molecular kinetic energy. However, a decline in adsorption capacity beyond 40°C indicates that the desorption process becomes more dominant at higher temperatures. This phenomenon might be attributed to the reduced thickness of the boundary layer surrounding the CNTs/MEFB, leading to decreased adsorbent accessibility [14].

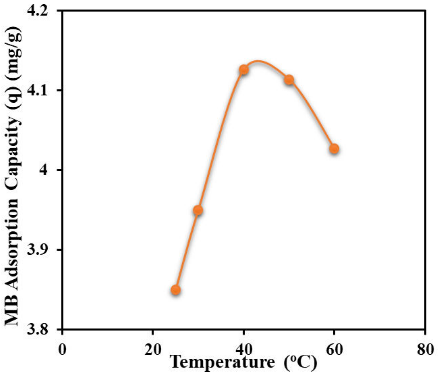

Fig. 4. The effect of temperature (°C) on MB uptake (q) (mg/g).

3.2 Adsorption isotherm study

3.2.1 Langmuir adsorption isotherm

The Langmuir model, as shown in Figure 5, effectively describes the adsorption of methylene blue onto CNTs/MEFB, with a high correlation coefficient ($R^2 = 0.995$). From Table 1, the maximum monolayer adsorption capacity q_m of CNTs/MEFB was determined to be (64.52 mg g^{-1}), indicating its ability to efficiently adsorb MB. This suggests that the adsorption process is primarily governed by the affinity of the binding sites within the CNTs for MB [8]. The equilibrium constant (K_L) associated with the binding energy of the sorption system was calculated as 0.096. This value suggests a homogeneous adsorbent surface and monolayer adsorption, favouring the Langmuir model over the Freundlich model [15].

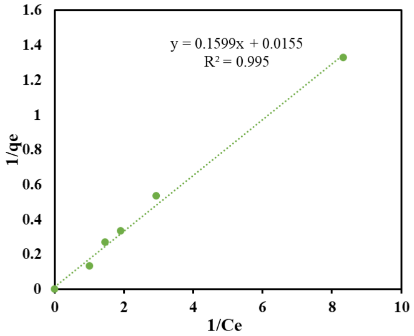

Fig. 5. Langmuir plot for adsorption of MB by CNTs/MEFB.

3.2.2 Freundlich adsorption isotherm

The Freundlich isotherm model, as depicted in Figure 6, also describes the adsorption of MB onto CNTs/MEFB, albeit with a lower correlation coefficient ($R^2 = 0.961$) compared to the Langmuir model. The Freundlich isotherm analysis yielded n and K_f values of 0.170 and 0.926 mg g^{-1}, respectively. The n value, less than unity, suggests a physisorption process, indicating unfavourable adsorption conditions and a relatively weak interaction between MB and CNTs/MEFB [15]. The corresponding values for the Freundlich parameters are listed in Table 1. The Freundlich equation reflects a gradual increase in adsorption with increasing concentration, as remaining adsorption sites exhibit lower affinity for MB.

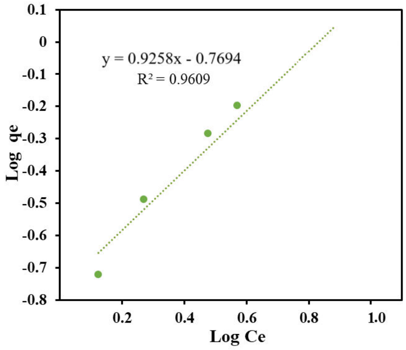

Fig. 6. Freundlich plot for adsorption of MB by CNTs/MEFB.

Table 1. Adsorption isotherm models with respective parameters for the adsorption of MB with CNTs/MEFB composite.

Models	**Parameters**	**Value**
Langmuir	q_m (mg g^{-1})	64.52
	K_L (L/mg)	0.096
	R^2	0.995
Freundlich	K_F (mg g^{-1})	0.926
	1/n	0.170
	R^2	0.961

4 Conclusion

Carbon nanotubes (CNTs) and modified empty fruit bunch (MEFB) demonstrate potential as an effective adsorbent for removing methylene blue (MB) from aqueous solutions. MB uptake increased with adsorbent dosage, with 0.25 g demonstrating superior performance to 0.1 g due to increased surface area availability. For initial MB concentration adsorption capacity was attained at 30 mg/l. The optimal pH for MB adsorption onto CNTs/MEFB was determined to be 8. This is likely due to electrostatic attraction between the negatively charged adsorbent and the cationic MB dye. Maximum adsorption occurred at 40°C, suggesting weak adsorption forces between the adsorbent and dye at higher temperatures. Langmuir isotherm modelling best represented the equilibrium data compared to Freundlich, as indicated by higher correlation coefficient (R^2) value. One potential area for future research is to explore the use of alternative adsorbents for dye removal. Investigating the adsorption capabilities of different materials could potentially lead to even more efficient and effective processes.

References

1. E. N. Seyahmazegi, R. Mohammad-Rezaei, & H. Razmi, Multiwall carbon nanotubes decorated on calcined eggshell waste as a novel nano-sorbent: Application for anionic dye Congo red removal. Chem. Eng. Res. Des. **109**, 824–834 (2016). https://doi.org/10.1016/j.cherd.2016.04.001
2. C.-Z Liang., S.-P Sun, F.-Y. Li, Y.-K., Ong, Y.-K., & T.-S. Chung, Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofiltration. J. Membr. Sci. **469**, 306–315 (2014). https://doi.org/10.1016/j.memsci.2014.06.057
3. X.-J. Liu, M.-F Li, & S. K. Singh, Manganese-modified lignin biochar as adsorbent for removal of methylene blue. J. Mater. Res. Technol. **12**, 1434–1445 (2021). https://doi.org/10.1016/j.jmrt.2021.03.076

4. M. J. Ahmad, R. Ismail, & F. A. Ghani, Review on socioeconomic and sustainability of oil palm plantations among rural communities in Malaysia, IOP Conf. Ser: Earth Environ. Sci., **1208**(1), 012054 (2023). https://doi.org/10.1088/1755-1315/1208/1/012054 (2023)
5. Y. Yang, Y. Piao, R. Wang, Y. Su, N. Liu, & Y. Lei, Nonmetal function groups of biochar for pollutants removal: A Review. J. Hazard. Mater. Adv. **8**, 100171 (2022). https://doi.org/10.1016/j.hazadv.2022.100171
6. A. Peigney, C. Laurent, E. Flahaut, Specific surface area of carbon nanotubes and bundles of carbon nanotubes. Carbon. **39**, 507–14(2001). https://doi.org/10.1016/S0008-6223(00)00155-X
7. N. S. J. M. L. Theo, Application of Oil Palm Empty Fruit Bunch as Adsorbent: A Review. Trans. Sci. Technol. **6**, 9-26. (2019).
8. M. Inyang, B. Gao, A. Zimmerman, M. Zhang, & H. Chen, Synthesis, characterization, and dye sorption ability of carbon nanotube–biochar nanocomposites. Chem. Eng. J. **236**, 39–46 (2014). https://doi.org/10.1016/j.cej.2013.09.074
9. E. Alver, A. Ü. Metin, & F. Brouers, Methylene blue adsorption on magnetic alginate/rice husk bio-composite. Int. J. Biol. Macromol. **154**, 104–113 (2020). https://doi.org/10.1016/j.ijbiomac.2020.02.330
10. A. A. Eljiedi, & A. Kamari, Removal of methyl orange and methylene blue dyes from aqueous solution using Lala Clam (orbicularia orbiculata) shell, in Proceedings of the International Conference on Education, Mathematics and Science 2016 (ICEMS2016) in Conjunction with 4th International Postgraduate Conference on Science and Mathematics 2016 (IPCSM2016), Perak, Malaysia, November 19 (2016), 1847. https://doi.org/10.1063/1.4983899
11. D. Pathania, S. Sharma, & P. Singh, Removal of methylene blue by adsorption onto activated carbon developed from *Ficus carica* bast. Arab. J. Chem. **10**, S1445-S1451 (2017). https://doi.org/10.1016/j.arabjc.2013.04.021
12. C. A. Policiano Almeida, T. M. Zanela, C. Machado, J. A. Altamirano Flores, L. F. Scheibe, N. P. Hankins, & N. A. Debacher, Removal of methylene blue by adsorption on aluminosilicate waste: Equilibrium, kinetic and thermodynamic parameters. Water Sci. Technol. **74,** 2437–2445 (2016). https://doi.org/10.2166/wst.2016.408
13. R. Salahshour, M. Shanbedi, & H. Esmaeili, Methylene blue dye removal from aqueous media using activated carbon prepared by Lotus leaves: Kinetic, equilibrium and thermodynamic study. Acta Chi. Slov. **68**, 363–373 (2021). https://doi.org/10.17344/acsi.2020.6311
14. M. Horsfall Jnr & A. I. Spiff, Studies on the effect of pH on the sorption of PB^{2+} and Cd^{2+} ions from aqueous solutions by Caladium bicolor (wild cocoyam) biomass. Electronic J. Biotechnol. **7,** (2004). https://doi.org/10.2225/vol7-issue3-fulltext-8
15. M.T.Yagub, T.K.Sen, & M.Ang, Removal of cationic dye methylene blue (MB) from aqueous solution by ground raw and base modified Pinecone Powder. Environ. Earth Sci. **71**, 1507–1519 (2023). https://doi.org/10.1007/s12665-013-2555-0