Malaysian Journal of Chemistry, 2024, Vol. 26(3), 264-272
(Special Issue: *The International Conference on Advanced Materials & Sustainable Energy Technologies 2023*)

Optimization Study of Methylene Blue Decolorization Using Waterfilter Prototype Embedded with Sugarcane Bagasse Biochar

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This study explored the utilization of sugarcane bagasse as an adsorbent in water filter prototype to remove methylene blue from coating industry wastewater. Sugarcane was selected due to its abundance as an agricultural waste material. This research was motivated by the lack of optimization studies on water filter adsorption efficiency for methylene blue removal from the coating industry wastewater as well as the harmful impact of methylene blue on human health. The pyrolysis process was employed to produce sugarcane bagasse biochar. The chemical and morphological characterization of sugarcane bagasse biochar was conducted using particle size analyzer, Fourier-transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy-energy dispersive X-ray analysis (FESEM-EDX). The FESEM-EDX analysis unveiled the porous structure of biochar, which facilitated the adsorption process. Optimization using Response Surface Methodology (RSM) led to a reduction in methylene blue absorbance from 3.91 to 0.22 under optimum conditions. These findings offer valuable insight into the potential of sugarcane bagasse biochar as a proficient adsorbent for methylene blue in treating wastewater from the coating industry.

Keywords: Sugarcane bagasse; biochar; adsorption; methylene blue; wastewater

Received: February 2024; Accepted: March 2024

Industrial, agriculture and domestic sectors consume more than 33% of the earth's renewable freshwater [1]. Over the past century, significant attention has been directed towards advancing pollution control technologies to effectively treat and manage wastewater generated by diverse industrial sectors. This attention has been focused on both research and development as well as applications. Methylene blue, which is frequently used to dye silk, wool, cotton, and paper, is one of the primary materials utilized in the dye and coating industries. This results in the production of industrial wastewater containing concerning amount of methylene blue in it. Methylene blue contamination poses several health risks to humans, including DNA mutation, mental disorders, carcinogenic effects of central nervous system dysfunction, kidney and liver damage, and dermatological diseases such as itching [2]. Treating wastewater with substantial amount of methylene blue before releasing it into the environment is of paramount importance due to its detrimental effects on water quality and perception [3].

Methylene blue and other textile colors are purportedly removed from industrial effluent using a variety of techniques. Among the techniques employed are liquid-liquid extraction [4], ultrafiltration [5], nano-filtration [6], microwave treatment [7], biodegradation [8], hybrid systems [9], coagulation [10], and adsorption/biosorption [11]. Amongst other materials, biochar has been extensively used in wastewater pollution treatment due to its high stability and adsorption capacity, outstanding surface characteristics, well-developed pore structure, and abundant surface functional groups [12]. Sugarcane bagasse, the residue obtained after the juice extraction process, has been identified as a potential precursor for biochar production due to its economic resource abundance and carbon-rich content, including cellulose and hemi-cellulose [13]. Biochar has also been shown to possess favourable properties as a bioadsorbent for methylene blue [14].

This study proposed an organic bioadsorbent material with the potential to be integrated into the wastewater treatment filtration system. Carbon-rich biochar was produced from sugarcane bagasse as the precursor via carbonization technique. Most of the bioadsorbents in the market are derived from charcoal residue undergoing high-temperature wood heating process, posing environmental concerns during their production process. However, the bioabsorbent in this study was produced from

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†Paper presented at the International Conference on Advanced Materials & Sustainable Energy Technologies 2023

absolute sugar-cane bagasse, a typical waste from local beverage industry. This biadsorbent was primarily derived from cellulose, which is a by-product from food processing industry, employing a waste-to-wealth approach to ensure the sustainability of feedstock. This study aimed to remove methylene blue from industrial wastewater to mitigate its harmful effects on humans and aquatic animals due to its toxic nature, and to enhance the environmental well-being in the future.

EXPERIMENTAL

Production of Biochar from Sugarcane Bagasse

Pre-treatment of Sugarcane Bagasse

Sugarcane bagasse was collected from a sugarcane juice stall in Pagoh, Johor. The sample was cleaned to remove any dirt and dried under sunlight for three days prior to cutting and further drying process in the oven at 70°C for about two hours. Finally, the sample was finely ground and sieved into particle size of 212 µm. This could ensure uniform heating of the sample during the pyrolysis procedure.

Carbonization of Sugarcane Bagasse

To produce biochar, sugarcane bagasse was carbonized in muffle furnace (Neytech 9493308 Vulcan Muffle Furnace, 550 Cu In). In this phase, the pulverized sugarcane bagasse was weighed and put into crucible. It was heated to 500°C in the muffle furnace at heating rate of 20°C per minute. The sample was then heated to 500°C for approximately an hour to eliminate any volatile substances. The residual carbon-rich material (biochar) was allowed to cool at room temperature prior to further use in wastewater treatment.

Filtration System Prototype Development

A simple set of household water filtration system (body diameter of 5 cm and height of 15 cm) was developed. The inner part of the filter was packed with sugarcane bagasse biochar. Wastewater containing methylene blue was passed through the water filter, and investigate the effects of dilution factors, wastewater to biochar ratio, and contact time were investigated. Adsorption efficiency was determined by wet and instrumentation analysis as described in the subsequent section.

Optimization Using Response Surface Methodology (RSM)

Based on the preliminary experiment, three factors, namely dilution factor (A), wastewater to biochar ratio (B), and contact time (C), were selected to be used in the Design Expert software via Response Surface Methodology (RSM) with methylene blue absorbance as the response. Every factor was adjusted into five levels: centre points (coded level 0), high level, low level, and two outer points corresponding to 1.68. Via Central Composite Design (CCD) in RSM, eight factorial points, six axial points, and six central points generated a total of 20 experimental runs.

The Design Expert software seeks the combination of factors which could provide the best conditions for optimum methylene blue filtration process.

Physicochemical Analysis

Ultraviolet-Visible Spectroscopy

UV analysis measures the absorbance or removal of specific contaminants in the treated wastewater, aiding in evaluating the efficiency of the biochar adsorbent in removing methylene blue. The best condition affecting the adsorption efficiency of methylene blue was determined, which was reflected by the reduction in color intensity in the wastewater samples. The efficiency of the bioadsorbent was determined by Cary 60 UV-Visible (UV-Vis) spectrophotometer from Agilent Technology (USA) at fixed wavelength of 615 nm for methylene blue solution.

Fourier Transform Infrared Spectroscopy

Functional groups of raw sugarcane bagasse precursor and biochar were analyzed using Perkin Elmer Fourier-transform infrared (FTIR) spectroscopy at wavelengths between 4000 cm^{-1} and 400 cm^{-1}.

Particle Size Analyzer

Bettersize 2000 laser particle size analyzer was employed to measure the size distribution of particles within the sample. This instrument characterizes sediment particles based on the diffraction of a laser light source.

Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray Analysis

Raw sugarcane bagasse and its biochar were analyzed in terms of morphological structure and elemental composition using Merlin ultra-high-resolution field emission scanning electron microscopy (FESEM) coupled with energy dispersive x-ray (EDX) at magnification of 20000x, respectively.

RESULTS AND DISCUSSION

Functional Group Analysis

FTIR analysis was conducted to identify various functional groups present in sugarcane bagasse before and after the pyrolysis process. Based on Figure 1, the spectra of sugarcane bagasse before pyrolysis showed three prominent and sharp peaks, namely 3355cm^{-1} for hydroxyl group (-OH), 1031cm^{-1} indicating C-O stretching representing cellulose and hemicellulose, and 2925cm^{-1} to 2860cm^{-1} indicating aliphatic CH_2 and CH, respectively [15]. According to the findings of Ban et al. (2022), the absorption band at 2960 cm^{-1} was attributed to the aromatic C-H bond in lignin, while 1031cm^{-1} indicated the C-O-C pyranose ring skeletal vibration [16]. For the sugarcane bagasse after pyrolysis, the peaks at 3355cm^{-1}, 1031cm^{-1}, and 2925cm^{-1} - 2860cm^{-1} were absent, but a new peak formed near 1580cm^{-1}, signifying C=C stretching for the lignin aromatic ring. Sugarcane bagasse contains various functional groups, such as carbohydrates, lignin, and hemicellulose, which are susceptible to thermal decomposition during pyrolysis. Elevated temperatures during pyrolysis disrupt chemical bonds, resulting in the release of volatile compounds and the breakdown of functional groups.

Particle Size Analysis

Particle size analysis served to distinguish between the particle dimensions of sugarcane bagasse and its biochar. The measurement of particle size was crucial to ensure methylene blue adsorption effectiveness as it was directly influenced by surface area and porosity.

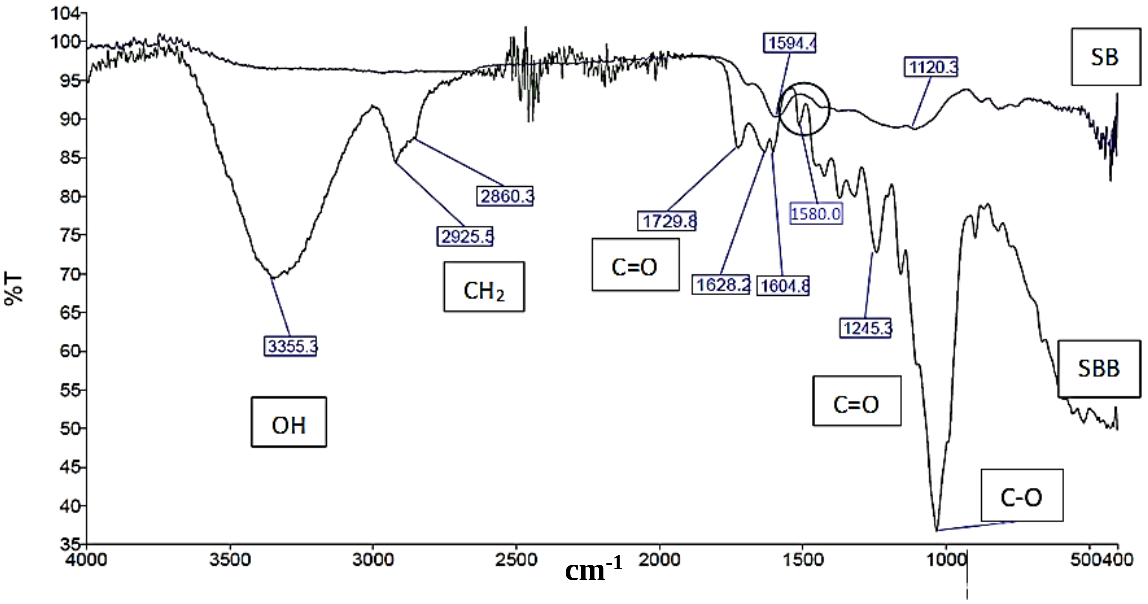
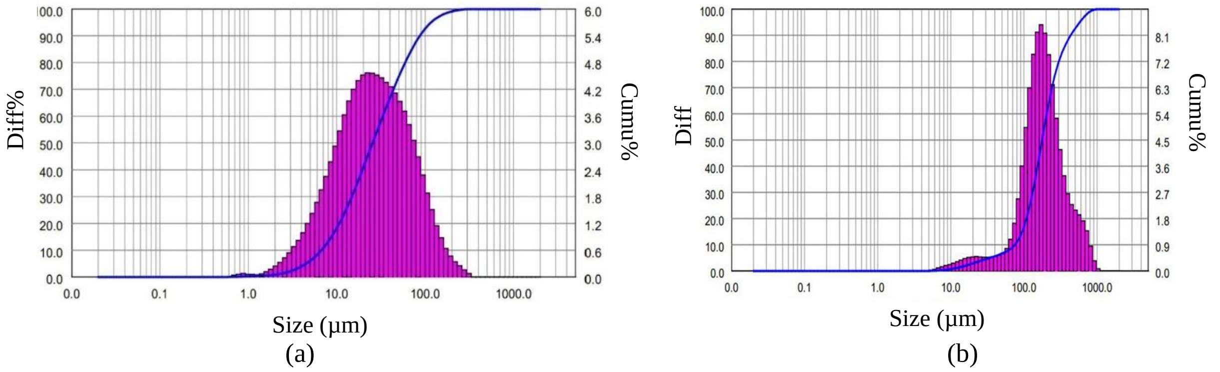


Figure 1. FTIR spectra of sugarcane bagasse (SB) and sugarcane bagasse biochar (SBB).



(a)

(b)

Figure 2. Particle size distribution of (a) sugarcane bagasse and (b) sugarcane bagasse biochar.

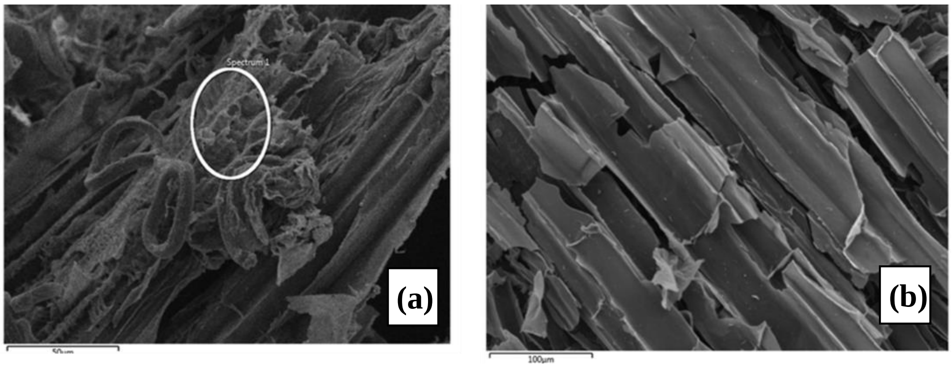


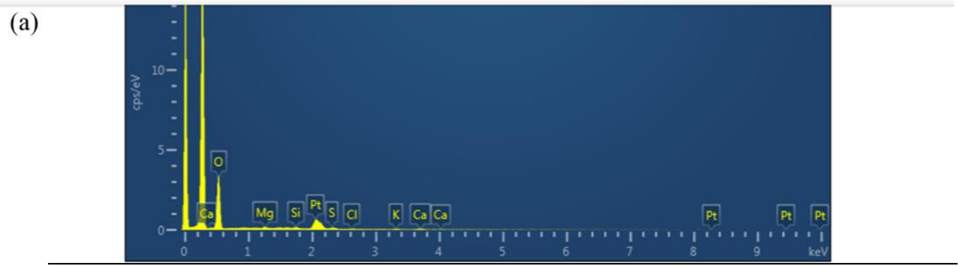
Figure 3. Surface morphological images of (a) sugarcane bagasse and (b) sugarcane bagasse biochar.

According to Figure 2, sugarcane bagasse displayed particle sizes ranging from 5.0 µm to 1000.0 µm. The smallest diameter size obtained was 5 µm at 0.01%, while the largest size obtained was 1000 µm at 16.82%. For biochar, the size distribution curve was shifted to smaller sizes in the range of 0.561 µm to 390.2 µm. The size of 25.45 µm represented the midpoint and covered 40% of the total graph area. Higher temperatures may promote the elimination of volatile and aliphatic compounds, yielding biochar with higher surface area and pore volume [17].

Morphological and Elemental Analysis

Figures 3 (a) and (b) show the morphological structures of both sugarcane bagasse and biochar produced from the pyrolysis process, respectively. Sugarcane bagasse is a lignocellulosic material with approximately 35–40% cellulose, 20–35% hemicellulose, 15–20% lignin, and 2–5% ash. As demonstrated in Figure 3, the FESEM image of the raw bagasse sample revealed various fiber types shapes. The majority of sugarcane bagasse was made up of fibrous bundles, comprising an inner layer with larger channel diameter and rigid outer layer, and has closely spaced vascular channels (5–17µm). Most of the visible particles were long, pore-filled tubular formations. Some of the fibers were found to be flaky and connected, while others appeared to be stiff and well-structured. The vascular system of plants is composed of these fibers. One possible explanation for the variation in the three functional units (cellulose, hemicellulose, and lignin) in fibers is their variance [18]. The micrograph of the raw sugarcane bagasse also displayed abundance of non-fibrous components scattered over the fiber surface. On the other hands, biochar showed dense, elongated structure that may be contributed by the carbon concentration process during pyrolysis. Similar trend is also depicted by the EDX results (Figure 4).

From Figure 4, it can be observed that the elemental composition of the biochar changed slightly during the pyrolysis process. This was indicated by the increase in carbon and oxygen elements due to the removal of volatile matters and the degradation of cellulose, hemicellulose and lignin at higher temperatures during the carbonization process.

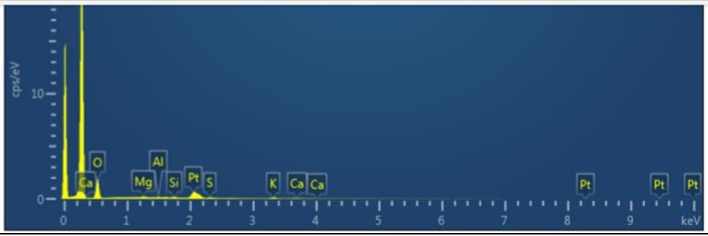


Spectrum 1

Element	Line Type	Weight %	Weight % Sigma	Atomic %
O	K series	22.17	0.25	17.77
C	K series	76.56	0.2o	81.75
Mg	K series	0.13	0.02	0.07
Ca	K serves	0.41	0.05	0.13
S	K series	0.22	0.04	0.09
K	K series	0.24	0.04	0.08

Cl	K series	0.11	0.03	0.00
Si	K series	0.15	0.03	0.07
Total		100.00		100.00

(b)



Spectrum 4

Element	Line Type	Weight %	Weight % Sigma	Atomic %
O	K series	12.18	0.15	9.51
C	K series	86.57	0.16	90.03
K	K series	0.54	0.04	0.17
Mg	K series	0. 15	0.02	0.08
S	K series	0.13	0.03	0.05
Al	K series	0.07	0.02	0.03
Si	K series	0.16	0.02	0.07
Ca	K series	0.20	0.04	0.06
Total			100.00	100.00

Figure 4. Elemental compositions of (a) sugarcane bagasse and (b) sugarcane bagasse biochar.

Optimization of Methylene Blue Absorbance

A total of 20 experimental runs via CCD) were conducted with the 2FI model identified as the best fit for the analysis. Table 1 presents the experimental and predicted values of methylene blue absorbance affected by three factors. The predicted absorbance from the experimental data was expressed in terms of coded factors as shown by Eq. 1.

Where, A, B, C, and D represent the independent variables of dilution factor, ratio of wastewater to biochar, and contact time, respectively. According to the analysis of variance, the F-value of 8.77 implied that the suggested model was significant with p-value of <0.0006. Additionally, this model exhibited good fit and significance as evidenced by the lack-of-fit with F-value of 2.25 and p-value of 0.1936. This model was appropriate for the data due to its insignificant lack of fit, with the possibility that the observed lack-of -fit was likely attributed to noise.

$$Y = 0.4571 - 0.2687 A + 0.1972 B - 0.3538 C -0.1867 AB +0.2982 AC -0.2382 B \qquad \text{(Eq. 1)}$$

Table 1. Experimental and predicted values of methylene blue absorbance.

Run	Factor 1 A: Dilution factor	Factor 2 B: Ratio of wastewater to biochar	Factor 3 C: Contact time minutes	Response 1: Methylene blue absorbance
1	20.0	65.0	5.5	0.1458
2	10.5	65.0	1.0	1.193
3	1.0	100.0	1.0	2.2821
4	1.0	30.0	10	0.2048
5	10.5	30.0	5.5	0.3646
6	10.5	65.0	5.5	0.2875
7	1.0	30.0	1.0	0.5071
8	20.0	30.0	1.0	0.1906
9	10.5	65.0	5.5	0.7463

10	10.5	100.0	5.5	0.4839
11	10.5	65.0	5.5	0.2715
12	20.0	30.0	10	0.1569
13	1.0	100.0	10	0.1028
14	10.5	65.0	5.5	0.2046
15	20.0	100.0	1.0	0.2945
16	10.5	65.0	10.0	0.2324
17	10.5	65.0	5.5	0.3994
18	10.5	65.0	5.5	0.2316
19	1.0	65.0	5.5	0.6103
20	20.0	100.0	10.0	0.2322

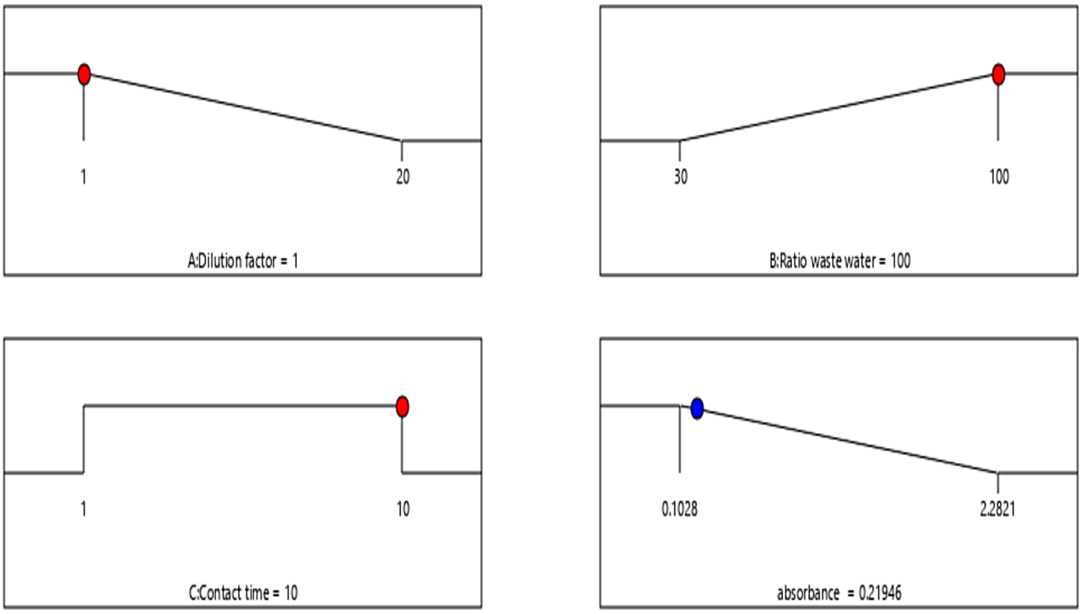


Figure 5. Optimum conditions for removal of methylene blue from industrial wastewater

Figure 5 displays the optimization results of the dilution factor, wastewater to biochar ratio, and contact time against methylene blue absorbance. Under optimum conditions, the filtration process using the water filter prototype produced the lowest UV absorbance of 0.22 at dilution factor of 1, wastewater to biochar ratio of 100:1, and contact time of 10 minutes. A significant reduction in methylene blue absorbance was visible when compared to the untreated wastewater (3.91) as illustrated in Figure 6. Minimum dilution factor was set to represent the most concentrated dilution intended to minimize water consumption and prevent its wastage. The wastewater to biochar ratio was set at 100:1 to promote maximum wastewater treatment with minimum biochar amount to address the substantial volume of industrial wastewater generated. Additionally, contact time of 10 minutes was allowed for efficient wastewater management and providing ample time for the biochar to interact with methylene blue.

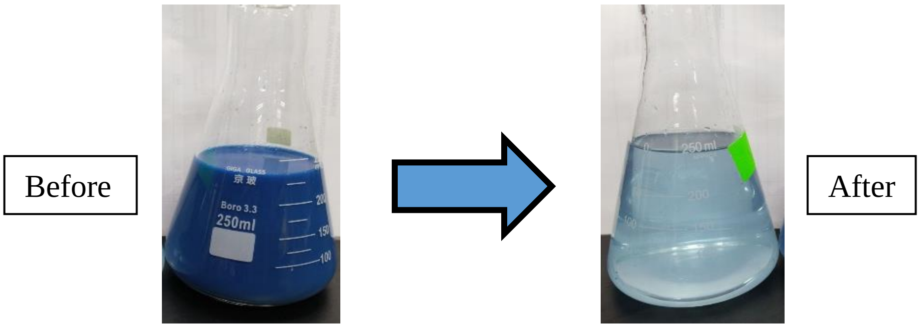


Figure 6. Wastewater color change after filtration process by sugarcane bagasse biochar water filter prototype at optimum conditions.

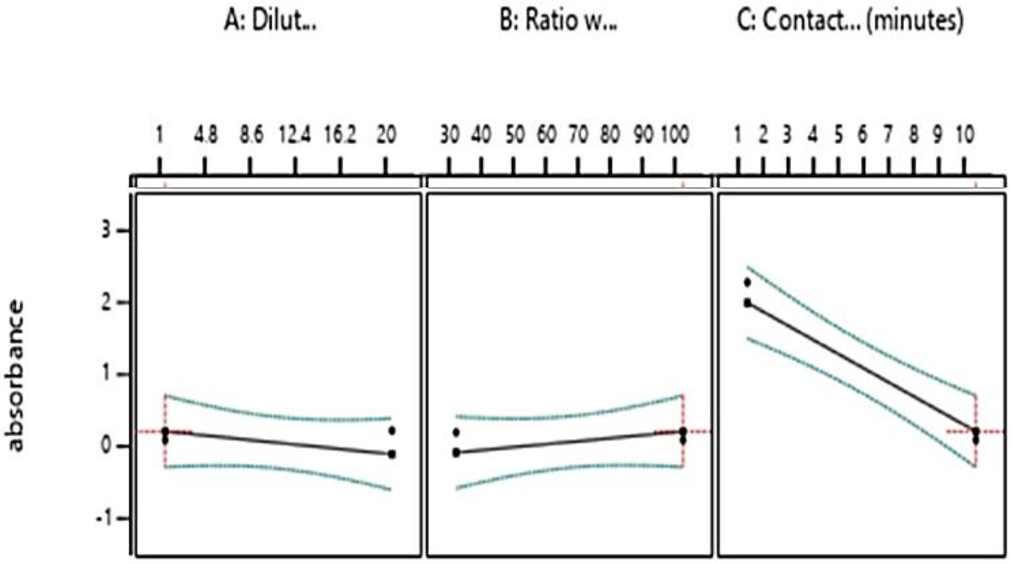
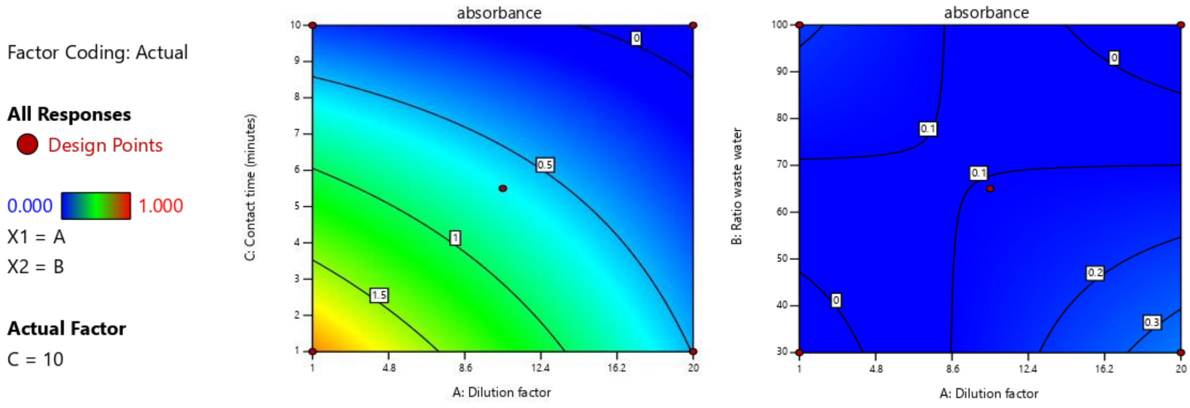


Figure 7. General trends of the effect of manipulated variables on methylene blue absorbance

Figure 7 illustrates the overall trend of methylene blue absorbance influenced by the three manipulated factors. Both dilution and wastewater to biochar ratio displayed a non-substantial outcome. The lack of insignificant persisted across scales varying from the most concentrated (1) to the most diluted wastewater (20), and from 30 to 100 wastewater to biochar ratio. However, the relationship between contact time and methylene blue absorbance yielded a significant finding between 1 to 10 minutes of filtration time. This underscored the crucial role of contact time in influencing the significant variation in methylene blue absorbance.

Figure 8 depicts the 2D diagram illustrating the relationship between two manipulated variables with the methylene blue absorbance. Figure 8 (a) shows the transition of color towards lower methylene blue absorbance with increasing contact time and dilution factor while maintaining constant wastewater to biochar ratio. This could be associated with the increased force, driving the movement of wastewater as the aqueous phase into the biochar, representing the solid phase. This movement may be facilitated by the concentration gradient, which denotes the difference in methylene blue concentration between two different regions to overcome the mass transfer resistance that occurs between the two phases [19]. In Figure 8 (b), there was no significant difference in methylene blue absorbance of at constant contact time of 10 minutes. These findings indicated that both factors played a minor role in the reduction of methylene blue in wastewater. However, there was an improvement demonstrated within a small range between 0.1 to 0.3 as the dilution factor approached 20 and wastewater to biochar ratio reached 100.



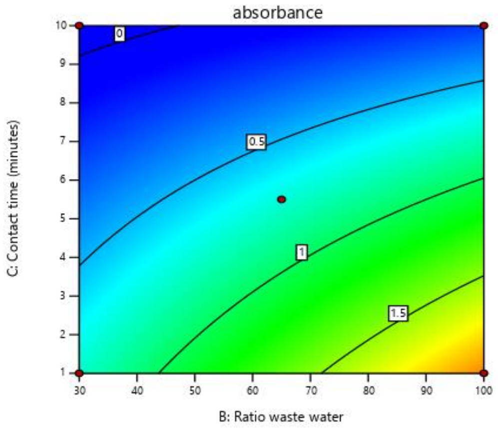


Figure 8. 2D diagram of effect of manipulated variables on methylene blue absorbance: (a) effect of dilution factor and contact time on methylene blue absorbance, (b) effect of wastewater to biochar ratio and contact time on methylene blue absorbance, (c) effect of dilution factor and wastewater to biochar ratio on methylene blue absorbance.

The slight increase in methylene blue absorbance can be attributed to the desorption process, where competition between compounds and ions in the solution for adsorption sites led to the displacement of methylene blue from the biochar. The result is in agreement with the previous study conducted by Zainuddin et al. 2023 [20]. Figure 8 (c) depicts the significant impact of contact time on the removal of methylene blue in wastewater treatment. Opposite trend was observed, where the absorbance value decreased as the ratio of wastewater to biochar increased, particularly at contact time below 8 minutes. This result suggested that the primary consideration in the development of water filter system for wastewater treatment should be the optimization of contact time.

CONCLUSION

In conclusion, this study successfully achieved its objective to develop a laboratory-scale prototype containing sugarcane bagasse to decolorize methylene blue from coating industry wastewater. The application of RSM enabled the determination of optimum conditions in terms of contact time, wastewater to biochar ratio and dilution factor to produce the lowest methylene blue absorbance. These findings highlight the promising potential of sugarcane bagasse as an environmentally friendly solution to address colour-related challenges in industrial effluents. Furthermore, these findings could become a solid groundwork for future research studies in development of water filter prototype incorporating bioadsorbents for an eco-friendly industrial wastewater management.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the TVET Applied Research Grant Scheme T-ARGS (T-ARGS/2024/BK01/00220) and Jabatan Pendidikan Politeknik dan Kolej Komuniti (JPPKK) for the financial support and Politeknik Tun Syed Nasir Syed Ismail for the opportunities provided to conduct this study. Appreciation is also extended to HueCoating Resources Sdn. Bhd. for their contribution of wastewater and valuable consultation.

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