Biochar Derived from Chopsticks as an Effective Biosorbent for Pollutant Removal from Wastewater

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Abstract

Dyes such as methylene blue have been found in wastewater and pose a threat to human health and the ecosystem. Removing pollutants from wastewater can be carried out through different methods, but a sustainable method of doing so should involve the use of readily available, low cost materials that can be processed through a method that is not energy-intensive. Carbon-rich solids such as biochar have been found to be effective in reducing the levels of cationic dyes like methyl violet, methylene blue, basic blue, crystal violet and rhodamine by using the electrostatic force of interaction as adsorption mechanism, though experiments using disposable chopsticks as a precursor have not been documented before. 2 types of biochar, derived separately from bamboo and wooden chopsticks, were pyrolysed at either 200ºC or 500ºC and used as absorbents for methylene blue in water. The structural characteristics and adsorption properties of chopstick biochar were analysed by Scanning electron microscopy, and the adsorption mechanism between chopstick biochar and methylene blue molecules was analysed using a UV-vis spectrophotometer. Results showed that biochar pyrolysed at higher temperatures (B5 and W5) were more effective in removing methylene blue solution compared to biochar pyrolysed at lower temperatures (B2 and B5). Wooden biochar (W2 and W5) were also more effective at removing MB compared to bamboo biochar (B2 and B5). Langmuir isotherm model was a better fit for all samples, suggesting that the adsorption by bamboo and wooden biochar is monolayer.

Keywords

Chopsticks, biochar, pollutant removal

1. Introduction

The rapid industrialisation of society has contributed greatly to water pollution, which is responsible for 1.2 million deaths per year [1]. Dye, a pollutant, is often discharged into water bodies. It has been estimated that 15% of total dyes produced worldwide are discharged to water bodies, which adversely affect aquatic ecosystems [2]. Dyes reduce the transparency of water and light penetration which influences photosynthesis and consequently reduces dissolved oxygen [2]. This will severely impact aquatic flora and fauna. Textile industries usually release a large amount of methylene blue (MB) dyes in natural water sources, which becomes a health threat to human beings and microbes. MB is toxic, carcinogenic, and non-biodegradable and can cause a serious threat to human health and destructive effects on the environment [3]. MB causes several risks to human health such as respiratory distress, abdominal disorders, blindness, and digestive and mental disorders. It also causes nausea, diarrhoea, vomiting, cyanosis, shock, gastritis, jaundice, methemoglobinemia, tissue necrosis, and increased heart rate, causing the death of premature cells in tissues and skin/eye irritations [3].

Synthetic dyes are relatively easy to detect but difficult to eliminate from wastewater and surface water ecosystems because of their aromatic chemical structure. Currently, removal of such chemicals from wastewater involves various techniques, including flocculation/coagulation, precipitation, photocatalytic degradation, biological oxidation, ion exchange, adsorption, and membrane filtration [4]. Activated carbon-based materials are the most commonly used adsorbents due to their high efficiency and the simple technology involved. However, such materials have a high production cost and low degree of regeneration.

Wooden and bamboo chopsticks show great potential in removing pollutants from wastewater as they are readily accessible and inexpensive. Chopsticks, which are rich in carbon, have the potential to serve as an effective biochar material. Making biochar from chopsticks can also alleviate the problem of waste as discarded chopsticks can be reused as biochar.

Carbon-rich solids such as biochar have been found to be effective in reducing the levels of cationic dyes like methyl violet, methylene blue, basic blue, crystal violet and rhodamine by using the electrostatic force of interaction as adsorption mechanism. [5] Although there have been studies on using chopsticks to make biochar electrodes [6] and chopsticks as renewable energy sources [7], research has not been done on the use of wooden and bamboo chopsticks to produce biochar to remove methylene blue dye.

Hence, this study aims to evaluate the effectiveness of biochar derived from bamboo and wooden chopsticks and hence test the effect of pyrolysis temperature on the adsorption of methylene blue from wastewater.

2. Materials and Methods

2.1. Chemicals and Materials

Bamboo and wooden chopsticks were sourced from local suppliers. Methylene blue solution was procured from GCE Laboratory Chemicals.

2.2 Biochar Preparation and Modification

Chopsticks were rinsed with distilled water and oven dried at 60°C for 2 hours. All chopsticks were pyrolysed at 200ºC for 2hrs and dried for 24hrs to obtain Bamboo 200°C (B2) and Wooden 200°C (W2) samples. Half of each batch of samples were further pyrolysed again at 500ºC to obtain Bamboo 500°C (B5) and Wooden 500°C (W5) samples. All 4 samples were grinded, then sieved to 120-250µm.

2.3 Characterisation of Biochar

The biochar particles were further analysed using a JEOL JSM-6100LA scanning electron microscope (SEM) in the Science Center Singapore lab.

2.4 Kinetics Experiments

Methylene blue (MB) was used as an adsorbent for adsorption experiments. 1000 mg/L of MB was prepared as a standard solution, which was then diluted into 40, 80, 120, 160 and 200 mg/L standard solutions using distilled water to create a MB calibration curve.

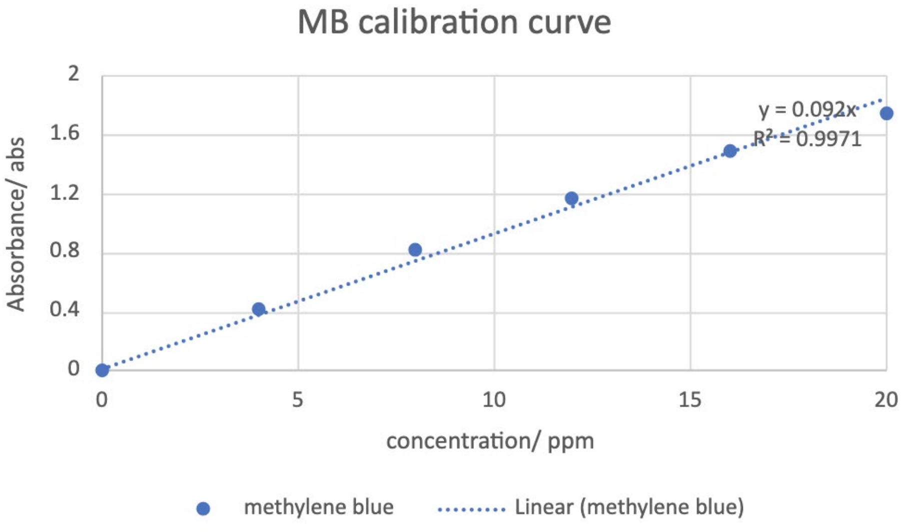


Figure 1: MB calibration curve

A kinetic study was then conducted using 100 mg/L MB standard solution, diluted from 1000 mg/L MB standard solution. 0.5g of B2, W2, B5 and W5 were added into 4 samples of 200mL MB solution respectively. The samples were shaken at 300 rpm in room temperature at fixed timings of 5, 10, 20, 30, 60, 120, 180, 300 min and 24 hours, and 2mL samples were then centrifuged at 10000 rpm for 5 mins.

Adsorption capacity was analysed using a UV-VIS spectrophotometer (IBM UV/Visible 9420 Spectrophotometer) at 664 nm. The adsorption capacity of the biochar samples were calculated and compared with the MB calibration curve (Figure 1).

2.4 Adsorption Experiments

The 1000 mg/L MB standard solution was then diluted into 20, 40, 60, 80 and 100 mg/L MB standard solutions. Adsorption isotherm studies were first conducted. 0.5g of each biochar sample (B2, W2, B5, W5) was added into different tubes, each with 200 mL MB solution with a mass concentration of 20, 40, 60, 80 and 100 mg/L. The samples were shaken for 1 hour at 300 rpm at room temperature, and then centrifuged at 10000 rpm for 5 mins.

Adsorption capacity was analysed using a UV-VIS spectrophotometer (IBM UV/Visible 9420 Spectrophotometer) at 664 nm. The adsorption capacity of the biochar samples were calculated and compared with the MB calibration curve (Figure 3).

2.5 Data Analysis

The adsorption isotherm studies were analysed using the Langmuir and Freundlich adsorption isotherm models:

<u>Langmuir adsorption isotherm model:</u>

$$C_e/q_e = (1/q_m)C_e + 1/((q_m)(kL))$$

Where C_e (mg/L) is the concentration of methylene blue at equilibrium, q_e is the equilibrium adsorption capacity (mg/g) of the biochar sample, q_m is the maximum adsorption capacity (mg/g) of the biochar sample, and kL is the adsorption constant. A graph of C_e/q_e against C_e was plotted, where the gradient of the slope is $1/q_m$ and vertical intercept is $1/((q_m)(kL))$.

<u>Freundlich adsorption isotherm model:</u>

$$\ln q_e = (1/n)\ln C_e + \ln k_f$$

Where C_e (mg/L) is the concentration of methylene blue at equilibrium, q_e is the equilibrium adsorption capacity (mg/g) of the biochar sample, k_F is the Freundlich constant and relates to adsorption capacity, and n corresponds to adsorption intensity. A graph of ln q_e against ln C_e was plotted. The gradient of the slope is represented by 1/n, while the vertical intercept is given by ln k_f.

3. Results and Discussion

3.1 Scanning Electron Microscopy

From Figure 2 and Figure 3, biochar is observed to have a rough, uneven surface and becomes porous after pyrolysis at higher temperatures. In addition, fragments of biochar tend to be smaller at higher pyrolysis temperatures, increasing surface area and thus predicted adsorption capacity. Those pyrolysed at 200ºC also tended to be long, thin fragments while those pyrolysed at 500ºC were broader and rounder. The wood biochar samples are also observed to splinter into further smaller pieces while the bamboo biochar generally has larger fragments.

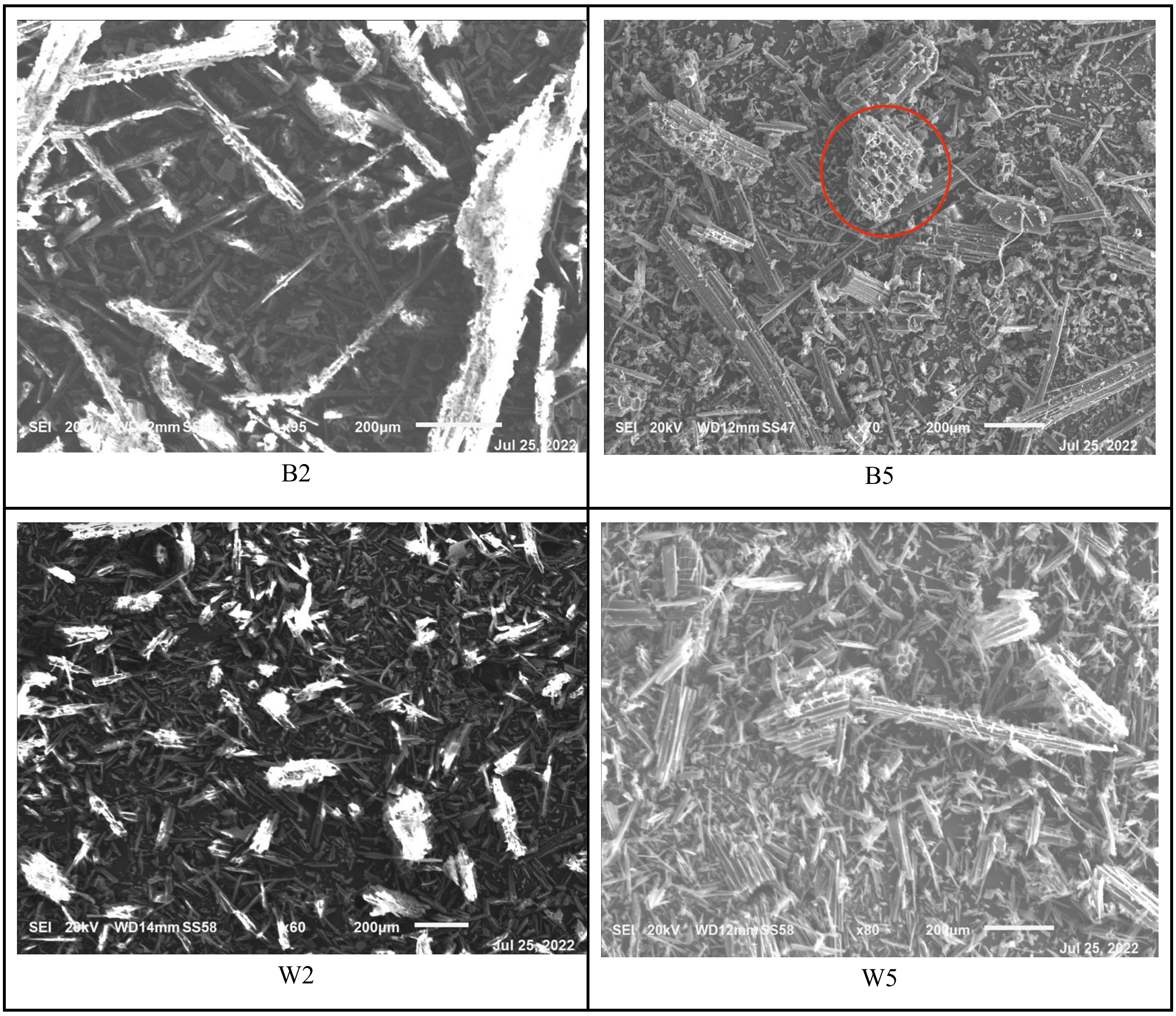


Figure 2: SEM images of biochar at 200µm

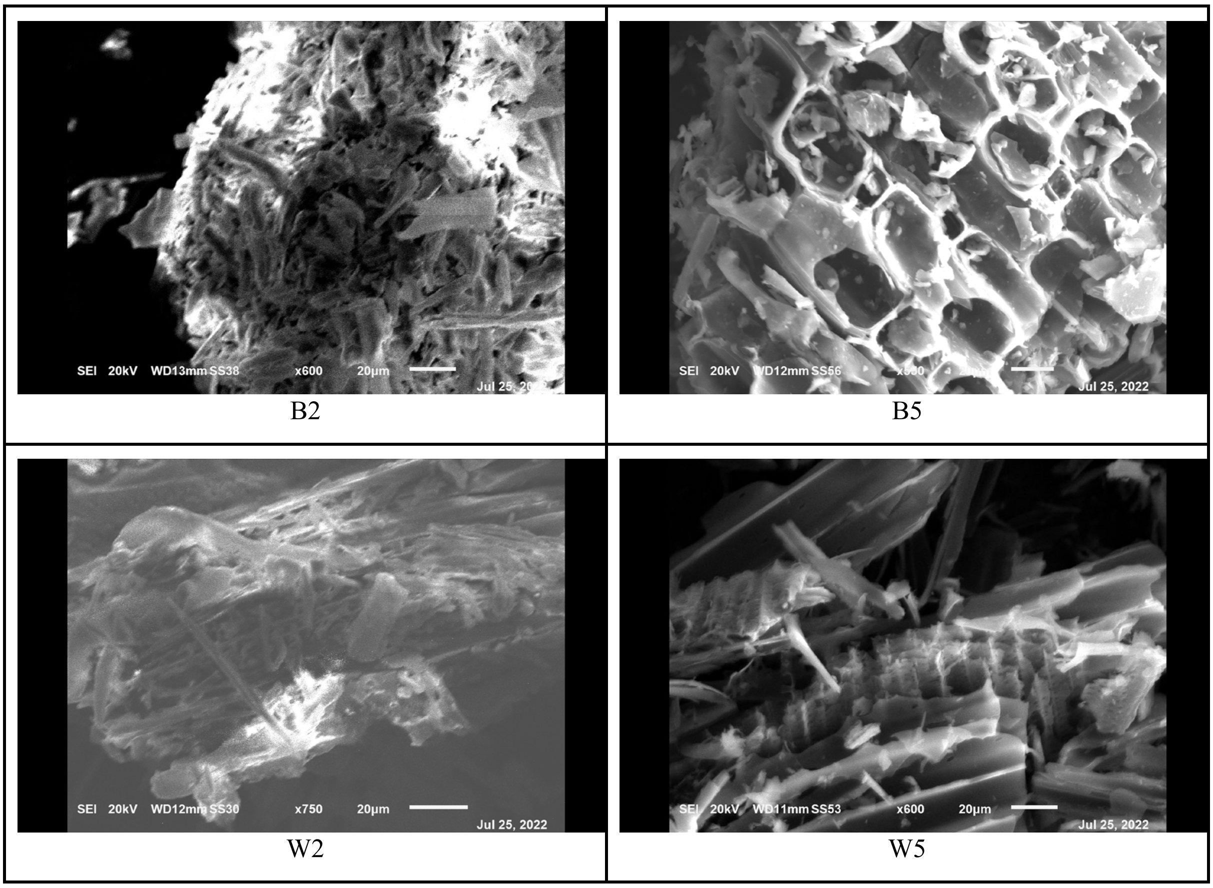


Figure 3: SEM images of biochar at 20µm

In addition, the analysis of the elemental composition of our biochar samples indicated that carbon and oxygen were major components of biochar, with trace amounts of sulphur and metal ions (Cu, Zn, K, Al) present.

3.2 Kinetic Studies

Our kinetic studies (Figure 4) indicate that enabling the samples to adsorb MB for prolonged periods of time has resulted in increased adsorption over time. However, the rate of increased adsorption tends to plateau off around the 300 min (5h) mark, hence, it is likely that an energy-efficient yet effective adsorption would take place within a 5h time period.

At the 20-minute mark, W2 and W5 had adsorption capacities of 9.80 mg/g and 9.67mg/g respectively, which is 1.5 times higher than B2's adsorption capacity of 6.15 mg/g and 3 times higher than B5's adsorption capacity of 3.87 mg/g. A similar trend is observed at the 300 min (5h) mark, whereby W2 and W5 had adsorption capacities of 18.87 mg/g and 18.22 mg/g, which is 1.5 times of B2's adsorption capacity of 11.15 mg/g and 2.5 times of B5's adsorption capacity of 7.72 mg/g. However, there is a greater deviation between W2 and W5 at the 24h mark. W2 had an adsorption capacity of 31.83 mg/g at 24h, which is higher than W5 at 25.42 mg/g. B2's adsorption capacity of 19.98 mg/g was higher than B5's adsorption capacity of 12.04 mg/g.

It can be concluded that the wood samples are more effective at adsorbing methylene blue than the bamboo samples, while those pyrolysed at 200ºC are more effective after the 300 min mark, with W2 being the most effective and B5 being the least effective at adsorbing methylene blue over the 24-hour period.

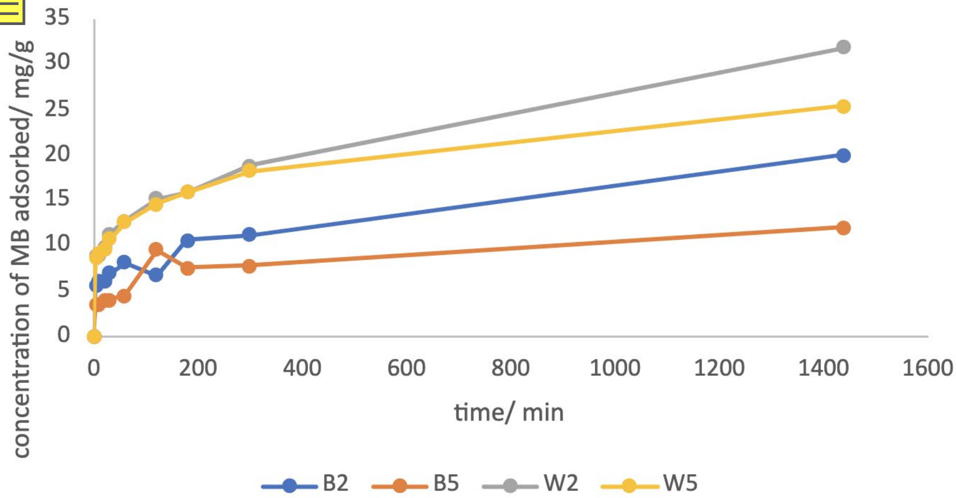


Figure 4: Graph of B2, B5, W2, W5 Kinetic studies

Comparing B2 and B5's adsorption capacities to the adsorption capacities of bamboo in other studies, we were able to obtain a higher mg/g value as compared to a research conducted on nitrate adsorption by bamboo biochar, where they obtained a mg/g value of 0.688 [6]. However, this could be due to the difference in chemicals adsorbed, whereby biochar could be more efficient in adsorbing dyes than ions.

3.3 Concentration Studies

The adsorption capacity of the wood biochar samples were significantly higher than that of the bamboo biochar samples (Figure 5). At 60 ppm MB solution, W5 and W2 had adsorption capacities of 18.05 mg/g and 14.33 mg/g, which is higher than B5 and B2 at 11.55 mg/g and 9.53 mg/g respectively.

However, those pyrolysed at 500ºC were better able to adsorb methylene blue than those pyrolysed at 200ºC, which contradicts our conclusion from the kinetic studies that chopsticks pyrolysed at 200ºC are more effective. This could be due to the fact that chopsticks pyrolysed at 200ºC were only definitively higher than those pyrolysed at 500ºC after the 300 min mark, but our concentration studies were conducted before the 300 min mark.

It can be concluded that wood samples are more effective at adsorbing methylene blue than the bamboo samples. In addition, we observed that while the peak adsorption capacity for most of the samples seem to be at a concentration of 60 ppm, W5 was able to further adsorb methylene blue at 80 ppm; this indicates that W5 is a more suitable adsorbent for higher concentrations of methylene blue relative to the other samples.

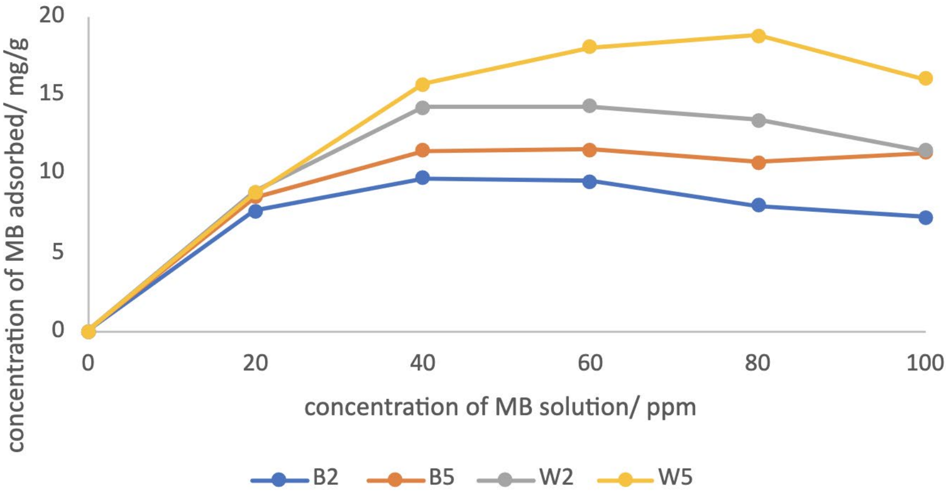
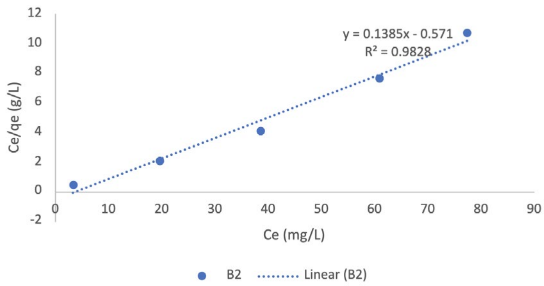


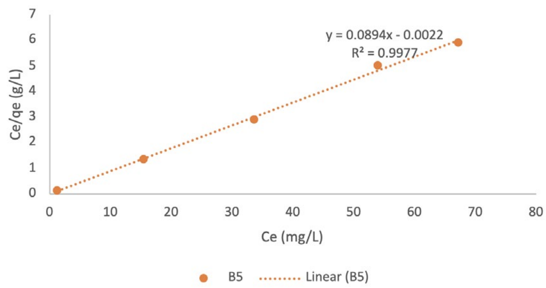
Figure 5: Graph of B2, B5, W2, W5 Concentration studies

The adsorption isotherm studies indicate that the adsorption mechanism of all 4 biochar samples largely agrees with the Langmuir adsorption isotherm model, with an $R^2 > 0.98$ for all 4 samples. This implies that the biochar samples largely conform to the key assumptions of the Langmuir model [8]:

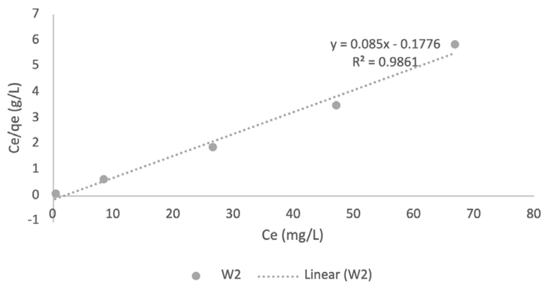
1. Adsorption only takes place on specific active sites of biochar [9].
2. All adsorption sites have equal adsorption energies.
3. Each site is only able to adsorb a single molecule of methylene blue, resulting in mono-layer adsorption.



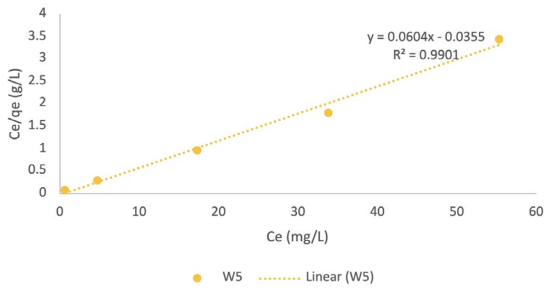
B2 Langmuir model



B5 Langmuir model



W2 Langmuir model



W5 Langmuir model

Figure 6: Graphs of Langmuir adsorption isotherm models

In contrast, the biochar samples largely deviate from the Freundlich adsorption isotherm model. Such deviation results in a range of R^2 values (Table 1) from $R^2 = 0.00009$ (B2) to $R^2 = 0.841$ (B5). These values imply that B5 somewhat adheres to the key assumption of the Freundlich model; taking into account the similarly high R^2 value B5 attained according to the Langmuir adsorption model, it can be inferred that the surface of B5 has both heterogeneous and homogeneous sites. The intermediate R^2 values of W2 and W5 indicate that the W2 and W5 samples have somewhat heterogeneous surfaces, but the higher R^2 values obtained from their Langmuir adsorption models indicate that they had predominantly homogeneous surfaces. The low R^2 value of B2 indicates that it does not adhere to the Freundlich adsorption model at all, and its surface is purely homogeneous.

Our findings regarding the bamboo biochar samples are mostly in line with a previous study done regarding the use of bamboo chopstick biochar [6]. However, B2's low R^2 value does not correlate with the high R^2 values achieved in the synthesis of biochar found in the abovementioned study. This could be due to the fact that it was pyrolysed at significantly lower temperatures than the samples in the above study (400-600ºC); this is supported by the fact that our samples pyrolysed at 500ºC tend to have significantly higher R^2 values in agreement with the Freundlich model than those pyrolysed at 200ºC.

Table 1: R^2 Values for Freundlich Model

Sample	B2	B5	W2	W5
R^2 value (3 sf)	0.000900	0.841	0.481	0.761

The equilibrium adsorption capacity, q_e, of the biochar samples (Table 2) depict a few key observations. Firstly, biochar pyrolysed at 500ºC had approximately 1.5 times the adsorption capacity of biochar pyrolysed at 200ºC, regardless of MB concentration and biochar material. This could be attributed to the greater porosity of samples pyrolysed at higher temperatures, which significantly increased the surface area and thus equilibrium adsorption capacity of biochar.

Secondly, the wood samples had almost twice the adsorption capacity of their corresponding bamboo biochar samples (B2 vs W2, B5 vs W5). From the morphology study of the various biochar samples, it was observed that the wood biochar samples splintered into smaller fragments than the bamboo biochar samples. Once again, this amplified the surface area of the wood biochar samples, thus increasing the adsorption capacity of the biochar.

Thirdly, our concentration studies (Figure 5) indicated that as the concentration of MB solution increased, the adsorption capacities of all 4 samples increased initially, but generally decreased as the concentration of MB increased from 60 ppm to 100 ppm. This implies that as MB concentration increases, due to the increase in ratio of substrate concentration to biochar, the adsorption capacity of biochar generally decreases beyond the saturation point.

Table 2: Adsorption Capacity of Biochar Samples

Sample	**Concentration of MB, C_e /mg L^{-1}**	**Equilibrium adsorption capacity of biochar, q_e /mg L^{-1} (2 dp)**
B2	20	7.70
	40	9.77
	60	9.53

	80	7.98
	100	7.23
B5	20	8.53
	40	11.49
	60	11.55
	80	10.78
	100	11.36
W2	20	8.84
	40	14.25
	60	14.33
	80	13.48
	100	11.48
W5	20	8.78
	40	15.74
	60	18.05
	80	18.84
	100	16.07

4. Conclusion

Biochar was successfully synthesised via pyrolysis of bamboo and wooden chopsticks. Biochar pyrolysed at higher temperatures (B5 and W5) were more effective in removing methylene blue solution compared to biochar pyrolysed at lower temperatures (B2 and B5). Wooden biochar (W2 and W5) were also more effective at removing MB compared to bamboo biochar (B2 and B5). Langmuir isotherm model was a better fit for all samples, suggesting that the adsorption by bamboo and wooden biochar is monolayer.

5. Future Work

In the future, the capability of used chopsticks in adsorbing a range of pollutants from wastewater, such as heavy metal ions and BPA, should be researched. In addition, an investigation into the effectiveness of magnetising the biochar samples, especially W2, in yielding promising results regarding wastewater treatment should be carried out.

6. Acknowledgements

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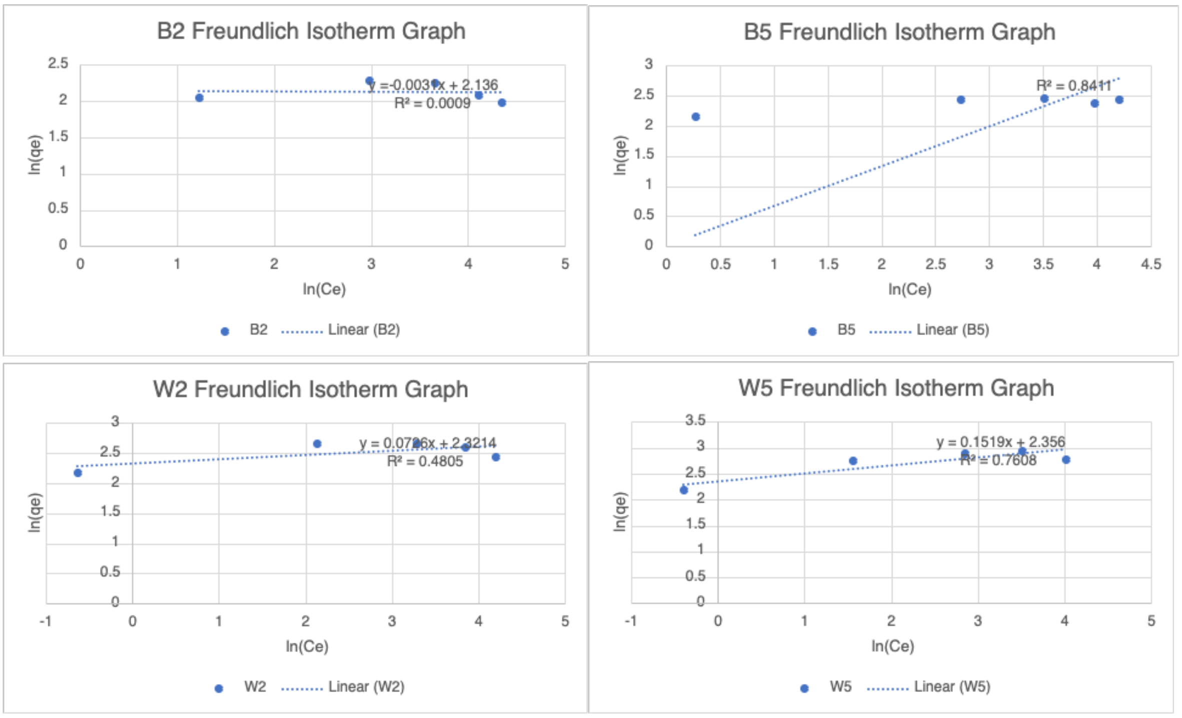
7. Appendix

Figure 7: Freundlich Model graphs



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