Adsorption of methylene blue on biochar

Evaluation of substrate adsorption performance within the Aquatuur project

HZ UNIVERSITY OF APPLIED SCIENCES
WATER TECHNOLOGY RESEARCH GROUP
07-02-2025

Interreg Vlaanderen-Nederland

Gefinancierd door de Europese Unie

Aquatuur

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EVALUATION OF SUBSTRATE ADSORPTION PERFORMANCE WITHIN THE INTERREG VLAANDEREN-NEDERLAND AQUATUUR PROJECT

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07-02-2025
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Final version

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1. INTRODUCTION

With a changing climate resulting in longer periods of drought and higher temperatures, in combination with a higher demand of fresh water due to economic growth, the Dutch National Institute for Public Health and the Environment (RIVM) expects shortages of drinking water availability by 2030 (Ministerie van Infrastructuur en Waterstaat, 2023). For agriculture and the industries surface water is a valuable fresh water source, that does not compete with drinking water production, but supply does not always meet demand.

In a previous project Fresh4Seas, HZ investigated the water quality of 3 waterbodies at the boarder between Belgium and The Netherlands. Isabellawatering was picked as the most promising surface water source as the EC values are close to fresh water. However, the parameters Manganese, Glyphosate, AMPA, BAM and Phenanthrene exceed the threshold of the Nota Grondwater (Letterie, 2022). Moreover, emerging contaminants like PFAS are also found in the Isabellawatering. Therefore the water needs to be treated. A common technology used to treat surface water to remove pesticides, metals and PAHs is by adsorption on activated carbon. However in this project it is researched if the components mentioned above can be removed by constructed wetlands. Several physical, chemical and biological processes that occur in wetlands remove substances. The wetlands should be designed in such a way that processes that remove the above mentioned pollutants are enhanced. Bacteria that are responsible for the biological breakdown require a certain hydraulic retention time. The addition of biochar, an organic material produced by means of pyrolysis, was proven to enhance the performance of constructed wetlands (Gupta et al., 2016) as it increase the retention time without requiring a larger surface area. In this research report several types of biochar will be tested on adsorption capacity in lab scale experiments using methylene blue as an adsorbate. Based on the results of this research the most suitable type of biochar will be selected to be used as an adsorbent in the constructed wetlands.

2. MATERIALS AND METHODS

To choose the appropriated biochar to be used together with the wetlands' substrate, laboratory tests were performed in the ecology laboratory of the HZ University of Applied Sciences (HZ UAS) (2022) and of the Joint Research Center Zeeland (2023 and 2024). As it was not possible to measure in this laboratory the compound of interest, glyphosate, due to the analysis complexity and equipment availability, the adsorption tests were done using methylene blue (MB) as the adsorbate. The goal was to use the MB removal percentage by each biochar, that is, their adsorption capacity, as an indicative of the best biochar to be used in the wetlands' pilot.

To accomplish this, a sequence of test trials was performed to enable a choice between six biochar types. The biochar types and some of their characteristics are presented in Table 1.

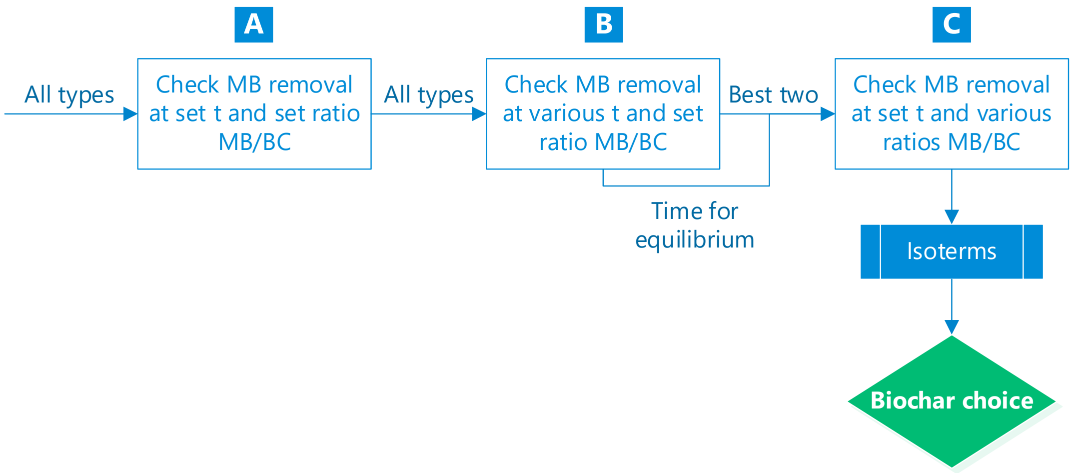
Table 1 Types of commercial biochar used in the tests

Id.	Biomass	Origin	Characteristics
BC1	Bonsai mix (biologically activated)	Greenwave Biochar (Netherlands)	• Activated with microorganisms • Fraction: from dust to max 3mm • Temperature of pyrolysis: Unknown
BC2	Bonsai *puur* (pure)	Greenwave Biochar (Netherlands)	• Fraction: from dust to max 3mm • Temperature of pyrolysis: Unknown
BC3	Cacao shell	HerbaCarbo GbR (Germany)	• Fraction: medium coarse to fine • Temperature of pyrolysis: 650-700 °C
BC4	Woodchips, barley husk, paper mud	Sonnenerde (Germany)	• Fraction: from very coarse to dust, varying sizes • Temperature of pyrolysis: 850 °C • Density: 408 g/L • pH: 10
BC5	Woodchips	HerbaCarbo GbR (Germany)	• Very coarse • Temperature of pyrolysis: 500-650 °C
BC6	Herbal pomace	HerbaCarbo GbR (Germany)	• Medium coarse to fine, soft structure • Temperature of pyrolysis: 600-700 °C • Density: 300 g/L

As seen in Table 1, not many characteristics of the biochar are known. The pyrolysis temperatures of BC1 and BC2 were not provided. Besides that, the biochar's particle size, porosity and surface area are not known. Their structure was analysed by sight and divided into dust, fine, medium and coarse. A limitation of this study is that the biochar used in the tests had to be a commercial type and one that could be delivered in rather large volumes (1 m^3), as the chosen type will be used in the wetlands' pilot. Most of the commercial biochar types found during this research did not presented this information.

The sequence of tests done in this methodology can be seen in Figure 1. Water management students of the HZ UAS performed the first two parts of this approach.

Figure 1 - Approach flowchart



The first trial of tests, here referred as A, had the goal to see how each biochar would act as an adsorbent and how much of the methylene blue they could remove. For this test, 0.1 g of each biochar was added to 20 ml solutions of 12 mg/L of MB with a set contact time (CT) of 2 hours (the detailed methodology can be seen in Appendix A)

To further investigate the relationship between methylene blue adsorption and the contact time, and mostly, to determine the contact time of equilibrium, the adsorption tests were repeated by varying the CT (part B). The following contact times were used: 2, 4, 5, 6, 7, 24, 41 and 48 h. The maximum contact time was chosen according to the expected hydraulic retention time (HRT) of the wetlands' pilot plant; which up to the moment of the tests, would be of either 24 or 48 hours. HRT and contact time do not have the same definition: the adsorption tests were done as batches, and the concentration changes in time up until equilibrium, and for the wetlands, the water would flow through the medium for this amount of time (similar to a plug flow), but the concentration also changes in space. However, the HRT was used to help and establish the longest test duration, as it is the longest time that the pollutant will be in contact with the biochar.

With the results obtained from the tests previously mentioned, two biochar types were chosen as the best performers and, therefore, to be further investigated. In this research, the biochar suitability, inferred here as the "best biochar", was evaluated not only for its capability of MB removal but also to how its properties (mostly size and density) could affect the wetlands.

Those two biochar types were tested, in part C, in solutions of different MB concentrations: 9.6, 13, 50, 150, 300, and 600 mg/L. The biochar mass was kept the same, 0.1 g, as well as the volume of the solutions, 20 ml, leading to the following ratios of MB(mg)/BC(g): 1.92, 2.6, 10, 30, 60, 120. The contact time was of 7 hours, to ensure that the equilibrium was reached, and was chosen based on the results obtained in phase B. The methodology followed the one explained in Appendix A, but with the MB concentrations as described above.

These tests enable the evaluation of the quantity of MB adsorbed into the biochar (q_e) regarding its concentration in the equilibrium (C_e). To calculate q_e, equation 1 was used:

$$q_e = \frac{V}{m}(C_o - C_e) \qquad (1)$$

Where, q_e is the MB absorbed into the biochar in the equilibrium (mg MB/g BC), V is the volume of the solution (L), m is the mass of biochar (g), C_o and C_e are the initial concentration and equilibrium concentration (mg/L), respectively.

Adsorption isotherms were made with those results to access the extension of the adsorption process. The data was fitted to two isotherms: Freundlich and Langmuir in which the R^2 was used to access the fit. With the isotherms, the adsorption process was evaluated whether favourable or not, and the maximum quantity of MB to be adsorbed by the biochar was calculated according to the Langmuir isotherm. The detailed methodology of the isotherms is presented in Appendix B.

3. RESULTS AND DISCUSSION

The methylene blue removal efficiencies per biochar type is shown in Figure 2 for the test of two hours of contact time. Furthermore, Figure 3 shows the results of part B, the variation of the MB removal per biochar type for the various contact times. As for the first eight hours several biochar have a similar behaviour, a zoomed version (1-8h) is presented in Figure 3 and the raw data is shown in Table 2.

Figure 2 - The removal efficiencies per biochar type (Part A)

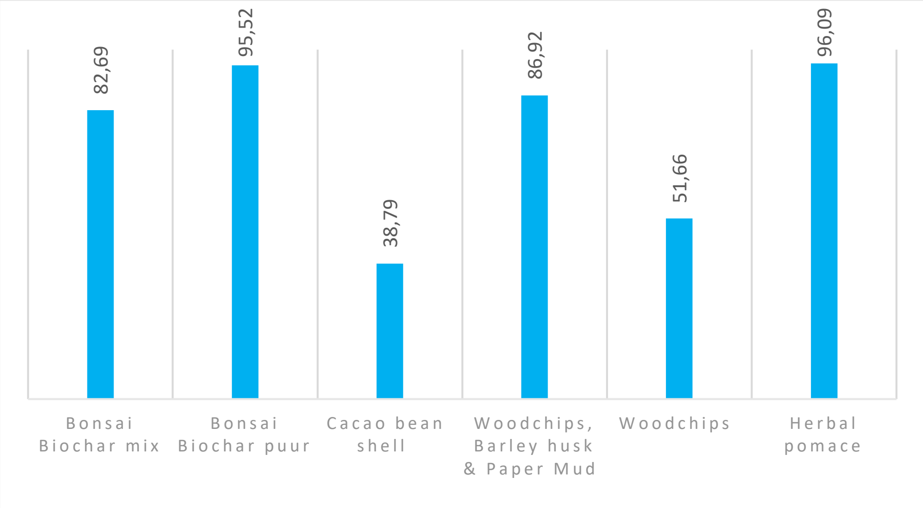
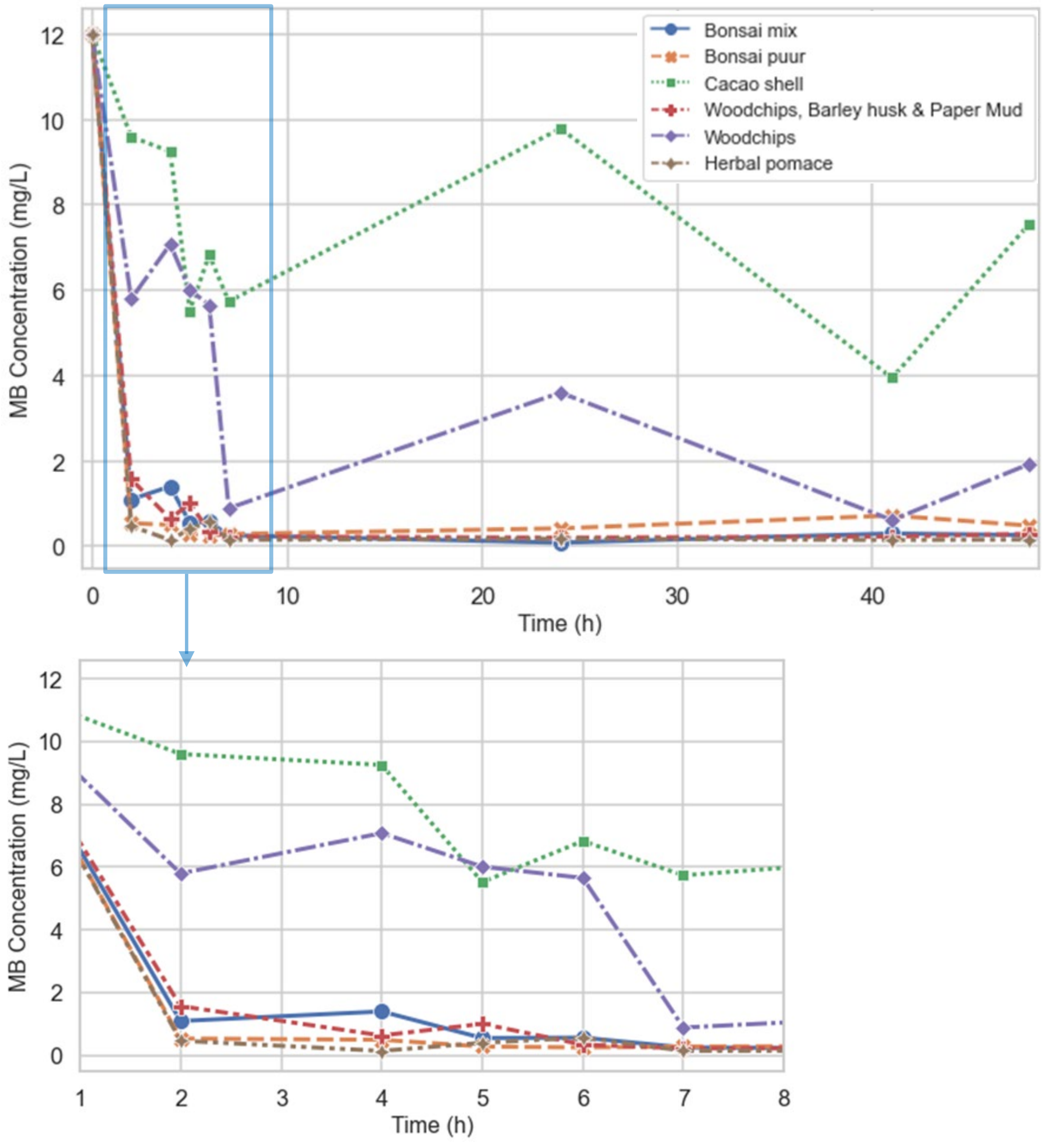


Table 2 - MB removal percentages per biochar for various contact times (Part B)

Time (h)	Bonsai Mix	Bonsai Puur	Cacao shell	Woodchips, Barley husk & Paper Mud	Woodchips	Herbal pomace
2	82.7%	95.5%	20.0%	86.9%	51.7%	96.1%
4	-	95.8%	22.9%	94.7%	41.0%	98.8%
5	85.9%	97.6%	54.0%	91.6%	49.9%	96.7%
6	89.7%	98.3%	43.1%	97.2%	52.9%	95.7%
7	93.1%	97.6%	52.2%	98.1%	92.6%	98.8%
24	91.6%	96.5%	18.4%	98.3%	70.0%	98.6%
41	91.2%	94.0%	67.1%	98.1%	94.9%	98.8%
48	92.0%	96.0%	37.2%	97.6%	84.0%	98.7%

Figure 3 - MB removal across time for various biochar types



The least performing biochar were BC3 and BC5 (cacao bean shell and woodchips, respectively), which are the coarser and larger types among the tested. This is probably the cause of the lower adsorption, because it provides a smaller surface area, which is known as directly proportional to the adsorption capacity. Besides that, the adsorption is not stable, as concentration peaks are seen at longer contact times, i.e. 24 and 48h, suggesting that desorption occurred.

Bonsai puur, the mixture of woodchips, barley husk and paper mud and the herbal pomace (BC2, BC4, BC6 respectively) were the best-performing biochar. The types BC1 and BC2 are from the same source, identified by the manufacturer as bonsai, with the exception that BC1 is activated with microorganisms. As BC1 has a lower adsorption capacity, it appears that the biological modification done by the added microorganisms worsen the interactions between the biochar and the dye.

Although BC2 presented one of the highest adsorption capacities, it was not chosen to be carried on to the final test due to its particle size. The really small fraction, almost as dust, is a constraint for its applicability in a constructed wetlands. There is the concern about such a fine biochar being dragged by water in the wetlands. As seen in Figure 3, BC6 is the one reaches both equilibrium and the highest removal faster. At 2h a removal of >98% was observed, and contact times ≥ 7 h the equilibrium was reached for most BC types. At 7h contact time BC4 reached a removal of >98% and also stayed stable for longer contact times. Hence, BC4 was chosen together with BC6 to be tested in Part C, and the contact time for equilibrium was set as 7 hours.

Figure 4 provides a visualization of both biochar types that were chosen to be used in Part C: BC4 and BC6. As seen in Figure 4(a), BC4 has a diverse structure: different sizes and likely various porosities. This is due to its source material, which is a mixture of woodchips, barley husk and paper mud. It varies from coarse parts, due to the woodchip, up to fractions like dust. BC6, Figure 4(b), is made from herbal pomace, therefore has a more even structure, varying from fine to medium sizes. It is seen that BC6 has also a darker colour than BC4, although its pyrolysis temperature is lower.

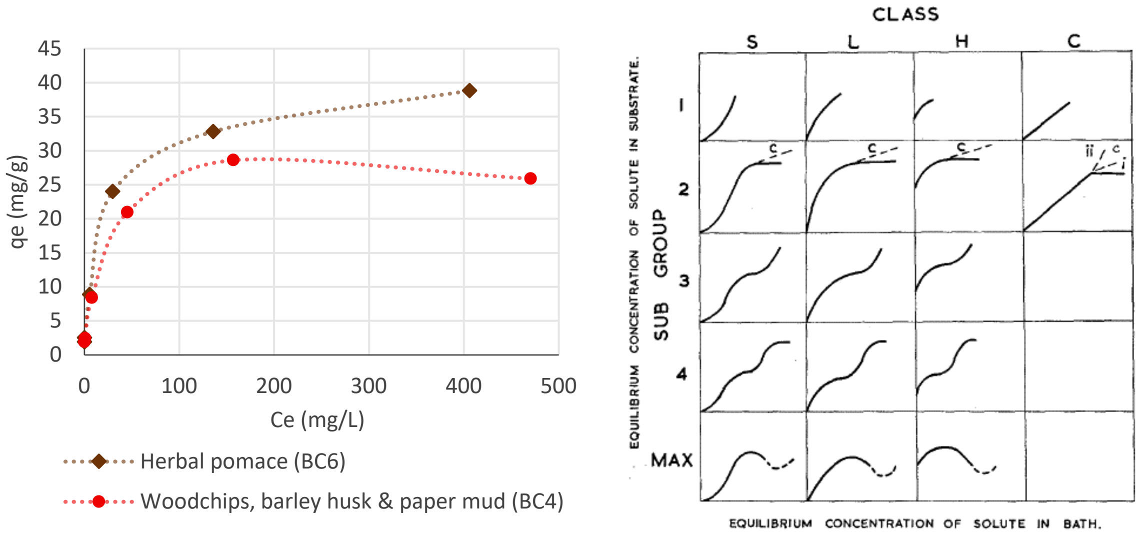
Figure 4 - Visualization of BC4 and BC6

(a) BC4

(a) BC6

Figure 5 (a) shows the variation of MB concentration in the substrate (q_e) with the MB concentration in the solution (c_e) during equilibrium, that is, contact time of 7 hours, for the various ratios of biochar BC4 and BC6 and MB concentration (Part C). According to Giles et. al (1960), the distribution seen in Figure 5 is related to the adsorbent–adsorbate affinity, which can be classified according to the isotherm shape, as seen in Figure 5 (b).

Figure 5 – Adsorption isotherm type



(a)

(b)
(Giles & Smith, 1973)

When comparing the obtained adsorption curves with the ones seen in Figure 5 (b), the curves likely follow the L class. The initial slope depends on the rate of change of site availability with an increase in solute adsorbed (Giles et al., 1960; Lawrence et al., 2000). The slope in L class shows that the sorbate has a high affinity with the sorbent surface, meaning that, at the first tested ratios, the highest fraction of MB is adsorbed onto the biochar. This happens up until the dosage of 30 mg MB/g BC. Once the mass of MB per mass of biochar increases, the chance that solute in solution attaches to an available site in the substrate decreases, which is seen by the flattening of the curve. This is caused by both the biochar adsorption capacity as well as by the equilibrium of MB in solution and MB in biochar.

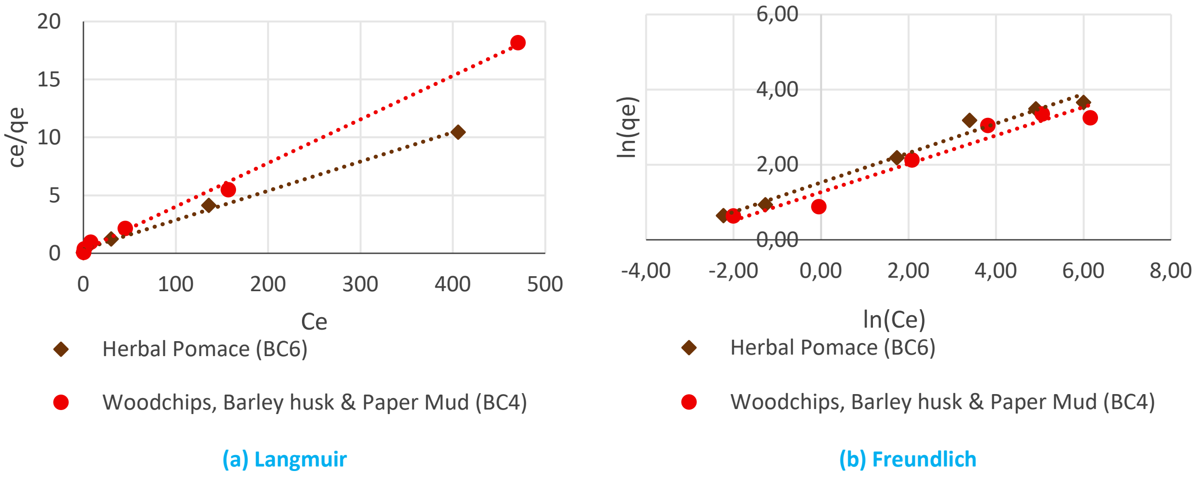
The subgroup classification is related to the shape of the upper section and slope change(s) (Hernández-Monje et al., 2021). BC6 is approaching subgroup 2 in the tested ratios. The curve is reaching a plateau which indicates that the biochar surface is getting saturated. When a plateau is reached, further adsorption can only take place on a new surface (Giles et al., 1960).

The initial slope of BC4 curve is similar to BC6, although the affinity of the MB with this biochar is lower than with BC6. However, the end part of the curve has a downward trend. It could be that the isotherm has achieved its maximum, in which the solute-solute interactions increase more than the substrate-solution. However, as this trend is not ‘strong’, this could also be due to variations from the experiment itself, which was done only in duplicate.

Besides that, it was noticed that for both BC types, the solution in the equilibrium of the final two ratios had a brown/greyish tone, unlike the others that were only blueish. There is the possibility that when in contact with high concentrations of methylene blue (ratios ≥ 60 MB(mg)/BC(g)), a component was leached into the solution and interfered with the measurements, as it added colour to the solution. This however has not been further investigated.

Furthermore, the isotherms were adjusted to Langmuir and Freundlich models. The results are presented in Figure 6.

Figure 6 – Langmuir and Freundlich adsorption isotherms of MB dye in BC4 and BC6



The Langmuir and Freundlich parameters were extracted from the graphs, in Figure 6, by using the methodology contained in Appendix B. The results are showed in Table 3.

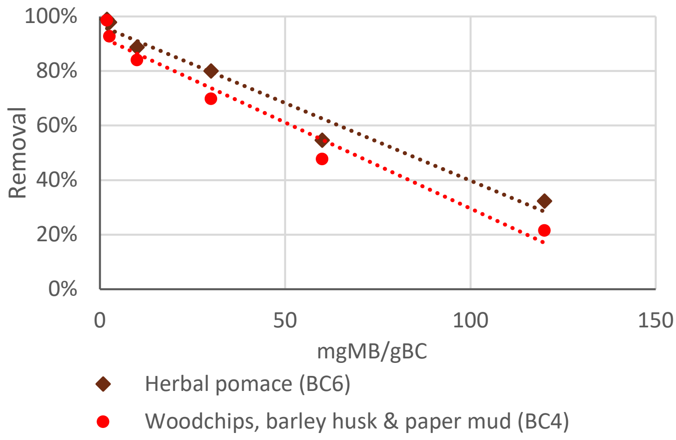
Table 3 – Parameters of adsorption isotherms of MB dye in BC4 and BC6

Adsorption model		BC4	BC6
Langmuir	q_m (mg/g)	26.60	39.68
	K_L (L/mg)	0.07	0.14
	R_L	0.26	0.21
	R^2	0.996	0.997
Freundlich	K_F (mg/g)	4.60	3.56
	n	2.55	2.65
	R^2	0.981	0.943

The R^2 values in Table 3 indicate how well the sorption mechanism follows the specified models. Both BC4 and BC6 follow the Langmuir sorption isotherm, which indicates a homogeneous distribution of MB over the BCs surface. The q_m indicates the maximum quantity of solute that can be adsorbed by the biochar. For BC4, this corresponds to 26.60 mg of MB per gram of biochar, and for BC6 this value is of 39.68 mgMB/gBC. However, according to Li et al. (2020), the regression q_m is only valid as the maximum capacity when the saturation isotherm is considered. That is, the maximum adsorption capacity is dependent on the solute initial concentration. As an example, BC6 had a q_m of 39.68 mg MB, but that was only achieved when 120 mg MB was dosed per g of biochar; this corresponds to only 32% of removal. Therefore, the isotherms do provide information over the relationship between solute concentration and adsorption, and can help on making decisions regarding the 'best' substrate for an specific case. They can also indicate the mass that will be adsorbed in relation to the ration of initial solute mass and mass of substrate added. However, the q_e is not constant and the q_m is only valid at saturation.

For an improved understanding, a better visualization of the change of MB removal per solute-substrate ratio is presented in Figure 7. It is seen that although the q_e increases, the removal decreases once the MB-BC ratio is higher.

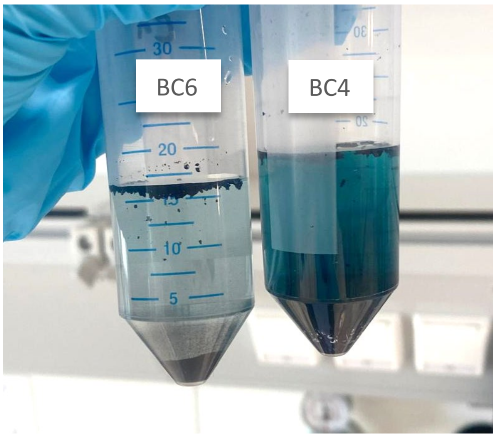
Figure 7 - MB removal per biochar at different solute-substrate ratios



The R_L factor, seen in Table 3 , is the separation factor that indicates if the adsorption is favourable or not. A value of $0 < R_L < 1$, such as the ones obtained (BC4: 0.26 and BC6:0.21) indicates, in general, that the adsorption is favourable (Hamdaoui & Naffrechoux, 2007; Mahajan et al., 2023).Regarding the Freundlich isotherm type, the R^2 for both biochar is strong, although slightly lower for BC6 (BC4: 0.98 and BC6: 0.94). The Freundlich isotherm does not provide an indication of maximum capacity but do provide an indication of favourable adsorption. Values of n as $1 < n < 10$ indicate a favourable adsorption, and $2 < n < 10$ provide good adsorption (Hamdaoui & Naffrechoux, 2007; O. Ifelebuegu, 2012).

Therefore, it is concluded that both biochar provided favourable adsorption of methylene blue. BC6 was slightly superior to BC4 in low concentrations, and increased the superiority for MB concentrations higher than 150 mg/L (corresponding to a solute-substrate ratio of 30 mg/g). This difference is shown in Figure 8.

Figure 8 - Comparison of MB removal between BC4 and BC6 (ratio 30 mgMB/gBC)



As for maximum capacity at saturation, BC6 outperforms again BC4. However, for the real application, i.e. glyphosate and manganese removal, the concentration will be low as the those micropollutants are found in ranges of µg/L in the targeted water. Nevertheless, the biochar was tested for MB removal, meaning that the removal performance and its saturation by glyphosate and manganese are unknown.

Finally, to further compare and make an advise on which biochar to use, their costs also need to be assessed. As both biochar come from Germany, transport costs will also have a substantial impact. It was calculated that a volume up to 5 m^3 of biochar will be needed for the wetlands (minimum is 3 m^3). Based on this information, costs were calculated and are provided in Table 4.

Table 4 - Costs for BC4 and BC6

	BC4		BC6	
	Types and volumes			
	3 m3	5 m3	5 m3	5 m3
Costs	BigBags	BigBags	BigBags	1L bag
Biochar	1340	2180	2000	1650
Transport	860	1122	490	490
Taxes	incld	incld	473.1	406.6
Total	**2200**	**3302**	**2963.1**	**2546.6**

CONCLUSION AND RECOMMENDATIONS

Bonsai puur, the mixture of woodchips, barley husk and paper mud and the herbal pomace are the best-performing biochar looking solely at removal efficiencies of methylene blue, 95.5%, 86,9% and 96.1% respectively.

The particle size of the Bonsai puur is very small which is undesirable for the use in constructed wetlands since the small particle size could lead to clogging or flushed out of the wetland. Therefore it is not advised to use Bonsai puur.

When comparing the adsorption capacity of the woodchip, barley husk and paper mud with the herbal pomace, herbal pomace seems to have a higher adsorption capacity (39.7mg/g VS 26.6mg/g), but this is only valid at the saturation point and for MB removal. It is also uncertain how both biochar types will perform on removing heavy metals, i.e. manganese, and pesticides, specially glyphosate, in a low magnitude of concentrations (µg/L).

When looking solely at performance based on removal efficiency and adsorption capacity, the herbal pomace is the most promising type of biochar. However, herbal pomace's structure is still small and the concern of it being flushed out of the constructed wetlands remains. Therefore, it is not advised to use only herbal pomace. Since the mixture of woodchips, barley husk and paper mud consists of different materials and of different particle sizes, in combination with the good results of adsorbing methylene blue, it can be considered a more diverse and widely applicable type of biochar. One downside of the mixture is that it has a higher cost.

Therefore, based on the findings of this research, but also on what is still uncertain, the recommendation is to use a mixture of both biochar types. This leads to four (different feedstocks) biochar types which increases the chances of successful adsorption of the targeted micropollutants. There is also a higher chance that (all of) the biochar is not carried by water away from the wetlands. Furthermore, both biochar types can also be supplied by the same company, HerbaCarbo[1], which should include the possibilities of transporting them together to the pilot location. The recommended ratio is of 70% woodchips, barley husk and paper mud and 30% of herbal pomace. In summary, the proposed mixture can benefit from having a higher diversity of materials, leading to higher diversity of adsorption capacity and of particle sizes.

[1] Although the mixture of woodchips, barley husk and paper mud is manufactured by Sonnenerde, HerbaCarbo is also one of the sellers.

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APPENDIX A

Methodology of Part A & B: MB removal at various contact times

Those tests were performed by the students Cheok Leng Chu, Dagmar Sinke, Tilia Battaglini-Fischer, and Wout Dreessen, of the Applications of water & pollution course of the HZ University of Applied Sciences. Tests were supervised by Bart Letterie, Iarima Mendonça and Maria van Schaik.

Batch adsorption tests were carried out by using biochar and methylene blue solution. The procedure consisted of adding 0.1g of biochar in 20 mL of a 12 mg MB/L solution into glass bottles (Khan et al., 2023; Zhang et al., 2020). The bottles were placed into an orbital shaker at 183 rpm for several contact times (specified by the test). Once the samples were taken from the orbital shaker the mixture was transferred into centrifuge tubes. The samples remained in the centrifuge for a total of 5 minutes at 3000 rpm. The samples were then left to settle for several hours to provide better separation of the biochar and the solution. After this, plastic pipettes were used to get the liquid phase from the test tubes to be measured in a spectrophotometer. The wavelength of 665 nm was used for the measurements, which is the maximum wavelength of MB in the visible spectrum.

The removal of MB was calculated as:

$$Removal\ (\%) = 100 \times \frac{(C_0 - C_e)}{C_o} \qquad \text{(A1)}$$

Where C0 and Ce are the initial and final MB concentrations (mg/L).

APPENDIX B

Equilibrium isotherms: Langmuir and Freundlich

(Atkins & de Paula, 2014)

Freundlich

The Freundlich isotherm is obtained by the following equation:

$$q_e = K_F \times C_e^{\frac{1}{n}} \qquad \text{(B1)}$$

Where q_e is the MB absorbed into the biochar in the equilibrium (mg MB/g BC), K_F is the Freundlich constant (mg/g), n is an empirical parameter and C_e is the concentration in the equilibrium. Equation B1 is then linearized to obtain the constants:

$$log q_e = \frac{1}{n} \times \log C_e + log K_F \qquad \text{(B2)}$$

To obtain the constants n and K_F, the graph of q_e x C_e needs to be done, by measuring the values for several ratios of BC:MB. In the case of this report, the mass of biochar was made constant, and the concentration of MB was varied.

With the graph it is possible to obtain the slope, which is the logK, which then allows to obtain the value of 1/n; or n.

Langmuir

The Langmuir isotherm is obtained by the following equation:

$$q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e} \qquad \text{(B3)}$$

Where q_e is the MB absorbed into the biochar in the equilibrium (mg MB/g BC), K_L is the Langmuir constant (L/mg), q_m is the maximum adsorption capacity (mg/g) and C_e is the concentration in the equilibrium. The linearization of B3 gives:

$$\frac{C_e}{q_e} = \frac{1}{q_m \times K_L} + \frac{1}{K_L} C_e \qquad \text{(B3)}$$

The graphical representation of C_e/q_e in function of C_e provides the slope $1/K_L$ and the intersection $1/(K_L.q_m)$.

With the values of K_L and q_m, it is possible to obtain the equilibrium parameter R_L, that will indicate if the adsorption if favorable or not.

$$R_L = \frac{1}{1 + q_m \times K_L} \qquad \text{(B4)}$$