Biochar: a low-cost adsorbent of Methylene Blue from aqueous solutions

J Kujawska and H Wasag

1 Lublin University of Technology, Faculty of Environmental Engineering, Nadbystrzycka 40B Street, Lublin 20-618, Poland

j.kujawska@pollub.pl

Abstract. Removal of Methylene Blue (MB) from aqueous solutions by compost-biochar and plant biomass-biochar mixtures is investigated under batch conditions to determine the adsorption capacity of biocarbons under variable parameters (initial Methylene Blue and biochar concentrations, temperature, pH of the solution). The experimental data have been computed using Freundlich adsorption isotherms. The adsorption percentage onto the biocarbons is shown to correlate linearly with the adsorbent quantity and concentration, MB-biochar contact time and pH. The results from the adsorption process are well correlated with the Freundlich model: \( R^2 > 0.989 \) for compost-biochar and \( R^2 > 0.977 \) for biomass-biochar. Biocarbons have been shown to be an effective and low-cost material for the removal of dye and colourisation from an aqueous solution.

1. Introduction

Biochar is a solid carbon residue produced during the low-temperature pyrolysis of carbon-rich biomass [1]. Physical and chemical properties of biochar depend on the type of combusted material [2]. Obtained primarily from waste, biochar is an inexpensive material whose potential in a range of applications, for example restoration of soils, water treatment, as a soil sequestration agent or a fertiliser, is a subject of extensive exploration.

Adsorption of pollutants from aqueous solutions with the use of biochar is a new chapter in the wastewater treatment technology, which is evidenced by a growing body of research in the field [3,4]. In recent years, researchers have been exploring the utilisation of biochar as a bioadsorbent of heavy metals from aqueous solutions (\( \text{Cd}^{2+} [5], \text{Pb}^{2+} [6], \text{Cu}^{2+} [7], \text{Zn}^{2+} [4] \)).

The purpose of this investigation has been to assess and compare the performance of two types of bioadsorbents in the removal of Methylene Blue (MB). Methylene Blue is a bright greenish-blue organic colourant representing phenothiazine compounds, which is chiefly used to dye bast (soft vegetable fibre such as jute, flax and hemp) and to a smaller extent paper, leather and mordanted cotton. It dyes silk and wool but exhibits low resistance to fading on these fibres [8]. Dyes are regarded to be the main pollutant in wastewater from the textile, leather, food processing, cosmetics, paper and dye industries [9]. Their decomposition products are highly hazardous and can be toxic to living organisms. Therefore, decolourisation of dyes is a crucial element of effluent treatment prior to their discharge into the water system. Industrial dye degradation is hampered by low reactivity of dye molecules, which are thus hard to remove from wastewater. Numerous physical and chemical methods of dye purification have been proposed: coagulation, ultrafiltration, electrochemical adsorption,
photooxidation [10,11]. Bioadsorption of dyes appears to possess the potential to become a cost-effective and simple dye removal solution.

The specific aim of the research is to assess whether biocarbon supplied by Fluid S.A. and biocarbon from municipal waste could serve as a low-cost adsorbent for the MB removal from an aqueous solution. The effect of MB-biochar contact time, MB dye concentration, biochar quantity, pH and temperature on Methylene Blue adsorption are studied. The adsorption isotherm is evaluated, presented and discussed.

2. Materials and Methods

2.1. Adsorbent
Two biocarbon adsorbents, supplied by Fluid S.A. (Sędziszów, Poland), were tested. The first material was fluid biochar obtained during a low-temperature heat-treatment (below 300 °C) of plant biomass performed in an anaerobic atmosphere with no chemical additives or catalysts. This biochar is a renewable biofuel, whose composition is as follows: 89% thermally tempered electric plant biomass, 3% binders and less than 10% moisture [12]. The other biocarbon is obtained from compost in a combined process of drying, degassing, thermolysis and combustion of pyrolysis gases carried out in a reactor at a temperature of approx. 650°C.

2.2. Sorbate
A commercial-grade basic dye Methylene Blue (C.I.No – 52015; C.I.Name – basic blue 9, chemical formula – C16H18ClN3S; molecular weight – 319.85 g/mol; λmax – 663 nm) supplied by Warchem, Marki, Poland.

The dye solution was prepared by dissolving 1.0 g of dye in deionized water in a 1-litre volumetric flask and made to a concentration of 1 g/l. The working solutions were obtained by diluting the dye stock solution in accurate proportions to needed initial concentrations (10–60 mg/l).

2.3. Instrumentation
The pH of the solutions was determined using a pH meter (ORION Model VERSA STAR). Methylene Blue absorption was measured with a UV-Visible spectrophotometer (Shimadzu Model UV-160 A) at 663 nm wavelength.

2.4. Batch adsorption experiments
The experiments were carried out in 250 ml flasks and the total volume of the reaction solution was 50 ml.

2.5. Effects of initial dye concentration
In batch experiments, a constant adsorbent-dye ratio was maintained: 0.1 g of biosolid adsorbent was mixed with 50 ml of dye solution. The initial MB concentrations (10, 20, 30, 40, 50, 60 mg/l) were produced using a rotary shaker at 150 rpm for 24 h in a process conducted at 24°C. Subsequently, the solution was separated from the solid phase in a 20-minute centrifugation (at 4,000 rpm). Then optimum initial dye concentration was identified.

2.6. Effect of contact time
The initial dye concentration was 30 mg/l. The effect of contact time was studied by shaking 0.1 g of the adsorbents at 24°C and pH = 6.0 for the period of 5, 10, 15, 20, 25, 30, 35, 40, 45, 60, 90, 120 or 240 min.

2.7. Effect of adsorbent dosage
The dosage-dependent MB removal capacity was studied for varying adsorbent dosages (0.05-0.20 g) in a 50 ml dye solution of 30 mg/l concentration, pH = 6.0 and shaken for 1.5 h in the case of the fluid biochar and 0.5 h for the biochar from municipal waste.
2.8. Effect of pH
The effect of pH on MB removal was established in the pH range from 2.0 to 10.0 with 0.1 g of the adsorbent for 1.5 h for the fluid biochar and 0.5 h for the bioadsorbent from municipal waste, in a 30 mg/l dye concentration. The initial solution pH was regulated using 0.1 M of H$_2$SO$_4$ or 0.1 M of NaOH.

2.9. Effect of temperature
The temperature-dependence of the adsorption process was tested in the range of temperatures 25-45°C.

The quantity of MB adsorbed onto the biocarbons ($q_e$) and the MB removal rate from the solution (R) were derived from the following formulas:

\[
q_e = \frac{V}{m}(c_0 - c_e) \tag{1}
\]

\[
\%R = \frac{c_0 - c_e}{c_0} \cdot 100 \tag{2}
\]

where: $c_0$ and $c_e$ – initial and equilibrium MB concentrations, respectively (mg/l); $V$ – MB solution volume (l); $m$ – mass of the adsorbent (g).

The obtained results served to calculate the sorption isotherms (Freundlich isotherm model) in the system of $\ln q_e = f(\ln C_e)$, and MB removal curves in the system of $R = f(C_0)$.

The Freundlich isotherm model [13] is expressed as:

\[
\ln q_e = \ln k + \frac{1}{n} \ln C_e \tag{3}
\]

where: $k$ and $n$ – adsorption capacity and adsorption intensity. These constants were determined from the intercept and slope of the linear plot of $\ln q_e$ versus $\ln C_e$, respectively.

3. Results and discussion

3.1. Effect of initial adsorbate concentration on adsorption
The quantity of adsorbed MB ($q_e$) and the MB removal rate (R) over 24 h onto the compost-biochar are shown in figure 1, and biomass-biochar in figure 2.

![Figure 1](image1.png)

**Figure 1.** The effect of MB concentration on MB adsorption onto compost-biochar (pH=6, T=24°C, compost-biochar dosage 0.1 g/l, contact time 24 h).

![Figure 2](image2.png)

**Figure 2.** The effect of MB concentration on the result of MB adsorption onto biomass-biochar (pH=6, T=24 °C, biomass-biochar dosage 0.1 g/l, contact time 24 h).
The results reveal a positive correlation between the increase in dye concentration and the increase in the quantity of adsorbed MB and the MB removal rate on both biochars. Since in both biochars the dye removal rate (99%) was constant at 30 mg/l MB concentration, therefore, the 30 mg/l concentration of MB was applied in subsequent experiments. The MB removal percentage rates by biochars did not display major differences between the tested adsorbents; however, the biomass-biochar mixture reached a 93% efficiency and compost-biochar 99%. Interesting results were obtained for the 10-20 mg/g range of initial concentrations. The Methylene Blue removal rate by the biomass-biochar mixture amounted to 70%, while in the case of compost-biochar – 98%.

3.2. Effect of contact time on adsorption process

The effect of Methylene-Blue-biochar contact time on MB adsorption onto the biochars is shown in figures 3 and 4.

![Figure 3](image1.png)  ![Figure 4](image2.png)

**Figure 3.** The effect of MB-biochar contact time on MB adsorption onto compost-biochar (pH=6, T=24 °C, compost-biochar dosage 0.1 g/l, contact time 24 h).

**Figure 4.** The effect of MB-biochar contact time on MB adsorption onto biomass-biochar (pH=6, T=24 °C, biomass-biochar dosage 0.1 g/l, contact time 24 h).

The Methylene Blue removal rate has been shown to increase over time, reaching the optimum after 90 min, in the case of biocarbon from municipal waste, or 30 min for the biomass-biochar adsorbent. Adsorption of Methylene Blue from aqueous solutions onto biochars intensifies progressively until equilibrium. Similar observations have been presented in other dye adsorption studies, e.g. by Kannan et al. and Al-Qadah [10, 14]. In the study of Methylene Blue adsorption onto waste sludge, by Sarioglu et al., adsorption peaked at 120 min [8]. In the study by Etim et al., in which coconut coir dust was used as the adsorbent, the equilibrium time was 20 min [15].

3.3. Effect of adsorbent dosage on adsorption

The dye uptake rates for the varying biochar dosage (0.05-0.2 g/50 ml) are specified in figures 5 and 6. The dye adsorption percentage is shown to rise with an increase in the adsorbent dosage, e.g. the increase from 0.05 to 0.15 led to the adsorption rate increase from 91.88% to 94.3% for the biomass-biochar and from 91.8% to 96% for the compost-biochar adsorbent. In adsorbent doses from 0.15 g to 0.2 g, the dye adsorption onto the biomass-biochar amounted to only 0.1, and onto the compost-biochar to 0.15 g, which indicates that adsorption is almost complete. A marked increase from 92.1% to 99.5% was observed following the dosage increase from 0.05 to 0.20 g. The increase in adsorption rate observed at a higher adsorbent dosage can be explained by an increase in the adsorption area and a greater number of adsorption sites [16].
The results indicate that there is a negative correlation between the quantity of adsorbed MB ($q_e$) and the increase in the adsorbent dosage, which may result from the overlapping or aggregation of dye-available adsorption sites on the adsorbent surface [17]. A similar trend is described by Etim et al. in the experiments on the removal of Methylene Blue from an aqueous solution by coconut coir dust and by palm, and El-Sayed’s study (2011) of Methylene Blue removal from an aqueous solution by palm kernel fibres [15, 17].

Adsorption onto the tested biochars approaches the equilibrium at the biochar dosage amounting to 0.1 g. A further increase in the dosage of biocarbons, from 0.1 g to 0.25 g did not improve the amount of adsorbed Methylene Blue. Hence, 0.1 g of biocarbons was determined as the optimum adsorbent dosage.

![Figure 5](image1.png)  ![Figure 6](image2.png)

**Figure 5.** The effect of adsorbent dosage on MB adsorption onto compost-biochar (pH=6, T= 24°C, compost-biochar dosage 0.1g/l, contact time 24h).

**Figure 6.** The effect of adsorbent dosage on MB adsorption onto biomass-biochar (pH= 6, T= 24°C, biomass-biochar dosage 0.1g/l, contact time 24h).

### 3.4. Effect of pH

The effect of the pH on the adsorption capacity of the biochars is given in figures 7 and 8. At pH 2, MB solutions exhibit low adsorption susceptibility – approx. 50% adsorption rate was recorded. The efficiency of the compost-biochar adsorbent in dye removal is positively affected by an increase in the pH: 94.8% at pH 4.0 and 96.3% at pH 6.0. With respect to the biomass-biochar adsorbent, the dye adsorption capacity was found to increase as well, from 91% at pH 4.0 to 96.3% at pH 6.0. Since pH 6 is the threshold level close to neutral, therefore, it is shown that adsorption cannot be conducted in an acidic environment. A further increase in the pH (up to 12) results in negligible changes in the dye removal percentage. Similar observations, i.e. indicating 6 as the optimal pH of the Methylene Blue solution have been reported by El-Sayed et al. (2011), Ponnusami et al. (2009), Sarioglu et al. (2006) or Etim et al. (2016) [8, 15, 17, 18].

### 3.5. Effect of temperature

In the present study, the effect of temperature on adsorption was investigated at free different temperatures (25, 35, 45°C). From the results presented below, it emerges that the temperature increase from 35°C to 45°C has a positive effect on the adsorption capacity of Methylene Blue onto the compost-biochar adsorbent, from 12.0 mg/g to 12.5 mg/g, and with respect to the biomass-biochar – from 11.50 mg/g to 11.7 mg/g. Elevated temperatures facilitate adsorption of methylene blue to biocarbons.
3.6. Adsorption isotherms
The adsorption mechanism is frequently described by means of equilibrium isotherms obtained from various Langmuir-Freundlich models [16]. The adsorption data obtained from the experiments were subjected to statistical analysis using the linear form of the Freundlich isotherm. The model expresses adsorption onto heterogeneous surfaces with an interaction between adsorbed molecules under the assumption that the adsorption energy decreases exponentially along with the filling of adsorption sites on the adsorbent [19].

Adsorption isotherms for Methylene Blue removal by the biochars in question are shown in figures 11-12. All isotherm models are shown to correlate well with the empirical data ($R^2 > 0.97$) (Table 1), thus indicating the validity of the adsorption data obtained in the study. A further sign of favourable adsorption is the value of $1/n < 1$ for Methylene Blue adsorption [20].

| Samples                      | Freundlich constants | $R^2$ |
|------------------------------|----------------------|-------|
| Adsorption of Methylene Blue onto compost-biochar | 1.42 1.01          | 0.989 |
| Adsorption of Methylene Blue onto biomass-biochar  | 1.49 1.02          | 0.977 |

4. Conclusions
Our experiments have demonstrated that biocarbons exhibit good adsorption capacity for removing cationic dyes, such as Methylene Blue, from aqueous solutions.

Compost-biochar dosed at 0.1 mg/g is capable of almost entirely ($R = 97 \%$) decolouring a 30 mg/g Methylene Blue solution. At pH = 6, the equilibrium adsorption occurs after 90 min.
At the same adsorbent dose and dye quantity, the biomass-biochar adsorbent achieves a comparable efficiency ($R = 91\%$), however, the equilibrium adsorption is attained at a shorter time, at pH = 6 after 30 min.

Adsorption parameters calculated from Freundlich isotherms provide a clear explanation of the mechanisms of the adsorption process as indicated by the good linear correlation coefficient values.

In additions, it has been revealed that should the process be carried out at the solution temperature above 25°C, it would be advantageous for the dye removal ratio. Nevertheless, the adsorption percentage obtained in the tests is high even at ambient temperature.

![Figure 9. Freundlich isotherm (compost-biochar).](image1)

![Figure 10. Freundlich isotherm (biomass-biochar).](image2)

References

[1] Li Q, Tang L, Hu J, Jiang M, Shi X, Zhang T, Li Y and Pan X 2018 *R. Soc. Open Sci.* **5** 180966
[2] Lee H W, Kim Y M, Kim S, Ryu C, Park S H and Park Y K 2018 *Carbon Let.* **26** 1–10
[3] Inyang M, Gao B, Yao Y, Xue Y and Zimmerman A R 2012 *Bioresource Technol.* **110** 50–6
[4] Chen X, Chen G, Chen L, Chen Y, Lehmann J, McBride M B and Hay A G 2011 *Bioresource Technol.* **102** 8877–84
[5] Saleh M E, Mahmoud A H and El-Refaey A A 2014 *Adv. Environ. Biol.* **8** 399–409
[6] Kolodynska D, Wentrzak R, Leahy J, Hayes M H B, Kwapinski W and Hubicki Z 2012 *Chem Eng J.* **197** 295–305
[7] Tong X and Xu R 2013 *J. Environ. Sci.* **25** 652–8
[8] Sarioglu M and Atay U A 2006 *Global NEST J* **8** 113–20
[9] Bhatnagar A. and Jain A K 2005 *J. of Colloid and Interface Sci*. **281** 49–55
[10] Kannan N and Sundaram M M 2001 *Dyes Pigm.* **51** 25–40
[11] Bhattacharyya K G and Sharma A 2005 *Dyes Pigm.* **65** 51–9
[12] www.fluid.com
[13] Mohanthy K, Jha M, Meikap B C and Biswas M N 2006 *Chem Eng J.* **117** 71–7
[14] Al-Qodah Z 2000 *Water Res.* **34** 4295–303
[15] Etim U J, Unmore S A and Eduok U M 2016 *J. Saudi Chem. Soc.* **20** S67-S76
[16] Kumar S, P., Ramalingam S, Senthilmarai C, Niranjanaa M, Vijayalakshmi P and Sivanesan S 2010 *Desalination* **261** 52–60
[17] El-Sayed G O 2011 *Desalination* **272** 225–32
[18] Ponnuasami V, Gunasekar V, Srivastava S N 2009 *J. Hazard. Mater.* **169** 119–27
[19] Crini G and Badot P M 2008 *Prog. Polym. Sci.* **33** 399–447
[20] Huang L, Zeng G, Huang D, Li L, Du C and Zhang L 2010 *Environ. Earth Sci.* **60** 1683–91.