BIOCHAR DERIVED FROM SLOW PYROLYSIS AND ITS APPLICATION AS SORBENT IN REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION

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In this study, biochar (BC) derived from slow pyrolysis of spruce sawdust and activated BC with HNO_3 were used as sorbents to remove methylene blue (MB) dye from the aqueous solution. BC was prepared by pyrolysis at temperatures of 200, 300, 400, and 500 °C. Based on the screening results, the two BCs (BC prepared at 400 °C and BC prepared at 500 °C) exhibiting a higher percentage of dye removal were selected to investigate further the effect of factors, including contact times 15, 30, and 60 minutes and the amount of dosage – BC 0.01, 0.03, 0.05 g / 8 mL. The sorption efficiency of MB was determined by measuring the absorbance of the solutions after sorption in a UV / VIS area of 665 nm. BC prepared at 500 °C was found to perform better than BC prepared at 400 °C and activated BC by HNO_3 and has more than 95 % rate of methylene dye adsorption.

KEYWORDS

spruce sawdust, biochar, chemical activation, adsorption, methylene blue

1 INTRODUCTION

Worldwide, 7.10^5 tons of 10,000 different dyes and pigments are produced and their market is raising every year. Approximately 10-15 % of dyes are discharged as effluent during dye applications in industries for the production of textiles, leather, paper, cosmetics, printing, and plastics [Hussain et al. 2019; Karthik et al. 2015]. Industries' wastewater can contain deleterious chemical compounds, which may be the primary sources of soil and aqueous contamination [Karthik et al. 2015]. The common pollutant of natural water bodies can be methylene blue (MB). It is a widely used organic cationic dye and after entering living organisms, MB can lead to neurotoxicity, encephalopathy, skin irritation, kidney, liver, and brain dysfunction [Fernando et al. 2021].

Among traditional water purification methods such as filtration, ion exchange, coagulation by lime, or using salts of iron/aluminium, adsorption has been proven to a be very effective methods. It offers the most promising, simple, and efficient technique and the use of low-cost adsorbents such as biochar from different types of biomass and other carbonaceous materials that make the dye removal process more economical [Sajjad et al. 2019].

Biochar (BC) is derived from any kind of biomass. It is a carbon-rich product that can be produced by several thermochemical processes: conventional carbonization or slow pyrolysis, fast pyrolysis, flash carbonization, and gasification [Lehmann and Joseph 2015]. The feedstock is dry biomass, most of which is composed of the three organic compounds cellulose, hemicellulose, and lignin [Hornung et al. 2021]. These behave differently during heat treatment and therefore the composition of the biomass directly influences the product yield and properties [Weber and Quicker 2018]. The feedstock used should be available and inexpensive for large-scale industrial applications and the adsorbent produced should have the optimal combination of porosity and surface functionality [Peiris et al. 2020]. These properties make BC an effective material for the removal of contaminants from wastewaters [Lonappan et al. 2016].

Generally, biomass is heated to temperatures between 300 and 800 °C, in which the maximum temperature, the heating rate, and the residence time determine the desired procedure (slow, fast, and flash pyrolysis). The products obtained are gas, liquid, and BC [Hussain et al. 2019]. Among the numerous pyrolysis techniques, slow pyrolysis is frequently used to produce BC due to its low-cost and simplicity and the highest quantity of BC [Fernando et al. 2021]. The properties of BC depend on a variety of parameters such as feedstock, processes, and process conditions. Quality defines the field of application [Hornung et al. 2021].

2 THEORETICAL BACKGROUND

Because it does not produce harmful residues and has the capacity to treat large volumes of water, adsorption is the best treatment process among other conventional water treatment methods. As far as the removal of dye from water is concerned, an adsorbent could be common materials, such as activated carbon, zeolites, activated alumina, silica gel and polymeric adsorbents [Deniz 2013]. But now the subject of interest for many researchers is the use of biomaterials instead of conventional materials for adsorption processes [Srivatsav et al. 2020].

In the past few years, extensive research has been done on different methods of pyrolysis, which can affect the conversion of biomass to BC. The nature of BC produced, as a result of pyrolysis, depends on many factors, such as biomass pretreatment, reactor type, and dimensions, pressure, residence time in the reactor [Li et al. 2020]. Compared to other processes, such as hydrothermal carbonization or hydrothermal liquefaction, pyrolysis has the advantage of being able to be used for a wide range of biomass and waste materials. BC can be modified in a multitude of ways for various purposes, some of which have been used in soil remediation, wastewater treatment, catalytic enhancer, etc. [Srivatsav et al. 2020]. Optimization of BC preparation and activation methods leads to an increase in BC yield, enhancing its pore size distribution and surface area [Sahu et al. 2020].

The environmentally friendly and versatile BC has been seen as a good material for treating wastewater, because of its adsorption properties. However, as an adsorbent, it works under specific conditions. The concentration of dye / BC, temperature, and pH of the solution plays important role in determining the efficiency of BC [Park et al. 2019; Mahmoud et al. 2020].

The mechanism of removal of dyes from wastewater using BC involves many complex interactions (both chemisorption and

physisorption) between the adsorbate (dye) and the adsorbent (BC). Depending on dyes, BC, and solvent, mechanisms, such as the pore-filling effect, van der Waals interaction, electrostatic interaction, chemical action, ion exchange, surface complexation, π-π interactions, cation-π interactions could play important roles in the adsorption process [Srivatsav et al. 2020]. BC produced by pyrolysis of mixed municipal discarded material at 300 °C for 12 h, has functional groups containing oxygen that are beneficial for the adsorption of methylene blue as well as graphitic structures suggesting potential sites for π-π interactions of – with methylene blue [Hoslett et al. 2020]. Liu et al. (2020) prepared biochar from wood powder and walnut shells by the limited oxygen pyrolysis process at a temperature of 550 °C. The evaluation of the adsorption performance using methylene blue (MB) as a pigment model showed that modified BC prepared from both biomasses had a mesoporous structure, and the pore size was larger in wood powder BC. To improve the physicochemical properties, different modifications such as concentrated sulfuric acid, phosphoric acid, $ZnCl_2$, and KOH were used. According to analyses, KOH effectively made holes in wood powder and walnut shells and activating reagents effectively expanded the specific surface area and increased the amount of adsorption. Chemical activation is a single-step method that involves the impregnation of chemicals such as KOH, H_3PO_4, H_2SO_4, NaOH, and K_2CO_3 in the precursor [Sahu et al. 2020]. Concentrated nitric acid is one of the other common oxidizing solutions. Treatment with HNO_3 increases the number of structures containing N-O bonds (nitro groups and nitrate complexes). Oxidation and nitration are the two reactions that occur during nitric acid activation [Sajjadi et al. 2018].

In the study by Guzel et al. (2017) the optimal BC based on oxidized weeds with HNO_3 was used as a sorbent to remove methylene blue (MB) dye from the aqueous solution. The results showed that the oxidized weed-based BC has a lower BET surface area, more oxygen functional groups, lower $pH_{pzc,}$ and higher MB index compared with the weed-based BC. Lonappan et al. (2016) compared the adsorption capacity of three different types of BC such as pine wood, pig manure, and cardboard with commercially available activated carbon. Experimental results showed that dye adsorption increased with the amount of BC at reduced concentrations. The adsorption capacities of BC varied with the source material and the method of preparation. The adsorption capacity for the cationic MB dye also increased with an increasing surface area of the BC.

3 METHODOLOGY

3.1 Preparation of Biochar and Characterization

The biomass (spruce sawdust) was supplied from central Slovakia, the region Liptov. The sawdust was dried in a TCN 50 PLUS dryer at a temperature of 100 °C for 48 hours and sieved at a size of 1.60 mm in maximum length. According to Zhang et al. (2016), crushing BC into powders destroys the pore structure, and the BC size was selected by sifting BC of the same size as the wood particles.

The preparation of BC was performed by slow pyrolysis in a LAC type LE 15/11 muffle furnace under controlled conditions, which were: nitrogen atmosphere (99.99 %) flow (20 mL / min), the residence time of 120 min, a heating rate of 10 °C / min and final temperature of 200, 300, 400 or 500 °C. Subsequently, the final product was cooled to room temperature in a desiccator. The yield was calculated as the ratio of the dry weight of the produced BC to the weight of the air-dried biomass.

To improve the adsorptive capacity, BC4 was activated by HNO_3. A gram of dried BC4 was treated with 25 mL of 65 % HNO_3 solution for one hour at 80 °C (reflux). After treatment, the samples were thoroughly washed with distilled water and dried at 105 °C to a constant weight [Guzel et al. 2017]. The chemically activated BC was named BCA.

The pH of BC was measured in a 1:20 ratio (BC : deionized water) after one hour of shaking on the shaker at 25 °C. Subsequently, the samples were allowed to stand for 30 min, and then the pH was measured using the electrode–glass electrode system. The pH meter was calibrated using buffers of pH seven and ten [Singh et al. 2017]. Generally, pH values were lower for BC samples produced at lower pyrolysis temperatures. As reported by Rehrah et al. (2014), the increase in pH at higher temperatures may be caused by the increased relative concentration of nonpyrolyzed inorganic elements in the feedstock and the formation of basic surface oxides at higher pyrolysis temperature.

The total acidity of the surface of BCA could be a result of the increase in surface acidic functional groups continuing to increase with the concentration of nitric acid or the duration of oxidation [Guzel et al. 2017].

The biomass was characterized by proximate analysis and biochars were characterized through scanning electron microscopy, elemental analysis, and Brunauer-Emmett-Teller surface area analysis.

Biochar	Temperature of pyrolysis [°C]	Residence time [min]	Yield [%]	pH
BC2	200	120	98.55	5.85
BC3	300	120	58.07	5.97
BC4	400	120	31.59	6.21
BC5	500	120	22.00	6.79
BCA (activated by HNO_3)	400	120	-	5.27

Table 1. Preparation of biochar samples and characterization and their preparation condition

As tab. 1 shows that the yield decreased with increasing pyrolysis temperature. According to Hernandez-Mena et al. (2014), it may be caused by the increased thermal degradation that occurs at elevated temperatures.

3.1.1 Proximate analysis

The proximate analysis yields the weight fractions of moisture, volatile matter (VM), ash, and fixed carbon (FC). To determine the moisture (M) of the biomass, a laboratory TCN 50 PLUS dryer was used. The biomass samples – 100 g were dried on a dry basis with moisture in an oven at 105 °C for 48 hours to remove excess moisture from the sample. Therefore, M is neglected for the purposes of the calculation. The determination of ASH in a biomass sample was performed according to the standard STN EN ISO 18122: Solid biofuels – Determination of ash content (ISO 18122:2015). Ash is the weight of residue obtained after the complete combustion of one gram of coal at 700-750 °C. Ash in % is:

$$\%A = \frac{weight\ of\ residue}{weight\ of\ samples} \times 100 \quad (1)$$

VM determination was performed according to the ISO 562:2010 standard on Hard coal and coke − determination of

the volatile matter. VM is the weight loss obtained by heating 1 g of sample coal at 900 ± 10 ºC for 7 minutes. VM in % is:

$$\%VM = \frac{weight\ of\ preheated\ sample - weight\ of\ sample\ after\ heating}{weight\ of\ precombustion\ sample} \times 100 \quad (2)$$

FC is a measure of the amount of nonvolatile carbon remaining in a coal sample. It is the calculated percentage of material that was lost during the testing for M, VM, and ASH:

$$FC(\%) = 100 - M(\%) - ASH(\%) - VM(\%) \quad (3)$$

Biomass samples	ASH [%]	VM [%]	FC [%]
Spruce sawdust	0.27	86.16	13.57

Table 2. Proximate analysis of biomass sample

3.1.2 Specific surface area

The nitrogen adsorption analyzer NOVA 2200e (the high-speed gas sorption analyzer Quantachrome Instruments) was used to determine the specific surface area. The data obtained were processed with NovaWin software and the specific surface area was calculated by the multipoint method and the Brunauer-Emmett-Teller (BET) method.

Biochar samples	Surface Area [m^2/g]	Outgas Time [h]	Outgas Temperature [ºC]
BC2	<1.0	70.0	150.0
BC3	<1.0	70.0	150.0
BC4	116.069	70.0	300.0
BC5	494.285	70.0	300.0
BCA	2.986	70.0	300.0

Table 3. Specific surface area (BET method) of biochar

3.1.3 Scanning Electron Microscopy Analysis (SEM)

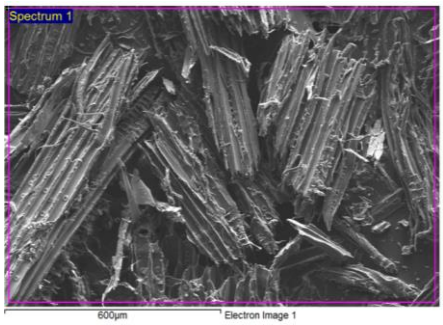
A Scanning Electron Microscope SEM (JEOL JSM 7600F with FEG cathode) was used to characterize the surface of the spruce sawdust and the various elements present in the sawdust were determined by an energy dispersive X-ray analyzer attached with the scanning electron microscope [energy-dispersion system EDS - Si (Li) detector X-Max 50 mm^2 (Oxford Instruments) and a wave-dispersive X-ray spectroscope (Inca Wave spectrometer, Oxford Instruments)]. The EDX study of the spruce sawdust shows the elemental composition of the adsorbent (Fig. 1), showing that the sawdust has a high percentage of carbon and oxygen. Generally, the chemical composition of spruce wood is C – 50 %, H – 6.27 %, O – 43.33 %, and N – 0.10 % [Neves et al. 2011]. The samples were vapor-deposited with a thin layer of amorphous carbon to increase electrical conductivity. For this reason, the percentage of carbon in the samples is slightly higher than the average values reported in the literature.

As reported by Guzel et al. (2017), oxidation of BCA becomes more severe with a higher concentration of nitric acid. Therefore, the carbon and hydrogen content decreases while the amounts of oxygen and nitrogen increase. The decrease of carbon is due to the destruction of the pore walls and the increase of nitrogen and oxygen is due to the formation of aromatic compounds containing functional groups of nitrogen and carbon-oxygen on the surface.

SEM images of biochar samples obtained at different temperatures are shown in Figs. 2-6. The surface morphology of the BC changed with the increase in the pyrolysis temperature. Few asymmetric small pores were observed on the surface of BC derived at lower temperatures (Figs. 2 and 3). This observation is consistent with the data reported from BET. The surface area for both BC2 and BC3 samples was less than 1 m^2 / g.

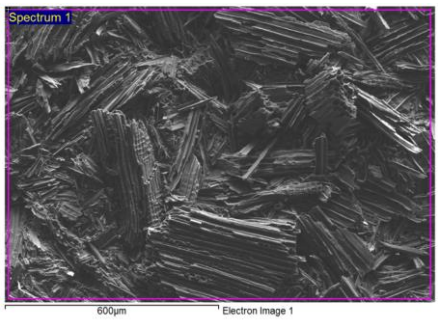
However, after pyrolysis at 400 and 500°C, the surface became porosity. The number of pores increased and several large pores were observed on the surface of BC4 and BC5. This observation is consistent with the data reported in Table 3, in which the increase in surface area was almost 4.2 times greater for BC5 than for BC4.

BC2



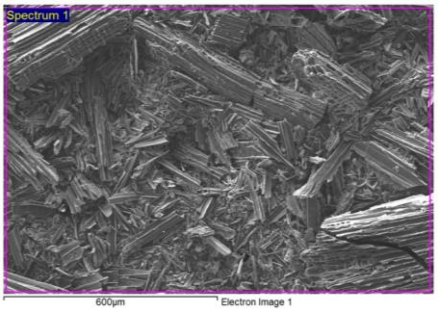
C [%]	N [%]	O [%]
60.76	3.70	35.54

BC3



C [%]	N [%]	O [%]
68.76	3.93	26.79

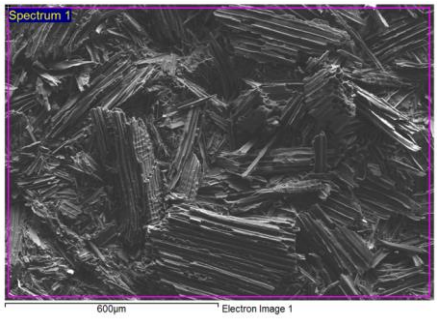
BC4



C [%]	N [%]	O [%]
72.18	4.33	23.50

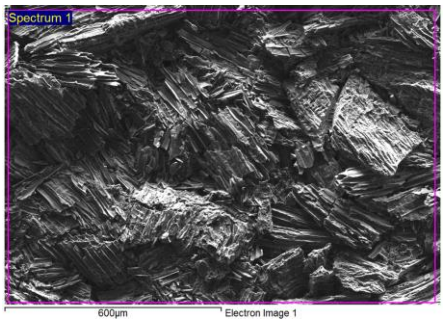
Figure 1. Elemental composition of pyrolyzed spruce sawdust and activated biochar

BC5



C [%]	N [%]	O [%]
74.97	4.46	21.10

BCA



C [%]	N [%]	O [%]
62.12	5.83	32.04

Figure 1. (continuation) Elemental composition of pyrolyzed spruce sawdust and activated biochar

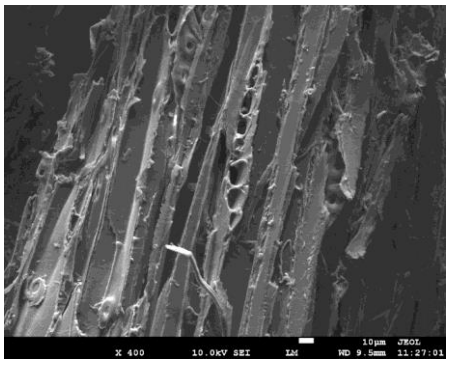


Figure 2. Surface detail of BC2 at 400x magnification

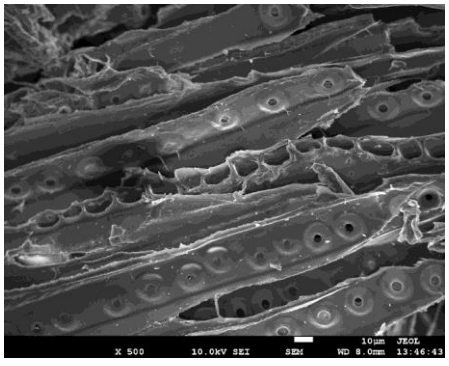


Figure 3. SEM photographs of BC3 at 500x magnification

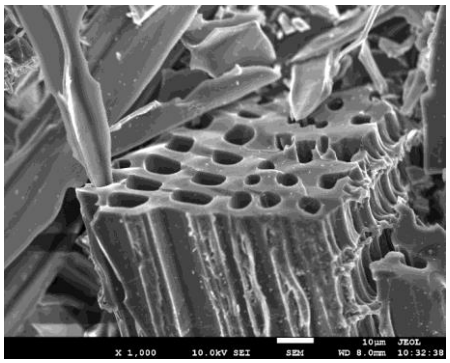


Figure 4. SEM photographs of BC4 at 1000x magnification

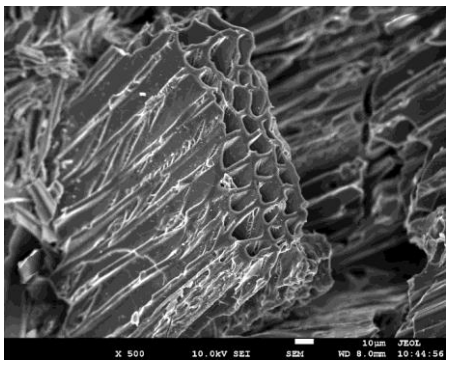


Figure 5. SEM photographs of BC5 at 500x magnification

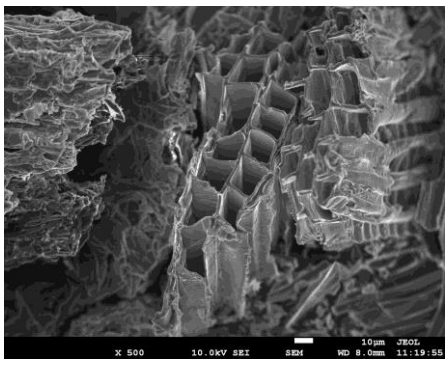


Figure 6. SEM photographs of BCA at 500x magnification

3.2 Sorption studies of methylene blue

The basic dye, MB (Type: cationic, Chemical formula: $C_{16}H_{18}ClN_3S$, Color index: Basic blue 9; *Mw*: 319.85 g/mol (anhydrous basis); *λmax*: 665 nm) was used as sorbate.

First, a screening test of BC produced for MB dye was carried out as follows: 0.01 g of BC produced were shaken for 24 h at 20 °C in 10 ml tubes containing 20 mg/L of MB in Mini Rocker–Shaker MR-1. Based on the screening results, the two BCs exhibiting a higher percentage of dye removal were selected to investigate further the effect of factors including contact times 15, 30, and 60 minutes and BC dosages 0.01, 0.03, and 0.05 g.

Adsorption experiments were performed to determine and compare the adsorption efficiency of different BC samples, depending on the effect of BC dose and contact time of each selected BC.

Exactly 0.01, 0.03, and 0.05 g of the selected biochars BC4, and BC5, BCA were shaken for 15, 30, and 60 min in 10 mL tubes containing 8 mL of MB dye solution 20 mg/L at a temperature of 20 ℃. After the adsorption test, BC was separated by centrifugation (Nahita Centrifuge model 2640-12) at 4000 rpm for 7 min to sediment small, undesirable particles of sorbent. The sorption efficiency of MB was determined by measuring

the absorbance of the solutions after sorption in 1 cm cuvettes using a GENESYS 8 spectrophotometer in a UV / VIS area of 665 nm.

The percentage of dye removal was determined, respectively, according to the equation:

$$\eta = \frac{A_0 - A_t}{A_0} \times 100 \quad (4)$$

where η (%) is the efficiency of adsorption, A_0 is the absorbance of the sample before adsorption, and A_t is the absorbance of the sample after adsorption. Experiments were tested in triplicate and the result was expressed as average.

4 RESULTS

For comparison, we used BC prepared at 400 and 500 °C. Figs. 7 and 8 show the sorption efficiency of MB in BC4 and BC5 at different doses of adsorbent and contact time. The adsorption efficiency of MB was studied by varying the amount of BC from 0.01, 0.03 to 0.05 g / 8 mL, while keeping other parameters constant, such as the initial concentration of 20 mg / L, the agitation rate of 120 rpm, the contact time of 15, 30, 60 min and the temperature of 20 °C. As can be seen in Fig. 7, the amount of adsorbent dose and the contact time of sorbate and sorbent has a relatively high impact on the efficiency of the sorption process. The removal efficiency of MB was found to increase slightly with the BC4 dose at contact times 15, 30, and 60 min at a constant concentration of MB. Due to the porous surface, BC4 has relatively good adsorption abilities with increased adsorbent dosage, as the particle size was kept constant, the surface area was directly proportional to the mass of adsorbent in the solution and hence the adsorption was increasing. On the contrary, as can be seen in Fig. 8, as the dose increased, the adsorption efficiency of BC5 increases rapidly. It was also found that the amount of adsorption capacity increases rapidly with increasing contact time. The higher sorption efficiency at 0.03 and 0.05 g of BCA may be due to an increased number of vacant active sites for adsorption at the surface of the adsorbent. As time progresses, this efficiency increases slightly due to the accumulation of dye particles at the vacant sites, leading to a decrease in the sorption rate.

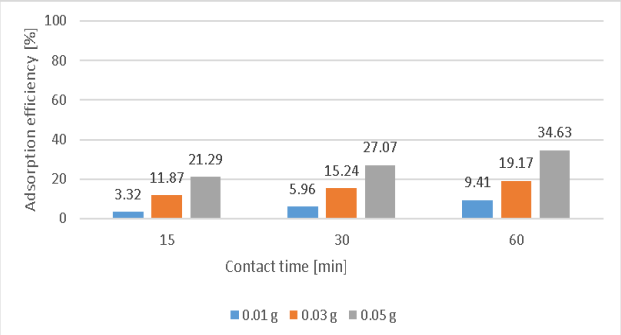


Figure 7. The plot related to the adsorption efficiency of MB in BC4 at different amounts of adsorbent dose and contact time

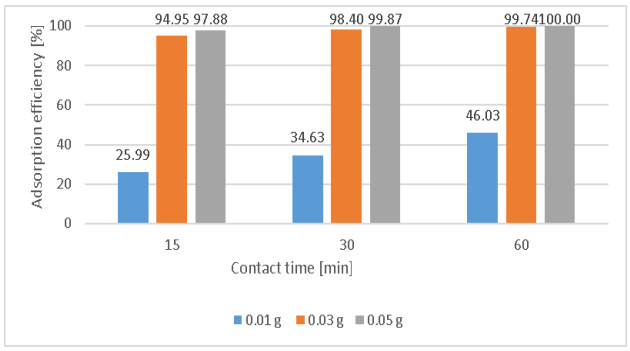


Figure 8. The plot related to the adsorption efficiency of MB in BC5 at different amounts of adsorbent dose and contact time

To increase adsorption capacity, BC4 was activated by HNO_3. This activated BC was named BCA. The sorption efficiency of BCA is shown in Fig.9. The amount of dye adsorption was found to increase with increasing contact time but decrease with an increasing amount of adsorbent dosage. Initially, the rate of increase in dye removal was rapid and then slowed with an increase in the adsorbent dose. It was observed that the increase in the dosage of adsorbent from 0.01 to 0.03 g and from 0.03 to 0.05 g at a contact time of 15 min resulted in a decrease in the amount of dye adsorbed (adsorbent efficiency) from 90.35 to 89.29 % and from 89.29 to 88.23 %. A similar trend of a slight decrease in adsorption efficiency with adsorbent dosage was also observed at contact times 30 and 60 min.

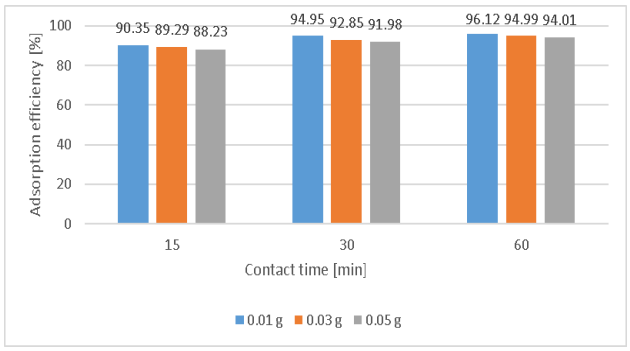


Figure 9. The plot related to the adsorption efficiency of MB in BCA at different amounts of adsorbent dose and contact time

5 DISCUSSION

Tab. 1 shows the percentage yield of BC derived from spruce sawdust at temperatures of 200-500 °C and a heating time of 120 min. Pyrolysis conditions cause a substantial impact on the properties of BCs produced, which significantly influenced the adsorptive performance. The BC yield decreased with increasing temperature, for example, the BC yield fell from 98.55 to 22.00 % when the temperature rose from 200 to 500 °C, respectively.

As Mahdi et al. (2017) stated in the study, the lower BC yield at higher pyrolysis temperature and heating time are attributed to the breakage of the cellulose and hemicellulose structure, leading to the release of organic molecules. Zhu et al. (2014) reported that BCs exhibiting high surface area and pore volume are excellent materials for organic pollutant adsorptions due to their strong affinity associated with a pore-filling effect. Additionally, as reported by Vyavahare et al. (2019), BC produced at higher charring temperature exhibited a large surface area and rough surface structure leading to efficient uptake of organic pollutants from the aqueous phase.

In our experiment, BC5 has a more than 95 % rate of methylene dye adsorption. According to Chaukura et al. (2017), it may be associated with the availability of active surface binding sites and the external surface adsorption behaviour that facilitates rapid dye sorption on the BC surface.

The pores in BC span several orders of magnitude and can be classified into macropores (with a diameter of the pore of 1000-0.05 µm), mesopores (0.05-0.002 µm), and micropores (0.05-0.0001 µm). Generally, the pore structure of BCs consists of micropores to a large extent, which may account for more than 80 % of the total pore volume. Porosity changes as a result of volatile gases that escape during the carbonization process and so does the total surface area of the biomass [Weber and Quicker 2018]. For most biomasses, a surface area of several hundred m^2 / g can be achieved under suitable carbonization conditions. Quicker and Weber (2016) reported that the surface areas of BCs produced from wood generally increase with increasing temperature. As expected, increasing the pyrolysis temperature promoted the development and formation of a highly porous structure in the BC produced, which manifests in the high surface area and pore volume obtained for the BC produced at 500 °C and has better sorption properties. And also as the study by Usman et al. (2015) demonstrated, the adsorption properties of BCs are highly influenced by feedstock composition and pyrolysis conditions.

Fig. 9 shows the sorption efficiency of BCA, which decreases with increasing dose of adsorbent. According to Nautiyal et al. (2016), the higher adsorption of dyes at a lower BC dose, due to the increase in the ratio of dye to adsorbent molecules, results in an improvement in the sorption capacity of the dyes. With an increase in BC dose, at fixed dye concentrations, there may be overlapping of binding sites and also insufficient availability of dye molecules for vacant active sites and thus showed a lower adsorption capacity at a higher dose.

The amount of adsorbent dose influences the degree of adsorption of dye. Even a small increase in the adsorbent dosage from 0.01 to 0.03 g caused the removal percentage to increase significantly (an almost threefold increase). A similar increase in the percentage of dye removal with a very small increase in adsorbent dosage was also observed in other studies, which concluded that the increase in adsorbent, dosage increased the active sites for adsorption as well the surface area of the adsorbent. However, the percentage of dye removal remained constant after a certain dose of BC due to the decrease in the amount of dye molecules adsorbed per unit mass of adsorbent [Nautiyal et al. 2016; Ganguly et al. 2020]. This decrease may be due to either narrowing of the pore entrances of oxygen groups formed on the entrance and walls of pores or to the destruction of the pore walls and the conversion of micropores and mesopores to macropores due to the strong oxidation conditions [Gokce and Aktaş 2014].

Guzel et al. (2017) pointed out changes in the elemental compositions of BC by activation with various concentrations of HNO_3. While the acid concentration increases, the carbon and hydrogen contents decrease, and the oxygen and nitrogen contents increase. The decrease of carbon and increase of nitrogen and oxygen may be due to the destruction of the pore walls, the formation of aromatic compounds containing nitrogen, and the formation of carbon-oxygen functional groups on the surface, respectively. Activation treatment processes can increase the total acidity of the surface that results from the increase in surface acidic functional groups, such as carboxylic, lactone, and phenol groups.

Although an increase in the BC surface area can improve adsorption [Zhang et al. 2012], the adsorption capacity is not exclusively dependent on the biochar surface area [Saarela et al. 2020].

6 CONCLUSIONS

The present study evaluated the impact of pyrolysis conditions on the characteristics of spruce sawdust BCs and their performance for the adsorption of MB. The sorption efficiency of BC4 and BC5 uptake was found to increase with an increasing amount of adsorbent dose and contact time; on the other hand, with the use of BCA, it decreased with an increasing amount of adsorbent dose. However, BC5 performed better than BC4 and activated BCA by HNO_3. Already using 0.03 g of BC5 and a contact time of 15 min, we achieved almost 95 % removal dye efficiency. Therefore, using this type of BC for the removal of dyes by sorption of MB from an aqueous solution eliminates the need for any chemical activation process, which can have a negative impact on the environment and thus has also potential as a sustainable adsorbent for rapid, efficient wastewater purification from industries for the production of e.g., textile, leather, paper, cosmetics, printing or plastics.

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