Methylene blue removal by adsorption on unmodified and modified wood sawdust

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INTRODUCTION

The textile industry is the most stable economic branch and the main carrier of economic development of many developing countries. During the production process, it uses a large amount of synthetic dyes of different composition. It is estimated that as much as 2/3 of the total world dye production is used by the textile industry (Bortolouz et al., 2020). However, the dye is not completely depleted in the production process due to the hydrolysis of the dye, so as such it can no longer be bound to the fiber. Therefore, 10-50 % of the initial dye concentration ends up in the wastewater, which becomes intensely colored (Janaki et al., 2013). It is estimated that 280,000 tons of dye per year enters wastewater (Bharagava & Pankaj, 2019). A low concentration of dye (<1.0 mg/dm³) is able to stain water bodies. Mashkoor & Nasar (2020) find such figures worrying because the dyes are highly toxic and cause major problems in aquatic ecosystems. The color of the water reduces the permeability of sunlight, which disrupts the photochemical and biological activities of aquatic organisms. Some types of dyes

Adsorption, as an easy and effective technique, is widely used to remove a large number of dyes from aqueous solutions. Activated carbon is the most desirable adsorbent, but due to its high cost, its use is limited. Proving the possibility of adsorption and its efficiency performed on cheap adsorbents is a great challenge and interest of many researchers in the past few decades.

In this paper, unmodified (P) and modified sawdust obtained in two ways (HCI treatment and NaOH treatment), labeled as P_{HCI} and P_{NaOH} , are used for the removal of the methylene blue dye. Adsorption experiments showed that the optimal time for adsorption is different, for the sample P_{NaOH} – 30 min, for the sample P – 45 min, and for the sample P_{HCI} – 60 min. By applying nonlinear kinetic models to the experimentally obtained data, it was found that the best model that describes this adsorption is pseudo-second-order model.

By examining the effect of pH values on adsorption, different results were obtained (for samples P and P_{HCI} the optimal pH value is pH=11, the P_{NaOH} sample is effective in a wider range of pH values).

The analysis of the effect adsorbent dose on adsorption process showed that the efficiency of dye removal decreases with increasing mass of adsorbents.

The obtained values of the coefficient of determination in Freundlich's model for samples of unmodified (P) and modified sawdust (P_{NaOH}) indicate that the adsorption of the methylene blue dye is multilayer type adsorption. For the P_{Hcl} sample, neither the Langmuir nor Freundlich model adequately described MB dye adsorption.

are considered carcinogenic and mutagenic for both animals and humans (Zhou et al., 2019). In general, paints are characterized by high thermal and photo stability, as well as a complex chemical structure that is not always known, which allows them to survive over a long period of time in the environment. Almost all synthetic dyes are produced using hydrocarbons, such as benzene, toluene, naphthalene and anthracene. In everyday life, they are present all around us, and their application continues to grow continuously (Buntić, 2017).

According to the chemical composition, dyes represent a type of organic compounds with a complex aromatic molecular structure, which makes them more stable and non-degradable (Saha et al., 2020). Color molecules consist of two key components: chromophores, responsible for color formation, and auxochromes, which can not only supplement the chromophore, but also make the molecule soluble in water and increase affinity for fibers during binding (Gupta & Suhas, 2009).

Before being discharged into the municipal or central industrial sewage system, the wastewater undergoes the following processes: pre-treatment, primary treatment, secondary treatment and final treatment (sludge treatment and its disposal).

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Currently, the most common processes are coagulation and flocculation, advanced oxidation, electrochemical, biochemical and adsorption processes (Bortolouz et al., 2020). Each of these processes has its advantages and disadvantages. The most common problems of these treatments are related to the high cost of treatment and disposal of sludge (Buntić, 2017).

Adsorption is one of the most popular physicochemical methods for removing many pollutants from wastewater, even dyes. The adsorption process is suitable for removing or concentrating contaminants from an aqueous solution, especially those that are not easily biodegradable or not biodegradable at all.

Adsorption involves the accumulation of adsorbates at the boundary between two phases. There are two types of adsorption: chemical adsorption (hemisorption) and physical adsorption (physisorption). The main difference between these two types of adsorption is that chemical adsorption involves the formation of strong chemical bonds between adsorbates and adsorbents through electron exchange, and is often irreversible. On the other hand, physical adsorption is characterized by weak Van der Waals or hydrogen bonds between the adsorbate and the adsorbent, and is also characterized by reversibility.

Over the past decades, a large number of researchers have conducted research with cheap adsorbents to prove that the adsorption process can be effectively performed on cheap adsorbents, and not only on more expensive adsorbents, such us activated carbon (Chikri et al., 2020; Rahimiani et al., 2020). The adsorbent is considered "cheap" if it is not dangerous for the environment, it is abundant in nature, and it is easily available, and requires very little processing (Yagub et al., 2014).

Sawdust from various types of wood plays an important role in the adsorption of pollutants from wastewater, because it contains numerous functional groups such as carboxyl, hydroxyl, phenolic, and amide groups in their structure, which may be suitable for adsorbing a large number of dyes. Moreover, sawdust can be modified with acid and alkali, increasing its adsorption properties. A large number of papers talk about the use of sawdust and modified sawdust as a cheap adsorbent for removing dyes from wastewater (Chikri et al., 2020).

The aim of this paper is to investigate the possibility of removing the methylene blue dye by various adsorption experiments on unmodified wood sawdust and wood sawdust that is modified in two ways (hydrothermal treatment with HCl and NaOH).

MATERIAL AND METHODS

Preparation of adsorbents

Wood sawdust formed as sawmill waste during the processing of beech and linden wood was used as an adsorbent. The sawdust was homogenized and dried in an oven at 105 °C for 24 h. Unmodified sawdust marked as P was used in adsorption experiments.

In the adsorption experiments modified sawdust was used. This modified sawdust was obtained by hydrothermal treatment with HCl (C=2M), and hydrothermal treatment with NaOH (C=2M).

The sawdust modification was performed in a glass balloon with a ground stopper, in a water bath with a shaker (*Memmert WNB 22, Germani*) at a temperature of T=85 °C, at the ratio of solid and liquid phase (S:L=1:10). The sawdust processing time was 5 h. At the end of the reaction time, the sample was first washed by decantation with distilled water until neutral pH was reached, then filtered through blue ribbon filter paper, and then dried in an oven at 105 °C for 24 h. In this way, adsorbent samples treated with HCI (P_{HCI}) and NaOH (P_{NaOH}) were obtained.

The identification of surface functional groups of the examined adsorbents was performed using with Fourier transform infrared spectroscopy using the ATR chamber (ATR - FTIR).

Preparation of adsorbate

Methylene blue dye previously dried at 105 °C was used as the adsorbent. From the basic dye solution (γ_0 =1000 mg/dm³), a working dye solution with a concentration of γ_1 =100 mg/dm³ was prepared by dilution and used in adsorption experiments.

Adsorption experiments

All adsorption experiments were performed at room temperature and atmospheric pressure using three adsorbents: unmodified sawdust (P), sawdust treated with HCl (P_{HCl}) and sawdust treated with NaOH (P_{NAOH}).

The samples of dried adsorbent (0.25 g) were weighed into laboratory beakers, and then a methylene blue adsorption solution with a volume of 50 cm³ was added. The beakers were placed on a magnetic stirrer, which provided intensive mixing during adsorption. After the set time, the separation of the solid from the liquid phase was performed by membrane filtration (*Sartorius, Membrane filter, Germani*), through 0.45 µm filter paper. The concentration of residual dye in the filtrates was determined by spectrophotometer (*Perkin Elmer, Lambda 25*) at the wavelength obtained experimentally – by determining the maximum of absorbance. In order to avoid errors due to the adsorption of dye on the membrane filter paper, the concentration of the working dye solution was determined on the spectrophotometer with prior filtration on the membrane filter paper.

The following experiments were used to test the efficiency and removal capacity of methylene blue dye by adsorption on unmodified sawdust and modified sawdust:

- Effect of contact time on adsorption of MB
- Effect of initial pH of dye solution on adsorption of MB
- Effect of adsorbent dose on adsorption of MB
- Effect of initial concentration of adsorbate on adsorption of MB

Effect of contact time on adsorption

To determine the optimal contact time, a dye solution with concentration of 100 mg/dm³ and pH value 6.60 (at T=24.2 °C) was used. The following times 5 min, 7 min, 10 min, 15 min, 30 min, 45 min, 60 min, and 120 min were used to examine the effect of contact time on the adsorption.

Effect of initial pH of dye solution on adsorption

Examination of the effect of pH value of the adsorption solution (concentration of γ_1 =100 mg/dm³) on the adsorption was performed at pH values: 3, 5, 7, 9, 11. The pH value was adjusted immediately before adsorption with 0.1M NaOH or 0.1M HCl. The duration of adsorption was taken from the determination of the effect of contact time on adsorption (60 min).

Effect of adsorbent dose on adsorption of MB

To analyze the effect of adsorbent dose on adsorption, adsorbent doses of 0.05 g; 0.10 g; 0.25 g; 0.50 g; 0.75 g; and 1.00 g were used. The duration of adsorption was 1 h. The pH value of the adsorption solutions was not adjusted for the P_{NaOH} sample (pH=6.60), while for the P and P_{HCI} samples the pH value was adjusted to pH=11.

Effect of initial concentration of adsorbate on adsorption of MB

To test the effect of initial adsorbate concentration on the adsorption of MB, adsorbent mass of 0.25 g and 50 cm³ of adsorption solution of the following concentrations were used: 100 mg/dm^3 , 200 mg/ dm³, 300 mg/dm³, 400 mg/dm³, 500 mg/dm³, 600mg/dm³ and 800 mg/dm³. The contact time between the adsorbate and the adsorbent was 60 minutes, at pH=11 for P and P_{HCI} samples, and at pH=6.60 for the P_{NaOH} sample.

Calculations

The adsorption capacity was calculated according to the following equation:

$$q_e = \frac{\left(\gamma_0 - \gamma_1\right) \cdot V}{m} \tag{1}$$

where q_e – the adsorption capacity (mg (residual dye)/g (adsorbent), γ_0 – initial concentration of working dye solution (mg/dm³), γ_1 – the concentration of dye solution after the adsorption treatment (mg/dm³), V – the volume of dye solution used in the experiment (dm³), *m* – adsorbent dose (g).

The efficiency od dye removal was calculated according to the following equation:

% Dye removal =
$$\frac{(\gamma_0 - \gamma_1)}{\gamma_0} \cdot 100$$
 (2)

Adsorption kinetics

The kinetic models, pseudo-first and pseudo-secondorder, are described by nonlinear equations, respectively, in accordance with Tran et al. (2017):

$$q_t = q_e \left(1 - e^{-k_t t} \right) \tag{3}$$

$$q_t = \frac{q_e^2 \cdot k_2 \cdot t}{1 + k_2 \cdot q_e \cdot t} \tag{4}$$

where q_e and q_t (mg/g) are the amounts of dye adsorbed per unit weight of adsorbent at equilibrium and at time t (min), k_1 (1/min) and k_2 (g/mg·min) represent pseudofirst and pseudo-second-order constants.

Adsorption izotherms

For the determination of the constants of the Langmuir isotherm in nonlinear form an equation in accordance with Tran et al. (2017) was used:

$$q_e = \frac{\left(Q_{\max}^0 \cdot K_L \cdot C_e\right)}{\left(1 + K_L \cdot C_e\right)} \tag{5}$$

where q_e (mg/g) is the amount of dye adsorbed per unit weight of adsorbent, C_e (mg/dm³) is the equilibrium concentration of adsorbate solution, K_L (dm³/mg) represents Langmuir isotherm constant and direct measure of adsorption, Q^0_{max} (mg/g) is the maximum amount of dye adsorbed per unit weight of adsorbate at full monolayer coverage.

The analysis of the Langmuir equation can also be achieved through the dimensionless equilibrium parameter R_L represented by the expression according to Tran et al. (2017):

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{6}$$

If the value of $R_L < 1$ adsorption is favorable, the value $R_L > 1$ represents unfavorable adsorption, $R_L = 1$ indicates linear adsorption, while the value $R_L = 0$ indicates irreversible adsorption.

For the determination of constants of the Freundlich isotherm in nonlinear form an equation in accordance with Tran et al. (2017) was used:

$$q_e = K_f \cdot C_e^n \tag{7}$$

where K_f (mg/g)/(mg/L)ⁿ is the parameter related to the binding capacity of the adsorbate, n (dimensionless) is the constant indicating the affinity of the adsorbent for the adsorbate, or the surface heterogeneity of the adsorbent, C_e (mg/dm³) is the adsorbate concentration at equilibrium.

"Solver" in Excel was used to calculate the parameters of kinetic models and adsorption isotherms by the nonlinear method, in accordance with the literature of Tran et al., (2017).

The mathematical function used in this paper, which describes the errors of regression analysis, is a

nonlinear χ -square test (χ^2), calculated by an equation in accordance with Tran et al. (2017):

$$\chi^{2} = \sum_{i=n}^{n} \frac{(q_{e,exs} - q_{e,\text{mod}\,el})^{2}}{q_{e,\text{mod}\,el}}$$
(8)

RESULTS AND DISCUSSION

The obtained results of adsorption experiments are presented graphically and tabularly.

Determination of absorbance maximum

The determination of the maximum absorbance of the methylene blue dye is shown in Figure 1.

Based on the shown results (Figure 1), it can be concluded that the maximum color absorption of methylene blue dye is at 664.21 nm, so all further determinations of dye concentration on the spectrophotometer were performed at this established wavelength.

FTIR analysis

Figure 1 shows numerous absorption peaks, which indicates the complexity of the structure of the tested adsorbents. It can be seen that the greater changes in sawdust structure were caused by modification with HCl treatment (Figure 2b) compared to NaOH treatment (Figure 2a). The wide absorption band that occurs in the P_{HCl} sample in the range of 3400 cm⁻¹ indicates the existence of the bound hydroxyl group, which is found in cellulose and lignin, and which adsorbs water on the sawdust surface. Strong elongation in this sample is also observed in the area

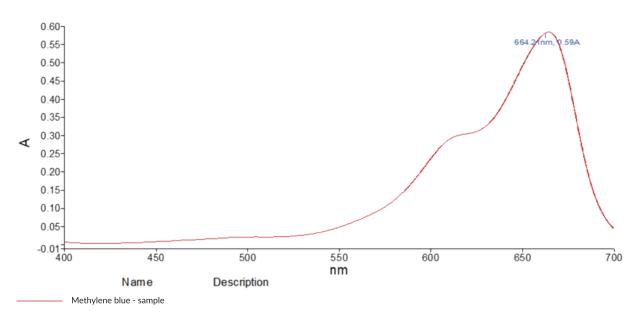


Figure 1. Graphical representation of the maximum absorbance of MB dye

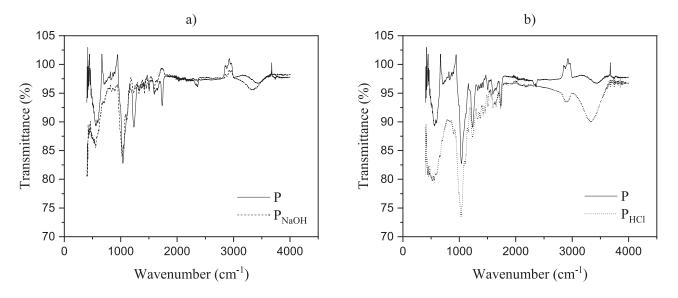


Figure 2. FTIR spectra of sawdust and modified sawdust with NaOH (a) and HCI (b)

of about 1000 cm⁻¹, which indicates C–O stretch that is specific for the lignin component from wood sawdust. Similar stretches were presented by Zou et al. (2013), obtained by treating sawdust with acetic acid.

Effect of contact time on adsorption

The binding time of the aqueous dye solution to the adsorbent has a great influence on the adsorption process (Wanyony & Onyari, 2014). The aim of the experiment is to establish the contact time of the adsorbent and the adsorbate at which the adsorption reaction reaches equilibrium. For this reason, the experiment was performed at different contact times (5 min, 7 min, 10 min, 15 min, 30 min, 45 min, 60 min, and 120 min), and the obtained results of adsorption capacity on sawdust (P) and modified sawdust (P_{NaOH} and P_{HC}) are shown in Figure 3.

The analysis of the obtained results (Figure 3) shows that with increasing contact time, the adsorption capacity and the efficiency of methylene blue dye removal increase, but unevenly for different adsorbents.

The adsorption capacity for a sample of sawdust modified with NaOH (P_{NaOH}) increases rapidly with increasing contact time, which can be attributed to the large amount of available adsorption sites. The rapid increase of the adsorption capacity of the MB dye

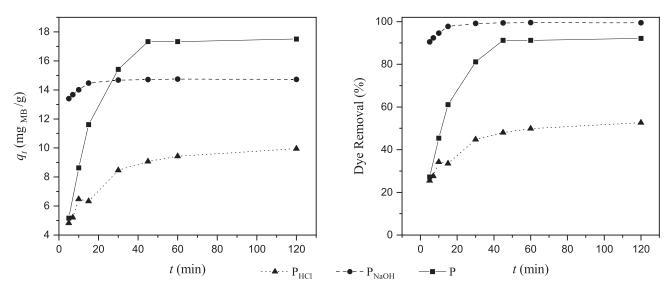


Figure 3. Effect of contact time on the adsorption capacity of MB and removal efficiency of MB dye by the adsorption on unmodified (P) and modified (P_{NaOH} , P_{Hcl}) sawdust (initial concentration of MB γ_0 = 100 mg/dm³, adsorbent dose γ =5 g/dm³, T=20 °C)

takes place within a few minutes due to the adsorption of the dye on the surface of the adsorbent particles, and after only 30 minutes it reaches an equilibrium with a removal efficiency of 99.12%. The difference in adsorption capacity of 5 min contact time (13.40 mg MB/g) and equilibrium capacity at 30 min contact time (14.67 mg MB/g) is very small.

A significantly slower adsorption is observed in samples of unmodified sawdust (P) and modified sawdust with HCI (P_{HCI}). It is seen that the adsorption on unmodified sawdust (P) reaches equilibrium after 45 min, with a dye removal efficiency of 92.23%. The difference in the adsorption capacity of methylene blue at 5 min contact time (5.17 mg MB/g), and the equilibrium capacity at 45 min contact time (17.33 mg MB/g) is significant.

Sawdust modified with HCl (P_{HCl}) reaches equilibrium after 60 min, with a dye removal efficiency of 52.63%. The difference in adsorption capacity after 5 min (4.82 mg MB/g) and equilibrium capacity after 60 min (9.43 mg MB/g) is not as significant as in sample P, but the adsorption capacity is significantly lower.

A review of the literature revealed that a number of authors found different values of the contact time required for the adsorption process to reach equilibrium:

- 85% of the methylene blue dye is removed in 60 minutes, and equilibrium is reached after 90 minutes, with the application of an activated carbon adsorbent (Pathania et al., 2013);
- adsorption of methylene blue dye on two types of adsorbent (red wood and beech wood) takes place quickly at the very beginning and lasts for several minutes (10 min), and after 50 min reaches the saturation point and the reaction slows down (M'hamdi et al., 2017);

- removal of the methylene blue dye on unmodified sawdust *Pinus elliottii* reaches equilibrium after 60 minutes, regardless of different dye concentrations (Bortolouz et al., 2020).

The main reason for achieving different contact times is most likely due to the different type of adsorbent used to remove the methylene blue dye (activated carbon, sawdust from different wood types), but it is evident that the difference in equilibrium is not significant.

For all of the following adsorption experiments, 60 minutes was used as the optimal contact time, due to the uniformity of the experiment.

Adsorption kinetics

To identify the step that determines the rate of the overall process of the adsorption of methylene blue dye on unmodified and modified sawdust, as well as to describe the mechanism according to which adsorption takes place, modeling of experimental data was performed. The most commonly used kinetic models of pseudo-first and pseudo-second-order in nonlinear form were applied to the experimentally obtained values of adsorption capacity. Table 1 presents the obtained parameters of the tested kinetic models in nonlinear form.

Based on the data obtained by modeling using nonlinear kinetic models (Table 1), the best agreement and the highest coefficient of determination are observed in the pseudo-second-order model for both unmodified sawdust P (R^2 =0.9851) and for modified sawdust P_{HCI} (R^2 =0.9876). The obtained results are in agreement with those by many authors who state that the adsorption of methylene blue dye on sawdust is best described by the kinetic model of the pseudo-second-order (Dulman 2009; M'hamdii et al., 2017; Yagub et al., 2014).

Model	Parametar	Parametar value		
		$P_{_{NaOH}}$	P _{HCI}	Р
Pseudo-first-order (PFO)	k ₁ (1/min)	85.73	85.73	85.73
	q _e model (mg∕g)	14.35	7.47	13.28
Parameters calculated from the model	R ²	0.9882	0.6396	0.5149
	X ² test	0.1545	3.7415	10.95
Decude second order (DEC)	k₂ (g/mg·min)	152.6	0.014	0.004
Pseudo-second-order (PSO)	q _e model (mg/g)	14.35	10.38	20.71
Parameters calculated from the model	R ²	0.9882	0.9876	0.9851
	X² test	0.1542	0.1506	0.3524

Table 1. Kinetics parametars for nonlinear modeling ($C_0 = 100 \text{ mg/dm}^3$; adsorbent dose=5 g/dm³, pH =6.60; T= 24.2 °C)

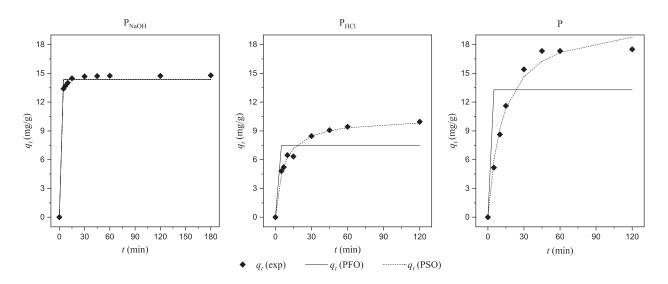


Figure 4. A comparative graphical representation of the adsorption capacities obtained experimentally and using a nonlinear kinetic model

A comparative graphical representation of the adsorption capacities obtained experimentally and using a nonlinear kinetic model of the pseudo-first and pseudo-second-order are shown in Figure 4.

Figure 4 shows that for the sample P_{NaOH} the values of adsorption capacity as well as the coefficients of determination obtained by applying the tested kinetic models in nonlinear form (Table 1) are completely identical. In this case, it is very difficult to determine which kinetic model best describes the examined adsorption, due to the very fast adsorption, in other words due to the very rapid increase in capacity followed by leveling and achieving equilibrium (Simonin, 2016). For a more precise determination of the adsorption rate, it is necessary to perform a series of experiments with a contact time of 1 min to 5 min.

Effect of initial pH of the dye solution on adsorption

The pH value of the dye solution is an important factor in any adsorption process because it can affect the active surface of the adsorbent, as well as the structure of the adsorbate. The change in pH value affects the dissociation of the functional groups of adsorbates and adsorbents (Khattri & Singh, 2009). The influence of pH value on adsorption was examined at the following pH values: 3, 5, 7, 9 and 11, and the obtained results are shown in Figure 5.

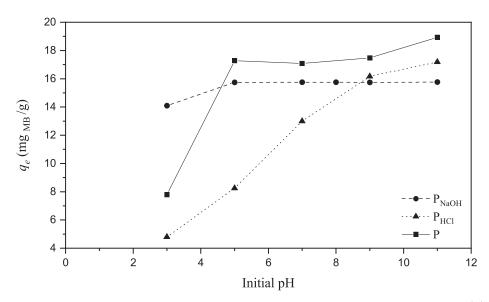


Figure 5. Effect of initial pH of dye solution on adsorption capacity of MB on unmodified (P) and modified ($P_{_{NaOH}}$, $P_{_{HC}}$) sawdust (initial concentration of MB γ_0 =100 mg/dm³, adsorbent dose γ =5 g/dm³, t=60 min, T=20 °C)

Adsorption capacity on unmodified sawdust (P) and modified sawdust with HCl (P_{HCl}) strongly depends on the pH value (Figure 5).

For the P_{HCI} sample, a constant increase in adsorption capacity was spotted, ranging from pH 3 (4.80 mg/g) to pH 9 (16.17 mg/g), to reaching the maximum value of adsorption capacity at pH 11 (17.19 mg/g).

For the P sample, a slightly different dynamics of the adsorption capacity increase was spotted compared to the P_{HCI} sample. From pH 3 (7.78 mg/g) to pH 5 (17.28 mg/g) there is a strong increase in the adsorption capacity, then the adsorption capacity in the range from pH 5 to pH 9 (17.48 mg/g) becomes insensitive to changes in pH, so that the maximum value of the adsorption capacity of the methylene blue dye would be reached at pH 11 (18.93 mg/g). This obtained effect of pH value on the adsorption capacity is in agreement with the authors Afroze et al. (2015); Chikri et al. (2020); Zou et al. (2013).

For the P_{NaOH} sample, a slightly different effect of pH value on the adsorption capacity is spotted in the pH range from pH=3 (14.09 mg MB/g) to pH=5 (15.74 mg MB/g), after which the adsorption capacity is constant and does not change with increasing pH values.

The increase in adsorption capacity with increasing pH values can be explained by the fact that at lower pH values the surface of the adsorbent is surrounded by H^+ ions. Competition between H^+ ions and methylene blue cations leads to prevention of dye adsorption and its fixation at the active sites of the adsorbent. At higher pH values, the concentration of H^+ ions decreases, which results in a good interaction between the dye ions and the active sites of the adsorbent, and ultimately leads to achieving maximum efficiency and adsorption capacity (M'hamdi et al., 2017).

Effect of adsorbent dose on adsorption

The effect of adsorbent dose on the efficiency of adsorbate removal is determined in order to perform the adsorption process as economically as possible, which implies the application of a minimum amount of adsorbent and efficient dye removal (Yagub et al., 2014). The results of the study of the effect of the adsorbent dose on the methylene blue dye removal capacity are presented in Figure 6.

The analysis of the obtained results (Figure 6) shows high values of adsorption capacity even at low adsorbent doses. Using the lowest mass of adsorbent (0.05 g), the adsorption capacity for P_{NaOH} is 64.73 mg/g; for P_{HCI} 47.09 mg/g, while for the sample P it is 36.42 mg/g. As the mass of the adsorbent increases, the adsorption capacity of all tested samples decreases, which is entirely in contrast to the increase in the available surface for adsorption. The reason for such behavior is better saturation of active adsorption sites at lower concentrations of adsorbents. Increasing adsorbent dose, lower yield occurs due to unsaturation of all adsorption sites (EI-Latif et al., 2009).

Equilibrium is reached at a mass of 0.75 g for all tested adsorbents, under the specified conditions.

Effect of initial adsorbate concentration on adsorption

The initial concentration of adsorbates has an important role on adsorption capacity because a constant mass of adsorbents can adsorb only a certain amount of adsorbates (Khattri & Singh, 2009). The effect of initial concentration of MB dye solution on the adsorption capacity on unmodified (P) and modified (P_{NaOH} ; P_{HCI}) sawdust is shown in Figure 7.

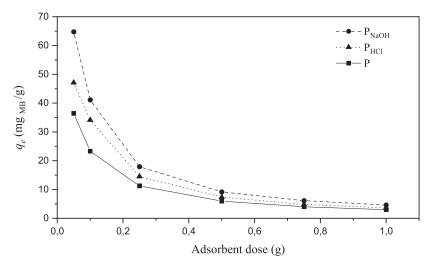


Figure 6. Effect of adsorbent dose on the adsorption capacity of MB on unmodified (P) and modified (P_{NaOH}, P_{HCI}) sawdust (initial concentration od MB γ_0 =100 mg/dm³, t=60 min; pH(P)=6.20; pH(P_{NaOH}, P_{HCI})=11)

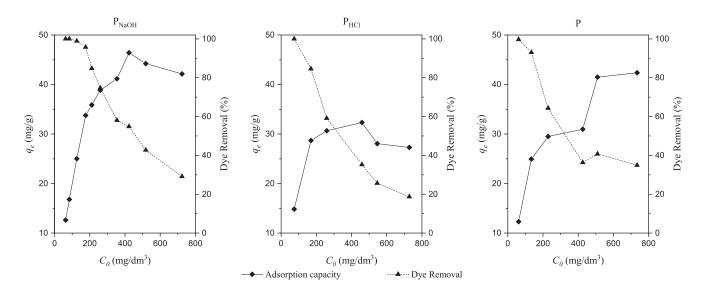


Figure 7. Effect of initial concentration of MB dye solution on adsorption capacity and removal efficiency of MB on unmodified (P) and modified (P_{NaOH}, P_{HCl}) sawdust (Adsorbent dose γ=5 g/dm³, t=60 min; pH(P)=6.20; pH(P_{NaOH}, P_{HCl})=11)

Figure 7 shows that the adsorption capacity increases with increasing initial MB dye concentration for all tested adsorbents.

The obtained dependence curves indicate that the adsorption capacity for the P_{NaOH} sample increases until it reaches its maximum of 46.41 mg/g corresponding to an initial dye concentration of 423.1 mg/dm³, while the equilibrium state is reached at an initial dye concentration of 518.0 mg/dm³, which is in correspondence with the equilibrium adsorption capacity of 44.23 mg/g.

The maximum adsorption capacity for the P_{HCI} sample is 32.34 mg/g corresponding to an initial dye concentration of 459.1 mg/dm³, while the equilibrium state is reached at an initial dye concentration of 545.8 mg/dm³.

For unmodified sawdust (P), the adsorption capacity gradually increases and reaches its maximum of 41.48 mg/g at an initial dye concentration of 509.6 mg/dm³. After reaching the maximum of adsorption, changes in the initial dye concentration have no effect on further increasing of the adsorption capacity due to saturation of the active sites of the adsorbent.

In contrast to the adsorption capacity, the removal efficiency decreases with increasing initial concentration (Figure 7). The lower the initial concentration of the paint solution, the more efficient the removal of MB paint is. After the saturation of the active sites of the adsorbent to which the dye binds, the adsorption decreases regardless of the residual amount of dye (Khattri & Singh, 2009).

In contrast to the adsorption capacity, the removal efficiency decreases with increasing initial concentration

(Figure 7). The lower the initial concentration of the dye solution, the more efficient the removal of MB dye is achieved. After the saturation of the active sites of the adsorbent to which the dye binds, the adsorption decreases regardless of the residual amount of dye (Khattri & Singh, 2009).

Adsorption isotherms

To optimize the removal conditions of methylene blue using unmodified (P) and modified sawdust ($P_{_{NaOH}}$ and $P_{_{HCI}}$), it is necessary to determine the adsorption capacity at different initial concentrations of methylene blue. The most commonly used Langmuir and Freundlich models were applied to the obtained equilibrium data.

Table 2 presents the obtained parameters of adsorption models in nonlinear form.

The values of the coefficient of determination using the Langmuir model for the tested samples P_{NaOH} (R^2 =0.5900) and P (R^2 =0.5463) do not show good agreement with the tested model in nonlinear form. The Q_m^0 values obtained by the nonlinear Langmuir model show lower values than the experimentally obtained ones, and amount to 41.75 mg/g for the P_{NaOH} sample (maximum experimentally obtained change capacity 46.41 mg/g), while the obtained Q_m^0 value for the P sample is 36.69 mg/g (maximum experimentally obtained capacity changes 42.37 mg/g).

The dimensionless parameter R_{l} , for all tested adsorbents is less than 1, which indicates favorable adsorption.

Model	Parametar	Parametar values		
		P _{NaOH}	P _{HCI}	Р
Langmuir	K _L (dm³/mg)	0.887	2.317	1.245
	Q_m^0 (mg/g)	41.75	29.55	36.69
Parametars calculated from model	R ²	0.5900	0.0000	0.5463
	RL	0.02-0.00	0.01-0.00	0.01-0.00
	χ²	1.6747	0.5684	12.839
Freundlich	n	0.087	0.000	0.177
	K _F (mg/g)/(mg/dm³) ⁿ	26.79	29.41	14.75
Parametars calculated from model	R ²	0.6083	0.0000	0.8566
	χ ²	1.1004	0.5755	3.9174

Table 2. Adsorption constants of tested isothermes using nonlinear models Adsorbent dose γ =5 g/dm³, t=60 min; pH(P)=6.20; pH(P_{NaOH}, P_{HCI})=11)

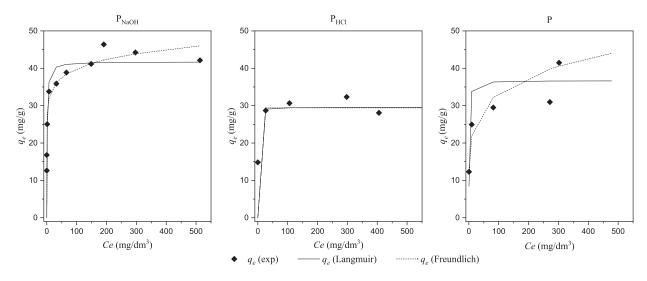


Figure 8. A comparative graphical representation of the adsorption capacities obtained experimentally and using nonlinear adsorption models of Langmuir and Freundlich

Determination coefficient in the Freundlich model is 0.6083 for P_{NaOH} , and 0.8566 for sample P, which indicates that the tested model corresponds much more to the experimentally obtained data. The obtained values of *n* are less than 1 for all tested samples of adsorbents, which indicates that it is a favorable adsorption, as obtained by Langmir's isotherm. The analysis error obtained by the χ^2 test shows lower values for the Freundlich model than for the Langmuir model.

Only for the P_{HCl} sample obtained the value of the Freundlich parameter n=0.000, which in combination with a value of R_{L} very close to 0.0 may indicate that it is an irreversible adsorption (Tran et al., 2017). It is specific for this sample that the determination factors for both tested models R^{2} =0.0000, which indicates that neither of the tested models describes well the adsorption of MB dye on this sample.

Various mechanisms of MB dye adsorption on sawdust have been published in numerous papers. It has been observed in the literature that the adsorption of MB on wood sawdust can be monolayer (a better derethmination coefficient was obtained for the linear Langmuir model according to Dulman et al. (2009) and El-Latif et al. (2009)) or multilayer (a better coefficient of determination was obtained for nonlinear Freundlich model according to Bartolouz et al. (2020)).

From the obtained results of modeling of adsorption isotherms, it can be stated that the adsorption of methylene blue dye on both unmodified (P) and modified sawdust (P_{NaOH}) is a heterogeneous process that is not limited to the monolayer formation.

A comparative graphical representation of the adsorption capacities obtained experimentally and using nonlinear adsorption models of Langmuir and Freundlich are shown in Figure 8.

CONCLUSION

In this paper, the possibility of using modified and unmodified wood sawdust as an adsorbent for the removal of methylene blue dye from aqueous solutions was investigated. Based on the results of this research, the following conclusions can be made:

- The analysis of the effect of contact time on the adsorption showed that adsorption increases with increasing contact time. The equilibrium contact time is different for different adsorbents. For the P_{NaOH} sample, the equilibrium contact time is 30 minutes with 99.12% process efficiency. Slower adsorption is observed with unmodified sawdust (P) which reaches equilibrium after 45 minutes, with 91.23% dye removal efficiency. The contact time required to reach equilibrium for the P_{HCI} sample is the longest time of 60 min, achieving 49.86% process efficiency.
- Based on the data obtained by modeling using nonlinear kinetic models, the best agreement and the highest coefficient of determination are discovered in the pseudo-second-order model for both unmodified sawdust (R^2 =0.9851) and modified sawdust P_{NaOH} (R^2 =0.9882) and P_{HCI} (R^2 =0.9876).
- The obtained results also show a significant influence of the pH value of the solution on the adsorption of the methylene blue dye. For modified P_{NaOH} sawdust, 100% dye removal efficiency is achieved at pH=5, while unmodified sawdust (P) and modified P_{HCI} sawdust require more alkaline conditions and only at pH=11 the greatest achieved efficiency is over 99.5%.
- The analysis of the effect of adsorbent dose on adsorption showed that the efficiency of dye removal decreases with increasing the dose of adsorbents. Using the lowest adsorbent concentration (1 g/ dm³), and a dye concentration of 100 mg/dm³, the adsorption capacity for P_{NaOH} is 64.73 mg/g; for P_{HCI} 47.09 mg/g, while for sample P it is 36.42 mg/g.
- The values of the coefficient of determination using Freundlich's model for the samples of unmodified (P) and modified sawdust (P_{NaOH}) indicate that the adsorption of the methylene blue dye is multilayer. For the P_{HCI} sample, neither the Langmuir nor the Freundlich model adequately described MB dye adsorption.

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Uklanjanje boje metilensko plavo adsorpcijom na nemodifikovanoj i modifikovanoj drvnoj piljevini

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Ključne riječi: drvna piljevina, metilen plavo, adsorpcioni eksperimenti. Tekstilna industrija predstavlja najstabilniju privrednu granu i glavni nosilac ekonomskog razvoja mnogih zemalja u razvoju. Tokom proizvodnog procesa koristi veliku količinu sintetičkih boja različitog sastava. 10–50 % od početne koncentracije boje završava u otpadnim vodama, koje postaju intenzivno obojene. Prije nego što se ispuste u komunalni ili u centralni industrijski kanalizacioni sistem, otpadne vode prolaze kroz postupke: predtretmana, primarne obrade, sekundarne obrade i završne obrade (obrada mulja i njegovo odlaganje). Adsorpcija, kao laka i efikasna tehnika se široko koristi za uklanjanje velikog broja boja iz vodenih rastvora. Aktivni ugalj je najpoželjniji adsorbent, ali je zbog visoke cijene, njegova upotreba ograničena. Dokazivanje mogućnosti izvođenja efikasne adsorpcije na jeftinim adsorbensima je veliki izazov i predmet naučnog interesovanja već nekoliko decenija.

U ovom radu za uklanjanje boje metilen plavo koristi se nemodifikovana (P) i modifikovana piljevina dobijena na dva načina (obradom sa HCl i obradom sa NaOH) i označena P_{HCl} i P_{NaOH}. Adsorpcionim eksperimentima ustanovljeno je da je optimalno vrijeme za adsorpciju različito, i iznosi za uzorak P_{NaOH} – 30 min, za uzorak P – 45 min, a za uzorak P_{HCl} – 60 min. Primjenom nelinearnih kinetičkih modela na eksperimentalno dobijene podatke ustanovljeno je da se najbolje slaganje uočava kod modela pseudo-drugog reda.

Ispitivanjem zavisnosti adsorpcije od pH vrijednosti dobijeni su različiti rezultati. Za uzorke P i P_{HCI} optimalna pH vrijednost je pH=11, dok je uzorak P_{NaOH} efikasan u širem opsegu pH vrijednosti).

Analizom zavisnosti adsorpcije od doze adsorbenata utvrđeno je da se efikasnost uklanjanja boje smanjuje sa povećanjem mase adsorbenata.

Dobijene vrijednosti koeficijenta determinacije kod Freundlich-ovog modela za uzorke nemodifikovane (P) i modifikovane piljevine (P_{NaOH}) ukazuju da je adsorpcija boje metilen plavo višeslojna. Za uzorak P_{HCI} ni Langmuir-ov ni Freundlich-ov model ne opisuje adekvatno adsorpciju boje MB.