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Scientific paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.5937/zasmat2301065D

Zastita Materijala 64 (1)
65 - 77 (2023)

Removal of bemacid red dye by adsorption on sawdust and carbonized sawdust

ABSTRACT

Today, huge amounts of coloured wastewater, released into ecosystems are a big problem, because they have harmful effects on humans, the environment, as well as the aquatic environment. One of the common treatments for removing dyes from wastewater is the adsorption process, with an emphasis on the use of cheap adsorbents. Therefore, the subject of this paper is the possibility of removing the anionic dye bemacid red (BR) on wood biomass sawdust and carbonized sawdust. The experiments examined the equilibrium contact time, the effect of initial pH, the effect of adsorbent dose, as well as the effect of the initial adsorbate concentration on the process of adsorption. By applying linear kinetic models, it was found that the adsorption process follows a pseudo-second-order kinetic model. It was found that pH does not have a significant effect on adsorption onto carbonized sawdust. By examining the effect of the initial adsorbent dose, it was found that optimal adsorption requires twice the mass of sawdust compared to carbonized sawdust. The use of linear adsorption isotherms shows better agreement with the Freundlich model for both adsorbents. The maximum adsorption capacity for sawdust is 30.18 mg/kg, while for carbonized sawdust it is 74.60 mg/kg. Use of sawdust and carbonized sawdust can be an effective adsorbent for removing the dye bemacid red from wastewater, which is confirmed by the experiment on a real sample of wastewater. The obtained efficiency of dye removal from real wastewater for sawdust is 42.9 %, and for carbonized sawdust 95.1 %.

Keywords: *Bemacid red, adsorption, wood sawdust, carbonized sawdust*

1. INTRODUCTION

A large proportion of industrial waste is effluents, loaded with various agents, which can cause environmental pollution. Dyes are a big problem in industrial wastewater. Due to a large number of produced products, the textile industry is one of the main users of dyes in the world – it uses two-thirds of the total world production of industrial dyes [1]. Coloured waters reduce the breakthrough of light and thus block photosynthesis in aquatic plants. In addition, synthetic dyes are hardly biodegradable compounds, and many of them are toxic, mutagenic and carcinogenic [2].

Therefore, researchers around the world have focused on removing dye from wastewater by various treatments: coagulation/flocculation, electrocoagulation, advanced oxidation processes, ion exchange, adsorption, sequencing batch reactors (SBR), membrane bioreactors (MBR), moving bed biofilm reactors (MBBR), and constructed wetlands (CW). All these purification processes have advantages, but also disadvantages such as high costs, secondary generation of pollutants, and very often inefficient removal of different types of dyes [3].

The adsorption technique, for removing dyes from wastewater, is relevant to researchers because of its simplicity, and the possibility of using different adsorbents. Activated carbon is one of the oldest and most widely used adsorbents, which is usually obtained from coal, but it is very expensive [4]. Therefore, various waste products from industry and agriculture, natural materials and bio sorbents are tested as potentially economical alternative adsorbents, because they require little processing, are easily available and are in abundance [5]. The adsorption technique using biomass has emerged as an alternative that has been widely studied because of its simplicity, and

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Paper received: 11. 07. 2022.
Paper corrected: 06. 09. 2022.
Paper accepted: 12. 09. 2022.
Paper is available on the website: www.idk.org.rs/journal

low cost. Natural adsorbents such as wood sawdust, garlic peel, rice husk, peel of various fruits, dates, cotton, seeds, and coffee husks, were used to remove various dyes from wastewater [6].

Numerous studies have shown the possibility of using sawdust, as an abundant by-product of the wood processing industry with a negligible price, to remove dye from wastewater. The main reason for the use of wood sawdust in adsorption processes for dye removal is the fact that this material basically consists of cellulose, hemicellulose and lignin. The importance of these compounds in the structure of adsorbents is so great that many researchers suggest their isolation before removing unwanted substances from water [1]. The sawdust in its structure contains numerous functional groups (carboxylic, hydroxyl, phenolic and amide) which are suitable for the adsorption of a large number of dyes. For a more efficient adsorption process, sawdust can be modified by different chemical treatments (with acids and alkalis) [7] or physical treatment (carbonization). The purpose of carbonization is to eliminate volatile substances from the raw material at relatively low temperatures (400 °C to 700 °C), which ultimately gives a product with a higher content of fixed carbon, and thus a greater specific surface area [5].

The rate and efficiency of dye biosorption are affected by different process parameters, so it is necessary to optimize the parameters for effective dye degradation, which include contact time, initial pH of the solution, temperature, dye concentration, and biomass concentration [8].

Synthetic anionic azo dye bemacid red (BR), meant for dyeing textiles of polyamide nature, was used for the performed experiments in this research. It is characterized by a high level of resistance to light, good migration power, and fast depletion even at low temperatures [9].

The aim of this research was to investigate the possibility of using wood and carbonized sawdust (beech+linden) from the territory of B&H, as an adsorbent, to remove the synthetic dye bemacid red from aqueous solutions. The obtained optimal adsorption conditions, both for wood sawdust and for carbonized sawdust, were applied to real wastewater, obtained after dyeing polyamide fabric with bemacid red dye.

Since there are no similar published works in our surroundings, it can be said that this is a pioneering work in this field.

2. EXPERIMENTAL PART

A mixture of beech and linden wood sawdust, obtained from the wood processing industry, was used as an adsorbent. These two adsorbents were prepared for adsorption experiments as follows: dried sawdust (obtained by drying in an oven at 105 °C for 8 h) and carbonized sawdust (obtained by annealing dried sawdust in an oven at 800 °C for 30 min, in the absence of oxygen).

The anionic synthetic dye bemacid red (BR) was used as the adsorbate. After drying at 105 °C and dissolving in distilled water, a basic BR dye solution with a concentration of 1 g/dm^3 was prepared. A working dye solution with concentration of 100 mg/dm^3 was prepared from the stock solution, and this concentration was used in adsorption experiments.

2.1. Characterization of the adsorbent

The characteristics of the adsorbent were examined by:

- FTIR analysis (Bruker, Tensor 27) in the wavelength region from 400 cm^{-1} to 4000 cm^{-1}.
- Determination of point of zero charge (pH_{zpc})

For the determination of pH_{zpc}, according to [4], 0.01 mol/dm^3 NaCl solution was used. In eight separate plastic test tubes, 25 cm^3 of NaCl solution was added, and the pH values were adjusted to 3; 4; 5; 6; 7; 8; 9; 10; 11 with the addition of 0.1 mol/dm^3 solution of HCl or NaOH. The adjusted pH represents the initial pH value (pH_i). After adding 0.1 g of adsorbent, the test tubes were closed and placed on the orbital shaker (Laboratory Instruments WiseShake SHO-2D witeg, Germani). Mixing was carried out at room temperature for 48 hours. After mixing the samples were filtered and the final pH was measured in the filtered samples (pH_f). The diagram of pHi versus ΔpH (pH_f-pH_i) has been plotted and the obtained cross-section on the x-axes represents the pH value at which the surface charge of the adsorbent is equal to 0 (pH_{zpc}).

2.2. Adsorption experiments

All adsorption experiments were performed at room temperature and atmospheric pressure with constant stirring on a magnetic stirrer, at an adsorbent dose of 5 g/dm^3. Separation of the solid and liquid phases was performed by membrane filtration (Sartorius, Membranfilter, Germany), through filter paper with a pore size of 0.45 μm. The concentration of dye residue in the solution was measured on a UV/VIS spectrophotometer (Perkin Elmer Lambda 25) at 504.9 nm. The efficiency of dye removal by adsorption on sawdust and carbonized sawdust was monitored by examining the effect of the contact time, the initial pH value of the adsorbate, the initial dose of the adsorbent, and the initial concentration of the adsorbate.

2.1.1. Effect of contact time on adsorption of BR

For determination of optimal contact time for adsorption, dye solution with a concentration of 100 mg/dm^3 and with an initial pH value (pH 6.06) was used. The examined contact times of the adsorbent and the adsorbate were: 5 min, 10 min, 15 min, 30 min, 45 min, 1 h and 3 h.

2.1.2. Effect of initial pH value on adsorption of BR

Examining the effect of the initial pH value on adsorption of BR dye required adjusting the pH of the dye solution, immediately before performing the experiment, by adding 0.1 M HCl or 0.1 M NaOH to the tested pH values: 3, 5, 7, 9, 11. The contact time used in this experiment was 1 h.

2.1.3. Effect of adsorbent dose on adsorption of BR

Table 1 shows the experimental conditions during the examination of the effect of the adsorbent dose.

Table 1. The experimental conditions during the examination of the effect of the adsorbent dose

Tabela 1. Uslovi ispitivanja zavisnosti adsorpcije boje BR od početne mase adsorbata

Experimental conditions	Adsorbents	
	Sawdust	Carbonized sawdust
Adsorbent dose (g/dm^3)	5; 10; 20; 25; 30; 35	2; 5; 10; 15; 20
Adsorbate volume (cm^3)	50	50
Adsorbate concentration (100 mg/dm^3)	100	100
pH value	3	6
Temperature (°C)	28.3	28.3
Contact time (min)	60	60

2.1.4. Effect of initial adsorbate concentration on adsorption of BR

The conditions for performing the experiment with sawdust as an adsorbent are: adsorbent dose 5 g/dm^3; contact time 60 min; pH 3; at different initial dye concentrations (25 mg/dm^3; 50 mg/dm^3; 75 mg/dm^3; 100 mg/dm^3; 200 mg/dm^3; 300 mg/dm^3; 500 mg/dm^3; 750 mg/dm^3; 1000 mg/dm^3).

The conditions for performing the experiment with carbonized sawdust as an adsorbent are: adsorbent dose 5 g/dm^3; contact time 120 min; pH 6; at different initial dye concentrations (25 mg/dm^3; 75 mg/dm^3; 100 mg/dm^3; 200 mg/dm^3; 500 mg/dm^3; 1000 mg/dm^3).

2.1.5. Simulations of real conditions

The dyeing process was performed at the solid:liquid ratio of 1:60 (5 g of fabric : 300 cm^3 of water). The dyeing process was performed according to the standard acid dyeing procedure as follows: about 200 cm^3 of distilled water was added to a 400 cm^3 beaker, followed by 1.8 g $(NH_4)_2SO_4$, and 0.2 cm^3 of 80% CH_3COOH (to adjust the pH to 5-6). The total volume of the fleet was adjusted to 300 cm^3 with distilled water. The prepared fleet was heated to 40 °C and then a polyamide fabric sample (5 g) was added and processed in the fleet for 15 min. Then 5 cm^3 of dye solution with a concentration of 5 g/dm^3 was added. The dyeing process of the polyamide fabric lasted 5 min at 40° C, and then the dyeing process was continued at the boiling temperature for another 30 min. The dyed sample was washed with cold water and left to dry.

The residual fleet after the dyeing process was used as an adsorbate in the adsorption process under the following conditions: adsorbate dose (sawdust and carbonized sawdust) 5 g/dm^3, contact time 1 h, adsorbate pH value: for adsorption on sawdust – pH 3 (T=26.2 °C), for adsorption on carbonized sawdust – without pH adjustment (pH 5.40 at T=24.3 °C).

2.1.6. Calculations

The adsorption capacity was calculated according to the following equation:

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

where q_e is adsorption capacity (mg/g), V is the volume of dye solution used in the experiment (dm^3), γ_0 is initial adsorbate concentration (mg/dm^3), γ_1 is adsorbate concentration after adsorption (mg/dm^3), m is adsorbate dose (g).

The efficiency of dye removal was calculated according to:

$$\text{Removal efficiency (\%)} = \frac{(\gamma_0 - \gamma_1)}{\gamma_0}\cdot 100 \qquad (2)$$

2.1.7. Adsorption kinetics

Kinetic models of pseudo-first-order (PFO), pseudo-second-order (PSO) and Elovich, are described by following linear equations, respectively, according to the literature [10]:

$$\ln(q_e - q_t) = -k_1 \cdot t + \ln(q_e) \qquad (3)$$

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

$$q_t = \frac{1}{\beta}\ln(t) + \frac{1}{\beta}\ln(\alpha\beta) \qquad (5)$$

where q_e and q_t (mg/g) are the amounts of dye substance adsorbed unit weight of adsorbent at equilibrium and at the time t (min), k_1 (1/min) and k_2 (g/mg·min) are PFO and PSO constants, α is initial rate of adsorption (mg/(g min)) and β is desorption constant (mg/g).

2.1.8. Adsorption isotherms

Langmuir adsorption model is described by the following linear equation, in accordance with the literature [10]:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^0_{\max}}\right) C_e + \frac{1}{Q^0_{\max} \cdot K_L} \qquad (6)$$

where q_e is the amount of adsorbed BR dye at equilibrium (mg/g), Q^0_{max} is the maximum amount of BR adsorbed per unit weight of adsorbate at full monolayer coverage (mg/g), K_L is Langmuir constant (dm^3/mg) and C_e is the equilibrium concentration of BR (mg/dm^3).

The separation factor, R_L, is calculated based on the Langmuir dependency graph:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \qquad (7)$$

where R_L is value that determines the type of adsorption, C_0 (mg/dm^3) is initial concentration of adsorbate. It is an irreversible process of adsorption when the value of R_L=0. When the values are 0<R_L<1, adsorption is favourable, while at values of R_L>1, adsorption process is unfavourable.

The linear form of the Freundlich isotherm is shown by the following equation in accordance with the literature [10]:

$$\log q_e = n \log C_e + \log K_f \qquad (8)$$

where q_e (mg/g) is amount of adsorbed substance, C_e (mg/dm^3) is equilibrium concentration of adsorbate in solution, K_f is the parameter related to adsorbate binding capacity, and n is constant indicating the affinity of the adsorbent towards the adsorbate, or the surface heterogeneity of the adsorbent.

3. RESULTS AND DISCUSSION

3.1. Characterization of the adsorbent

The characteristics of the adsorbents were determined by FTIR analysis and by determination of point of zero charge (pH_{zpc}).

3.1.1. FTIR analysis

The results of FTIR analysis for tested adsorbents are shown in Figure 1.

Figure 1 shows completely different FTIR spectra for sawdust and carbonized sawdust, which indicates that the structure of sawdust is completely changed after its physical activation. A great similarity, in contrast, can be seen between the FTIR spectra of carbonized sawdust and commercial activated carbon powder.

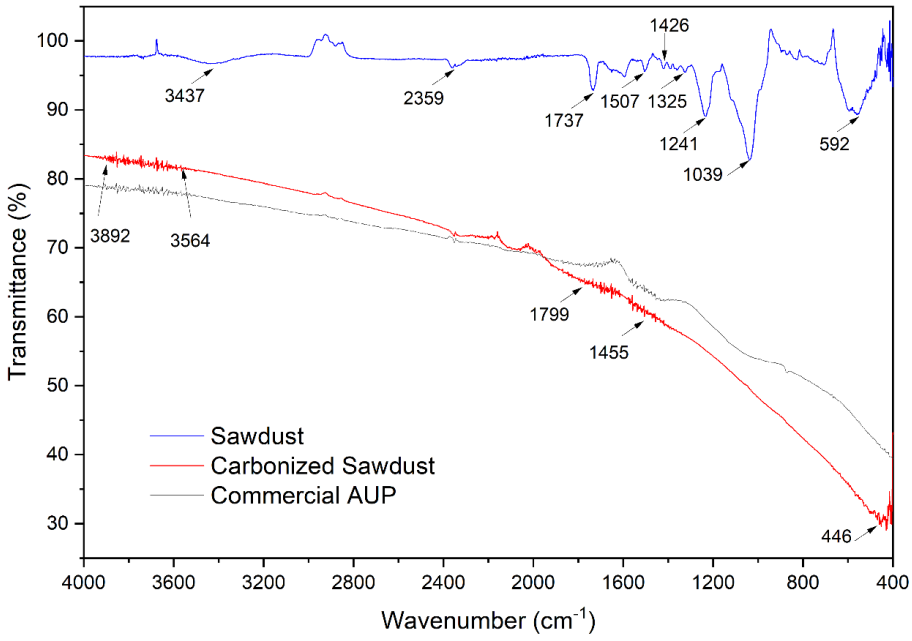

Figure 1. FTIR spectra of sawdust, carbonized sawdust and commercial activated carbon powder

Slika 1. FTIR spektar piljevine, karbonizovane piljevine i komercijalnog aktivnog uglja u prahu

The FTIR spectra of sawdust shows the presence of functional groups that are characteristic for macromolecules present in wood (cellulose, hemicellulose and lignin).

Minor peaks that occur in the region of 3437 cm^{-1} refere to the stretching of aromatic and aliphatic O–H groups present in the primary components of wood: cellulose, hemicellulose and lignin [2]. The quite larger band that occures at 1737 cm^{-1} is due to the presence of C=O groups from hemicellulose. Peaks in the area from 1650 cm^{-1} to 1507 cm^{-1} refer to the stretching of C=C aromatic group in the structure of lignin [1, 2]. In the area from 1426 cm^{-1} to 1325 cm^{-1} angular deformation of –CH group originating from cellulose and hemicellulose can be observed. The band at 1241 cm^{-1} is in association with stretching of C–O from methoxy groups from lignin, and the band at 1039 cm^{-1} is due to stretching of C–O groups from cellulose. Smaller peaks that appear in the region around 800 cm^{-1} are related to the deformations of the –CH groups substituted in the aromatic ring. Bands in the region of 592 cm^{-1} are the result of deformation of C–C bonds in the aromatic ring [1].

Physical activation of sawdust removes volatile substances from sawdust, and increases the content of fixed carbon [5]. The FTIR spectra of carbonized sawdust do not show particularly expressive bands, but some stretching that originate from functional groups containing oxygen, such as hydroxyl groups (at 3892 cm^{-1} to 3564 cm^{-1}), and carboxyl groups (at 1799 cm^{-1} to 1455 cm^{-1}) can be observed, but without dominant peaks.

3.1.2. Determination of point of zero charge (pH_{zpc}).

Determination of point of zero charge was carried out in the wide range of pH values: 3; 4; 5; 6; 7; 8; 9; 10; 11. The results for pH_{zpc} are shown in Figure 2.

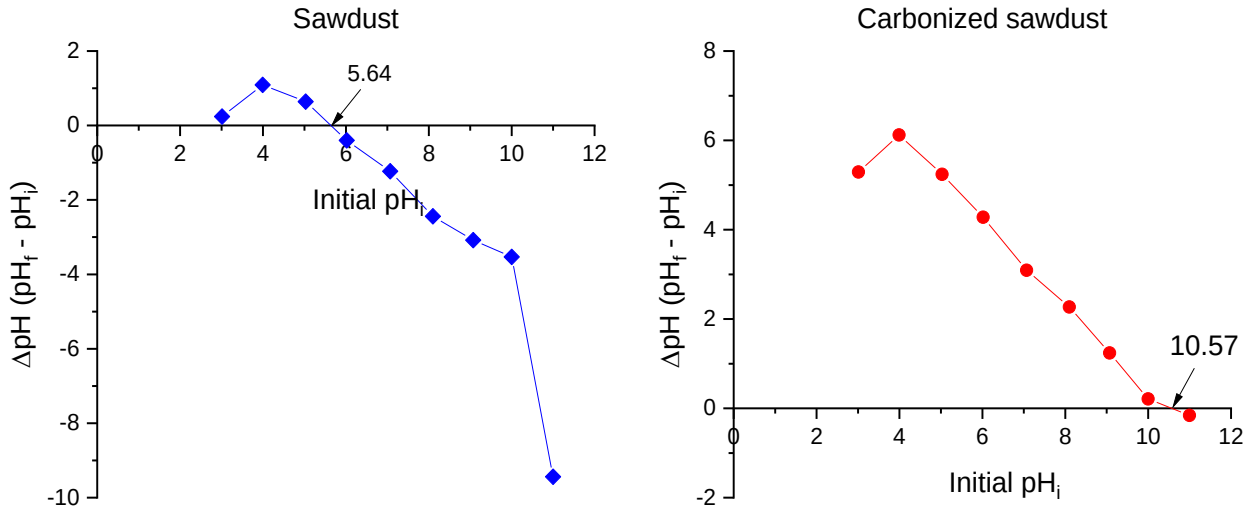

Figure 2. Point of zero charge (pH_{zpc}) for sawdust and carbonized sawdust

Slika 2. Tačka nultog naelektrisanja (pH_{zpc})za piljevinu i karbonizovanu piljevinu

The obtained results (Figure 2) show that at pH value of 5.64, the surface charge of sawdust is equal to 0. This means that the surface of the sawdust at pH < pH_{zpc} is positively charged, and that in a narrow range of pH values (from 3 to 5.64) it can adsorb anionic dyes. Carbonized sawdust at pH value of 10.57 shows a point of zero charge, which means that its surface is positively charged and favorable for anionic dye adsorption in a significantly larger pH range (from 3 to 10.57). The surfaces of adsorbents at pH values above pH_{zpc} are negatively charged, and therefore unfavorable for anion adsorption.

3.2. Effect of contact time on adsorption

Determining the contact time required to reach equilibrium is the first step in the investigation of adsorption processes. Effect of contact time on adsorption process of BR dye, for sawdust and carbonized sawdust, is shown in Figure 3.

Based on the obtained results (Figure 3), it can be observed that the adsorption of dye on sawdust initially increases with contact time, and the equilibrium was reached at contact time of 60 min. Accordingly, the adsorption time in all subsequent experiments, with sawdust as adsorbent, was 60 min.

Adsorption of dye on carbonized sawdust required a slightly longer contact time (about 120 min) to reach an equilibrium state.

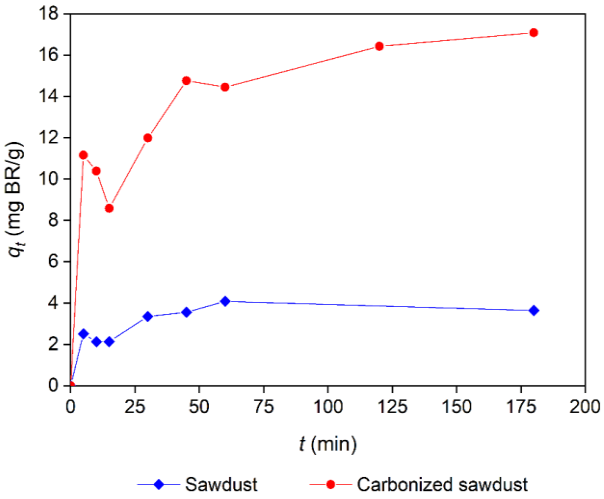

Figure 3. Effect of contact time (t) on adsorption capacity of BR dye (q_t) (γ_{dye}=100 mg/dm^3, $\gamma_{adsorbent}$=5 g/dm^3, pH=6.06, T=24.2 °C)

Slika 3. Zavisnost kapaciteta adsorpcije boje BR, q_t, od kontaktnog vremena, t (γ_{boje}=100 mg/dm^3, $\gamma_{adsorbenta}$=5 g/dm^3, pH=6,06, T=24,2 °C)

The obtained different equilibrium contacts times for the removal of BR dye from aqueous solutions depend on both, the nature of the adsorbent and the adsorbate, which is shown in Table 2.

Table 2. Literature review of equilibrium contact time for azo dyes and low-cost adsorbents

Tabela 2. Literaturni pregled ravnotežnog vremena kontakta azo boja i jeftinih adsorbenasa

Adsorbate (azo dyes)	Low cost adsorbent	Contact time	Ref.
Bemacid red	Date activated charcoal	60 min	[9]
Bemacid red	Washed Grape Winery Waste	60 min	[11]
Bemacid red	TiO_2	30 min	[12]
Bemacid red	Modified fly ash	60 min	[12]
Acid Yellow 29	Modified sawdust	30 min	[13]
Allura red	Wood sawdust and modified sawdust	20 min	[14]

There are three time periods that are characteristic for adsorption processes [5]. In the first period, the adsorption process is very fast, and the adsorption capacity is higher due to the high availability of active sites on the adsorbent. In the second period, the adsorption rate decreases due to the occupancy of active sites. Finally, the adsorption process reaches the saturation stage, when the adsorbate is no longer removed, due to the lack of active sites on the adsorbent. Some authors point out that rapid adsorption takes place on the surface of the adsorbent, followed by diffusion and adsorption on the inner surface of the adsorbent [14]. The mentioned periods are also visible on the Figure 3,

The reason for achieving different contact times should most probably be a consequence of the pore size of the used adsorbents. An adsorbent with a larger pore diameter allows faster migration of molecules, more precisely faster adsorption, but also faster desorption, and usually has a longer equilibrium contact time [15].

3.2.1. Adsorption kinetics

The determination of the contact time allows obtaining key information about the adsorption rate of the BR dye on the tested adsorbents. Based on the obtained data, it is possible to establish which mechanism the given adsorption process takes place. The most commonly used pseudo-first-order, pseudo-second-order kinetic models and the Elovich model in linear form were applied to the experimentally obtained adsorption capacity values. Table 3 presents the obtained parameters of the investigated kinetic models in linear form.

Based on the data obtained using linear kinetic models, the best agreement and the highest coefficient of determination were obtained using the pseudo-second-order kinetic model for both tested adsorbents. The obtained coefficients of determination for the tested adsorbents are quite high: for sawdust R^2=0.9932, and for carbonized sawdust R^2=0.9927. A high value of the coefficient of determination is not the only indicator of good agreement with the pseudo-second-order model. A good agreement with this model is also confirmed by comparing the values of the adsorption capacity obtained experimentally (q_e *exp.*) with values calculated from the kinetic model (q_e *model*). In the experiment with sawdust, the highest obtained adsorption capacity is 4.082 mg/g, while according to the pseudo-second-order model, the highest adsorption capacity is 3.754 mg/g. It is similar with carbonized sawdust, the highest experimentally obtained adsorption capacity is 17.09 mg/g, and the adsorption capacity calculated from the model is 17.58 mg/g.

Table 3. Parameters of investigated kinetic models in linear form (γ_0=100 mg/dm^3, adsorbent dose = 5 g/dm^3, pH = 6.06, T= 24.2 °C)

Tabela 3. Parametri ispitivanih kinetičkih modela u linearnom obliku (γ_0=100 mg/dm^3, koncentracija adsorbenta = 5 g/dm^3, pH = 6.06, T= 24.2 °C)

Model	Parameter	Parameter values	
		Sawdust	Carbonized sawdust
Pseudo-first-order	k_1 (1/min)	0.012	0.034
Parameters calculated from the model	R^2	0.1778	0.9272
	q_e model (mg/g)	1.23	13.10
	$q_e$exp.(mg/g)	4.08	17.09
Pseudo-second-order	k_2 (g/mg·min)	0.075	0.007
Parameters calculated from the model	R^2	0.9932	0.9927
	q_e model (mg/g)	3.75	17.57
	$q_e$exp(mg/g)	4.08	17.09
Elovich	α (mg/g·h)	1.547	6.781
	β (mg/g)	1.358	0.337
Parameters calculated from the model	R^2	0.8300	0.8694

Based on the data obtained using linear kinetic models, the best agreement and the highest coefficient of determination were obtained using the pseudo-second-order kinetic model for both tested adsorbents. The obtained coefficients of determination for the tested adsorbents are quite high: for sawdust R^2=0.9932, and for carbonized sawdust R^2=0.9927. A high value of the coefficient of determination is not the only indicator of good agreement with the pseudo-second-order model. A good agreement with this model is also confirmed by comparing the values of the adsorption capacity obtained experimentally (q_e *exp.*) with values calculated from the kinetic model (q_e *model*). In the experiment with sawdust, the highest obtained adsorption capacity is 4.082 mg/g, while according to the pseudo-second-order model, the highest adsorption capacity is 3.754 mg/g. It is similar with carbonized sawdust, the highest experimentally obtained adsorption capacity is 17.09 mg/g, and the adsorption capacity calculated from the model is 17.58 mg/g.

Modelling of the experimentally obtained data for adsorption capacities with the pseudo-first-order kinetic model did not give satisfactory values (Table 2), although the determination coefficient of the pseudo-first-order kinetic model for carbonized sawdust is quite high (R^2=0.9272). The mechanism of BR dye adsorption on investigated adsorbents is not well described with Elovich model, which is shown in Figure 4.

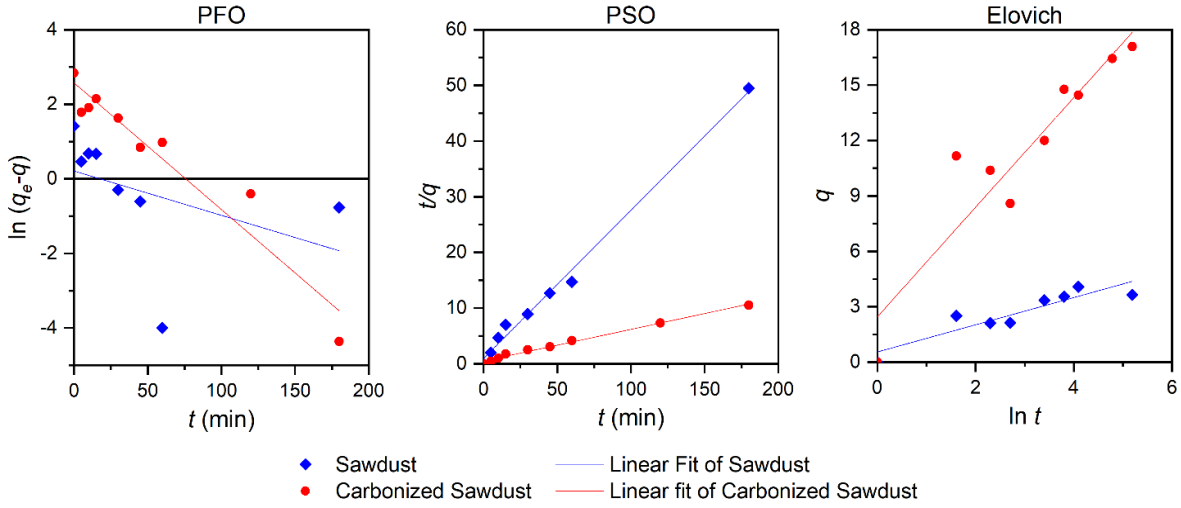

Figure 4. Graphic representation of the investigated kinetic models in linear form for sawdust and carbonized sawdust

Slika 4. Grafički prikaz ispitivanih kinetičkih modela u linearnom obliku za piljevinu i karbonizovanu piljevinu

Adsorption of BR dye on wood sawdust pre-treated with NaOH revealed a better agreement between the experimental data and the kinetic model of PSO [2].

According to Boudia et al. [9] it was found that the adsorption kinetics of BR dye on date activated carbon also follows a pseudo-second-order model.

In the column adsorption of Basic Red 2 (BR2) on activated carbon, it was found that there is no agreement between the experimental adsorption capacity (q_{exp}) and the adsorption capacity (q_1) obtained from the pseudo-first-order model. On the contrary, there is quite good agreement between the experimental (q_{exp}) and theoretical adsorption capacities (q_2) with the pseudo-second-order model [16].

3.3. Effect of pH on the adsorption capacity

Variations in the pH value affect the reactions between the dye molecules, but also change the surface charge of the adsorbent. In general, low or high pH value favours the adsorption of anionic or cationic dyes [17]. Therefore, the effect of different pH values on adsorption capacity was examined in this paper. Investigated initial pH values of dye solution were: 3, 5, 7, 9 and 11, and the obtained result of pH impact on adsorption capacity are shown in Figure 5.

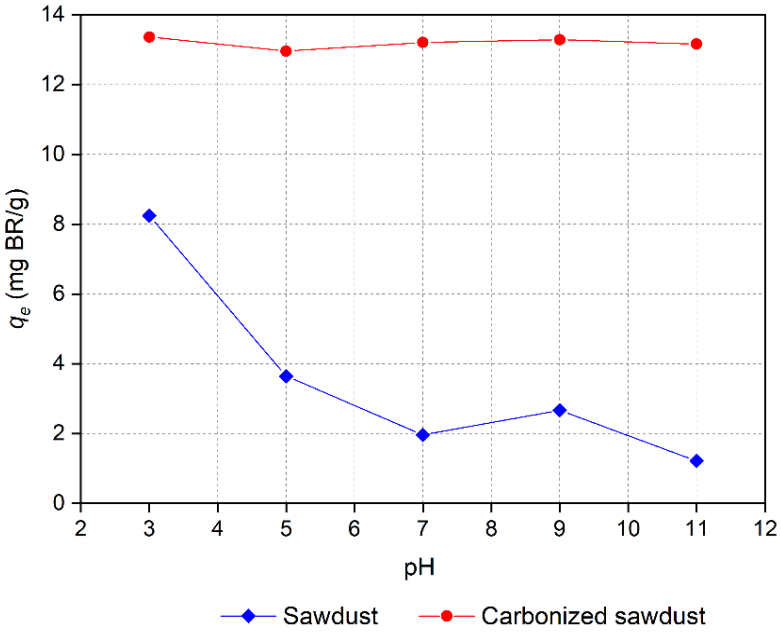

Figure 5. Effect of pH value on adsorption capacity of BR dye on sawdust and carbonized sawdust (γ_{dye}=100 mg/dm^3, $\gamma_{adsorbent}$=5 g/dm^3, T=24.2 °C)

Slika 5. Zavisnost kapaciteta adsorpcije boje BR od pH vrijednosti za piljevinu i karbonizovanu piljevinu (γ_{boje}=100 mg/dm^3, $\gamma_{adsorbenta}$=5 g/dm^3, T=24.2 °C)

Figure 5 shows that the pH value of the adsorbate has a different effect on the BR dye removal capacity on the tested adsorbents. Adsorption on sawdust shows a great dependence on the pH value. The highest value of the adsorption capacity is achieved in the acidic solution, at pH=3 (8.25 mg/kg). As the pH value increases, the adsorption capacity on sawdust decreases significantly, and at an initial pH of 11 has value of 1.22 mg/kg. The obtained results are in agreement with the results obtained by determining pH_{zpc} (Figure 2). The removal of BR dye by adsorption on sawdust in an acidic medium is explained by the presence of carboxylic and phenolic groups present on the surface of the adsorbent. The surface of the adsorbent (sawdust) is positively charged and attracts negatively charged dye particles. Therefore, the maximum adsorption of anionic dyes on the cellulose material is achieved at a pH value of 3-4 [4,18,19]. The maximum adsorption of BR dye of 98.9% on lignocellulosic material (brewery waste) was achieved at a pH value of 2 [8]. This statement also indicates the mechanism of adsorption of bemacid red dye on sawdust, which is the ion exchange mechanism. In order to prove it experimentally, it is necessary to regenerate the adsorbent, and then repeat the adsorption on the regenerated adsorbent.

However, in the case of adsorption on carbonized sawdust, the pH value has no great influence on the adsorption capacity, which remains constant at all tested pH values (about 13.2 mg/kg). Carbonized sawdust has pH_{zpc} at pH 10.57 (Figure 2) so its surface is positively charged in the entire range of examined pH values that show the effect of pH on adsorption process (3 to 11), which favors the binding of the anionic dye, so the adsorption capacity remains approximately constant.

The process of dye adsorption on activated carbon is associated with the presence of conjugated bonds on the carbon surface, which are non-localized and very active. The acidity or basicity of the surface is explained by reactions:

$$\text{Adsorbent} - OH^- + H^+ \rightarrow \text{Adsorbent} - OH_2^+ \quad (9)$$

$$\text{Adsorbent} - OH^- + H^+ \rightarrow \text{Adsorbent} - O + H^+ \quad (10)$$

In most cases, it was observed that the adsorbent adsorbs anions at lower pH values due to the presence of H^+ ions. However, if the pH value increases, the functional groups on surface of the carbon are deprotonated, which changes the polarity, and the adsorption of the dye is enabled [15].

Also, it is visible that carbonized sawdust has a significantly higher adsorption capacity than adsorption on sawdust. The reason is most likely the significantly more developed surface of the carbonized sawdust, with a wide range of pore sizes (from visible cracks to cracks of molecular dimensions) [16].

3.3. Effect of adsorbent dose on adsorption capacity

The effect of adsorbent dose on adsorption capacity is shown in Figure 6.

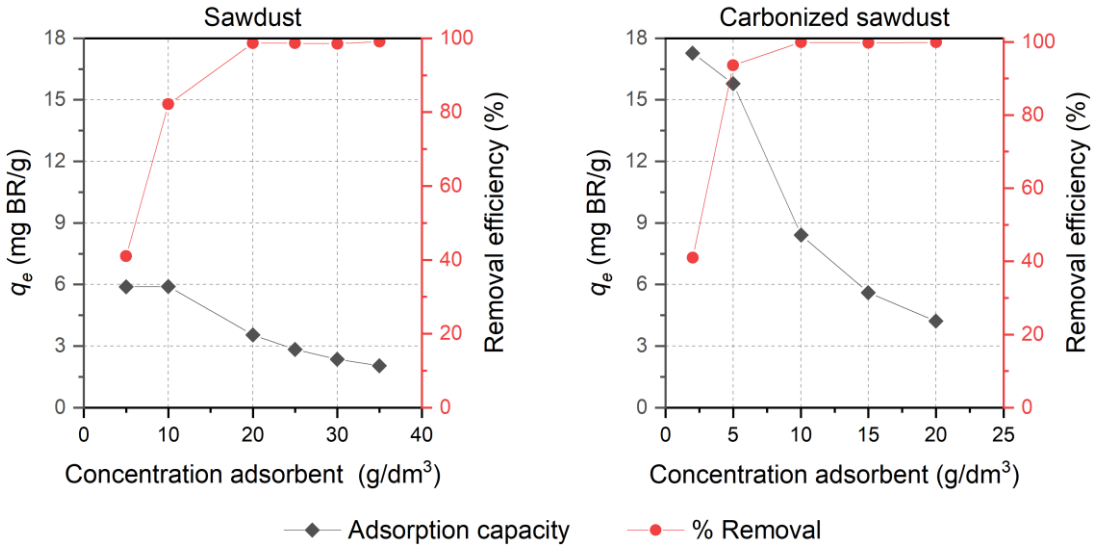

Figure 6. Effect of adsorbent dose on adsorption capacity and removal efficiency of BR dye (γ_{dye}=100 mg/dm^3, $pH_{sawdust}$=3.04, $pH_{carbonized\ sawdust}$=6.01; T=28.3°C, $t_{sawdust}$=1 h, $t_{carbonized\ sawdust}$=2 h)

Slika 6. Zavisnost kapaciteta adsorpcije i efikasnosti uklanjanja boje BR od mase adsorbenta (γ_{boje}=100 mg/dm^3, pH $_{piljevina}$=3.04, pH $_{kar.\ pilj.}$=6.01;T=28.3°C, $t_{pilj.}$=1 h, $t_{karb.pilj.}$=2 h)

From Figure 6, it can be seen that the efficiency of BR dye removal increases with the increase in adsorbent dose, while the adsorption capacity decreases. The reason for such a contradiction can be explained by the concentration gradient.

The lowest adsorption capacity for sawdust is 2.03 mg/g, and it is observed at the highest doses of adsorbent, with the highest removal efficiency of 99.1%. In contrast, the highest adsorption capacity of 5.89 mg/g was obtained at the lowest dose of adsorbent, but also with the lowest efficiency of 41.0 %. For the adsorption on the sawdust and for following process conditions: dye concentration 100 mg/dm^3, *T*= 28.3°C, pH= 3.04, contact time 1 h, the optimum adsorbent dose is 10 g/dm^3.

Significantly higher adsorption capacities were achieved by using carbonized sawdust. The highest adsorption capacity of 17.27 mg/g was achieved with the lowest adsorbent dose, with a removal efficiency of 41.0%. For the adsorption on the carbonized sawdust and for following process conditions: dye concentration 100 mg/dm^3, *T*= 28.3°C, pH= 3.04, contact time 1 h, the optimum adsorbent dose is 5 g/dm^3.

Obtained results are in accordance with the literature. By the adsorption of azo dye Allura red (AC) on sawdust, it was found that the percentage of dye removal increased with the increase in the adsorbent dose, from 40% to 80% [14] while for the adsorption of BR dye on date activated carbon, it was found that the adsorption rate increases with an increase in the adsorbent dose from 25% to 95% [9].

3.4. Effect of adsorbate concentration on the adsorption capacity

The effect of BR dye concentration on the adsorption capacity, when using sawdust and carbonized sawdust, is shown graphically in Figure 7. It can be seen that the efficiency of BR dye removal decreases with increasing adsorbate concentration, while on the other hand, the adsorption capacity increases.

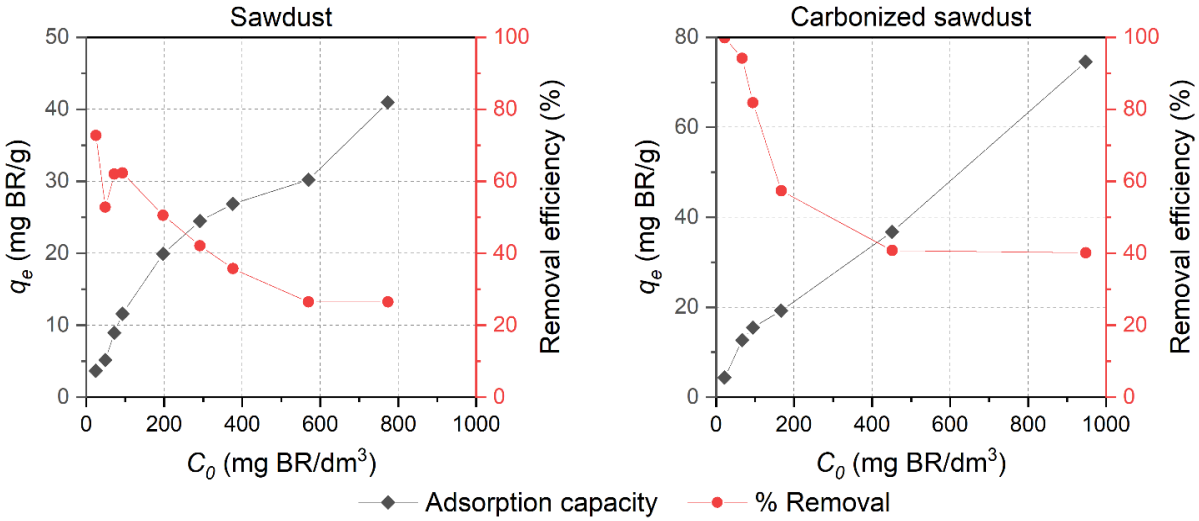

Figure 7. Effect of initial concentration of adsorbate on adsorption capacity and removal efficiency of BR dye ($\gamma_{adsorbent}$=5 g/dm^3, $pH_{sawdust}$ =3.01, $pH_{Carb.\ sawdust}$=6.01, T=28.4 °C)

Slika 7. Zavisnost kapaciteta adsorpcije i efikasnosti uklanjanja boje BR na piljevini od početne koncentracije adsorbata ($\gamma_{adsorbenta}$=5 g/dm^3, $pH_{pilj.}$=3.01, , $pH_{Karb.\ pilj.}$=6.01; T=28.4 °C)

This phenomenon can be explained by the fact that a high initial dye concentration gives a higher concentration gradient between the liquid and solid phase, which increases the adsorption capacity [9].

3.4.1. Adsorption isotherms

The most commonly used Langmuir and Freundlich adsorption models in linear form were applied to the experimentally obtained results for the adsorption capacity of bemacid red dye. The obtained adsorption isotherm constants are presented in Table 4.

Table 4. Adsorption constants of tested isotherms using linear models (Adsorbent dose = 5 g/dm^3, pH=3.01, T=28.4 °C, contact time 1 h (sawdust); pH= 6.01, T=28.2 °C, contact time 2 h (carbonized sawdust)

Tabela 4. Adsorpcione konstante ispitivanih izotermi primjenom linearnih modela (Koncentracija adsorbensa = 5 g/dm^3, pH=3.01, T=28.4 °C, Vrijeme adsorpcije 1 h (piljevina); pH= 6.01, T=28.2°C, Vrijeme adsorpcije 2 h (karbonizovana piljevina)

Model	Parameter	Parameter values	
		Sawdust	Carbonized sawdust
Langmuir	K_L (dm^3/mg)	0.008	0.011
	Q^0_{max} (mg/g)	44.84	74.07
Parameters calculated from the model	R^2	0.9441	0.7898
	R_L	0.142 – 0.836	0.107 – 0.786
Freundlich	n	0.548	0.255
	K_F (mg/g)/(mg/dm^3)^n	9.226	1.325
Parameters calculated from the model	R^2	0.9506	0.9100

The parameters of the adsorption isotherms presented in Table 4 show that the adsorption of bemacid red dye on sawdust and carbonized sawdust is better described by the Freundlich model than by the Langmuir model. The coefficient of determination for sawdust according to the Freundlich model is 0.9506, and for carbonized sawdust 0.9100, indicating good agreement with experimental data. The obtained values for the affinity constant for the adsorbate (n) are less than 1, which with the values of the dimensionless parameter R_L, also less than 1 for both adsorbents, indicate favourable adsorption. The adsorption curve has a concave shape. Also, the low values of the K_L Langmuir model constant indicate a high affinity between the bemacid red dye and the tested adsorbents. All above-mentioned indicates that everything is referring to a favourable multilayer adsorption. A graphical representation of the examined adsorption isotherms in linear form is presented in Figure 8.

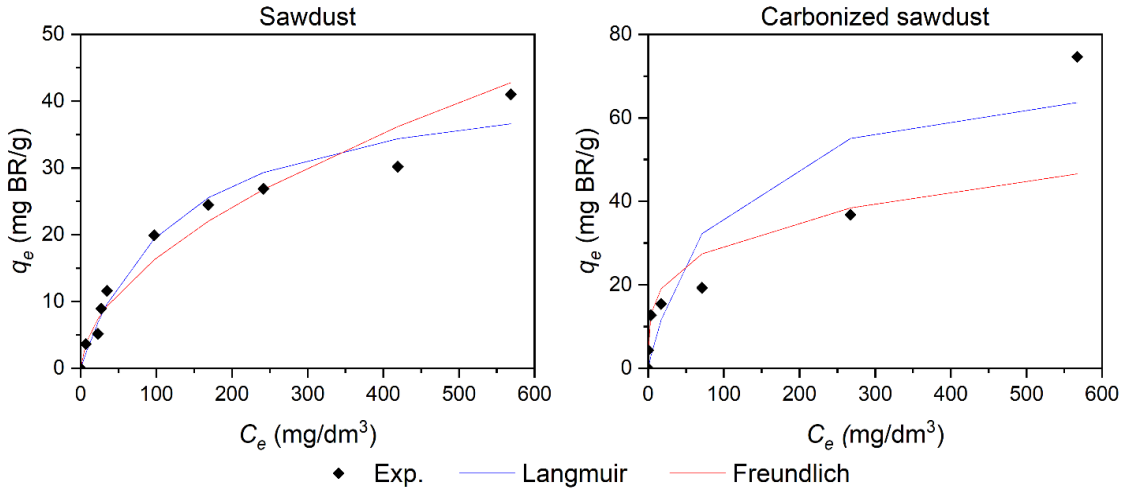

Figure 8. Graphical representation of examined models of adsorption isotherms in linear form for sawdust and carbonized sawdust

Slika 8. Grafički prikaz ispitivanih modela adsorpcionih izotermi u linearnom obliku za piljevinu i karbonizovanu piljevinu

A literature review of the obtained results for adsorption capacity of acid dyes on sawdust is presented in Table 5.

Table 5. Literature review of adsorption capacity data of azo dyes on low-cost adsorbents

Tabela 5. Literaturni pregled kapaciteta adsorpcije azo boja i jeftinih adsorbenasa

Adsorbent (azo dyes)	Low-cost adsorbents	Adsorption Capacity (mg/g)	References
Bemacid red	Washed Grape Winery Waste	65.5	[11]
Bemacid red	Prickly pear (species of cactus)	12.45	[2]
Allura red	Natural Sawdust	25.88	[14]
Acid Yellow 29	Ailanthus altissima Sawdust	13.00	[13]
Bemacid red	Brewery waste	152.0	[20]
Bemacid red	Sawdust	30.18	In this paper
Bemacid red	Carbonated sawdust	74.60	In this paper

3.5. Simulations of real conditions

By using waste water, obtained by dyeing polyamide fabric with BR dye, the real conditions of performing the adsorption process were simulated. The optimal adsorption parameters for each adsorbent were applied in the experiment with wastewater, and the obtained results are shown in Figure 9.

Using sawdust, the removal efficiency of BR dye is 42.9%, while carbonized sawdust shows almost complete dye removal (95.1%). By applying it to real waste water, the possibility of removing BR dye on the tested adsorbents was confirmed.

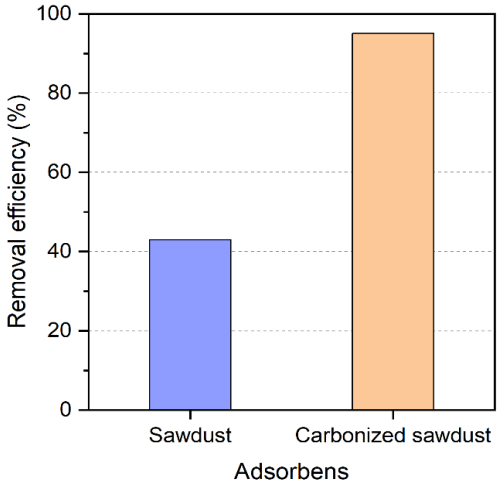

Figure 9. Removal efficiency of BR dye from a real sample of wastewater using the tested adsorbents (γ_{dye}=4.77 mg/dm^3, $\gamma_{adsorbent}$=5 g/dm^3, t=1 h, $pH_{sawdust}$=3.02, $T_{sawdust}$=26.2 °C; $pH_{carb.\ sawdust}$=5.40, $T_{carb.\ sawdust}$=24.3°C)

Slika 9. Efikasnost uklanjanja boje BR iz realnog uzorka otpadne vode primjenom ispitivanih adsorbenta (γ_{boje}=4,77 mg/dm^3, $\gamma_{adsorbenta}$=5 g/dm^3, t=1 h, $pH_{Sawdust}$=3.02, $T_{Sawdust}$=26.2 °C; $pH_{Carb.\ sawdust}$=5.40, $T_{Carb.\ sawdust}$=24.3°C)

5. CONCLUSION

Adsorption can be a cheap process because it allows the use of waste material as an adsorbent. The use of tested adsorbents (sawdust and carbonized sawdust) has its advantages, but also disadvantages. In the adsorbent preparation phase, dried sawdust is preferable to carbonized sawdust due to less energy and time consumption. However, dried sawdust, in order to achieve optimal adsorption conditions, requires a pH value of around 3, which represents an additional consumption of chemicals, and after treatment requires the adjustment of the pH value of the waste water before discharge. On contrary, adsorption on carbonized sawdust is insensitive to changes in pH value, which indicates savings in time and chemicals, with higher initial investment costs, but also higher removal efficiency. In order for sawdust and carbonized sawdust to be used as cheap adsorbents for bemacid red dye removal, it is necessary to conduct additional research that would include the regeneration of used adsorbents, as well as adsorption on regenerated adsorbents.

When it comes to sawdust as a waste material, it is certain that it has a future as an adsorbent in various adsorption processes. However, it is also certain that its application will require a lot of additional research.

6. REFERENCES

[1] J.Bortoluz, F.Ferrarini, L.R.Bonetto, J.da Silva Crespo, M.Giovanela (2020) Use of low-cost natural waste from the furniture industry for the removal of methylene blue by adsorption: isotherms, kinetics and thermodynamics, Cellulose, 27, 6445-6466. (https://doi.org/10.1007/s10570-020-03254-y)

[2] A.Fekaouni, G.Henini, Y.Laidani (2022) Evaluation of *Opuntia Ficus* indica as an economic adsorbent for anionic red bemacid dye from aqueous solution, Cellulose Chemistry and Technology, 56(3-4), 427-442. (https://www.cellulosechemtechnol.ro/pdf/CCT3-4(2022)/p.427-442.pdf)

[3] S.Dutta, B.Gupta, S.K.Srivastava, A.K.Gupta (2021) Recent advances on the removal of dyes from wastewater using various adsorbents: a critical review, Materials Advances, 2, 4497-4531. (https://doi.org/10.1039/D1MA00354B)

[4] V.Gupta, A.Agarwal, M.K.Singh, N.B.Singh (2019) Kail sawdust charcoal: a low‑cost adsorbent for removal of textile dyes from aqueous solution, SN Applied Sciences 1:1271. (https://doi.org/ 10. 1007/s42452-019-1252-3)

[5] R.Chikri , N.Elhadiri, M.Benchanaa, Y.El maguana (2020) *Efficiency of Sawdust as Low-Cost Adsorbent for Dyes Removal*, Review Article, Journal of Chemistry, 2020, ID 8813420, 17 page. (https://doi.org/10.1155/2020/8813420)

[6] F.Ouazani, A.Iddou, A.Aziz (2017) Biosorption of bemacid red dye by brewery waste using single and poly-parametric study, Desalination and Water Treatment, 93, 171-179. (https://doi.org/ 10.5004/dwt.2017.21413)

[7] L.G.Morão, G.Dilarri, C.R.Corso (2017) An approach to textile dye removal using sawdust from Aspidosperma polyneuron, International Journal of Environmental Studies, 74(1), 75-85. (http://dx.doi.org/10.1080/00207233.2016.1236651)

[8] F.Ouazani, H.Benchekor, Y.Chergui, I.Abdelkader, A.Abdellah (2020) Linearized form effect on estimation adsorption parameters of three industrial dyes by lignocellulosic sorbent, Journal of Environmental Health Science and Engineering, 18, 1045-1055. (https://doi.org/10.1007/s40201-020-00526-4)

[9] R.Boudia, G.Mimanne, K.Benhabib, L.Pirault-Roy (2019) *Preparation of mesoporous activated carbon from date stones for the adsorption of Bemacid Red*; Water Science and Technology, 79(7), 1357-1366. (https://doi.org/10.2166/wst.2019.135)

[10] H.N.Tran, Sh-J.You, A.H.Bandegharaei, H-P.Chao. (2017) Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. *Water Research*, 120, 88-116. (https://doi.org/10.1016/j.watres.2017.04.014)

[11] Y.Chergui, A.Iddou, H.Hentit, A.Aziz, J-C.Jumas (2019) *Biosorption of Textile Dye Red Bemacid ETL Using Activated Charcoal of Grape Marc (Oenological By-Product)*, Key Engineering Materials, 800, 151-156. (https://doi.org/10.4028/www.scientific.net/KEM.800.151)

[12] A.Duta, M.Visa (2015) Simultaneous removal of two industrial dyes by adsorption and photocatalysis on a fly-ash–TiO_2 composite, Journal of Photochemistry and Photobiology A: Chemistry, 306, 21-30. (http://dx.doi.org/10.1016/j.jphotochem. 2015.03.007)

[13] N.ur Rahman, I.Ullah, S.Alam, M.S.Khan, L.Ali Shah, I.Zekker, J.Burlakovs, A.Kallistova, N. Pimenov, Z.Vincevica-Gaile, Y.Jani, M.Zahoor (2021) Activated Ailanthus altissima Sawdust as Adsorbent for Removal of Acid Yellow 29 fromWastewater: Kinetics Approach, Water, 13, ID 2136,. (https://doi.org/ 10.3390/w13152136)

[14] T.K.Saha, R.K.Bishwas, S.Karmaker, Z.Islam (2020) Adsorption Characteristics of Allura Red AC onto Sawdust and Hexadecylpyridinium Bromide-Treated Sawdust in Aqueous Solution, ASC Omega, 5(22), 13358-13374. (https://doi.org/ 10. 1021/acsomega.0c01493)

[15] K.Y.Foo & B.H.Hameed (2010) An overview of dye removal via activated carbon adsorption process; Desalination and Water Treatment, 19, 255-274. (https://doi.org/10.5004/dwt.2010.1214)

[16] B.Acemioğlu, G.N.Karata., M.H.Güler, G.M.Erta, M.H.Alma (2019) Adsorption of basic red 2 dye by activated biomass charcoal in batch and column systems; International Journal of Chemistry and Technology, 3(2), 136-145. (https://doi.org/10.32571/ijct. 650476)

[17] S.Dutta, B.Gupta, S.K.Srivastava, A.K.Gupta (2021) Recent advances on the removal of dyes from wastewater using various adsorbents: a critical review, Materials Advances, 2(14), 4497-4531. (https://doi.org/10.1039/D1MA00354B)

[18] F.Ferrero (2007) Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust; Journal of Hazardous Materials, 142, 144-152. (http://dx.doi.org/10.1016/j.jhazmat. 2006.07.072)

[19] D.Suteu, D.Bilba, C.Zaharia, A.Popescu (2008) fifth edition of: "Colloque Franco-Roumain de Chimie Appliquée, Bacău, Romania, proceedings, p. 293-302.) (https://www.researchgate.net/publication/ 267394345_Removal_of_dyes_from_textile_waste water_by_sorption_onto_ligno-cellulosic_materials

[20] F.Ouazani, Y.Chergui, S.Benhammadi, A.F.Z.Saidi (2022) Three Level Design to Estimate Dyes Adsorption Parameters using Oenological By-Product as Adsorbent, Journal of Environmental Treatment Techniques, 10(1), 134-142. (https://doi.org/10.47277/JETT/10(1)142)

IZVOD

UKLANJANJE BOJE BEMACID RED ADSORPCIJOM NA PILJEVINI I KARBONIZOVANOJ PILJEVINI

Ogromne količine obojene otpadne vode, ispuštene u ekosisteme danas predstavljaju veliki problem, jer imaju štetne efekte na čoveka, životnu i vodenu sredinu. Jedan od postupaka uklanjanja boja iz otpadnih voda jeste proces adsorpcije, sa naglaskom na upotrebu jeftinih adsorbenata. Zbog toga je i tematika ovog rada mogućnost uklanjanja anjonske boje bemacid red (BR) na piljevini drvne biomase i karbonizovanoj piljevini. Provedenim eksperimentima ispitano je ravnotežno vrijeme kontakta, uticaj pH vrijednosti, zavisnost adsorpcije od mase adsorbenta, kao i zavisnost adsorpcije od početne koncentracije adsorbata. Primjenom linearnih kinetičkih modela ustanovljeno je da proces adsorpcije prati kinetički model pseudo drugog reda. Adsorpcija na karbonizovanoj piljevini ne pokazuje značajniju zavisnost od pH vrijednosti. Ispitivanjem zavisnosti adsorpcije od početne mase adsorbenta ustanovljeno je da je za optimalnu adsorpciju potrebna duplo veća masa piljevine u odnosu na karbonizovanu piljevinu. Primjena linearnih adsorpcionih izotermi pokazuje bolje slaganje sa Freundlichovim modelom za oba adsorbensa. Maksimalni kapacitet adsorpcije za piljevinu iznosi 30.18 mg/kg, dok je za karbonizovanu piljevinu 74.60 mg/kg. Dobijeni rezultati pokazuju da primjena piljevine i karbonizovane piljevine može biti efikasan adsorbens za uklanjanje boje bemacid red iz otpadnih voda,što je i potvrđeno na realnom uzorku otpadne vode. Dobijena efikasnost uklanjanja boje iz realnih otpadnih voda, dobijene nakon bojenja poliamidne tkanine bojom bemacid red, za piljevinu iznosi 42.9 %, a za karbonizovanu piljevinu 95.1 %.

Ključne riječi: *bemacid red, adsorpcija, drvna piljevina, karbonizovana piljevina*

Naučni rad
Rad primljen: 11. 07. 2022.
Rad korigovan: 06. 09. 2022.
Rad prihvaćen: 12. 09. 2022.
Rad je dostupan na sajtu: www.idk.org.rs/casopis