Toxic dye removal by thermally modified lignocellulosic waste in a three-phase air-lift reactor: Kinetic insights

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Abstract

This paper investigates the influence of the air flow rate in a three-phase air-lift reactor on the sorption of toxic dye, Brilliant green, onto a promising and efficient sorbent, sour cherry stone biochar. In order to gain a comprehensive insight into the sorbent/sorption behaviour, sour cherry stone biochar was characterized by Fourier transform infrared spectroscopy with attenuated total reflection, pH of the suspension, point of zero charge, scanning electron microscopy with energy-dispersive X-ray spectroscopy and X-ray diffraction. The experiments were performed in an air-lift reactor using airflows of 2.50 and 5.55 dm^3 h^{-1}. The experimental data of sorption kinetics experiments were fitted by non-linear form of pseudo-first and, pseudo-second models as well as the Weber-Morris model based on intraparticle diffusion. The overall sorption rate was found to be limited by the Brilliant Green mass transport rate to the sorbent at a lower airflow and thus mixing intensity, while it was kinetically controlled at a higher rate following the pseudo-second order kinetic model. Furthermore, sorption at lower air flow was delayed by mass transfer resistance through the liquid boundary layer surrounding sorbent particles. Presented results clearly indicate that airflow intensity plays a significant role in the overall sorption kinetics and support possible application of the applied biochar for efficient Brilliant Green sorption.

Keywords: Biowaste; sour cherry stone; pyrolysis, sorption; Brilliant green; kinetic study.

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1. INTRODUCTION

Some of the most pronounced global problems that mankind is facing today are environmental pollution and increased energy consumption. The main reasons for these problems are rapid industrial and technological developments, population growth and urbanization, as well as resource depletion. Consequently, large amounts of wastewater loaded with different organic and inorganic pollutants are generated every day, representing a huge burden on the environment. Considering that water is one of the finite natural resources, the global demand for preserving its quality is dramatically increasing [1,2]. Among various pollutants, synthetic dyes from different industries (especially from textile, leather, paper, cosmetics, tanning, printing, *etc.*) may be particularly hazardous to humans and aquatic life either because they are toxic, carcinogenic, teratogenic or mutagenic, or due to the change of water colour and prevention of sunlight permeation [1]. Having in mind the estimated future increase in the global dye market [3], an increase in the resulting water pollution is expected. The main challenges connected to the treatment of wastewater contaminated with dyes are caused by their composition and relatively high stability and resistance to degradation by oxidizing agents, aerobic digestion, heat, and light [4].

Brilliant green (BG) is a toxic, positively charged (cationic), organic dye mostly used in textile, paper, rubber, printing, and other dye-based industries [5]. It is well known that cationic dyes are more toxic than anionic ones and that they can cause serious health problems in some cases, even at extremely low concentrations (~1 mg dm^{-3}) [6]. Harmful

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effects of BG in small doses are mainly connected to the gastrointestinal and respiratory tracts causing irritation and symptoms such as vomiting, diarrhoea, kidney irritation, nausea, coughing, and shortness of breath, while in larger doses BG may cause methemoglobinemia, cardiovascular collapse and death due to respiratory failure [5]. In addition, prolonged exposure can cause organ damage [4,7]. Therefore, it is necessary to reduce the level of the BG dye present in the wastewater before it is discharged into the environment.

Biodegradation of dyes, although very attractive, is not practical for BG removal since it may generate metabolites that are highly toxic, carcinogenic, and mutagenic [5]. Other commonly used methods for dye removal are chemical coagulation, oxidation, membrane processes, sorption, and ion exchange, but most of those processes also have some drawbacks, such as large sludge generation, high capital investments or operating costs, membrane fouling, *etc.* [8]. Although sorption has its own drawbacks, among which are sorbent regeneration problems, its advantages have made it the most promising method for continuous removal of dyes at large scale even from highly loaded wastewater [9]. By this process dyes can be removed in a simple, efficient, cost effective and environmentally friendly manner [10,11].

Many different materials have been tested and used as sorbents among which biochar has been identified as one of the potential sorbents for wastewater treatment. Biochar is produced by thermochemical decomposition of biomass in the absence of oxygen. It is a solid, carbon rich material with excellent properties (abundance of surface functional groups, chemical stability, high porosity and high surface area [12]), that make it an attractive sorbent for different applications. In addition, energy and environment inputs for biochar production are lower than those in the other frequently applied technologies for producing sorbents like activated carbon or ionic resins. For example, biochar production costs may be up to six times lower than those of the commercial activated carbon [7]. Besides its efficacious removal of many various pollutants [1,10,13], another issue that makes biochar so attractive is the wide range of waste materials that may be used for its production, which helps in avoiding landfill disposal. In Serbia, large amounts of biowaste from agriculture and food industry may be used for biochar production. Among them, fruit stones are some of the materials that represent promising candidates for further investigations. Serbia is known for its rich fruit-growing tradition and cultivation of various types of fruit, among which sour cherries are one of the most abundant in these regions. According to the data from the Statistical office of the Republic of Serbia [14], the average yearly production of sour cherries in Serbia is 164,000 t. The resulting waste may be used as raw material for biochar production, thus reducing waste disposal and obtaining promising sorbent for pollutants removal.

Kinetics of the sorption process determines the rate and efficiency of sorbate molecules binding to the surface of a sorbent material, where the overall rate of the process is determined by the slowest step. Within the sorption process, there are few steps that may determine the overall rate: film diffusion, pore diffusion and sorption on the solid surface itself. In the cases where the sorption is fast, the process rate is determined by the first two rates i.e. transport of the molecules to the solid surface. For such systems, the increase in mixing will lead to increased overall sorption rates. In addition, it is necessary to minimize the costs of the purification process using the cheapest possible methods and equipment for its accomplishment. Air-lift reactors (ALR) are almost the ideal candidates for such processes. As the first advantage, construction of these reactors is simple without any moving parts [15]. Compared to bubble columns, ALRs have better performance for treating suspensions due to lower energy inputs [16]. Compared to the reactors with mechanical mixing ALRs demand lower power inputs for the same level of mixing, which is of essential importance for low price/high volume processes which is surely the wastewater treatment [17]. Thus, energy demands of ALRs may be three times lower as compared to mechanically mixed reactors indicating the efficient use of energy [18]. In addition, performance of those reactors is almost the same for small and large scale geometries and they can easily work even with high amounts of solid phase [19]. Finally, these reactors can be easily operated in continuous mode [20,21].

The aim of this study was to examine the influence of mixing on the kinetics of dye removal in an ALR system. Sour cherry stone (SCS) was used to produce biochar (SCS-B), a novel efficient dye sorbent, which was characterised by various techniques. A crucial aspect of this study involved determining kinetics of the BG removal process under different airflow conditions. Two kinetic models (pseudo-first and pseudo-second) and one mass transport model (intraparticle diffusion) were tested to interpret the experimental data and explain the influence of mixing on the sorption mechanism of BG onto biochar.

2. EXPERIMENTAL

2. 1. Material

SCSs were collected from the local Serbian fruit processing factory. Collected stones were separated from soft fruit residues, washed in water and dried at room temperature. In order to reduce their size, a vibratory disk mill "Siebtechnik - T S250" (Siebtechnik GmbH, Germany) was used. The particles were sieved into different particle size fractions. For the purpose of this investigation, SCSs with particle size between 0.2 to 0.3 mm were used. The SCSs were pyrolysed in a Nabertherm 1300 muffle furnace (Nabertherm, Germany), at 500 °C for 1.5 h in argon atmosphere, with a heating rate of 10 °C min^{-1}. Finally, the produced SCS-B was kept in vials closed with polypropylene caps before use.

BG was purchased from Sigma-Aldrich, USA. Chemical properties of BG are listed in Table 1. The dye concentration of 1000 mg dm^{-3} was diluted to the experimental solution concentration of 50 mg dm^{-3}, with initial pH of 6.8.

Table 1. Chemical properties of Brilliant green [7]

Name	Brilliant green
Molecular formula	$C_{27}H_{34}N_2O_4S$
Molecular weight, g mol^{-1}	482.63
λ_{max} / nm	624
Solubility in water at 25 °C, g dm^{-3}	100

An internal loop air-lift reactor (with characteristics presented in Table 2) made of Pyrex glass with a concentric draft-tube (Fig. 1) was used in sorption experiments.

Table 2. Geometric characteristics of the experimental ALR

Total / Working volume, dm^3	0.3 / 0.150
Total / Liquid height, m	0.46 / 0.19
Height or the riser draft-tube, m	0.15
Reactor / riser outer diameter, m	0.035 / 0.021
Sparger type	Perforated disc with 8×1 mm orifices

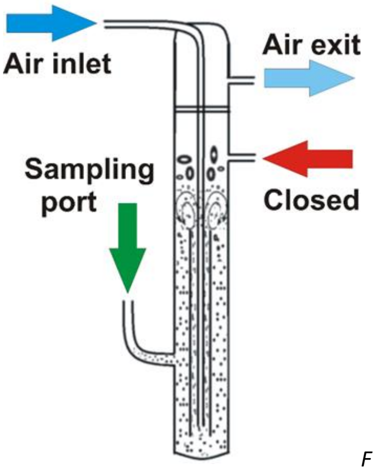


Figure 1. Air-lift design

2. 2. Sorbent characterisation

Various characterisation methods were used to study the physico-chemical properties of SCS-B.

Fourier-transform infrared spectroscopy with attenuated total reflection (FTIR-ATR) was applied to biochar before and after BG sorption in order to examine functional groups responsible for binding of the dye. FTIR analysis was performed using a Thermo Nicolet 6700 FTIR instrument (International Equipment Trading Ltd., USA) in the range of 400 to 4000 cm^{-1}. A background scan was acquired before scanning the samples.

pH values of suspensions (pH_{sus}) of the sorbent in water were determined by using the ASTM D6851-02 standard. A certain dose of sorbent (0.2 g) was added to 30 cm^3 of distilled water and kept in a closed container with mixing at room temperature for 72 h. Then, pH_{sus} was measured by a pH meter SensION3 (Hach, USA).

pH_{pzc} values of SCS and SCS-B were determined according to Milonjić *et al.*[22]. Initial pH values (pH_i) of 50 cm^3 of 0.01 mol dm^{-1} of KNO_3 solutions were adjusted in the range of 2 to 10 and were accurately noted. Then, 0.1 g of the sorbent was added to each solution and shaken for 24 h at 150 rpm. After determined period, the final pH value (pH_f) was measured and recorded.

Surface morphology of SCS and SCS-B was analysed using scanning electron microscopy (SEM), as well as Energy Dispersive X-Ray analysis (EDX) to map the presence of particular components on material surfaces. The SEM-EDX analysis was performed by a JEOL JSM-6610 LV SEM instrument (JEOL Ltd. Japan), on samples covered with a thin layer of gold.

X-ray diffraction (XRD) analysis was used to identify the crystallinity of biochar by a PW-1710 instrument (Philips, Netherlands) with Cu Kα radiation (λ = 1.54178 nm). The 2θ angle was scanned in an interval of 2θ (5 to 30°) with an angular increment of 0.02° and a time step of 1 s.

2. 3. Sorption kinetics

Sorption experiments were carried out in the internal loop ALR at two different airflows of 2.55 and 5.50 dm^3 h^{-1}, provided by using an air pump (LABOPORT N 86 KT.18, Germany). The process parameters were adopted from our previous study [7], which describes detailed investigations of BG removal by biochar of similar composition. In accordance with previous findings, 150 cm^3 of BG solution with the initial concentration of 50 mg dm^{-3} was mixed in ALR with 0.3 g of SCS-B for 120 min, at room temperature and at the selected airflow. Samples of 2 cm^3 were taken at different time intervals (0.5, 1, 2, 5, 15, 30, 45, 60, 75, 90, 105, 120 min), measured at 624 nm using a UV/VIS spectrophotometer (Spekol 1300, Analytik Jena, Germany) and then returned to the ALR. All experiments were performed in duplicate, and average values are presented.

The effectiveness (R) and the final sorption capacity at applied operational parameters (q_f) of BG sorption by SCS-B were calculated using Equations (1) and (2):

$$R = \frac{C_i - C_f}{C_i} 100 \tag{1}$$

$$q_f = \frac{(C_i - C_f)V}{m} \tag{2}$$

where C_i and C_f are initial and final concentration of BG, respectively, V is the volume of the dye solution and m is the mass of the sorbent.

In order to describe and analyse kinetics of the sorption process of BG on SCS-B, the experimental data were fitted using pseudo-first and pseudo-second models, as well as the Weber-Morris model based on intraparticle diffusion. These models are listed in Table 3.

Table 3. Models/equations used to asses Brilliant green sorption

Name of kinetic model	EEquation	Parameter	Ref.
Pseudo-first order	$q_t = q_e (1 - e^{-k_1 t})$	q_t / mg g^{-1}: mass of the sorbate per mass of the sorbent at any time t q_e / mg g^{-1}: sorption capacity at equilibrium k_1 / min^{-1}: the pseudo-first order rate constant	[23]
Pseudo-second order	$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{1}{q_e}}$	k_2 / g mg^{-1} min^{-1}: the pseudo- second order rate constant	[24]
Weber-Morris model based on intraparticle diffusion	$q_t = K_d t^{0.5} + C$	K_d / mg g^{-1} $min^{1/2}$: the intra-particle diffusion parameter C / mg g^{-1}: intercept	[25]

3. RESULTS AND DISCUSSION

3. 1. Sorbent characterisation

Pyrolysis causes significant changes in physical and chemical properties of the raw material. The obtained FTIR-ATR spectra are used to identify surface functional groups of biochar before and after BG sorption. As can be seen in Figure 2, the FTIR spectra were similar, indicating that the BG sorption process had negligible effects on functional groups of biochar. The peak at 2649 cm^{-1} indicates the presence of aliphatic groups (-CH_n) in biochar [26]. The band at 1697 cm^{-1} corresponds to the stretching vibration of carbonyl (C=O) groups [27], while the peak at 1580 cm^{-1} is related to C=O stretching and aromatic C=C vibrations [26]. After the sorption of BG, new peaks appeared between 1439 and 1329 cm^{-1} which were assigned to the N-H bending vibration and the C-N stretching vibration, revealing that BG sorption involved the interaction of amino groups on the biochar surface with BG molecules [28]. The strong peak at 1173 cm^{-1} was related to the C-O stretching vibration of phenolic hydroxyl groups on the surface of biochar, which interacted with the C=O group of BG through hydrogen bonding, leading to the split of this peak into two new peaks at 1187 and 1156 cm^{-1}. The peaks observed in the range of 749 and 874 cm^{-1} in biochar were attributed to the presence of aromatic compounds, with no significant effect on dye sorption [29].

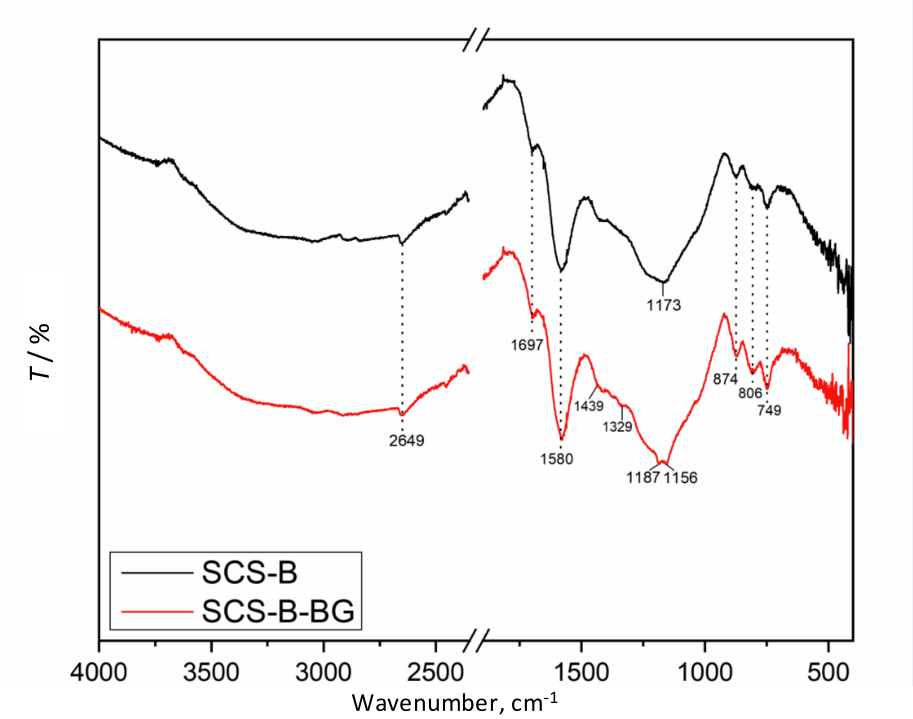


Figure 2. FTIR-ATR spectra of SCS-B before and after dye sorption

When distilled water comes in contact with a sorbent, the pH value changes due to the interaction with acidic and alkali groups on its surface. Contact pH or pH_{sus} is an indicator of the acid-alkali nature of a material surface [30]. pH_{sus} of the SCS-B was found to be 6.48, which is higher than the measured pH_{sus} value of the SCS amounting to 4.11. The low alkalinity of pH_{sus} for biochar can be attributed to the presence of acidic functional groups, such as carboxyl and phenolic groups, the presence of which was proven by FTIR. These findings are consistent with the results of Antanasković *et al.* [7], reporting that biochar originating from peach stone was more alkaline (6.91) than the native material (5.14).

The point of zero charge (pH_{pzc}) represents a pH value at which the surface of a sorbent exhibits a zero charge. The values of the pH_{pzc} may suggest possible electrostatic interactions between the sorbent and sorbate in a dye solution. At pH values below the pH_{pzc}, the material surface is positively charged, favouring the attraction of negatively charged ions, while at solution pH values above pH_{pzc}, the sorbent surface is negatively charged and can attract positively charged ions [31]. As can be seen in Figure 3, the pH_{pzc} value for SCS was 5.00, while that of SCS-B was 6.60. Thus, SCS demonstrated neutrality within a limited initial pH range (6-7), whereas the SCS-B exhibited neutrality in a wide range of initial pH values (6-9). It was expected that the pH_{pzc} of biochar would be higher than that of raw materials due to the elimination of acidic groups and creation of basic functional groups during pyrolysis. Since the pH value of the BG solution(6.8) is higher than the pH_{pzc} value, surfaces of the biochar remain negatively charged, which favours sorption of cations, such as BG [32].

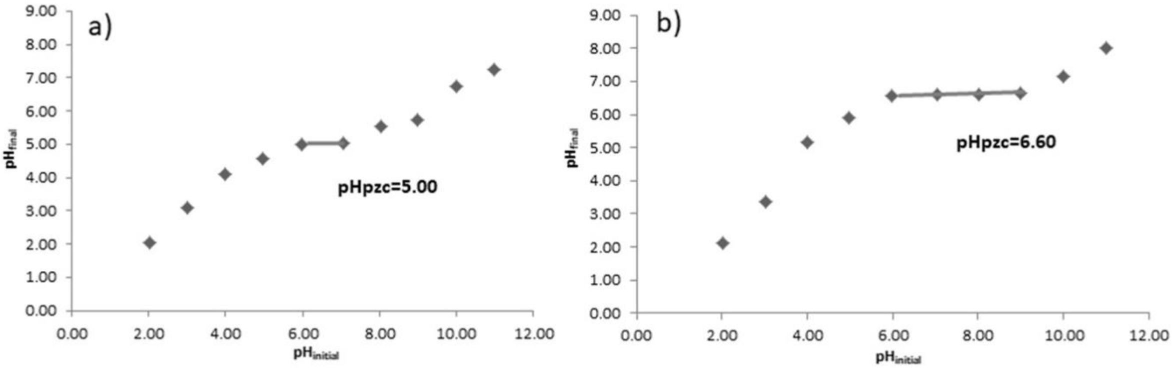
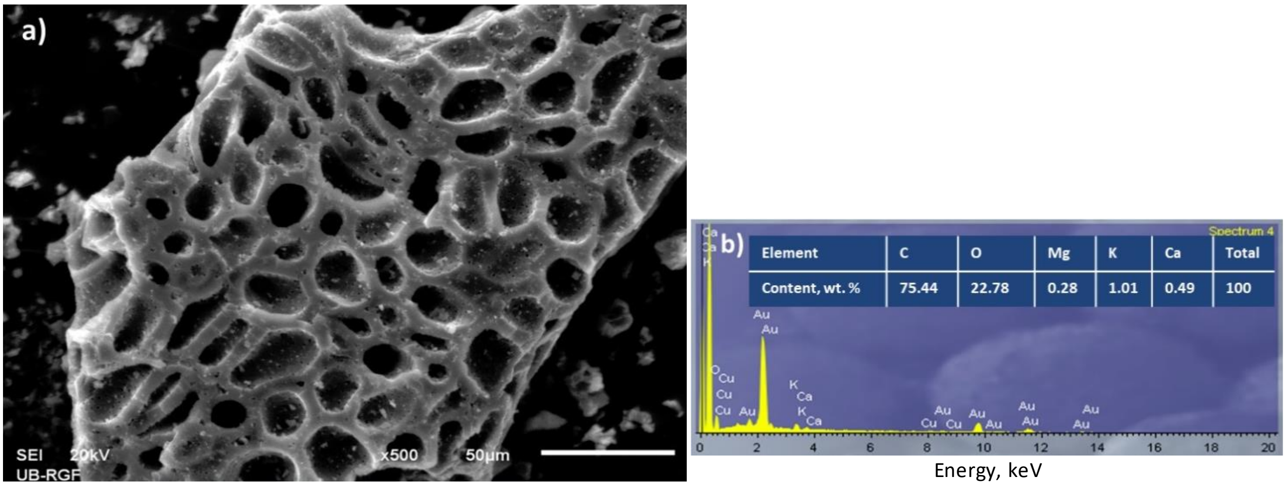


Figure 3. Determination of final pH values in the suspensions as functions of the initial values for a) SCS; b) SCS-B

SEM was used to closely examine morphology of the material surface. SCS-B has a porous structure with irregular pores of various sizes and shapes (Fig. 4a), which is a result of decomposition and volatilisation of the main components (hemicellulose, cellulose and partial lignin) during pyrolysis, which increased the surface area of the obtained biochar promoting later sorption of the dye. Using a similar material (cherry stone), Pehlivan and Kahraman [33], also confirmed that pyrolysis of lignocellulosic biomass produces a porous material with a large number of cracks and channels. The EDX analysis (Fig. 4b) revealed that the biochar was composed mainly of carbon (75.44 %), followed by oxygen (22.78 %), while the presence of magnesium, calcium and potassium was only 0.28, 1.01 and 0.49 %, respectively. These results indicated that carbon is the dominant element, as expected, while oxygen is also present, dominantly by oxygen-containing functional groups such as a carbonyl (also shown by the FTIR analysis). Similar findings were obtained by the EDX analysis previously [13], for biochar of a similar lignocellulosic structure (made from peach stone).



Element	C	O	Mg	K	Ca	Total
Content, wt. %	75.44	22.78	0.28	1.01	0.49	100

Figure 4. SEM-EDX analysis of the SCS-B: a) SEM micrograph (scale bar: 50 μm); b) EDX analysis results

The XRD pattern for SCS-B is shown in Figure 5. The appearance of two broad diffraction peaks at 2 θ of 20 to 30° and 41°, corresponding to the 002 and 100 reflection planes, respectively, indicates an amorphous structure, and presence of carbon and graphite. The high peak at 24° originates from high carbon (C_{12} to C_{60}) concentration, due to high pyrolysis temperature (500 °C) [34]. The peak at 41° belongs to the C (100) plane of condensed carbonized structures [35]. These results confirmed the amorphous structure of SCS-B, which lacks a long-range order in atomic/molecular arrangement, resulting in a porous and disordered structure [36]. Such structure contributes to the surface area increase, which improves the availability of active sites on for sorption of the large dye molecules.

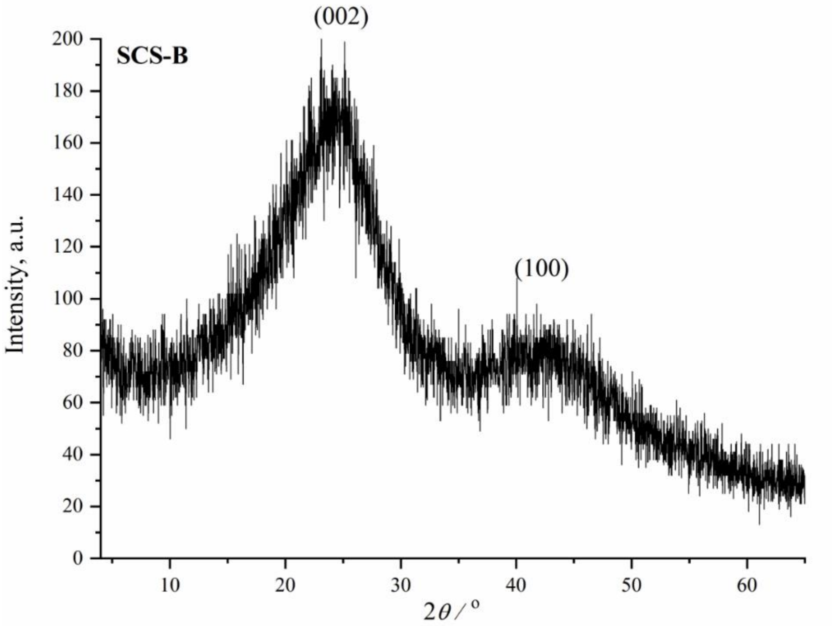


Figure 5. XRD pattern of SCS-B

3. 2. Sorption kinetics

Studies of sorption kinetics provide insights into the overall rate of the sorption process, which is a crucial factor in evaluating the efficiency of the sorbent, as well as insights into the sorption mechanism [37]. The sorption process is affected by numerous parameters and one of them is mixing, which was examined in this study. The influence of mixing at airflow rates of 2.55 and 5.50 dm^3 h^{-1} on the overall rate of dye sorption was investigated using two reaction kinetic models (pseudo-first order and pseudo-second order) and one intraparticle diffusion model. The models were applied in nonlinear forms and fitted using nonlinear regression analysis using OriginPro (2021 version) software. Figure 6 illustrates the time-dependent profiles of sorption of BG onto SCS-B, and application of the two kinetic models, while the related parameters are summarized in Table 4.

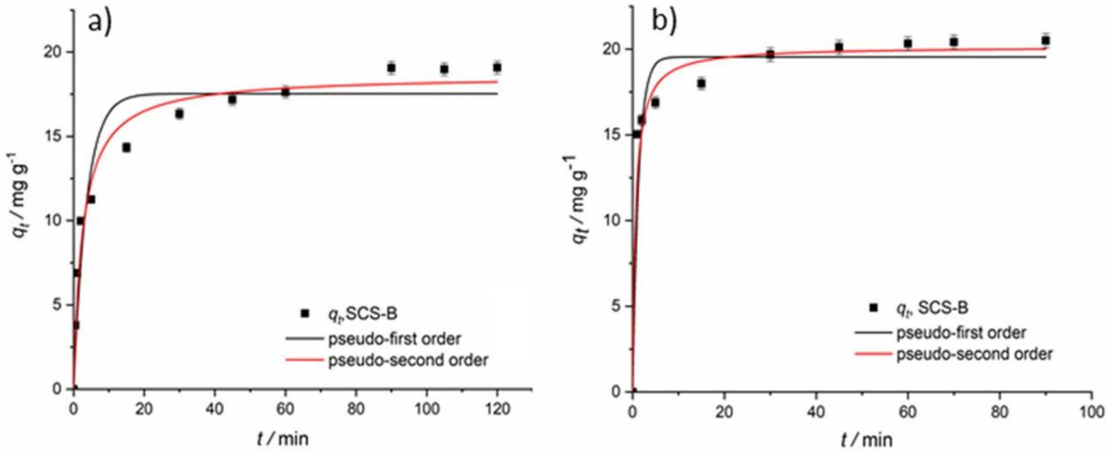


Figure 6. Sorbed BG per mass of SCS-B (q_t) as a function of time: experimental data (symbols) and the best fit predictions of the pseudo-first and pseudo second order kinetics with airflow: a) 2.55 dm^3 h^{-1}; b) 5.50 dm^3 h^{-1}

With the use of a higher airflow (Fig. 6b), equilibrium is reached in approximately 45 min, which is almost twice as fast as it is at the lower airflow rate (Fig. 6a), clearly indicating the effects of mass transport. The increased airflow enhances the external mass transfer, allowing BG molecules to reach the SCS-B surface more rapidly. Thus, the application of the higher airflow of 5.50 dm³ h⁻¹ has shown to be more effective in removing BG. After only 5 min, almost 70 % of dye was removed, while with the use of the airflow of 2.55 dm³ h⁻¹ only 48 % was removed. Also, the statistical parameters of the models fitting (R^2 and χ^2) were lower for the lower airflow. Higher internal circulation has the potential to influence the overall rate of dye sorption by increasing the mass transport rate to the surface and possibly within the pores of the biochar [38]. Lowering of the external mass transport limitations and the diffusion distance through the film induced the higher sorption rate and the increase in the apparent overall rate constant.

Data presented in Table 4 demonstrate that reaction kinetic models have shown higher correlation with the data at the higher flowrate than at the lower where the influences of mass transport are not negligible. These data show that for the higher airflow rate, the pseudo-first order model does not fit the experimental data well, which can be also observed in Figure 6b. The correlation coefficient (R^2) for the pseudo-second order was higher (0.9892) then for the pseudo-first order (0.9700), while the chi-squared value (χ^2) was lower (0.5308) compared to the value of the pseudo-first model (1.4697). Additionally, the experimental equilibrium sorption capacity q_{exp} value (20.49 mg g^{-1}) is very close to the calculated q_{calc} values (20.15 mg g^{-1}) for the pseudo-second order kinetic model, indicating again that mass transport limitations become less prominent at the higher airflow and better mixing. Giri *et al.* [39] also reported that the pseudo second-order kinetic model could effectively explain sorption of BG using the corncob biochar, with the sorption capacity of 5.73 mg g^{-1}.

The application of the intraparticle diffusion model provides a deeper understanding of the rate limiting steps in the two experimental set-ups realized in the present study. In specific, as mentioned above, the sorption process involves several steps. Initially, the sorbate molecules migrate from the bulk solution to the liquid boundary layer, and this step depends on agitation and solution homogeneity. In the next step, these molecules diffuse through the liquid boundary layer at the sorbent surface, where they bind to the active sites, while one part of the molecules pass through the sorbent micropores and reach the interior where they bind. The overall sorption rate will be controlled by the slowest of those processes or the rate-limiting step [40].

The resistance to mass transfer within the liquid film surrounding the particle is only significant during the initial phase of diffusion [41]. Examining sorption, it is usually assumed that the sorbent particles are spherical, which leads to the expression for the initial phase $q_t/q_e < 0.4$ [42]. Accordingly, the intraparticle diffusion model was applied to the experimental data in the initial period ($q_t/q_e < 0.4$), presented in Figure 7, while the model parameters are listed in Table 4.

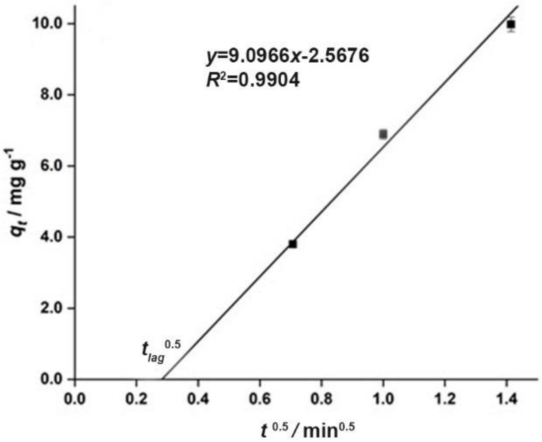


Figure 7. Application of the intraparticle diffusion model (lines) on the experimental data (symbols) of BG sorption on SCS-B in the initial period ($q_t/q_e < 0.4$) at airflow 2.55 dm^3 h^{-1}

Under the airflow of 2.55 dm^3 h^{-1}, the experimental data showed a straight line with a negative y-axis intercept (C = -2.57 mg g^{-1}) and a positive x-axis intercept ($t_{\mathrm{lag}}^{0.5}$) of 0.282 min$^{0.5}$ leading to the lag time of 0.08 min. The negative value of C indicates the effect of external film diffusion resistance, which limits the sorption rate alongside intraparticle diffusion [42,43]. Consequently, sorption is delayed for less than 5 s due to the external diffusion resistance of the film.

This short delay in sorption suggests that the resistance of the outer diffusion film was low or that other factors had a minor effect on the sorption delay. These findings are consistent with the results reported by Zhu et al. [44] who observed a negative C value and delayed sorption during the sorption of pyridine onto polymeric adsorbents.

Applying a higher airflow rate, 5.50 dm³ h⁻¹, the process was observed to be kinetically controlled, rather than controlled by intraparticle diffusion. The increased airflow rate resulted in a significant reduction of the sorbate boundary layer and the film mass transfer resistance around the sorbent particles [45]. It might be assumed that film diffusion was so rapid that it was not experimentally observed in the measurements, as the first sampling point was after 1 min, potentially after the initial phase had already been finished. The higher mixing induced by the higher airflow velocity enhances the transport rate of the dye, reducing the time dye molecules spend on the sorbent surface and consequently decreasing the diffusion time [46]. Perez Cadena *et al.* [47] investigated biological decolorization of Amaranth dye with *Trametes polyzona* in an air-lift reactor under three airflow regimes. They have concluded that the rate of decolourisation is a function of the aeration regime, where the higher aeration rate is associated with the faster decolourisation rate.

Table 4. Sorption kinetic parameters of BG removal by SCS-B with different airflows

Model	Parameter	Flow of 2.55 dm³ h⁻¹	Flow of 5.50 dm³ h⁻¹
Pseudo-first order	q_{exp} / mg g⁻¹	19.09	20.49
	q_{calc} / mg g⁻¹	17.53	19.54
	k_1 / min⁻¹	0.272	0.762
	R^2	0.9169	0.9700
	χ^2	3.360	1.4697
Pseudo-second order	$q_{e,\mathrm{calc}}$ / mg g⁻¹	18.62	20.15
	k_2 / g mg⁻¹ min⁻¹	0.021	0.075
	R^2	0.9688	0.9892
	χ^2	1.2616	0.5308
Intraparticle diffusion	K_d / mg g⁻¹ min$^{1/2}$	9.10	-
	C / mg g⁻¹	-2.57	-
	R^2	0.9904	-

The sorption capacity (obtained from experimental kinetic studies under applied operational parameters) of SCS-B towards BG, has been compared with other biochars reported in the literature, which is presented in Table 5. The sorbent prepared in this study exhibited relatively high sorption capacity for BG of 20.49 mg/g, which represents the significant basis for further research.

Table 5. Comparison of calculated sorption capacities of various biochars for removal of BG dye

Biochar	Parameter pH	 C_i / mg L⁻¹	 t / h	q_{exp} / mg g⁻¹	Ref.
Soybean straw	8.0	500	1	12.53	[5]
Peach stone	7.0	50	2	31.00	[7]
Corncob	8.1	50	3.5	5.73	[39]
Rice straw	7.0	20	3	17.61	[48]
Sour cherry stone	6.8	50	2	20.49	This study

4. CONCLUSION

In this paper, lignocellulosic waste material, originating from the food industry, was pyrolysed to produce biochar, which was then examined as a sorbent. This study demonstrates the influence of the mixing within the air-lift reactor on the overall rate of sorption of toxic dye, BG, onto the biochar. The results of the biochar characterization indicate an amorphous and porous structure, with a negatively charged surface, making it highly suitable for efficient sorption of cationic dyes, such as BG. The overall sorption rate was found to be limited by the BG mass transport rate to the sorbent at a lower airflow and thus mixing intensity, while it was kinetically controlled at a higher rate following the pseudo-second order kinetic model. The findings highlight the significant role that mixing had on the sorption process, leading to improved removal of the toxic dye with the airflow increase. Applying higher airflow rate, the process reached equilibrium almost twice faster compared to the lower rate. The use of a higher airflow reduces the influence of the liquid boundary layer indicating again that mass transport limitations become less prominent at the higher airflow and better mixing, resulting in enhanced convective mass transfer, induced by the increase in the liquid velocity, which facilitates the dye molecules transport to the sorption sites. The obtained results indicate that three-phase air-lift reactors may be promising equipment for sorption processes allowing lower energy inputs.

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Uklanjanje toksične boje termički modifikovanim lignoceluloznim otpadom u trofaznom "air-lift" reaktoru: uvid u kinetiku procesa

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(Naučni rad)

Izvod

Ovaj rad istražuje uticaj protoka vazduha u trofaznom pneumatskom reaktoru sa recirkulacijom (air-lift) pri sorpciji toksične boje Brilliant Green, pomoću sorbenta na bazi bio čađ, i dobijenog od koštica višnje. U cilju karakterizacije sorbenta korišćene su sledeće metode: infracrvena spektroskopija sa Furijeovom (Fourier) transformacijom i prigušenom totalnom refleksijom, pH vrednost suspenzije, tačka nultog naelektrisanja, skenirajuća elektronska mikroskopija sa energetski disperzivnom rendgenskom spektroskopijom i difrakcija rendgenskih zraka. Eksperimenti su izvedeni u air-lift reaktoru pri protoku vazduha od 2.50 i 5.55 dm^3 h^{-1}. Eksperimentalni podaci kinetike modelovani su nelinearnim oblicima pseudo-prvog i pseudo-drugog reda, kao i Weber-Morrisovim modelom, koji se zasniva na unutar-čestičnoj difuziji. Pokazano je da je pri nižem protoku i intenzitetu mešanja, brzina sorpcije boje Brilliant Green ograničena brzinom prenosa mase ka sorbentu, dok je pri većem protoku rekacija kinetički kontrolisana u skladu sa pseudo-drugim kinetičkim modelom. Pored toga, pri nižem protoku, sorpcija je odložena usled otpora prenosa mase kroz granični sloj tečnosti oko čestica sorbenta. Prikazani rezultati jasno ukazuju da intenzitet protoka vazduha ima značajnu ulogu u ukupnoj kinetici sorpcije i podržavaju moguću primenu biočadji za efikasnu sorpciju boje Brilliant green.

Ključne reči: otpadna biomasa; koštice višnje; piroliza; sorpcija; Brilliant green; kinetika