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Cladium mariscus Saw-Sedge versus Sawdust—Efficient Biosorbents for Removal of Hazardous Textile Dye C.I. Basic Blue 3 from Aqueous Solutions

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Abstract: Bio-based waste materials are more often used as effective and cheap adsorbents to remove toxic organic compounds such dyes. Batch adsorption of C.I. Basic Blue 3 (BB3) onto *Cladium mariscus* saw-sedge was studied in comparison with sawdust obtained from various species of wood in order to explore their potential application as low-cost sorbents for basic dye removal from wastewaters. The effect of phase contact time (1–240 min), initial dye concentration (50–200 mg/L), and the auxiliaries presence (10–60 g/L NaCl and 0.1–0.75 g/L anionic surfactant) on BB3 uptake was investigated. The adsorption kinetic data followed the pseudo-second order equation rather than pseudo-first order one. The equilibrium adsorption data were analyzed using the Langmuir, Freundlich, and Tempkin isotherm models. The monolayer sorption capacities decreased from 44.29 to 42.07 mg/g for *Cladium mariscus* saw-sedge and from 28.69 to 27.5 mg/g for sawdust with temperature increasing from 20 to 50 °C. The thermodynamic parameters such as the change in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were calculated, too.

Keywords: low-cost sorbent; basic blue dye; removal; sew-sedge; sawdust

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1. Introduction

Industrial operations in dye production plants, dye-house, paper plants, plastic- and food-processing plants, as well as petroleum and cosmetics release large quantities of effluents containing dyes. These wastewaters cause the accumulation of dyestuffs in the environment, creating a grave problem [1,2]. It has been found that even a minimal amount of dye (<1 ppm) makes the effluents strongly colored [3]. According to Ecological and Toxicological Association of Dyes and Organic Pigments Manufactures (ETAD), BB3 dye, in addition to the basic dyes such as Blue 81, Red 12, Violet 16 or Yellow 21, is classified as toxic [4]. The dyestuffs not only impede the penetration of light into the water and retard photosynthetic activity, but also enlarge microtoxicity to aquatic life [5,6]. Thus, it is pivotal to remove dyes from effluents, and make water reusable for various industrial and agricultural purposes. The most prominent physicochemical methods of wastewater purification are: coagulation, flocculation, flotation, oxidation, filtration, as well as adsorption [7–9]. In the papers by Holkar et al. [10] and Hasanbeigi and Price [11] advantages and drawbacks of these methods were scrupulously described. Their effectiveness depends on many parameters. The yardstick of their application in the technology of wastewater purification is not only noxious substance degradation, but also process economy [12,13]. Taking the above into account, there exists a need to find efficient and cheap alternatives for dyestuff removal. Biosorption is one of them.

There are multitude literature reports on the application of plant biosorbents for purification of wastewaters containing dyestuffs. They are characterized by accessibility and very low costs of exploitation, which is very desirable as far as the process economy is considered. These materials are formed as a result of grinding or crumbling the above-ground parts of plants (sprouts, bark, leaves, and fruit) or their roots. It should be mentioned that some of these biosorbents are created from substances requiring utilization and are not widely applied, e.g., peels and fruit stones, nut shells, cones, etc. [13]. The aforementioned materials are built from biopolymers, mainly lignocellulose (lignin, cellulose, and hemicellulose) and tanning agents, which enable the binding of chemical compounds owing to the existence of specific functional groups, mainly hydroxyl, carboxylic, carbonyl, thiol, and amine ones in their structure [14]. Biosorption mechanism can be complex including many physicochemical processes such as absorption, adsorption (physical and chemisorption), ion exchange, complexation, or microprecipitation.

As follows from the literature review, the cationic dye BB3 was removed from aqueous solutions using the following adsorbents: *Bacillus catenulatus* [15], *Sphagnum Magellanicum* peat [16], *Spirogyra* sp. biomass [17], pomelo peel [18], activated carbons [19–21], cement kiln dust [22], fly ash [23], sepiolite [23], and cation exchange resins [24]. *Cladium mariscus* (L.) overgrows peat bogs in the eastern part of Lublin district (Chełm region). This plant along with other rush plants were partially removed from peat bogs in order to preserve already existing species, thus to keep and increase population of *Acrocephalus paludicola* (a very rare bird from the *Passeriformes* order, which is becoming extinct). The biomass obtained in this way was mainly used for the production of pellet and briquette. However, it can be also applied as a biosorbent. For the contrast sawdust, formed as a waste product of woodworking (cutting, planting, and turning of different species of wood) was applied for BB3 uptake, too. The adsorption kinetics, isotherms, and thermodynamics were investigated for determination of adsorptive properties of these materials depending on the phase contact time, initial dye concentration, additives (salt and surfactant) presence, and temperature using the batch adsorption method.

2. Materials and Methods

2.1. Adsorbents and Adsorbate Characteristics

Cladium mariscus was collected in south-eastern region of Poland (Chełm, Lubelskie voivodship). The leaves of the plant were washed with distilled water cut and dried at 105 °C for 24 h. The wood sawdust obtained from the local sawmill (Poznan, Poland) was washed with distilled water and dried (at 105 °C for 24 h). The elemental analysis of the sorbents was made using a Vario El Cube instrument (Elementar Analysensysteme GmbH, Germany). In order to characterize the parameters of the porous structure of *Cladium mariscus* saw-sedge and sawdust, the specific surface area BET and pore volume were determined using an Accelerated Surface Area and Porosimetry 2020 instrument (Micromeritics Instrument Co., USA). The characteristics of used sorbents are listed in Table 1.

Table 1. Low-cost sorbents characteristics.

Parameter	*Cladium mariscus* Saw-Sedge	Sawdust
Elemental analysis	48% C, 7.1% H, 0.95% N, 0.4% S	49.5% C, 8.8% H, 0.4% N, 0.5% S
Specific surface area BET (m^2/g)	0.60	1.17
Volume of the pores (cm^3/g)	0.01	0.58

FT-IR analysis of *Cladium mariscus* saw-sedge and sawdust before and after sorption of C.I. Basic Blue 3 was performed by using a VERTEX 70 spectrophotometer (Bruker, Germany). Sorbents were analyzed in a form of tablets (ca. 250 mg of anhydrous KBr mixed with 1.5 mg of the sample). Spectra were recorded over a wavenumber range of 4000–400 cm^{-1}, with a resolution of 0.5 cm^{-1}.

C.I. Basic Blue 3 dye (BB3) is 3,7-bis (diethylamino) phenoxazin-5-ium chloride. It is also known as Astrazon Blue FGRL. This cationic dye is the commercial product of Sigma-Aldrich (Germany) and was used without purification (dye content 25%). An accurately weighted amount of the dye was dissolved in the doubly distilled water to prepare stock solution. The experimental solutions of desired concentrations were obtained by successive dilutions.

Sodium chloride of analytical grade was purchased from POCh (Poland). The anionic surfactant sodium dodecyl sulfate (SDS) was obtained from Sigma Aldrich (Germany).

2.2. Kinetic Studies

Determination of the kinetic parameters of BB3 sorption on *Cladium mariscus* saw-sedge and sawdust was a significant part of the work. For this purpose, calculations were performed to determine the amount of dye retained by the low-cost sorbents, which is essential for defining kinetic models such as the pseudo-first order [25], pseudo-second order [26], and intraparticle diffusion [27]. The amount of dye adsorbed at time *t* by *Cladium mariscus* saw-sedge or sawdust, denoted as q_t, was calculated from the equation:

$$q_t = \frac{(C_0 - C_t)}{m} V \tag{1}$$

where C_0 and C_t are the concentrations of BB3 in the solution before and after sorption, respectively (mg/L), V is the volume of the solution (L), and m is the weight of dry low-cost sorbent (g).

The accurately weighed samples of low-cost sorbents (0.2 g) were shaken at 180 cpm at a constant temperature 20 °C using a laboratory shaker Elpin Plus 358A (Elpin Plus, Lubawa, Poland) with 20 mL aqueous solutions containing known amount (50, 100, or 200 mg/L) of dye. The concentration of BB3 in the solution after predetermined time intervals was measured using the UV–vis method (at λ_{max} = 654 nm; Agilent Cary 60, USA).

2.3. Isotherm Studies

In order to determine the equilibrium adsorption parameters according to the Freundlich [28], Langmuir [29], and Temkin [30] isotherm models, it was necessary to calculate the amount of dye adsorbed at equilibrium by *Cladium mariscus* saw-sedge or sawdust, q_e (mg/g) as:

$$q_e = \frac{(C_0 - C_e)}{m} V \tag{2}$$

where C_0 and C_e are the liquid-phase concentrations of C.I. Basic Blue 3 before sorption and at equilibrium state, respectively (mg/L), V is the volume of solution (L), and w is the weight of dry low-cost sorbent (g).

Equilibrium studies were performed in a set of Erlenmeyer flasks (100 mL) where 20 mL of BB3 solutions with the increasing initial concentrations were placed. The mass of 0.2 g sorbents was added to each flask and kept in an isothermal shaker at 20, 30, 40, and 50 °C for 24 h to reach equilibrium. The original pH of the solutions was used, which was around 4.3. Aqueous samples were taken from the solutions and the dye concentration was analyzed using the UV–vis spectrophotometer.

Effects of the auxiliaries addition on the dye uptake at equilibrium were studied by shaking the sorbents (0.2 g) with the 50 mg/L dye solution (20 mL) containing from 25 to 100 g/L of NaCl or from 0.1 to 0.75 g/L of sodium dodecyl sulfate at 20 °C. The dye concentration after sorption was measured spectrophotometrically at the maximum absorbance wavelength. All adsorption experiments were performed in triplicates with the reproducibility ±5%.

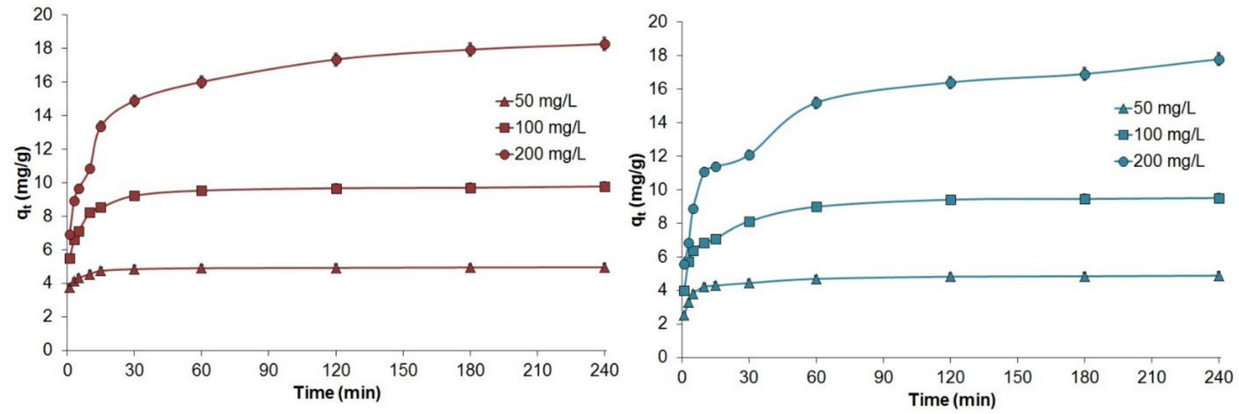
2.4. Desorption Study

Desorption tests of *Cladium mariscus* saw-sedge and sawdust adsorbents were performed using the batch technique at 20 °C (laboratory shaker Elpin Plus 358A, Elpin Plus, Poland). Adsorbents loaded with BB3 dye (sorption conditions: C_0 = 100 mg/L, V = 20 mL t = 240 min m = 0.2 g) was added to conical flasks containing 50 mL of 0.1 M HCl, 0.1 M NaOH or 0.1 M NaCl, and stirred for 240 min. The dye concentration after desorption test was determined spectrophotometrically at the maximum absorbance wavelength in order to calculate the regeneration efficiency (%RE) of the adsorbent.

3. Results and Discussion

3.1. Kinetic Adsorption

In the case of adsorption application for the removal of industrial dyes, it is pivotal to evaluate kinetic parameters that can facilitate process designing under real conditions. Kinetic models are based on determination of the amount of adsorbate retained per gram of adsorbent as a function of time (q_t). The comparison of the amounts of BB3 removed from aqueous solutions of different initial dye concentrations (50, 100, and 200 mg/L) at a specified time intervals (from 1 to 240 min) by the sawdust and *Cladium mariscus* saw-sedge is presented in Figure 1.



(**a**) (**b**)

Figure 1. Adsorption of BB3 onto (**a**) sawdust and (**b**) *Cladium mariscus* saw-sedge a function of phase contact time and dye initial concentration.

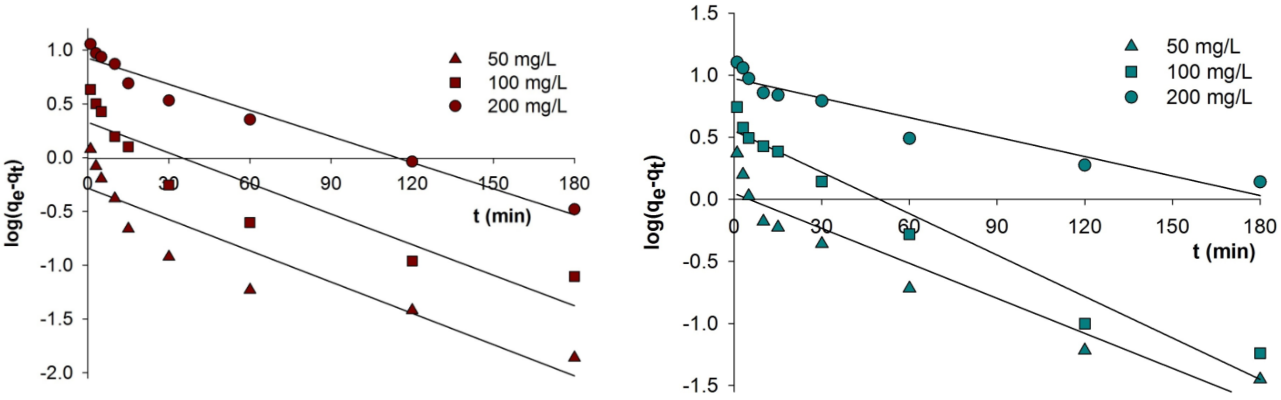
The equilibrium state for both biosorbents was practically attained after 60 min in the case of solutions containing 50 mg/L and 100 mg/L of BB3. Increasing the initial BB3 concentration to 200 mg/L increases phase contact time necessary to reach equilibrium (up to 240 min).

The pseudo-first order kinetic model (PSO) introduced by Lagergren [25], the pseudo-second order kinetic model (PSO) defined by Ho and McKay [26] as well as intraparticle diffusion model (IP) by Weber and Morris [27] were applied for determination of kinetic parameters and adsorption mechanism. According to the assumptions of PFO kinetics, the rate of reaction is directly proportional to the logarithmic difference between the equilibrium capacity and the amount of adsorbate retained by the adsorbent at a given time. The Lagergren model is described by Equation (3):

$$log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \tag{3}$$

where q_e is the amount of BB3 adsorbed at equilibrium (mg/g), q_t is the amount (mg/g) of BB3 retained at time t, and k_1 is the adsorption rate constant from PFO kinetic model (1/min).

The equilibrium adsorption capacity (q_e) as well as the pseudo-first order adsorption rate constant (k_1) were calculated using the experimentally based plot log(q_e-q_t) vs. t (Figure 2). Table 2 presents the values of kinetic adsorption rate constants (k_1) determined for depending on the concentrations of BB3.



(**a**) (**b**)

Figure 2. Pseudo-first order kinetic model for BB3 adsorption on (**a**) sawdust and (**b**) *Cladium mariscus.*

Table 2. Pseudo-first order, pseudo-second order, and intraparticle diffusion kinetic parameters for adsorption of BB3 onto sawdust and *Cladium mariscus* saw-sedge.

Kinetic Model	Parameter	Initial Concentration of BB3 (mg/L)					
		50	100	200	50	100	200
		Sawdust			*Cladium mariscus*		
	$q_{e,exp}$ (mg/g)	4.96	9.77	18.26	4.87	9.51	18.28
PFO	$q_{e,cal}$ (mg/g)	0.52	2.13	8.40	1.12	3.57	9.40
	k_1 (1/min)	0.022	0.022	0.019	0.022	0.026	0.012
	r^2	0.844	0.854	0.966	0.906	0.959	0.914
PSO	$q_{e,cal}$ (mg/g)	4.96	9.82	18.50	4.90	9.64	18.24
	k_2 (g/mg min)	0.27	0.06	0.01	0.11	0.03	0.01
	h (mg/g min)	6.74	5.52	3.31	2.564	2.732	2.201
	r^2	0.999	0.999	0.999	0.999	0.999	0.996
IP	k_{ip} (mg/g $min^{0.5}$)	0.069	0.290	1.010	0.103	0.485	0.896
	C_{ip}	4.41	7.39	8.66	3.88	5.29	7.88
	r^2	0.781	0.926	0.844	0.999	0.986	0.929

The determination coefficients (r^2) calculated from the PFO kinetic model for sawdust are in the range 0.844–0.966, but in the case of *Cladium mariscus* saw-sedge they varied from 0.906 to 0.959 for the analyzed initial concentrations. This points to the average fit of the PFO equation to the experimental sorption data. Amounts of BB3 adsorbed at equilibrium obtained from the calculations ($q_{e,cal}$) also differed from those determined experimentally ($q_{e,exp}$). Distinctly, much better fitting was detected using the PSO model, which is discussed in the next paragraph.

The pseudo-second order kinetics are presented by Equation (4):

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

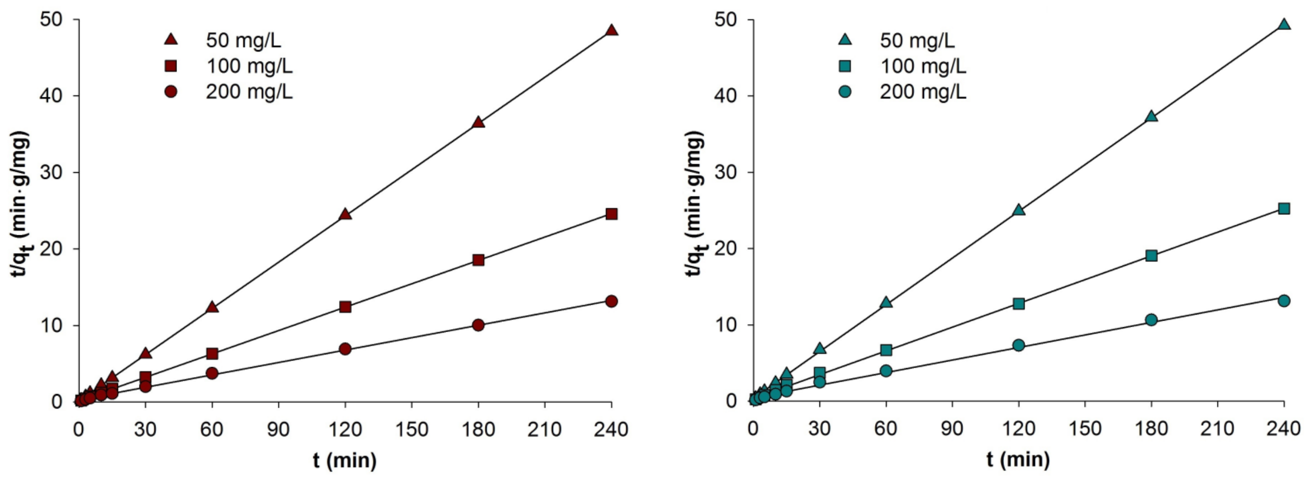
where q_e and q_t are the amounts (mg/g) of BB3 adsorbed at equilibrium and at time t (min), respectively, and k_2 is the adsorption rate constant of the PSO adsorption (g/mg min).

The initial adsorption rate, h (mg/g min) is denoted as (5):

$$h = k_2 q_e^2 \quad (5)$$

The k_2 and q_e values can be calculated from the dependence of t/qt vs. t.

Adsorption kinetics of BB3 using sawdust and *Cladium mariscus* saw-sedge as effective biosorbents from solutions of the initial concentrations 50–200 mg/L were very well described using the PSO kinetic model. This was evidenced by the values of determination coefficients (r^2) of the plot t/q_t vs. t (Figure 3). Independent of the BB3 initial concentration and the applied adsorbent, they were 0.999. It should be also stressed that the calculated amounts of BB3 retained by the biosorbents ($q_{e,cal}$) based on the PSO kinetic model were consistent with the experimental data ($q_{e,exp}$). In the case of the initial sorption rate (h), a growing tendency with the increasing adsorbate concentration was not observed, which can be associated with heterogeneity of the biosorbents of natural origin. However, k_2 determined by means of the applied model decreases with the increasing initial concentration of BB3.



(**a**) (**b**)

Figure 3. Pseudo-second order kinetic model for BB3 adsorption on (**a**) sawdust and (**b**) *Cladium mariscus.*

Other scientists also determined adsorption kinetics of BB3 as compatible with the PSO equation using various adsorbents [15–19,31,32]. The kinetic parameters obtained by them are depicted in Table 3.

Table 3. The kinetic parameters describing the adsorption of BB3 on the selected adsorbents.

Adsorbent	Type of Kinetic	r^2	k_1 or k_2 (1/min) or (g/mg min)	BB3 Concentration (mg/g)	Ref.
Bacillus catenulatus	PFO	0.986	0.17	500	[15]
Sphagnum Magellanicum peat	PSO	0.999	0.08	50	[16]
		0.999	0.02	100	
		0.999	0.01	200	
Spirogyra sp. biomass	PSO	0.999	0.03	15	[17]
Pomelo peel	PSO	0.997	0.04	20	[18]
		0.999	0.03	30	
		0.996	0.01	40	
Activated carbon	PSO	0.990	0.001	20	[19]
Chitosan-based adsorbent	PSO	0.994	0.02	20	[32]
Sawdust	PSO	0.999	0.27	50	This study
		0.999	0.06	100	
		0.999	0.01	200	
Cladium mariscus saw-sedge	PSO	0.999	0.11	50	This study
		0.999	0.03	100	
		0.996	0.01	200	

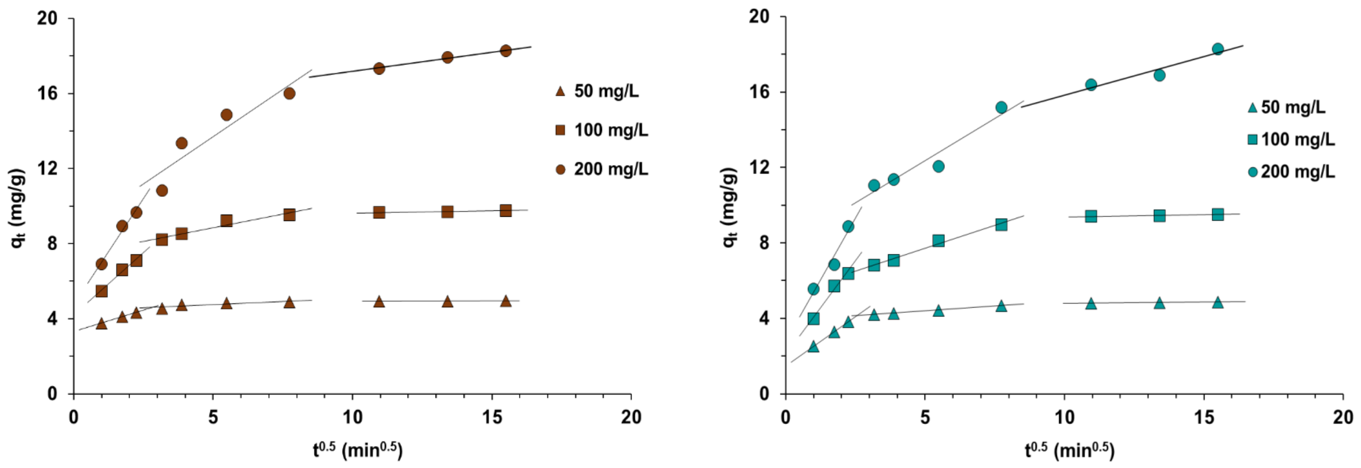
The intraparticle diffusion model (IP) was proposed by Weber and Morris in 1962 and is described by the following Equation (6) [27]:

$$q_t = k_{ip}t^{0.5} + C_{ip} \tag{6}$$

where k_{ip} (mg/g min$^{0.5}$)—intraparticle diffusion rate constant, C_{ip}—intercept.

It is mainly used to describe the process of adsorption occurring on highly porous adsorbents. The rate limiting step of the sorption process is the diffusion of adsorbate in the pores of the adsorbent particles, and the influence of other processes on the total speed of the process can be neglected.

In the case of BB3 adsorption on selected biosorbents, the q_t vs. $t^{0.5}$ plot presented in Figure 4 shows a multi-linearity, in which three stages can be distinguished. The first part of the plot can be attributed to BB3 adsorption on the surface of the sawdust and *Cladium mariscus* saw-sedge. The second stage is gradual adsorption, where intraparticle diffusion limits the speed of the dye uptake. The third part corresponds to the final equilibrium state, in which BB3 molecules move from larger pores to micropores, which makes the sorption slower.



(**a**) (**b**)

Figure 4. Intraparticle diffusion kinetic model for BB3 adsorption on (**a**) sawdust and (**b**) *Cladium mariscus*.

The k_{ip} and C_{ip} (proportional to the film thickness surrounding the adsorbent particles) as well as r^2 calculated in the investigated systems are listed in Table 2. The intraparticle rate constants for BB3-sawdust were found to be in range of 0.069–1.010 mg/g $min^{0.5}$ and C_{ip} increased from 4.41 to 8.66 mg/g with increased concentration of BB3 from 50 to 200 mg/L. However, r^2 vales were lower compared with the PSO model, which indicates that the intraparticle diffusion is not an important step to limit the adsorption rate. In case of BB3 adsorption on the *Cladium mariscus* saw-sedge, r^2 were higher (from 0.929 to 0.999) which means that the intraparticle diffusion has a significant impact on the dye adsorption rate.

3.2. Isotherm of Adsorption

Adsorption isotherms describe the process parameters in equilibrium. An indispensable element of dyestuff removal from aqueous solutions is the fitting of the obtained experimental data to a proper model of isotherms [33]. The analysis of the adsorption isotherms provides valuable information about the process character and mechanism. The Freundlich [28], Langmuir [29], and Temkin [30] models were applied for determination of adsorption isotherms of BB3 on sawdust and *Cladium mariscus* saw-sedge. The studies were carried out as a function of different temperatures (20, 30, 40, and 50 °C).

The Langmuir isotherms model assumes the monolayer adsorption covering. The number of adsorbed molecules corresponds to that of active centers on the adsorbent surface. Based on the above assumptions the equation of the Langmuir isotherm is as follows (7):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{7}$$

where Q_0 is the maximum BB3 uptake (mg/g), b (L/mg) is the Langmuir constant, and C_e is the equilibrium concentration of BB3 (mg/L).

The Freundlich isotherm model is most frequently used for description of the adsorption process proceeding on the adsorbents characterized by the heterogeneous structure. The model of Freundlich isotherm is described by Equation (8):

$$\log q_e = log k_F + \frac{1}{n} log C_e \tag{8}$$

where k_F (mg/g) and n are the Freundlich constants, and C_e is the equilibrium concentration of BB3 (mg/L).

If $n < 1$, adsorption is of a chemical character, while $n > 1$ adsorption is of a physical character.

As follows from the Temkin isotherm model, the sorbent surface is heterogeneous and a drop in adsorption heat is associated with the adsorbent–adsorbate interactions. This is described by Equation (9):

$$q_e = \left(\frac{RT}{b_T}\right)\ln A + \left(\frac{RT}{b_T}\right) lnC_e \quad (9)$$

where R is the gas constant (8.314 J/mol K), T is the temperature (K), A (L/g) and b_T (J/mol) are the Temkin constants, and C_e is the equilibrium concentration of BB3 (mg/L).

Figures 5–7 illustrate the fitting of the equilibrium data to the aforementioned models. The parameters of the Langmuir, Freundlich and Temkin isotherms, calculated from the following graphs: C_e/q_e vs. C_e, log q_e vs. log C_e and q_e vs. ln C_e are listed in Table 4.

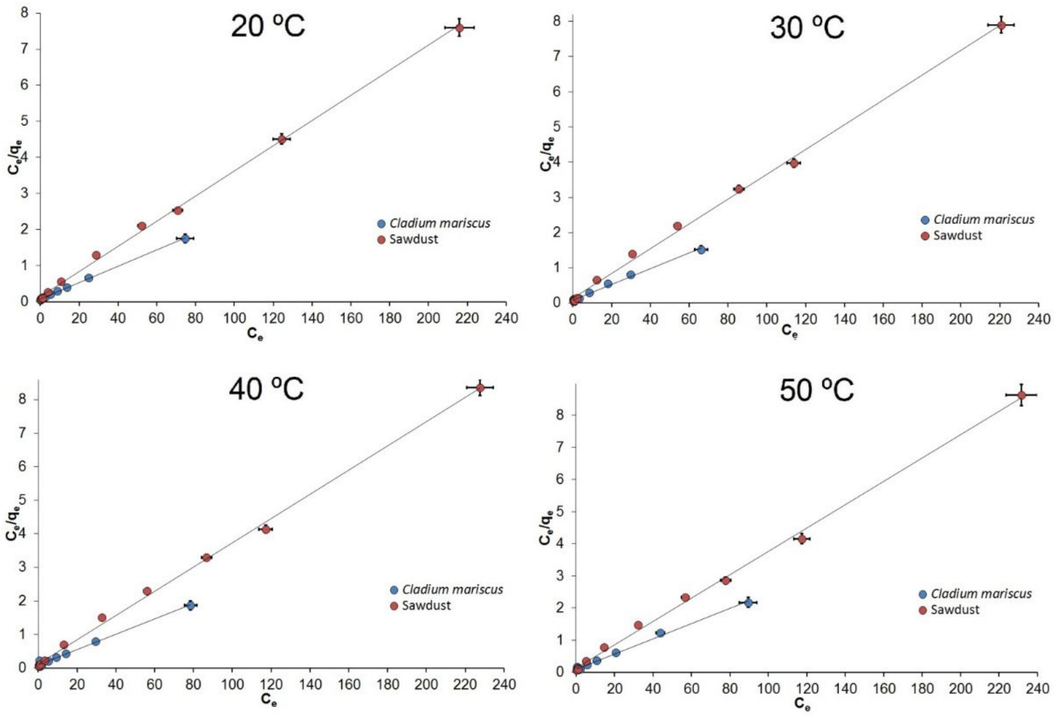


Figure 5. Langmuir isotherm model for BB3 adsorption on sawdust and *Cladium mariscus* saw-sedge at different temperatures.

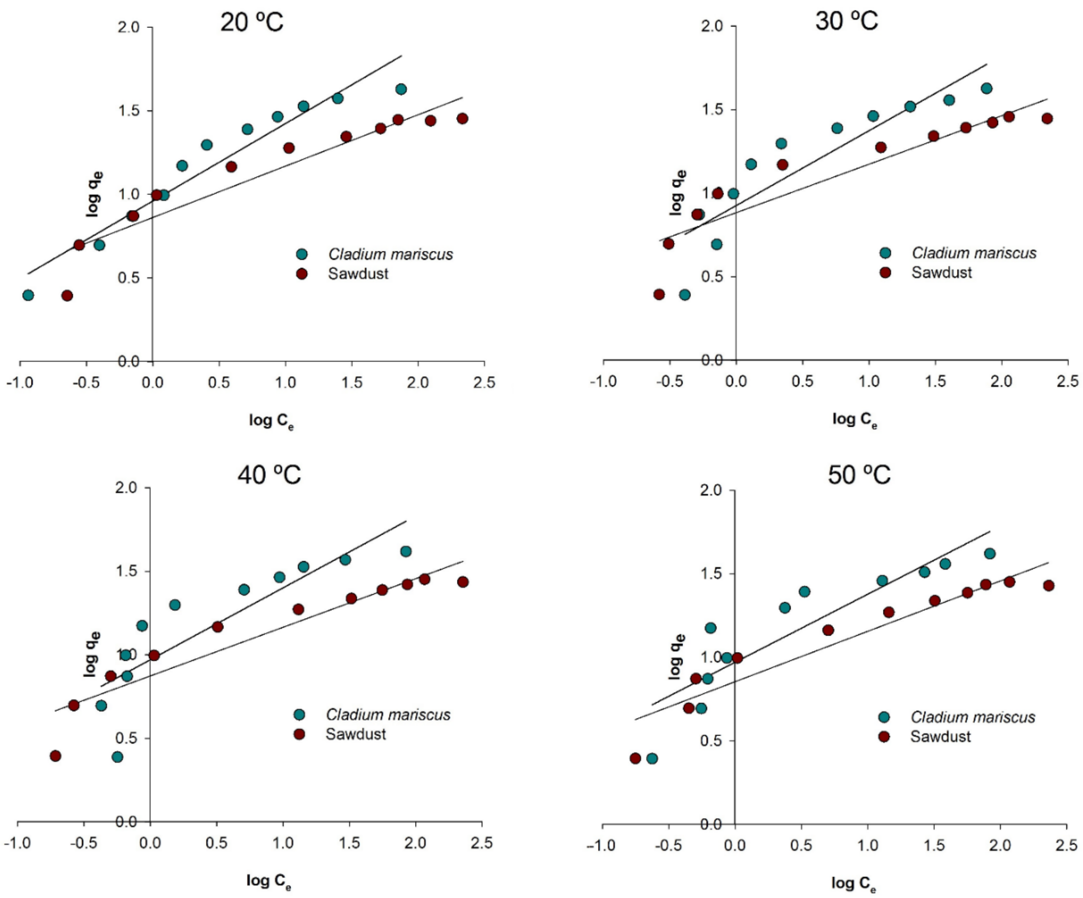


Figure 6. Freundlich isotherm model for BB3 adsorption on sawdust and *Cladium mariscus* saw-sedge at different temperatures.

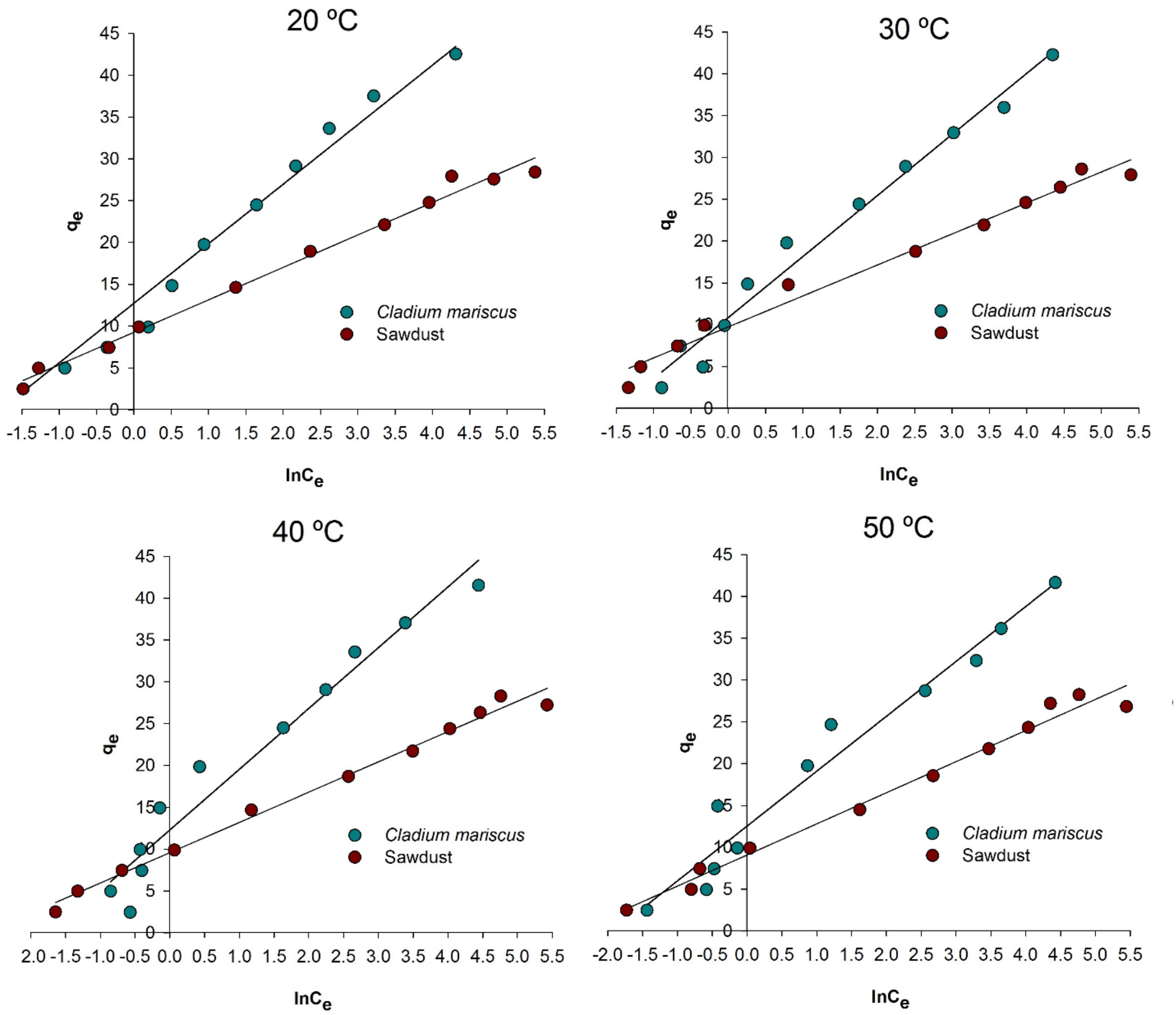


Figure 7. Temkin isotherm model for BB3 adsorption on sawdust and *Cladium mariscus* saw-sedge at different temperatures.

Table 4. Isotherm constants for BB3 adsorption on sawdust and *Cladium mariscus* saw-sedge at 20–50 °C.

Adsorbent	T (°C)	Langmuir Parameters			Freundlich Parameters			Temkin Parameters		
		r^2	Q_0 (mg/g)	b (L/mg)	r^2	k_F (mg/g)	n	r^2	b_T (J/mol)	A (L/g)
Sawdust	20	0.999	28.69	0.26	0.891	7.27	3.25	0.990	638.02	10.87
	30	0.998	28.35	0.27	0.848	7.64	3.45	0.982	668.02	13.81
	40	0.998	27.73	0.28	0.888	7.47	3.44	0.990	684.09	14.06
	50	0.998	27.50	0.29	0.901	7.14	3.32	0.983	665.29	11.47
Cladium mariscus	20	0.999	44.29	0.28	0.929	9.12	2.16	0.966	347.91	5.98
	30	0.994	44.62	0.27	0.819	9.49	2.24	0.970	337.51	5.77
	40	0.991	43.93	0.25	0.740	9.32	2.30	0.958	331.55	5.24
	50	0.995	42.07	0.23	0.795	8.48	2.31	0.975	352.66	4.74

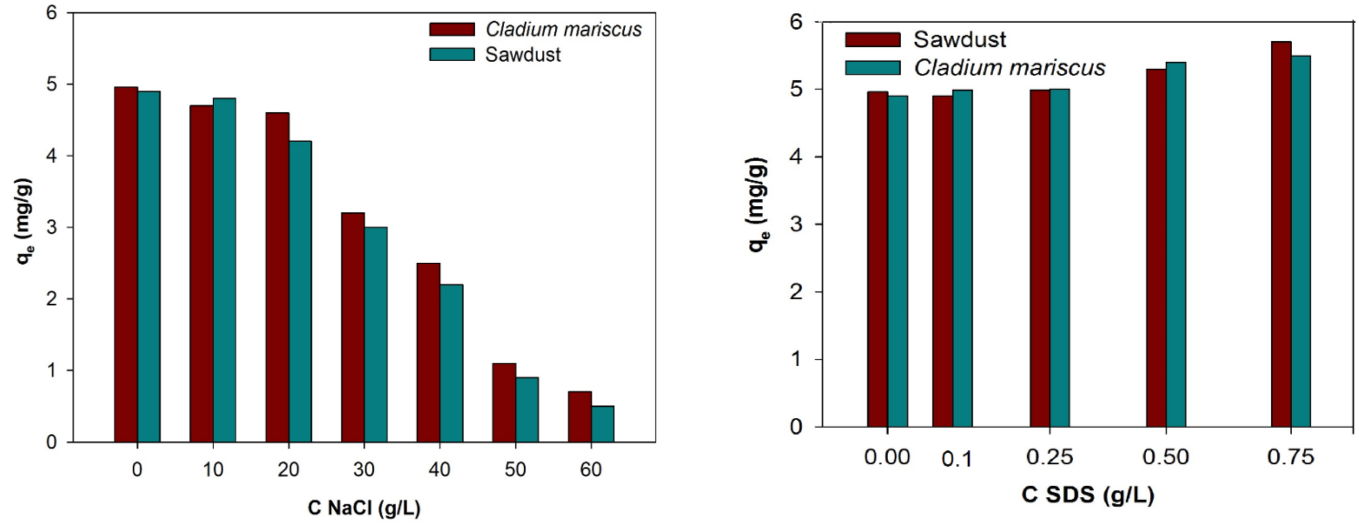
The analysis of the results shows that adsorption of BB3 independent of temperature was best fitted by the Langmuir model using both sorbents: sawdust and *Cladium* *mariscus* saw-sedge, which was confirmed by the high values of r^2 (0.998–0.999). In the case of the Freundlich model, the r^2 values were lower, i.e., in the range 0.740–0.891. The Langmuir model allowed to determine the monolayer sorption capacities of the adsorbents—28.69 mg/g for sawdust and 44.29 mg/g for *Cladium mariscus* (at 20 °C). The comparison of the maximum monolayer adsorption capacity of other adsorbents for BB3 based on the literature review is presented in Table 5. Comparison of the sorption capacities of other materials of natural origin with respect to sawdust and *Cladium mariscus* saw-sedge supported the applicability of the undertaken studies. It should be mentioned that sorption properties of adsorbents of natural origin are largely conditioned by geographical situation. While determining the isotherms using the Freundlich model, there was also estimated the heterogeneity coefficient (n), which, independent of the adsorbent and temperature, assumed a value above 1. This indicates the physical character of adsorption. Taking into consideration the values of the Temkin constant b_T pertaining to the sorption capacity with respect to sorption heat, it can be stated that the value of sorption heat increases (linearly) in the layer. The reason may be interactions between the adsorbent and the adsorbate molecule being in contact with it. As follows from the experimental data, this parameter reached the value 638.02 J/mol for sawdust and 347.91 J/mol for *Cladium mariscus* and saw-sedge.

Table 5. Comparison of adsorption capacity of low-cost adsorbents towards BB3.

Kind of Adsorbent	q_m (mg/g)	Ref.
Green algal *Spirogyra* sp.	71.4	[17]
Cladium mariscus sew-sedge	44.4	This study
Sphagnum Magellanicum Peat	40.6	[16]
Quaternized sugar cane bagasse	37.6	[2]
Activated sludge biomass	36.5	[1]
Sawdust	28.7	This study
Pomelo peel	23.9	[18]
Sugarcane bagasse	23.6	[18]
Ethylenediamine-modified rice hull	3.29	[5]
Wood activated charcoal	0.59–0.64	[20]

3.3. Salt and Surfactant Impact on BB3 Uptake

Textile wastewaters often contain a number of metal ions, salts, surfactants, organic and inorganic acids and bases, as well as reducing and oxidizing agents. Depending on intensity of dyeing, the amounts of these substances in dyeing baths can be added in a wide range from 30 to 1500 g/kg of fabrics [24]. Additives remain in wastewaters at the level close to the initial concentration (part deposits on the textile) as they do not wear but only create proper conditions for dyeing. Therefore, the additives can influence the dyes sorption process. BB3 adsorption on both sorbents was slightly negatively affected with an increase in NaCl concentration from 10 to 30 mg/L. When the sodium chloride concentration was higher than 40 g/L, the amount of BB3 retained by both biosorbents dropped gradually due to a competition between the chloride anions and the dyestuff anions (Figure 8).



(**a**) (**b**)

Figure 8. Influence of (**a**) NaCl and (**b**) SDS concentration on BB3 uptake by sawdust and *Cladium mariscus* saw-sedge.

Similar results were described by Dogan et al. [34] who studied the adsorption of Maxilon Yellow 4 GL and Maxilon Red GRL dyes on kaolinite in the presence of NaCl, as well as by Genc and Oguz [35] who investigated C.I. Acid Yellow 99 and C.I. Acid Red 183 removal by granulated blast furnace slag and furnace bottom ash in the presence of KCl. In the system containing 100 mg/L BB3 and 25–100 g/L NaCl, there were not observed essential changes in the capacities of Amberlite XAP 1180 and Dowex Optipore SD2 despite relatively large amounts of salt in the order 100 g/L, but in the case of the cation exchanger Lewatit MonoPlus SP112, the capacity decreased with the increasing NaCl concentration [24].

Surface active substances such as SDS are applied in the textile industry for fiber chemical treatment. They decrease surface tension of water, increase fiber wettability, thus facilitating the same the dyestuff contact with the fabric surface and removal of dirt. In order to check the effect of SDS concentration on BB3 sorption, the SDS concentration was varied between 0.1 and 0.75 g/L while the initial dye concentration was maintained at 50 mg/L. The dye–surfactant aggregates (micelles) of various nature are formed in the system depending on the SDS concentration. They can undergo sorption and additionally increase capacity as was observed for the sorption of BB3 on sawdust and *Cladium mariscus* saw-sedge. In agreement with the paper by Janos and Šmídová [36], a crucial mechanism of dyes sorption in the presence of surfactants are hydrophobic interactions, the effect of which is the increase in their sorption. This phenomenon was also observed for the sorption of C.I. Acid Orange 7 and C.I. Basic Blue 9 on oxyhumolite [37], C.I. Basic Blue 9, C.I. Basic Greek 4, and C.I. Basic Violet 10 on the cheap sorbent formed in the reaction of humus acids with iron salts [38,39].

3.4. Thermodynamic Parameters of the Adsorption

The next section of the paper was the study of thermodynamic aspects of BB3 adsorption on sawdust and *Cladium mariscus* saw-sedge. The investigations were carried out at 20, 30, 40, and 50 °C. Therefore, the change in free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) was calculated from Equations (10) to (12):

$$\Delta G^o = -RT lnK_c \quad (10)$$

$$lnK_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (11)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (12)$$

where $\Delta G°$ is the change in free energy of the system (kJ/mol), $\Delta H°$ is the change in free enthalpy of the system (kJ/mol), $\Delta S°$ is the change in free entropy of the system (kJ/mol K), R is the gaseous constant (8.314 J/mol K), K_C is the reaction equilibrium constant (L/mg), and T is temperature (K).

Changes in enthalpy and entropy were calculated using the dependence ln K_c vs. $1/T$ (Figure 9), from the slope $(-\frac{\Delta H^o}{R})$ and intercept $\left(\frac{\Delta S^o}{R}\right)$ of the plot. The obtained results are presented in Table 6.

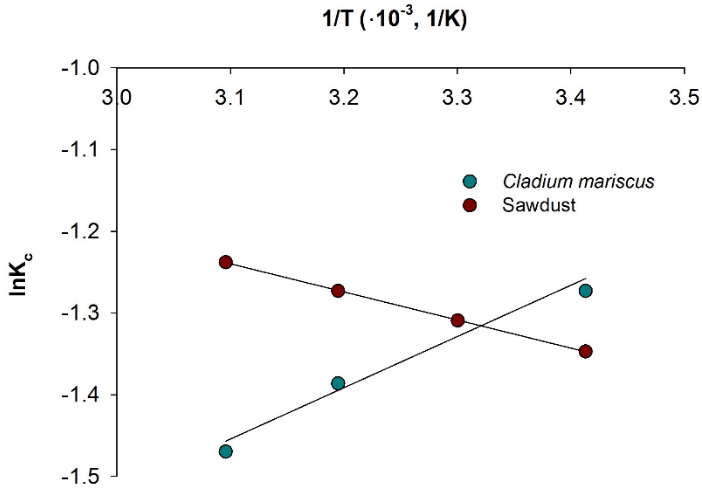


Figure 9. Estimation of thermodynamic parameters for the adsorption of BB3 onto sawdust and *Cladium mariscus* saw-sedge.

The positive values of $\Delta H°$ pinpoint the endothermic character of the process for sawdust. However, application of *Cladium mariscus* saw-sedge generate the negative value of $\Delta H°$ proving exothermic character of adsorption. Moreover, the capacity of a given material towards BB3 decreases insignificantly with the increasing temperature. The positive values $\Delta G°$ for BB3 adsorption at all four temperatures indicate the intrinsic sense of the process. With the increasing temperature, spontaneity of the process grows, which is consistent with the endothermic nature of the process.

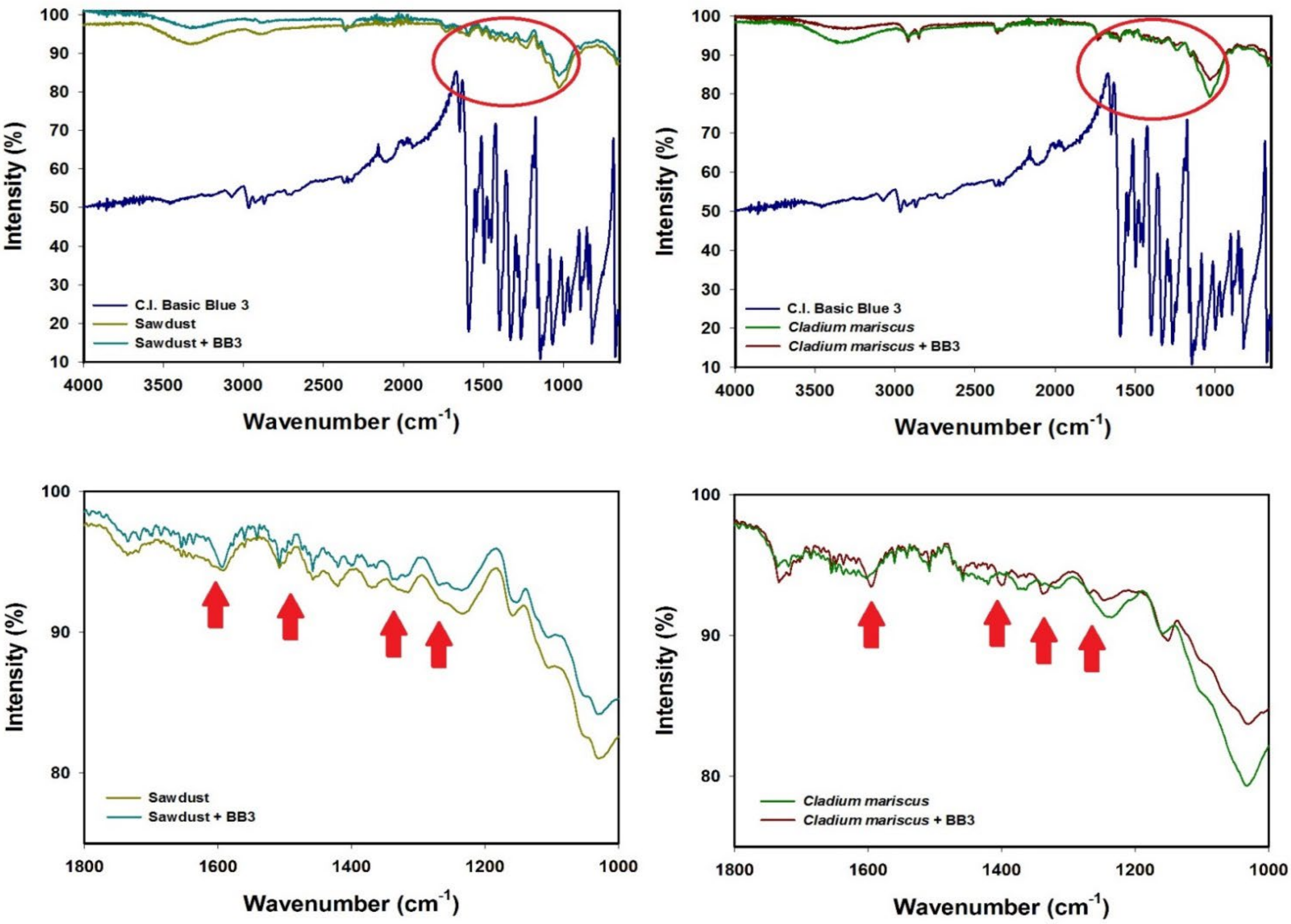
Table 6. Thermodynamic parameters of BB3 adsorption onto sawdust and *Cladium mariscus* saw-sedge.

Adsorbent	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)			
			20 °C	30 °C	40 °C	50 °C
Sawdust	2.83	−1.43	3.28	3.30	3.31	3.32
Cladium mariscus	−4.30	−28.28	3.10	3.30	3.61	3.95

What is more, negative values of entropy change ($\Delta S°$) in the discussed system describe randomness in the adsorbent and adsorbate interactions. Carrying out studies on BB3 adsorption on other materials the researchers obtained similar results. Barsanescu et al. [23] and Khataee et al. [17], in their analyses, determined thermodynamic parameters to acquire better knowledge about mechanism of BB3 adsorption on the weak acid acrylic resin and green algal *Spirogyra* sp. The results obtained by them also confirm the endothermic nature of the BB3 uptake. However, it should be highlighted that both research groups obtained positive values of entropy change, which might be caused by the greater randomness of interactions on the phase contact surface. The discrepancy in the $\Delta H°$ values may be due to the adsorbent's composition.

3.5. FT-IR Studies and Mechanism of Biosorption

The images presented in Figure 10 show the FT-IR spectra of BB3, *Cladium mariscus* saw-sedge, sawdust, and products after the BB3 adsorption by both materials. The obtained spectra exhibit the presence of a number of various signals; thus, the most important wavenumber range is presented in magnification. The FT-IR spectrum of BB3 displays the signals at 2951 and 2862 cm^{-1} related to the stretching vibrations of C–H bonds in the –CH_3 groups. Four signals in the wavenumber range 1600–1450 cm^{-1} can be assigned to the C_{Ar}=C_{Ar} vibrations of aromatic rings in the dye molecule. The signals related to the bending and deformational vibrations of C_{Ar}–H bonds are located at 1405 and 813 cm^{-1}, respectively. The spectra show also peaks at 1330 and 1145 cm^{-1} representing the asymmetric and symmetric vibrations of C–O–C bonds. The signal located at 1270 cm^{-1} refers to the C–N bonds.



(**a**) (**b**)

Figure 10. The FTIR spectra of BB3 and biosorbents before and after dye adsorption: (**a**) sawdust and (**b**) *Cladium mariscus* saw-sedge.

Based on the FT-IR spectra it can be concluded that *Cladium mariscus* saw-sedge and sawdust exhibit a similar chemical structure, mainly composed of cellulose, hemicellulose, and lignin. The evidence of this is occurrence of the signals at 2940 cm^{-1} attributed to the stretching vibrations of C–H bonds and those in the range 1550–1450 cm^{-1} related to the vibrations of C=C aromatic bonds [40]. Additionally, the signal at 1233 cm^{-1} in the sawdust spectrum can be assigned to the presence of the hemicellulose units [41]. It is worth emphasizing that in the spectrum of *Cladium mariscus* saw-sedge signals at 3425, 1739, and 1243 cm^{-1} indicate the presence of –OH groups, C=O, and C–OH bonds, respectively. Whereas in the sawdust spectra, the peaks at 3410, 1732, and 1031 cm^{-1} confirm the presence of similar functional groups in this material. Occurrence of hydroxyl and carbonyl groups in the structure of the sorbents facilitates effective adsorption of BB3 [42].

The results of the FT-IR analysis after dye sorption on the natural materials indicate changes arising from the attachment of BB3. Among others, in these spectra, the signals in the wavenumber range 1600–1400 cm^{-1} related to the C_{Ar}=C_{Ar} stretching vibrations of aromatic bonds can be observed (changes are shown with arrows). These signals possess maxima at the same wavenumber as the spectrum of the dye. Additionally, there are also bands at 1340 and 1270 cm^{-1}, assigned to the C–O–C and C_{Ar}–N bonds (changes are shown with arrows). The presence of these signals, characteristic of the structure of BB3, confirmed the effective sorption of the dye. Moreover, in the spectra of biosorbents after BB3 adsorption, decrease in the intensity of the bands related to the –OH and C=O groups can be observed. This fact indicates that these groups are predominantly involved in the dye removal.

3.6. Desorption Study

Desorption test is a very important aspect in the adsorption technique as it shows the potential regeneration of the adsorbent and possibility of its reuse. This is very important parameter, which confirms adsorbate/adsorbent interactions. Regeneration experiments were performed using different eluting agents: 0.1 M HCl, 0.1 M NaOH, and 0.1 M NaCl. The efficiency of the desorption process was low for all the eluting agents used (did not exceed 6%) for *Cladium mariscus* saw-sedge, the values of %RE were equal to 3.2% (HCl), 5.1% (NaOH), and 3.0% (NaCl). However, for sawdust, the values of %RE were equal to 2.8% (HCl), 4.4% (NaOH), and 2.7% (NaCl).

4. Conclusions

The paper presents the studies on adsorption of BB3 from an aqueous solution on the two bio-waste adsorbents: *Cladium mariscus* saw-sedge and sawdust. The PSO kinetic model described adsorption of BB3 onto *Cladium mariscus* saw-sedge and sawdust better than the PFO or IP. The sorption capacities (Q_0 obtained from the Langmuir model) were found to be 28.69 mg/g for sawdust and 44.29 mg/g for *Cladium mariscus* saw-sedge (at room temperature). The values of Q_0 decrease insignificantly with the temperature increase. Increasing the sodium chloride concentration in the system from 10 to 60 g/L in the presence of 50 mg/L BB3, there was observed a decrease in the q_e values. The presence of an additive such as sodium dodecyl sulfate caused an increase in the capacities of *Cladium mariscus* saw-sedge and sawdust. Positive values of ΔG were obtained in the temperature range 20–50 °C and proved the spontaneity of BB3 adsorption on both sorbents. The FT-IR studies revealed different types of interactions between BB and the biosorbents under investigation.

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