USE OF SAWDUST IMMOBILISED ON CHITOSAN FOR DISPOSAL OF DYES FROM WATER SOLUTIONS

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Abstract

In this article, the sorption properties of chitosan hydrogel beads, beech sawdust and sawdust immobilised on chitosan in relation to Reactive Black 5 (RB5) and Basic Violet 10 (BV10) dyes were compared. In the conducted research, the sorption capacities of the sorbents, sorption pH and the point of zero charge (pH_{ZPC}) were determined. For the description of the obtained results, the double Langmuir model has been used. The highest effectiveness of the cationic and anionic dye removal on chitosan hydrogel beads and sawdust immobilised on chitosan was obtained at pH 4, whereas on sawdust, the pH was 3. The best sorbent in relation to the RB5 dye was obtained using chitosan hydrogel beads, and in relation to BV10, it was sawdust. The maximum sorption capacity of chitosan in relation to RB5 was 875.66 mg/g, whereas the sorption capacity of sawdust in relation to BV10 was 30.15 mg/g. The research has shown that the sorbent in the form of sawdust immobilised on chitosan had a high sorption capacity in relation to anionic as well as cationic dyes. Immobilisation of sawdust on chitosan led to the creation of a universal sorbent in relation to cationic and anionic dyes.

Key words: *sorption, chitosan, sawdust, immobilisation, Reactive Black 5, Basic Violet 10*

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1. Introduction

Dyes are widely used i.a. in the textile, tanning, paper, food and pharmaceutical industries. Along with the development of technology and industry, more attention is being paid to water pollution caused by dyes. It is estimated that the world production of dyes has reached almost 10^6 tons per year [1]. Because of the high solubility of dyes and low susceptibility of certain materials for staining, up to 50% of dye is released into wastewater after the dyeing process [2]. The dyes in an aqueous environment are visible even at low concentrations (1 mg/dm^3) and may significantly disturb the process of photosynthesis [3]. The majority of coloured substances are minimally biodegradable, so the discolouration of waste water using biological methods is not effective. The effectiveness of industrial wastewater decolourisation with the use of conventional systems of wastewater treatment rarely exceeds 50–60% [4].

The effective wastewater decolourisation methods include physico-chemical methods, such as coagulation, ozonation and ultra/nanofiltration. However, these methods have many disadvantages: the drawbacks of coagulation are the creation of large amounts of sludge and the increase in salinity wastewater [5]; for ozonation, there is a risk of incomplete oxidation of dyes [6]; and for ultra/nanofiltration, there is the high price and the requirement of pre-treatment of wastewater [7].

One of the more efficient and environmentally friendly methods for the removal of dyes from wastewater is the sorption process. Among the various techniques used for the discolouration of wastewater, sorption can be classified into methods that do not require large investments. Despite this, practical application of these methods encounters a number of limitations: primarily, the high cost of sorbents and difficulties in its application and regeneration. Thus, much research is focused on finding cheap and effective sorbents [8].

Chitosan sorbents can be an alternative for the commonly used active carbon. Chitosan is obtained chemically from chitin, which is extracted from the waste products of industrial processing of seafood [9]. Due to its cationic character, chitosan is characterised by a high ability to remove acid and reactive dyes, whereas it shows a low affinity towards cationic dyes.

Cheap and widely available natural products and waste from industry and agriculture can be used as sorbents with a high ability to remove cationic dyes. Sawdust can be an alternative sorbent, having a high affinity towards cationic dyes due to its high content of cellulose, hemicellulose and lignin rich in hydroxyl groups [10,11]. However, this product, in contrast to chitosan sorbents, has a very low sorption capacity with respect to anionic dyes. A major drawback of sawdust is also the difficulty in separating them from the purified solution, limiting its practical usage.

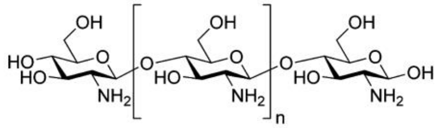
In order to obtain a universal sorbent that has a high sorption capacity towards both anionic and cationic dyes, immobilisation of sawdust on chitosan hydrogel beads is proposed in the present paper. This study involved comparing the sorption properties of chitosan hydrogel beads, sawdust, and sawdust immobilised on chitosan with respect to Reactive Black 5 and Basic Violet 10 dyes.

2. Materials and methods

2.1 Chitosan

Chitosan used in the study came from the Heppe Medical Chitosan GmbH in Halle (Germany). The chitosan specification provided by the manufacturer is presented in the Table 1.

Table 1. The chitosan specification

	Chitosan
Structural formula	
Deacetylation degree	82.6–87.5% (average of 85.0%)
Origin of the material	Shrimp shells

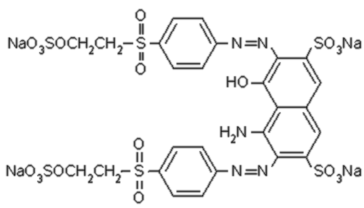
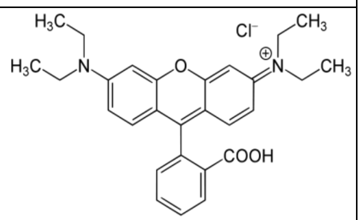
2.2 Sawdust

Beech sawdust to be used in the study, provided by the "Kaczkan" (Poland) company, is a waste product from wooden floor production. Moisture content in the material reaches 7% (w/w). The composition of the product is as follows (expressed in % (w/w) of dry matter): 41.0% cellulose, 27.9% hemicellulose, 26.7% lignin, 0.1% ash, ca. 4.3% extracts and other components.

2.3 Dyes

Both Reactive Black 5 (RB5) and Basic Violet 10 (BV10) dyes used in the study were purchased at the "Boruta" Dye Production Plant, SA (Poland). The characteristics of the above dyes are provided in Table 2.

Table 2. Characteristics of dyes used in the study

Dye name	**Reactive Black 5 (RB5)**	**Basic Violet 10 (BV10)**
Structural formula		
Molecular weight	991 g/mol	479 g/mol
ë$_{max}$	600 [nm]	554 [nm]
Character of dye	acidic (anionic – reactive)	basic (cationic)

3. Methods

3.1. Preparation of chitosan sorbent in the form of hydrogel beads

Chitosan in an amount of 25 g d.m. was dissolved in 975 g of a 5% acetic acid solution. The obtained chitosan mixture was added to a 2 M solution of sodium hydroxide. Chitosan solution in 2 M NaOH was immediately subjected to the gelling process. The formed hydrogel beads were left in the solution of NaOH for 24 hours.

Afterwards, the chitosan beads were rinsed with distilled water to remove the remaining NaOH from their surface. The appearance and form of sorbents are shown in Fig. 1.

CHITOSAN HYDROGEL BEADS

SAWDUST

IMMOBILIZATION OF SAWDUST ON CHITOSAN HYDROGEL BEADS (mass ratio 1:1)

Figure 1. The appearance and form of sorbents

3.2 Preparation of sawdust

Beech sawdust was sifted in order to isolate a single fraction, and then it was washed with 2 M sulfuric acid to remove water-soluble substances. The reaction lasted 24 hours; after that time, the sawdust was washed with 1 M NaOH and then with distilled water to reach the pH of the filtrate – 7.0. The sorbent was then dried in an oven at 110°C.

3.3 Preparation of chitosan–sawdust beads

After the initial preparation, sawdust was added in an amount of 25 g to a chitosan gel, having a role of a carrier, prepared from 25 g of dry mass of chitosan dissolved in 5% acetic acid. The obtained mixture was added dropwise to a 2 M NaOH solution to form the beads. The beads were left for 24 hours in the solution of sodium hydroxide and then washed with distilled water to remove the remaining NaOH.

3.4 Study on the pH impact on dye sorption efficiency

An amount of 1 g d.m. of each sorbent was weighed in 250 cm^3 conical flasks and then a dye solution (200 cm^3) at pH 2.0–11.0 was added. The flasks were placed on a shaker (150 rpm). After 2 hours of the sorption process, the solution samples were taken (10 cm^3) to determine the concentration of the remaining dyes. Study parameters are summarised in Table 3.

Table 3. Parameters of the research on the optimal pH of the sorption of dyes

Sorbent concentration [g/dm^3]	Dye	Sorbat concentration [mg/dm^3]	Tested pH of the sorption [pH]	Sorption time [h]
5	RB5	100	2, 3, 4, 5, 6, 7, 8, 9, 10, 11	2
5	BV10	10	2, 3, 4, 5, 6, 7, 8, 9, 10, 11	2

3.5 Determination of the maximum sorption capacity

An amount of 1 g d.m. of each sorbent was weighed, along with 200 cm^3 of solution of the tested sorbate, in 250 cm^3 conical flasks. Solutions had optimal pH set out in point of 3.4 of the article. The flasks were placed on a shaker (200 rpm). After 24 and 72 hours, the dye concentration remaining in the solution was marked. Based on these results, the maximum sorption capacity of sorbents was determined. Parameters of these studies are summarised in Table 4.

Table 4. Research parameters to determine the maximum capacity three sorbents in relation to RB5 and BV10

Sorbent concentration [g/dm^3]	**Sorbent**	**Sorbat**	**Sorbat concentration [mg/dm^3]**	**Sorption time [h]**
5	Chitosan beads	RB5	10, 25, 50, 100, 200, 300, 500, 750, 1000, 1500, 2000	24/72
	Sawdust		10, 25, 50, 100, 200, 300, 500, 750, 1000, 1500, 2000	24/72
	Chitosan–sawdust beads		10, 25, 50, 100, 200, 300, 500, 750, 1000, 1500, 2000	24/72
5	Chitosan beads	BV10	1, 2, 5, 10, 25, 50, 75, 100, 150, 200	24/72
	Sawdust		1, 2, 5, 10, 25, 50, 75, 100, 150, 200	24/72
	Chitosan–sawdust beads		1, 2, 5, 10, 25, 50, 75, 100, 150, 200	24/72

3.6 Determination of zeta factor

In order to determine the pH_{ZPC} of sorbents, 50 ml of 0.01 M KNO_3 solution with an initial pH (pH_0) of 3–12 was added to the conical flask. To each flask, 1 g of sorbent was also added, and then the mixture was stirred for 24 hours. After this time, the final pH of the solution was measured. The pH_{ZPC} value was determined based on the curve. The zero point for beech sawdust was located at the intersection of the curve defining the relationship of ÄpH and pH_0 with the axis of a graph on which pH_0 is marked [12].

3.7 Computational methods

The amount of dye absorbed was calculated using equation (1):

$$\mathbf{Qs} = \frac{(\mathbf{Co} - \mathbf{Cs}) \cdot \mathbf{V}}{\mathbf{m}} \tag{1}$$

where:

Qs – mass of dyes sorbed [mg/g]
Co – the initial concentration of dye [mg/dm^3]
Cs – concentration of dyes after sorption [mg/ dm^3]
V – volume of the solution [dm^3]
m – mass of the sorbent [g]

To determine the maximum sorption capacity, three different models of sorption were used. The homogeneous Langmuir model (2):

$$q_e = \frac{q_{max} \cdot K_c \cdot C}{1 + K_c \cdot C} \qquad (2)$$

where:

q_e – equilibrium amount of dyes absorbed [mg/g]
q_{max} – maximum sorption capacity of sorbent monolayer [mg/g]
K_c – constants in Langmuir equation [dm^3/mg]
C – concentration of dyes remaining in the solution [mg/dm^3]

Double Langmuir model (3):

$$Q = \frac{b_1 \cdot K_1 \cdot C}{1 + K_1 \cdot C} + \frac{b_2 \cdot K_2 \cdot C}{1 + K_2 \cdot C} \qquad (3)$$

where:

Q – actual adsorption of sorbate on a sorbent [mg/g.d.m]
b_1 – maximum adsorption capacity of a sorbent (I type active sites) [mg/g.s.m]
b_2 – maximum adsorption capacity of a sorbent (II type active sites) [mg/g.s.m]
K_1; K_2 – Langmuir equation constants [dm^3/mg]
C – the concentration of dye remaining in the solution [mg/dm^3]

The heterogeneous Freundlich model (4):

$$q_e = K \cdot C^n \qquad (4)$$

where:

q_e – equilibrium amount of dyes sorbed [mg/g]
C – concentration of dyes remaining in solution [mg/dm^3]
K – equilibrium sorption constant in the Freundlich model
n – heterogenity parameter

Fitting of the experimental data for the mathematical models determined using the correlation coefficient R^2 (5):

$$R^2 = \frac{\Sigma\left(q_{cal} - \bar{q}_{exp}\right)^2}{\Sigma\left(q_{cal} - \bar{q}_{exp}\right)^2 + \Sigma\left(q_{cal} - q_{exp}\right)^2} \qquad (5)$$

where:

R^2 – correlation coefficient – a measure of data alignment to the model
q_{exp} – the experimental data – amount of dyes sorbed [mg/g]
q_{cal} – theoretical data resulting from the model – amount of dyes sorbed [mg/g]

4. Results and Discussion

4.1 Effect of pH on the effectiveness of dye sorption

The sorption effectiveness of the Reactive Black 5 dye on chitosan beads and sawdust immobilised on chitosan depends largely on the initial pH of the solution. Chitosan sorbents at pH 2–3 dissolved completely, making it impossible to perform the analysis. The sorption of the Reactive Black 5 dye on chitosan beads and chitosan–sawdust beads occurred most efficiently at an initial pH of 4 (Fig. 2). The beneficial effect of a low pH on the sorption of anionic dyes on chitosan sorbents is also confirmed in the literature [13,14]. The effectiveness of the Reactive Black 5 dye removal onto sawdust, regardless of the pH, was low and ranged between 1 and 9%. Based on the obtained results, the next investigation of anionic dye sorption on sawdust began at an initial pH of 3. According to the literature, the decrease in the pH of the solution means a higher positive charge of the sorbent as a result of the increased amount of H^+, which also results in stronger interactions with negatively charged dye [15].

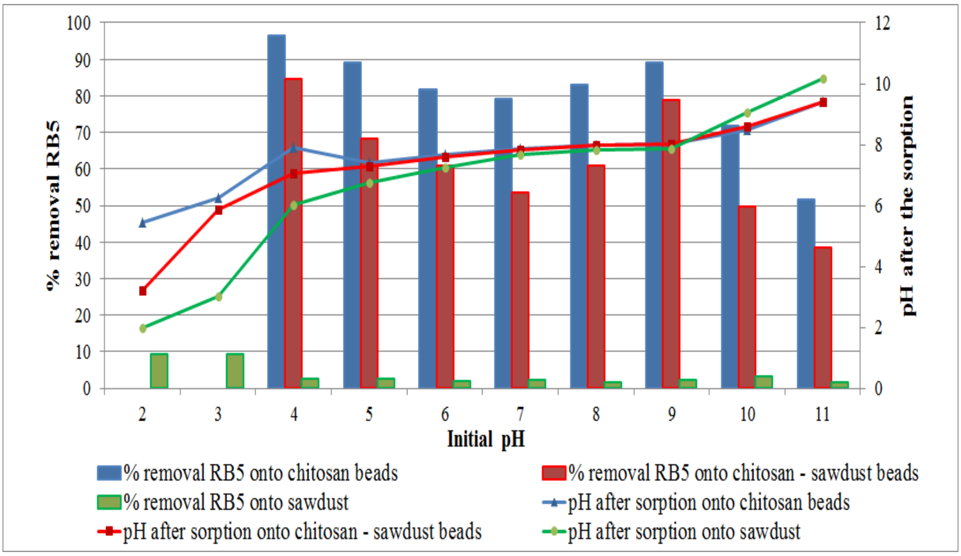


Figure 2. Effect of pH value on the effectiveness of Reactive Black 5 sorption

The influence of the pH on the sorption effectiveness of Basic Violet 10 dye on chitosan sorbents was small (Fig. 3). The obtained effectiveness of cationic dye removal at the very diverse pHs of 4 and 11 did not differ more than 5%. The lack of results for chitosan beads and sawdust immobilised on chitosan at pH 2–3 is connected with the complete dissolution of the sorbents. The research of the sorption capacity of chitosan sorbents for Basic Violet 10 was carried out at pH 4. In the case of sawdust, remarkable differences in cationic dye removal depending on the initial pH of the solution were observed. The highest sorption effectiveness of 78% was obtained at pH 3. Moreover, high effectiveness of BV10 sorption at a pH below 4 has been demonstrated in the literature [16,17,18]. According to Anandkumar and others [19], at a pH below 3.5, particles of Basic Violet 10 remain in the monomeric form and may easily enter the structure of the sorbent, above pH 3.5, the particles of the dye aggregate and the sorption is restricted.

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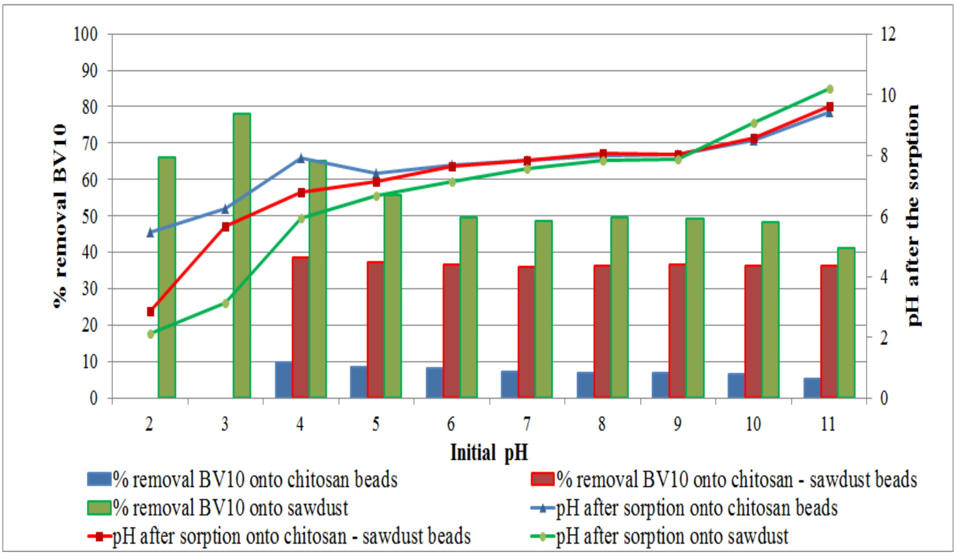

Figure 3. Effect of pH value on the effectiveness of Basic Violet 10 sorption

The chitosan sorbent had a huge influence on the pH change during sorption. In chitosan, the initial pH of the solution was in the range of 4–8, and after sorption, the pH was within 7.9–7.98; for sawdust immobilised on chitosan, the pH was 7.05–8.99 (Fig. 2 and 3). The pH_{ZPC} for both sorbents was around 7.98 (Fig. 4). The sawdust had a small influence on the change in initial pH of the solution, showing a range of 2–3; the given starting range of the pH of the solution after sorption was 2–3.04 (Fig. 2 and 3). The initial pH of the solution was 4–8, and after sorption, it was 6.02–7.81. The system was maintaining the pH close to pH_{ZPC} = 7.81 (Fig. 4). pH changes in the solution result from the buffer properties of chitosan, which causes the solution to approach pH close to pH_{ZPC} (pH of zero charge).

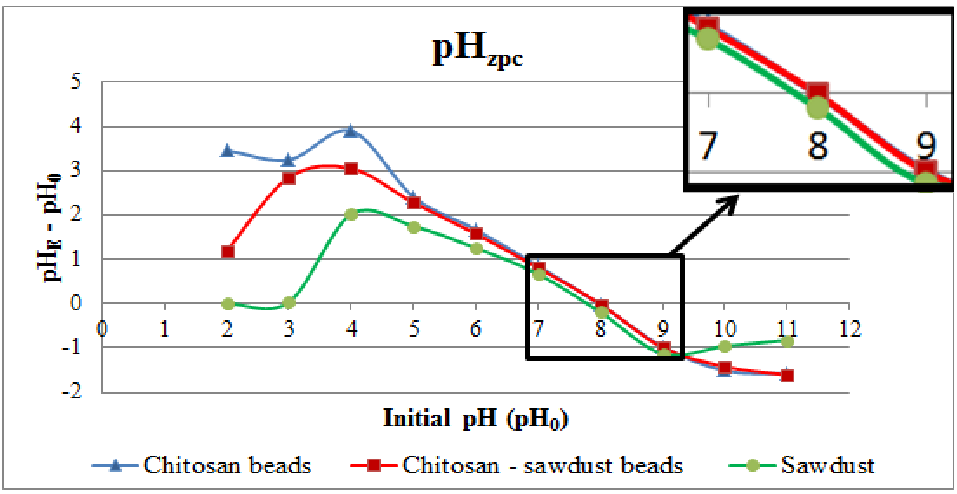

Figure 4. The pH of the solution before and after sorption of dyes depending on the initial pH of the solution

4.2 Maximum sorption capacity

Based on preliminary studies, the research enabling the determination of the maximum sorption capacity for all the sorbents was conducted. The obtained data was described by the heterogeneous Langmuir, double Langmuir and Freundlich models. For these models, the constants were determined using the nonlinear regression method. The measure of fitting of the curve to the experimental data was R^2 factor (Table 5). In all cases, the double Langmuir model showed the best fit to experimental data showed, which might indicate that the sorbents have at least two types of sorption centre [20].

In Figures 5 and 6, the sorption isotherms of the Reactive Black 5 and Basic Violet 10 dyes on chitosan beads, beech sawdust and sawdust immobilised on chitosan are shown, and in Table 5, the match factors and reaction constants are presented.

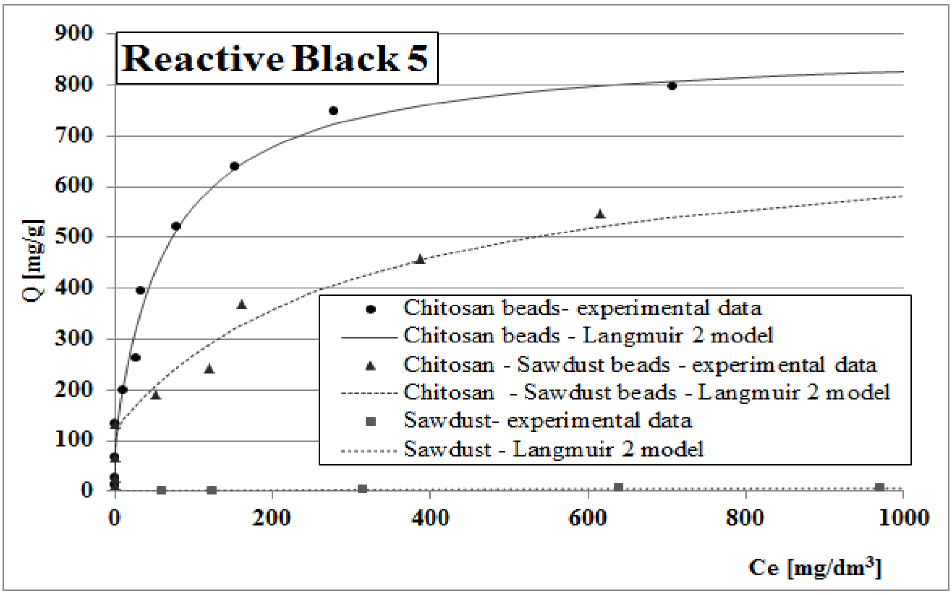

Figure 5. Experimental results and isotherms for the Langmuir 2 sorption of Reactive Black 5 after 72 h

The data presented in the table 5 shows that chitosan beads have the highest effectiveness for anionic dye removal. The maximum sorption capacity for chitosan beads in relation to Reactive Black 5 was 875.66 mg/g. The high ability of anionic dye removal by the chitosan beads results from the chemical structure of the polymer. Chitosan has numerous amino groups in its structure, which are responsible for the sorption of anions [21].

The highest capacity in relation to the cationic dye was sawdust. The maximum sorption capacity of sawdust in relation to Basic Violet 10 was 30.15 mg/g. Similar abilities of cationic dye removal were obtained using natural products such as Indian Rosewood sawdust [22], banana peel [23] or hazelnut shells [24]. In order to obtain a universal sorbent showing high sorption capacity for both anionic and cationic dyes, a sorbent in the form of sawdust immobilised on chitosan has been proposed in the present work. The sorption capacity in relation to the anionic dye was 720.7 mg/g, and for the cationic dye, it was 24.10 mg/g.

A sorbent in the form of sawdust immobilised on chitosan showed significantly higher sorption capacity in relation to cationic dyes than hydrogel chitosan beads. Previous work using composites of chitosan with montmorillonite (natural silicate) to remove Congo red [25] and Rhodamine 6G [26] came to similar conclusions. Also, according to Chang and Juang [27], the sorption capacity of a composite of chitosan with clay activated in relation to methylene blue is multiple times higher than chitosan beads alone.

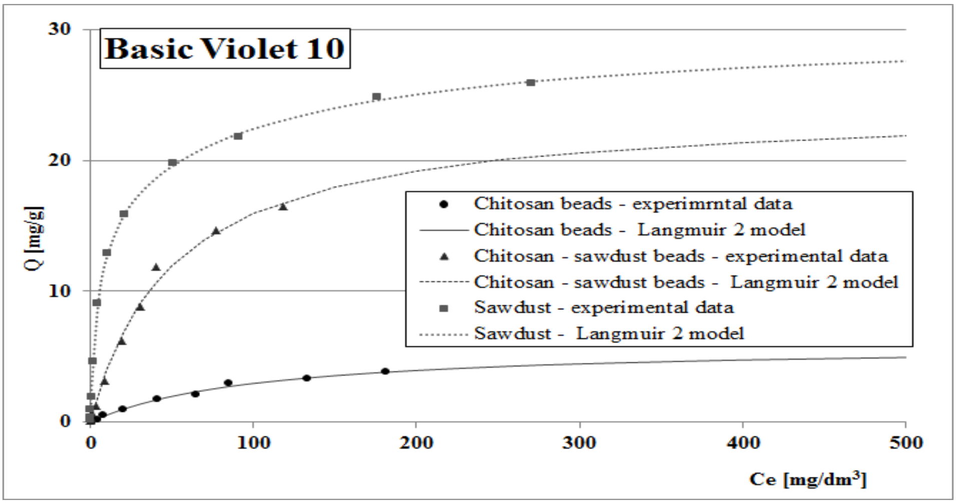

Figure 6. Experimental results and isotherms for the Langmuir 2 sorption of Basic Violet 10 after 72 h

Table 5. Constants in the Langmuir 2 equation and sorption capacity

Dye	Time of sorption	Sorbent	Qmax [mg/g]	Langmuir 2 model constants					
				b_1	k_1	b_2	k_2	R^2
RB5	24 h	Chitosan beads	688.60	114.43	1.004	574.17	0.002	0.999
		Chitosan–sawdust beads	500.18	83.18	0.678	416.99	0.001	0.999
		Sawdust	13.90	1.83	0.005	12.08	0.001	0.996
	72 h	Chitosan beads	875.67	104.47	2.432	771.19	0.015	0.991
		Chitosan–sawdust beads	720.70	120.96	5.136	599.74	0.003	0.993
		Sawdust	16.69	4.95	0.004	11.75	0.000	0.999
BV10	24 h	Chitosan beads	5.79	2.92	0.010	2.87	0.010	0.997
		Chitosan–sawdust beads	23.88	12.54	0.018	11.34	0.018	0.998
		Sawdust	28.99	3.68	2.204	25.32	0.031	0.999
	72 h	Chitosan beads	5.95	2.95	0.010	3.00	0.010	0.993
		Chitosan–sawdust beads	24.10	15.01	0.020	9.09	0.020	0.997
		Sawdust	30.15	16.75	0.216	13.39	0.009	0.999

5. Conclusions

Considering the deteriorating state of surface waters, it is important to find a universal and cheap sorbent, that can remove both cationic and anionic dyes. The polymer characterised by the high ability to remove acidic and reactive dyes is chitosan. Cationic dyes with high effectiveness might be removed by cheap and widely accessed natural products and waste from industry, i.e. sawdust. In this paper, it has been proposed to join these two ingredients and create a sorbent in the form of sawdust immobilised on chitosan. The maximum sorption capacity in relation to the anionic dye was 720.7 mg/g, and the capacity in relation to the cationic dye was 24.10 mg/g. The conducted research indicated that sawdust immobilised on chitosan shows a significantly higher sorption capacity in relation to cationic dyes than chitosan hydrogel beads.

The effectiveness of dye removal significantly depended on the pH in which the process was carried. The pH at which the sorption process was the most effective was set at pH 4 for chitosan sorbents and pH 3 for sawdust. The obtained results were described by the double Langmuir model, as this model showed the best fit to the experimental data (R^2>0.99). High values of the isotherm match factor of the double Langmuir model to the obtained experimental data might indicate the bonding of the dyes by at least two types of sorption centres.

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