THE COMBINATION OF WASTE PRODUCTS FROM CHITIN AND SAWDUST TO REMOVE ANIONIC AND CATIONIC DYES

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Abstract

The application of the immobilisation method – which consists of immobilising modified sawdust in a carrier, a chitosan gel – enabled the development of a new sorbent. By combining waste products from chitin and sawdust, the properties of both adsorbents were utilised. This paper evaluated the adsorption efficiency of four dyes – Reactive Yellow 84, Reactive Black 8, Basic Violet 10 and Basic Green 4 – on four adsorbents – chitin flakes, chitosan flakes, chitosan beads and sawdust immobilised in chitosan beads. The latter adsorbent showed good adsorption properties for both anionic and cationic dyes. The experimental results showed a relationship between the amount of adsorbed and desorbed dye and the type of adsorbent. Chitin flakes showed the lowest adsorption capacity, regardless of the type of dye. The immobilisation of modified sawdust in chitosan had a particularly positive effect on the binding efficiency of cationic dyes.

Keywords: *chitin flakes, chitosan flakes, chitosan beads, modified chitosan in sawdust, cyclic adsorption/desorption*

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1. Introduction

The ability of different types of adsorbents to bind to dyes depends on both the type of adsorbent and the structure of the dye; this phenomenon has been well documented in the literature. The practical application of the adsorption process for the removal of dyes from wastewater still faces a number of limitations. Among the most important is the lack of a universal adsorbent that would be highly effective regardless of the type of dye (anionic or cationic) and could be used under flow conditions [1]. The costs associated with separating the adsorbent in the form of powders or flakes from the purified solution also play an important role: if this could be done at a relatively low cost, it would allow the adsorbent to be reused in subsequent adsorption and desorption cycles. These disadvantages can be eliminated by immobilisation.

Agricultural and forestry wastes such as sawdust and bark can be used successfully as adsorbents, mainly due to their wide availability, physicochemical properties and low costs associated mainly with transportation from storage sites to landfills [2–4]. Sawdust is a major by-product of the wood industry; it is mostly used as fuel or as packaging material [5]. Sawdust accounts for about 10% of the wood processed in sawmills. It is also a by-product of cutting and milling, among other activities, in wood-processing companies.

Lignincellulose biomass is widely available and inexpensive. Its sources include growing resources of coniferous and deciduous trees, reeds, some types of grasses, plantations of fast-growing trees (willows, poplars and eucalyptus), wood waste, straw, hay, crop stalks, wood waste from the pulp and paper industry, corn cobs, waste from the milling industry, the oil industry, waste wood construction materials, and paper and municipal waste. It is estimated that the annual production of terrestrial plant biomass is about 170 billion tonnes. Only about 6 billion tonnes of biomass are used, and only 3% of this amount is used outside the agricultural and food industry [6].

Researchers have described the adsorption of dyes, toxic salts, metals or oils from aqueous solutions using sawdust as a sorbent. Sawdust, which contains organic components such as lignins, cellulose and hemicellulose with polyphenolic groups, is a promising and effective material for the removal of dyes [5, 7–10]. The adsorption capacity achieved by sawdust adsorbents in the published studies show a rather wide range due to the differences in the type of sawdust and the method used for their preparation and modification [11, 12], The adsorption capacity of raw sawdust can range from 27.4 [13] to 398.8–526 mg/l [8, 14] depending on the tree species, the processing method and the colourant.

The use of chitin and chitosan as adsorbents is economically advantageous. Both chitin and chitosan occur in considerable quantities in nature and their extraction does not involve large financial costs [15–17]. Chitin is obtained from natural resources, while the preparation of chitosan involves the use of inexpensive and widely available chemical reagents [18]. Thanks to this versatility, both chitin and chitosan can be used in various forms: as flakes, in gels, as various types of beads [19–21] or as fibres and membranes [22]. Like chitin, chitosan is easily biodegradable and non-toxic [23]. In addition, it has a number of other properties: high chemical reactivity, high bioactivity, high stability and a high adsorption capacity. The sorption properties of chitosan are used to remove dyes, heavy metals and other toxic substances that pollute water.

Chitosan has attracted particular attention as a complexing agent due to its low cost compared with activated carbon and its numerous functional groups – amino and hydroxyl. Biosorbents based on chitin and chitosan represent effective materials and have a very high affinity for many classes of dyes [9, 20, 21, 24–27]. Chitosan has been used as an adsorbent to remove acid dyes [24, 28–33]. These studies have reported an adsorption capacity of > 1000 mg/g of sorbent, confirming the usefulness of chitosan for the removal

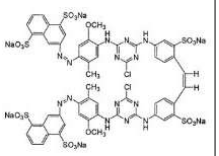
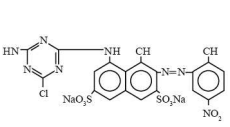
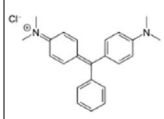
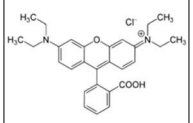
of dyes. The application of the immobilisation method – which consists of immobilising modified sawdust in a carrier, a chitosan gel – enabled the development of a new adsorbent [23, 34, 35]. The combination of waste products from chitin and sawdust utilises the properties of both adsorbents. Immobilised modified sawdust in chitosan gel exhibits good adsorption properties for both anionic and cationic dyes so that the adsorption process can be used to remove dyes under dynamic conditions.

2. Materials and Methods

2.1. Dyes

Dyes from ZPB 'Boruta' SA (Poland) were used in this study. Due to their widespread use in industry, anionic (reactive) and cationic (basic) dyes were used. Table 1 shows the chemical characteristics of the dyes employed in this study.

Table 1. The characteristics of the anionic and cationic dyes used in this study.

Name	Reactive Yellow 84 (RY84)	Reactive Black 8 (RB8)	Basic Green 4 (BG4)	Basic Violet 10 (BV10)
Structural formula				
Chemical formula	$C_{52}H_{38}Cl_2N_{18}O_{26}S_8$	$C_{19}H_{11}C_lN_8Na_2O_{10}S_2$	$C_{27}H_{28}N_2O_8$	$C_{28}H_{31}C_lN_2O_3$
Molecular mass [g/mol]	1628	657	365	479
λ_{max} [nm]	356	657	618	554
Type of dye	Anionic (reactive)	Anionic (reactive)	Basic (cationic)	Basic (cationic)
Dye class	Double azo dye	Azo dye	Triphenyl-methane	Triphenyl-methane
Dye application	Dyeing of polyester, cotton and synthetic silk	Dyeing of natural silk and wool	Dyeing of wool, cotton, silk, leather and paper	Dyeing of cotton, paper and leather; production of printing and painting dyes

2.2. Adsorbents

Adsorbent 1 – chitin flakes. Krill chitin from the Institute of Sea Fisheries in Gdynia with a dry matter content of 95.64%, an ash content of 0.32% and a degree of deacetylation of < 3% was used for the study. The commercial chitin flakes were washed with distilled water and 6 N hydrochloric acid (HCl) before adsorption to loosen the structure and to remove calcium and magnesium ions as well as fat residues. It was then rinsed with distilled water to neutralise the pH of the filtrate.

Adsorbent 2 – chitosan flakes. The chitosan used in the study was prepared from chitin, which was washed with distilled water and HCl and then boiled for 3 h in a water bath with a 70% potassium base. After cooling, the flakes were rinsed with distilled water until neutral and drained in a vacuum. The degree of deacetylation was 75%.

Adsorbent 3 – chitosan beads. Chitosan in the form of flakes with a degree of deacetylation of 85%, a viscosity of 100 mPa/s and a dry substance content of 86.8% was obtained from Heppe (Germany). Fifty grams of chitosan, dissolved in 2% acetic acid, was dropped into 5% sodium hydroxide (NaOH) using a micropipette and incubated in the solution for 24 h. The size of the beads was controlled based on the size of the micropipette (3 mm).

Adsorbent 4 – beads of modified oak sawdust immobilised in chitosan. Oak sawdust from the local sawmill in Naterki, a waste product from the treatment of oak wood that has undergone modification, was used. The fibre fractions were determined based on the chemical analysis method according to Van Soest et al. [36]. This method involves the selective isolation of different fractions under specific conditions using surface-active compounds. The characteristics of the raw material, expressed in % (w/w) in relation to the dry mass, are listed in Table 2.

Table 2. Characteristics of the oak sawdust used in this study.

Component	Percent of dry matter content
Cellulose	45.0
Hemicellulose	28.9
Lignins	22.7
Ash	0.1
Extracts and other ingredients	3.3

2.2.1. Modification of the Sawdust

Fifty grams of sawdust was mixed with 50 g of concentrated sulphuric acid (H_2SO_4) and heated at 150°C for 24 h. The sawdust was washed with distilled water and incubated in 1% sodium carbonate for 12 h to remove residual H_2SO_4. The resulting modified sawdust was dried at 105°C for 24 h and then sieved through a sieve with a mesh size of 1 mm [5, 11].

2.2.2. Preparation of Modified Sawdust Immobilised on Chitosan

Twenty-five grams of modified sawdust was added to 25 g of chitosan dissolved in 5% acetic acid. To create the beads, a mixture of modified sawdust and chitosan was dropped into 5% NaOH using a micropipette and incubated in the solution for 24 h. The resulting beads were drained, washed and stored in distilled water.

2.2.3. Determination of the Efficiency of Dye Adsorption/Desorption

Adsorption and desorption was assessed for Reactive Yellow 84 (RY 84), Reactive Blue 8 (RB8), Basic Violet 10 (BV10) and Basic Green 4 (BG4). For the anionic dyes (RY84 and RB8), adsorption was carried out at pH 5 and desorption was carried out at pH 10. For the cationic dyes (BV10 and BG4), adsorption was carried out at pH 10 and desorption was carried out at pH 3. The reaction of the solutions was adjusted with HCl and NaOH solutions. The concentration of the adsorbent was constant in all experiments (1 g/l). The adsorption (120 min) and desorption (30 min) times were determined using the studies shown in Figures 1 and 2.

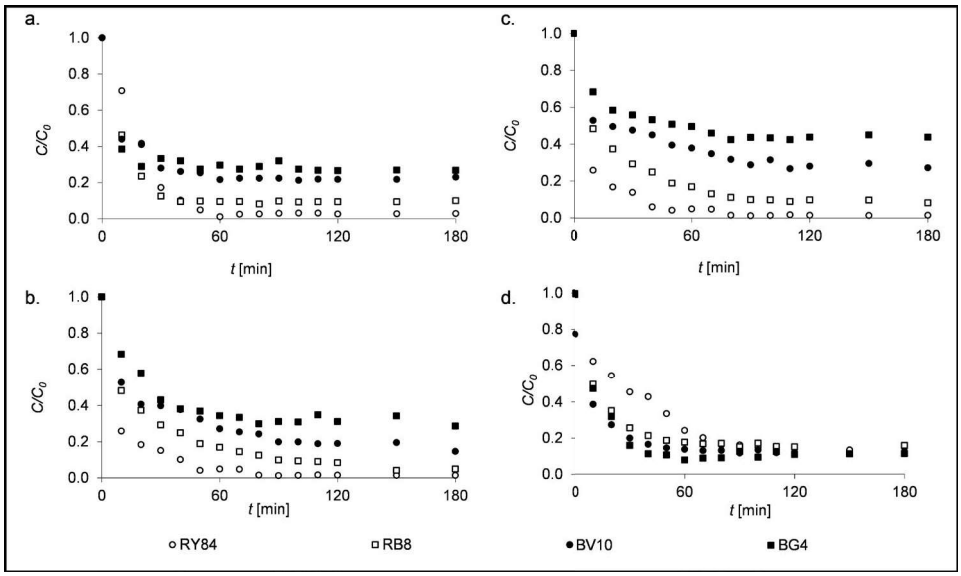


Figure 1. Changes in the dye concentration over time during adsorption on (a) chitin flakes, (b) chitosan flakes, (c) chitosan beads and (d) sawdust immobilised on chitosan beads. Abbreviations: BG4, Basic Green 4; BV10, Basic Violet 10; RB8, Reactive Blue 8; RY84, Reactive Yellow 84.

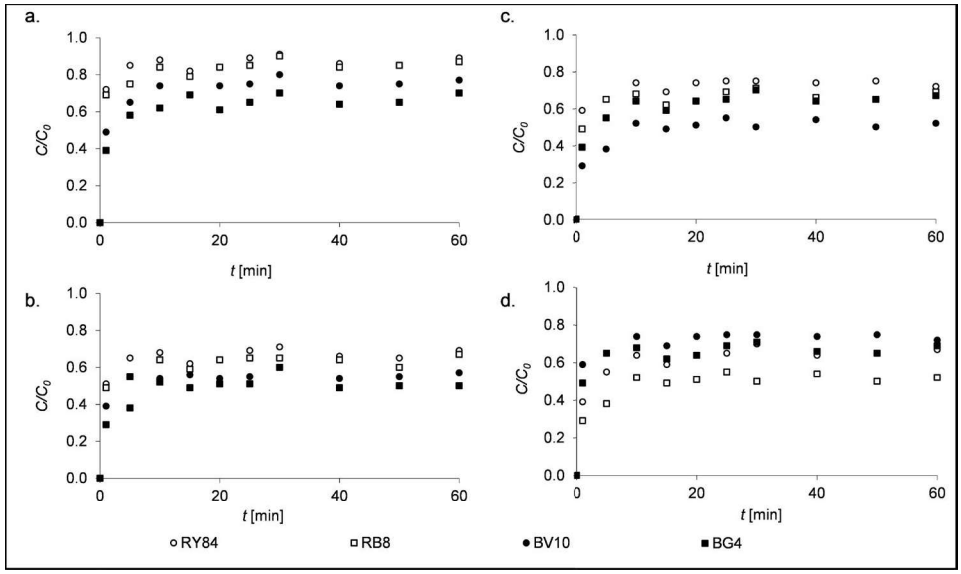


Figure 2. Changes in dye concentration over time during desorption from (a) chitin flakes, (b) chitosan flakes, (c) chitosan beads and (d) sawdust immobilised on chitosan beads. Abbreviations: BG4, Basic Green 4; BV10, Basic Violet 10; RB8, Reactive Blue 8; RY84, Reactive Yellow 84.

2.3. Analytical Methods

The samples taken for analysis were decanted and centrifuged at 10,000 rpm for 15 min. The concentration of dye remaining in the solution was determined using a standard curve prepared with a SP-3000 ultraviolet–visible (UV–Vis) spectrophotometer (VWR In-ter-national LLC., Canada). Distilled water was used as the blank.

2.4. Calculation Methods

The amount of dye adsorbed from the solution was determined by the change in the concentration of dye remaining in the solution and calculated using equation (1):

$$Q_s = \frac{C_0 - C_s}{m} \tag{1}$$

The symbols in this equation mean the following:

Q_s – amount of adsorbed dye [mg/g dry matter (DM)];
C_0 – initial concentration of the dye [mg/l];
C_s – concentration of the dye after adsorption [mg/l];
m – concentration of mass of the adsorbent in tested sample [g DM/l].

A double-Langmuir model was used to describe the results of the experimental adsorption. The model assumes that the surface of the adsorbent is energetically heterogeneous and has adsorption centra with different binding energies of adsorbates. Each type is described by Langmuir's isotherm equation [37–39] and the active sites are characterised by constants labelled K_1 and b_1 and K_2 and b_2, respectively, as shown in equation (2). This model has been used successfully to interpret the results of metal adsorption by activated sludge and to evaluate metal adsorption in soils [37].

$$Q = \frac{b_1 \cdot K_1 \cdot C}{1 + K_1 \cdot C} + \frac{b_2 \cdot K_2 \cdot C}{1 + K_2 \cdot C} \tag{2}$$

The symbols in this equation mean the following:

Q – amount of adsorbed dye [mg/g DM];
b_1, b_2 – adsorption capacity in active sites of the first and second type [mg/g DM];
K_1, K_2 – constants in Langmuir's equation [l/mg DM];
C – concentration of dye in the solution at equilibrium [mg/l].

The total adsorption capacity (b) is equal to the sum of the maximum adsorption capacity determined for the first and second types of active sites ($b = b_1 + b_2$). K_1 and K_2 characterise the adsorption affinity of the dye to the active sites of the first and second types, respectively, and correspond to the reciprocal of the equilibrium concentration of the dye at which the adsorption capacity is more than half the maximum capacity of b_1 or b_2. A larger K indicates an increase in the adsorption affinity of the dye to the active sites of the adsorbent. The constants K_1 and K_2 and the maximum adsorption capacity (b_1 and b_2) were determined by non-linear regression. The R^2 coefficient was used as a measure of the fit of the curve (with the determined parameters) to the experimental data.

The amount of desorbed dye was calculated from equation (3):

$$Q_d = \frac{C_d - C_s}{m} \tag{3}$$

The symbols in this equation mean the following:

Q_d – amount of desorbed dye [mg/g DM];
C_0 – concentration of the dye before desorption [mg/l];
C_d – concentration of the dye after desorption [mg/l];
m – concentration of mass of the adsorbent in the tested sample [g DM/l].

The desorption of dyes from aqueous solutions on the tested adsorbents was evaluated based on the relationship between the mass of dye adsorbed on the adsorbent Q (mg/g DM) and its equilibrium concentration C [mg/l].

The single-Langmuir model was used to describe the experimental results of desorption. It is shown in equation (4):

$$Q = \frac{b \cdot K \cdot C}{1 + K \cdot C} \tag{4}$$

The symbols in this equation mean the following:

- Q – amount of adsorbed dye [mg/g DM];
- b – adsorption capacity [mg/g DM];
- K – constant in Langmuir's equation [l/mg DM];
- C – concentration of dye in the solution, at equilibrium [mg/l].

The constants K and b were determined by non-linear regression. R^2 was used as a measure of the fit of the curve (with the determined parameters) to the experimental data.

3. Results and Discussion

The combination of chitin and sawdust via immobilisation of sawdust in chitosan aimed to create an adsorbent that would have good adsorption properties for both anionic and cationic dyes and high adsorption and desorption efficiency. The adsorption and desorption of the dyes was evaluated based on the relationship between the mass of dye adsorbed on the adsorbent (Q) and its equilibrium concentration (C). The double-Langmuir model, equation (2), and the single-Langmuir model, equation (4), were used to describe the experimental results. Figures 3–6 show the relationship between the amount of dye adsorbed and desorbed on adsorbents 1–4, the equilibrium concentration and the Langmuir isotherms. The constants K and b determined from equations (2) and (4) for all dyes tested are presented in Tables 3 and 4, respectively.

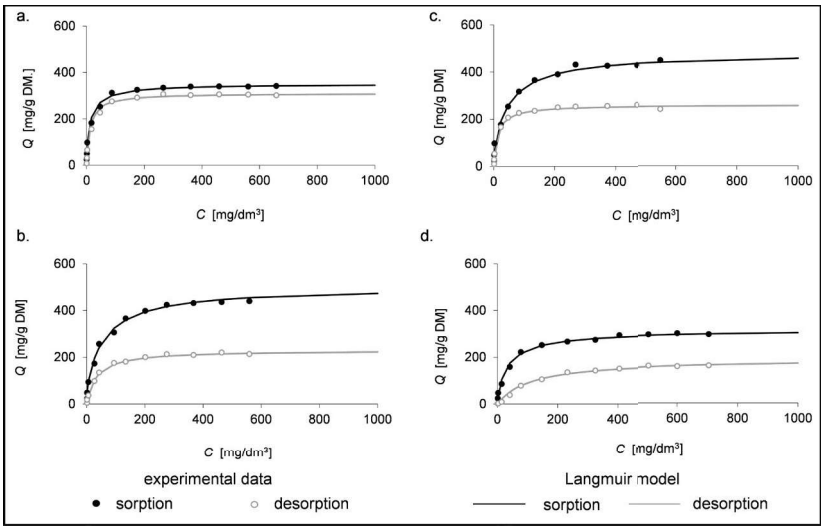


Figure 3. The experimental data compared with the adsorption determined from the double-Langmuir isotherm and the desorption isotherm determined from the Langmuir equation model for Reactive Yellow 84 on (a) chitin flakes, (b) chitosan flakes, (c) chitosan beads and (d) sawdust immobilised on chitosan beads.

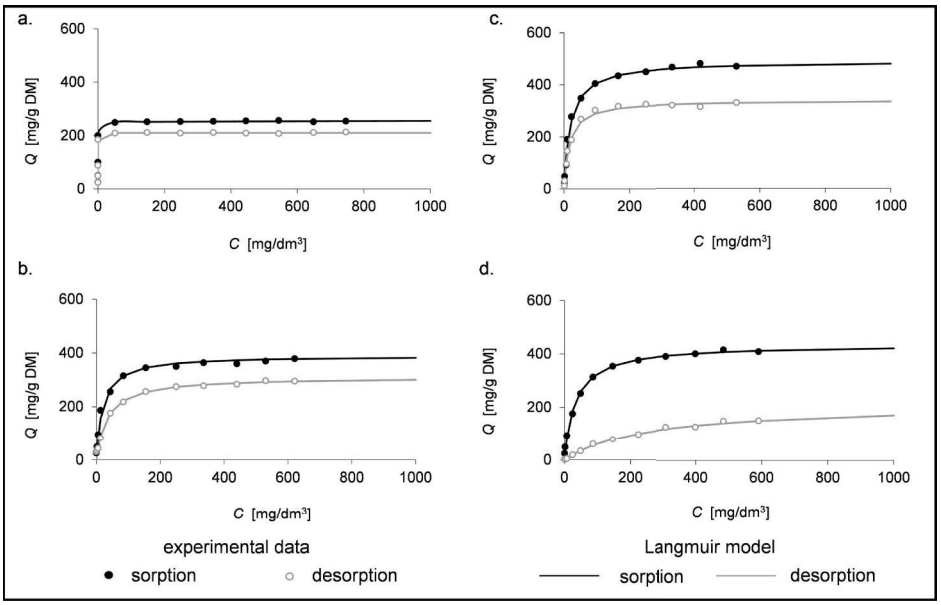


Figure 4. The experimental data compared with the adsorption determined from the double-Langmuir isotherm and the desorption isotherm determined from the Langmuir equation model for Reactive Blue 8 on (a) chitin flakes, (b) chitosan flakes, (c) chitosan beads and (d) sawdust immobilised on chitosan beads.

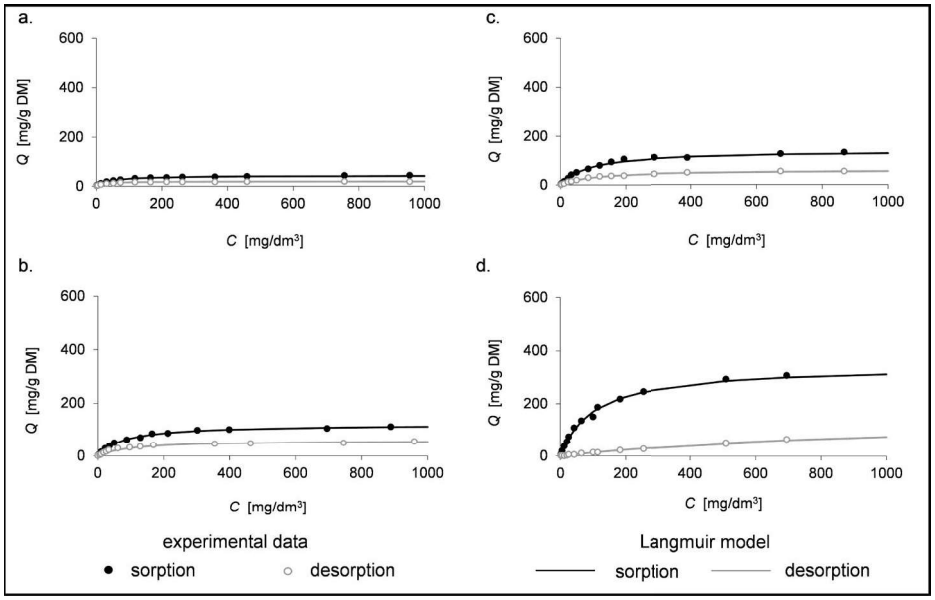


Figure 5. The experimental data compared with the adsorption determined from the double-Langmuir isotherm and the desorption isotherm determined from the Langmuir equation model for Basic Violet 10 on (a) chitin flakes, (b) chitosan flakes, (c) chitosan beads and (d) sawdust immobilised on chitosan beads.

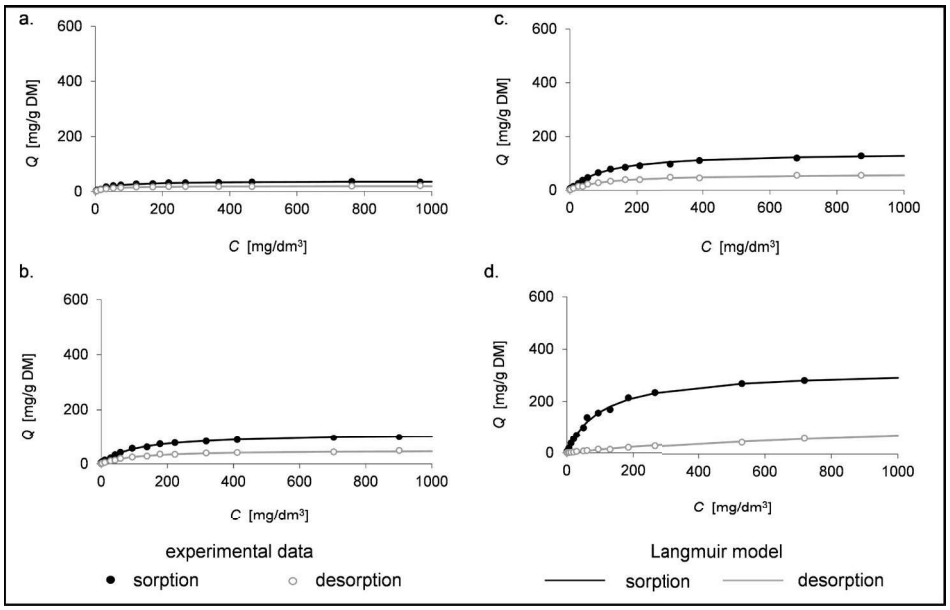


Figure 6. The experimental data compared with the adsorption determined from the double-Langmuir isotherm and the desorption isotherm determined from the Langmuir equation model for Basic Green 4 on (a) chitin flakes, (b) chitosan flakes, (c) chitosan beads and (d) sawdust immobilised on chitosan beads.

Based on the data, regardless of the dye tested, the adsorption capacity of chitin flakes was the lowest compared with the other three adsorbents. Moreover, the efficiency of adsorption on chitin flakes depended strongly on the type of dye. The amount of anionic dyes bound to chitin flakes ranged from 180 mg/g DM (RB8) to 350 mg/g DM (RY84), while for the cationic dyes it was significantly lower, ranging from 38 mg/g DM (BG4) to 44 mg/g DM (BV10) (Table 3). Analysis of the adsorption and desorption isotherms of the tested dyes on chitin flakes revealed a high desorption efficiency. The course of the adsorption and desorption isotherms was very similar.

A higher degree of chitosan deacetylation had a significant effect on the amount of dye removed [40–44]. For chitosan flakes, chitosan beads and sawdust immobilised on chitosan beads, there was an increase in the adsorption capacity of all tested dyes (Figures 3–6, Table 3). Both tested cationic dyes showed the largest increase in the adsorption capacity compared with chitin flakes. The amount of BV10 and BG4 increased to 120 and 110 mg/g DM, respectively, when bound to chitosan flakes (an increase of about 2.8 compared with chitin flakes), to 140 mg/g DM when bound on chitosan beads (a 3.7-fold increase compared with chitin flakes) and to 340 and 320 mg/g DM, respectively, when bound to sawdust immobilised on chitosan beads (an increase of 7.7 and 8.4 times, respectively). The results showed that the modification of chitosan by immobilisation with sawdust increased the adsorption of cationic dyes.

The use of chitosan beads had no effect on the adsorption capacity. The adsorption capacity of the chitosan beads was higher or at a similar level to that of the chitosan flakes for all the tested dyes. The adsorption capacity for the anionic dyes ranged from 390 to 500 mg/g DM for chitosan flakes and from 480 to 490 mg/g DM for chitosan beads. For the cationic dyes BV10 and BG4, the adsorption capacity

was 110 and 140 mg/g DM, respectively. The sawdust immobilised on chitosan beads reduced the adsorption capacity by about 10% compared with chitosan beads.

Analysis of the adsorption and desorption isotherms of chitosan flakes, chitosan beads and sawdust immobilised on chitosan beads revealed that, in case of the anionic dyes, a significant increase in the adsorption capacity did not lead to a corresponding increase in the amount of desorbed dye compared with chitin flakes. The desorption isotherms differed significantly from the adsorption isotherms (Figures 3–6).

A different mechanism of dye binding on the four tested adsorbents is evidenced by the *K* values, which describe the affinity of the adsorbate to the adsorbent (Table 3). K_1 determined for the chitin flakes was high for RB8 (50 l/mg), which could indicate strong binding of this dye to chitin flakes. K_1 for the cationic dyes BV10 and BG4 determined using the double-Langmuir model was more than 1000 times lower. The adsorption affinity of the tested dyes to the other three adsorbents was significantly lower and there were no significant differences depending on the type of dye. K_1 was between 0.01 and 0.7 l/mg for chitosan flakes, chitosan beads and sawdust immobilised on chitosan beads. K_2, describing the affinity for the second type of active site, was between 0.01 and 0.05 l/mg regardless of the adsorbent. The only exception was RB8 adsorbed on chitin flakes, for which K_2 was an order of magnitude lower at 0.001 l/mg.

A double-Langmuir model was also used to describe the desorption process, but for all tested dyes and adsorbents, the K_2 and b_2 values were very small; thus, they can be omitted. The desorption of the tested dyes was described successfully with the single-Langmuir model (Table 4).

Table 3. The *K* and *b* values determined from the double-Langmuir model, equation (2), for adsorption.

Constants from the double-Langmuir model												
Dye	**Chitin flakes**						**Chitosan flakes**					
	K [l/mg DM]		*b* [mg/g DM]			R^2	*K* [l/mg DM]		*b* [mg/g DM]			R^2
	K_1	K_2	b_1	b_2	*b*		K_1	K_2	b_1	b_2	*b*	
RY84	1	0.05	90	260	350	0.994	0.70	0.015	80	420	500	0.991
RB8	50	0.001	250	10	260	0.999	0.05	0.05	380	10	390	0.992
BV10	0.04	0.012	25	19	44	0.991	0.01	0.015	40	80	120	0.994
BG4	0.04	0.01	22	16	38	0.991	0.01	0.01	40	70	110	0.994
Dye	**Chitosan beads**						**Sawdust immobilised on chitosan beads**					
	K [l/mg DM]		*b* [mg/g DM]			R^2	*K* [l/mg DM]		*b* [mg/g DM]			R^2
	K_1	K_2	b_1	b_2	*b*		K_1	K_2	b_1	b_2	*b*	
RY84	0.4	0.017	90	390	480	0.992	0.08	0.02	130	200	380	0.991
RB8	0.05	0.05	480	10	490	0.991	0.03	0.03	380	55	435	0.997
BV10	0.01	0.01	40	100	140	0.992	0.01	0.01	140	200	340	0.996
BG4	0.01	0.01	40	100	140	0.991	0.01	0.01	130	190	320	0.996

Abbreviations: BG4, Basic Green 4; BV10, Basic Violet 10; DM, dry matter; RB8, Reactive Blue 8; RY84, Reactive Yellow 84.

Table 4. The values of K and b determined from the Langmuir model, equation (4), to describe desorption.

Constants from Langmuir equation												
Dye	**Chitin flakes**			**Chitosan flakes**			**Chitosan beads**			**Sawdust immobilised on chitosan**		
	K	b	R^2	K	b	R^2	K	b	R^2	K	b	R^2
RY84	1	0.05	90	260	350	0.994	0.70	0.015	80	420	500	0.991
RB8	50	0.001	250	10	260	0.999	0.05	0.05	380	10	390	0.992
BV10	0.04	0.012	25	19	44	0.991	0.01	0.015	40	80	120	0.994
BG4	0.04	0.01	22	16	38	0.991	0.01	0.01	40	70	110	0.994

Abbreviations: BG4, Basic Green 4; BV10, Basic Violet 10; DM, dry matter; RB8, Reactive Blue 8; RY84, Reactive Yellow 84.

Based on the K and b values, the significantly higher absorption capacity of the chitosan flakes for the anionic dyes compared with chitin flakes had no effect on the amount of desorbed dye. The desorption of the anionic dyes from chitin flakes was 310 mg/g DM (RY84) and 210 mg/g DM (RB8), which accounted for 89% and 81% of the amount of adsorbed dye, respectively. The shape of the adsorption isotherm and the high K_1 values determined for the chitin flakes suggest chemical adsorption. However, this was not confirmed by the desorption results. The chitin flakes showed the highest desorption efficiency regardless of the type of dye. The chitosan flakes, chitosan beads and beads of modified sawdust immobilised on chitosan beads had a significantly lower desorption efficiency for the anionic dyes, ranging from 26% (RB8, chitosan flakes) to 79% (RB8, chitosan flakes).

Dye loss during the dyeing process is estimated to be around 10%–50% for anionic dyes and up to 5% for cationic dyes [20, 21]. Because anionic and cationic dyes can be present in the tanks at the same time, it is important to use adsorbents that allow their simultaneous and effective removal.

Researchers have compared the adsorption capacity of chitosan in the form of flakes and beads, similarly to the present study, but have not provided a clear correlation between the extent of dye binding and the type of adsorbent (flakes and beads). Wu et al. [45] investigated the binding efficiency of Reactive Red 222 (RR222) to flakes and beads of chitosan obtained from shrimp, lobsters and crabs. The capacity was 1026–1106 mg/g for chitosan beads, significantly higher (2–3.8 times) compared with chitosan flakes (293–494 mg/g). Lazaridis and Keenan [46] evaluated the adsorption of RB5 on chitosan beads. The adsorption capacity of 238 mg/g, lower than the capacity of 1000 and 936 mg/g determined by Gibbs et al. [47] and Elwakeel et al. [48] for chitosan flakes.

Kyzas and Lazaridis [49] investigated the adsorption of Reactive Yellow 3RS (RY3RS) and Basic Yellow 37 (BY37), on chitosan flakes and beads. Chitosan flakes showed a higher absorption capacity for both dyes, but this difference was not as significant as in other studies. The adsorption capacity for RY3RS was 373 mg/g for chitosan flakes and 311 mg/g for chitosan beads. The adsorption capacity for BY37 was 254 mg/g for chitosan flakes and 137 mg/g for chitosan beads.

In the present study, sawdust immobilised on chitosan beads showed a good adsorption capacity for the tested anionic and cationic dyes. The adsorption capacity determined for the anionic dyes was slightly lower or comparable to that determined for the chitosan flakes and beads. The decrease in capacity was 12%–21% compared with chitosan beads.

This decrease can be explained by the fact that for sawdust immobilised on chitosan beads, 50% of the weight was chitosan and 50% was modified sawdust. The combination of chitosan and modified sawdust did not affect the binding efficiency of anionic dyes. Sawdust immobilised on chitosan beads had a particularly positive effect on improving the binding efficiency of cationic dyes compared with chitosan beads. Moreover, sawdust immobilised on chitosan beads showed good desorption of all tested dyes.

Based on the K_1 values, the affinity of the chitin flakes for the two tested anionic dyes was markedly higher than the affinity for the two tested cationic dyes. Similarly, Akkaya et al. [33, 50] reported that chitin flakes had a high affinity for Reactive Yellow 2 (RY2) and RB8 as well as indigo carmine and trypan blue based on the adsorption isotherms. The other adsorbents had much lower affinity for all dyes, denoted by the lower K_1 values. The K values in the present study are comparable with the results of Kyzas and Lazaridis [49]. For BY37, the K value was 0.0302 l/mg for chitosan beads and 0.0167 l/mg for chitosan flakes, and for RYG3RS, the K value was 0.0649–0.0542 l/mg. Wu et al. [45] reported a K value of 0.2 l/mg for RR 222 adsorption on spheres, higher than the K value determined for chitosan flakes (0.052 l/mg). The authors explained these results based on the larger adsorption surface and the looser pore structure of the chitosan beads compared with the chitosan flakes, which facilitated the adsorption of RR222. The K_2 values were comparable regardless of the adsorbent and the dye, ranging from 0.001 to 0.05 l/mg. The combination of both immobilised sawdust and chitosan beads resulted in a similar adsorption affinity for both anionic and cationic dyes.

The efficiency of adsorption of anionic and cationic dyes on each component of sawdust immobilised on chitosan beads depends on several factors. The surfaces of cellulosic adsorbents become negatively charged when they come into contact with water. The binding of cationic dyes (e.g. BV10 and BG4) occurs mainly by ion exchange adsorption. On the other hand, the anions of anionic dyes (e.g. RY84 and RB8) are repelled when they approach a negatively charged surface, which is why the removal efficiency is lower. The adsorption process on nitrogen-containing biological adsorbents, which include chitin and chitosan, is different compared with cellulose-containing adsorbents. The chemical structure of these adsorbents enables the binding of anionic dyes by ion exchange adsorption and by hydrogen bonds or intermolecular interactions caused by van der Waals forces, which leads to an increase in adsorption affinity.

The K value can indicate the mechanism of dye binding to the tested adsorbents. Different K_1 and K_2 values may indicate a different type of binding of the dye to the first and second types of active sites of adsorbents. High values indicate strong chemical binding while lower values indicate weaker physical binding. The higher K_1 values in the present study could indicate that there is chemical binding at the first type of active site, especially in case of chitin. On the other hand, the lower K_2 values could indicate weaker physical binding of the second type of active site. This desorption results support this view. The total amount of dye released was equal or close to the amount of dye bound to the second type of active site during adsorption.

An adsorbent may be used in several ways. It may be used once and then disposed of – for example, by incineration or disposal in a landfill – or regenerated. From an economic point of view, methods that allow the regeneration of the adsorbent and the recovery of the desorbed substance are more favourable. Therefore, the efficiency of recovery of the adsorbed components also determines the possibility of using the adsorbent. Repeated use of the adsorbent should maintain its adsorption capacity (maximum adsorption capacity) and not cause physical changes or damage.

In the present study, desorption was carried out by changing the pH of the solution. Although the double-Langmuir model was also used to describe the desorption process,

the K_2 and b_2 values were very small. This indicates that desorption occurs from one type of active site. Consistently, the single-Langmuir model adequately described the data, as confirmed by the R^2 values.

4. Conclusions

This paper presented the production and efficiency of adsorption and desorption of anionic and cationic dyes on chitin flakes, chitosan flakes, chitosan beads and modified sawdust on chitosan beads. Chitin flakes showed the lowest binding efficiency for anionic and cationic dyes, but the highest desorption efficiency. Chitosan flakes and beads showed a much higher adsorption capacity, particularly for the anionic dyes. Compared with chitin flakes, the increase in adsorption efficiency was not associated with an increase in desorption efficiency. In addition, they had a significantly lower adsorption capacity. Based on the results, it can be concluded that the combination of two adsorbents with different properties allowed for the removal of both anionic and cationic dyes, especially the latter, by adsorption with high efficiency.

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