USE OF CHITOSAN ADSORBENTS FOR DYE REMOVAL IN THE AIR-LIFT REACTOR

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Abstract

Adsorption tests in the air-lift reactor were carried out for six dyes – four anionic (RR11, RB5, RB8, and RR18) and two cationic (BV10 and BG 4) – as well as three adsorbents – chitosan flakes, chitosan in the form of beads, and modified sawdust immobilised in chitosan (adsorbent 3). The dye concentration in the inflow to the reactor in all the conducted test series was 10 mg/dm³; the amount of adsorbent was also constant at 10 g dry matter (d.m./dm³, and the flow rate was 0.1 V/h. For all tested dyes, the obtained maximum adsorption capacity was high and ranged from 3802 to 2203 mg/g d.m. for chitosan flakes, from 3312 to 2076 mg/g d.m. for chitosan beads, and from 2734 to 2148 mg/g d.m. for modified sawdust immobilised in chitosan. The immobilisation of sawdust on chitosan resulted in effective adsorption of both anionic and cationic dyes.

***Keywords**: chitosan; chitosan beads; modified sawdust immobilised in chitosan, dye*

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1. Introduction

Adsorption can be carried out under dynamic or static conditions. Dynamic adsorption can be used in a single- or multi-stage batch system either co-currently or counter-currently. The speed of the process depends on the size of the adsorbent particles: the smaller the particles, the faster the process. For this reason, it is advisable to use dust adsorbents [1]. However, there are problems with removing the adsorbent from the purified solution.

Moving or fixed bed reactors are most often used for dynamic adsorption. In both fixed and moving bed adsorbers, the adsorbent with an exhausted adsorption capacity must be discharged periodically for regeneration and replacement. Reactors can be used in the pharmaceutical industry, for environmental protection and forage production, and in many areas of the economy [2]. Depending on the method of supplying energy, the reactors can be divided into mechanically driven (e.g., mixer tanks and multistage columns with mixer), hydraulically driven (e.g., jet bioreactors and pneumatically driven such as bubble columns), and air-lift reactors.

Conventional reactors in which gas is a factor forcing the movement of liquids are now increasingly used in the chemical industry, biotechnology, and wastewater treatment. The intensive development of biotechnology in recent years has led to many modifications of the reactors used. Air-lift reactors are one of the most important groups of reactors that use air as a carrier. These reactors are attractive for both chemical and biological processes and, due to their advantages, have found wide applications mainly in biotechnology and wastewater treatment [3]. The classification of air-lift reactors depends on the type of internal or external recirculation. A characteristic feature of these reactors is a very clear circulation of the liquid mass [2, 4]. The advantages of air-lift reactors include a simple structure, no moving parts, and high efficiency of gas-liquid mass exchange. In the case of air-lift reactors, disadvantages are poor mixing, limited to low-viscosity media, and the occurrence of foaming. However, these factors do not significantly affect the efficiency of the reactor when the adsorption is carried out in it.

The mechanism of dye elimination from aqueous solutions is closely related to the chemical structure of the adsorbent. Adsorbents that contain cellulose adsorb basic dyes through electrostatic attraction and ion exchange. The acidic dyes on these adsorbents are bound by physical adsorption and the process is reversible. Chitosan is one of the few biopolymers that shows a basic character. Nitrogen-containing adsorbents, including chitin, have a much greater adsorption capacity for acidic dyes than basic dyes. This property is due to the presence of free amine (NH_2) groups; hence, chitosan has a very high adsorption capacity towards anionic dyes.

Chitin is a natural polymer of acetylated or non-acetylated glucosamine that is increasingly used in medicine, pharmacology, biotechnology, plant protection, and environmental protection. In addition to good adsorption properties, it is non-toxic, shows hydrophilic properties, is biocompatible, and is relatively resistant to biodegradation. The most important parameters characterising chitin are the molecular weight and the degree of acetylation (the percentage of *N*-acetylglucosamine in the chitin or chitosan chain). It is believed that the lower the degree of acetylation, the higher the activity of the polymer. Chitosan can be obtained either by an enzymatic process or by chemical deacetylation of chitin, which simultaneously degrades the chain and reduces the molecular weight of the polymer. Studies of chitosan as an adsorbent for the removal of acidic dyes have been presented by numerous authors [5-11]. The obtained adsorption capacities exceeding 1000 mg/g of adsorbent confirm the usefulness of chitosan for dye removal.

Agricultural and forestry waste, such as sawdust and bark, can be used successfully as adsorbents, mainly due to their wide availability, physical and chemical properties, and low costs related to transport from storage sites to disposal sites [12]. Several studies have evaluated the adsorption of dyes, toxic salts, metals, or oils from aqueous solutions using sawdust as an adsorbent. Sawdust contains organic ingredients such as lignin, cellulose, and hemicellulose with polyphenolic groups and is a promising and effective material in removing dyes [13-17].

These studies have reported a relatively wide range of adsorption capacities of sawdust adsorbents, a phenomenon that results from the difference in the type of sawdust used as well as the methods used for their preparation and modification [15, 18, 19]. The adsorption capacity of raw sawdust, depending on the type of tree, method of preparation, and dye, can be from 27.4 mg/dm^3 [20] to 398.8-526 mg/dm^3 [21].

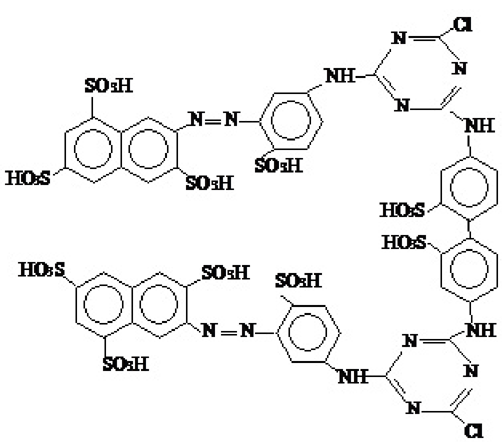
The aim of the study was to test the effectiveness of various chitosan adsorbents, namely chitosan flakes, chitosan beads, and sawdust immobilised in chitosan, to remove dyes with different reactive groups. The tests were carried out under flow conditions in an air-lift reactor to check the applicability of this type of reactor in practice.

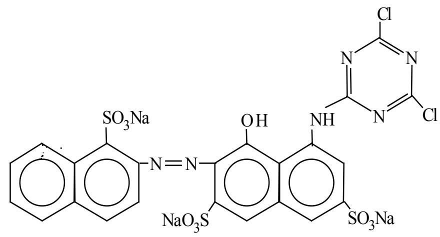
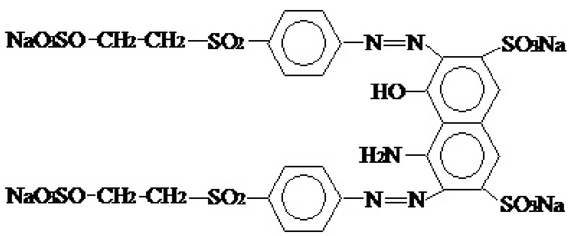
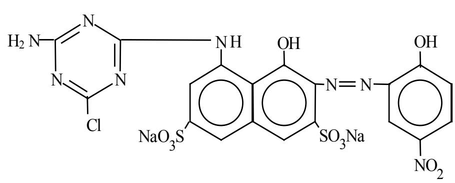
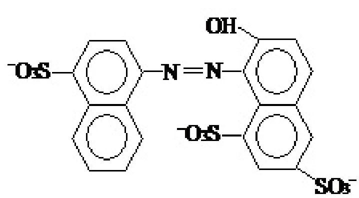
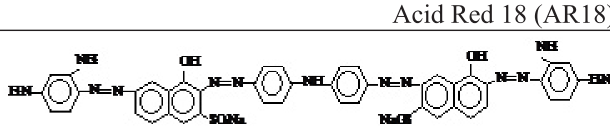
2. Research Methodology

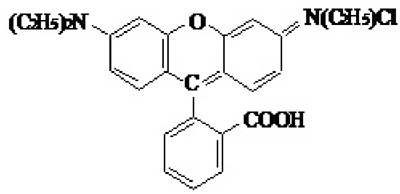
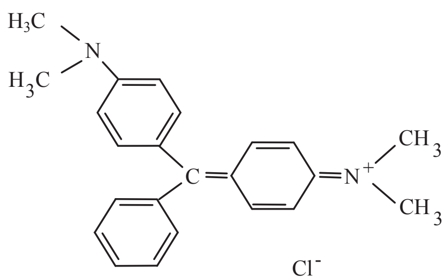
2.1. Dyes

Dyes from ZPB ‘Boruta’ SA were used in the research. Due to their widespread use in industry, dyes belonging to four classes were used in this research: reactive, acidic, direct (anionic dyes), and basic (cationic dyes). Table 1 shows the chemical characteristics of the tested dyes.

Table 1. Characteristics of the tested dyes.

Dye class	Structural formula	Molecular mass [g]
Reactive	 Reactive Yellow 84 (RY84)	1701

Dye class	Structural formula	Molecular mass [g]
Reactive	 Reactive Red 11 (RR11)	767
	 Reactive Black 5 (RB5)	992
	 Reactive Black 8 (RB8)	657
Acidic	 Acid Red 18 (AR18)	508
Direct	 Direct Black 22 (DB22)	993

Dye class	Structural formula	Molecular mass [g]
Basic	 Basic Violet 10 (BV10)	450
	 Basic Green 4 (BG4)	927

2.2. Adsorbents

2.2.1. Chitin

Krill chitin obtained from the Sea Fisheries Institute in Gdynia was used. It has a dry matter (dm) content of 95.64%, an ash content of 0.32%, and a degree of deacetylation <3%.

Before adsorption, commercial chitin was washed with distilled water and 6 N hydrochloric acid (HCl), in order to loosen the structure and remove calcium and magnesium ions and fat residues. Then, it was rinsed with distilled water until the filtrate pH was neutral.

2.2.2. Adsorbent 1: Chitosan Flakes

The chitosan was prepared from chitin washed with distilled water and HCl, boiled for 3 h in a water bath with 70% potassium base. After cooling, the chitosan was washed with distilled water until the reaction was neutral and filtered off in a vacuum. The degree of deacetylation of the obtained chitosan was 75%.

2.2.3. Adsorbent 2: Chitosan Beads

Fifty grams of chitosan, dissolved in 2% acetic acid, was dripped with a micropipette into 5% sodium hydroxide (NaOH) and incubated for 24 h. The resulting beads were filtered, rinsed, and stored in distilled water. The size of the dripped beads (3 mm) was controlled by the size of the micropipette.

2.2.4. Adsorbent 3: Beads of Modified Oak Sawdust Immobilised in Chitosan

The study used oak sawdust from the local sawmill in Naterki, a waste product from the processing of oak wood, which was modified as follows. Fifty grams of sawdust was mixed with 50 g of concentrated sulphuric acid (H_2SO_4) and heated at 150°C for 24 h. Then, the sawdust was washed with distilled water and soaked in 1% sodium carbonate for 12 h to remove residual H_2SO_4. The modified sawdust prepared in this way was dried at 105°C for 24 h and then sieved through a sieve with a mesh of 1 mm [15, 18]. The modified sawdust was then immobilised in chitosan. Twenty-five grams of modified sawdust was added to 25 g of chitosan dissolved in 5% acetic acid. Hardening of the beads consisted of dropping a mixture of modified sawdust and chitosan into 5% NaOH with a micropipette and incubating it for 24 h. The obtained beads were filtered, washed, and stored in distilled water.

Determination of the Influence of the Type of Adsorbent and Dye on the Effectiveness of Adsorption in the Air-Lift Reactor

The tests were carried out in an air-lift circulation reactor with a circular cross-section, the diagram of which is shown in Figure 1. The volume of the reactor is 0.77 dm^3. The lower part of the reactor is shaped like a truncated cone and contains nozzles that supply air and the dye solution. The dye solution is supplied by a peristaltic pump. The outflow nozzle is in the upper part of the reactor. There is a centrally located partition inside the reactor and a pocket settler at the reactor outflow.

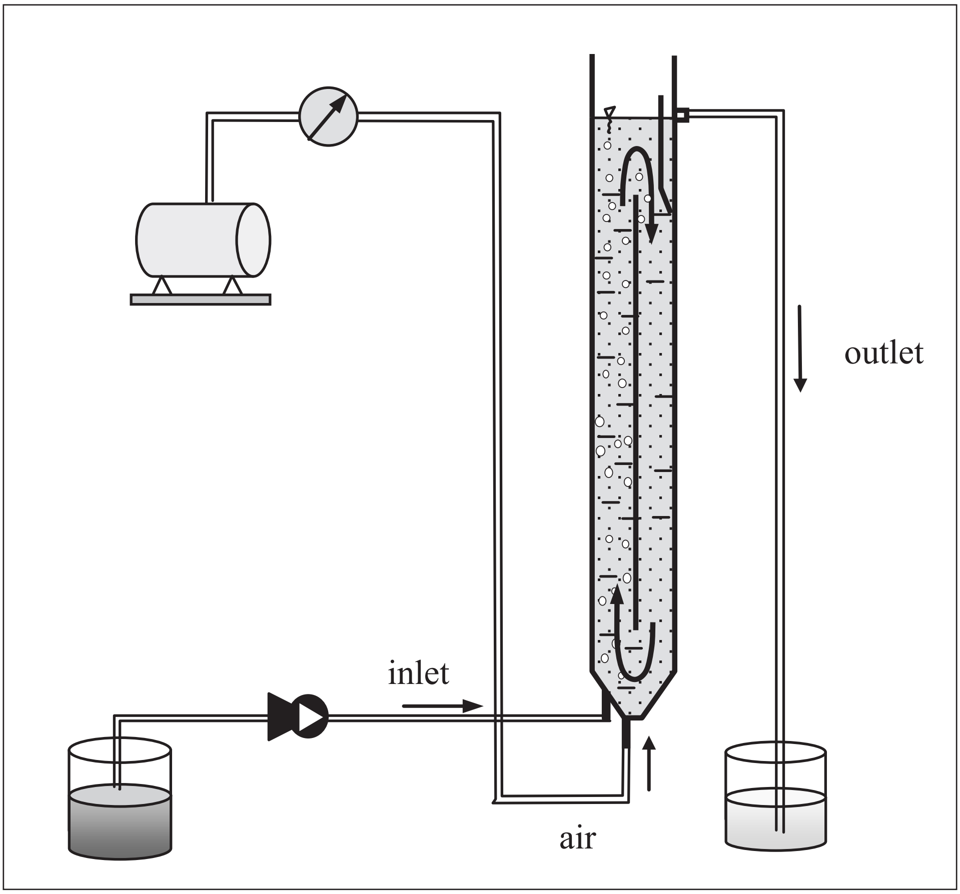


Figure 1. A diagram of the air-lift reactor.

The tests were carried out for six dyes – RR11, RB5, RB8, RR18, BV10, and BG4 (Table 1) – and three adsorbents – chitosan in the form of flakes, chitosan in the form of beads, and modified sawdust immobilised in chitosan. The pH of the solution was 5 for anionic dyes and 10 for cationic dyes. The technological assumptions of the tests are presented in Table 2.

Table 2. Technological assumptions of the dye adsorption tests on chitin in the air-lift reactor.

Parameter		Unit	Value
Flow rate of the solution	(q)	V/h	0.1
Flow rate of the air	(q)	dm^3/h	50
Adsorbent concentration	(m)	g d.m./dm^3	10
Inflow dye concentration	(C_0)	mg/dm^3	10

Note. d.m. – dry matter; V – reactor volume.

The efficiency of the process was calculated by measuring decolourization. At regular time intervals (10 min), several samples were taken and then centrifuged at 10000 rpm for 10 min. The residual dye concentration was measured spectrophotometrically. In total, 18 test series differing in the type of adsorbent and dye were carried out. In each series, the tests were carried out until the dye concentration in the outflow of the reactor was equal to the initial concentration in the inflow. Based on the tests, the breakthrough time ($C = 0.05 \times C_0$) and the maximum adsorption capacity of the tested adsorbents ($C = C_0$) were determined.

2.4. Calculation Methods

The amount of dye adsorbed under flow conditions was calculated from equation (1):

$$Q = \frac{\sum_{\tau=1}^{n}((C_k - C_\tau) \cdot q \cdot \tau)}{V \cdot m} \quad (1)$$

where:

Q – amount of adsorbed dye [mg/g d.m.]
C_k – average dye concentration in the reactor outflow in the control sample (without adsorbent) [mg/dm^3]
C_τ – average dye concentration in the reactor outflow in the time τ [mg /dm^3]
q – flow rate of the dye solution to the reactor [dm^3/h]
τ – adsorption time [h]
V – reactor volume [dm^3]
m – concentration of adsorbent in the reactor [g d.m./dm^3]

3. Results and Discussion

Two parameters of the reactor seem to be the most important for adsorption: the total mass of the dye that can be removed – and, therefore, the volume of the effluent of the assumed quality that can be obtained as a result of operating the reactor – and the nature of the adsorption curve between the breakthrough point ($C = 0.05 \times C_0$) and the point of depletion of the adsorption capacity of the adsorbent ($C = 0.90 \times C_0$) [7, 22].

The breakthrough curves obtained in six test series showing the changes in the dye concentration in the reactor outlet depending on time for adsorbents 1, 2, and 3 are shown in Figure 2. Table 3 shows the determined maximum adsorption capacities of the tested adsorbents and the total reactor operating time, when the dye concentration in the effluent was equal to that of the incoming dye ($C = C_0$).

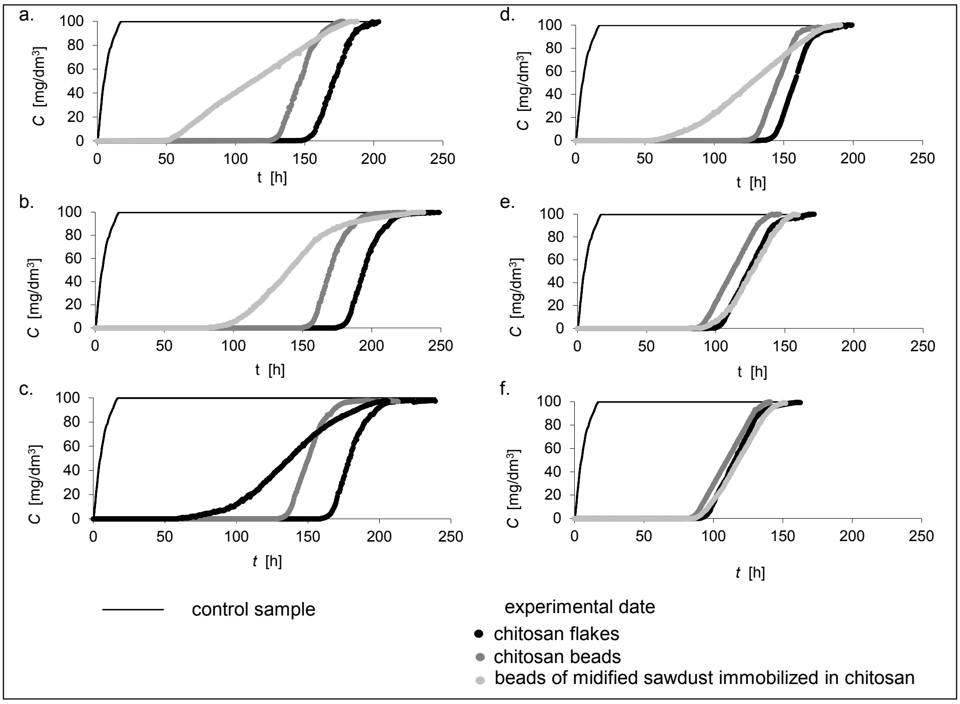


Figure 2. Breakthrough curves showing changes in the concentration of the dye remaining in the solution for RR11 (a), RB5 (b), RR8 (c), AR18 (d), BV10 (e), and BG4 (f). See Table 1 for details on the dyes.

Table 3. Adsorption capacities and reactor operating times.

Dye	Adsorbent 1		Adsorbent 2		Adsorbent 3	
	Q mg/g d.m.	τ h	Q mg/g d.m.	τ h	Q mg/g d.m.	τ h
RR11	3315	203.5	2822	179	2148	187.5
RB5	3802	252	3312	227	2734	241
RB8	3512	239	2924	213	2336	206
AR18	3046	199	2798	175	2392	191
BV10	2371	171	2121	147	2391	159.5
BG4	2203	162.5	2076	140.5	2236	152

Note. See Table 1 for details on the dyes. d.m. – dry matter.

The maximum adsorption capacity was obtained for anionic dyes and adsorbent 1: from 3802 mg/g d.m. (RB5) to 3046 mg/g d.m. (AR18). For adsorbent 2, there was a decrease in the yield for all dyes, with capacities ranging from 3312 mg/g d.m. (RB5) to 2076 mg/g d.m. (BG4). BG4 had the greatest decrease (94%). Adsorbent 3 presented different *Q* and *t* values compared with adsorbents 1 and 2. The combination of chitosan, an effective adsorbent of anionic dyes, and modified sawdust, an effective adsorbent of cationic dyes, increased the adsorption capacity of cationic dyes by 11%-13% (2391 mg/g d.m. for BV10 and 2236 mg/g d.m. for, BG4) compared with adsorbent 2; the values are comparable to adsorbent 1. There was lower but still high adsorption efficiency for the anionic dyes (RR11, RB5, RB8, and AR18) – from 2734 to 2148 mg/g d.m. This could be due to the fact that adsorbent 3 contains a 1:1 ratio of chitosan to modified sawdust, so the amount of chitosan in the reactor in the case of adsorbent 3 was lower than that of adsorbent 2 (the other half was modified sawdust). Taking into account the amount of chitosan in adsorbent 3, it can be seen that in the case of anionic dyes, from 737 mg/g d.m. (RR11) to 1174 mg/g d.m. (RB8) of the dye was adsorbed on modified sawdust (Table 4), representing 34%-45% of the total adsorption capacity of adsorbent 3. The amount of cationic dye adsorbed on the modified sawdust in adsorbent 3 was from 1331 (BG4) to 1198 mg/g d.m. (BV10). The adsorption of both dyes was >50% of the total adsorption capacity of adsorbent 3 (Table 4).

Table 4. Comparison of adsorption capacities of adsorbents 2 and 3.

Dye	Adsorption capacity mg/g d.m.				
	Adsorbent 2		Adsorbent 3		
	1 g d.m. chitosan/dm^3	* 0.5 g d.m. chitosan/dm^3	0.5 g d.m. chitosan + 0.5 g d.m. modified sawdust	0.5 g d.m. chitosan/dm^3	0.5 g d.m. modified sawdust
RR11	2822	1411	2148	1411	737
RB5	3312	1656	2735	1656	1079
RB8	2924	1462	2636	1462	1174
AR18	2798	1399	2392	1399	993
BV10	2121	1060	2391	1060	1331
BG4	2076	1038	2236	1038	1198

Note. * Adsorption capacity of adsorbent 2, assuming that the adsorbent is 50% chitosan. See Table 1 for details on the dyes.

The possibility of using an adsorbent on a technical scale is determined by how much of the adsorption capacity is used considering the assumed adsorbate removal efficiency and the reactor operating time between adsorbent exchanges. Table 5 presents the degree of use of the adsorption capacity at two characteristic points of the breakthrough curve: the breakthrough point ($C = 0.05 \times C_0$) and the adsorption capacity exhaustion point ($C = 0.90 \times C_0$).

There was a high degree of use of the adsorption capacity for chitosan in the form of flakes (adsorbent 1) and beads (adsorbent 2), regardless of the type of dye. For anionic dyes, the use of chitosan in the form of flakes ranged from 92.6% (RB5) to 86.5% (AR 18), and for chitosan in the form of beads, it ranged from 91.5% (RB5) to 89.0% (RR11). In the case of cationic dyes, the use of chitosan in the form of flakes and beads was lower, ranging from 83.6% (V10) to 79.5% (BG4). The modified sawdust in chitosan (adsorbent 3) showed lower use of the adsorption capacity for anionic dyes. This outcome was due to the fact that chitosan accounted for 50% of the dry weight of adsorbent 3 (Table 5).

Table 5. Use of the total adsorption capacity with the assumed dye removal efficiency.

Dye	Degree of use of the adsorbent (%)					
	Adsorbent 1		Adsorbent 2		Adsorbent 3	
	$C = 0.05C_0$	$C = 0.90 \times C_0$	$C = 0.05 \times C_0$	$C = 0.90 \times C_0$	$C = 0.05 \times C_0$	$C = 0.90 \times C_0$
RR11	90.2	99.7	89.0	99.6	48.0	99.3
RB5	92.6	99.7	91.5	99.6	69.0	98.5
RB8	91.7	99.3	89.3	99.0	58.2	99.2
AR18	86.5	99.4	89.3	99.5	54.2	99.5
BV10	83.6	99.2	80.7	99.6	77.4	99.7
BG4	82.2	99.2	79.5	99.7	77.4	99.6

Note. See Table 1 for details on the dyes.

For most adsorption in water and wastewater, the breakdown curves take the characteristic ‘S’ shape, but the slope of the curve varies depending on the process. For all test series, the tangents at $C/C_0 = 0.5$ were determined. To evaluate the course of the adsorption process under dynamic conditions, the *a* parameter was used, determined as the tangent to the breakthrough curve at the point $C/C_0 = 0.5$. Figure 3 shows the relationship between C/C_0 and the adsorbate volume V that flowed through the reactor. The tangents to the breakdown curves at the point $C/C_0 = 0.5$ were determined for all the test series. Then, the slope coefficients of *a* were determined for the tangents, the values of which are presented in Table 6.

Table 6. Values of the slope coefficients of *a*.

Dye	Adsorbent 1	Adsorbent 2	Adsorbent 3
RR 11	0.420	0.408	0.100
RB 5	0.557	0.515	0.180
RB 8	0.495	0.434	0.150
AR 18	0.475	0.418	0.130
BV 10	0.310	0.297	0.280
BG 4	0.290	0.277	0.270

Note. See Table 1 for details on the dyes.

There was a clear tendency of the slope of the tangent to change depending on the type of adsorbent. The highest values of the coefficient were recorded for adsorbent 1, and the lowest for adsorbent 3, regardless of the type of dye. The type of adsorbent had the strongest influence on the shape of the breakthrough curve for anionic dyes. In the case of cationic dyes, the differences between the values of coefficient *a* were much smaller, only about 10%.

Based on the conducted research, it can be concluded that the values of coefficient *a*, describing the slope of the tangent, were high when the adsorption process in dynamic conditions was most favourable. Then, the time at which the adsorbate was effectively bound to the adsorbent ($C < 0.05 \times C_0$) was extended, and after high adsorbent saturation with the adsorbate, there was a rapid increase in the concentration of the adsorbate in the outflow. Along with the decrease in the value of *a*, the time during which the dye was bound with high efficiency on the adsorbent was reduced, and the use of the total

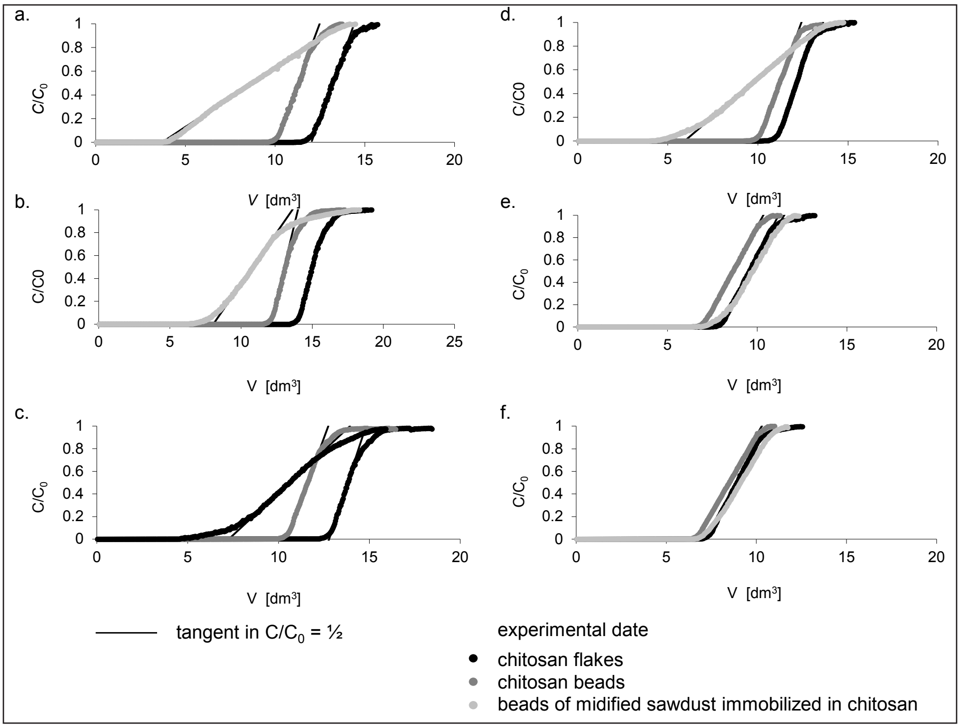


Figure 2. Changes in dye concentration in the reactor outflow depending on the volume of dye solution supplied during adsorption on chitin: RR11 (a), RB5 (b), RR8 (c), AR18 (d), BV10 (e), and BG4 (f). See Table 1 for details on the dyes.

adsorbent capacity of the adsorbent decreased. This dependence was observed regardless of the type of dye and the type of adsorbent.

The use of the adsorption capacity of chitosan flakes and beads at the breakthrough point of the reactor exceeded 90% for anionic dyes and about 80% for cationic dyes. Compared with the literature, the degree of chitosan utilisation during adsorption in the air-lift reactor obtained in our research was very high. In a previous paper, the degree of chitosan utilisation during t adsorption of RB5 ranged from 37.8% to 68.7%, depending on the dye concentration in the inflow, the inflow intensity, the mass of chitosan in the reactor, or the size of chitosan flakes [7]. The results from the present study showed that the adsorption of both anionic and cationic dyes in the air-lift reactor was characterised by much higher use of the maximum adsorption capacity of the tested adsorbents.

4. Summary

Tests under flow conditions in the air-lift reactor showed that for all tested dyes, the obtained maximum adsorption capacity was high and ranged from 3802 to 2203 mg/g d.m. for chitosan flakes, from 3312 to 2076 mg/g d.m. for chitosan beads, and from 2734 to 2148 mg/g d.m. for modified sawdust immobilised in chitosan. The adsorbent consisting of a combination of chitosan and modified sawdust was particularly effective in adsorbing cationic dyes. The adsorption capacities for BV10 and BG4 during adsorption on this adsorbent were higher by about 7%-13% compared with the capacities obtained for chitosan beads.

Based on the conducted tests, the value of the tangent slope *a* depends on the effectiveness of the adsorption process under dynamic conditions. The higher the constant values, and the longer the reactor is operated, the dye concentration in the outflow was equal to $C = 0.05 \times C_0$ was extended. Along with the decrease in the value of *a*, the time during which the dye was bound to the adsorbent was reduced, and the utilisation of the total adsorption capacity of the adsorbent decreased. This dependence was observed regardless of the type of dye and the type of adsorbent.

To sum up, under dynamic conditions, the use of adsorbents in the form of beads (adsorbents 2 and 3) was more advantageous, due to the reactor operation and the loss of the adsorbent, compared with the flake adsorbent (adsorbent 1). The maximum adsorption capacity was higher compared with the maximum adsorption capacity obtained under static conditions for all the dyes tested. Adsorbent 3, which is a combination of chitosan and modified sawdust, was particularly effective against cationic dyes. The adsorption capacities of adsorbent 3 for BV10 and BG4 were higher than those obtained for chitosan alone in the form of beads (adsorbent 2).

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