

REUSABILITY OF CHITOSAN AND SAWDUST-MODIFIED CHITOSAN FOR ADSORPTION/DESORPTION OF ANIONIC AND CATIONIC DYES

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Abstract

We explored the multiple uses of chitosan in the form of beads and beech sawdust immobilised in chitosan to remove anionic (Reactive Yellow 85 and Reactive Blue 5) and cationic (Basic Violet 10 and Basic Green 4) dyes. For both anionic dyes, with the next adsorption/desorption cycle, the amount of dye accumulated in the adsorbent increased, which resulted in a decrease in the desorption efficiency. The number of possible adsorption/desorption cycles was regulated by the occupation of all active sites. We observed the opposite trend for the cationic dyes: the charge accumulated in the adsorbent after both adsorption and desorption decreased with subsequent cycles. Despite the low accumulated charge compared with the total adsorption capacity of the adsorbents, it was impossible to further adsorb and desorb the dye. The results demonstrated that for both adsorbents tested, it was possible to carry out 6–7 adsorption/desorption cycles, but the desorption efficiency decreased with each cycle.

Keywords: *chitosan, sawdust modified in chitosan, cyclical adsorption/desorption*

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1. Introduction

The treatment of wastewater from the textile industry creates many problems [1]. The variety of dyes used today and the constant changes in production technologies make it difficult to develop a simple, universal, effective, and economical method to remove dyes from wastewater. Due to the diverse susceptibility of materials to dyeing and the high solubility of dyes, even as much as half of the dye used in the process ends up in the sewage. This creates a problem especially due to the significant amounts of water used in the textile industry, which shows the greatest demand for dyes [2–4]. Some of the dyes that enter the environment after the purification process can cause serious changes to aquatic ecosystem, including limiting the access of sunlight to deeper layers of water and reducing the diffusion of atmospheric oxygen into the water, which in total reduces photosynthesis [5]. This further leads to the formation of anaerobic conditions in water reservoirs and, consequently, the collapse of the aquatic ecosystem. Moreover, dyes and their decomposition products often show toxic properties and limit the life functions of aquatic organisms.

These negative effects make it necessary to search for new innovative methods enabling highly effective removal of hazardous coloured substances. Biological and physicochemical methods are used to treat coloured wastewater. The main disadvantage of biological methods using, for example, activated sludge are long retention times of sewage in the bioreactor, from 20 h to 10 days. In the group of methods of chemical removal of dyes from wastewater, the most common methods are coagulation and electrocoagulation [6, 7], the advantage of which is the short time of wastewater treatment compared with biodegradation. Recently, in order to increase the efficiency of removing dyes from wastewater, advanced oxidation process (AOP) methods have been increasingly used, especially with the participation of several oxidising agents [8, 9]. The use of ultraviolet (UV) radiation allows the removal of 10%–20% of the dye, while the combination of UV and hydrogen peroxide (H_2O_2) allows almost complete removal of colour from textile wastewater [10]. Another group of wastewater decolourisation methods are membrane processes, mainly reverse osmosis and nanofiltration [11, 12], which ensure nearly 100% removal of dyes from aqueous solutions. The major disadvantages of reverse osmosis are high water losses, high operating costs, most often associated with the need to replace membranes, the formation of large amounts of hydrated sludge, and the need to pre-treat wastewater to prevent clogging of the membranes and the formation of a concentrate in which there are coloured substances in an unchanged chemical form.

Adsorption is considered to be one of the most effective, economical, and environmentally friendly methods of removing pollutants from wastewater [13]. The advantages of adsorption are low costs, often limited to the cost of the adsorbent or its transport, the effective removal of toxic substances, and additional reagents are not needed. Adsorption does not cause sludge formation or salinity of the wastewater. The adsorption process is based mainly on the proper selection of the adsorbent. Cheap adsorbents of natural origin, mainly waste from agriculture or various industries, are becoming more and more popular. In the adsorption process, it is important to properly select the adsorbent depending on the nature of the contamination. The following have been used to remove dyes from wastewater: activated carbon produced from various types of organic materials; clay minerals; zeolites; ferric substances and minerals from the silicon dioxide group; and chitin, chitosan, cellulose, lignin, and waste materials, often by-products of industrial processes in the food industry, agriculture, and the wood processing industry. Much hope is associated with the use of modified natural adsorbents, which are an innovative alternative to traditional commercial adsorbents [14–17]. The ability to bind dyes by various types of adsorbents is related to both the type of adsorbent and the structure of the dye.

The most important limitations of the widespread use of adsorption processes is the lack of a universal adsorbent that, regardless of the type of dye (anionic, cationic), would be highly effective. Other important factors are the costs associated with the separation of the adsorbent in the form of dust or flakes from the purified solution, as well as the mechanical strength that enables multiple uses of the adsorbent in subsequent adsorption and desorption cycles. These disadvantages can be eliminated, for example, by using immobilisation processes.

In the present study, modified sawdust was immobilised in chitosan gel carrier to develop a new adsorbent. The combination of chitin and sawdust waste products takes advantage of the properties of both adsorbents. Modified sawdust immobilised in chitosan gel shows good adsorption properties for anionic and cationic dyes and improves the mechanical properties, allowing the use of the adsorption process to remove dyes under dynamic conditions.

2. Materials and Methods

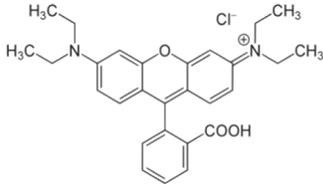
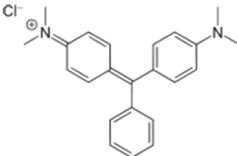
2.1. Dyes

Dyes from ZPB 'Boruta' SA were used in this study. Due to the widespread use in industry, dyes belonging to two classes were used in this study: reactive (anionic dyes) and basic (cationic dyes). Tables 1 and 2 show the chemical characteristics of the anionic and cationic dyes tested, respectively.

Table 1. Characteristics of the anionic dyes used in this study.

| Dye name | Reactive Black 5 (RB5) | Reactive Yellow 84 (RY84) |
|------------------------|---|--|
| Structural formula | | |
| Chemical formula | $C_{26}H_{21}N_5Na_4O_{19}S_6$ | $C_{52}H_{38}Cl_2N_{18}O_{26}S_8$ |
| Molecular mass | 991 g/mol | 1628 g/mol |
| λ_{max} | 600 nm | 356 nm |
| Type of dye | Anionic (reactive) | Anionic (reactive) |
| Dye class | Double azo dye | Double azo dye |
| Dye application | Dyeing of cotton, viscose, wool, and polyamide fibres | Dyeing of polyester, cotton, and synthetic silk |
| Other commercial names | Begazol Black B Diamira Black B Remazol Black B | Active Yellow HE-4R Apollocion Yellow H-E4R Lamafix Yellow HER |

Table 2. Characteristics of the basic dyes used in this study.

| Dye name | Basic Violet 10 (BV10) | Basic Green 4 (BG4) |
|--------------------|---|--|
| Structural formula |  |  |
| Chemical formula | $C_{28}H_{31}ClN_2O_3$ | $C_{27}H_{28}N_2O_8$ |
| Molecular mass | 479 g/mol | 365 g/mol |
| λ_{max} | 554 nm | 618 nm |
| Type of dye | Basic (cationic) | Basic (cationic) |
| Dye class | Triphenylmethane | Triphenylmethane |
| Dye application | Dyeing of cotton, paper, and leather Production of printing and painting dyes | Dyeing of wool, cotton, silk, leather, and paper |

2.2. Adsorbents

2.2.1. Adsorbent 1: Chitosan Beads

Chitosan in the form of flakes with a degree of deacetylation of 85%, a viscosity of 100 mPa·s, and a dry matter content of 86.8% (Heppe, Germany) was used. First, 50 g of chitosan, dissolved in 2% acetic acid, was dripped with a micropipette into 5% sodium hydroxide (NaOH) and left in the solution for 24 h. The resulting beads were drained, rinsed, and stored in distilled water. The size of the beads (3 mm) was controlled by the size of the micropipette.

2.2.2. Adsorbent 2: 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, was used and modified. To modify sawdust, 50 g of sawdust was mixed with 50 g of concentrated sulfuric acid and heated for 24 h at 150°C. Then, the sawdust was washed with distilled water and soaked in 1% sodium carbonate for 12 h to remove residual sulfuric acid. The modified sawdust prepared this way was dried at 105°C for 24 h, and then sieved through a sieve with a mesh of 1 mm [15, 18].

To immobilise the modified sawdust in chitosan, 25 g of modified sawdust was added to 25 g of chitosan dissolved in 5% acetic acid. The beads were hardened by dropping a mixture of modified sawdust and chitosan into 5% NaOH with a micropipette and leaving it in the solution for 24 h. The obtained spheres were drained, washed, and stored in distilled water.

2.2.3. Determining the Number of Dye Adsorption/Desorption Cycles

The cyclic adsorption and desorption of RY84, RB5, BV10, and BG4 for adsorbents 1 and 2 was evaluated. The anionic dye adsorption was carried out at pH 5 and desorption at pH 10; cationic dye adsorption was carried out at pH 10 and desorption at pH 3. The pH of the solutions was adjusted with hydrochloric acid (HCl) and NaOH. The initial concentration of all dyes tested was constant at 50 mg/l. The concentration of adsorbent in all trials was

constant at 1 g/l. The adsorption (120 min) and desorption (30 min) times were determined based on previous studies.

2.3. Analytical Methods

Samples taken for analysis were decanted and centrifuged for 15 min at 10,000 rpm. The concentration of the dye remaining in the solution was determined using a SP-3000 ultraviolet-visible (UV-VIS) spectrophotometer (OPTIMA INC., Japan), based on a standard curve. Distilled water was used as the blank.

2.4. Calculations

The amount of dye adsorbed from the solution was determined based on the change in the concentration of the dye remaining in the solution and was calculated from Equation 1:

$$Q_s = \frac{C_0 - C_s}{m} \quad (1)$$

where:

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

The amount of desorbed dye was calculated from Equation 2:

$$Q_d = \frac{C_d - C_s}{m} \quad (2)$$

where:

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

Accumulation of the dye was calculated with Equation 3:

$$Q_k = Q_s - Q_d \quad (3)$$

where:

- Q_k – amount of accumulated dye [mg/g DM];
- Q_s – amount of adsorbed dye [mg/g DM];
- Q_d – amount of desorbed dye [mg/g DM].

3. Results and Discussion

The possibility of using the adsorbent in practice is determined by the efficiency of recovering the adsorbed components in as condensed a form as possible. When reusing an adsorbent, it should maintain its adsorption capacity (maximum adsorption capacity) and not cause any physical changes or damage.

In the literature, the effectiveness of adsorption and desorption is most often assessed based on a single cycle, and the few studies that examine subsequent cycles usually consider only one adsorbent and an adsorbate. There are relatively few studies of cyclic adsorption/desorption, on the basis of which it is possible to assess the ability to use an adsorbent multiple times to adsorb various compounds – for example, dyes or metals.

We performed cyclic adsorption and desorption studies for four dyes (RY84, RB5, BV10, and BG4) and two adsorbents, namely chitosan beads (adsorbent 1) and beads immobilised in chitosan-modified sawdust (adsorbent 2). We investigated the adsorption of the dyes from the solution based on the change in the concentration of the dye remaining in the solution, determined with Equation 1. We calculated the amount of desorbed dye by using Equation 2 and dye accumulation by using Equation 3. We continued the experiment until the amount of dye adsorbed/desorbed in the next adsorption/desorption cycle did not change.

Figure 1 shows the amount of RY84 and RB5 anionic dyes adsorbed and accumulated on chitosan beads. For both dyes, there was a decrease in the adsorption and desorption efficiency in the subsequent cycles (Figure 1a and 1b). The decrease in adsorption and desorption efficiency of RY84 was slower compared with RB5, and only in the sixth cycle was the adsorption and desorption efficiency close to zero. The amount of bound and released RB5 was low already from the third cycle (Figure 1b). This may be due to the different method of dye binding and the different molecular weight of the dyes tested. RY84 has a much higher molar mass (1628 g/mol) than RB5 (991 g/mol), which may result in slower penetration into the adsorption sites of the adsorbent, and a relatively high desorption efficiency would indicate the physical nature of the bond. In the case of RB5, the low efficiency of adsorption and especially desorption, already from the second cycle, may indicate a permanent bond of RB5 with chitosan in the form of beads. This is shown in the graphs of the accumulation of both anionic dyes in the chitosan beads in the subsequent cycles (Figure 1c and 1d). The amount of RY84 permanently bound to the adsorbent did not change from the fifth cycle, and RB5 was practically permanently bound to adsorbent 1 from the second cycle. The results prove the possibility of using chitosan adsorbent in the form of beads to remove anionic dyes, but without the possibility of regeneration, especially in the case of RB5.

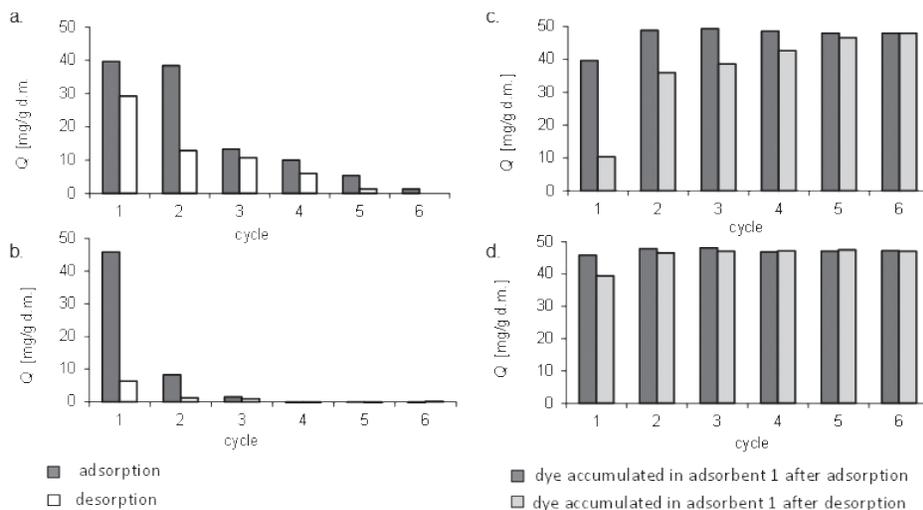


Figure 1. The amount of adsorbed (a) Reactive Yellow 84 (RY84) and (b) Reactive Black 5 (RB5) and accumulated (c) RY84 (d) RB5 in the adsorption/desorption cycles on chitosan beads (adsorbent 1).

The cationic dyes BV10 and BG4 showed different results. There were six adsorption/desorption cycles, but the load of the dye accumulated in adsorbent 1 was significantly lower compared with the anionic dyes (Figure 2c and 2d) and reached a maximum of about

16% of the initial charge. The subsequent adsorption/desorption cycles did not increase the accumulation of the dye on the adsorbent. Despite the much lower efficiency of binding and accumulation of these dyes on the chitosan beads, there was a high ability to regenerate the adsorbent. Only in the sixth adsorption/desorption cycle were there no changes in the amount of adsorbed or desorbed dye (Figure 2). The results indicate the possibility of regenerating adsorbent 1 when removing cationic dyes, but the amount of cationic dyes removed is relatively low, which is disadvantageous and excludes practical use.

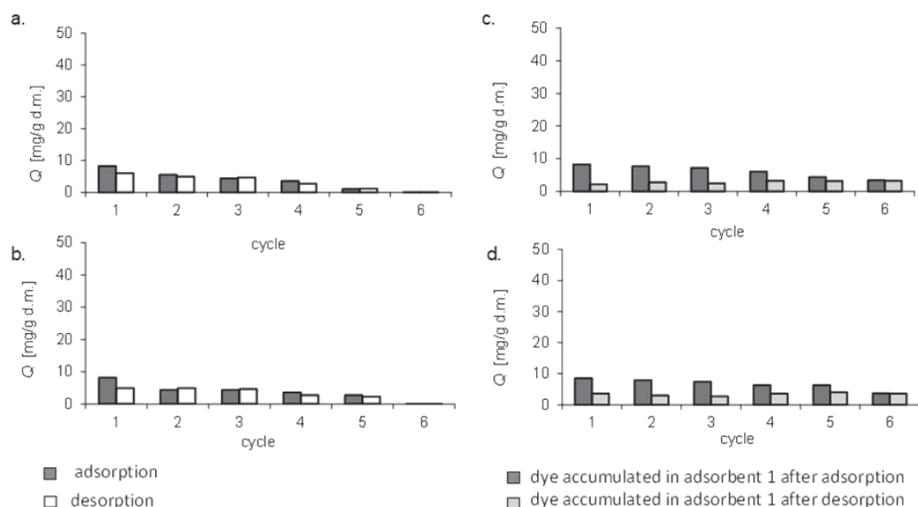


Figure 2. The amount of adsorbed (a) Basic Violet 10 (BV10) and (b) Basic Green 4 (BG4) and accumulated (c) BV10 and (d) BG4 in the adsorption/desorption cycles on chitosan beads (adsorbent 1).

Immobilisation of modified sawdust in chitosan had a very positive effect on the removal of cationic dyes without significantly reducing the binding efficiency of anionic dyes. Figures 3 and 4 show the cyclic adsorption and desorption of the anionic dyes RY84 and RB5 and the cationic dyes BV10 and BG4, and the accumulation of these dyes on beads of sawdust immobilised in chitosan (adsorbent 2).

When analysing the changes in the amount of dye accumulated on adsorbent 2 (Figures 3 and 4), similarly to adsorbent 1 the amount of adsorbed RY84 and RB5 was always higher compared with the amount of desorbed dye. Moreover, with the next adsorption/desorption cycle, the amount of dye accumulated in the adsorbent increased (Figure 3c and 3d). This means that also in case of the adsorbent 2, the number of possible adsorption/desorption cycles for the anionic dyes was related to the adsorbent reaching its total adsorption capacity.

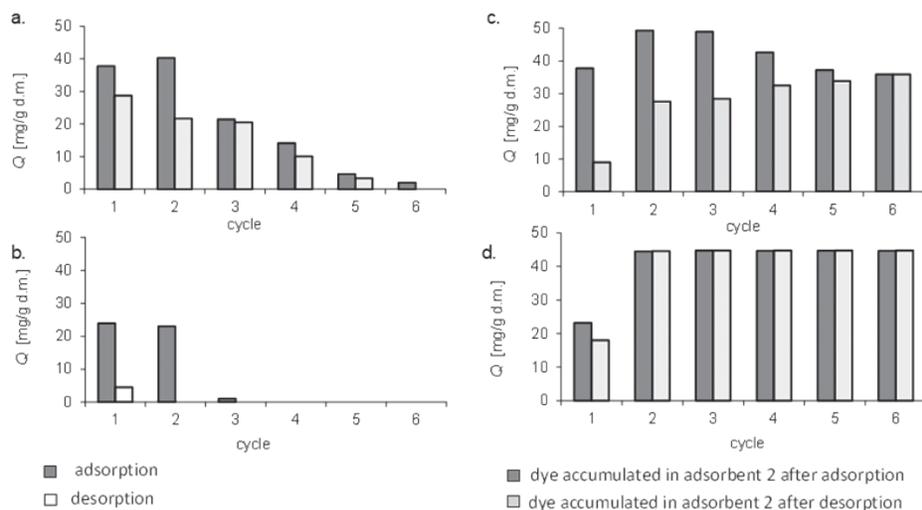


Figure 3. The amount of adsorbed (a) Reactive Yellow 84 (RY84) and (b) Reactive Black 5 (RB5) and accumulated (c) RY84 and (d) RB5 in the adsorption/desorption cycles on modified sawdust in chitosan (adsorbent 2).

Immobilisation of modified sawdust in chitosan had a positive effect on the cyclic adsorption/desorption of the two cationic dyes (Figure 4). For both dyes, the number of cycles increased to 7, and the binding efficiency in the first cycle increased from 16% to 97%. Accumulation of cationic dyes in adsorbent 1 was low from the first cycle (Figure 2), while in the case of adsorbent 2, which combined chitosan and modified sawdust, the amount of dye accumulated after adsorption during the first two cycles was much higher, reaching about 96%, but decreased with each subsequent cycle. The dye load in adsorbent 2 after adsorption and desorption was always lower compared with the load in the previous cycle (Figure 4c and 4d).

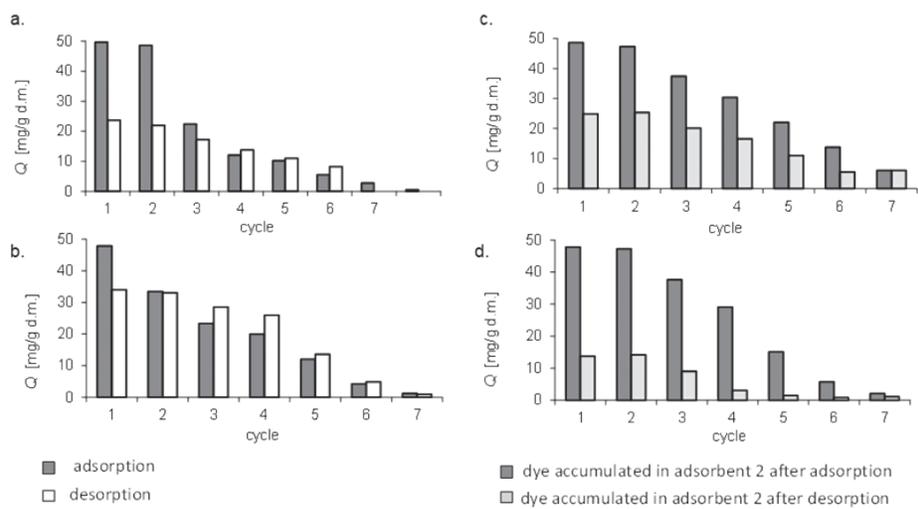


Figure 4. The amount of adsorbed (a) Basic Violet 10 (BV10) and (b) Basic Green 4 (BG4) and accumulated (c) BV10 and (d) BG4 in adsorption/desorption cycles in modified sawdust in chitosan (adsorbent 2)

Based on the obtained results, it can be concluded that:

- for anionic dyes, the number of possible adsorption/desorption cycles resulted from occupying all active sites – the adsorbent did not bind or release the dye to the solution, and the charge accumulated in the adsorbent after adsorption and after desorption was equal;
- for cationic dyes, after finishing the process of cyclic adsorption/desorption, adsorbent 1 in the form of chitosan beads was only filled with 12% (BV10) and 4% (BG4) of the dye. Despite the low accumulated charge compared with the total adsorption capacity, it was impossible to adsorb and desorb more dye. There was an analogous mechanism for adsorbent 2. This may be due to the occupation of active sites by the ions of the NaOH and HCl solutions used to control the pH, or it may also be the result of a permanent positive charge on the surface, which resulted in repulsion of cationic dyes.

The literature most often assesses the efficiency of desorption based on a single cycle, and the tests in cycles usually concern one adsorbent and adsorbate or only assess the efficiency of adsorption in subsequent cycles. There are relatively few studies of cyclic adsorption/desorption, an approach that allows assessing how many times the adsorbent can be used for various compounds, including dyes and metals, and the mechanism by which the dye, metal, or other impurity accumulates in the adsorbent. As our own research has shown, the mechanism of adsorption/desorption is also important, as it determines the possibility of carrying out subsequent cycles.

According to Tisser *et al.* [19], who evaluated the desorption of rhodamine dye from wool, desorption can be due to the deprotonation of cation and amine groups present in the sample under alkaline conditions. During desorption, the negatively charged surface of the sample will increase, thereby repelling dye molecules to the aqueous medium, a phenomenon that allows the functional groups to be vacant for the next adsorption cycle.

Chiou and Li [20] explained the desorption mechanism as deprotonation of positively charged amino groups in alkaline solutions, so the electrostatic interactions between chitosan and the dye are weaker, which results in the dye leaving the chitosan adsorption site. The authors presented the adsorption capacity of chitosan beads during adsorption/desorption/adsorption of RR189. Similarly to our research, they carried out adsorption at pH 3 and desorption at pH 10. The adsorption capacity in the first cycle was 1616 mg/g and the desorption capacity was 591 mg/g. The adsorption capacity in the second cycle was comparable to that of the first cycle.

Kyzas and Lazaridis [21] attributed the decrease in desorption/adsorption efficiency in subsequent cycles to either a higher swelling degree of the flake adsorbent or to a different distribution of the active sites of the adsorbent, which may reduce desorption. In the first cycle, for both cationic and anionic dyes, they noted higher adsorption efficiency on chitosan flakes. However, in subsequent cycles, also regardless of the type of dye, the authors found a decrease in the effectiveness of adsorption on chitosan in the form of flakes of up to 15%, while the differences in the cycles of adsorption and desorption on chitosan beads did not exceed 5%.

Zhou *et al.* [22] analysed the possibility of using a chitosan-based adsorbent multiple times. The authors showed three incomplete adsorption/desorption cycles of two anionic dyes, Acid Orange 7 (AO7) and Acid Orange 10 (AO10), using modified chitosan. They carried out desorption by changing the pH of the solution from 3 to 10. The adsorption efficiency in the second cycle was 81.1% and 87.8% for AO7 and AO10, respectively, of the capacity obtained in the first cycle. The authors attributed the decrease in the amount of absorbed dye to the fact that in an alkaline solution, positively charged amino groups are

deprotonated and the electrostatic interactions between chitosan and anionic dye molecules are weakened significantly.

In research on simultaneous adsorption of cationic and anionic dyes using chitosan/electrospun sodium alginate nanofibre composite sponges, Zhao *et al.* [23] presented six adsorption/desorption cycles for AB113 and RhB. They reported a slight decrease in the adsorption capacity in subsequent cycles to about 89% and 85%, respectively, of the initial values. According to the authors, this decrease may result from the dye molecules not being completely desorbed or the adsorption sites no longer existing in the elution process, causing the degradation of adsorption performance. Other researchers have also presented similar reasons for the decline in the effectiveness of adsorption and desorption. According to Wan *et al.* [24], the occlusion of some active sites by dye molecules, which were challenging to desorb due to strong chemical interactions with the hydrogel surface, may be the cause of the decrease in adsorption after each desorption.

Based on the conducted research, we conclude that the combination of modified sawdust and chitosan produces an adsorbent that effectively removes both anionic and cationic dyes. It is possible to reuse, in the adsorption and desorption cycles, chitosan in the form of beads and modified sawdust immobilised in chitosan for anionic dyes, but the process is effective only in the initial cycles.

4. Conclusions

The possibility of using an adsorbent multiple times determines its practical application. For all anionic dyes, the desorption efficiency decreased along the subsequent adsorption/desorption cycle, which resulted in an increase in the amount of dye accumulated in the adsorbent. The number of possible cycles for anionic dyes depended on the dye accumulation in the adsorbent. We observed the opposite tendency for cationic dyes, for which the charge accumulated in the adsorbent after adsorption and desorption decreased with subsequent cycles. Cationic dyes have a high affinity for cellulose adsorbents and anionic dyes have a high affinity for adsorbents with a positive charge, such as chitosan. We have presented a novel adsorbent – beech sawdust immobilised in chitosan – that effectively binds both anionic and cationic dyes. We found that chitosan beads could be used only once, while sawdust immobilised in chitosan could periodically adsorb and desorb cationic dyes and thus could be used multiple times.

5. Acknowledgements

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