CYCLIC SORPTION AND DESORPTION OF REACTIVE DYES ONTO CHITOSAN BEADS

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Abstract
The study was undertaken to analyze cyclic sorption and desorption of four reactive dyes: Reactive Yellow 84, Reactive Red 11, Reactive Black 5 and Reactive Black 8. onto chitosan beads. In all experimental series, dye and sorbent concentrations were constant and reached 50 mg/dm³ and 1 mg d.m./dm3, respectively. Determinations were conducted to investigate the effect of the sorbent on the effectiveness of dye removal. The number of feasible sorption/desorption cycles ranged from 6 to 3 and was found to depend on the type of dye tested. For all dyes examined, the quantity of dye accumulated onto chitosan beads and released from the solution was determined after each process of sorption and desorption.

Key words: *chitosan, cyclic sorption/desorption, reactive dyes.*

1. Introduction

Color is a visible contamination. Even low concentrations of dye in water may be the cause of water withdrawal from retail distribution, even if its toxicity is relatively low. Dyes not absorbed in the dyeing process as well as other chemicals used in the successive stages of the production process reach wastewaters and pose potential environmental hazard [1]. By reducing light penetration, color inhibits photosynthesis and growth of fauna and flora, and finally may bear toxic effects on live organisms [2].

Dyes are organic compounds containing in their molecules chromophore groups that render color and auxochrome groups that intensify color. Depending on their structure, they may form anions or cations in aqueous solutions, owing to which a dye molecule may be permanently bound with polymeric material. Dyes are compounds acknowledged as resistant to biochemical degradation, inducing skin irritations and allergies, as well as frequently toxic, carcinogenic and mutagenic [3]. For this reason, improvement of methods for their elimination is of outmost significance.

Studies have proved that currently sorption is one of the most effective and attractive processes of dye removal from wastewaters. In addition, it is relatively inexpensive due to the possibility of applying appropriate renewable adsorbents [4].

One of the most common materials used for dye removal from wastewaters is activated carbon. It has been extensively tested, yet relatively high costs of its operation and problems with its regeneration have restricted its large-scale application. Hence, other natural, inexpensive, easily-renewable materials often being waste products of various industry branches are still sought for [5].

Contemporarily, more and more frequently adsorption process are run with the use of biosorbents, i.e. substances of plant or animal origin (usually by-products), e.g. bark rich in tannins, marine plants, humus, moss peat, modified cotton, wool, chitin, chitosan and alginate. Another type of biosorbents are microorganisms – pure bacterial cultures, activated sludge, biomass being a waste product in the pharmaceutical industry, and algae. Biosorbents include also biopreparations, e.g. immobilized microorganisms, mixtures of biosorbents with the addition of minerals, and APV hardened peat.

The application of chitosan as an adsorbent has raised interest mainly owing to a high number of its functional groups – amine and hydroxylic ones, which are characterised by a high catalytic absorption potential thus enabling the absorption of anionic dyes through electrostatic attraction [6].

Chitin, being a natural polysaccharide, occurs in exosceletons of marine animals (crustacea), insects and in cell walls of mushrooms. This biopolymer is composed, primarily, of repeating fragments of acetylated glucosamine and these with usually a low content of non-acetylated glucosamine. An important characteristics of chitosan is its deacetylation degree (DD), i.e. the higher the degree of deacetylation, the better the adsorption properties [7]. Chitin is widely applied as an adsorbent for a variety of substrates due to its good adsorption and hydrophilic potential. In terms of abundance, it is the second – after cellulose – polymer occurring in nature. The annual production of this anionic polymer is almost

comparable with that of cellulose [8]. Taking this into account, it seems a more attractive sorbent as compared to the activated carbon. It is additionally characterised by susceptibility to biodegradation and by fine bactericidial properties.

The objective of this study was to determine the number of feasible adsorption and desorption cycles of reactive dyes onto chitosan in the form of beads and to assay the quantity of dye absorbed and released in the successive cycles. The study was conducted with 4 reactive dyes, i.e.: Reactive Yellow 84 (RY 84), Reactive Red 11 (RR 11), Reactive Black 5 (RB 5), and Reactive Black 8 (RB 8).

2. Materials and methods

2.1. Dyes

Due to their common application, the following dyes belonging to the class of reactive dyes (anionic dyes) were used in the study (***Table 1***).

Table 1. *Characteristics of the dyes examined.*

Dye	Reactive group	Structural formula	Molecular weight, g/mole
Reactive Yellow 84	chlorotriazine		1701
Reactive Red 11	chlorotriazine		767
Reactive Black 5	vinylsulfone		991
Reactive Black 8	chlorotriazine		656,5

2.2. Sorbent

Preparation of chitosan beads

Analyses were conducted with chitin of krill obtained from the Sea Fisheries Institute in Gdynia, with dry matter content of 95.64%, ash content of 0.32%, and deacetylation degree below 3%. Before sorption, commercial chitin was rinsed with distilled water and 6 N hydrochloric acid in order to loosen its structure and wash out calcium ions, magnesium ions and lipid residues, next rinsed with distilled water until a neutral reaction of the filtrate. Afterwards, chitin was cooked for 3 h on a water bath with 70% potassium base. After cooling, the chitin was again flushed with distilled water until a neutral reaction and filtrated off under vacuum.

50 g of chitin dissolved in 5% acetic acid were instilled with a micropipette to 5% NaOH and left in the solution for 24 h. The size of the instilled beads was controlled by the size of the micropipette and was 3 mm. The resultant beads were filtrated, rinsed with distilled water and kept in distilled water until used.

2.3. Analytical methods

In each of the samples, the concentration of dye left in the aqueous solution was controlled with the spectrophotometric method. Samples to be analyzed were collected (10 cm^3), decanted and centrifuged for 15 min at 10,000 r.p.m. The concentration of the remaining dye was determined acc. to standard curves in a UV-VIS Spectrophotometer SP-3000.

Wavelength at which extinction was read out was determined for each of the analyzed dyes (***Table 2***).

Table 2. *Wavelength at extinction measurement of the dyes examined.*

Dyes	Wavelength λ (nm)
RY84	383
RR11	543
RB5	597
RB8	587

3. Results and discussion

Analyses of cyclic sorption/desorption were carried out for four dyes – RY84, RR 11, RB5 and RB8, and chitosan in the form of beads used a sorbent. The process of sorption was run at pH 5.0 and that of desorption at pH 12.

The effectiveness of dye adsorption and desorption from a solution was determined based on changes in the concentration of dye left in the solution.

The quantity of adsorbed dye was computed from the following equation:

$$Q_s = (C_0 - C_s)/m \tag{1}$$

Q_s – quantity of adsorbed dye, mg/g d.m.

C_0 − initial concentration of dye, mg/dm^3

C_s − concentration of dye after sorption, mg/dm^3

m − concentration of sorbent in the sample, g d.m./dm^3

The quantity of desorbed dye was computed from the following equation:

$$Q_d = (C_d - C_s)/m \qquad (2)$$

Q_d − quantity of desorbed dye, mg/g d.m.

C_0 − Concentration of dye before desorption, mg/dm^3

C_d − concentration of dye after desorption, mg/dm^3

m − concentration of sorbent in the sample, g d.m./dm^3

Accumulation of dye was computed from the following dependency:

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

Q_k − quantity of accumulated dye, mg/g d.m.

C_s − quantity of absorbed dye, mg/g d.m.

C_d − quantity of desorbed dye, mg/g d.m.

Results of the study demonstrating sorption and desorption of the four dyes examined in the cycles were presented in *Figure 1*.

Analyses demonstrated that the number of feasible sorption/desorption cycles onto chitosan beads ranged from 6 (RY 84 and RR 1) to 3 (RB5). These results are better than
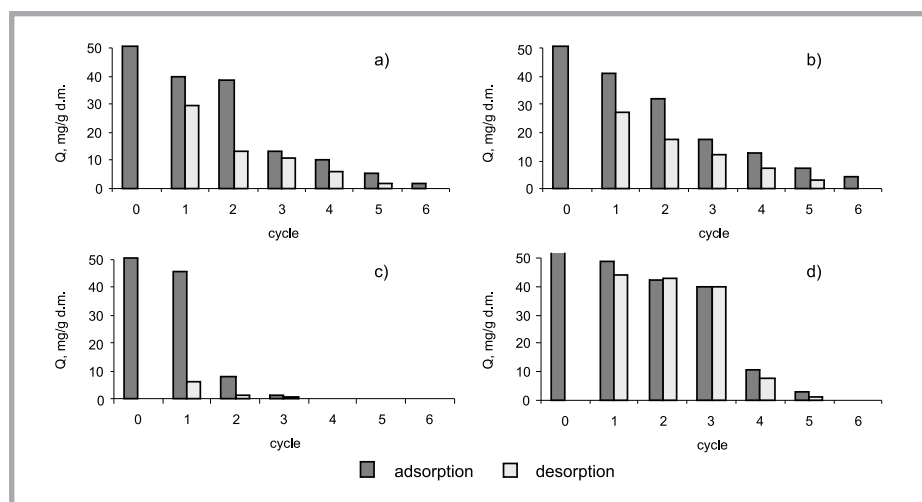

Figure 1. Quantity of Q dye adsorbed and desorbed in sorption/desorption cycles: a) RY84, b) RR 11, c) RB 5, d) RR8.

findings of other authors. Asouhidou et al. [9] managed to run three sorption/desorption cycles of reactive dyes on different activated carbons, however in the third cycle process effectiveness was low and reached ca. 7%. Other authors who were investigating cyclic sorption/desorption onto chitin reported to run from 2 to 5 cycles [10-13].

When analyzing changes in the quantity of dye adsorbed and desorbed in the sorbent (*Figure 1*), it may be observed than in the case of three out of four dyes examined the quantity of adsorbed dye was higher than the quantity of desorbed dye. An opposite tendency was noted for the RB 8 dye. The quantity of adsorbed dye was very high in the first three cycles as compared to the quantity of desorbed dye, whereas the effectiveness of both sorption and desorption was observed to decrease significantly beginning from the fourth cycle (*Figure 1.d*).

Thus, the quantity of RY 84, RR 1 and RB 5 dyes accumulated in the sorbent was observed to increase with each successive sorption/desorption cycle (*Figures 2.a, 2.b,* and *2.c*). The number of feasible sorption/desorption cycles for these dyes was, thus, linked with the fact of almost complete filling of the sorbent with the dye and with permanent occupation of active sites capable of absorbing and removing dye.

In the case of the RB 8 dye, after completion of cyclic sorption/desorption the sorbent was filled with the dye only in ca. 10% (*Figure 2.d*). The diminished effectiveness of adsorption and desorption in the subsequent cycles may result from a variety of reasons. For instance, the course of successive cycles may be affect by the type of solutions used for desorption. Chern and Wu [14] suggest that reduced effectiveness of adsorption and desorption of dyes in the subsequent cycles may be due to the fact that ethyl alcohol applied in the desorption process may occupy active centres in which acidic dyes: Red, Yellow and Mustard Yellow, were usually adsorbed.
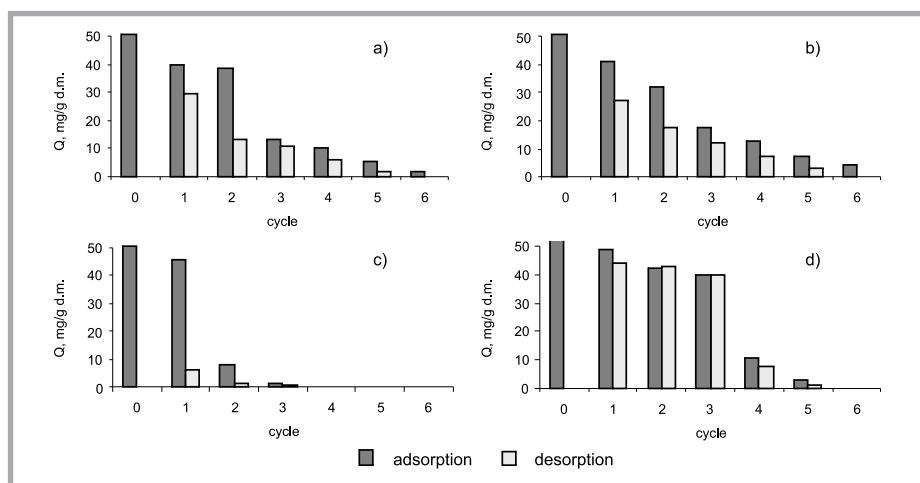
Figure 2. *Quantity of dye accumulated in sorption/desorption cycles: a) RY84, b) RR 11, c) RB 5, d) RR8.*

4. Conclusions

The study was undertaken to analyze cyclic sorption and desorption of four reactive dyes: Reactive Yellow 84, Reactive Red 11, Reactive Black 5 and Reactive Black 8. onto chitosan beads. It demonstrated that the number of feasible sorption/desorption cycles ranged from 6 to 3 and was determined by the type of dye examined. The highest number of the sorption/desorption cycles reaching 6 was run for only two out of four dyes tested, i.e. for RY 84 and RR11. They both belong to dyes with the chlorotriazine active group. In contrast, the lowest number of the cycles (3) was run in the case of RB5 dye, which possessed the vinylsulfone active group. After each sorption and desorption process determinations were conducted for the quantity of dyes accumulated on chitosan beads and dyes released from the solution. The results obtained indicate that in the case of three dyes, i.e. RY 84, RR 11 and RB 5, the reduction in the number of feasible sorption/desorption cycles was due to the depletion of active sites of the sorbent being occupied by the dye. A different mechanism was observed in the sorption/desorption cycles of the fourth dye analyzed in the study, namely RB 8. Its accumulation onto chitosan beads after all desorption cycles was low. The diminished quantity of the dye adsorbed in the two last cycles enabled 5-fold utilization of the sorbent.

5. *References*

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