EFFECT OF PH VALUE AND ADSORBENT CONCENTRATION ON THE EFFECTIVENESS OF ADSORPTION ONTO CHITIN AND CHITOSAN

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Abstract
The study was aimed at determining the effectiveness of reactive dye RB5 removal in the adsorption process onto chitin and chitosan as affected by the quantity of an adsorbent and pH value of the solution. The experiment was conducted at two concentrations of a sorbent, i.e. 1 and 5 mg d.m./dm^3 and at three values of the reaction, i.e. pH 3.0, pH 5.0, and pH 9.0. The kinetics of RB5 sorption onto chitin and chitosan was described with the use of Langmuir model. In the case of both adsorbents examined, the highest adsorption capacity was achieved at pH 3.0 and adsorbent concentration of 1 g d.m./dm^3. Increasing pH value up to pH 5.0 and 9.0 and adsorbent concentration in the sample from 1 to 5 g d.m./dm^3 caused a decrease in the quantity of dye absorbed.

Key words: *chitin, chitosan, reactive dye RB5.*

1. Introduction

The process of adsorption enables removing not only color-producing compounds but also other substances posing threat to the natural environment from water. Processes of dyes removal from wastewaters require substantial financial outlays. In contrast to chemical and physical processes, including: chemical and electrochemical oxidation, coagulation, membraneous processes, flocculation or ionic exchange, the process of adsorption does not require relatively high financial expenditures, whereas appropriately selected adsorbents - characterized by easy availability and the feasibility of regeneration - may assure high effectiveness of contaminants removal [1].

Chitin is a natural polysaccharide of β-N-acetylglucosamine. It is an organic compound constituting skeletons of the arthropods [2]. It also occurs in insects and in cellular walls of mushrooms. It is one of the key natural polymers occurring world wide [3]. It is currently estimated that the annual quantity of synthesized chitin is almost comparable with the quantity of produced cellulose [4]. Chitin displays good sorptive properties against dyes, especially having been deacetylated. Being a natural polymer of acetylated or non-acetylated glucosamine, it is extensively applied in medicine, pharmacology, biotechnology, plant protection or environment protection. Apart from good sorptive properties, it demonstrates also hydrophilic properties, susceptibility to biodegradation as well as antibacterial properties.

The undertaken study was aimed at determining the effectiveness of reactive dyes removal from aqueous solutions in the adsorption process. Analyses were conducted with two adsorbents: chitin and chitosan applied at concentrations of 1 and 5 g d.m./dm^3. An adsorbate was a reactive dye – Vinyl Sulfone Black – RB 5. Assays were carried out at three pH values, i.e. pH 3.0, pH 5.0 and pH 9.0.

The scope of the research included: determination of the effect of chitin and chitosan concentration on the effectiveness of RB 5 dye adsorption, determination of the effect of pH value on the effectiveness of RB 5 dye adsorption onto chitin and chitosan, and determination - under test conditions - of the adsorption capacity and adsorption affinity of the adsorbents.

2. Materials and Methods

2.1 Characteristics and preparation of adsorbents

The experiment was carried out on krill chitin obtained from the Sea Fisheries Institute in Gdynia. It was characterized by dry matter content of 95.64% and ash content of 0.32%.

- *chitin* – a weighed portion of commercial chitin (10 g) was poured with distilled water at a 1:10 ratio (w/w) and left for 24 h at room temperature for swelling. Swollen chitin was transferred onto a Buchner funnel and filtered off under vacuum. A weighed portion of chitin after swelling was rinsed with 6 N HCl, flushed with distilled water until neutral reaction of filtrate and filtered off under vacuum. Next, 18% KOH solution was added to chitin which was then cooked for 3 h on water bath. After cooling down, chitin was flushed with distilled water until neutral reaction and filtered off under vacuum; DD 5%

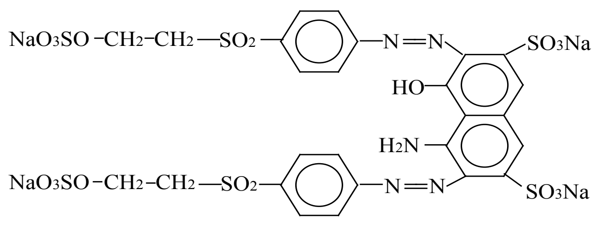

***Figure 1**. The structure of reactive dye Black 5.*

- *chitosan* – a weighed portion of chitin after swelling was rinsed with 6 N HCl and flushed with distilled water until neutral reaction of the filtrate and filtered off under vacuum. Next, 70% KOH solution was added to chitin which was then cooked for 3 h on a water bath. After cooling down, chitin was flushed with distilled water until reaching neutral reaction of the filtrate and filtered off under vacuum; DD 75%

Deacetylation degree of chitin and chitosan was analyzed according to Roberts [5].

2.2. Characteristics and preparation method of dyes.

In the experiments there was used reactive dye Black 5, produced by ZPB „Boruta" SA in Zgierz. The structure of reactive dye RB5 is displayed in ***Figure 1***.

A stock solution of the dye was prepared by weighing 1 g of pure dye in the powdered form. Next, the dye was quantitatively transferred to a 1 dm^3 measuring flask which was next filled up with distilled water with pH 6.0. Dye's concentration in the working solutions accounted for: 25; 50; 100; 200; 300; 400; 500; 600; 700; 800; 900 and 1000 mg/dm^3, respectively for chitin and chitosan.

2.3. Experimental procedures

2.3.1. Analyses under static conditions

In order to determine the adsorption capacity of chitin or chitosan, 1 and 5 g d.w./dm^3 of the sorbent was weighed into 200 cm^3 Erlenmeyer flasks and supplemented with 100 cm^3 of the working solution of the dye at an appropriate concentration, i.e. from 25 to 1000 mg/dm^3 for chitin and chitosan.

Samples were fixed on a shaker and shaken for 2 hours at a constant rate of 200 r.p.m. After shaking, the samples were sedimented for 1 minute. Dye solution was decanted and centrifuged for 10 minutes in an MPW 210 centrifuge at 10 000 r.p.m. After centrifugation, the samples were collected for determination of dye concentration. The concentration of dye was determined with the spectrophotometric method using a UV-VIS Spectrophotometer SP 3000. Absorbance values was measured at λ_{max} = 597 nm.

3. Results and discussion

The efficiency of adsorption of a dye from solution was analyzed based on changes in its concentration in the solution.

The quantity of the adsorbed dye was calculated from the following dependence:

$$Q = \frac{C_0 - C}{m} \quad (1)$$

where:
Q – the quantity of dye absorbed, in mg/g d.w.
C_o – initial concentration of dye, in mg/dm^3
C – concentration of dye after sorption, in mg/dm^3
m – sorbent mass, in g $d.w./dm^3$

The results obtained were analyzed with the use of the two-site Langmuir's model (2). Adsorption efficiency of RB5 from aqueous solutions onto chitin (*sorbent 1*) and chitosan (*sorbent 2)* was analyzed based on a dependency between the quantity of adsorbed dye *Q* in mg/g d.w. and its equilibrium concentration *C* in mg/dm^3.

$$Q = \frac{b_1 \cdot K_1 \cdot C}{1 + K_1 \cdot C} \quad (2)$$

Q – mass of dye adsorbed onto sorbent, in mg/g d.m.,
b – maximum adsorption capacity of sorbent, in mg/g d.w.,
K – a constant in Langmuir equation, in dm^3/mg,
C – dye concentration in the solution, in mg/dm^3.

Experimental results indicating a correlation between the quantity of adsorbed dye and the equilibrium concentration as well as isotherms determined from the Langmuir's equation were presented in ***Figure 2*** and ***3. Table 1*** collates values of K_1 and *b*, calculated from the Langmuir's equation, that describe affinity and adsorption capacity for the two adsorbents examined.

Analyses conducted in the study demonstrated that increasing pH values resulted in diminishing adsorption capacity in the case of both chitin and chitosan. Yet, the effect of pH value on the quantity of dye absorbed was diversified. In the case of chitin, increasing pH value from 3.0 to 5.0 was observed to diminish its adsorption capacity by ca. 80%, whereas the successive increase in pH value up to 9.0 was no longer observed to have a significant effect on its adsorption capacity (tab. 1). During adsorption onto chitosan, likewise in the case of chitin, the pH value also affected the effectiveness of the sorption process. However, in contrast to the adsorption onto chitin, increasing the pH value from 5.0 to 9.0 evoked a successive decrease in the quantity of the dye absorbed, which was not observed in the case of chitin (tab.2). Analogous results, pointing the influence of the pH value on the quantity of dye absorbed, were reported in other works of, among others: Chiou and Li [5], Klimiuk et al. [6], Filipkowska [7], Filipkowska [8], Hasan et al. [9], and Al.-Degs et al. [10].

In the presented study, assays of reactive dye RB5 adsorption were conducted at two concentrations of both adsorbents examined – 1 and 5 g d.m./dm^3. The total adsorption capacities determined from the Langmuir's model for the adsorbent applied at the concentration of 5 g d.m./dm^3 were lower as compared to those determined for adsorbent concentration of 1 g d.m./dm^3 in all experimental series run in the study. It points to the fact that increasing the quantity of an adsorbent in a sample does not result in an increase in the quantity of dye removed, and that a higher quantity of chitin or chitosan in the sample was not completely utilized. Only in the case of samples with chitin at pH 5.0 and pH 9.0 were the values of the adsorption capacity comparable at adsorbent concentrations of 1 and 5 g s.m./dm^3.

In addition, the conducted study enabled monitoring the influence of pH value and adsorbent concentration on adsorption affinity. In the series in which chitin was used as an adsorbent, likewise in the case of the adsorption capacity, the highest adsorption affinity described with a constant *K* in the Langmuir's model was obtained at pH of the solution reaching 3.0. Increasing the pH value to 5.0 and 9.0 resulted in a significant decrease in the value of the *K* constant, i.e. from 80 to 90% depending on the series. The study showed the adsorption affinity to be additionally affected by adsorbent concentration in the sample. Increasing chitin concentration from 1 to 5 d.m./dm^3 was also found to decrease the value of the *K* constant, which is likely to indicate the weaker binding of RB 5 dye with chitin. Such a tendency was not observed in the samples with chitosan. In turn, increasing the pH value did not evoke such a considerable decrease in the adsorption affinity and, simultaneously, adsorbent quantity was not confirmed to affect the adsorption affinity.

4. Conclusions

The study demonstrated the feasibility of applying chitin and chitosan as adsorbents of Vinyl Sulfone Black – RB 5 from aqueous solutions. The effectiveness of the adsorption process on both adsorbents was found to depend on the type and concentration of adsorbent applied as well as on the pH value of the solution. Chitosan turned out to be a more effective adsorbent of RB 5 dye than chitin. The adsorption capacity of chitosan ranged from 86 mg/g to 800 mg/g d.m., whereas that of chitin – from 19 mg/g to 162 mg/g d.m. The adsorption capacity of chitosan was nearly 5-fold higher as compared to that of chitin. Better effects of RB 5 removal from aqueous solutions were achieved for adsorbent concentration of 1 g/dm^3. An exception were results obtained for chitin at pH reaching 5.0 and 9.0, where the quantity of dye removed from chitin applied at concentrations of 1 g/dm^3 and 5 g/dm^3 was alike. The adsorption capacity of both adsorbents was affected, to a great extent, by the pH value of the solution. The best results were achieved at pH=3.0. Increasing the pH value of the solution caused a reduction in the adsorption capacity and thus diminished the effectiveness of RB 5 dye removal. The highest adsorption capacity accounting for 800 mg/g d.m. was obtained for chitosan at pH = 3.0, whereas the lowest one – accounting for 19 mg/g d.m. – for chitin at pH = 9.0.

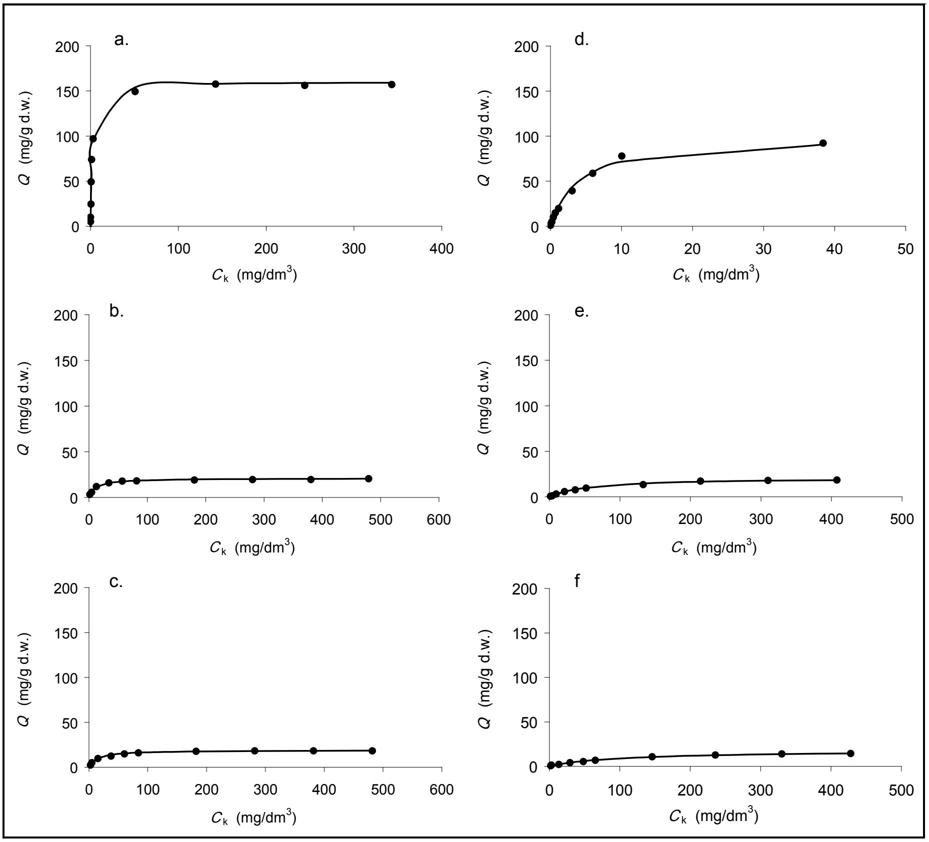

Figure 2. *Experimental results of Reactive Black 5 adsorption on chitin and approximation of adsorption with Langmuir isotherms plotted from Langmuir equation; a - 1 g d.m. chitin/dm^3 and pH 3.0; b - 1 g d.m. chitin/dm^3 and pH 5.0; c - 1 g d.m. chitin/dm^3 and pH 9.0; d - 5 g d.m.chitin/dm^3 and pH 3.0; e - 5 g d.m. chitin/dm^3 and pH 5.0; f - 5 g d.m. chitin/dm^3 and pH 9.0.*

Table 1. *Constants in Langmuir equation applied for adsorption onto chitin.*

pH	Quantity of sorbent					
	1 g d.m./dm^3			5 g d.m./dm^3		
	Constants in Langmuir equation					
	K mg/dm^3	b mg/g d.m.	R^2	K mg/dm^3	b mg/g d.m.	R^2
3.0	0.50	160	0.986	0.250	100	0.993
5.0	0.09	21	0.994	0.017	21	0.995
9.0	0.07	19	0.993	0.010	18	0.994

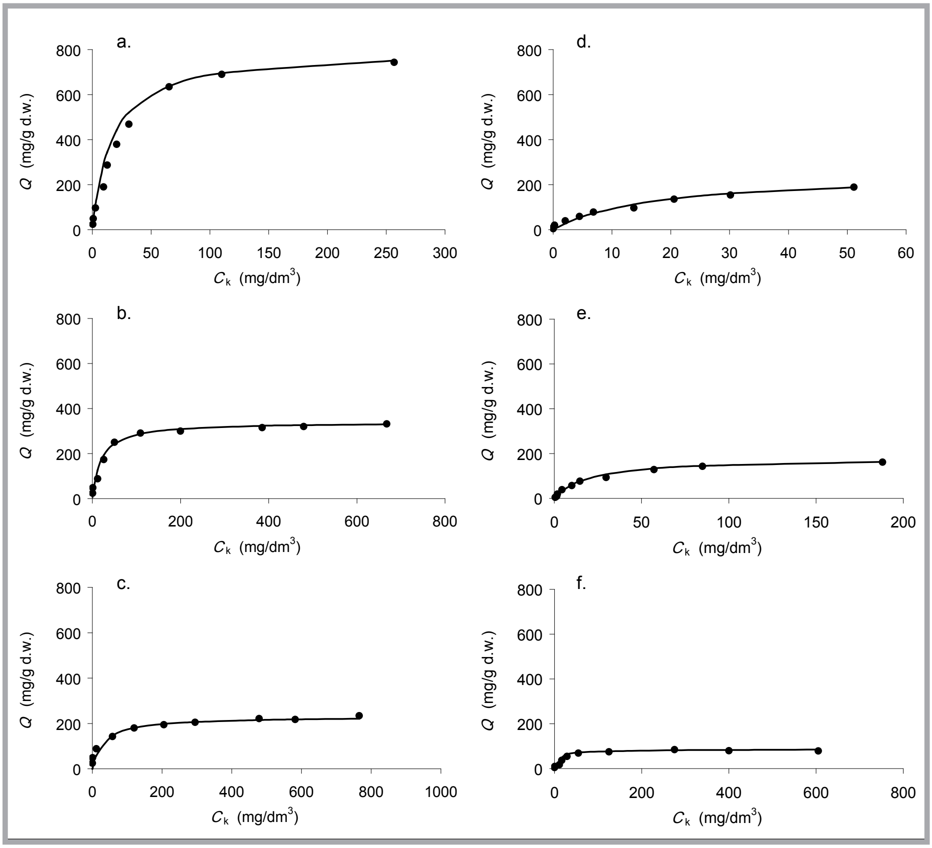

Figure 3. *Experimental results of Reactive Black 5 adsorption on chitosan and approximation of adsorption with Langmuir isotherms plotted from Langmuir equation; a – 1 g d.m. chitosan/dm³ and pH 3.0; b – 1 g d.m. chitosan/dm³ and pH 5.0; c – 1 g d.m. chitosan/dm³ and pH 9.0; d – 5 g d.m.chitosan/dm³ and pH 3.0; e – 5 g d.m. chitosan/dm³ and pH 5.0; f – 5 g d.m. chitosan/dm³ and pH 9.0.*

Table 2. *Constants in Langmuir equation applied for adsorption onto chitosan.*

pH	Quantity of sorbent					
	1 g d.m./dm3			5 g d.m./dm3		
	Constants in Langmuir equation					
	K mg/dm3	b mg/g d.m.	R2	K mg/dm3	b mg/g d.m.	R2
3.0	0.06	800	0.966	0.06	250	0.975
5.0	0.05	340	0.974	0.05	180	0.990
9.0	0.03	230	0.926	0.02	90	0.955

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