

# Description of the Adsorption and Desorption of Black 5 onto Chitin and Chitosan – Isotherm Equations

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## Abstract

*The sorption and desorption of a reactive dye – Black 5, commonly used in the textile industry, from aqueous solutions onto chitin and chitosan was studied. Following the adsorption of the dye at pH 3, its desorption was carried out at pH 11. Equilibrium isotherms were analysed using the following isotherms: the Freundlich, the Langmuir, the two-site Langmuir and the three-parameter Redlich-Peterson. All four isotherm equations showed a good fit to experimental data. The best-fitting isotherm was the two-site Langmuir, i.e. the heterogeneous model.*

**Key words:** adsorption, chitin, chitosan, reactive dye Black 5, isotherm equations.

and consequently reaching the natural environment. Reactive dyes are the most common type used due to their advantages, such as bright colours, excellent colour fastness and ease of application. Many reactive dyes are toxic for some organisms and may cause the direct destruction of creatures in water. [7].

Colour effluence is one of the main problems connected with dye production and the textile industry. Therefore, decolourisation has been the subject of research in recent years. Dye removal is a complex and expensive process. Methods such as chemical and electrochemical oxidation, membrane processes, coagulation-flocculation, adsorption and ion exchange are recommended. One of the most effective methods applied for contaminant removal is the process of adsorption [4, 8 - 15]. Of great significance, thus, is the selection of an appropriate sorbent characterised by a high effectiveness of dye removal for a relatively low cost. This has resulted in growing interest in dye removal technology with the use of inexpensive and natural sorbents. The application of waste material in decolouration has recently become a subject of great concern [8, 16 - 18]. In addition, great attention is paid to the elaboration of technologies with the use of effective and recoverable sorbents, including chitin.

Chitin is a natural polymer of acetylated and chitosan - non-acetylated glucosamine that displays a very good adsorption capability and is applied for the removal of heavy metals, dyes, detergents, phenols etc. As a sorbent, chitin and chitosan are characterised by a high adsorption capacity, high affinity to reactive dyes and the possibility of effective regeneration. Furthermore it is safe for the environment and utilisable after re-

generation, which is beneficial from an economic point of view [19].

The process of adsorption is characterised by a very high effectiveness of contaminant removal, which consists in the selective transfer of a substance dispersed in a solution onto the surface or into the interior of an adsorbent.

The adsorption process proceeds in several stages. The first stage involves the migration of an adsorbate to the outer surface of an adsorbent, which is determined by the diffusion rate of contaminant molecules in the liquid phase. Another step is the process of external diffusion in adsorbent pores, followed by adsorption onto their surface. In turn, the desorption consists in the release of molecules from the adsorbent's surface, the diffusion of molecules in the pores of granules to the adsorbent's surface, and the diffusion of molecules from the adsorbent's surface to a liquid flux. The rate of each of these processes is always determined by the rate of the slowest stage.

Usually, due to a lack of sufficient data, accurate prognosis of the stages and rates of the proceeding reactions is impossible. Equations of sorption isotherms describing the process under equilibrium conditions may provide information as well as more intelligible solutions to this complex problem. Isotherm equations do not serve as an in-depth analysis of the complicated stages of adsorption mechanisms, including external mass transfer, diffusion in the adsorbent's pores, ionic exchange and chemisorption. In practice, equilibrium equations are applied to design systems exploiting adsorption. However, the technological assumptions adopted and parameters of equilibrium models determined often enable to eluci-

## ■ Introduction

Production plants of dyes and rubber, as well as the textile, cosmetic, leather and food industries constitute a major source of surface water contamination with dyes. The problem is of great importance, especially for the textile industry, where practically all fibres, yarns and fabric manufactured from wool [1], cellulose and polyester-cellulose blends [2] are dyed with different dyeing processes [3]. Of great importance here is Black 5. In the textile industry, ca. 1,000 litres of water are necessary to produce each 1,000 kg of a product [4]. The market offers over 100,000 dyes, and their annual production exceeds 7·10<sup>5</sup> tons [5, 6]. The problem of waste-water decolourisation is especially important in Poland and other European countries, where as a result of economical transformations a great amount of small dye-houses exists instead of great texture manufactures. The imperfection of the dyeing process contributes to considerable amounts of colour compounds, from 2 to 50%, being discharged into the sewage system

date the mechanism of sorption, as well as the properties of an adsorbent and its affinity to adsorbate [20].

The objective of the study was to determine the effectiveness of the adsorption and desorption of reactive dye RB5 onto chitin and chitosan. The processes of sorption and desorption were described by means of four models: the Freundlich, the Langmuir, the two-site Langmuir and the three-parameter Redlich-Peterson .

## Experimental

### Characteristics and preparation method of chitin

An experiment was carried out on krill chitin obtained from the Sea Fisheries Institute in Gdynia. The chitin was characterized by a dry matter content of 95.64% and ash content of 0.32%. The average size of the chitin flake used in the study was  $314 \times 184 \mu\text{m}$ . Analyses of dye adsorption were carried out on modified chitin and chitosan. The preparation procedure for chitin and chitosan is given below:

□ *sorbent 1* – a weighed portion of commercial chitin (10 g) was poured into distilled water at a 1:10 ratio (w/w) and left for 24 h at room temperature to swell. The swollen chitin was transferred to a Büchner funnel and filtered off under a vacuum. The deacetylation degree of the prepared chitin reached  $DD = 5\%$ . The structural formula of chitin is presented in *Figure 1.a*.

□ *sorbent 2* – a weighed portion of chitin after swelling was rinsed with 6 N HCl and flushed with distilled water until a neutral reaction of the filtrate and filtered off under a vacuum. Next, 70% KOH solution was added to the chitin, which was then cooked for 3 h in a water bath. After cooling down, the chitin was flushed with distilled water until a neutral reaction of the filtrate and filtered off under a vacuum. The structural formula of chitin is presented in *Figure 1.b*. The deacetylation degree of the chitosan prepared reached  $DD = 75\%$

### Characteristics and preparation method of dyes

In the experiments use was made of a reactive dye of the vinylsulfone group – Black 5 (RB5), produced by ZPB 'Boruta' SA in Zgierz (Poland), the characteris-

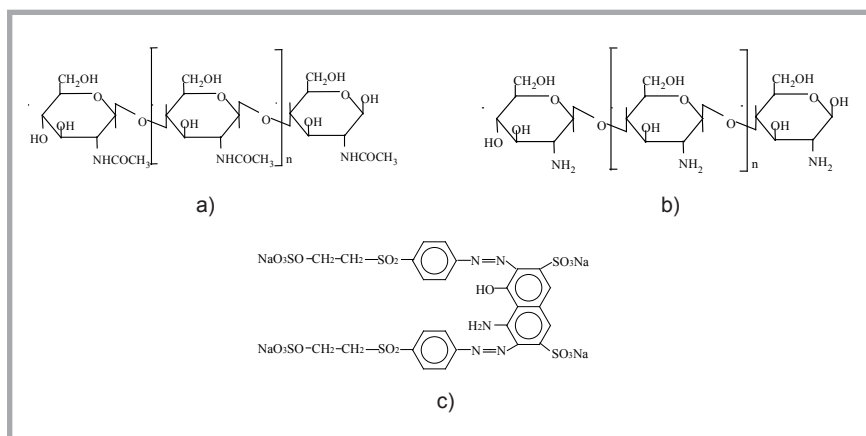


Figure 1. Chemical structure of molecule: a) chitin, b) chitosan and c) reactive dye Black 5.

Table 1. Characteristics of the dye.

Dye	Reactive group	Structural formula	Class	Molecular weight, g/mole
Reactive Black 5	Vinylsulfone	dye - $\text{O}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$	diazo-bis(sulphatoethylsulphonate)	991

tics and structures of which are provided in *Table 1* and *Figure 1.c*.

A stock solution of the dye was prepared by weighing 1g of pure powdered dye, transferring it quantitatively to a 1dm<sup>3</sup> measuring flask and supplementing it with distilled water at pH 6.0. The concentration of the dye in the solution was 1000 mg/dm<sup>3</sup>. The stock solution was used to prepare working solutions of the dye, the concentration of which in those solutions ranged from 1 to 500 for chitin and from 25 to 1000 mg/dm<sup>3</sup> for chitosan.

### Analytical methods

In order to determine the adsorption capacity of *sorbent 1* or *2*, 0.1 g d.m. of the sorbent was weighed in 200 cm<sup>3</sup> Erlenmeyer flasks and supplemented with 100 cm<sup>3</sup> of the working solution of the dye at an appropriate concentration. The adsorption process was carried out at pH = 3.0 – chitin and pH = 5.0 – chitosan.

Samples were fixed on a shaker and shaken for 2 hours at a constant rate of 200 r.p.m. After having been shaken, the samples were sedimented for 1 minute. The dye solution was then decanted and centrifuged for 10 minutes in an MPW 210 centrifuge at 10 000 r.p.m. After centrifugation, samples were collected for determination of the dye concentration. To assay the dye concentration, the solution was adjusted to pH 6. The concentration of dyes was determined by the spectrophotometric method using a UV-VIS Spectrophotometer - SP 3000. The

wavelength at which the absorbance was measured was  $\lambda = 597 \text{ nm}$

Analyses of the desorption efficiency of reactive dyes from the two sorbents examined were carried out after the prior adsorption process at pH = 11 [21].

## Results and discussion

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

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

$$Q_s = (C_0 - C_s)/m \quad (1)$$

where:

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

$C_0$  – initial concentration of dye in mg/dm<sup>3</sup>

$C_s$  – concentration of dye after adsorption in mg/dm<sup>3</sup>

$m$  – chitin mass in g d.m./dm<sup>3</sup>

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

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

where:

$Q_d$  – the quantity of dye desorbed in mg/g d.m.

$C_d$  – concentration of dye after desorption in mg/dm<sup>3</sup>

$C_s$  – concentration of dye before desorption (after adsorption) in mg/dm<sup>3</sup>

$m$  – chitin mass in g d.m./dm<sup>3</sup>

The results obtained were analysed with the use of the Freundlich, Langmuir, two-site Langmuir and Redlich-Peterson models.

The Freundlich model is an empirical sorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expressed by equation:

$$Q = k \cdot C^{1/n} \quad (3)$$

where:

- $Q$  – mass of dye adsorbed onto chitin in mg/g d.w.
- $C$  – dye concentration in the solution in mg/dm<sup>3</sup>
- $k$  – a constant in the Freundlich equation in (mg/g d.w.)/(dm<sup>3</sup>/mg)<sup>1/n</sup>
- $1/n$  – a constant in the Freundlich equation.

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The Freundlich equation suffers from a limitation in that it does not have a fundamental thermodynamic basis because it does not reduce to Henry's law at lower concentrations [20, 22 - 24].

The Langmuir model is a theoretical equilibrium isotherm relating the amount of solute sorbed on the surface to the concentration of solute. This equation is derived from simple mass action kinetics, assuming chemisorption. This model is based on two assumptions that the forces of interaction between sorbed molecules are negligible, and once a molecule occupies a site no further sorption takes place. Theoretically, a saturation value is therefore reached beyond which no further sorption takes place. Moreover this equation can reduce to Henry's law at lower initial concentrations. Alternatively, at a higher concentration, it predicts the monolayer sorption capacity [23]. The saturated monolayer sorption capacity can be represented by the expression:

$$Q = b \cdot K \cdot C / (1 + K \cdot C) \quad (4)$$

where:

- $Q$  – mass of dye adsorbed onto chitin in mg/g d.w.
- $b$  – maximum adsorption capacity of chitin in mg/g d.w.
- $K$  – a constant in the Langmuir equation in dm<sup>3</sup>/mg
- $C$  – dye concentration in the solution in mg/dm<sup>3</sup>.

The two-site Langmuir model takes into account the fact that the adsorbent's sur-

face is energetically heterogeneous and possesses adsorption centers with different energy levels of binding adsorbate molecules. Each of their types is described by an isotherm of the Langmuir equation [25 - 29], and the active sites are characterised by constants reaching  $K_1$ ,  $b_1$  and  $K_2$ ,  $b_2$ , respectively.

$$Q = b_1 \cdot K_1 \cdot C / (1 + K_1 \cdot C) + b_2 \cdot K_2 \cdot C / (1 + K_2 \cdot C) \quad (5)$$

- $Q$  – mass of dye adsorbed onto chitin in mg/g d.m.
- $b_1$  – maximum adsorption capacity of chitin at type I active sites in mg/g d.w.
- $b_2$  – maximum adsorption capacity of chitin at type II active sites in mg/g d.w.
- $K_1$  – a constant in the Langmuir equation in dm<sup>3</sup>/mg
- $K_2$  – a constant in the Langmuir equation in dm<sup>3</sup>/mg
- $C$  – dye concentration in the solution in mg/dm<sup>3</sup>.

The total adsorption capacity of chitin ( $b$ ) is equal to the sum of the maximum adsorption capacity determined for type I and type II active sites ( $b = b_1 + b_2$ ). Constants  $K_1$  and  $K_2$  characterise the adsorption affinity of a dye to the active sites of type I and type II, respectively, and correspond to a converse of the equilibrium concentration of the dye at which the adsorption capacity of chitin is equal to over half the maximum capacity of  $b_1$  or  $b_2$ . Higher values of constant  $K$  indicate an increase in the adsorption affinity of the dye to the active sites of chitin.

Constants  $K_1$  and  $K_2$  as well as the maximum adsorption capacity ( $b_1$  and  $b_2$ ) were determined by the method of non-linear regression.

The Redlich-Peterson isotherm contains three parameters and includes features of both the Langmuir and Freundlich models [22, 29]. It can be described as:

$$Q = b \cdot C / (1 + K \cdot C^g) \quad (6)$$

where:

- $Q$  – mass of dye adsorbed onto chitin in mg/g d.m.
- $b$  – a constant in the Redlich-Peterson equation in dm<sup>3</sup>/g d.w.
- $K$  – a constant in the Redlich-Peterson equation in (dm<sup>3</sup>/mg)<sup>g</sup>
- $g$  – a constant in the Redlich-Peterson equation, which lies between 0 and 1

$C$  – dye concentration in the solution in mg/dm<sup>3</sup>.

At a low concentration the Redlich-Peterson isotherm approximates to Henry's law, whereas at a high concentration its behaviour approaches that of the Freundlich isotherm.

The adsorption efficiency of RB5 from aqueous solutions onto chitin and chitosan was analysed based on a dependency between the amount of adsorbed dye  $Q$  in mg/g d.m. and its equilibrium concentration  $C$  in mg/dm<sup>3</sup>.

Experimental results indicating a correlation between the quantity of adsorbed and desorbed dye, the equilibrium concentration and isotherms determined from the Langmuir equation are presented in **Figures 2** and **3**.

In the description of experimental data referring to the adsorption of reactive dye RB5 onto chitin and chitosan, use was made of four models: the Freundlich, Langmuir, two-site Langmuir and Redlich-Petersen. All the isotherms applied fitted well to experimental data. In the case of data determined for both adsorbents analysed, the best-fitting model was achieved after the application of the two-site Langmuir isotherm (5) (**Table 2**). A very good fit of experimental data to the model applied was also obtained in the case of the Langmuir isotherm (4) – adsorption onto chitosan. That model, however, was unsuitable for the description of RB5 adsorption onto chitin, where the fit was found to be the worst out of the four models applied (**Figure 2.a**, and **Table 2**).

The study demonstrated that the quantity of dye adsorbed varied significantly depending on the adsorbent. The adsorption capacity of chitin determined from the two-site Langmuir model reached 260 mg/g d.m., whereas it was 2.5-fold higher for chitosan - 650 mg/g d.m, which was due to an increase in the deacetylation degree of the adsorbent applied. The deacetylation degree of chitin used in the study accounted for 5%, whereas that of chitosan - 75%. Adsorption capacities determined from the Langmuir model were comparable with those determined from the two-site Langmuir model, which could be observed especially in the case of chitosan, where both the models fitted very well to experimental data ( $b$  values

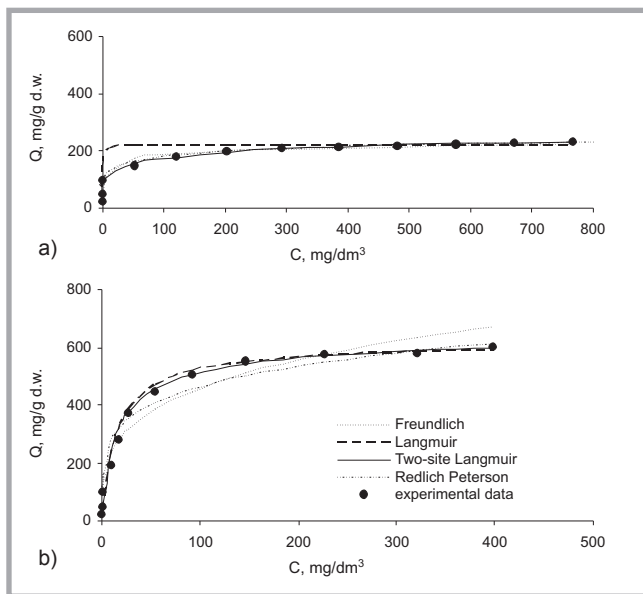


Figure 2. Experimental data and adsorption isotherms of Black 5 on: a) chitin & b) chitosan.

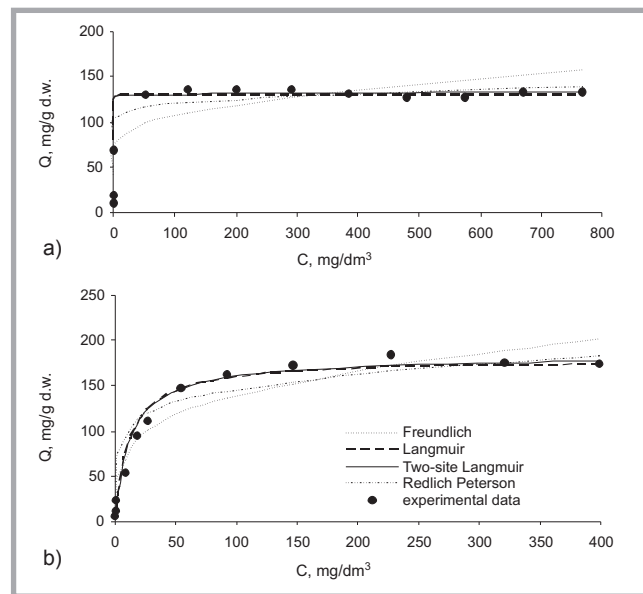


Figure 3. Experimental data and desorption isotherms of Black 5 on: a) chitin & b) chitosan.

Table 2. Isotherm parameters for Black 5.

Model	Equation	Parameters	adsorption				desorption			
			chitin		chitosan		chitin		chitosan	
			Value	R <sup>2</sup>	Value	R <sup>2</sup>	Value	R <sup>2</sup>	Value	R <sup>2</sup>
Freundlich	$Q = k \cdot C^{1/n}$	k 1/n	85 0.15	0.919	125.8 0.28	0.931	21.9 0.29	0.763	9 0.49	0.918
Langmuir	$Q = b \cdot K \cdot C / (1 + K \cdot C)$	K b	22 220	0.874	0.05 640	0.987	22 130	0.994	0.08 180	0.979
Langmuir 2	$Q = b_1 \cdot K_1 \cdot C / (1 + K_1 \cdot C) + b_2 \cdot K_2 \cdot C / (1 + K_2 \cdot C)$	K <sub>1</sub> b <sub>1</sub> K <sub>2</sub> b <sub>2</sub>	70 130 0.005 130	0.998	0.09 480 0.009 170	0.989	25 130 0.001 7	0.995	0.08 180 0.001 10	0.980
Redlich Petersen	$Q = b \cdot C / (1 + K \cdot C^n)$	K b n	2.47 260 0.88	0.821	3.5 650 0.8	0.928	2.2 145 0.89	0.512	6 164 0.70	0.831

were very similar for both models, reaching 640 and 650 mg/g d.m.).

The desorption of reactive dye RB5 onto chitin and chitosan was also described by means of the four models used in the adsorption description. As for adsorption, higher desorption values,  $R^2$ , were obtained for the two-site Langmuir model, yet they were only negligibly better than in the case of the Langmuir model. Thus, it may be stated that both these models describe well the process of RB5 desorption onto both chitin and chitosan. The least fit of the model to experimental data was reported for the Redlich-Petersen isotherm.

In contrast to the adsorption process of RB5 onto chitin and chitosan, during desorption, differences in the quantity of desorbed dye between both these sorbents were not so significant. The  $b$  value,

describing the quantity of dye released was 1.38-fold higher for chitosan – 190 mg/g d.m. and 180 mg/g d.m., depending on the model, than for chitin – 137 mg/g d.m. and 130 mg/g d.m., respectively.

Values of  $K_1$  constants in the Langmuir equation and two-site Langmuir equation (type I of active sites) describing the adsorptive affinity of RB5 to the adsorbent were very high in the case of chitin, i.e. 22 and 70 dm<sup>3</sup>/mg, and considerably lower in the case of chitosan, i.e. 0.05 and 0.09 dm<sup>3</sup>/mg.

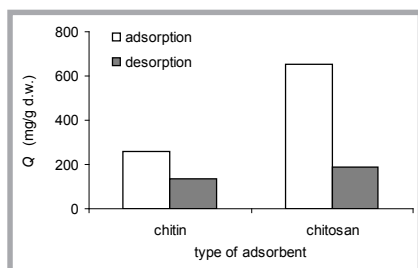
In the two-site Langmuir model describing the process of desorption, values of constants  $K_2$  and  $b_2$  were very low, implying that the desorption process was proceeding from one type of active site and that desorption from the second type of site, as compared to the first type, may

be omitted for it does not determine the effectiveness of the process. With this assumption, the two-site model attains the form of a single Langmuir equation, and experimental results of RB5 desorption onto both chitin and chitosan may be successively described by means of the single Langmuir model.

Comparing the quantity of desorbed dye to that of adsorbed dye, it may be concluded that the effectiveness of desorption from chitin was higher than that from chitosan and, depending on the model, accounted for 59% (Langmuir model) and 53% (two-site Langmuir model) of the quantity of adsorbed dye.

In the case of chitosan, the effectiveness of the desorption process was ca. two times lower, reaching ca. 29% of the quantity of dye adsorbed.





**Figure 4.** Quantity of adsorbed and desorbed Black 5 dye onto chitin and chitosan (two-site Langmuir model).

Constants determined from the two-site Langmuir model suggest mechanisms of RB5 binding onto chitin and chitosan. Substantial differences in the values of constants  $K_1$  and  $K_2$ , describing the adsorptive affinity of the adsorbate to the adsorbent, are likely to indicate a varied mode of dye binding at type I and type II active sites both in the case of chitin and chitosan. The constants  $K_1$  determined for type I active sites were higher, which may point to chemical binding, especially in the case of chitin. The binding at type II active sites, which is described by constants  $K_2$ , was of a different character, which is indicated by low values of the adsorptive affinity. This is likely to indicate weaker physical binding. Such a suggestion was confirmed by results obtained from the desorption process. The total quantity of dye released was equal or similar to that of dye bound during adsorption at type II active sites, i.e. 137 mg/g. d.m. (desorption  $b = b_1 + b_2$ ) and 130 mg/g. d.m. (adsorption -  $b_2$  constant) in the case of chitin, and 190 mg/g. d.m. (desorption  $b = b_1 + b_2$ ) and 170 mg/g d.m. (adsorption -  $b_2$  constant) in the case of chitosan.

In technological systems in which the adsorption process is utilised for the removal of contaminants, both the regeneration efficiency of the adsorbent applied and the possibility of its multiple use are of great significance. Comparison of the quantity of adsorbed and desorbed Black 5 dye is shown in **Figures 4**.

Thus, in contrast to other sorbents, after dye adsorption, chitin is characterised by a high capacity for regeneration [21, 30]. Chitin and chitosan are also known and utilised as sorbents for the removal of metals. Literature data indicates that the adsorption efficiency of metals onto chitin or chitosan is remarkably lower compared to that of dyes [31 - 33]. In the research by Filipkowska [30], it was

possible to carry out ca. 100 adsorption/desorption cycles for Brilliantorange 3R, whereas in the case of the other dyes the number of cycles was lower but still considerably higher than that reported elsewhere.

## Conclusions

1. The study presented shows that all four isotherm equations, i.e. the Freundlich, Langmuir, two-site Langmuir and Redlich-Peterson models, represented well the sorption and desorption of reactive Black 5 onto chitin and chitosan.
2. The best fit of the model to experimental data in both the adsorption and desorption processes for both adsorbents applied was obtained when the two-site Langmuir isotherm was applied.
3. The quantity of RB5 adsorbed onto chitosan (650 mg/g d.m.) was 2.5-fold higher than that onto chitin (260 mg/g d.m.). In the desorption process, the quantity of dye released from chitosan was 1.38-times higher than that released from chitin. When comparing the quantity of desorbed dye to that of adsorbed dye, it can be concluded that in the case of chitin the efficiency of desorption was the highest.
4. Constants determined from the two-site Langmuir model suggest varied mechanisms of RB5 binding at type I and type II active sites. The first type of active site, displaying a high adsorptive affinity, suggests the chemical binding of RB5. The adsorptive affinity determined for type II active sites was substantially lower, which may point to a weaker binding of RB5 and the desorption of dye from type II active sites, described in the model with constants  $K_2$  and  $b_2$ .

## References

1. Musnickas J., Rupainytė V., Treigienė R., Ragelienė L.; *Fibres & Textiles in Eastern Europe*, 2005, 13(6) pp. 65-69.
2. Blus K., Paluszkiwicz J., Czajkowski W.; *Fibres & Textiles in Eastern Europe*, 2005, 13(6) pp. 75-78.
3. Perkowski J., kos., Żyła R., Ledakowicz S.; *Fibres & Textiles in Eastern Europe*, 2005, 13(6) pp. 59-64.
4. Garg V. K., Amita M., Kumar R., Gupta R.; *Dyes and Pigments*, 2004, 63, pp. 243-250.
5. Pearce C. I., Lloyd J. R., Guthrie J. T.; *Dyes and Pigments*, 2003, 58, pp. 179-196.

6. McMullan G., Meehan C., Conneely A., Kirby N., Robinson T., Nigam P., Banat I. M., Marchant R., Smyth W. F.; *Applied Microbiology and Biotechnology*, 2001, 56, pp. 81-87.
7. Papic S., Koprivanac N., Bozic AL., Metes A.; *Dyes and Pigments*, 2004, 62, pp. 291-298
8. Al-Degs Y., Khraishah A. M., Allen S. J., Ahmad M. N.; *Water Research*, 2000, 34(3) pp. 927-935.
9. Acemioğlu B.; *Journal of Colloid and Interface Science*, 2004, 274, pp. 371-379.
10. Walker G. M., Hansen L., Hanna J.-A., Allen S. J.; *Water Research*, 2003, 37, pp. 2081-2089.
11. Sun Q., Yang L.; *Water Research*, 2003, 37, pp. 1535-1544.
12. Chiou M. S., Li H. Y.; *Chemosphere*, 2003, 50, pp. 1095-1105.
13. Majeti N. V., Kumar R. A.; *Reactive and Functional Polymers*, 2000, 46, pp. 1-27.
14. Wu F.-Ch., Tseng R.-L.; *Juang R.-S.; Water Research*, 2000, 35(3) pp. 613-618.
15. Garg V. K., Gupta R., Yadav A. B., Kumar R.; *Bioresource Technology*, 2003, 89, pp. 121-124.
16. Namasivayam C., Kavitha D.; *Dyes Pigments*, 2002, 54, pp. 47-58.
17. Figueiredo S. A., Loureiro J. M., Boaventura R. A.; *Water Research*, 2005, 39, pp. 4142-4152.
18. Özacar M., Şengil İ. A. A.; *Process Biochemistry*, 2005, 40, pp. 565-572.
19. Karcher S., Kornmüller A., Jekel M.; *Water Research*, 2000, 35(14) pp. 3309-3316.
20. Kumar K. V., Sivanesan S.; *Journal of Hazardous Materials*, 2005, B123, pp. 288-292.
21. Filipkowska U. *Adsorption Science and Technology*, 2006, 24(9) pp. 781-795.
22. Kumar K. V., Sivanesan S.; *Journal of Hazardous Materials*, 2005, B126, pp. 198-201.
23. Kumar K. V., Sivanesan S.; *Dyes and Pigments*, 2007, 72, pp. 124-129.
24. Wang X.-S., Qin Y.; *Process Biochemistry*, 2005, 40, pp. 677-680.
25. Wang S., Zhu Z. H.; *Journal of Hazardous Materials*, 2005, B126, pp. 91-95.
26. Machida M., Kikuchi Y., Aikawa M., Tatumoto H.; *Physicochem. Eng. Aspects*, 2004, 240, pp. 179-186.
27. Cheung C. W., Chan C. K., Porter J. F., McKay G.; *Journal of Colloid and Interface Science*, 2001, 243, pp. 328-336.
28. Hinz Ch.; *Geoderma*, 2001, 99, pp. 225-243.
29. Ho Y.-S., Chiu W.-T., Wang Ch.-Ch.; *Bioresource Technology*, 2005, 96, pp. 1285-1291.
30. Filipkowska U.; *Environmental Technology*, 2008, 29(6) pp. 681-690.
31. Benguella B., Benaissa H.; *Water Research*, 2000, pp. 36:2463-2474.
32. Wu F.-Ch., Tseng R.-L., Juang R.-S.; *Water Research*, 2000, 35(3) pp. 613-618.
33. Sağ Y., Akay Y.; *Process Biochemistry*, 2000, 36, pp. 157-173.

Received 03.02.2009      Reviewed 22.03.2009