

THE INFLUENCE OF CHITOSAN DEACETYLATION DEGREE ON REACTIVE BLACK 5 SORPTION EFFICIENCY FROM AQUEOUS SOLUTIONS

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Abstract

In the paper sorption capacity of chitosan having a deacetylation degree DD=75%, DD=85% and DD=90% relatively to the Reactive Black 5 were compared. Studies on the effectiveness of the dye sorption were carried out in a wide pH range – from 3 to 11. For each of the tested chitosan sorbents, sorption capacity has been determined. The results were described by isotherms Freundlich and Lagmuir isotherms, and a double Langmuir isotherm.

Sorption of Reactive Black 5 most efficiently occurred at pH 4. At pH <4 chitosan sorbents underwent dissolution, regardless of the degree of deacetylation.

The efficiency of dye sorption increased with the degree of deacetylation. The sorption capacity calculated after 12 h of the chitosan sorption with DD=75%, DD=85% and DD =90% was, relatively to the Reactive Black 5, respectively 433.03 mg/g and 464.52 mg/g and 532.14 mg/g.

The impact of the deacetylation degree on pHzpc (zero point of charge) of the sorbent was also examined. Along with the increase in the deacetylation degree the value of chitosan pHzpc increased as well and at DD=75% DD=85% and DD=90%, pHzpc amounted respectively 7.6, 7.7 and 7.8.

Key words: *chitosan, deacetylation degree, sorption, Reactive Black 5*

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1. Introduction

Chitosan is a polysaccharide derived from chitin, the second, after the cellulose, most abundant biopolymer in nature. Chitin is the main building material of arthropods body armor and part of the cell walls of fungi, some algae and bacteria. It is estimated that the annual production of chitin by living organisms is about 10^{11} Mg [1]. The main source of chitin are waste products of marine crustaceans processing industry. According to the literature, from this source more than 200 000 Mg of pure chitin per year can be acquired [2, 3]. For this reason, the chitin appears to be an available and cheap material. Chitosan can be obtained as a result of a simple reaction of chitin deacetylation (Fig.1). Chitosan as one of the few biopolymers exhibits a basic character. The property is due to the presence of free groups ($-NH_2$). By having amine functional groups, chitosan has a high sorption capacity for impurities of anionic character. Chitosan absorbs and easily removes nutrients such as nitrate [4] and phosphate [5] from aqueous solutions. Chitosan shows the greatest suitability on the sorption of anionic dyes [6, 7, 8, 9].

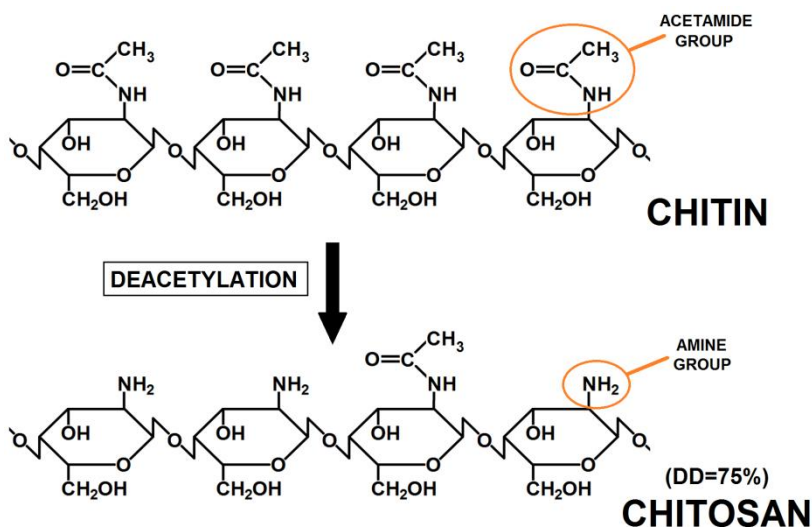


Figure 1. Diagram of the chitin deacetylation process, chitosan preparation

As reported by the literature [3, 10], the degree of deacetylation, which translates to the content of amino groups in sorbent can have a significant impact on the sorption properties of chitosan. The amount of research on the relationship between the degree of deacetylation and the sorption capacity of chitosan relatively to dyes seems to be insufficient.



In this work the sorption capacity of chitosan having a deacetylation degree DD=75% (CHs-75), DD=85% (CHs-85), and DD=90% (CHs-90) with respect to popular industrial dye Reactive Black 5 (RB5) is compared.

2. Material and methods

2.1. Materials

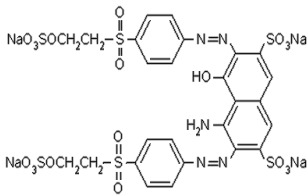

Chitosan, in the form of flakes (DD=75/85/90%), was purchased from Heppel Medical Chitosan GmbH, Halle (Saale), Germany. Specifications provided by the manufacturer of chitosan has been presented in Table 1.

Table 1. Specification of chitosan used in the study

Shape and appearance of the chitosan			
	Yellow petals diameter 2-3 mm	Yellow petals diameter 2-3 mm	Light yellow petals diameter 1-2 mm
Appearance of 1% aqueous solution (in 5% CH ₃ COOH)	Dark yellowish	Yellowish	Light yellow
Degree of deacetylation	75 %	85 %	90 %
Viscosity	100 mPas	100 mPas	100 mPas
Ash content	< 1.0 %	< 1.0 %	< 1.0 %
Dry mass content	> 85% (ident. 86.8 %)	> 85% (ident. 88.6 %)	> 85% (ident. 88.8 %)
Heavy metal content	< 40 ppm	< 40 ppm	< 40 ppm
Raw material source	Crab shells	Crab shells	Crab shells

Reactive Black 5 (RB5) was produced by "Boruta" SA Dyes Production Plant. The dye characteristics has been compiled in Table 2.

Table 2. Characteristics of the dye Reactive Black 5

Reactive Black 5 characteristics (RB5)		Structural formula	Appearance (in the form of the powder)
Molar mass	991 g/mol		
λ_{max}	600 [nm]		
Dye type	acidic- anionic, reactive		
Dye class	diazo		
Functional groups	vinylsulfone		
Usage	dyeing of cotton, viscose, wool, polyamide fibers		

2.2. Methods

2.2.1. Preparation of chitosan sorbent in the form of hydrogel beads

To the beaker of 1 L 25g d.m. chitosan flakes and 975 g - 5% solution of acetic acid was added and the solution was stirred mechanically until homogeneous. The solution was added dropwise to a 2M NaOH solution to form beads with a diameter of 2.0 - 2.2 mm. Moulded chitosan beads were kept in a solution of NaOH for 24 h, then were washed with distilled water until neutral reaction. Thus prepared, the sorbent was kept in distilled water at 4 ° C. Prepared chitosan sorbents having a deacetylation degree of 75% (the CHs-75), 85% (CHs-85) and 90% (the CHs-90) are shown in Figure 2.

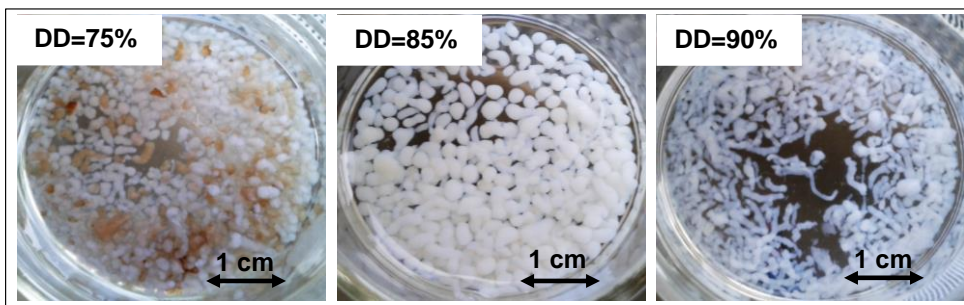


Figure 2. Chitosan hydrogel beads (ready for sorption)

2.2.2. Determination of the optimal pH value of dye sorption

To the conical flasks of 300 mL chitosan sorbent in an amount of 0.2 g d.m._{CH₅} was weighed and then the dye solution (200 mL) at pH 3,0-11,0 was added. The flasks were placed on a shaker (150 r.p.m.). After 2 h the process of sorption of the solution, samples were taken (10 mL) in order to determine the concentration of the remaining dye. The most important parameters of this study are summarized in Table 3.

Table 3. Studies parameters on the effect of pH on the sorption efficiency

Tested sorbents	Sorbent conc. [g s.m. _{CH₅} /L]	Tested dye	Dye conc. [mg/L]	Tested pH of the sorption	Stirring speed (r.p.m.)	Sorption time [h]	Temp. (°C)
CHITOSAN DD=75% CHITOSAN DD=85% CHITOSAN DD=90%	1.0	RB5	200	3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0	150 (stirrer)	2	22

2.2.3. Determination of sorption capacity chitosan sorbent

To 10 conical flasks (vol. 300 mL) chitosan sorbent in an amount of 0.2 g d.m._{CH₅} was weighed. To the flask 200 mL of dye solution was added, with the optimum sorption pH (defined in section 2.2.2) and the dye concentration in the range from 100 to 4000 mg/L. The flasks were placed on a shaker (150 r.p.m.). At the appointed time, the samples were taken (10 mL) to determine the concentration of the remaining dye. Parameters of this study are summarized in Table 4.

Table 4. Research parameters on the determination of sorption capacity

Tested sorbents	Sorbent conc. [g s.m. _{CH₅} /L]	Tested dye	Dye conc. [mg/L]	pH of the sorption	Stirring speed (r.p.m.)	Sorption time [h]	Temp (°C)
CHITOSAN DD=75% CHITOSAN DD=85% CHITOSAN DD=90%	1.0	RB5	100, 250, 500, 750, 1000, 1500, 2000, 2500, 3000, 4000	optimal (point 2.2.2)	150 (stirrer)	12	22

2.2.4. Determination of the dye concentration in solutions

The concentration of the dye in the solution was determined by spectrophotometric method using a Genesys 20 spectrophotometer of Thermo Scientific (USA). Spectrophotometer with parameters set for the RB5 dye ($\lambda_{\max} = 600$ nm, the conversion factor = 41.3), automatically calculated its concentration in a given sample.

2.2.5. Computational methods

The amount of dye adsorbed on the chitosan sorbent was calculated from the equation (1):

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

where:

- Q_s – mass of absorbed dye (static conditions) [mg/g.d.m.]
- C_0 – initial dye concentration [mg/L]
- C_s – dye concentration after the sorption [mg/L]
- V – solution capacity [L]
- m – mass of the sorbent [g.d.m.]

To determine the maximum sorption capacity, three adsorption isotherms: Langmuir, Langmuir 2 (Langmuir double equation) and Freundlich were used. Langmuir isotherm equation is shown below (2):

$$Q_s = \frac{q_{\max} \cdot K_c \cdot C}{1 + K_c \cdot C} \quad (2)$$

where:

- Q_s – mass of absorbed dye (static conditions) [mg/g.d.m.]
- q_{\max} – maximum sorption capacity in Langmuir equation [mg/g d.m.],
- K_c – constants in Langmuir 2 equation [L/mg]
- C – dye concentration remaining in the solution [mg/L]

Langmuir 2 isotherm is presented in equation (3).

$$Q_s = \frac{b_1 \cdot k_1 \cdot C}{1 + k_1 \cdot C} + \frac{b_2 \cdot k_2 \cdot C}{1 + k_2 \cdot C} \quad (3)$$

where:

- Q_s – mass of absorbed dye (static conditions) mg/g.d.m.]
- b_1 – maximum sorption capacity of the sorbent (active sites of the I type) [mg/g.d.m]
- b_2 – maximum sorption capacity of the sorbent (active sites of the II type) [mg/g.d.m]
- $k_1; k_2$ – constants in Langmuir 2 equation [L/mg]
- C – dye concentration remaining in the solution [mg/L]

Freundlich isotherm equation is presented below (4).

$$Q_s = K \cdot C^n \quad (4)$$

where:

- Q_s – mass of absorbed dye (static conditions) [mg/g.d.m.]
- C – dye concentration remaining in the solution [mg/L]
- K – sorption equilibrium constant in Freundlich model
- n – constant in Freundlich model

Constants in the Langmuir, Langmuir 2 and Freundlich equations were calculated using Statistica 12.5.

Matching the experimental data to a mathematical models were calculated using the determination coefficient R^2 (5)

$$R^2 = \frac{\sum(q_{cal} - \bar{q}_{exp})^2}{\sum(q_{cal} - \bar{q}_{exp})^2 + \sum(q_{cal} - q_{exp})^2} \quad (5)$$

where:

- R^2 – determination coefficient – measure of data alignment to the model
- q_{exp} – experimental data - amount of sorbed dye [mg/g d.m.]
- q_{cal} – theoretical data resulting from the model - amount of sorbed dye [mg/g d.m.]

3. Results and discussion

3.1. Influence of pH

The sorption of the RB5 dye on the hydrogel chitosan beads occurred most efficiently at pH 4.0. Chitosan at lower pH underwent dissolution and lost sorption properties. Therefore, the results of sorption at pH 3.0 were not included in the graphs. RB5 sorption efficiency on the chitosan sorbents clearly decreased with pH increasing, with the lowest value at pH 10.0-11.0 (Fig. 3).

For the trend obtained amine functional groups of chitosan are responsible. At low pH, most of the $-NH_2$ groups are protonated ($-NH_3^+$), which enhances sorption of the negatively charged RB5. With increasing pH, the number of chitosan $-NH_3^+$ groups decreases, which results in weaker bonding of the dye. At pH 10-11 RB5 sorption is further limited by the competition with OH^- ions.

The effectiveness of RB5 adsorption independently from the initial pH, increased with the chitosan deacetylation degree. For chitosan sorbents, the higher the deacetylation degree, the more free amino groups in the polysaccharide structure. The chitosan amino groups, which are the result of acetamide deacetylation of functional groups are the sorption centers of greatest importance when bonding anionic dyes [11, 12]. Larger amount of amino groups results in a greater sorption capacity of chitosan.

Chitosan sorbents exhibited the ability to change the pH of the solution, in which the sorption took place. In the case of CHs-75, for the initial pH values of 4.0-9.0, at the end of the sorption process the solution reached value in the range 7.22-7.65 pH, CHs-85 values between 7.33-7.79, CHs-90 in the range of 7.40-7.82. pH changes in the solution result from the buffer properties of chitosan, which causes the solution to approach pH close to pH_{ZPC} (pH of zero charge).

The ability of chitosan sorbents to neutralize acidic (pH <7) or alkaline (pH > 8) aqueous solutions are their undoubted advantage. Assuming that the sorbents are used for pre-treatment of industrial wastewater, the problem of the wastewater pH neutralization before it is introduced into the sewage system or before the next stage of purification is solved.

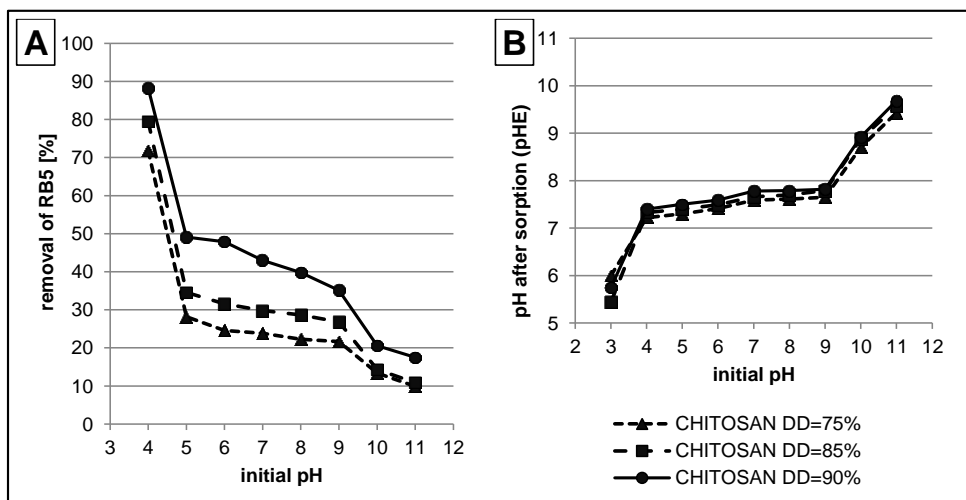


Figure 3. A) Influence of pH on the RB5 sorption effectiveness with the chitosan sorbents B) The influence of the chitosan sorbents on the pH change of the solution; temp. 22°C.

Determined on the basis of Figure 4, the point of zero charge for CHs-75 was 7.6 and for pH_{ZPC} CHs-85 and 90 respectively 7.7 pH_{ZPC} and 7.8 pH_{ZPC} . Chitosan pH_{ZPC} values increased with the rise in deacetylation degree. The obtained result can be explained by the fact, that the higher chitosan deacetylation degree indicates higher number of free amino groups in the structure of the sorbent. Free amino groups, capable of protonating of chitosan are responsible for the basic character of the sorbent.

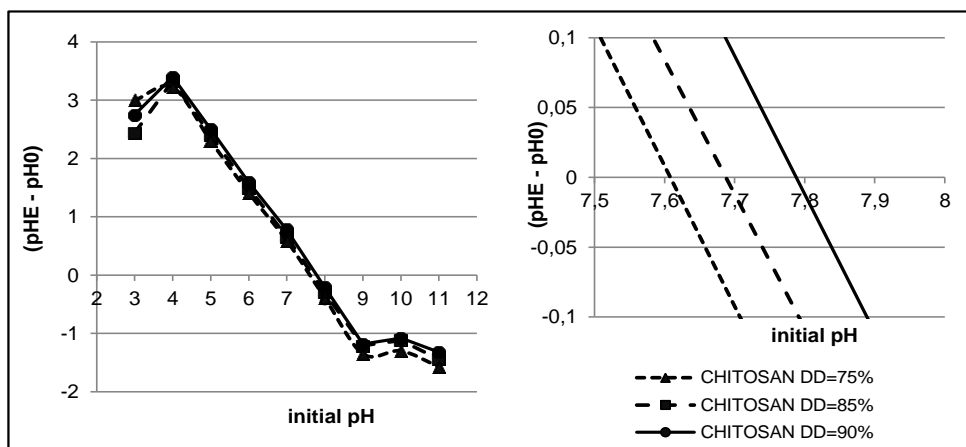


Figure 4. The difference between the pH of the solution at the beginning and at the end of the sorption depending on the initial pH of the solution (the titration method of determining pH_{ZPC} of the solution). Temp. 22°C. **pHE**- the final pH (at the end of the process). **pH0**- the initial pH

3.2. Sorption capacity

To describe the experimental data obtained three adsorption models: Langmuir, Langmuir 2 (double Langmuir equation) and Freundlich have been adjusted (Figure 5). Constants determined on the basis of the models above were summarized in Table 5.

Table 5. Constants determined from Langmuir's model, Langmuir's 2 model and from Freundlich's model

Type of sorption model	Constants/units		Type of chitosan sorbent		
			CHITOSAN DD=75%	CHITOSAN DD=85%	CHITOSAN DD=90%
Langmuir 2 model	$Q_{(12h)} (b_1+b_2)$	[mg/g]	433.03	464.52	532.14
	b_1	[mg/g]	237.60	243.20	245.69
	k_1	[L/mg]	36.299	34.866	34.342
	b_2	[mg/g]	195.43	221.32	286.45
	k_2	[L/mg]	0.0024	0.0024	0.0025
	R^2		0.9980	0.9973	0.9987
Langmuir model	$Q_{(12h)}$	[mg/g]	387.34	400.13	444.68
	K_c	[L/mg]	0.1551	0.1888	0.4208
	R^2		0.8132	0.7937	0.7810
Freundlich model	n	-	0.1075	0.1131	0.1213
	K	[L/mg]	180.37	179.49	190.83
	R^2		0.9915	0.9907	0.9801

In all the conducted series the Langmuir 2 model showed best fit to the experimental data. Therefore, constants and adsorption capacities calculated from the Langmuir model 2 were used to discuss the results. The values of b_1 and b_2 indicate the capacity of sorption centres of the sorbent, while k_1 and k_2 constants are a measure of the dye affinity to the active sites [13].

Constants calculated from the Langmuir 2 model - k_1 and k_2 , had similar values for CHs-75, CHs-85 and CHs-90. This is due to the identical functional groups and similar sorbent structures. CHs-75 sorption capacity obtained after 12 h relatively to the RB5 was 433.03 mg/g. Compared with the CHs-75, the sorption capacities of CHs-85 and CHs-90 were 7.3% and 22.9% higher and amounted to 464.52 mg/g and 532.14 mg/g. Sorption capacities of chitosan sorbents ($b_1 + b_2$) increased with the degree of deacetylation. Larger sorption capacity of chitosan with higher deacetylation degree resulted from higher number of free amino groups, that is, the main sorption centers of chitosan towards the RB5 sorption.

The increase in the sorption capacity and the degree of deacetylation has been observed also in studies on sorption of Cr (VI) [10] and food dyes [14] on chitosan flakes. This suggests that whatever the form of chitosan sorbent (flakes / hydrogel), sorption capability increases with the degree of deacetylation. In the case of commercial use of chitosan sorbents, the deacetylation degree will most likely be one of the most important parameters describing the properties of the product.

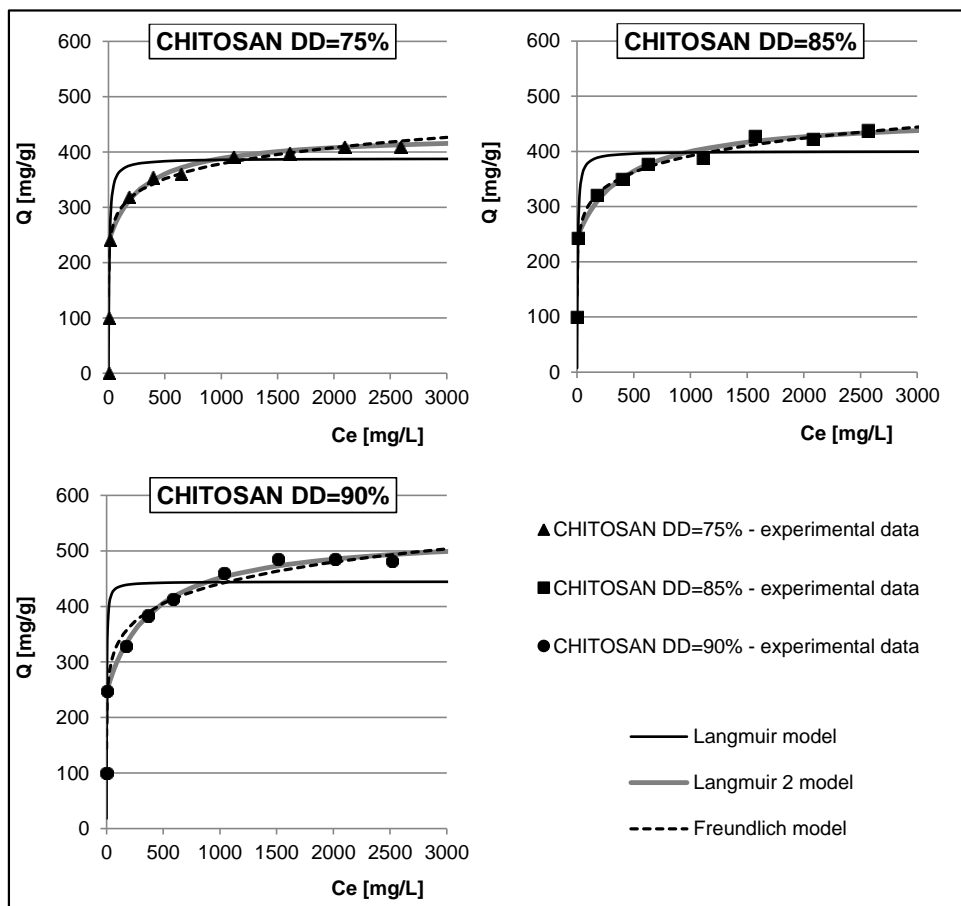


Figure 5. Isotherms of RB5 sorption on chitosan sorbents; temp. 22°C

4. Conclusion

RB5 sorption efficiency on the chitosan sorbents, irrespective of the pH of the solution increases with an increase in degree of deacetylation. This is due to the fact that a higher deacetylation degree results in a higher amount of free amino groups which are responsible for sorption of anionic dyes.

With the increase in the degree of deacetylation also the value pH_{ZPC} (point of zero charge) of the sorbent is increased. It is also a result of the greater amount of free amino groups, responsible for basic character of the sorbent.

In the pH range of 4-11, RB5 sorption efficiency of on the chitosan sorbents increases with decreasing pH value. Sorption at $pH < 4$ results in chitosan dissolving regardless of the degree of deacetylation.

Buffering capability of chitosan, which results in the pursuit of a solution to a pH close to pH_{ZPC} is its unquestionable advantage. In the case of the use of chitosan for treatment of industrial wastewater, the problem of neutralization the pH of waste water before it is introduced into the sewage system or into the next stage of purification is eliminated.

5. Acknowledgments

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6. References

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