

THE USE OF ACTIVE CARBON IMMOBILISED ON CHITOSAN BEADS FOR RB5 AND BV10 DYE REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract

This paper presents the adsorption of dyes – the anionic Reactive Black 5 (RB5) and cationic Basic Violet 10 (BV10) dyes – on activated carbon (AC) immobilised on chitosan (CHs). The results were compared with the removal efficiency of RB5 and BV10 on the individual sorbents: chitosan beads and activated carbon. In this study, the sorption capacities of the sorbents, sorption pH and the point of zero charge (pH_{ZPC}) were determined. For the description of the obtained results, the Freundlich, Langmuir and double Langmuir models were used. The results show that the developed sorbent (CHs-AC) is effective for both types of dye (RB5 or BV10) over a broad pH range 4–10, which makes it a universal sorbent. The maximum sorption capacity of CHs-AC with RB5 was 639.8 mg/g, while for BV10 it was 50.7 mg/g.

Key words: chitosan, activity carbon, adsorption, immobilisation

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1. Introduction

The processes of dye application on different types of products require water in the amount ranging from 80 to 250 L/kg of product. During colouring, huge amounts of sewage containing detergents, non-organic salts, alkalis and dyes are created [1]. Dyes are compounds that are difficult to remove in the biodegradation process, insusceptible to light, chemical substances and heat. Partial biodegradation of these compounds might lead to the creation of toxic and more damaging products [2, 3]. To purify this kind of sewage, many methods have been proposed, such as chemical oxidation, ultrafiltration, ionic exchange or nanofiltration [4, 5]. When each of these methods is used separately, they do not give satisfactory effects; therefore, they are combined into multistage systems of purification. The disadvantages of these systems are their significant energy requirement and high cost of investment, which has led to the search for better technologies of dye removal. One fairly cheap and effective method for this is the process of adsorption [6, 7].

Traditional adsorbents applied in water and sewage purification are active carbons (AC), which provide high effectiveness. Adsorption on AC has a wide range of uses. It is used for the removal of colour, taste, smell and organic and non-organic contamination from drinking water. Another use was found in medicine, as the purification of air and most importantly in the purification of industrial wastewater [8]. Considering the high cost of dye removal from wastewater with the use of active carbon, natural sorbents that are able to remove contamination with lower investment expenditure are gaining more attention [9].

Chitosan (CHs) is highly bonded with great amounts of dye groups. Only basic dyes are characterised by low bonding to CHs. Moreover, pH has an important role in sorption effectiveness: a low pH causes the protonation of free amino groups, which is the reason that anionic dye particles can be attached.

A sorbent of combined CHs and AC, created as a result of immobilisation of AC on CHs hydrogel beads, might be universal and show high sorption capacity for all anionic and cationic dyes.

The purpose of the study was to evaluate the use of active carbon immobilised on chitosan hydrogel beads for removal of both anionic (RB5) and cationic (BV10) dyes from aqueous solutions. The obtained results were compared with the effectiveness of RB5 and BV10 removal on the single sorbents of chitosan beads and active carbon.

2. Materials and Methods

2.1 Characteristics and preparation of adsorbents

2.1.1 Activated carbon

Activated carbon F400 (Fig 1.), commonly used for wastewater treatment processes, was used to carry out the study. Carbon was purchased from Chemviron Carbon (Belgium). The sorbent in the form of granules was rinsed with distilled water before use in order to remove the microsuspension.

Activated carbon F400 parameters:

- Specific surface: min 1050 m²/g
- Granulation: 0.6–1.2 mm
- Iodine value: min 1000 mg/g
- Moisture: 5%
- Hardness: min 94%
- Bulk density: 420±30 g/L



Figure 1. Activated carbon

2.1.2 Chitosan beads

The studies used chitosan in the form of flakes with a deacetylation degree (DD) = 85%, viscosity of 100 mPa/s and a dry matter content of 86.8% originating from the German company Heppe.

In order to prepare the sorbent, 25 g of d.m. CHs flakes, 50 g of acetic acid (99.5%) and 925 g of distilled water were added to a beaker with a capacity of 1 L.

The beaker was stirred mechanically until a homogenous mass was formed and then left to stand for 24 h to vent. The concentration of the prepared mixture was 2.5% CHs. The solution was added dropwise to a 2 M NaOH solution and, as a result, beads with a diameter of 2.0–2.2 mm formed. During gelation of the sorbent, NaOH solution was stirred with a magnetic stirrer (300 rpm).

The prepared CHs beads (Fig 2.) were kept in a solution of NaOH for 24 h and then washed with distilled water until neutral. This ready-to-use sorbent was kept in distilled water at 4°C.



Figure 2. Chitosan beads

2.1.3 Activated carbon immobilised on chitosan beads

Activated carbon was added in an amount of 25 g to a CHs gel, which had the role of carrier and was prepared from 25 g of dry mass of CHs dissolved in 5% acetic acid. The obtained mixture was added dropwise to a 2 M NaOH solution to form the beads. The beads were left for 24 h in the solution of NaOH and then washed with distilled water to remove the remaining NaOH.



Figure 3. Activated carbon immobilised on chitosan

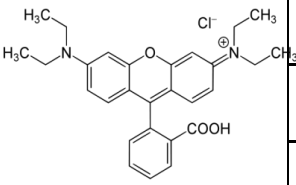
2.2 Characteristics and preparation of dyes

The experiments were conducted using the Reactive Black 5 and Basic Violet 10 dyes produced by ZPB “Boruta” SA in Zgierz (Poland). The structure of the reactive dye is presented in Table 1.

A stock solution of dye was prepared by weighing 1.00 g of pure powdered dye. The dye was quantitatively transferred into a 1000 cm³ measuring flask, which was then filled with distilled water. The dye concentration in the solution reached 1000 mg/L. The stock solution was used to prepare working solutions.

Table 1. Characteristics of the dyes

Reactive Black 5 (RB5)				
	Molar mass	991 g/mol	Application	Dyeing of cotton, viscose, wool, polyamide fibres
	λ_{max}	600 [nm]		
	Type	anionic/reactive	Other commercial names	Begazol Black B, Celmazol Black B, Diamira Black B, Levafix Black E-B, Primazin Black BN, Remazol Black
Chemical structure	Class	Diazo		

Basic Violet 10 - (BV10)				
	Molar mass	479 g/mol	application	Dyeing of cotton, paper, leather Preparation of printing inks/painting inks
	λ_{\max}	554 [nm]		
	Type	Cationic/basic	Other commercial names	Rhodamine B, Futramine D, Peltol D, Basic Red RB, Basazol Red 71 L, Violet B
Chemical structure	Class	Triphenylmethane		

2.3 Determination of the optimal pH of the adsorption process

In order to determine the optimal pH value of the adsorption process, aqueous solutions were prepared with a dye concentration of 100 mg/L and pH of 1–11. Adsorbent in the quantity of 0.1 g d.m. and 100 cm³ of dye solutions with pH 1–11 were added to each of the conical flasks (250 cm³). Next, the flasks were placed on a magnetic stirrer, and the concentration of adsorbate in the solution was determined after 2 h of adsorption.

2.4 Determination of the maximum adsorption capacity

In order to determine the adsorption capacity of the three tested sorbents: chitosan beads (CHs), activated carbon (AC) and activated carbon immobilised on chitosan beads (CHs-AC), 0.1 g d.m. of each sorbent was weighed into 250 cm³ Erlenmeyer flasks and supplemented with 100 cm³ of the working solution of the dye at concentrations of 10–2000 mg/L (RB5) and 1–200 mg/L (BV10) and optimal pH values. Flasks thus prepared with solutions and sorbents were set on a shaker (150 rpm). After 24 and 72 h, flask samples were taken to determine the quantity of dye remaining in solution. The concentrations of dye after shaking were determined by the colourimetric method using a spectrophotometer (UV-VIS SP 3000).

2.5 Determination of zeta factor

In order to determine the pHz_{PC} of sorbents, 50 mL of 0.01 M KNO₃ solution with an initial pH (pH₀) from 3 to 12 was added to the conical flask. To each flask, 1 g of sorbent was also added and then the mixture was stirred for 24 h. After this time, the final pH of the solution was measured. The pHz_{PC} value was determined based on the curve. The zero point for beech sawdust was located at the intersection of the curve defining the relationship between Δ pH and pH₀, with the axis of a graph on which the pH₀ is marked.

2.6 Analytical methods

The concentration of dye left in the aqueous solution was determined spectrophotometrically in each sample. Samples to be analysed were collected (10 cm³), decanted and centrifuged for 15 min at 10,000 rpm. To assay the dye concentration, the solution was adjusted to pH 6. The concentration of the remaining dye was determined according to standard curves in a UV-VIS SP-3000 spectrophotometer. The wavelength at which absorbance was measured was determined for each of the dyes examined (Table 1).

2.6 Calculation methods

The effectiveness of dye adsorption from the solution was analysed based on changes in their concentration in the solution.

The quantity of adsorbed basic and acid yellow was calculated from the formula (1):

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

where:

- Q – mass of adsorbed dyes [mg/g d.m.],
- C_0 – initial concentration of dyes [mg/L],
- C – dye concentrations after adsorption [mg/L],
- M – mass of adsorbent [g d.m.].

Experimental data were described using three models – the Freundlich model, the Langmuir model and the heterogeneous Langmuir model (double Langmuir equation). Sorption on sorbents that have a microporous or non-uniform surface may be described by the Freundlich model. In the Freundlich theory, the number of active centres may be greater than the number of molecules that have been sorbed. This model, as compared to the Langmuir model, does not preclude the formation of a sorbate multilayer on the surface of the sorbent. The Freundlich isotherm equation (2) is below:

$$Q = K_F C^{1/n} \quad (2)$$

where:

- Q – equilibrium amount of dyes absorbed [mg/g s.m.];
- C – concentration of dyes remaining in the solution [mg/L],
- K – constant of sorption equation [-];
- n – constant of Freundlich equation [-].

The Langmuir model presumes that the sorbate creates a monolayer. Sorbate molecules binding with active sites of the sorbent can have a physical (hydrogen or electrostatic interaction), or chemical (chemisorption) character. This theory requires that the particles do not form a multilayer, and do not interact with each other. Sorbed particles can however move in the monolayer, (change the active centres), but may also be replaced by a sorbate derived from outside the monolayers. The mass, which will be absorbed by a substance depends on the maximum sorbent monolayer capacity (q_{\max}) and sorbent for sorbate affinity. The Langmuir isotherm equation (3) is shown here:

$$Q = \frac{K_c \cdot q_{\max} \cdot C}{1 + K_c \cdot C} \quad (3)$$

where:

- Q – equilibrium amount of dyes absorbed [mg/g s.m.];
- q_{\max} – maximum sorption capacity of sorbent monolayer [mg/g s.m.];
- K_c – constant in the Langmuir equation [L/mg];
- C – concentration of dyes remaining in the solution [mg/L].

The Langmuir 2 model differs from the Langmuir model, because it assumes that the sorbent has two types of active centres on its Surface that have a different degree of sorbent affinity.

The amount of substance that will undergo sorption depends on the sorption capacity of of the active sites of type I and II ($q_{\max 1}$ and $q_{\max 2}$) and the degree of affinity for the

active centres of the sorbent to the sorbate (k_1 and k_2). Equation (4), presenting Langmuir 2 isotherm, can be found below:

$$Q = \frac{k_1 \cdot q_{\max 1} \cdot C}{1 + k_1 \cdot C} + \frac{k_2 \cdot q_{\max 2} \cdot C}{1 + k_2 \cdot C} \quad (4)$$

where:

- Q – equilibrium amount of dyes absorbed [mg/g s.m];
- $q_{\max 1}$ – maximum sorption capacity of sorbent (active site of the first type) mg/g s.m];
- $q_{\max 2}$ – maximum sorption capacity of sorbent (active site of the second type) mg/g s.m];
- $k_1; k_2$ – constants in the Langmuir 2 equation [L/mg];
- C – concentration of dyes remaining in the solution [mg/L].

Constants in the equations of Freundlich, Langmuir and Langmuir 2 were calculated with the use of Statistica 12:

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

where:

- R^2 – correlation coefficient – a measure of data alignment to the model;
- q_{exp} – the experimental data – sorbed amount of dyes [mg/g s.m.];
- q_{cal} – theoretical data resulting from the model – sorbed amount of dyes [mg/g s.m.].

The program STATISTICA 10.0 was used to determine the fit of the curves (with the determined constant) to the experimental data with the use of non-linear estimation by the method of least squares, at a significance level of $p < 0.05$.

3. Results and discussion

3.1. Effect of pH on the effectiveness of the dyes sorption

Figure 4 shows the change in efficiency of the adsorption of the anionic dye RB5 and the cationic BV10 with the three adsorbents tested: chitosan beads (CHs), activated carbon (AC) and activated carbon immobilised on chitosan beads (CHs-AC). Sorbents containing chitosan (CHs and CHs-AC) underwent dissolution at $pH < 4$ hence it was impossible to determine the effectiveness of the sorbent for sorption at $pH 2$ or 3 .

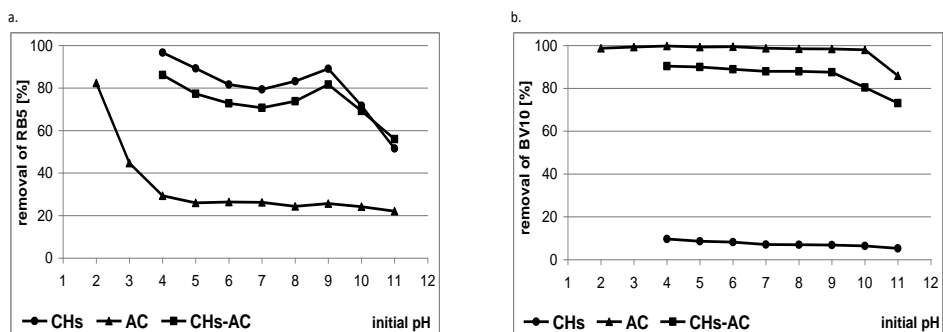


Figure 4. Effect of pH on the efficiency of dye sorption a. RB5, b. BV10

The effectiveness of RB5 sorption on CHs and CHs-AC was the highest at pH 4, and slightly decreased with increasing pH by weight with initial pH of 4–9. A decrease in the efficiency of sorption for both sorbents occurred at pH 10 and 11. RB5 sorption on AC most efficiently occurred at pH 2. Changing the initial sorption pH to 3 or 4 reduced the amount of RB5 binding on AC. A further increase in pH had no significant effect in the early effectiveness of RB5 sorption on AC.

The beneficial effect of low pH for the adsorption of anionic dyes on chitosan has been confirmed in previous studies [10–15]. This is due to the electrostatic interaction of the anionic dye with a negative charge and the chitosan adsorbent with a positive charge. At low pH, there is further protonation of chitosan amine groups that electrostatically attract the anionic dye. The increase in pH at which the adsorption is carried out is associated with the appearance of an increasing amount of OH⁻ groups in the solution, which consequently leads to a change in charge of the adsorbent and the electrostatic repulsion of a negatively charged dye. Reduction of the efficiency of RB5 adsorption at high pH may also result from competition of the anionic dye with the OH⁻ ions for active sites of the adsorbent.

In the case of the cationic BV10, there was a different trend. A high efficiency of adsorption for AC and CHs-AC was observed, along with a significantly lower efficiency for CHs. However, an influence of the initial pH on the adsorption efficiency of the solution was not observed (Fig. 3b). The high BV10 sorption efficiency at pH <4 is also confirmed by the literature [16–18].

The high adsorption efficiency of the cationic BV10 at low pH may result from the presence of the carboxyl group in the dye molecule. The decrease in the binding efficiency at the highest values of initial pH of the solution (10 and 11) may be due to plurality of negatively charged OH⁻ groups, which caused both the adsorbent and dye to be negatively charged and repel each other.

Figure 5 shows the pH change in the dye solution after adsorption. Significant changes were observed after the adsorption reaction compared with the initial pH of the solution. In the case of RB5 for the initial pH range of 4–9 for all adsorbents tested, the pH after the adsorption was in the pH range of 7–8. A similar tendency was observed for the cationic dye BV10 during adsorption on CHs and CHs-AC.

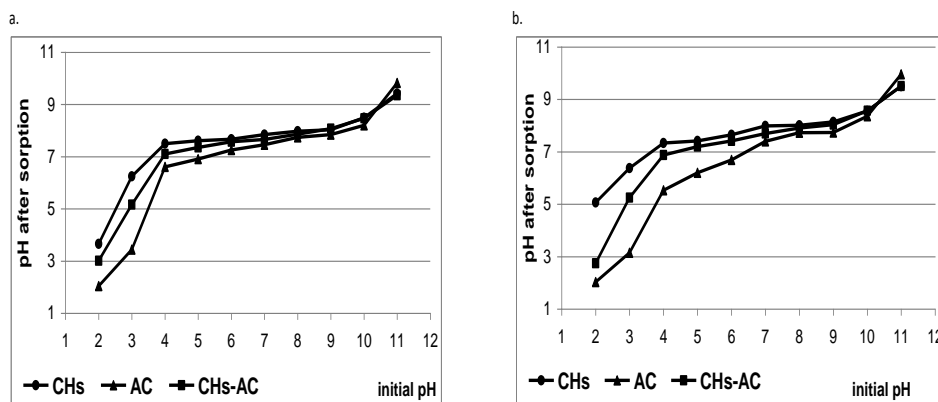


Figure 5. Change in pH of the solution after sorption a. RB5, b. BV10

The pH of the solution during adsorption always endeavored to obtain a pH similar to pH_{ZPC} of the tested sorbent (Fig. 6). The pH_{ZPC} point value, determined for CHs, CHs-

AC and AC were 7.98, 7.82 and 7.64, respectively. The pH_{ZPC} value is related to the nature of the adsorbent and its possession of functional groups.

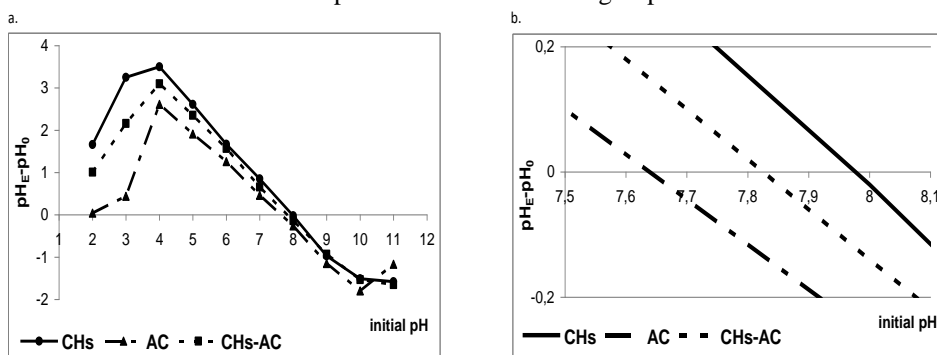


Figure 6. Determination of pH_{ZPC} of the sorbents

Adsorption capacity studies presented in the work were conducted at a pH of 4 with regard to the pH of the effluent colour range.

3.2 The maximum sorption capacity of the adsorbent

Experimental results of the RB5 and Basic Violet 10 BV10 dyes adsorption from the aqueous solution and isotherms determined from the Langmuir 2, Langmuir and Freundlich equations are presented in Figures 7 and 8.

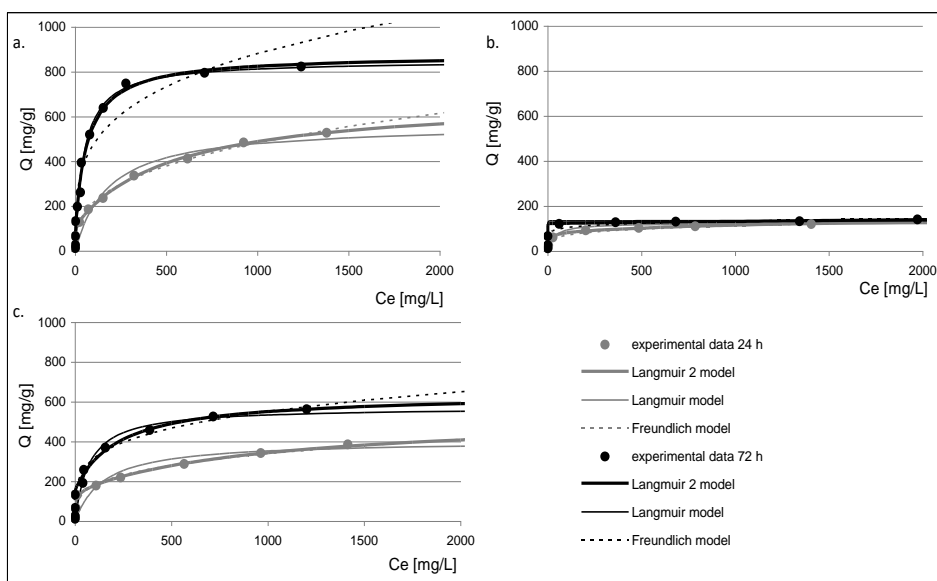


Figure 7. Experimental results RB5 onto a. chitosan beads (CHs), b. activated carbon (AC), c. activated carbon immobilised on chitosan beads (CHs-AC) and adsorption isotherms determined from the Langmuir 2, Langmuir and Freundlich models

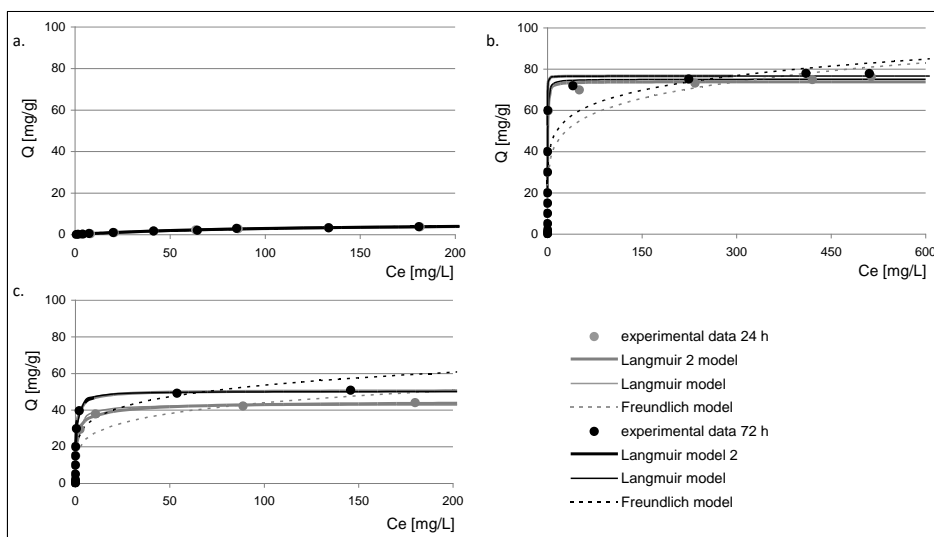


Figure 8. Experimental results for BV10 and RB5 onto a. chitosan beads (CHs), b. activated carbon (AC), c. activated carbon immobilised on chitosan beads (CHs-AC) and adsorption isotherms determined from the Langmuir 2, Langmuir and Freundlich models

Tables 2–4 show the constants from the Langmuir 2, Langmuir and Freundlich models. On the basis of the determination coefficient R^2 , it can be stated that the results of the experimental adsorption for RB5 and BV10 on the three adsorbents tested – CHs, AC and CHs-AC – best are best described by the double Langmuir model. This is confirmed by the binding of the tested dyes in different active centres among the groups [19]. These can form amino and acedamide chitosan groups.

Table 2. Reactive Black 5 (RB5) and Basic Violet 10 (BV10) adsorption constants determined from the Langmuir 2 model for the tested adsorbents

Dye	Time of sorption	Sorbent	Langmuir 2 (constants)					
			Q	q_{max1}	k_1	q_{max2}	k_2	R^2
			[mg/g d.m.]	[mg/g d.m.]	[L/mg]	[mg/g]	[L/mg]	-
RB5	24 h	CHs	688.60	114.44	1.004	574.17	0.002	0.999
		AC	161.70	84.02	0.113	77.68	0.001	0.995
		CHs-AC	535.85	150.81	0.227	385.04	0.001	0.992
	72 h	CHs	875.66	104.47	2.432	771.19	0.015	0.991
		AC	210.15	123.86	22.790	86.29	0.001	0.977
		CHs-AC	639.83	159.34	20.336	480.49	0.004	0.991
BV10	24 h	CHS	5.79	2.92	0.0101	2.87	0.010	0.997
		AC	81.96	60.60	4.799	21.36	0.007	0.941
		CHs-AC	44.54	32.14	4.168	12.40	0.075	0.981
	72 h	CHs	5.95	2.95	0.010	3.00	0.010	0.993
		AC	82.26	62.37	28.80	19.89	0.012	0.974
		CHs-AC	50.71	28.73	22.510	21.98	0.463	0.997

Table 3. Reactive Black 5 (RB5) and Basic Violet 10 (BV10) adsorption constants determined from the Langmuir model for the tested adsorbents

Dye	Time of sorption	Sorbent	Langmuir (constants)		
			q_{max}	K_c	R^2
			[mg/g]	[L/mg]	-
RB5	24 h	CHs	566.82	0.006	0.962
		AC	125.79	0.030	0.934
		CHs-AC	405.95	0.007	0.910
	72 h	CHs	851.15	0.022	0.978
		AC	135.89	20.008	0.956
		CHs-AC	573.25	0.014	0.932
BV10	24 h	CHS	5.79	0.0101	0.997
		AC	72.52	3.780	0.927
		CHs-AC	40.61	2.758	0.968
	72 h	CHs	5.95	0.010	0.993
		AC	74.61	22.658	0.960
		CHs-AC	45.83	8.657	0.965

Table 4. Reactive Black 5 (RB5) and Basic Violet 10 (BV10) adsorption constants determined from the Freundlich model for the tested adsorbents

Dye	Time of sorption	Sorbent	Freundlich (constants)		
			k	n	R^2
RB5	24 h	CHs	44.126	0.3468	0.996
		AC	28.352	0.2012	0.972
		CHs-AC	51.298	0.2742	0.990
	72 h	CHs	140.124	0.2665	0.935
		AC	64.896	0.1058	0.961
		CHs-AC	106.576	0.2383	0.970
BV10	24 h	CHS	0.165	0.6113	0.978
		AC	26.614	0.1801	0.862
		CHs-AC	17.013	0.2064	0.841
	72 h	CHs	0.170	0.6080	0.981
		AC	32.906	0.1513	0.874
		CHs-AC	23.456	0.1793	0.861

The data in Table 2 shows that the chitosan beads (875.66 mg/g d.m.) are capable of the most efficient removal of the anionic dye RB5 from aqueous solutions, due to a number of amino groups present in chitosan [20]. The lowest adsorption capacity was obtained for activated carbon (210.15 mg/g d.m.).

In the case of the cationic dye, the opposite tendency was observed. The most effective adsorbent was activated carbon (82.26 mg/g d.m.) and the best adsorption capacity was obtained for the beads of chitosan (5.95 mg/g d.m.). Immobilisation of activated carbon in chitosan resulted in the highest amount of dye removed, for both anionic and cationic dyes (50.71 and 639.83 mg/g d.m., respectively).

These values are comparable with the capacities obtained by Aguiar et al. [21], who studied the adsorption of three dyes: anionic dyes reactive red 120 (RR120), procion red MX-5B (PRMX-5B) and acid blue 25 (AB-25) on three types of activated carbon, Norit, WV1050 and Maxsorb. The values obtained for the adsorptive capacity of Norit were the lowest and ranged from 148 mg/g d.m. (RR120) to 245 mg/g d.m. (AB25). Adsorption for WV1050 ranged from 277 mg/g d.m. for RR120 to 905 mg/g d.m. for PRMX1050. The authors obtained the highest effectiveness for Maxsorb: from 690 mg/g d.m. for RR120 to 1200 mg/g d.m. for PRMX1050. McKay et al. [22] investigated the binding of three acid dyes, Acid Blue 80 (AB80), Acid Yellow 117 (AY117) and Acid Red 114 (AR114), to granular activated carbon. The resulting adsorption capacities were within the range of 103.73 to 185 mg/g. The adsorption capacities of sorbents presented in the literature of biological origin are much lower compared with commercial activated carbon used in this study.

In work by McKay et al. [23], the adsorptive removal of basic dyes (acridine orange: AO, and azure B: AzB) was presented onto a novel activated carbon prepared from brown linseed (*Linum usitatissimum L.*) deoiled cake with phosphoric acid activation. The adsorption capacity of the adsorbent tested by the authors was 205.6 mg/g for AO and 124.0 mg/g for AzB. Even lower values were obtained Aboua et al. [24] while examining the dye adsorption onto activated carbon from the shells of Macoré fruit. The amount of removed methylene blue (MB) was 6.85 mg/g and methylene orange (MO) was 2.96 mg/g.

The adsorbent presented in this study therefore demonstrates capacities that are attractive for the removal of dyes from wastewater from different types of industries prior to introduction into the sewage system, which is often a problem.

The study showed different binding mechanisms of the tested dyes, RB5 and BV10, on three adsorbents. Analysing the k constants, designated with a double Langmuir model, it can be seen that the k_1 constants were much higher than the k_2 constants, indicating stronger binding of dyes in the active sites of the first type. The k_2 constants were low for both dyes and all adsorbents irrespective of the duration of the adsorption step. In the case of k_1 constants, an impact on the value of both types of dye and duration of the adsorption process was noticeable. After 24 h of adsorption, the RB5 adsorption affinity with respect to CHs was high (1.004 L/mg), and it was low with respect to AC (0.013 L/mg). The opposite trend occurred in the case of BV10. High affinity was designated relative to AC (4.799 L/mg) and low relative to CHs (0.0101 L/mg). This would demonstrate strong binding of the RB5 dye with CHs and much weaker binding with AC, while in the case of BV10, there was strong binding with AC and weak binding with CHs. After 72 h of adsorption, a marked increase in affinity for both dyes and all adsorbents was seen. The most significant increase was noted in the case of AC. The constant k_1 for RB5 increased by about 100x to 22.79 L/mg, and in the case of BV10, it increased more than seven times to 28.8 L/mg. Comparably high values were obtained for the CHs-AC adsorbent. This demonstrates a strong and lasting binding. It can be assumed that the AC had a decisive influence on this binding. To create an adsorbent that will permanently bind every type of dye, this may be provided by the use of active carbon within the adsorbent, as well as by a long adsorption process.

4. Conclusions

Due to its basic nature, chitosan is an efficient sorbent for anionic dyes ($Q_{\max}=875.7$ mg RB5/g), but it is ineffective for the sorption of cationic dyes ($Q_{\max}=5.9$ mg BV10/g). Immobilisation of activated carbon on chitosan hydrogel beads significantly improved the sorption properties of the chitosan sorbent with respect to BV10. The

developed sorbent (CHs-AC) is therefore effective for both types of dyes (RB5/BV10) over a broad pH range 4–10, which makes it a universal sorbent. The maximum sorption capacity of CHs-AC for RB5 is 639.8 mg/g, while for BV10 it is 50.7 mg/g.

5. Acknowledgements

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