THE USE OF POLYSACCHARIDES FOR ACID RED 18 ANIONIC DYE REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract

In the paper, the adsorption of Acid Red 18 (AR18) on chitosan (CHs), sodium carboxymethyl cellulose (CMC) and agar (AGA) was researched. The adsorption capability of biosorbents was examined as a function of initial pH, time of contact and influence of initial concentration of dye. The adsorption kinetics was compared with the pseudo 1. and 2. order models. It was found that the dye adsorption occurred in accordance with the pseudo 2. order model. The experimental data of adsorption in the equilibrium state was analysed with the use of isotherms of the Freundlich, Langmuir and double-Langmuir models. It was found that for the description of dye adsorption on adsorbents, the double-Langmuir model was suitable, which was demonstrated by the determined values of the average relative error (ARE). The highest adsorption capacity and affinity to AR 18 was obtained for CHs, at 81.7 mg/g d.w and 0.997 L/mg, respectively. The experimental results show that CHs seems to be a promising biosorbent for AR 18 dye removal from aqueous solutions.

Key words*: dye, carboxymethylcellulose, agar,* chitosan, adsorption

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1. Introduction

Wastewater from the textile, pulp and paper, chemical, leather, food and cosmetic industries contains dyes and is thus a dangerous source of pollution to the environment [1]. Wastewater containing dyes poses huge difficulties in purifying processes because of the complex structure of the dye molecule. Even small amounts of dyes are undesirable, because they stain water, making it unaesthetic, and disrupt life processes in the water. Most dyes are non-biodegradable, impair the penetration of light into the water and inhibit photosynthesis, increasing chemical and biological oxygen demand. Some dyes might also have toxic or even carcinogenic and mutagenic properties in relation to living organisms.

Synthetic dyes can be divided according to the chemical structure into three categories: cationic, non-ionic and anionic. Among the anionic dyes, it is possible to distinguish among direct, reactive and acidic dyes [2]. These are water-soluble dyes, which have good dyeing durability. They are characterised by an average endurance to light and wet factors and give the colouring of high brightness and purity. Due to their properties they, form a group of compounds difficult to remove by conventional wastewater treatment systems and remain in treated sewage unchanged, posing a serious threat to surface waters [3].

Currently, for colourful wastewater treatment, methods such as precipitation, ultrafiltration, ion exchange, electrodialysis or reverse osmosis are being used [4, 5]. The following methods are mostly used for the removal of high concentrations of contamination; however, they are not useful in the purification of large amounts of wastewater with low concentrations of dyes, where its use becomes energy consuming and leads to the creation of huge amounts of secondary contamination. The alternative to these processes are biotechnological processes, such as biosorption or bioaccumulation.

In biosorption, low cost biological materials are frequently used, namely alive or dead microorganisms. The interactions between microorganisms (yeast, bacteria, fungi, algae) and dyes depend on their chemical properties [6]. In recent years, for the removal of organic contamination, including dyes, polymer adsorbents have been used with increased frequency because they can easily be recovered from wastewater [7, 8]. Natural polymers, including polysaccharides used for the removal of the dyes from wastewater, are substances such as cellulose, chitin, chitosan and agar [9–12].

The use of biosorbents in the technologies of water and wastewater purification requires fundamental research enabling the determination of the sorption properties of biomass. This will allow the design process to continue and guidelines for the design of technical installations to be further developed. This research can include the recognition of mechanisms of ion bonding, the determination of kinetics and equilibrium of the biosorption process, and the influence of process parameters on the efficiency of the process. Mathematical modelling of the process enables the kinetic and equilibrium parameters to be determined, which is extremely useful in the planning of the technological installation. In the present work, for the adsorption of the AR18 anionic dye, chitosan, carboxymethyl cellulose (CMC) and agar were used. The adsorption kinetics was determined with the use of pseudo 1. and 2. order models, whereas the experimental data of adsorption in the equilibrium state was analysed with the use of isotherms of Freundlich, Langmuir and double-Langmuir models.

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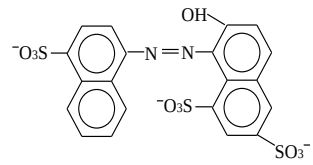
2. Materials and methods

2.1. Materials

Sodium carboxymethyl cellulose (CMC) was prepared by dissolving 2 g of carboxymethyl cellulose sodium salt (Sigma-Aldrich Poland cas. 9004-32-4) in 100 g of distilled water, and then 0.1 M $Al_2(SO_4)_3$ was added dropwise. Gelled grains were left in the solution for 24 h and then washed with distilled water. Agar (Sigma-Aldrich Poland cas. 9002-18-0) was prepared by dissolving 2 g of powder in 100 g of distilled water in a water bath at 100°C, cooled to 50°C, and then the distilled water mixed with vegetable oil in the ratio 2:10 was added dropwise. The obtained grains were washed with a solution of detergent to remove the oil and then with distilled water. In the research, chitosan from crab shells in the form of flakes (DD=90%) was used and it was purchased from Heppe Medical Chitosan GmbH, Halle (Saale), Germany.

Acid Red 18 (AR 18) was produced by "Boruta" SA Dyes Production Plant. The dye characteristics have been compiled in Table 1.

Table 1. Characteristics of the dye Acid Red 18

Structural formula	
Molecular formula	$C_{20}H_{11}N_2Na_3O_{10}S_3$
Name	Acid Red 18
Working class	acid
Chemical class	azo
Molecular weight	604.5
Wavelength λ	508

2.2. Sorption study

The research was conducted in the pH range 1–10 and with a dye concentration of 100 mg/L. Biosorbents (CMC, agar, chitosan) in the amount of 4 g each were put into a 250 cm^3 reaction vessel. Then 50 cm^3 of the solution of the tested dye, having previously been subjected to adjustment of pH using 0.01 M NaOH or 0.01 M HNO_3 to achieve the specified value, was added and this was shaken at 180 rpm for 2 h.

In the study of adsorption of the AR 18 dye onto biosorbents, the time necessary to obtain the equilibrium of the reaction was determined. To achieve equilibrium, 20 g of biosorbent was measured into the reaction vessel, and 500 mL of the AR 18 solution at a concentration of 100 mg/L was added. The reaction vessel was then put on the magnetic stirrer. Subsequently, in the time interval of 0–240 min, the solution was sampled and the concentration of the dye remaining in solution was determined.

The concentrations of dye in solution as well as the value of the maximum concentration were selected in such a way as to obtain the course of the adsorption isotherm up to the complete saturation of the active sites of the sorbents with the dye. For this study, the model solutions of the dye at concentrations of 1 to 600 mg/L were prepared. Then 8 g of biosorbent was added to 250 cm^3 reaction flasks along with

100 cm^3 of the dye solution of determined pH. The reaction flasks were shaken for 2 h at 180 rpm.

2.3. Calculation methods

The amount of the adsorbed dye in the equilibrium state Q_{ad} was calculated from the balance of mass with the equation:

$$Q_{ad} = \frac{(C_0 - C_{ad})}{m} \qquad (1)$$

where:
C_0 – initial concentration of the dye in the solution (mg/L); C_{ad} – concentration of the dye in the solution in the equilibrium state after adsorption (mg/L); m – the concentration of the used adsorbent (g/L).

The influence of the pH on the sorption effectiveness (η_s) was assessed based on the percentage amount of dye in the adsorbent and calculated from the equation:

$$\eta_{ad} = \frac{Q_0 - Q_{ad}}{Q_{ad}} \cdot 100 \qquad (2)$$

where:
Q_0 – the amount of dye in solution before adsorption (mg/g d.w.); Q_{ad} – the amount of dye in the adsorbent after adsorption (mg/g d.w.).

2.3.1 The study of adsorption kinetics of the dye

The evaluation of adsorption effectiveness included the determination of adsorption kinetics, i.e. reaction order and rate constants. Analysing the data from the literature, it is possible to notice that for the description of the dye adsorption kinetics, the reactions of the pseudo 1. order and pseudo 2. order models were used [14–16].

The reaction rate constants were calculated with Lagergren's equation, which consists of the analysis of correlations between the mass of dye adsorbed by 1 g of adsorbent and time, and is defined as the pseudo-n-order reaction. The order of reaction was determined by using determination factor (R^2) as selection criteria.
Equation for a pseudo 1. order reaction:

$$\frac{dQ_t}{dt} = k_1 \left(Q_{ad} - Q_t\right) \qquad (3)$$

where:
Q_{ad} – the amount of dye adsorbed in the equilibrium state (mg/g d.w.), Q_t – the amount of dye adsorbed on the surface of the sorbent in the time unit (mg/g d.w.), k_1 – rate constant for a pseudo 1. order adsorption (1/m), t – time

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Model of pseudo 2. order reaction:

$$\frac{dQ_t}{dt} = k_2\left(Q_{ad} - Q_t\right)^2 \qquad (4)$$

where:
k_2 – rate constant for pseudo-second-order adsorption [mg/(g·min)].

2.3.2 Isotherm models

The adsorption of the dye in the equilibrium conditions was marked based on the course of the adsorption isotherms and maximum adsorption capacity determined from the Freundlich, Langmuir and double Langmuir equations. The adsorption process lasts until the adsorption equilibrium state between adsorbent and adsorbate is established, and this can be presented as:

$$q = f(C,T) \qquad (5)$$

where:
q – the amount of adsorbed adsorbate in the surface layer of 1g of adsorbent (mg/g), C – the equilibrium concentration of the adsorbate (mg/dm^3), T – temperature (°C).

At constant temperature, in the equilibrium conditions, the dependence of $q = f(C)$ is described mathematically with the use of adsorption isotherms. For the description of the experimental results of adsorption, the Freundlich, Langmuir and double Langmuir models were used (2).
Freundlich model:

$$q_e = K_F C_e^{1/n} \qquad (6)$$

where:
q_e – the amount of adsorbed sorbate on sorbent in the equilibrium state (mg/g d.w.), C_e – the equilibrium concentration of the adsorbate in the solution (mg/L), K_F – constant in the Freundlich equation connected with the ability of adsorption, $1/n$ – measure of the adsorption intensity. For $n = 1$ the division of the sorbate between two phases depends on the concentration. For $1/n < 1$ the isotherm has the course of the Langmuir isotherm. For $1/n > 1$ the adsorption has a cooperative character.

Langmuir model:

$$q_e = \frac{Q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e} \qquad (7)$$

where:
Q_{max} – maximum adsorption capacity of monolayer (mg/g d.w.), b – the adsorption equilibrium constant (L/mg).

Langmuir model (2):

$$q_e = \frac{Q_1 \cdot b_1 \cdot C_e}{1 + b_1 \cdot C_e} + \frac{Q_2 \cdot b_2 \cdot C_e}{1 + b_2 \cdot C_e} \qquad (8)$$

where:

Q_1, Q_2 – maximum adsorption capacity of monolayer 1 (Q_1) and 2 (Q_2) (the size of adsorption is equivalent to the filling of monolayer) (mg/g d.w.); b_1, b_2 – the equilibrium constant of the monolayer adsorption 1 (b_1) and 2 (b_2) (L/mg).

3. Results and discussion

3.1. The influence of the pH on the sorption effectiveness

Analysing the results, it was noted that the adsorption ability of the biosorbents depended on the applied pH. The results of AR 18 adsorption depending on the pH of are shown in Figure 1.

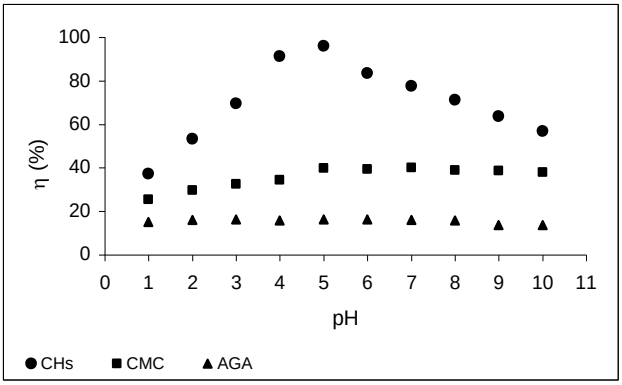

Figure 1. Effectiveness of AR 18 adsorption at different pH (C_0 = 100 mg/L, temp. 25°C).

The research has shown that the biggest influence of the pH on the effectiveness of AR 18 dye adsorption was observed in case of CHs. The optimum pH was contained in the narrow range of pH, from 4.0 to 5.0, where the efficiency of AR 18 removal was 94% on average. An important change in the dye bonding was noticed in the pH range of 1 to 3 and from 6 to 10. The effectiveness of AR 18 removal from the solution in these ranges were 53.4% and 56.3%, respectively. Similar results, but with a wider range of pH values, were obtained by Yan et al. [13]. While carrying out the study of the adsorption effectiveness of anionic dyes (AO 10, AO 7, AR 18 and AG 25) with the use of chitosan (CTS-beads) and chitosan modified with benzaldehyde (CTSN-beads), the authors demonstrated that the proper pH range for CTS-beads is 5–7, whereas for CTSN-beads a wider range of pH 3–9 might be used.

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The efficiency of dye adsorption on CMC was lower in comparison with CHs and remained at 46% in the pH range from 6.0 to 10.0, whereas lower efficiency was observed in an acidic environment (pH 1–5) and was 32%. Previous research of the adsorption of methylene blue on CMC showed that the maximum adsorption of the dye also occurred in the pH range of 6–7, but a further increase in pH caused a significant decrease in the process efficiency [10].

In the case of AGA in the whole examined range of pH, the adsorption of the dye was much lower (15%) in comparison with CHs and CMC.

A high adsorption efficiency of AR 18 on chitosan in a pH range of 4–5 resulted from chitosan protonation. The increase in pH value caused mutual repulsion of dye ions and OH^- ions, which reduced the adsorption. For the remaining biosorbents, the adsorption efficiency did not result from protonation; therefore, the pH change did not substantially affect the amount of adsorbed dye."

In further research of AR 18 adsorption on tested biosorbents, the pH of the solution was kept in the range of 4–5.

3.2. The study of adsorption kinetics of the dye

The results of the dependence between the mass of the adsorbed dye and the time of the adsorption are shown in Figure 2, and the determined reaction rate constants from the pseudo first order and pseudo second order equations are shown in Table 2.

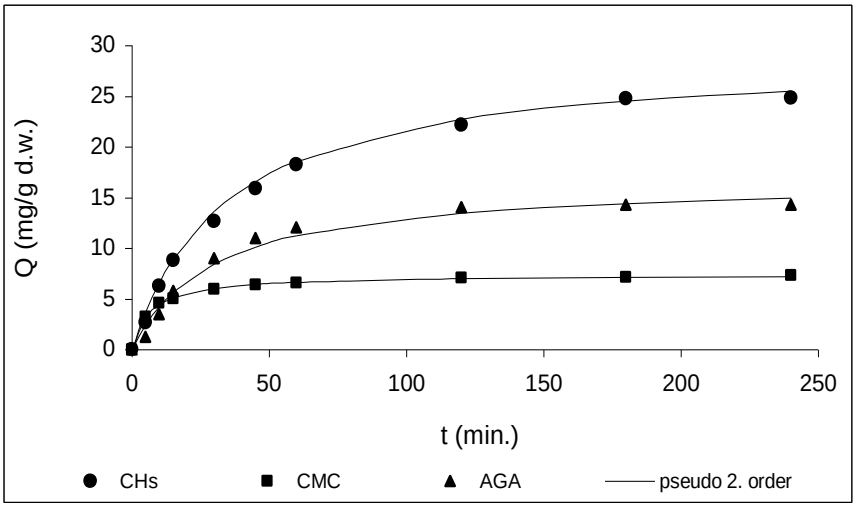

Figure 2. Diagram of the sorption kinetics of CHs, CMC and AGA for the AR 18 dye (C_0 = 100 mg/L, pH 4.5 ± 0.5, temp. 25°C).

In order to examine the influence of time of contact on AR 18 adsorption, experiments were carried out for three tested biosorbents. The necessary time to reach the equilibrium state was about 120 min. An equally short equilibrium time (<120 min) was obtained by Gao et al. [16] in a study of AR 18 adsorption on natural polymer chitosan (CTS) and siliceous mesoporous SBA-15, which indicated that multimolecular adsorbents are beneficial for quick mass transfer.

Based on the present results, the adsorption of the AR 18 dye was according to the pseudo 2. order reaction. This is also compatible with results obtained by other authors for the adsorption of this dye [17–19].

Table 2. The values of the kinetic constants of the adsorption of AR 18 dye for the tested biosorbents.

Pseudo 1. order reaction			
Biosorbents	Q_{ad} (mg/g d.w)	k_1 (1/min)	R^2
CHs	24.4	0.025	0.9968
CMC	6.6	0.325	0.9859
AGA	14.7	0.033	0.9985
Pseudo 2. order reaction			
Biosorbents	Q_{ad} (mg/g d.w.)	k_2 (g/mg·min)	R^2
CHs	29.2	0.001	0.9990
CMC	7.4	0.020	0.9990
AGA	16.8	0.002	0.9991

3.3. Isotherm models

The experimental results of the amount of bonded AR 18, depending on the concentration of dye left in the solution, and the Freundlich, Langmuir and Langmuir (2) isotherms determined based on them are shown in Figure 3.

From the data presented in Figure 3, the results show that the isotherms of the Freundlich, Langmuir and Langmuir (2) models exhibit a high fit of the experimental results of AR 18 adsorption by the CMC and AGA adsorbents, while in the case of CHs, the isotherms of the Langmuir and Freundlich models were significantly different from the experimental data; only the Langmuir (2) model reflected the obtained results of AR 18 adsorption. The highest efficiency of AR 18 removal in the examined range of initial concentrations of dye was obtained for CHs: 87% on average. A significantly lower efficiency of adsorption was noted in CMC and AGA: 22% and 30%, respectively.

In order to analyse the obtained results of AR 18 dye adsorption on CHs, CMC and AGA, in Table 3, the constants determined from the Freundlich, Langmuir, Langmuir (2) equations and the factor of determination, R^2, as a measure of the fit of model isotherms to experimental data are presented.

Based on the R^2 value, it was difficult to judge the usefulness of the adsorption model equations for the description of experimental data. The values of this factor were very high (0.9943–0.9986) for the Langmuir (2) model and slightly lower yet still high (0.9581–0.9936) for the Langmuir and Freundlich models (Table 3).

The average relative error (ARE) was more useful in this regard. The minimisation of the average relative error (*ARE*) was computed as follows in order to show how well the equilibrium models agree with experimental results [20]:

$$\mathrm{ARE}\ (\%) = \frac{100}{z}\sum_{i=1}^{z}\left(\frac{\left|q_{exp} - q_{calc}\right|}{q_{exp}}\right)_i \qquad (9)$$

where:

z is the number of data points; q_{exp} and q_{calc} are the experimental sorption capacity and the sorption capacity calculated with the theoretical models.

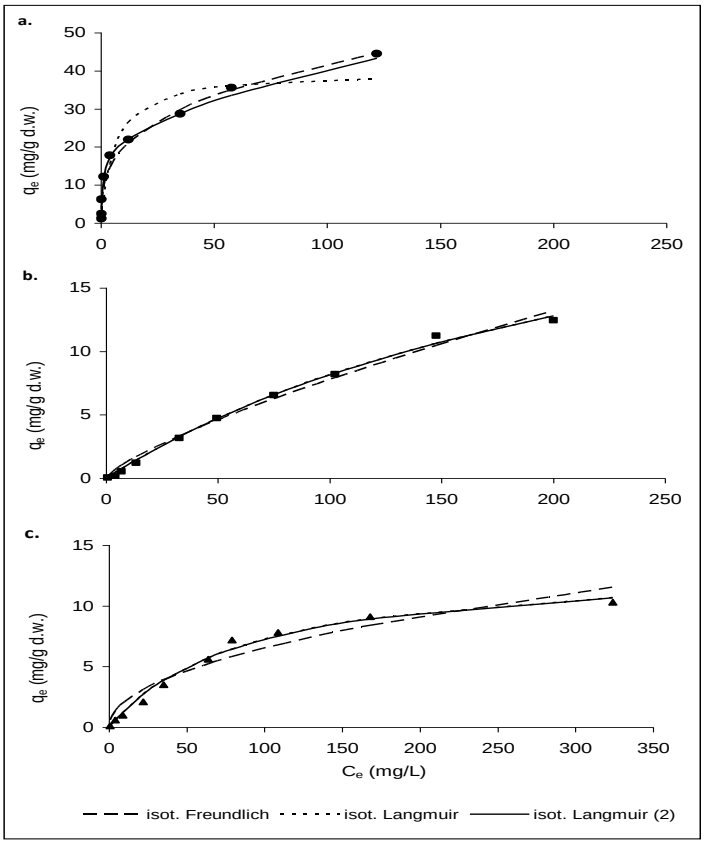

Figure 3. The experimental results of AR 18 dye adsorption and the isotherms determined from the Freundlich, Langmuir and Langmuir (2) equations. a. CHs, b. CMC, c. AGA (pH 4.5 ± 0.5, temp. 25°C).

Table 3. The values of constants determined based on Freundlich, Lagmuir and double Langmuir equations for the adsorption of the AR 18 dye on biosorbents.

Models	**Constants**	**Biosorbent**		
		CHs	**CMC**	**AGA**
Freundlich model	K_F	9.3	0.2	0.7
	1/n	0.327	0.759	0.486
	R^2	0.9934	0.9936	0.9675
Langmuir model	Q_{max}	39.9	29.7	13.6
	b	0.163	0.004	0.011
	R^2	0.9581	0.9983	0.9982
Langmuir (2) model	b_1	0.992	0.004	0.011
	b_2	0.005	0.004	0.011
	Q_1	20.1	14.8	2.2
	Q_2	61.6	14.8	11.4
	Q_1+Q_2	81.7	29.6	13.6
	R^2	0.9986	0.9982	0.9943

The values were differential, which enabled the choice of model that precisely reflected the obtained experimental data of AR 18 adsorption (Figure 4).

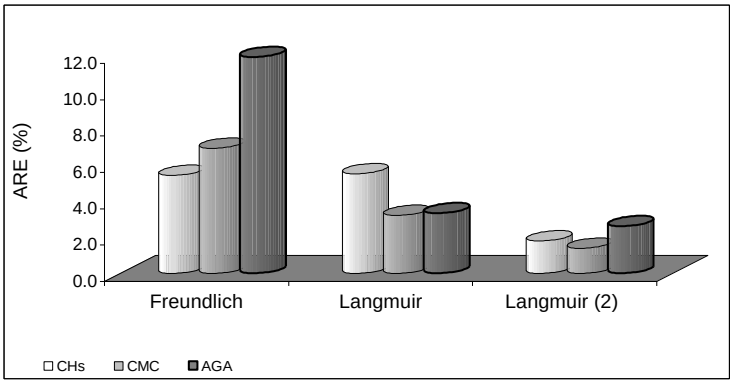

Figure 4. The values of average relative error (ARE%) for tested biosorbents described by Freundlich, Langmuir and Langmuir (2) isotherms.

High values of ARE% between 6% and 12% obtained for the Freundlich isotherm demonstrated the poor suitability of this model for the description of AR 18 adsorption on the tested biosorbents. The analysis of the value of relative error showed that the Langmuir (2) model had the best fit of obtained experimental data of AR 18 adsorption on the tested biosorbents. The highest value of error in case of Langmuir (2) isotherm was noted for AGA (2.6%), whereas the lowest was noted for CMC (1.4%).

Determined form the Langmuir (2) model, adsorption capacities depended on the type of sorbent (Table 3). The lowest value of q_{max} constant was for CMC (13.6 mg/g d.w.), while an adsorption capacity of more than six times higher was shown by CHs. The highest obtained values of the constant (*b*) demonstrating the affinity of the adsorbent to adsorbate was also noted for CHs, and the lowest for CMC: 0.997 and 0.008 L/mg, respectively.

4. Conclusion

The research of the adsorption of AR 18 on the tested biosorbents (CHs, CMC and AGA) showed that the amount of adsorbed dye depended on the pH and their initial concentrations. The highest efficiency of dye removal from the solution depending on the initial concentration was obtained for CHs (87%). The values of the correlation factor R^2 demonstrated that the adsorption kinetics of the AR 18 dye on tested biosorbents occurred according to the reaction of pseudo 2. order model, which indicates that the process had a chemical character. The reaction equilibrium appeared before 180 min. The analysis of the value of relative error (ARE) inicated that the best fit to the experimental data of AR 18 adsorption on biosorbents was shown by the Langmuir (2) model. The highest values of the q_{max} and *b* constants determined from the Langmuir (2) model were obtained for CHs: 81.7 mg/g d.w and 0.997 L/mg, respectively. Based on these results, it is possible to state that CHs is an effective adsorbent that could be used for anionic dye removal. Furthermore, it is possible to obtain CHs at relatively low costs, and this process is environmentally friendly, so it constitutes a viable replacement of synthetic polymer adsorbents, carbons and other widely used adsorption materials.

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5. Acknowledgements

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