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## Biosorption of Congo Red and Methylene Blue by pretreated waste *Streptomyces fradiae* biomass – Equilibrium, kinetic and thermodynamic studies

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**Abstract:** Pretreated waste *Streptomyces fradiae* biomass was utilized as an eco-friendly sorbent for Congo Red (CR) and Methylene Blue (MB) removal from aqueous solutions. The biosorbent was characterized by Fourier transform infrared spectroscopy. Batch experiments were conducted to study the effect of pH, biosorbent dosage, initial concentration of adsorbates, contact time and temperature on the biosorption of the two dyes. The equilibrium adsorption data were analysed using Freundlich and Langmuir models. Both models fitted well the experimental data. The maximum biosorption capacity of the pretreated *Streptomyces fradiae* biomass was 46.64 mg g<sup>-1</sup> for CR and 59.63 mg g<sup>-1</sup> for MB, at a pH 6.0, with the contact time of 120 min, the biosorbent dosage of 2 g dm<sup>-3</sup> and the temperature of 298 K. Lagergren and Ho kinetic models were used to analyse the kinetic data obtained from different batch experiments. The biosorption of both dyes followed better the pseudo-second order kinetic model. The calculated values for  $\Delta G$ ,  $\Delta S$ , and  $\Delta H$  indicated that the biosorption of CR and MB onto the waste pretreated biomass was feasible, spontaneous, and exothermic in the selected temperature range and conditions.

**Keywords:** waste biomass; water treatment; dyes; biosorption.

### INTRODUCTION

Synthetic dyes are used in food, textile and paper, plastic, printing, leather and pharmaceutical industries. Worldwide, the production of synthetic dyes reaches 800 000 t/year, and from 60 to 70 % of this production goes to azo dyes.<sup>1</sup>

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Most of the azo dyes are characterized by a high resistance to chemical, thermal and photochemical effects; moreover, they cannot be subjected to biological degradation, which determines their high persistence in the environment.<sup>2</sup> Azo dyes exhibit toxic effects on living organisms and can release mutagenic and carcinogenic substances.

Conventional methods have been reported for dye removal (chemical precipitation, activated carbon adsorption, reverse osmosis, solvent extractions and oxidation by ozone), but they often produce the hazardous by-products and generate large amounts of solid waste, which requires costly disposal or regeneration methods.<sup>3,4</sup> Among these methods the adsorption is considered as an effective method for dye removal. The most commonly used adsorbent is the activated carbon, but its disadvantages are the high costs of production and regeneration.<sup>5,6</sup>

In recent years biosorption has become an economic and eco-friendly alternative method for removal of metals, dyes, phenols, fluoride, and pharmaceuticals from solutions.<sup>7,8</sup> Biosorption is a metabolically passive process, performed by the materials of biological origin, not by living biomass. A wide variety of biomasses from different origins have been used for dye removal from aqueous solutions, like bacteria, yeast, fungi and algae,<sup>9-13</sup> unmodified and modified chitosan,<sup>14,15</sup> low-cost agricultural wastes,<sup>16-18</sup> etc.

*Streptomyces* is a genus consisted of Gram-positive bacteria. The Gram-positive bacteria have a greater sorption capacity due to their thicker peptidoglycan layer connected by amino acid bridges. Embedded in the Gram-positive bacterial cell wall are polyalcohols, some of which are lipid linked to form lipoteichoic acids.<sup>19</sup> Among the functional groups presented on the bacterial cell wall are carboxyl, phosphonate, amine and hydroxyl groups.<sup>20</sup>

The *Streptomyces* genus produces two-thirds of the clinically useful antibiotics and other bioactive compounds with remarkable importance.

The antibiotic fermentation industry generates large amounts of waste which is disposed of by incineration. This unnecessary biomass, after suitable pretreatment, has been used for biosorption of metals and dyes from aqueous solutions.<sup>21-24</sup>

Congo Red (CR) is a benzidine-based anionic diazo dye that can cause allergic reactions and can be metabolized to benzidine – a carcinogenic product.<sup>25</sup>

Methylene Blue (MB) is a tricyclic phenothiazine cationic dye used in different fields: textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries.<sup>26</sup> In high doses the dye can cause toxicity and it is also harmful if swallowed; it irritates the eyes, respiratory system and skin.<sup>27</sup> CR and MB are widely employed as a model anionic and cationic dyes in adsorption studies using low-cost biosorbents.

The aim of this research was to evaluate for the first time the biosorption capability of waste pretreated *Streptomyces fradiae* biomass, obtained from tylosin production, as an eco-friendly biosorbent for the removal of CR and MB

from model aqueous solutions. In batch mode the different process parameters were optimized. The equilibrium, kinetic and thermodynamic parameters of the dyes biosorption by the waste *Streptomyces fradiae* biomass were investigated.

## EXPERIMENTAL

### *Preparation and characterisation of the biosorbent*

The waste *Streptomyces fradiae* biomass from tylosin production was provided by “Biovet” AD, Peshtera, Bulgaria. The lipids of the biomass were extracted with chloroform/methanol by the Folch method to prevent the aggregation of the biosorbent during biosorption experiments.<sup>28</sup> The obtained biomass was washed several times with deionized water until pH 6 for the filtrate was reached, and oven-dried at 80 °C for 12 h. The dried biomass was ground and sieved (100 mesh sieve) and stored in desiccator until further use.

Surface functional groups of the *Streptomyces fradiae* biomass before and after CR and MB sorption were recorded on Thermo Nicolet Avatar 330 Fourier Transform Infrared Spectrometer. Potassium bromide disks were prepared by mixing 2 mg of biosorbent samples with 200 mg of KBr, at resolution of 4 cm<sup>-1</sup>.

### *Adsorbates*

Methylene Blue (MB, color index number: 52015, chemical formula – C<sub>14</sub>H<sub>18</sub>ClN<sub>3</sub>S, molecular weight: 319.86 g mol<sup>-1</sup>, 98 % dye content) and Congo Red (CR, color index number: 22120, chemical formula – C<sub>32</sub>H<sub>22</sub>N<sub>6</sub>Na<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, molecular weight: 696.66 g mol<sup>-1</sup>, 98 % dye content) were purchased from Sigma–Aldrich.

Stock solutions of each dye (500 mg dm<sup>-3</sup>) were prepared in deionized water. Working solutions with desired concentrations were prepared daily, by the dilutions with deionized water. The dye concentrations were determined spectrophotometrically on a UV/Vis spectrophotometer Ultrospec 3300.

The absorbance of MB was measured at 663 nm. The maximum absorption wavelength of CR as a function of pH was determined, and specific pH standard calibration curves were generated. The absorption was measured at 570 nm (pH range 2–3), 506 nm (pH 4) and at 498 nm (pH range 5–8).<sup>29</sup>

### *Biosorption experiments*

In order to evaluate the effect of pH, biosorbent dosage, initial CR and MB concentrations, contact time and temperature, a set of biosorption experiments were conducted in 250 cm<sup>3</sup> Erlenmeyer flasks, at a constant agitation speed of 250 rpm in a batch mode. The experiments were carried out by varying: the initial pH of the solution from 2.0 to 8.0; the biosorbent dosage from 0.5 to 4 g dm<sup>-3</sup>; the initial concentrations of each dye from 25 to 200 mg dm<sup>-3</sup>; the contact time from 5 to 180 min, and the temperature from 298 to 313 K. The initial pH of dye solutions was adjusted with 1 M HCl or 1 M NaOH in the range from 2.0 to 8.0. At the end of the biosorption process, the biosorbent was separated from the solution by centrifugation at 2500 rpm for 10 min and the residual dye concentration was determined as listed above.

Blanks, containing dyes but no biosorbent, were used for each series of experiments. All experiments were performed in triplicate. For all graphical representations, the mean values of the three independent experiments were considered, but the standard deviations within the triplicates were too small to be plotted as an error bar (< 1 %).

The amount of dye adsorbed per unit of biosorbent (mg dye per g of dry biomass) and the removal efficiency *R* (%) were calculated from the determined concentrations.

## RESULTS AND DISCUSSION

*Characterization of the biosorbent*

The FTIR spectrum of the unloaded biomass (Fig. S-1 of the Supplementary material to this paper) has shown several bands. The broad and strong band between 3500 and 3200  $\text{cm}^{-1}$  was assigned to the overlapping of  $-\text{OH}$  and/or  $-\text{NH}$  stretching vibrations. The peaks at 2924 and 2854  $\text{cm}^{-1}$  confirmed the presence of  $-\text{CH}$  symmetric and asymmetric stretching vibrations of  $-\text{CH}_2$  groups. The amide I band,  $-\text{C}=\text{O}$  stretching vibration appears at 1653  $\text{cm}^{-1}$ . The peak at 1542  $\text{cm}^{-1}$  could be assigned to amide II, and it could be due to  $-\text{NH}$  bending and  $-\text{CN}$  stretching vibrations of  $-\text{C}(=\text{O})-\text{NH}-$  group in its transformations. Sometimes asymmetric stretching vibration of the carboxylic anion group ( $-\text{C}(=\text{O})-\text{O}^-$ ) appears around this wavenumbers.<sup>30</sup> The peak observed at 1456  $\text{cm}^{-1}$  was due to a  $-\text{CH}_2$  scissoring or  $-\text{CH}_3$  anti-symmetrical bending vibration. The weak band at 1227  $\text{cm}^{-1}$  can be attributed to a  $-\text{C}=\text{O}$  stretch.<sup>31</sup> The peak around 1057  $\text{cm}^{-1}$  could be caused by the stretching of phosphate groups. Therefore, the FTIR analysis of the biosorbent revealed the presence of hydroxyl, carboxyl, amino, and phosphate groups on the biomass surface.

The spectra obtained after MB and CR biosorption (Figs. S-2 and S-3 of the Supplementary material, respectively) showed the changes in the form and in the intensity of the band at 3420  $\text{cm}^{-1}$ . It was also shifted to 3410 and 3411  $\text{cm}^{-1}$  after MB and CR biosorption, indicating the interactions between MB and CR molecules and/or  $-\text{OH}$  and  $-\text{NH}$  groups of the biosorbent. The bands at 2924 and 2854  $\text{cm}^{-1}$  almost disappeared after the biosorption of the two dyes. The bands from 1700 to 1100  $\text{cm}^{-1}$  revealed a change in their form and intensities. The band at 1057  $\text{cm}^{-1}$  also lost its intensity and shifts to 1062  $\text{cm}^{-1}$  for the MB and CR loaded biomass.

The FTIR spectra revealed possible interactions between the two dyes and the hydroxyl, amino, carboxyl and phosphate groups present on the biosorbent surface.

*Effect of pH*

The pH is one of the important process parameters affecting the biosorption removal, because it determines the chemistry of the dye solution and the activity of the functional groups present on the surface of the biosorbents.<sup>32</sup> In general, as the pH of the solution increases, the removal of basic dyes is enhanced, while the removal of acidic dyes is reduced. At low pH values the surface of the biosorbent is positively charged (protonated functional groups) and opposes the biosorption of cationic species, but when the pH of the solution is increased, the biosorbent surface becomes negatively charged (deprotonation of functional groups) and the electrostatic interactions occurred between the oppositely charged sorbate and sorbent.

The obtained removal efficiencies for CR and MB as function of initial pH are presented in Fig. 1.

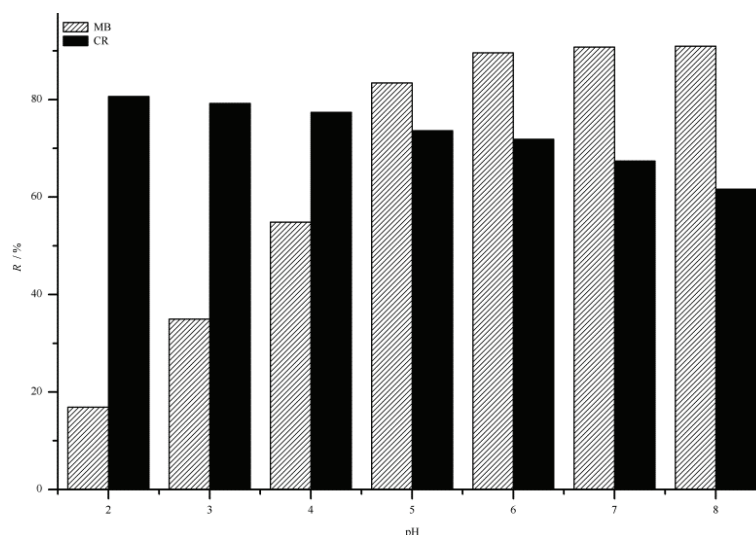


Fig. 1. Effect of pH on MB and CR removal efficiency onto waste pretreated *S. fradiae* biomass ( $c_0 = 50 \text{ mg dm}^{-3}$ ,  $W = 2 \text{ g dm}^{-3}$ ,  $V = 0.1 \text{ dm}^3$ ,  $T = 298 \text{ K}$ ,  $t = 120 \text{ min}$ ).

With the increasing of the initial pH of the solutions from 2.0 to 6.0 the removal efficiency of MB increased from 16.90 to 89.60 %. Further increasing in the pH did not affect the removal of this cationic dye. Similar results were obtained by other researchers.<sup>33,34</sup>

For CR, the removal efficiency decreased slowly with the increasing of the initial pH of the solution, from 80.66 % at pH 2.0 to 61.60 % at pH 8.0. The calculated uptakes were 20.16 and 15.04  $\text{mg g}^{-1}$ , respectively. The pH has a little effect on the CR biosorption by the pretreated *Streptomyces fradiae* biomass. This fact gives potential for practical use, because it is costly, difficult and environmentally hostile to decrease the pH of wastewaters to pH 2.0. Zhang *et al.*<sup>35</sup> studied the biosorption of CR onto living *Streptomyces sp* LH1 biomass, and observed the maximum removal of 97.5 % for 50  $\text{mg dm}^{-3}$  initial dye concentration at pH 2.0, on the other hand Bhattacharyya and Sharma<sup>36</sup> reported that the pH of the solution played minimal effect on the CR biosorption.

Considering the removal efficiencies and biosorption capacities, obtained in our study, all further biosorption experiments were carried out at initial pH 6.0.

#### *Effect of biosorbent dosage*

The effect of biosorbent dosage on the removal of MB and CR at the initial concentration of 50  $\text{mg dm}^{-3}$  is shown in Fig. 2.

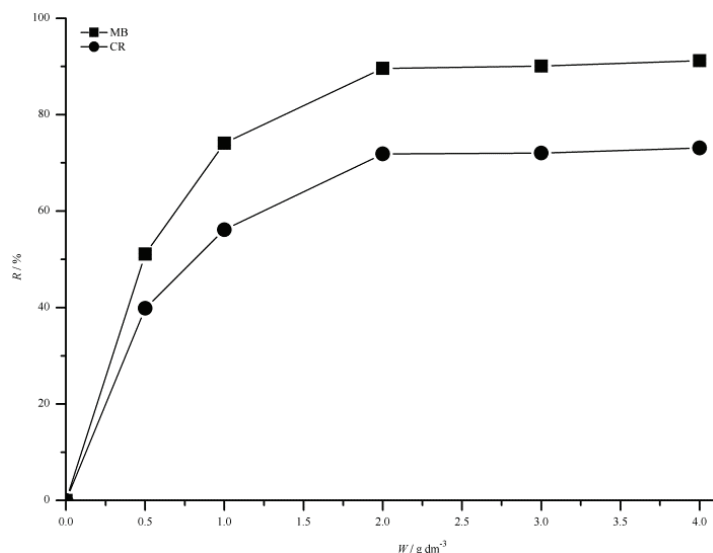


Fig. 2. Effect of biosorbent dosage on MB and CR removal efficiency onto waste *S. fradiae* biomass ( $c_0 = 50 \text{ mg dm}^{-3}$ , pH 6.0,  $V = 0.1 \text{ dm}^3$ ,  $T = 298 \text{ K}$ ,  $t = 120 \text{ min}$ ).

The removal efficiency increased from 51.08 to 91.20 % when the biosorbent concentration increased from 0.5 to  $4 \text{ g dm}^{-3}$  for MB and from 39.86 to 73.10 % for CR, respectively. Mane *et al.* explained this phenomenon with the greater surface area and the availability of more sites for biosorption.<sup>37</sup> However, the biosorption capacity decreased. This fact can be attributed to the overlapping or aggregation of biosorbent particles. All further experiments were conducted with  $2 \text{ g dm}^{-3}$  amount of biosorbent.

#### *Biosorption kinetics and effect of contact time*

The kinetic profiles of CR and MB biosorption onto waste pretreated waste biomass *Streptomyces fradiae* are shown in Fig. 3.

As it can be seen from Fig. 3, the uptake of the dyes was rapid in the first 40 min. This rapid phase was followed by a secondary slower phase until equilibrium was reached at 80 min for MB and 70 min for CR, respectively. The rapid phase could be explained with the availability of enough free active binding sites on the biosorbent surface, but during the second phase, the number of binding sites is limited and the effectiveness decreased. Further biosorption experiments were carried out for a contact time of 120 min.

The obtained kinetic data were analysed with pseudo-first<sup>38</sup> and pseudo-second<sup>39</sup> order kinetic models.

The parameters of pseudo-first-order and pseudo-second-order models were estimated with the aid of the non-linear regression. The obtained data and the correlation coefficients are presented in Table I.

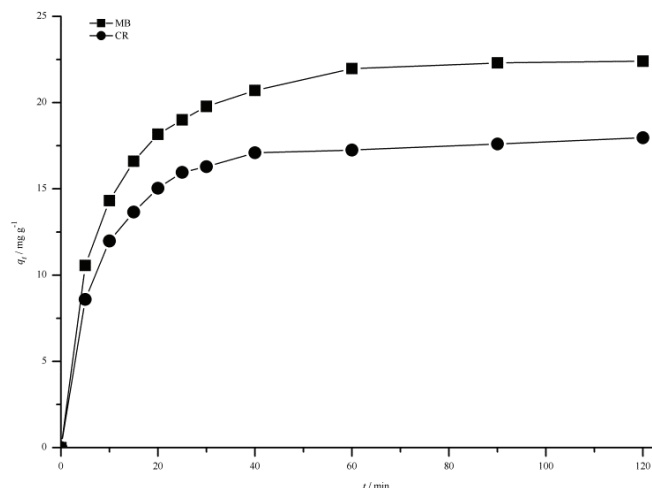


Fig. 3. Effect of contact time on MB and CR biosorption onto pretreated *S. fradiae* biomass ( $c_0 = 50 \text{ mg dm}^{-3}$ , pH 6.0,  $V = 0.1 \text{ dm}^3$ ,  $W = 2.0 \text{ g dm}^{-3}$ ,  $t = 120 \text{ min}$ ,  $T = 298 \text{ K}$ ).

TABLE I. Parameters of pseudo-first and pseudo-second-order kinetic models

Parameter	Dye	
	MB	CR
$q_e^{\text{exp}} / \text{mg g}^{-1}$	22.40	17.96
Pseudo-first-order kinetic model		
$q_e^{\text{cal}} / \text{mg g}^{-1}$	14.37	7.11
$k_1 \times 10^{-2} / \text{min}^{-1}$	5.62	4.09
$R^2$	0.9906	0.9086
Pseudo-second-order kinetic model		
$q_e^{\text{cal}} / \text{mg g}^{-1}$	24.04	18.96
$k_2 \times 10^{-2} / \text{g mg}^{-1} \text{ min}$	0.644	1.04
$R^2$	0.9996	0.9962

The obtained results indicated that the biosorption of MB and CR onto the pretreated waste biomass followed the pseudo-second order kinetic model. The correlation coefficients ( $R^2$ ) were close to 1. This value indicated a good correlation with the experimental data. The calculated equilibrium uptake,  $q_e^{\text{cal}}$ , was in good agreement with the experimental values,  $q_e^{\text{exp}}$ . The pseudo-second kinetic model has been one the most frequently used, and the grand advantage of this model is its accuracy in describing the whole range of the experimental kinetic data.<sup>40,41</sup>

#### *Effect of initial dye concentration and biosorption models*

The biosorption capacity of waste pretreated *Streptomyces fradiae* biomass for MB and CR was studied for different initial dye concentrations and the obtained data are shown in Fig. 4.



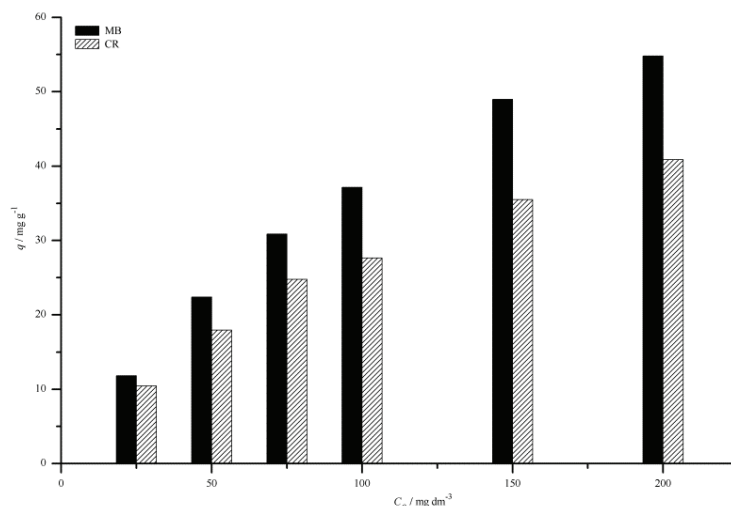


Fig. 4. Effect of initial concentration on biosorption of MB and CR onto waste pretreated *S. fradiae* biomass ( $W = 2 \text{ g dm}^{-3}$ ;  $V = 0.1 \text{ dm}^3$ ; pH 6.0;  $t = 120 \text{ min}$ ,  $T = 298 \text{ K}$ ).

The biosorption capacity increased with the rise of the initial dye concentration because of the high driving force for mass transfer. At higher concentrations, MB and CR, the removal efficiency decreased, due to the saturation of the binding sites on the biosorbent surface.

For the evaluating and the comparing of the biosorption capacities of MB and CR by the pretreated waste biomass of *S. fradiae*, Langmuir and Freundlich isotherm models were applied.<sup>42</sup>

The constant  $b$ , obtained from Langmuir equation, was used to determine the suitability of the biosorbent to sorbate by the Hall separation factor ( $R_L$ , dimensionless).<sup>43</sup>

$$R_L = \frac{1}{1 + bc_0} \quad (1)$$

where  $c_0$  is the highest initial sorbate concentration ( $\text{mg dm}^{-3}$ ). There are four probabilities for the  $R_L$  value: for favourable adsorption  $0 < R_L < 1$ ; for unfavourable adsorption  $R_L > 1$ ; for linear adsorption  $R_L = 1$  and for irreversible adsorption  $R_L = 0$ .

The Langmuir and Freundlich linear plots are shown in and Figs. 5 and 6.

The calculated adsorption isotherm constants for MB and CR and correlation coefficients are presented in Table II.

The biosorption of MB and CR on the waste pretreated *Streptomyces fradiae* biomass fitted well to both Langmuir and Freundlich isotherm models, the correlation coefficients ranged from 0.9647 to 0.9813. The homogeneous and heterogeneous distribution of the active sites on the surface of the studied biosorbent could



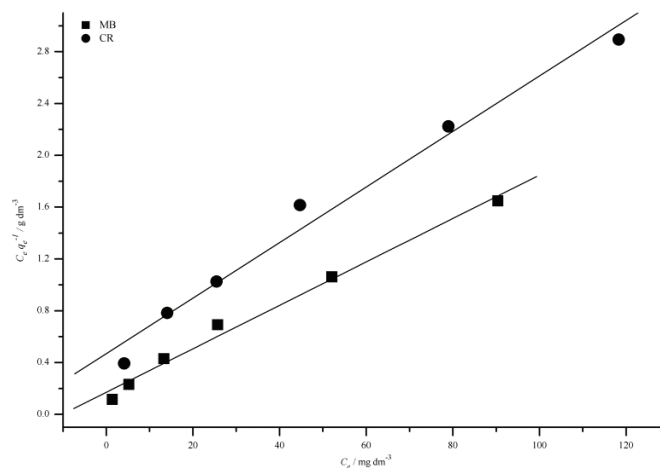


Fig. 5. Langmuir isotherm model for MB and CR.

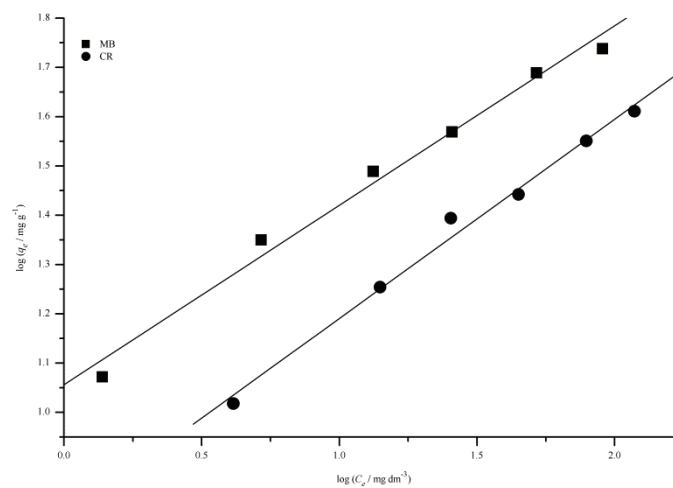


Fig. 6. Freundlich isotherm model for MB and CR.

TABLE II. Adsorption isotherm constants for MB and CR biosorption

Parameter	Dye	
	MB	CR
Langmuir isotherm		
$q_{max} / \text{mg g}^{-1}$	59.63	46.64
$b / \text{dm}^3 \text{mg}^{-1}$	0.098	0.046
$R^2$	0.9785	0.9647
Freundlich isotherm		
$n$	2.75	2.47
$K_F / \text{mg g}^{-1} \text{dm}^{3/n} \text{mg}^{-1/n}$	11.38	6.11
$R^2$	0.9746	0.9813

explain this result. The calculated  $R_L$  values were 0.048 and 0.098 for MB and CR.

Values of 2.75 and 2.47 were obtained for  $n$  with the Freundlich isotherm, for the biosorption of MB and CR, respectively. These values indicated that the adsorption process was favourable under the studied conditions.

#### *Effect of temperature and biosorption thermodynamics*

The effect of temperature on the removal efficiency of MB and CR was studied at three temperatures: 298, 303 and 313 K (Fig. 7).

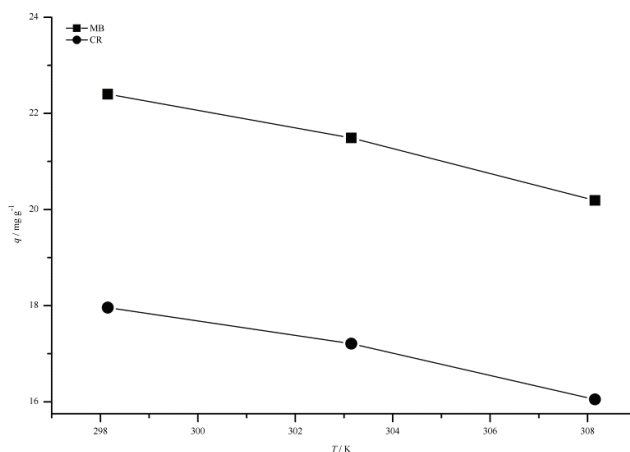


Fig. 7. Effect of temperature on MB and CR uptake.

The biosorption experiments were conducted with  $2 \text{ g dm}^{-3}$  of biosorbent,  $50 \text{ mg dm}^{-3}$  initial concentration of each dye, and initial pH 6.0. The removal efficiency for MB decreased from 89.60 to 80.76 %, and for CR from 71.86 to 64.20 % when the temperature increased from 298 to 313 K. The similar results were obtained by Nacèra and Aicha<sup>23</sup> for MB biosorption on waste *Streptomyces rimosus* biomass and by Acemioğlu *et al.*<sup>33</sup> for MB biosorption on *Aspergillus wentii*.

In order to describe the thermodynamic behaviour of the biosorption of MB and CR on waste pretreated *Streptomyces fradiae* biomass, the thermodynamic parameters were calculated:  $\Delta G$  – change in Gibbs energy,  $\text{J mol}^{-1}$ ;  $\Delta H$  – change in enthalpy,  $\text{J mol}^{-1}$ ;  $\Delta S$  – change in entropy,  $\text{J K}^{-1} \text{ mol}^{-1}$ ;  $K_d$  – the distribution coefficient, found from the ratio of the dye concentration adsorbed ( $c_{\text{ad,e}}$ ) to the dye concentration ( $c_e$ ) in the solution at equilibrium.<sup>43</sup>

The values of  $\Delta H$  and  $\Delta S$  were obtained from the slope and intercept of the plot of  $K_d$  versus  $T^{-1}$ . The obtained values of the thermodynamic parameters of MB and CR biosorption are given in Table III.

The negative values of Gibbs energy change in the temperature range 298–313 K showed the spontaneity of the MB and CR biosorption process. The dec-

rease in the values of  $\Delta G$  with the increase in temperature confirmed the diminishing of the spontaneity of the biosorption, so the process turned out unfavourable at higher temperatures. The negative values of the standard enthalpy were due to the exothermic nature of the biosorption of CR and MB. The negative  $\Delta S$  values suggested the decrease in randomness at the solid/liquid interface during biosorption.

TABLE III. Thermodynamic parameters calculated for MB and CR biosorption on waste pretreated *Streptomyces fradiae* biomass

Dye	$T / K$	$K_d$	$\Delta G / J \text{ mol}^{-1}$	$\Delta H / kJ \text{ mol}^{-1}$	$\Delta S / J K^{-1} \text{ mol}^{-1}$
MB	298	8.61	-5354.24	-35.04	-100.07
	303	6.13	-4637.15		
	313	4.19	-3723.05		
CR	298	2.55	-2320.17	-17.47	-50.94
	303	2.21	-1996.15		
	313	1.79	-1491.06		

The maximum biosorption capacities of dyes by various biosorbents vary as a function of experimental conditions – biosorbent dosage, initial dye concentration, pH, equilibrium time and temperature. The biosorption capacities obtained for CR and MB in this study were compared with the other microbial biosorbents.

Table IV outlines  $q_{\max}$  values (obtained from Langmuir isotherm model) for CR and MB biosorption.

TABLE IV. Comparison of biosorption capacities of waste pretreated *Streptomyces fradiae* biomass with other microbial biosorbents

Dye	Biosorbent	$q_{\max} / \text{mg g}^{-1}$	Experimental conditions	Ref.
MB	<i>S. rimosus</i>	34.34	pH natural; $V = 0.1 \text{ dm}^3$ ; $W = 25 \text{ g dm}^{-3}$ ; $C_0 = 10\text{--}150 \text{ mg dm}^{-3}$ ; 293 K	23
	<i>B. subtilis</i>	169.49	pH 6–8; $V = 0.1 \text{ dm}^3$ ; $W = 1 \text{ g dm}^{-3}$ ; 293 K; $t = 30 \text{ min}$	45
	<i>S. fradiae</i>	59.63	pH 6; $V = 0.1 \text{ dm}^3$ ; $W = 2 \text{ g dm}^{-3}$ ; $C_0 = 25\text{--}200 \text{ mg dm}^{-3}$ ; 298 K; $t = 2 \text{ h}$	This work
CR	<i>R. arrhizus</i>	49	pH natural; $V = 0.025 \text{ dm}^3$ ; $W = 1.5 \text{ g dm}^{-3}$ ; $C_0 = 25\text{--}1000 \text{ mg dm}^{-3}$ ; $t = 30 \text{ min}$	46
	<i>Dietzia</i> strain	170.34	pH 3; $V = 0.1 \text{ dm}^3$ ; $W = 5 \text{ g dm}^{-3}$ ; $C_0 = 10\text{--}100 \text{ mg dm}^{-3}$ ; 313 K; $t = 12 \text{ h}$	47
	<i>Streptomyces sp. LHI</i>	38.12	pH 5; $V = 0.1 \text{ dm}^3$ ; $W = 20 \text{ g dm}^{-3}$ ; $C_0 = 20\text{--}60 \text{ mg dm}^{-3}$ ; 298 K; $t = 24 \text{ h}$	35
	<i>S. fradiae</i>	46.64	pH 6; $V = 0.1 \text{ dm}^3$ ; $W = 2 \text{ g dm}^{-3}$ ; $C_0 = 25\text{--}200 \text{ mg dm}^{-3}$ ; 298 K; $t = 2 \text{ h}$	This work

Two biosorbents are showing higher maximum biosorption capacities for MB and CR sorption, but the species they are made from were specially cul-

tivated and then killed for the preparation of the biosorbents, which leads to the increase in process cost. It also has to be mentioned that the maximum biosorption capacity of CR was achieved at acidic pH, different temperature and different amount of sorbent and a contact time of 12 h. The waste pretreated *Streptomyces fradiae* biomass is competitive with other reported biomasses – byproducts of fermentation industries (*Streptomyces rimosus* and *Rhizopus arrhizus*).

#### CONCLUSIONS

Waste pretreated *Streptomyces fradiae* biomass, obtained from the tylosin production, can be used as an effective eco-friendly biosorbent for the cationic (MB) and the anionic (CR) dye removal from aqueous solutions. The pretreated biomass, and MB and CR loaded biomasses were characterized by FTIR spectroscopy and the possible role of hydroxyl, amino, carboxyl and phosphate groups presented on the biosorbent surface were revealed. By the set of experiments the optimum biosorption conditions were found: initial pH 6.0; contact time of 120 min; biosorbent dosage of  $2 \text{ g dm}^{-3}$ ; initial concentration range from 25 to  $200 \text{ mg dm}^{-3}$  and temperature of 298 K. The main advantage of the pretreated biosorbent is that the pH has an insignificant effect on the biosorption of the anionic dye. This gives a potential for practical use, because it is costly and difficult to decrease the pH of the wastewaters to acidic pH.

The equilibrium data for MB and CR biosorption fitted well into the Langmuir and Freundlich models. The pseudo-second order kinetic model describes the biosorption kinetic of the both dyes better. The thermodynamic studies showed that the biosorption of MB and CR was exothermic and spontaneous in nature.

The present study gives the important data about the utilization of waste pretreated *Streptomyces fradiae* biomass as the biosorbent for anionic and cationic dyes removal from aqueous solutions. The majority of biosorption studies use only one dye in batch systems. The dyes containing effluents are composed of more than one dye, and in addition the contaminants such as metal ions and surfactants are present.

Future studies will be directed to the regeneration of the biosorbent and the biosorption.

#### SUPPLEMENTARY MATERIAL

FTIR spectra of waste and biosorbents are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

## ИЗВОД

БИОСОРПЦИЈА КОНГО-ЦРВЕНОГ И МЕТИЛЕНСКО-ПЛАВОГ БИОМАСОМ  
ПРЕДТРЕТИРАНОГ ОТПАДА ОД *Streptomyces fradiae* – РАВНОТЕЖНА, КИНЕТИЧКА  
И ТЕРМОДИНАМИЧКА ИСПИТИВАЊА

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Коришћена је биомаса од предтретираног отпада *Streptomyces fradiae* као еколошки прихватљив сорбент боја конго-црвене (CR) и метиленско плаве (MP) за уклањање из водених раствора. Овај биосорбент је окарактерисан инфрацрвеном спектроскопијом са Фуријеовом (Fourier) трансформацијом. Шаржни експерименти су спроведени ради испитивања ефекта рН, дозирања биосорбента, почетне концентрације адсорбата, контактнoг времена и температуре на биосорпцију. Подаци о адсорпционој равнотежи су анализирани моделима Фројндлиха (Freundlich) и Ленгмира (Langmuir). Резултати су поређени са експерименталним подацима. Максимални биосорпциони капацитет овакве биомасе је био 46,64 mg g<sup>-1</sup> за CR и 59,63 mg g<sup>-1</sup> за MP, при рН 6,0 и време контакта 120 min, при дози биосорбента 2 g dm<sup>-3</sup> и температури 298 K. Кинетички подаци добијени из различитих шаржних експеримената су анализирани моделима Лажергрена (Lagergren) и Хоа (Ho). Боље слагање је добијено помоћу кинетичког модела псеудо-другог реда. Израчунате вредности за  $\Delta G$ ,  $\Delta S$  и  $\Delta H$  указују на то да је биосорпција CR и MP на предтретирану отпадну биомасу изводљива, спонтана и егзотермна у одабраном опсегу температура и услова.

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