

Original Research

COMPARATIVE KINETIC ANALYSIS OF CATIONIC DYES ADSORPTION ONTO  
SUSTAINABLE LIGNOCELLULOSIC BIOSORBENTS

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Jovana Perendija<sup>1,a\*</sup>, Verica Ljubić<sup>1,b</sup>, Dragana Milošević<sup>1,c</sup>, Slobodan Cvetković<sup>1,d</sup>,  
Mihal Đuriš<sup>1,e</sup>, Željka Milovanović<sup>1,f</sup>

<sup>1</sup> University of Belgrade, Institute of Chemistry, Technology and Metallurgy, National Institute of the  
Republic of Serbia, Njegoševa 12, 11001 Belgrade, SERBIA

<sup>a</sup> <https://orcid.org/0000-0002-6318-9053> <sup>b</sup> <https://orcid.org/0000-0002-8648-6421>

<sup>c</sup> <https://orcid.org/0000-0003-3548-6832> <sup>d</sup> <https://orcid.org/0000-0003-4417-4443>

<sup>e</sup> <https://orcid.org/0000-0002-1585-7707> <sup>f</sup> <https://orcid.org/0000-0002-1998-5239>

Abstract

*This study evaluates the biosorption performance of sorghum-, hemp-, and hop-based biosorbents for the removal of methylene blue (MB) and malachite green (MG) from aqueous solutions. A rapid initial uptake of both dyes was observed due to the abundance of available active binding sites, followed by a gradual decrease in adsorption rate until equilibrium was reached. Kinetic analysis revealed that the pseudo-second-order (PSO) model best describes the adsorption process for both MB and MG on all investigated biosorbents ( $R^2 = 0.999$ ), indicating that chemisorption is the dominant mechanism. The hemp-based biosorbent exhibited the highest rate constant  $k_2$  and the fastest equilibrium time for MB removal (180 min), while sorghum and hop reached equilibrium after 360 min. For MG removal, hemp and sorghum achieved equilibrium after 180 min, whereas hop required 360 min. The intra-particle diffusion (IPD) model indicated a multi-stage adsorption process, where both film diffusion and intra-particle diffusion contribute, with boundary layer effects playing an important role. Overall, the results demonstrate that the investigated biosorbents are effective for MB and MG removal, with hemp showing the most favorable kinetic performance.*

**Keywords:** biosorption, kinetic study, malachite green, methylene blue, waste biomass.

INTRODUCTION

Industrial activities and rapid population growth have significantly contributed to water pollution. Nowadays, substantial efforts are focused on controlling pollutant levels in water in order to mitigate their adverse effects on ecosystems, biodiversity, and, most importantly, human health [1]. Among various water contaminants, synthetic cationic dyes represent a serious environmental concern due to their ability to reduce light penetration and photosynthetic activity, thereby degrading aquatic ecosystems [2]. According to available reports, approximately 12% of the annual production of cationic dyes is discharged into industrial wastewater streams, contributing considerably to environmental pollution [3]. Widely used dyes such as malachite green and methylene blue may adversely affect reproductive and immune systems even at low exposure levels and have been reported to exhibit carcinogenic and mutagenic properties [4].

\* [j.nikolic@ihtm.bg.ac.rs](mailto:j.nikolic@ihtm.bg.ac.rs)

Among the numerous methods applied for the treatment of dye-contaminated wastewater, adsorption has emerged as one of the most effective and economically favourable approaches. In recent years, increasing attention has been directed toward the use of waste biomass materials as bio-based adsorbents due to their biodegradability, renewability, availability, and high adsorption efficiency [5]. The biomasses investigated in this work represents a widely available lignocellulosic material characterized by large number of different functional groups, a well-developed fibrous structure, and favourable surface properties that may enhance the removal of organic dyes from aqueous solutions. The sorghum, hemp, and hop biomasses used in this study contain cellulose, hemicellulose, and lignin, whose functional groups enable interactions with dye molecules through electrostatic interactions, hydrogen bonding,  $\pi$ - $\pi$  interactions, etc.

Biosorption kinetics were investigated as an important aspect of understanding the mechanisms governing dye removal, with the aim of determining the biosorption rate and identifying the potential rate-controlling steps of the process. Therefore, the objective of this study was to evaluate and compare the biosorption kinetic parameters of malachite green and methylene blue onto biosorbents derived from sorghum, hemp, and hop in a batch system, as well as to assess differences in the efficiency of cationic dye removal from aqueous solutions.

## **MATERIALS AND METHODS**

### **Material**

#### ***Preparation of Biosorbent***

The waste biomasses used in this study were obtained from the Institute of Field and Vegetable Crops, Backi Petrovac, Serbia. Waste stems of sorghum, hemp, and hop were chopped and washed with deionized water, air-dried under ambient conditions, and subsequently oven-dry at 65 °C for 24 h. The dried biomasses were ground into fine particles and sieved using a laboratory sieve. The biomass fraction with a particle size smaller than 0.519 mm was used in all biosorption experiments.

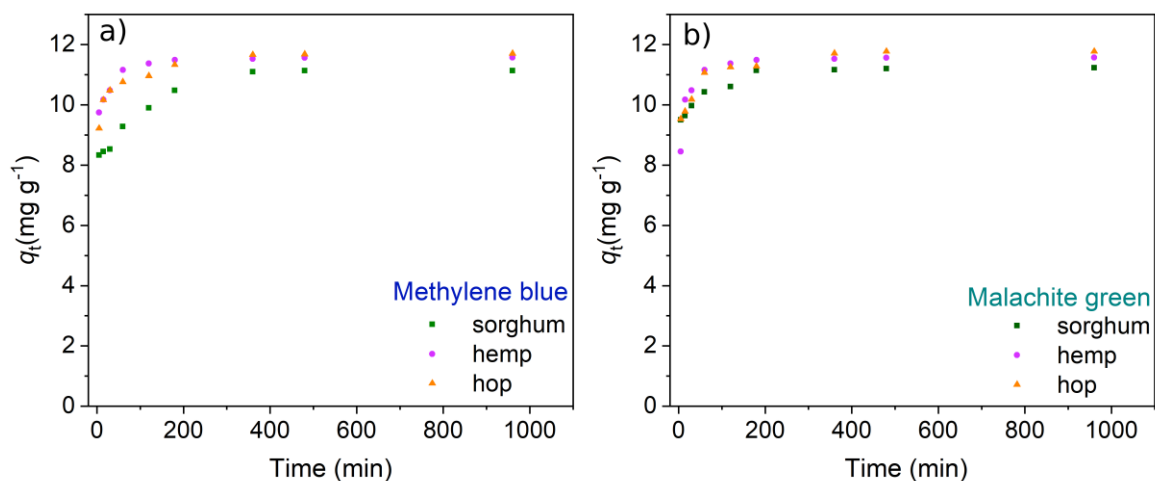
#### **Biosorption experiments**

Batch biosorption experiments were conducted to evaluate the performance of sorghum-, hemp-, and hop-based biosorbents for the removal of methylene blue (MB) and malachite green (MG) and from aqueous solutions. The experiments were carried out in 50 mL Erlenmeyer flasks by mixing the biosorbents with aqueous dye solutions containing MB or MG. The kinetic study was performed to investigate the effect of contact time on the biosorption capacity under the following conditions: contact time ranging from 5-960 min, biosorbent dose of 2.5 g L<sup>-1</sup>, initial dye concentration of 30 mg L<sup>-1</sup>, pH of 6.5, and temperature of 25 °C. After biosorption, the samples were filtered through a 0.22  $\mu$ m nylon syringe filter, and the residual dye concentrations were determined using a UV-Vis spectrophotometer (Lambda 25/35/45, PerkinElmer). The biosorption capacity ( $q_e$ ) (mg g<sup>-1</sup>), as well as the parameters of the pseudo-first-order (PFO), pseudo-second-order (PSO), and intra-particle diffusion (IPD) models were calculated according to the equations reported by Perendija *et al.* [6].

## RESULTS AND DISCUSSION

In this study, the effect of contact time on the biosorption of methylene blue (MB) and malachite green (MG) onto sorghum-, hemp-, and hop-based biosorbents was investigated in detail. In the initial stage of biosorption (5–30 min), a rapid uptake of both dyes was observed due to the abundance of available active binding sites on the biosorbent surfaces. This creates a strong driving force for mass transfer and enables rapid diffusion of dye molecules from the solution to the biosorbent surface. As contact time increases, the biosorption rate gradually decreases as these active sites become progressively occupied by MB and MG molecules, leading to a reduction in available binding capacity.

For MB biosorption (Figure 1a)), equilibrium was reached after 360 min using sorghum and hop, while hemp achieved equilibrium more rapidly, after 180 min. Beyond these time points, no significant changes in adsorption capacity were observed, confirming that equilibrium conditions had been established. These results suggest that the hemp-based biosorbent exhibits the fastest adsorption kinetics and the shortest time required to reach equilibrium for MB removal. In the case of MG biosorption (Figure 1b)), equilibrium was reached after 180 min using sorghum and hemp, whereas hop required 360 min to reach equilibrium, reflecting slower adsorption kinetics compared to the other two biosorbents. The adsorption capacity values obtained for both dyes using all three materials were very similar, with hop showing the highest adsorption capacity. Overall, these results indicate that all three biosorbents are comparably effective for dye removal under the applied conditions, differing primarily in the rate of equilibrium attainment.



**Figure 1** Effect of contact time on the biosorption of a) MB; b) MG onto sorghum, hemp, and hop

Kinetic PFO, PSO, and IPD models, were applied to describe the adsorption rate and process mechanism. According to results presented in Table 1 and Table 2, the PSO model provided the best fit for both MB and MG adsorption onto all investigated biosorbents, as evidenced by very high correlation coefficients ( $R^2 = 0.999$ ) and close agreement between experimental and calculated  $q_e$  values. This demonstrates that chemisorption is the dominant mechanism controlling the biosorption process. The hemp-based biosorbent exhibited the highest pseudo-second-order rate constant ( $k_2$ ) for MB removal, reflecting the fastest adsorption kinetics and the shortest equilibrium time among the investigated materials.

**Table 1** Kinetic parameters obtained by linear regression analyses of PFO, PSO, and IPD kinetic models applied to the experimental data for biosorption of MB onto sorghum, hemp, and hop biosorbents

| Model parameters                                      | Sorghum               | Hemp                  | Hop                    |
|-------------------------------------------------------|-----------------------|-----------------------|------------------------|
| <b>Experimental</b>                                   |                       |                       |                        |
| $q_{e, \text{exp}} (\text{mg g}^{-1})$                | 11.1                  | 11.6                  | 11.7                   |
| <b>PFO</b>                                            |                       |                       |                        |
| $q_{e, \text{cal}} (\text{mg g}^{-1})$                | 3.91                  | 1.13                  | 1.99                   |
| $k_1 (\text{min}^{-1})$                               | $1.26 \times 10^{-2}$ | $1.02 \times 10^{-2}$ | $0.995 \times 10^{-2}$ |
| $R^2$                                                 | 0.957                 | 0.918                 | 0.982                  |
| <b>PSO</b>                                            |                       |                       |                        |
| $q_{e, \text{cal}} (\text{mg g}^{-1})$                | 11.2                  | 11.6                  | 11.7                   |
| $k_2 (\text{g mg}^{-1} \text{min}^{-1})$              | $1.02 \times 10^{-2}$ | $4.15 \times 10^{-2}$ | $1.98 \times 10^{-2}$  |
| $R^2$                                                 | 0.999                 | 0.999                 | 0.999                  |
| <b>IPD</b>                                            |                       |                       |                        |
| <b>I stage</b>                                        |                       |                       |                        |
| $k_{\text{dif}} (\text{mg g}^{-1} \text{min}^{-0.5})$ | 0.191                 | 0.193                 | 0.179                  |
| $C_1$                                                 | 7.74                  | 9.42                  | 9.23                   |
| $R^2$                                                 | 0.925                 | 0.929                 | 0.735                  |
| <b>II stage</b>                                       |                       |                       |                        |
| $k_{\text{dif}} (\text{mg g}^{-1} \text{min}^{-0.5})$ | 0.032                 | 0.004                 | 0.018                  |
| $C_2$                                                 | 10.3                  | 11.4                  | 11.2                   |
| $R^2$                                                 | 0.317                 | 0.742                 | 0.405                  |

**Table 2** Kinetic parameters obtained by linear regression analyses of PFO, PSO, and IPD kinetic models applied to the experimental data for biosorption of MG onto sorghum, hemp, and hop biosorbents

| Model parameters                                       | Sorghum               | Hemp                  | Hop                   |
|--------------------------------------------------------|-----------------------|-----------------------|-----------------------|
| <b>Experimental</b>                                    |                       |                       |                       |
| $q_{e, \text{exp}} (\text{mg g}^{-1})$                 | 11.2                  | 11.6                  | 11.8                  |
| <b>PFO</b>                                             |                       |                       |                       |
| $q_{e, \text{cal}} (\text{mg g}^{-1})$                 | 1.42                  | 1.28                  | 1.99                  |
| $k_1 (\text{min}^{-1})$                                | $8.66 \times 10^{-3}$ | $10.6 \times 10^{-3}$ | $9.63 \times 10^{-3}$ |
| $R^2$                                                  | 0.887                 | 0.891                 | 0.946                 |
| <b>PSO</b>                                             |                       |                       |                       |
| $q_{e, \text{cal}} (\text{mg g}^{-1})$                 | 11.3                  | 11.6                  | 11.8                  |
| $k_2 (\text{g mg}^{-1} \text{min}^{-1})$               | $2.49 \times 10^{-2}$ | $3.84 \times 10^{-2}$ | $1.98 \times 10^{-2}$ |
| $R^2$                                                  | 0.999                 | 0.999                 | 0.999                 |
| <b>IPD</b>                                             |                       |                       |                       |
| <b>I stage</b>                                         |                       |                       |                       |
| $k_{\text{dif1}} (\text{mg g}^{-1} \text{min}^{-0.5})$ | 0.137                 | 0.299                 | 0.217                 |
| $C_1$                                                  | 9.20                  | 8.51                  | 9.05                  |
| $R^2$                                                  | 0.931                 | 0.707                 | 0.908                 |
| <b>II stage</b>                                        |                       |                       |                       |
| $k_{\text{dif2}} (\text{mg g}^{-1} \text{min}^{-0.5})$ | 0.005                 | 0.004                 | 0.025                 |
| $C_2$                                                  | 11.1                  | 11.3                  | 11.1                  |
| $R^2$                                                  | 0.901                 | 0.741                 | 0.389                 |

A similar trend was observed for MG adsorption, where hemp also showed the highest  $k_2$  value, while sorghum displayed slightly slower kinetics. Nevertheless, both biosorbents reached equilibrium within the same time interval. In contrast to PSO, the PFO model showed a poorer fit, as reflected by lower correlation coefficients and significant deviations between experimental and calculated  $q_e$  values, suggesting that physisorption alone does not

adequately describe the systems. The results obtained from the IPD model revealed multi-linear plots with positive intercepts, confirming that intra-particle diffusion is not the sole rate-controlling step in the biosorption processes. The positive intercepts further indicate the contribution of boundary layer (film) diffusion, particularly during the initial stages of biosorption. Although intra-particle diffusion may contribute to the internal transport of dye molecules within the biosorbent particles, the results suggest that its contribution is secondary and does not govern the overall biosorption rate. This is further supported by the significant decrease in the correlation coefficient in the second stage of the IPD plots (MB removal by all biosorbents and MG removal by hop), showing that the model does not adequately describe this stage of the process. Overall, the biosorption process appears to be primarily governed by chemisorption and surface adsorption, while film diffusion and intra-particle diffusion act as supporting mechanisms for all biosorbents used for MB and MG removal.

## CONCLUSION

The investigated sorghum-, hemp-, and hop-based biosorbents showed similar potential for the removal of MB and MG from aqueous solutions. Biosorption was characterized by rapid initial uptake followed by a slower approach to equilibrium, with hemp exhibiting the fastest kinetics and the shortest equilibrium times. Kinetic modeling showed consistent trends for all three biosorbents, with the pseudo-second-order model providing the best fit for both dyes, indicating that chemisorption is the dominant mechanism. In contrast, the pseudo-first-order model showed a poorer fit to the experimental data. The intra-particle diffusion model suggested that biosorption proceeds through multiple stages and is not governed solely by intraparticle diffusion. Positive intercepts indicated the contribution of boundary layer diffusion, particularly at the early stages of biosorption. Overall, the process is controlled by a combination of surface biosorption and diffusion mechanisms.

## ACKNOWLEDGEMENT

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