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ADSORPTION OF AN ORGANIC POLLUTANT ONTO BIOCHAR DERIVED FROM SOUR CHERRY STONE

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Abstract: *In the last decade, the expansion of industrial and agricultural activities has led to the significant rise of organic pollutants, contributing to serious environmental contamination. Biochar has received considerable attention as a low-cost and environmentally friendly adsorbent for a wide range of pollutants. In this paper, waste sour cherry stones, originating from the local fruit industry, were used as a raw material for biochar production via slow pyrolysis. The obtained biochar was characterized by SEM-EDX analysis, which revealed a porous and irregular surface morphology. The adsorption of the cationic dye Malachite green (MG) onto biochar was investigated in stirred batch system at pH 6, 25 ℃, adsorbent dosage of 2 g/L, initial dye concentration of 15-400 mg/L for 24 h. To assess the adsorption capacity of biochar for MG, the experimental data were analyzed by non-linear fitting of the Langmuir, Freundlich, and Sips adsorption isotherm models. The maximum adsorption capacity of 116.33 mg/g was obtained by Sips model, indicating combined adsorption on heterogeneous surfaces. The utilization of waste sour cherry stones for biochar production offers an effective approach for reducing waste disposal problems and producing a novel and sustainable adsorbent with promising potential for removal of organic pollutants from aqueous solutions.*

Keywords: *lignocellulosic waste, pyrolysis, dye removal, isotherms*

1. INTRODUCTION

Global population growth, urbanization, industrial expansion, and evolving lifestyles have contributed to the growing release of potentially polluting substances into the environment, placing considerable strain on water resources. Worldwide assessments indicate that water pollution is a critical environmental challenge, with repercussions felt globally, posing severe threats to human health, food security, and ecosystem functioning [1]. Of particular concern are organic pollutants, whose persistent nature allows them to remain in water systems for extended periods. These pollutants include a wide range of compounds such as pharmaceuticals, dyes, pesticides, and industrial chemicals, as well as hazardous organic substances that may originate from the chemical industry and military activities. Due to their toxicity, persistence, semi-volatile nature, and resistance to natural biodegradation, these compounds pose significant risks to both ecosystems and human health [2,3]. Furthermore, the persistence of organic pollutants can lead to their bioaccumulation and biomagnification through food chains [4].

Among these contaminants, organic dyes constitute a significant class of pollutants due to their widespread industrial use and direct release into aquatic systems. In particular, Malachite Green (MG) has been extensively studied as a model dye, owing to its high toxicity, chemical stability, complex structure and resistance to conventional degradation processes. This dye is widely used in the textile industry, as a therapeutic agent in aquaculture, and for food-related applications [5]. Prolonged exposure to this dye has been associated with potential carcinogenic and mutagenic effects [6]. In order to effectively remove MG from contaminated water, various treatment technologies have been developed, among which adsorption has been widely recognized as one of the most effective methods due to its cost-effectiveness, simplicity, and operational flexibility [2,6].

In recent decades, various materials have been investigated as adsorbents for organic pollutants, while

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biochar has emerged as a promising material for environmental applications. Biochar is a stable carbon-rich material produced through the pyrolysis of biomass under oxygen-limited conditions, which is widely recognized for its low cost, abundant feedstock availability, and versatile applications in environmental remediation [7,8]. Due to the highly porous structure, large specific surface area, and diverse surface functional groups (hydroxyl, phenolic and carboxyl groups), biochar exhibits excellent adsorption capacity toward various organic and inorganic contaminants [5,8].

Despite these advances, there is a growing need to develop feedstock-specific biochars that align with the principles of green chemistry and circular economy, transforming local agricultural by-products into high-value environmental solutions. In the present study, biochar produced from fruit waste industry was evaluated as a low-cost and sustainable adsorbent for the removal of MG from aqueous solutions and represents a basis for further investigations aimed at developing cost-effective and efficient adsorbents for organic pollutant removal. The results provide a basis for further research on the application of the obtained biochar for the removal of other organic pollutants, such as fuel residues and pesticides, from water contaminated by military activities.

2. MATERIALS AND METHODS

Sour cherry stones (*Prunus cerasus L.*) were obtained from the local fruit processing company "Fruvita", where they are generated as a waste by-product. The collected stones were separated from fruit residues, thoroughly washed with tap water, and dried at room temperature prior to further processing. The dried material was subsequently pyrolysed to produce biochar. Pyrolysis was carried out in a Nabertherm 1300 muffle furnace (Nabertherm, Germany) at 500 °C for 90 minutes under an argon atmosphere. After cooling, the produced biochar was ground and sieved to obtain a particle size fraction between 0.1 and 0.5 mm.

The yield of produced biochar is calculated according to the following Equation (1):

$$Yield(\%) = \frac{mass\ of\ pyrolised\ sampel\ (g)}{mass\ of\ raw\ sampel\ (g)}\ x\ 100 \qquad (1)$$

Produced biochar was characterised by using the SEM-EDX analysis by JEOL JSM-6610 LV SEM (JEOL Ltd., Japan). Prior to analysis, the samples were coated with a thin layer of gold. EDX measurements were conducted at an accelerating voltage of 20 kV, a probe current of approximately 13 nA, a working distance of 10 mm, a magnification of 500×, and an acquisition live time of 100 s. The elemental composition obtained by EDX analysis was expressed as weight percentages (wt. %).

Malachite green, also known as Basic Green 4 was supplied by Sigma-Aldrich, (USA) and used as received without further purification. A stock solution (1000 mg/L) was prepared by accurately dissolving the required amount of dye in distilled water, and working solutions of different concentrations were subsequently obtained by serial dilution of this stock solution.

The adsorption isotherms were performed in batch mode at 25 °C. Briefly, 0.1 g of biochar was added to 50 mL of MG solutions with initial concentrations ranging from 15 to 400 mg/L. The systems were equilibrated for 24 h, after which the residual dye concentration was determined spectrophotometrically by measuring the absorbance by UV/VIS spectrophotometer (Spekol 1300, Analytik Jena, Germany) at 614 nm. The adsorption capacity q (g/mg) was calculated using Equation (2):

$$q_e = \frac{V\ x\ (C_i - C_f)}{m} \qquad (2)$$

where C_i and C_f are the equilibrium and initial concentrations of dye (mg/L), respectively, V is the volume of dye solution (L) and m is the amount of the sorbent (g).

The equilibrium data were analyzed using Langmuir, Freundlich, and Sips isotherm models, which are described in detail in our previous study [7]. The best fitting model was determined by the highest correlation coefficients (R^2) and the lowest chi-squared value (χ^2).

3. RESULTS AND DISCUSSION

Schematic illustration of the adsorbent preparation and adsorption experiment is provided in Figure 1.

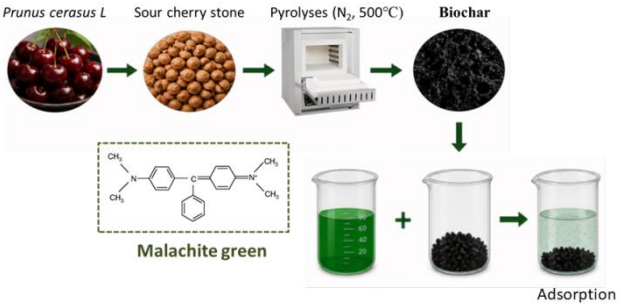


Figure 1. Schematic diagram of the experiment

The obtained biochar yield was 26.73%, which is typical for biochar produced from fruit stones [9,10].

To investigate the surface morphology and elemental composition of the biochar, SEM–EDX analysis was performed and presented in Figure 2. The biochar exhibited irregular and heterogeneous morphology with visible pores of different sizes and shapes. The observed porous features may be associated with the thermal decomposition of lignocellulosic components, including cellulose and hemicellulose, during pyrolysis. The decomposition of these components is accompanied by the release of volatile compounds, which may contribute to the formation of voids and channels within the carbon matrix [11]. The EDX analysis indicated that carbon was the dominant element in the biochar (81.37%), followed by oxygen (18.44%). These results are in agreement with the study by Lopičić et al., [12] who investigated the SEM–EDX characteristics of biochar derived from plum stones.

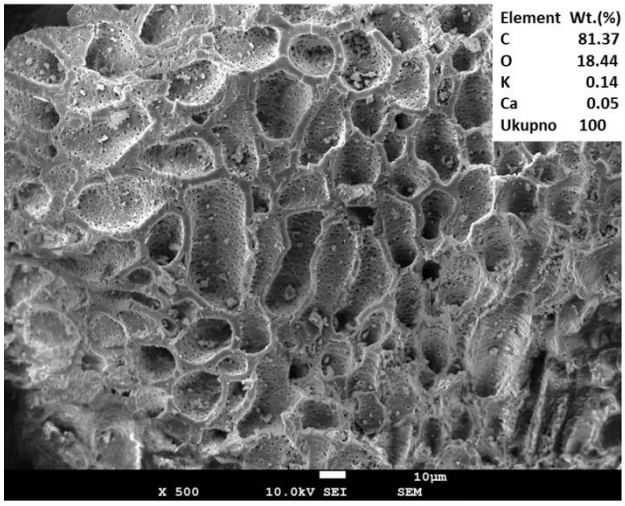


Figure 2. SEM-EDX micrographs of the biochar from Sour cherry stone

To elucidate the nature of the interaction between MG and biochar, adsorption isotherm analysis was performed. The experimental data were fitted using the Langmuir, Freundlich, and Sips isotherm models and presented in Figure 3, while the corresponding parameters are listed in Table 1.

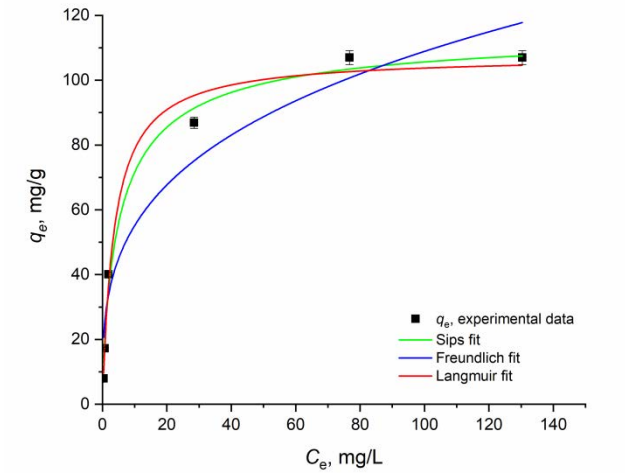


Figure 3. Isotherm model fitting of MG adsorption on biochar

The suitability of the applied isotherm models for describing MG adsorption was evaluated using the correlation coefficient (R^2) and chi-square (χ^2) values as statistical criteria. According to the data presented in Table 1, the Sips model provided the best fit for MG adsorption onto biochar. The Sips model exhibited the highest R^2 value (0.991) and the lowest χ^2 value (2.657), indicating that MG adsorption onto biochar occurs on heterogeneous surface sites with varying energies. The Sips heterogeneity parameter s was 0.791, which confirms a heterogeneous adsorption surface with non-uniform binding energies. The maximum predicted adsorption capacity obtained from the Sips model was 116.332 mg/g. Das et al., [5] reported the similar adsorption capacity of 120.50 mg/g for MG removal by NaOH-activated biochar derived from agricultural waste. Considering that the biochar used in this study was not activated, the obtained results highlighting the potential of the biochar derived from waste sour cherry stones for further optimization and application in the removal of organic pollutants from aqueous solutions. Future studies should evaluate the applicability of the biochar in real water matrices, where competing dissolved components may affect the adsorption process. The desorption of the adsorbed dye, together with the regeneration and reuse of the biochar, should also be evaluated to determine the potential for repeated application and the economic feasibility of the adsorption process. In addition, the obtained biochar may be further investigated as a low-cost adsorbent for the treatment of contaminated water resulting from military activities, particularly where locally available waste-derived materials may be advantageous.

Table 1. Isotherm parameters for the adsorption of MG onto biochar

Isotherm model	Parameter	Value
Langmuir	q_e, mg/g	107.551
	K_L	0.273
	R^2	0.985
	$\chi 2$	7.374
Freundlich	K_F	27.904
	n	0.296
	R^2	0.931
	χ^2	9.696
Sips	q_e, mg/g	116.33
	K_S	0.259
	s	0.791
	R^2	0.991
	χ^2	2.657

4. CONCLUSION

This study demonstrates that biochar derived from agro-industrial waste can be used as an efficient, low-cost, and sustainable adsorbent for the removal of organic pollutants from aqueous systems, such as MG. Conversion of fruit industry waste into a functional adsorbent not only provides an effective approach for wastewater treatment, but also contributes to waste valorization and the reduction of environmental burdens in accordance with the principles of the circular economy.

Among the investigated isotherm models, the Sips model showed the best agreement with the experimental data, indicating heterogeneous adsorption behavior, with a maximum adsorption capacity of 116.33 mg/g. The high adsorption capacity may be associated with the porous morphology observed by SEM, which may facilitate the uptake of relatively large dye molecules. These findings provide a basis for future studies focused on the optimization, potential surface modification, and application of biochar derived from sour cherry stones for the removal of organic pollutants from aqueous solutions.

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