Exploring the potential of hemp seed shells as dye removal from waters to a sustainable economy

E. Muñiz, P. Diaz, L. Taboada-Ruiz, M. Díaz-Somoano, B. Ruiz

Department of Sustainable Chemical Processes, Instituto de Ciencia y Tecnología del Carbono (INCAR), CSIC, Oviedo, Spain
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Corresponding author email: mercedes@incar.csic.es
Presenting author email: l.taboada@incar.csic.es

Introduction

Recent years have witnessed a considerable surge in the cultivation of hemp, largely attributable to its incorporation into numerous industrial sectors (Ahmed et al., 2022). The products of greatest interest are hemp seeds and fibre. The growing demand for these products creates a significant opportunity. However, in order to guarantee the sustainability of this type of activity, it is necessary to look for solutions that allow the use and revaluation of the waste generated. In this context, a promising approach involves the recovery of lignocellulosic waste as adsorbents for the removal of pollutants from water (Moscariello et al., 2021). The objective of this work is the characterization of the residues generated during the extraction of hemp oil and its evaluation as biosorbents in water treatment processes. In order to achieve this objective, hemp seed shells (HSS) are selected as biosorbents for the removal of a toxic dye from waters: malachite green (MG) (Lellis et al., 2019). Subsequently, the selected waste will be subjected to a mild alkaline chemical treatment, called mercerization, in order to increase the adsorption capacity of the material (Luchese et al., 2024; Prem Kumar et al., 2022).

Materials and Methods

Hemp wastes were supplied by an agro-food industry in northern Spain (Asturias). Mercerized biosorbents, i.e. chemically treated hemp seed shells (HSS-MER), were prepared by soaking the biomass into a 5 % NaOH solution (50 g hemp/l) for an hour at room temperature. Then they were neutralized with HCl 0.2 M and washed with distilled water several times. Finally, they were oven-dried (100 ºC, 12 h). Hemp seed shells washed with distilled water (HSS-WW) were used as reference material. Then, they were oven-dried (100 ºC, 12 h).

Adsorption experiments were performed in batch by changing the different reaction parameters in order the select the optimal reaction conditions: pH (2-8), initial dye concentration (C): 5-100 mg/l, dosage of biosorbent (D): 0.5-2 g/l, contact time (t): 5 min-24 h, and temperature (T): 293-333 K. Following the completion of this first stage, desorption experiments and reusability of the biosorbents were studied. To do so, saturated biosorbents were treated with several eluents: distilled water, sodium hydroxide (0.1 M), hydrochloric acid (0.1 M), acetic acid (0.1 M) and potassium chloride (0.1 M). A total of 3 cycles were done and biosorbents were washed until neutral pH and dried between cycles to remove any residual eluent.

To determine the concentration of dye in the liquid phase, UV-Vis spectroscopy at the maximum wavelength of the dye, previously obtained, was used (618 nm). To calculate the biomass retention capacity (q, (mg/g) and efficiency (E, %), Eq. 1 and 2 were used. To calculate the regeneration efficiency (E_R, %), Eq. 3 was applied.

$$q\ [mg/g] = \frac{C_0 - C_f}{m} \times V \qquad \text{Eq. 1}$$

$$E\ [\%] = \frac{C_0 - C_f}{C_0} \times 100 \qquad \text{Eq. 2}$$

$$E_R\ [\%] = \frac{quantity\ of\ dye\ desorbed\ (mg)}{quantity\ of\ dye\ initially\ sorbed\ (mg)} \times 100 \qquad \text{Eq. 3}$$

All experiments were carried out by triplicate to ensure the reproducibility of the results.

Results and Discussion

The experimental findings from the preliminary biosorption tests (Table 1) demonstrate that HSS-MER exhibits a higher adsorption capacity in comparison to the reference material. This observation suggests that the mercerization process has induced a modification in the material's chemical structure. When reaction conditions are modified and optimized (Table 1), it is possible to achieve more than 80% removal of MG with HSS-WW and almost 100% removal with HSS-MER. This indicates that hemp wastes can be successfully employed as dye sorbents.

Table 1. Retention capacities and efficiencies of biosorbents in preliminary experiments and after optimization of reaction conditions.

Sample	Reaction conditions	q (mg/g)	E (%)
HSS-WW	pH:6, C_{MG}: 10 mg/l, D: 1 g/l, t:1 h, T: 293 K	6.21	62.9
HSS-MER	pH:6, C_{MG}: 10 mg/l, D: 1 g/l, t:1 h, T: 293 K	9.21	93.9
HSS-WW*	pH: 6, C_{MG}: 25 mg/l, D: 1 g/l, t: 24 h, T: 333 K	20.8	83.3
HSS-MER*	pH: 6, C_{MG}: 50 mg/l, D: 1 g/l, t: 24 h, T: 333 K	49.1	98.6

*Experiments after optimization of reaction conditions.

Kinetic studies indicate that adsorption on MG dye is followed by a pseudo-second order (PSO) kinetic model in both materials. HSS-WW follows Langmuir model and HSS-MER, Freundlich isotherm model.

Desorption tests show that regeneration could be possible in an acidic environment, by utilizing acetic acid as eluent (Figure 1). A recovery efficiency (E_R) of almost 35 % is possible and retention capacities at second and third cycles are up to 20 %. Whilst the retention capacities demonstrated in these regeneration studies are not particularly elevated, it is imperative to acknowledge that the reversibility of the process is not a pivotal consideration when utilizing such a cost-effective material.

Figure 1. Elution liquid obtained after desorbing experiments (cycle 1) with HSS-MER in H_2O, NaOH (0.1 M), HCl (0.1 M), KCl (0.1 M) and AcOH (0.1 M).

Conclusions

The findings of this study illustrate the potential benefits of hemp seed shells in the elimination of MG within water systems. Following the alkaline treatment, HSS-MER exhibited a greater number of oxygenated groups, associated with the presence of cellulose, which enhanced the biosorption capacity of the material. As it was shown, a simple and soft chemical treatment can convert a residue into a sustainable and cheap adsorbent for water treatment.

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