chemistry proceedings

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Proceeding Paper

The Preparation of the Natural Plant "Casuarina Equisetifolia" as a Biosorbent for "Bemacid Red" Dye Removal †

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† Presented at The 28th International Electronic Conference on Synthetic Organic Chemistry (ECSOC 2024), 15–30 November 2024; Available online: https://sciforum.net/event/ecsoc-28.

Abstract: This study evaluates the ultrasound-assisted biosorption of Bemacid Red dye (BR) from aqueous solutions using Casuarina Equisetifolia needles (CEP), an eco-friendly and cost-effective biosorbent. Characterization techniques, including FTIR, SEM, XRD, TGA, and pHpzc, were used. Key parameters like contact time, dye concentration, dosage, pH, and temperature were optimized. Kinetic studies followed the pseudo-second-order model, while biosorption data fit the Sips isotherm. The process was exothermic, with $\Delta H = -18.3$ kJ/mol, confirming physical adsorption. CEP demonstrates the potential for practical dye removal and environmental purification applications.

Keywords: anionic dyes; biosorbent; biosorption; ultrasound

Citation: Feddane, S.; Oukebdane, K. The Preparation of the Natural Plant "Casuarina Equisetifolia" as a Biosorbent for "Bemacid Red" Dye Removal. *Chem. Proc.* **2024**, *6*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Name

Published: 15 November 2024

1. Introduction

Industrial activities, particularly in the textile sector, contribute significantly to water pollution by introducing harmful dyes into aquatic environments. These pollutants can be nonionic, cationic, or anionic dyes, and often evade removal through conventional water treatment methods, leading to heightened toxicity and environmental hazards. Dyes are widely used in food, textiles, and biological applications [1–3]. They are toxic and extremely difficult to decompose, as they are a combination of aromatic rings and auxochrome fragments [(-NH2) groups and phenol hydroxyl groups] with chromophores such as nitro (-NO2), azo (-N=N-),nitroso (-N=O), and ketone groups (-C=O). Their per-sistence in water and potential toxicological effects upon ingestion, inhalation, or skin contact necessitates the development of advanced removal techniques [4–6].

Various chemical, physical, and biological methods, including ozonation, photocatalysis, and microbial degradation, have been investigated for dye removal. However, these methods often suffer from limitations such as the formation of harmful by-products or low efficiency in treating large volumes of wastewater. Biosorption has emerged as a preferred technique due to its simplicity, efficiency, and low cost-effectiveness [7–10]. Moreover, it has been shown that combining biosorption with ultrasound significantly improves efficiency while lowering costs. Ultrasonic irradiation, through acoustic cavitation, accelerates chemical reactions and mass transfer, further enhancing the biosorption process by reducing pollutant concentration [11].

Casuarina Equisetifolia (Figure 1) is a common evergreen tree often referred to as ironwood, whistling pine, bulkoak, and beefwood, typically found in coastal regions. It is known for its ability to fix nitrogen and possesses antimicrobial qualities. It contains compounds such as tannins, triterpenes, and proline, along with various phytochemicals like ellagic acid, gallic acid, quercetin, and catechin. Casuarina Equisetifolia has been extensively used in coastal landscaping, agricultural enhancement, and as an ornamental shade tree, as well as for firewood and windbreaks [12].

In this study, the ultrasound-assisted biosorption of Bemacid Red dye (BR) from an aqueous system using Casuarina Equisetifolia needles (CEN); an inexpensive, environmentally friendly, and efficient biosorbent, was evaluated. The biosorbent was characterized by the Fourier-transform infrared spectroscopy (FTIR), Scanning electronic microscopy (SEM), X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA), and the point of zero charge (pHpzc). The effects of different analytical parameters; including contact time, initial dye concentration, biosorbent dosage, pH, and temperature, were in-vestigated to optimize the biosorption process. Kinetic, thermodynamic, and isothermal biosorption studies were performed to elucidate the mechanisms and efficiency.

Figure 1. Casuarina Equisetifolia plant.

2. Materials and Methods

The BR dye (λmax = 508 nm, $C_{24}H_{20}O_6S_2N_4NaCl$, M = 583 g/mol, 98% purity) was sourced from the textile industry in Soitex-Tlemcen, Algeria. The initial pH was adjusted using HNO_3 or NaOH, with measurements taken using an Adwa AD1030 pH meter. The point of zero charge (pHpzc) of the biosorbent was determined via the salt addition method with a KNO_3 solution (0.1 mol/L). Ultrasonic-assisted biosorption was performed in an ultrasonic bath. The concentration of BR dye was measured at 508 nm using a UV-visible spectrophotometer (Analytik Jena Specord 210 Plus), following a calibration curve established under identical conditions. Fourier Transform Infrared spectroscopy (PerkinElmer version 10.4.00) was employed to identify the functional groups of CEN, while morphological analysis of the biosorbent was conducted using SEM; the sample was coated with 15 nm of gold and examined under a microscope at an accelerating voltage of 20 kV. A centrifuge (SIGMA model 2–6) was used to expedite phase separation, and distilled water was utilized throughout the experimental procedures.

CEN was collected from the Tlemcen region (northwest Algeria), washed with distilled water to eliminate dust, and then dried in an oven at 60 °C for 24 h until a constant weight was reached. The dried needles were blended and sieved to achieve various particle sizes using a laboratory sieve shaker (ORTO ALRESA). The BR solution was prepared by dissolving an appropriate amount of BR powder in distilled water, with diluted solutions made from the stock solution.

The biosorption efficiency of the prepared CEN biosorbent was evaluated using the anionic BR dye. Various parameters were studied, including initial pH (ranging from 2 to 9), biosorbent dose (0.001 g to 0.1 g), sonication time (1 to 15 min), initial dye concentration (5 to 100 ppm), and temperature (17 to 65 °C). The biosorbent mass was added to 10 mL of dye solution. The removal percentage and biosorption capacity (the amount of dye biosorbed per mass of biosorbent) were calculated using the following equations [13]:

$$R(\%) = (C_0 - C_e)/C_0 \times 100 \quad (1)$$

$$Q = ((C_0 - C) \times V)/m \quad (2)$$

where, Q is the biosorption capacity ($mg.g^{-1}$), C_0 and C_e are respectively the initial and equilibrium concentrations of BR (ppm), V is the volume of the BR solution (mL) and m is the weight of biosorbant (g).

3. Results and Discussion

3.1. Characterization of the Biosorbent

The CEN surface morphology displayed significant irregularity, as shown in Figure 2. The specific surface area was measured at 351 m^2/g. Fourier Transform Infrared (FTIR) analysis, depicted in Figure 3, revealed several functional groups: a broad peak at 3429 cm^{-1} corresponding to –OH stretching, a peak at 2923 cm^{-1} indicating alkyl C-H stretching, and a peak at 1627 cm^{-1} attributed to carboxylate ions ($-COO^-$). Additionally, a smaller peak at 1451 cm^{-1} was linked to N-H stretching of amine groups, suggesting the presence of proline in CEN. Other notable peaks included one at 1317 cm^{-1} for C-O stretching and a stronger peak at 1035 cm^{-1} for C-N stretching of aliphatic amines.

Furthermore, determining the point of zero charge (pHpzc) is crucial for biosorption studies, as it indicates the pH at which the surface charges of the biosorbent are balanced. Below this pH, the surface carries a positive charge, while above it, the surface becomes negatively charged. According to the results in Figure 4, the pH_{PZC} value was equal to 5.0.

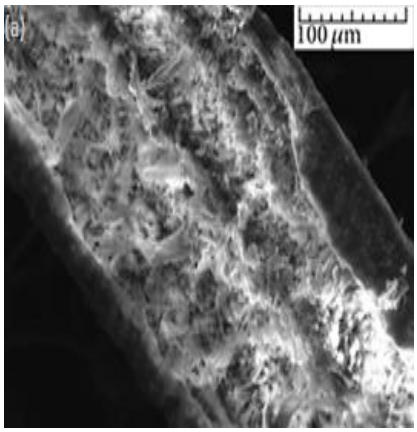

Figure 2. SEM spectra of CEN.

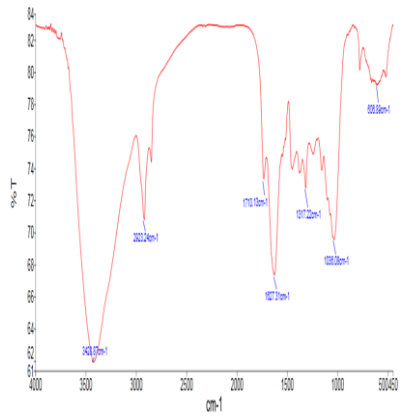

Figure 3. FTIR Spectra of *CEN*.

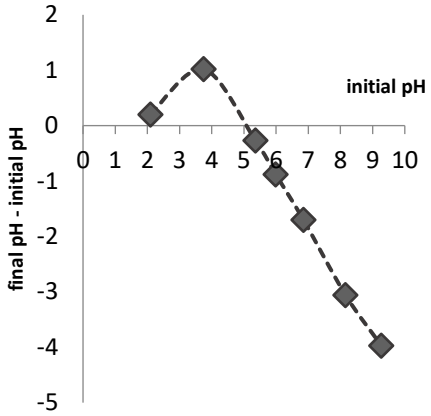

Figure 4. pH of zero point charge of the *CEN* (pH_{pzc}).

3.2. Effect of Biosorption Parameters

3.2.1. Effect of Sonication Time

Based on the results shown in Figure 5, the percentage of dye removal increases rapidly during the initial phase. This is due to the abundance of active sites available, which allows for the fast biosorption of BR onto the CEN surface [14]. Afterward, the biosorption rate gradually slows down until equilibrium is reached at 7 min.

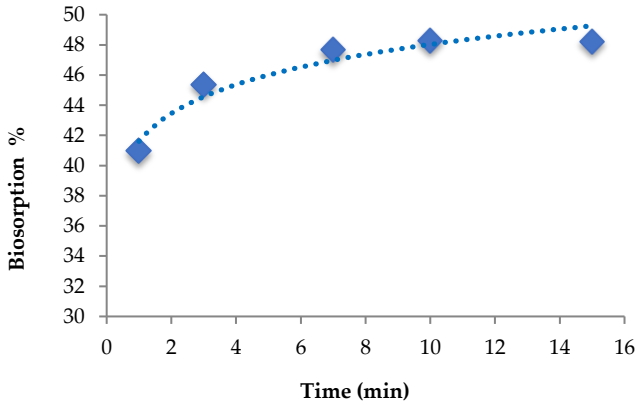

Figure 5. Effect of sonication time on BR biosorption.

3.2.2. Effect of Initial pH

Figure 6 shows that BR biosorption is highest at pH 2, with 71% removal, and decreases with increasing pH, stabilizing beyond pH 5. The CEN surface is positively charged below its pH_{PZC} (5 ± 0.1), attracting the negatively charged BR. In basic conditions, OH^- ions compete with BR for sorption sites, reducing efficiency. So it suggests that the biosorption of BR onto *CEN* depends mainly on ionic interaction. The same observations are reported by Oukebdane et al. [15] for BR removal, and Kooh et al. [16] for another anionic dye removal. In order to replicate real-life conditions and better assess the efficiency of biosorption in real effluents, we chose to work with the natural pH of the BR (pH = 6) without any adjustment.

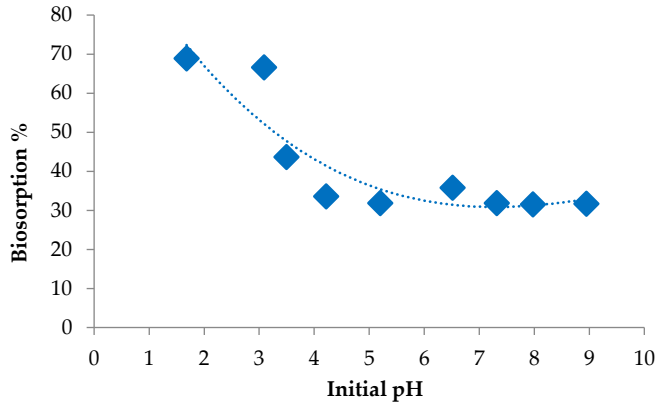

Figure 6. Effect of pH on BR biosorption.

3.2.3. Effect of Biosorbent Dose

The maximum dye removal percentage was obtained using 0.05 g (Figure 7). This was explained by the fact that with increasing dose, the available sites for biosorption also increased which led to the increase in biosorption yields. At higher biosorbent doses, the reactive sites would be excessive to accommodate more dye molecules, which justifies the equilibrium plateau after a biosorbent dose of 0.05 g [17].

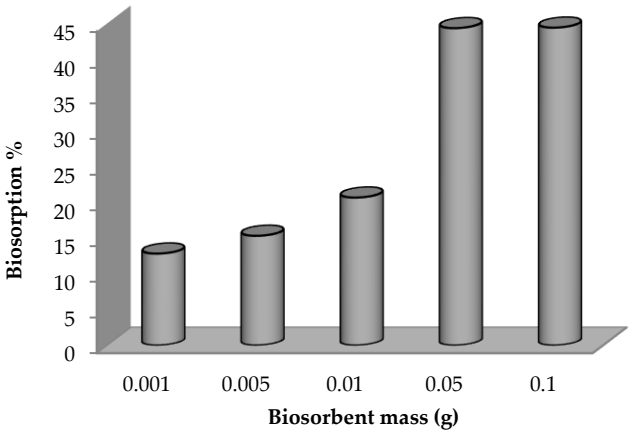

Figure 7. Effect of biosorbent dose on BR biosorption.

3.2.4. Effect of Initial Dye Concentration

The effect of initial dye concentration is shown in Figure 8. A rapid increase in the removal percentage of BR can be observed, and it is a function of the increase in the initial concentration. This trend gets closer to its maximal value, and then it remains constant beyond the concentration 50 ppm. This is due to the saturation of CEN's active sites with the dye molecules and thus, the biosorption process slows down and finally reached equilibrium [18].

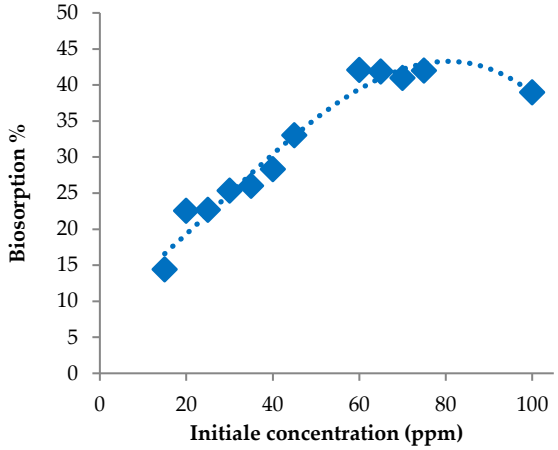

Figure 8. Effect of initial concentration on BR biosorption.

3.2.5. Effect of Temperature

Figure 9 shows the effect of temperature on the biosorption of BR onto CEN. It was observed that the biosorption percentage slightly decreases with increasing temperature, indicating the exothermic nature of the biosorption process. This decrease in biosorption with increasing temperature may be due to the weakening of sorptive forces between the active sites of CEN and BR molecules, additionally, this may be attributed to the escaping tendency of the BR from the solid phase to the bulk phase with the rise in temperature of the solution [19].

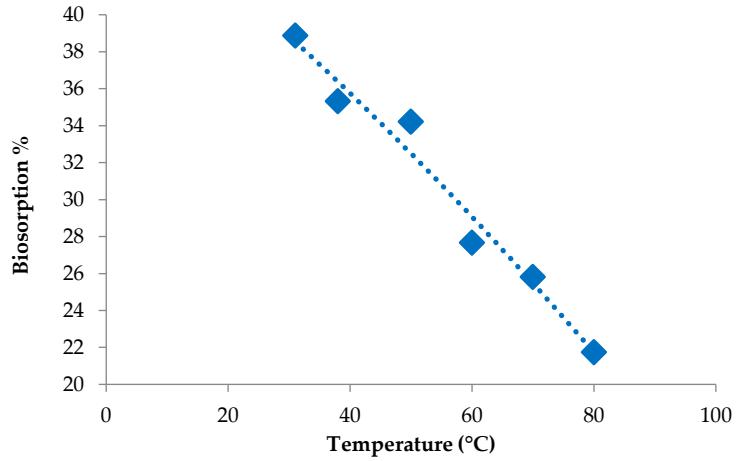

Figure 9. Effect of temperature on BR biosorption.

4. Conclusions

The study of BR dye removal onto CEN was investigated with the developement the biosorption technique that represents a practical and environmentally friendly approach that satisfies the requirements of green chemistry. The discoloration can be rapidly observed during 7 min. The effect of initial pH interestingly; the removal yield of BR dye was remarkably high at pH 2.0. The thermodynamic parameters of BR dye biosorption indicated that the biosorption is exothermic. CEN used in this study is freely and abundantly available. It is clear that the characteristics of CEN make it a suitable biosorbent for practical application and it can be exploited for the development of extraction and purification.

Author Contributions:

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: All authors would like to convey our obligation to Management and the Principal.

Conflicts of Interest: The authors declare no conflict of interest.

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