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Equilibrium and Kinetic Study of Photocatalytic Degradation of Tartrazine Using Biochar Using Microwave Assisted Pyrolysis from *Theobroma cacao L.* Husk Doped with Iron †

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Abstract: The microwave-assisted pyrolysis (MAP) process involved placing acid-pretreated biomass (CPH) in a domestic microwave oven at 600 W for 15 min. This was followed by a doping process with iron salts (+2, +3) to obtain BCCPH-Fe. Characterization of BCCPH-Fe was carried out using surface analysis (BET), thermogravimetric analysis (TGA), particle size distribution, and Fourier Transform Infrared Spectroscopy (FTIR). Subsequently, the photodegradation process was performed using three different light sources, with tartrazine as the adsorbate. The effect of pH on photodegradation was studied, and the percentage of degradation was evaluated through equilibrium and kinetic studies. The amount of BCCPH-Fe, tartrazine concentration, and exposure time to the light source were also evaluated. The best conditions for the photodegradation process were: 254 nm light source, pH of 5, 1 g/100 mL BCCPH-Fe, 25 ppm tartrazine concentration, and 40 h exposure time. Under these conditions, a 93.45% removal of tartrazine was achieved. The experimental data of the adsorption equilibrium best fit the Langmuir-Hinshelwood model, while the adsorption kinetics best fit the pseudo-first-order model. The apparent kinetic constant was 0.04053 [h^{-1}], and the correlation coefficient was 0.98667. In conclusion, photodegradation using BCCPH-Fe can be an effective method for the removal of tartrazine from wastewater, offering a sustainable alternative to traditional methods.

Keywords: biochar; microwave assisted pyrolysis; tartrazine

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1. Introduction

Synthetic dye pollution in water bodies poses a significant threat to aquatic ecosystems. This study proposes an innovative and sustainable solution: the use of iron-doped cocoa husk biochar as a photocatalyst for the degradation of tartrazine, a common azo dye [1].

Biochar, a porous carbonaceous material, offers high adsorption capacity and chemical stability. Doping it with iron introduces new active sites that favor the generation of free radicals during photocatalysis, accelerating dye degradation [3]. This strategy combines the advantages of biochar (sustainability, low cost) with the catalytic activity of iron, offering a promising alternative to conventional photocatalysts [4].

2. Materials and Methods

A carbonaceous biomaterial was developed from cocoa husks through pyrolysis and subsequent iron doping. The obtained biochar was characterized by BET, TGA, and FTIR analysis. BET analysis revealed a high surface area, indicating its potential for adsorption and catalytic activity. TGA analysis showed that the iron-doped biochar exhibited improved

thermal stability compared to the undoped biochar. FTIR analysis confirmed the successful incorporation of iron into the biochar structure.

The iron-doped biochar was evaluated for its ability to photodegrade tartrazine under different conditions. The results demonstrated that the biochar exhibited optimal performance at a pH of 5 and under UV irradiation at 254 nm. Increasing the catalyst concentration and irradiation time led to enhanced tartrazine degradation, but beyond certain thresholds, further improvements were limited. The biochar was found to be effective in degrading tartrazine concentrations up to 25 ppm.

These findings suggest that the iron-doped biochar has significant potential as a sustainable and efficient photocatalyst for the treatment of wastewater contaminated with tartrazine. Future studies could explore its applicability to other types of dyes and emerging contaminants, as well as investigate the long-term stability and reusability of the material. Additionally, optimizing the synthesis process and exploring different iron doping methods could further enhance the catalytic performance of the biochar.

3. Results and Discussion

3.1. Obtaining BCCPH-Fe

The study focused on the production and characterization of iron-doped biochar derived from cocoa husk biomass. Initially, the biomass underwent an acid pretreatment to remove impurities and increase its porosity. This pretreatment decomposes the lignocellulosic components of the biomass, facilitating its subsequent conversion into biochar.

Subsequently, a microwave-assisted pyrolysis process was carried out to obtain the biochar. During this stage, the biomass decomposes into biochar, gases, and tar. The resulting biochar was doped with iron, which involves the incorporation of iron particles into its structure. This doping process increases the mass of the material and confers new catalytic properties.

3.2. BCCPH-Fe Characterization

FTIR, BET, and TGA analyses provided valuable information about the structure and composition of the iron-doped biochar. FTIR analysis confirmed the successful incorporation of iron onto the biochar surface, evidenced by the appearance of characteristic bands of iron compounds such as Fe_2O_3, Fe-O, and Fe-O-OH. Additionally, a significant interaction between iron and the functional groups of the biochar was observed, forming coordination complexes.

BET analysis revealed a decrease in the specific surface area and pore volume of the biochar after iron impregnation, suggesting that iron particles blocked part of the material's porosity. However, the presence of iron within the porous structure could generate new active sites and modify the selectivity of the material.

TGA analysis showed an increase in the ash content of the iron-doped biochar, confirming the incorporation of the metal into the material's structure and the formation of stable iron oxides at high temperatures.

3.3. Experiments

3.3.1. Equilibrium Studies

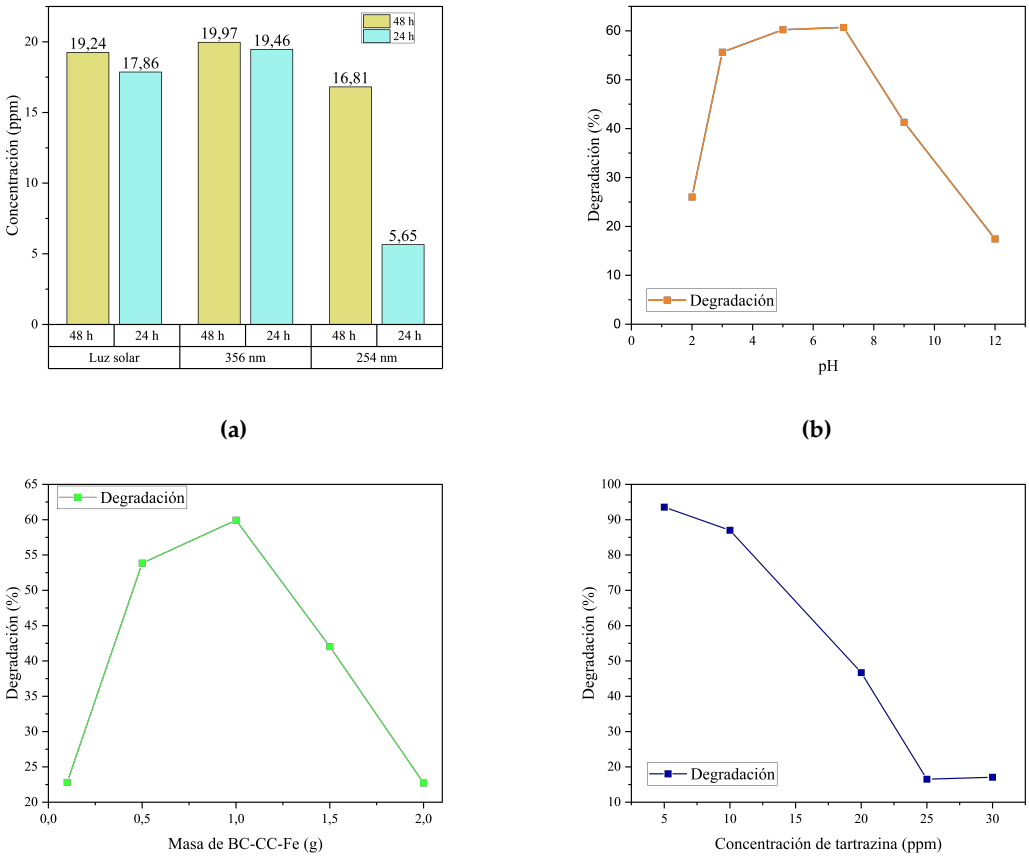

Figure 1. (**a**) Experiments conducted with different light sources determined that ultraviolet C radiation (UV-C), with a wavelength of 254 nm, was the most effective for dye degradation, achieving up to 75% removal. The high energy associated with UV-C facilitates photodegradation processes, breaking the dye's chemical bonds more efficiently. Therefore, 254 nm UV-C light was selected for the following stages of the study. (**b**) The results indicate that the optimal pH range for tartrazine photodegradation is between 5 and 7, reaching up to 61% degradation. A pH of 5 was selected for subsequent experiments due to its similarity to the natural pH of tartrazine solutions (5.5–6.2 pH). This pH favors a negative charge on the biochar surface, which can promote the adsorption and subsequent degradation of the dye. (**c**) The best amount of biochar for tartrazine degradation was evaluated. It was found that 1 g of biochar provided the highest degradation efficiency (60%). Smaller amounts generated competition for active sites, while larger amounts saturated the material. (**d**) The optimal tartrazine concentration for the experiment was found to be 25 ppm. At this concentration, an equilibrium was reached between the adsorption of tartrazine molecules onto the active sites of the biochar and their subsequent degradation.

3.3.2. Kinetic

The kinetic study was determined under the best conditions, where data on % Removal of Concentration with respect to time is available. From the Langmuir-Hinshelwood equation, we have:

$$r = -\frac{dC}{dt} = k * \frac{K * C}{(1 + K * C)} \quad (1)$$

The Langmuir-Hinshelwood equation depends on the dye concentration [3]. Tartrazine has a concentration of 20 ppm (equivalent to $3.75 * 10^{-5} \frac{\text{mol}}{\text{L}}$). Therefore, the kinetics take the form of a pseudo-first-order equation.

$$r = -\frac{dC}{dt} = k_{ap} * C \quad (2)$$

where k_{ap} is the apparent kinetic rate constant and C is concentration. This equation can be integrated. Therefore, we will have:

$$\ln \frac{C_o}{C} = k_{ap} * t \quad (3)$$

This equation is used to linearize the obtained data.

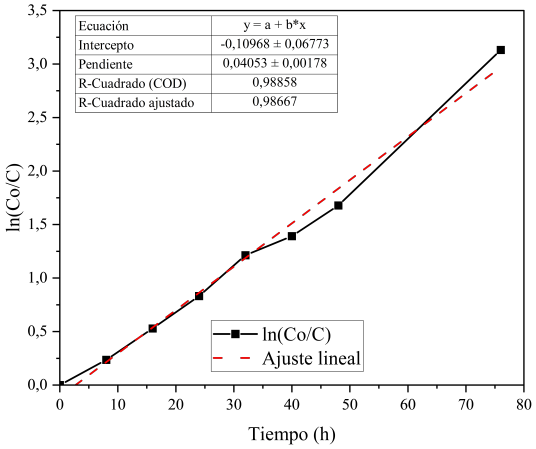

Figure 2. Linealización del estudio cinético ln $\frac{C_o}{C}$ vs t.

The slope with a value of 0.04053 corresponds to the value of k_{ap}. These data are accurate with respect to the mathematical study carried out due to its correlation coefficient R^2 being 0.98667. The kinetic study determines that the photodegradation of tartrazine fits a Langmuir-Hinshelwood kinetic model, with a pseudo-first-order reaction.

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