Photocatalysis process using Zeolitic Imidazolate Framework-8

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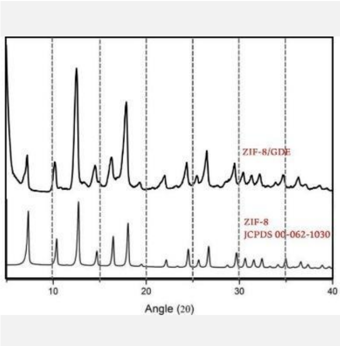

Photocatalysis is a process that involves accelerating a chemical reaction using catalysts and different light sources. The catalyst used in this project is known as ZIF-8 (Zeolitic Imidazolate Framework-8), which is a porous material from the family of Structured Organic Metals (MOFs). Through various studies, ZIF-8 has proved to be an excellent catalyst. It contains active sites that interact with the reactant molecule, has a large surface area and is chemically stable. The material's organic structure is susceptible to generating electron pairs, with functional groups assigned to catalyst structures that enable chemical reactions, such as the decomposition of organic compounds. The aim of this study was to evaluate the efficiency of ZIF-8 in a photocatalysis process for organic dyes degradation.

Introduction

The accelerated growth of industrialization has sparked great global concern due to the impacts of industrial discharge on the environment, directly affecting water bodies, fauna and human beings. The intensification of water pollution is attributed to the spread of emerging organic pollutants, such as pharmaceuticals, herbicides, pesticides and other contaminants. These pollutants can unbalance aquatic ecosystems and pose serious risks to human health [1].

The leather industry, together with the textile industry, are examples of production activities that contribute to the contamination of natural waters. This is due to the significant generation of effluents from dyeing processes using reactive dyes. Although these dyes are not considered intrinsically toxic, they can undergo partial degradation, either through biological processes or other treatment methods. This partial degradation process can result in the formation of even more toxic compounds when the partially degraded molecules bind to others, exacerbating the environmental impact [2].

Dyes can also reach water collection and treatment plants, damaging public supplies and contaminating the soil near water sources. In this scenario, another concern arises: although some bacteria present in the soil help degrade the dyes, they can generate carcinogenic compounds as a by-product. These compounds, when they infiltrate water and soil, pose a serious problem for agricultural crops, which are essential for human and animal nutrition. Faced with this significant threat, it is imperative to develop new treatment methods for these effluents, guaranteeing low levels of contaminants [3].

Heterogeneous photocatalysis has been widely used to treat pollutants, due to its high rate of degradation of organic compounds through catalytic reductions and oxidation formed by semi-reactions caused by electrons and photo-generated holes [4,5].

New materials with the potential to be photocatalysts must be researched. Among these materials, Metal–organic frameworks (MOFs) stand out. Zeolite imidazolate frameworks (ZIFs), a subclass of MOFs, compose of transition metal ions [Zn(II), Co(II)] and imidazolate linkers which form 3D tetrahedral frameworks [6].

This study aims to evaluate the effectiveness of Zeolitic Imidazolate Framework-8 catalyst for the degradation of textile dyes.

Material and Methods

To verify the photocatalytic activity of ZIF-8 previously synthesized by the group [7,8], two textile dyes were used - red and turquoise dye quimacryl - at a concentration of 1 g·L^{-1}.

After checking the initial peak concentration of the solution with the organic compound, duplicates were made by mixing 0.1 g of the ZIF-8 catalyst in 100 mL of the liquid solution made previously.

The reactions took place in duplicate in a photoreactor consisting of four germicidal lamps (18 W) and a stirring plate.

The duplicates were stirred on a magnetic stirrer in a closed environment exposed only to ultraviolet light, so that the photocatalysis process could begin. Samples were taken every 30 min of stirring and exposure to visible light and their concentrations were recorded using data from a spectrometer.

The quantitative determination of the chemical elements present in ZIF-8 was performed by X-ray

fluorescence (XRF) analysis (Epsilon 1, Malvern Panalytical).
BET surface area, pore volume and distribution were obtained by physical nitrogen adsorption (Novatouch LX2, Quantachrome). In Gas Sorption Analysis the catalyst was subject to vacuum degassing pretreatment at 200 °C for 2 h to remove moisture and volatile compounds.

Results and Discussion

XRD was performed on the material previously obtained by the group to verify its crystalline structure (Graphical Abstract). The result confirmed that the material is characterized as ZIF-8. The chemical composition of the catalyst determined by XRF is reported in Table 1. Table 2 shows the value obtained for the specific surface area, volume and pore radius for ZIF-8.

Table 1. Composition of ZIF-8.

Catalyst	Zn (% w/w)	Others (% w/w)
ZIF-8	99.115	0.885

Table 2. Specific surface area, volume and pore radius.

Catalyst	S_BET ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Average pore radius (nm)
ZIF-8	1045.998	0.5855	1.1245

The sample has a specific surface area of 1046 $m^2 \cdot g^{-1}$, as expected for a MOF. The average pore diameter is in the range of 2-50 nm, characterizing it as mesoporous. The adsorption isotherm is of type IV-H1, typical of mesoporous systems.
The preliminary results obtained in the photocatalytic tests are shown in Figure 1. The absorbances taken every 30 min stabilized over time, with a final degradation of 13% for Red dye and 22% for Turquoise dye. The results obtained did not demonstrate high effectiveness of ZIF-8 catalyst in the process of deteriorating the dye in water using photocatalysis.

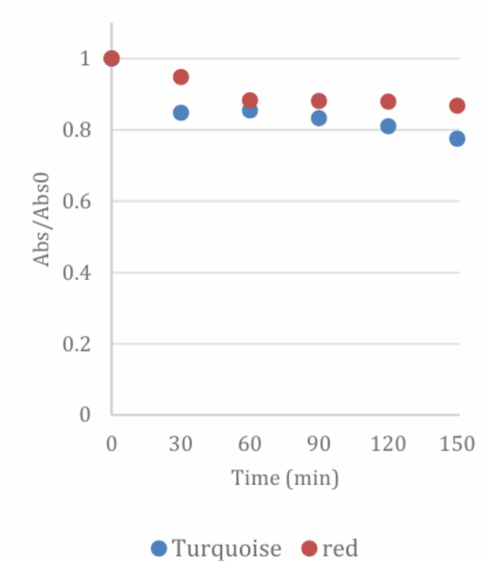

Figure 1. Textile dye degradation using ZIF-8.

Zinc compounds are known to be photoactive materials, but an electron/hole pair combination may be occurring in the MOF structure, thus preventing high efficiency. For future studies, metals will be added to the MOF to improve their photocatalytic activity.

Conclusions

ZIF-8 has promising characteristics, such as large surface area (1046 $m^2 \cdot g^{-1}$), but did not demonstrate high efficiency in this photocatalysis process. It degraded 13% of the Red dye and 22% of the Turquoise dye. Further studies, such as metal addition, are necessary to improve the structure of this MOF for application in photocatalysis.

Acknowledgments
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