Photocatalytic Application of Iron-Doped Clinoptilolite Catalysts for Reactive Blue Dye Degradation

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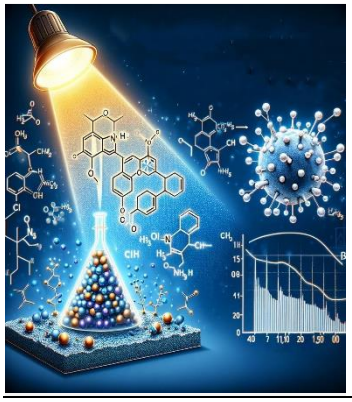

Catalysts based on clinoptilolite doped with different iron percentages (2.5% and 5% w/w) were synthesized and their photocatalytic activity was evaluated for degrading Reactive Blue dye under a 35W Xenon lamp after PAS analysis (Band Gap energy around 2 eV). A Box-Behnken experimental design was employed to investigate the photo-Fenton process, varying catalyst concentration, pH, and reaction time, with the response variable being the yield obtained by UV-VIS absorption spectroscopy. Subsequently, the kinetic curve under optimal conditions displayed degradation rates above 95%. Thus, the synthesis route proved efficient, and the photo-Fenton process successfully operated with light sources beyond the UV range. This study offers a promising approach for water decontamination from textile dyes, proposing an alternative to TiO_2 and UV lamp-based advanced oxidative processes.

Introduction

The inadequate disposal of industrial waste has become one of the primary causes of water pollution [1]. In particular, textile effluents, mostly composed of dyes, pose a serious risk due to visual pollution, interfering with photosynthesis processes, and health hazards from their carcinogenic and mutagenic behavior [2]. As described by [3], the use of advanced oxidative processes has proven effective in combating the presence of such contaminants. Titanium dioxide (TiO_2) is one of the most commonly used materials in this application; however, according to [4], its usage has limitations due to rapid electron/hole pair recombination and a high Band Gap energy, restricting it to light sources in the UV range. On the other hand, a material that has been gaining prominence is natural zeolites, such as clinoptilolite, for promoting selective chemical reactions and exhibiting ion exchange capacity [5]. In this context, this study aimed to investigate an alternative approach to Reactive Blue dye degradation through the synthesis and application of clinoptilolite-based catalysts doped with different iron percentages (2.5% and 5% w/w) in a photo-Fenton process assisted by a 35W Xenon lamp.

Material and Methods

For the synthesis, the following route was employed: magnetic stirring of 10g of clinoptilolite in a solution containing the necessary mass of $FeCl_3 \cdot 6H_2O$ for iron contents for 48 hours, followed by vacuum filtration using common filter paper and drying in an oven at 60°C for one hour. With the catalysts prepared, the Band Gap energy determination was performed using the Photoacoustic Spectroscopy technique to assist in the selection of the light source. Finally, the reaction tests were carried out in borosilicate batch reactor (Figure 1) and consisted of 15 duplicate experiments following a Box-Behnken experimental design with 3 levels taken from [6]: pH (2, 3, and 4), catalyst concentration (100, 250, and 400 mg/L), and reaction time (30, 60, and 90 min), with the response variable being the average yield obtained by UV-VIS absorption spectroscopy. Each test involved agitation in the dark for two hours of 40 mL of a 20 ppm Reactive Blue solution containing the catalyst at the specified concentration and pH, followed by the addition of 2 mL of hydrogen peroxide. Subsequently, the 35W Xenon lamp was switched on and kept on for the specified time in the experimental design.

Figure 1. Photoreactor.

Results and Discussion

The spectra of the catalysts (2.5Fe-Clp and 5Fe-Clp)

and unmodified Clinoptilolite (Clp) are depicted in Figure 2, from which the Band Gap value can be obtained using method reported by [7]. The values for 2.5Fe-Clp, 5Fe-Clp, and Clp were respectively 2.38, 2, and 2.64 eV. Thus, it can be observed that the catalysts exhibit an optical transition range between 400 and 700 nm, encompassing the visible spectrum, and that a higher iron percentage implies a lower Band Gap energy. Based on this, the lamp selection was limited to those that best fit within this range, departing from conventional choices of UV lamps. Therefore, considering factors such as availability and cost, the decision was made to use a 35W Xenon lamp.

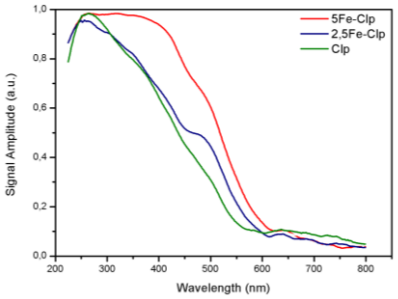

Figure 2. Normalized spectra.

From the experimental design, the optimal conditions of pH, catalyst concentration and reaction time were respectively 2, 400 mg/L and 60 min for 2.5Fe-Clp and 2, 100 mg/L and 60 min for 5Fe-Clp. Thus, it can be affirmed that both exhibited better performance at a more acidic pH and intermediate reaction time, while concerning the concentration, for a higher iron percentage present in the catalyst, a lesser amount of it was required. Consequently, the kinetic curves presented in Figure 3 were constructed in these conditions to illustrate the evolution of this process over the time the lamp remained on.

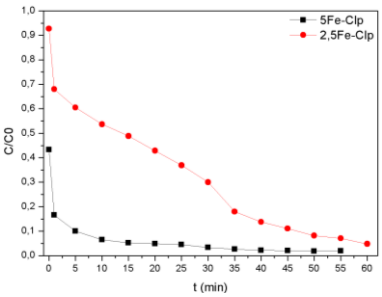

Figure 3. Kinetic curves.

It is noticeable that both catalysts exhibited satisfactory results, with degradation rates equal to 95.21% for 2.5Fe-Clp and 98.06% for 5Fe-Clp concerning the original concentration of the dye in solution. It is also worth noting that the difference between the initial points is attributed to the two-hour stirring period in the dark, i.e., prior to the onset of the photo-Fenton reaction. This indicates that the 5Fe-Clp catalyst was capable of removing more contaminant from the solution compared to the other, with this removal attributed to adsorption on the catalyst's surface.

Conclusions

It was demonstrated that the synthesis route used was an economical, simple, and efficient alternative for the impregnation of Fe^{3+} into Clinoptilolite, and that the photo-Fenton process can be carried out with lamps outside the UV range, bringing it closer to possible applications under natural light. Furthermore, with the factorial study conducted through the Box-Behnken design, it was possible to map the best conditions of pH, catalyst concentration and reaction time necessary to ensure high degradation rates, optimizing the process, as illustrated by the kinetic curves. Therefore, the two catalysts represent a promising alternative for Reactive Blue dye degradation, contributing to the fight against water bodies pollution by textile effluents.

Acknowledgments

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