

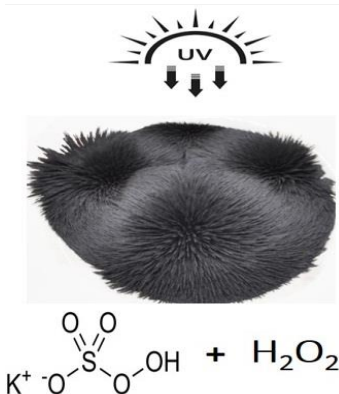
## Enhanced degradation of textile dye using heterogeneous photo-Fenton process using magnetic catalyst and oxidant synergy

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O. R. S. Rocha<sup>1</sup>, R. V. S. Aquino<sup>2</sup>, R. F. Carvalho<sup>1</sup>, E. J. M. Dantas<sup>1</sup>, J. G. A. Pacheco<sup>1</sup>

(1) Universidade Federal de Pernambuco, Avenida dos Economistas, s/n, Cidade Universitária, Recife, Brazil

(2) Universidade Federal de Santa Catarina, Campus Universitário João David Ferreira Lima, Florianópolis, Brazil  
email of the 1<sup>st</sup> author: otidene.rocha@ufpe.br



This study investigated the degradation of Yellow Remazol 145 (YR145) textile dye using advanced oxidation processes (AOPs) that combine radiation, photocatalyst, and oxidants in the heterogeneous photo-Fenton process. Magnetite was employed as a magnetic solid catalyst, while persulfate (PS), peroxymonosulfate (PMS), and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were utilized as chemical oxidants. XRD analysis confirmed the successful formation of magnetite as the catalyst, exhibiting its characteristic peaks. The heterogeneous photo-Fenton process with PMS achieved the highest degradation rates (58%). Combining PMS and  $\text{H}_2\text{O}_2$  in a 1:1 ratio further enhanced the degradation to 88%. After 5 consecutive cycles, the process efficiency decreased by only 9%, demonstrating the viability of applying heterogeneous photo-Fenton with oxidant synergy for YR145 degradation. The findings indicate that the heterogeneous photo-Fenton process with magnetite as the catalyst and PMS/ $\text{H}_2\text{O}_2$  as oxidants presents high potential for efficient and reusable degradation of YR145 textile dye.

### Introduction

Textile effluents are highly colored due to the presence of dyes, which are not fixed to the fibers during the dyeing process and end up in wastewater [1]. Biological methods could be applied to treat this type of effluent, however, dyes have low biodegradability and resistance to degradation. As an alternative to this problem, photo-Fenton is a non-selective advanced oxidation process that can oxidize complex organic molecules, such as dyes, and can even achieve the mineralization of these contaminants.

For this, oxidants, an energy source (such as ultraviolet radiation), and an iron source are used to generate oxidizing radicals, such as hydroxyl ( $\text{HO}\cdot$ ). The conventional photo-Fenton process uses hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and  $\text{Fe}^{2+}$  in aqueous phase, however, some modifications can be applied to improve the oxidation efficiency [2].

One modification involves using different types of sulfur-based oxidants, such as persulfate (PS) and peroxymonosulfate (PMS). Combining these oxidants with  $\text{H}_2\text{O}_2$  can increase degradation rates due to the synergistic effect of these species, as demonstrated in the study by Baradaran and Sadegui [3] on the degradation of comassie brilliant blue, where the use of hydrodynamic cavitation with persulfate/hydrogen peroxide increased TOC removal by about 20% compared to using  $\text{H}_2\text{O}_2$  alone.

Another modification being applied to the process is the use of solid catalysts as iron sources. This process, known as heterogeneous photo-Fenton, offers advantages over the homogeneous process by making it possible to recover and reuse the catalyst due to the magnetic properties of iron oxides [4].

In this context, the objective of this work was to apply the heterogeneous photo-Fenton process with combined

oxidants and the use of the magnetic catalyst magnetite for the degradation of the textile dye yellow remazol 145 (YR 145). Studies were carried out to choose the best process, the effect of using combined oxidants, and catalyst reuse.

### Material and Methods

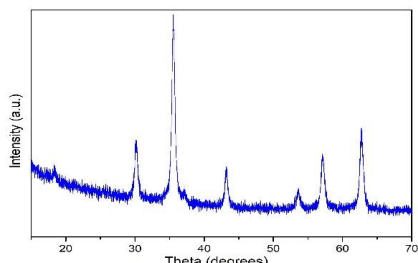
The iron catalyst (magnetite) was synthesized based on the work of Tahifi and Montazer [1]. The material was characterized by X-ray diffractometry (XRD, Rigaku SmartLab) using an angular range of 3-70° and a step of 0.02°.

A model contaminant was used, an aqueous solution of Yellow Remazol 145 textile dye at a concentration of 50  $\text{mg}\cdot\text{L}^{-1}$  at pH 3. The degradation experiments were carried out in a batch photocatalytic reactor containing a magnetic stirrer, a UVC lamp (ILUMISAMPA, 30 W), and cylindrical containers containing 200 mL of solution. Preliminary tests were carried out combining the action of radiation, oxidants (sodium persulfate and potassium peroxymonosulfate), and the catalyst. In the best process, a synergy test was performed between the best oxidant and hydrogen peroxide (ratio of 1:1). The total test time was 120 minutes. Under the best conditions, a reuse study was carried out. The catalyst was separated from the samples using a magnet. The dye concentration was determined in a spectrophotometer (Spectroquant Pharo 300) at  $\lambda = 420$  nm with subsequent conversion of absorbance to concentration.

### Results and Discussion

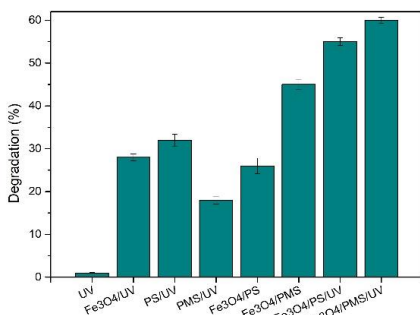
The X-ray diffractogram for the synthesized magnetite is presented in Figure 1. According to the diffractogram, only peaks relative to magnetite were observed in the crystalline phase. The  $2\theta$  values containing the characteristic peaks were 30.1°, 35.5°, 43.2°, 53.6°, 57.1° and 62.8°, which is in agreement with the Inorganic

Crystal Structure Database (ICSD 50567).



**Figure 1.** XRD diffractogram of the catalyst.

Figure 2 compares the individual and combined processes between the catalyst, oxidants, and radiation. Photolysis showed less than 2% degradation, while  $\text{Fe}_3\text{O}_4/\text{UV}$ ,  $\text{PS}/\text{UV}$ , and  $\text{PMS}/\text{UV}$  had efficiencies between 18 and 32%. In the heterogeneous Fenton-type process using  $\text{PMS}$  as the oxidant, the oxidative power was improved and the degradation reached 45%. In the heterogeneous photo-Fenton process, the degradation rate reached about 60% in 120 minutes of reaction. This is due to the combined action of the oxidizing agents with radiation, shifting the reaction equilibrium towards the formation of reactive oxygen species (ROS). Thus,  $\text{Fe}_3\text{O}_4/\text{PMS}/\text{UV}$  was considered the best process for YR145 oxidation.



**Figure 2.** Comparison of YR145 degradation under various AOP processes.

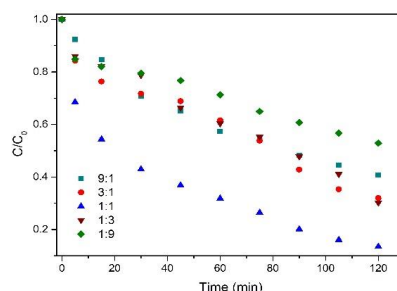
## Conclusions

It was possible in this work to observe the influence of the synergistic use of oxidants in a heterogeneous photo-Fenton process for the degradation of YR145. The best process obtained was  $\text{Fe}_3\text{O}_4/\text{PMS}/\text{UV}$ , which combined with  $\text{H}_2\text{O}_2$  in the  $\text{PMS}/\text{H}_2\text{O}_2$  ratio of 1:1 presented almost 90% degradation. In the reuse tests, an efficiency of around 80% was achieved even after 5 reaction cycles, showing the potential of magnetite as a magnetic catalyst and activating agent for the oxidants used.

## References

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After selecting the  $\text{Fe}_3\text{O}_4/\text{PMS}/\text{UV}$  process, the effect of hydrogen peroxide in combination with  $\text{PMS}$  at different molar ratios was observed, as shown in Figure 3. The system with the lowest observed efficiency was the  $\text{PMS}/\text{H}_2\text{O}_2$  ratio of 1:9, showing that the decrease in sulfate radical generation was not beneficial to the process. The ratios of 9:1, 3:1, and 1:3 showed similar behaviors, with no significant difference in degradation. However, in  $\text{PMS}/\text{H}_2\text{O}_2$  1:1, almost 90% degradation of YR145 was observed, demonstrating that the synergy of oxidants in the appropriate proportion is interesting for optimizing the process efficiency. Hydroxyl radicals can act as less selective agents, which increases the effectiveness in oxidizing the organic groups present in the dye structure, while sulfate radicals have a longer half-life, acting for a longer time in degradation [5].



**Figure 3.** Degradation of YR145 in heterogeneous photo-Fenton using different ratios of  $\text{PMS}/\text{H}_2\text{O}_2$ .

With the  $\text{PMS}/\text{H}_2\text{O}_2$  ratio of 1:1 in the  $\text{Fe}_3\text{O}_4/\text{PMS}/\text{UV}$  system, a catalyst reuse study was carried out in different degradation cycles. Between cycles, the catalyst was separated with the aid of a magnet and washed with distilled water. Total degradation, after 120 minutes of the 1st cycle, was observed to be 88%. The following cycles showed 87%, 86%, 81% and 79% degradation, with a 9% drop between the first and fifth cycles. It is observed that the catalyst remained efficient even with possible iron leaching at pH 3 after the reaction cycles, suggesting that iron in the form of a cation may have effectively participated in the process.