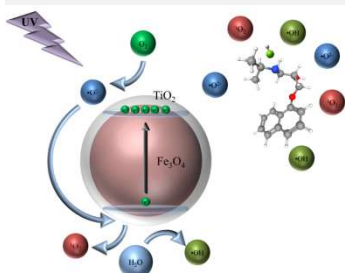


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This work had the intended to prepare  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  core-shell nanoparticles using different ratios of  $\text{Fe}_3\text{O}_4$  to serve as a photocatalyst for an Advanced Oxidative Process (AOP) in the decomposition of propranolol hydrochloride, exploiting its potential to reduce electron recombination and its reuse by magnetic separation. In this study, a  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  core-shell photocatalyst was successfully synthesized by hydrothermal method. It was shown that the degradation of propranolol was optimal for  $\text{Fe}_3\text{O}_4:\text{TiO}_2$  at a proportion of 1:22 which reached 70% degradation after 60 min under UV light, demonstrating efficiency and effectiveness in removing pharmaceutical pollutants and indicating great potential for practical applications.

## Introduction

In the context of environmental problems caused by the creation and use of new synthetic substances, emerging pollutants are in evidence, given their widespread use and its potential as water contaminant [1]. The propranolol is a drug with potential toxicity already detected in surface water, being persistent and bioaccumulative, thus considered an emerging pollutant of interest [2] [3] [4]. With that in mind, the use of alternative methods, such as Advanced Oxidative Processes (AOP's), is a promising alternative. Among these methods, heterogeneous photocatalysis is a degradation method of organic molecules that shows robust results, especially when using  $\text{TiO}_2$  associated with UV radiation [5]. However, the recovering process of these particles after the photocatalysis have a high cost, so the association with magnetic materials can facilitate separation and improve contaminant degradation due to synergistic effects [6]. Therefore, in this work  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  core-shell nanoparticles were prepared using different proportions of  $\text{Fe}_3\text{O}_4$  to serve as a photocatalyst of a AOP for the decomposition of propranolol hydrochloride, aiming to reduce electron recombination and its reuse by magnetic separation.

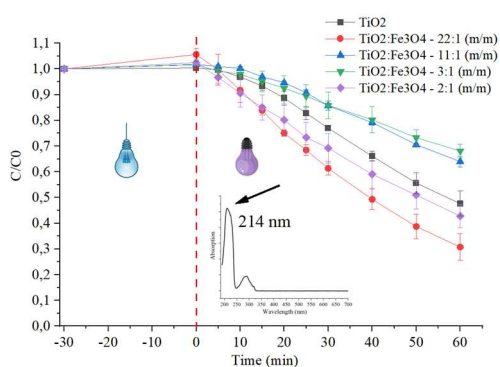
## Material and Methods

The  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  core-shell nanoparticles were prepared using different ratios  $\text{Fe}_3\text{O}_4$  (1,0; 0,6; 0,2 e 0,1 g). The procedure consists in the preparation of two solutions (A and B). In solution A magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles were dispersed in 50 ml of absolute ethanol. This mixture was homogenized in an ultrasonic equipment (Soniscs INC, Model VCX

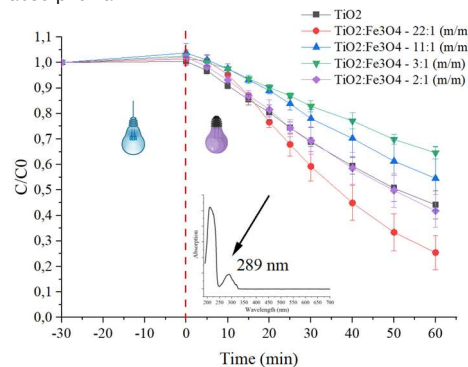
750) for 5 min, at frequency of 60 kHz. To this mixture, 0,12 g of EDTA was added repeating the homogenization by ultrasound for the same amount of time. Solution B consists of the slow addition of 8 ml of titanium isopropoxide in 120 ml of absolute ethanol and 7 ml of glacial acetic acid, under stirring for 30 min. Subsequently, solution B was poured into solution A and homogenized again for 5 min via ultrasound. Afterwards, the solution A+B was transferred to a hydrothermal reactor, which was placed in an oven for 10 h at 160 °C. After that, this solution was filtered and the resulting solid was dried at 100 °C for 12 h. The drug degradation reactions were carried out in a jacketed reactor that contained a UV light source (80 W) and an aeration system. The initial concentration of propranolol hydrochloride was 25 mg/L and the catalyst was 1,0 g/L, which were dispersed in 1,5 l of water. Initially, the system was maintained for 30 min in the absence of light to evaluate the adsorption effect. After this period the lamp was activated. The samples collected at each time period were analyzed in a spectrophotometer at wavelengths of 214 and 289 nm.

## Results and Discussion

Figures 1 and 2 represent the reduction of chromophore groups present in the drug. It is observed that in the proportion of  $\text{TiO}_2:\text{Fe}_3\text{O}_4$  equal to 22:1 there is an optimization of the process.



**Figure 1** Removal kinetics of the chromophore group with absorption at 214 nm.



**Figure 2** Removal kinetics of the chromophore group with absorption at 289 nm.

The results suggest that the presence of magnetite does not simply help to separate the photocatalyst,

### Conclusions

In this study, a  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  core-shell photocatalyst was successfully synthesized by hydrothermal method. The degradation efficiency of propranolol was optimal for  $\text{Fe}_3\text{O}_4:\text{TiO}_2$  at a proportion of 1:22 which reached 70% degradation after 60 min under UV light. Therefore, this photocatalyst is promising for effective and efficient removal of pharmaceutical pollutants, indicating the great potential of this one for practical applications.

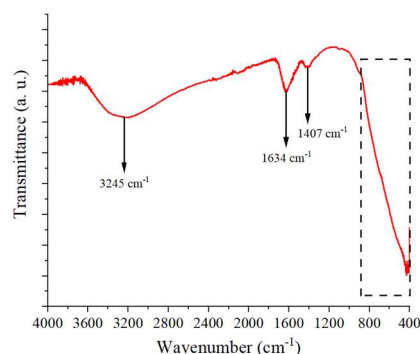
### Acknowledgments

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it also improved the degradation of the contaminant. This fact may be associated with the formation of a heterojunction between the structures, which leads to a reduction in the recombination of electron/vacancy pair due to the transference of electrons from the  $\text{Fe}_3\text{O}_4$  particles to  $\text{TiO}_2$  [6]. Figure 3 showed the FTIR spectra of  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  core-shell structure. The strong adsorbing peaks at  $3425\text{ cm}^{-1}$  and  $1634\text{ cm}^{-1}$  can be attributed to the stretching vibration of -OH and H-O-H bending vibration, which showed that sample contained the surface OH or adsorbed water, respectively. The peak at  $1407\text{ cm}^{-1}$  is recognized as CH=CH bonds, due to the  $\text{TiO}_2$  precursor. The wideband at  $400\text{-}900\text{ cm}^{-1}$  is known as the Ti-O-Ti and Fe-O vibrations. This peak is wider because of the coincidence of the Ti-O band with Fe-O peaks [7,8].



**Figure 3**  $\text{Fe}_3\text{O}_4@\text{TiO}_2$  1:22 FTIR.