

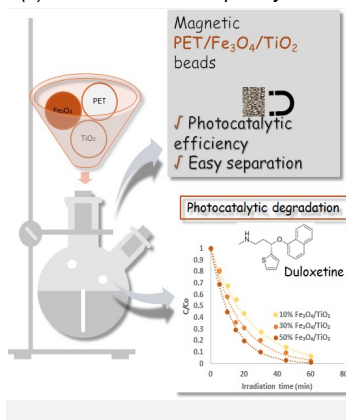
Magnetically separable PET-TiO₂/Fe₃O₄ photocatalyst for degradation of the antidepressant drug duloxetine

POSTER
Ph.D. Student: Y
Journal: YES

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Heterogeneous photocatalysis has been proved to be a powerful, tool for the degradation of many organic compounds. However, the challenge of separating the catalyst after treatment significantly impedes its practical application. In this regard, magnetic-nanocomposite- PET/TiO₂ beads were synthesized and assessed as photocatalysts for duloxetine's degradation. First, magnetic Fe₃O₄/ TiO₂ nanoparticles were synthesized and then incorporated into PET matrix, which originated from post-consumer bottles, to form PET-TiO₂/Fe₃O₄ composite beads. The synthesized nanocomposites were characterized with various characterization techniques such as FTIR, SEM, XRD and TGA. All composites were capable of degrading the target compound within 60 minutes. Parameters like the Fe₃O₄/TiO₂ content or the mass of catalyst appear to affect the reaction rate. Experiments in higher loaded matrices like wastewater or leachate retard the degradation of the target compound.

Introduction

Heterogeneous photocatalysis is a promising technique for the elimination of organic pollutants from water and wastewater. Based on its photoactivity, low price, stability and availability, TiO₂ powder has become the standard semiconductor used in most of the photocatalytic studies. TiO₂ is usually used in a slurry system, due to its large surface area available for high photocatalytic efficiency [1]. However, the post separation and recovery of the photocatalyst particles after water/wastewater treatment remains a challenge. In this context, techniques that can facilitate the recovery of utilized catalyst will come a long way in making photocatalysis a more environmental-friendly process [2].

To address these challenges, up to now, the immobilization of the TiO₂ catalyst on different supporting materials such as polymers has been successfully applied [3]. Consequently, the main scope of the study was the immobilization of TiO₂ particles on recycled polyethylene terephthalate (rPET). Moreover, the incorporation of Fe₃O₄ in the nanocomposites was also conducted in order to offer facile recovery from the treated water by simple magnetic force and reduce the separation cost. As a result, three different photocatalysts were synthesized with different inorganic filler (10, 30 and 50 wt% Fe₃O₄-TiO₂) and their photocatalytic efficiency was tested towards the elimination of the antidepressant duloxetine. Antidepressants have been detected in surface waters and in treated drinking waters at low concentrations revealing the inefficiency of water treatment technologies to efficiently remove these compounds.

Consequently, the main objectives of the study were (a) to synthesize three different PET/Fe₃O₄/TiO₂ beads (b) to characterize the

nanocomposites with various techniques, (c) to evaluate their effectiveness in degrading duloxetine in aqueous solutions (d) to examine the effect of various factors like the Fe₃O₄/TiO₂ content or the mass of catalyst (e) to evaluate the effect of water matrix on duloxetine's degradation.

Material and Methods

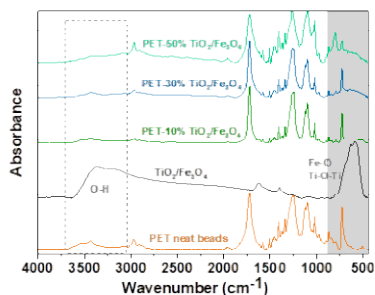
P25 TiO₂ was supplied by Evonik. rPET was provided by post-consumer bottles. Firstly, magnetic Fe₃O₄ nanoparticles were synthesized with the precipitation method. Then, the TiO₂ nanoparticles were decorated with magnetic Fe₃O₄ nanoparticles employing a sol-gel method, and then the hybrid nanoparticles were embedded into the PET matrix, forming the magnetic immobilized PET-TiO₂/Fe₃O₄ composite beads. Photocatalytic experiments were conducted in an Atlas suntest CPS+ pyrex reactor employed with a xenon lamp. Analysis of duloxetine concentration in the treated solution was conducted using a Shimadzu LC-MS system operating in SIM mode at 298 m/z.

Results and Discussion

Various characterization techniques such as such as FTIR (Figure 1a), XRD (Figure 1b), and SEM-EDX, indicated that TiO₂/Fe₃O₄ nanoparticles were successfully immobilized on PET beads. Moreover, the chemical structure of TiO₂/Fe₃O₄ content was not altered after its immobilization. According to SEM micrographs, the EDX analysis and the back scattering detector, the inorganic nanoparticles were uniformly and regularly dispersed in the composite beads. Regarding the thermal performance of the manufactured composite beads, it was proved by DSC and TGA thermographs that the thermal properties of the PET-TiO₂/Fe₃O₄ beads had been slightly altered in accordance with the

content of the inorganic filler. Moreover, from the obtained TGA data we may conclude that the char amount increases by increasing $\text{TiO}_2/\text{Fe}_3\text{O}_4$ content, due to its inorganic and not degrading character.

a)



b)

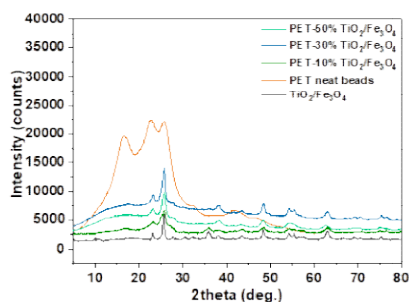


Figure 1. FTIR spectra (a) and XRD patterns (b) of neat PET beads, $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles and $\text{PET}/\text{Fe}_3\text{O}_4/\text{TiO}_2$ beads

Preliminary results revealed that the addition of the catalyst strongly accelerates the degradation of the parent compound while no adsorption was recorded on the magnetic beads surface. Experiments with the different composites showed that increase of the inorganic content causes an increase of the reaction rate (**Figure 2**) while other parameters like the concentration of the catalyst also affect the degradation kinetics.

Conclusions

Three different magnetic $\text{PET}/\text{Fe}_3\text{O}_4/\text{TiO}_2$ composites were successfully synthesized with varying inorganic content (10, 30 and 50 wt% $\text{Fe}_3\text{O}_4/\text{TiO}_2$). All catalysts were efficient in degrading duloxetine, however the $\text{PET}-50\% \text{Fe}_3\text{O}_4/\text{TiO}_2$ composite achieved higher reaction rates and complete degradation of the target compound within 60 minutes of treatment. Other factors like the mass of catalyst or the aqueous matrix also appeared to affect the treatment process.

References

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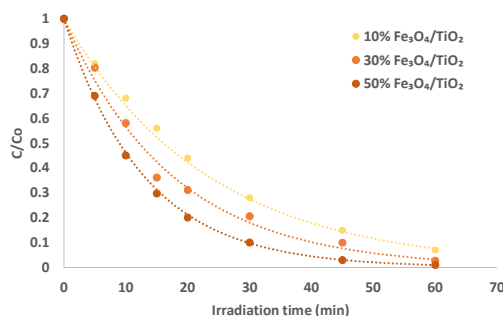


Figure 2. Photocatalytic degradation of duloxetine with different magnetic $\text{PET}/\text{Fe}_3\text{O}_4/\text{TiO}_2$ beads

In order to study the effect of matrix, experiments with the most efficient composite were conducted in wastewater and leachate (**Figure 3**). Obviously, the degradation of the target compound proceeds in a slower rate compared to ultra-pure water due to the scavenging effect of the organic and inorganic constituents [4].

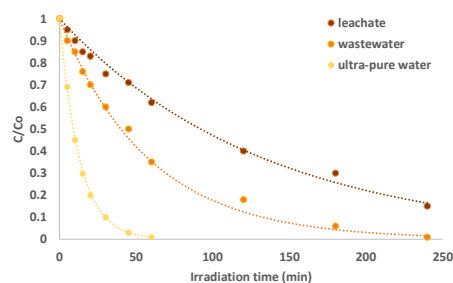


Figure 3 Photocatalytic degradation of duloxetine in different aqueous matrices