# Photocatalytic Degradation Of The Antibiotic Ceftazidime using immobilized $TiO_2$ on Floating Polyethylene Terephthalate Spheres

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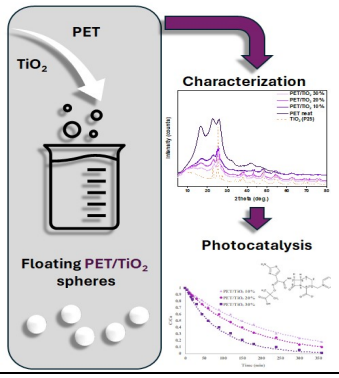


The application of $TiO_2$ as a powder requires energy costing separation stages to remove the catalyst at the end of the process. Thus, immobilization of the catalyst can be an attractive solution. Under this light, three different PET/TiO2 photocatalytic spheres were synthesized and evaluated towards the photocatalytic degradation of the antibiotic ceftazidime. The PET/$TiO_2$ spheres with different contents of $TiO_2$ filler (10% wt, 20% wt and 30% wt) were synthesized by using an anti-solvent precipitation method and were characterized by different techniques, such as FTIR, SEM, XRD, TGA and DSC. Among the different composites, PET/TiO2 30%wt spheres proved to be the most efficient catalyst, achieving almost complete degradation of ceftazidime within 6 h of treatment. The stability and reuse of the synthesized catalysts were also evaluated. Furthermore, the effect of matrix was examined, revealing slower kinetics in high loaded matrices.

## Introduction

Advanced oxidation processes (AOPs) have been widely applied for the elimination of pharmaceuticals from water matrices. Among these various processes, heterogenous photocatalysis is a very promising technique combining many advantages like the ease of use, sustainability, and the eco-friendly nature. One of the most applied catalysts is $TiO_2$ with many benefits like high efficiency, non-toxicity and low cost [1]. However, powdered catalysts such as $TiO_2$ appear to be problematic especially in large-scale units, as they require an energy-consuming post separation step, or they can agglomerate, disperse the incident light flux, or leach into the effluent. In order to overcome these drawbacks, immobilization of the catalyst on various substrates have been explored. Polymers have been successfully employed as matrices for $TiO_2$ immobilization due to their outstanding properties like flexibility, low-cost production, mechanical stability, and durability [2]. Poly(ethylene terephthalate) (PET) has been proved as a dynamic candidate for supporting material in $TiO_2$-photocatalysis due to its low-cost, high mechanical properties, flexibility, recyclability, and omnipresence in our daily life [3].

Under this light, the main scope of this study was to and apply a, recycled, and widely available material for the immobilization of $TiO_2$. The new catalysts were tested towards the photocatalytic degradation of the antibiotic ceftazidime (CFZ). The target compound is one of the most frequently used β-lactam antibiotics presenting low biodegradability and thus surviving wastewater treatment. Consequently, the objectives of the study were (a) to synthesize three different PET/$TiO_2$ catalysts (10% wt, 20% wt and 30% wt $TiO_2$) (b) to characterize them with various techniques, (c) to evaluate their effectiveness in degrading ceftazidime in aqueous solutions (d) to examine their recyclability and (e) to evaluate the effect of water matrix on ceftazidime's degradation.

## Material and Methods

PET was provided by post-consumer bottles. P25-$TiO_2$ from Evonik was used as catalyst. LC–MS grade solvents (methanol/water) were supplied by Merck and Fisher. CFZ was of high purity (>98%) and supplied by Sigma-Aldrich (Germany). Ultra-pure water was used for the preparation of all solutions throughout the experimental work. For the preparation of the catalytic spheres via the precipitation into an anti-solvent, a mixture of chloroform/trifluoroacetic acid (85/15% v/v, Alfa Aesar, pur. >99%) was utilized to dissolve the post-consumer PET bottles, whereas acetone (Sigma Aldrich, ≥99.5%) was used as the anti-solvent. The photocatalytic experiments were conducted using an Atlas suntest CPS+ reactor employed with a xenon lamp. Analysis was performed using a Shimadzu LC-MS system.

## Results and Discussion

As far as the characterization of the synthesized PET/$TiO_2$ is concerned, FTIR, XRD, SEM, DSC and TGA analysis proved that $TiO_2$ was successfully immobilized on the PET spheres. TGA and DSC thermographs revealed that the thermal properties of PET have not been altered after the immobilization of the catalyst indicating its efficiency for application as photocatalytic support. According to SEM images the semiconductor was uniformly dispersed in the composite spheres, as also proven by the EDX analysis and the back scattering detector. Finally, XRD patterns (**Figure 1**) showed that crystallinity of the composite materials is gradually decreased due to the reduced ability of PET macromolecules to be folded in crystalline structure.

The photocatalytic degradation of ceftazidime under the three PET/$TiO_2$ catalysts id depicted in figure 2. As it can be observed better results were acquired with the catalyst with the higher inorganic content (PET/TiO2 30%wt), eliminating the target compound within 360 min of treatment.

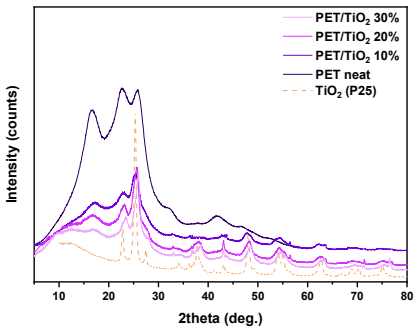


**Figure 1.** XRD patterns of neat PET spheres, PET/$TiO_2$ composite spheres, and $TiO_2$ (P25) nanoparticles

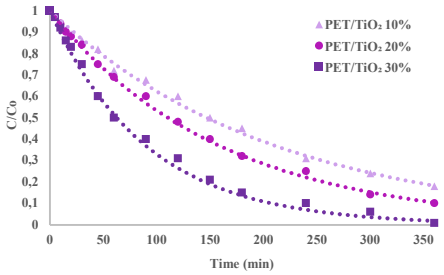


**Figure 2.** Photocatalytic degradation of CFZ in the presence of the three different PET/$TiO_2$ spheres.

The synthesized catalysts were also tested for two consecutive cycles exhibiting good stability (**Table 1**), however, after the second cycle their performance was decreased due to a decay on the polymeric surface caused by the attack of hydroxyl radicals.

Application of the most efficient catalyst on the degradation of CFZ in more loaded matrices (wastewater, leachate) revealed that more prolonged times are required for complete degradation.

**Table 1.** Photocatalytic rate constants (k, $min^{-1}$) of CFZ in the presence of the three PET/$TiO_2$ spheres for two consecutive cycles and the calculated Δk (%) values.

| | PET/$TiO_2$ 10%wt | | | PET/$TiO_2$ 20%wt | | | PET/$TiO_2$ 30%wt | | |
|---|---|---|---|---|---|---|---|---|---|
| **Compound** | **1st run** | **2nd run** | **Δk%** | **1st run** | **2nd run** | **Δk%** | **1st run** | **2nd run** | **Δk%** |
| Ceftazidime | 0.0050 | 0.0049 | 2% | 0.0067 | 0.0063 | 5.9% | 0.0110 | 0.0108 | 1.8% |

## Conclusions

Immobilization of $TiO_2$ was successfully conducted on recycled PET spheres in three different percentages (10, 20 and 30% wt). All synthesized catalysts were able to degrade the antibiotic ceftazidime however higher efficiency was exhibited by the PET/$TiO_2$ 30%wt catalyst. The nanocomposites appear to be stable for two consecutive cycles while their performance in more loaded matrices is retarded, requiring more prolonged irradiation times for complete degradation of the target compound.

***References***

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