

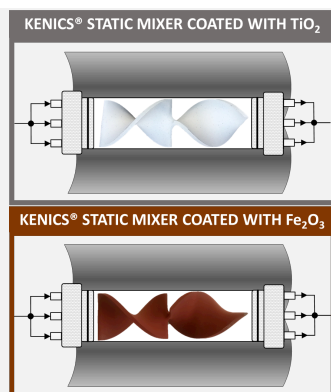
Intensification of Heterogeneous Photocatalysis by Applying a Kenics® Static Mixer as Catalyst Support

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Despite scientific community's efforts, overcoming mass and photon transfer limitations remain a main challenge for heterogeneous photocatalysis with immobilized catalysts. Here, a Kenics® static mixer was used for the first time as catalyst support for heterogeneous photocatalysis in tubular reactors. This permitted not only to take advantage of the enhanced mass transfer supplied by the intense mixing, but also to provide a total illumination of the photocatalyst surface area with front-irradiation mechanism by using sunlight combined with compound parabolic collectors. Stainless steel Kenics® static mixers were coated with TiO₂ or Fe₂O₃ photocatalyst and applied for oxytetracycline (OTC) degradation in aqueous solutions. The photocatalytic efficiency was evaluated as a function of different parameters: (i) catalyst deposition technique (dip coating or spray coating), (ii) photocatalyst film thickness, (iii) oxidant (H₂O₂) concentration, and

Introduction

Heterogeneous photocatalysis with immobilized catalysts have been recognized as a very promising technology for the degradation of organic contaminants in water. A multitude of support materials has been tested, such as those based on silica, quartz, cellulose, ceramics, clays, stainless steel or organic polymers [1], and various support shapes have been adopted, such as plates [2], spheres [3], rings [4], nanotubes [5], fibers [6] and monolithic structures [7]. Despite all the efforts, overcoming mass and photon transfer limitations remain a main challenge for heterogeneous photocatalysis with immobilized catalysts. Mass transfer problems can be solved by applying static mixers. Commercial static mixers, such as Kenics®, Sulzer® and Karman®, have been widely applied in chemical, petrochemical, pharmaceutical, food engineering, pulp and paper, and water and wastewater treatment industries [8]. The Kenics® static mixer was the first static mixer produced and is broadly considered the leader in design and technology. It is composed of alternated right- and left-hand helical mixing elements that direct the fluid flow radially toward the pipe walls and back to the center. Simultaneously, patterns of flow division are produced, with the number of divisions growing exponentially for each succeeding element. Intense mixing is provided under both laminar and turbulent flow conditions. By using laminar flow regime instead of turbulent, the friction between fluid and catalyst surface is reduced, preventing catalyst detachment from the support, and the energy for liquid pump operation is diminished. To our knowledge, the use of commercial static mixers in heterogeneous photocatalytic reactors only refers to the employment of catalysts in suspension.

The current study wanted to go further, focusing on the use a stainless steel Kenics® static mixer as catalyst support for heterogeneous photocatalysis in tubular reactors. This allowed not only to improve mass transfer due to a high degree of mixing, but also to provide a total illumination of the photocatalyst surface area with front-irradiation when using sunlight combined with compound parabolic collectors (CPCs). Sanded stainless steel Kenics® static mixers were coated with TiO₂ or Fe₂O₃ photocatalyst and utilized for the degradation of a model compound – antibiotic oxytetracycline (OTC) – in aqueous solution. The photocatalytic efficiency was evaluated as a function of different parameters: (i) catalyst deposition technique (dip coating or spray coating), (ii) photocatalyst film thickness (amount of photocatalyst deposited in the static mixer surface), (iii) oxidant (H₂O₂) concentration, and (iv) number of static mixing elements.

Material and Methods

TiO₂ (Aeroxide® P25 powder) and Fe₂O₃ aqueous suspensions of 2% (w/v) with the addition of two drops of TritonTM X-100 per 100 mL of aqueous suspension were prepared. TiO₂ deposition was carried out by dip or spray coating methods, while Fe₂O₃ deposition was performed only by spray coating technique. The dip coating method was performed in an automatic dip coating unit RDC 15 from Bungard Elektronik using a speed of insertion of 8 cm min⁻¹, a speed of drawing of 3 cm min⁻¹ and a dipping time of 30 s. One, five or ten dips were executed. After each layer deposition, the static mixer was dried at 60 °C for 30 min. The spray coating method employed a nozzle that sprayed the catalyst suspension over the static mixer surface

while it was placed in a heating plate at 200 °C. The amount of catalyst was controlled by the application of 25, 50 or 75 mL of catalyst aqueous suspension to get a catalyst amount of ≈ 0.5 , ≈ 1.0 or ≈ 1.5 g, respectively. After spray deposition, the static mixer was dried on the heating plate for 20 min and then cooled at room temperature.

Two flow systems were applied: one of 1.8 L capacity and the other of 5.5 L capacity. They were mainly composed of: (i) a jet photoreactor made of borosilicate tube with 0.271 L or 0.719 L capacity allocated in the focus of a CPC structure and filled with a Kenics® static mixer with two or six helical mixing elements, respectively (static mixer volume of 31 or 93 cm³, and surface area of 190 or 570 cm², respectively), and (ii) a recirculation cylindrical glass vessel thermostatically controlled and magnetically stirred. For the system with two static mixing elements it was used simulated sunlight as radiation source (solar radiation simulator Atlas, model Suntest XLS+), while for the system equipped with six static mixing elements it was used natural sunlight as radiation source.

OTC was determined by reversed-phase HPLC. Dissolved organic carbon (DOC) was determined in a Shimadzu TOC-V_{CSN} analyzer.

Results and Discussion

Firstly, the heterogeneous TiO₂ photocatalysis was assessed by varying the photocatalyst deposition method, the photocatalyst dosage, and the amount of H₂O₂ added as electron acceptor to avoid electron(e⁻)/hole(h⁺) pairs recombination. Regardless of the TiO₂ dosage, faster OTC and DOC removals were attained for TiO₂ photocatalysis using the spray coating technique compared to the dip coating method. This suggests the achievement of better TiO₂ film morphological properties using the former technique. By using spray coating, the OTC removal increased for higher TiO₂ dosages until the application of 50 mL of TiO₂ suspension. For this catalyst amount, a catalyst film, able to completely absorb the front-irradiation, is likely to be generated. Thicker catalyst films did not increase the degradation rate since the diffusional length of e⁻/h⁺ pairs to the catalyst-liquid interface remained unaffected. H₂O₂ amounts of 77 and 154 mg L⁻¹ were applied. Maximum OTC abatement was achieved in the presence of 77 mg L⁻¹ of H₂O₂, indicating the maximization of the inhibition of e⁻/h⁺ pairs recombination. Moreover, the reuse ability was examined by carrying out three consecutive OTC degradations using the same catalyst film deposited in the static mixer and fresh OTC solutions. Similar OTC and DOC decays were achieved, thereby indicating no deterioration of the TiO₂ catalyst film. Furthermore, no TiO₂ leaching was occurring since null absorbances were detected during reactions, measured at a wavelength of 500 nm, for which the absorbance of the TiO₂ slurry is detected even in very small

amounts.

Afterwards, the heterogeneous Fe₂O₃ photocatalysis in the presence of H₂O₂ and using the spray coating method was assessed by changing the photocatalyst dosage, and also the amount of H₂O₂. Faster OTC and DOC decays were achieved for higher Fe₂O₃ amounts, which can be ascribed not only to the generation of more e⁻/h⁺ pairs but mainly to the improvement of photo-Fenton reactions in heterogeneous phase and also in homogeneous phase since some iron leaching occurred in all Fe₂O₃ experiments, being more pronounced for higher catalyst dosages (0.30, 0.58 and 0.68 mg L⁻¹ of total dissolved iron for experiments using 25, 50 and 75 mL of Fe₂O₃ suspension, respectively). The improvement on OTC abatement from 50 to 75 mL of Fe₂O₃ suspension was smoother, suggesting the absorption of almost all front-irradiation by the catalyst film formed by the application of 50 mL of Fe₂O₃ suspension. As regards the influence of H₂O₂ concentration, increasing OTC removals were achieved for rising H₂O₂ amounts from 0 to 154 mg L⁻¹, which can be attributed not only to the inhibition of e⁻/h⁺ pairs recombination and enhancement of heterogeneous photo-Fenton reactions, but mainly to the occurrence of homogeneous photo-Fenton reactions in higher extent since a higher amount of iron was leached in the trial using 154 mg L⁻¹ of H₂O₂ compared to the one using 77 mg L⁻¹ of H₂O₂ (0.68 mg L⁻¹ versus 0.24 mg L⁻¹). The reuse ability was assessed by carrying out three consecutive Fe₂O₃/H₂O₂/UV reactions using the same catalyst film produced by spray coating with 75 mL of Fe₂O₃ suspension. Similar OTC and DOC decays were attained, despite the aforementioned reported iron leaching.

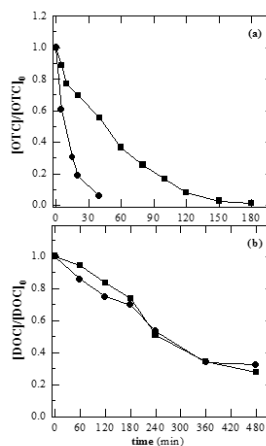


Figure 1. Comparison of TiO₂ photocatalysis using 50 mL of TiO₂ suspension deposited by spray coating and 77 mg L⁻¹ of H₂O₂ (■) and Fe₂O₃ photocatalysis using 75 mL of Fe₂O₃ suspension deposited by spray coating and 154 mg L⁻¹ of H₂O₂ (●) in terms of normalized OTC decay (a) and normalized DOC decay (b) as a function of time for the

degradation of 20.0 mg L⁻¹ OTC solutions at the system using two static mixing elements, pH=4.5, 25 °C and flow rate of 100 L h⁻¹.

The application of TiO₂ or Fe₂O₃ as photocatalyst was compared. Fe₂O₃ photocatalyst led to faster OTC removals compared to TiO₂ (Fig. 1a), exhibiting a degradation rate of 0.3 mmol_{OTC} m⁻³_{illuminated volume} s⁻¹ that contrasts with a value of 0.05 mmol_{OTC} m⁻³_{illuminated volume} s⁻¹ for TiO₂. This can be mainly ascribed to the action of hydroxyl radicals produced from photo-Fenton reactions in Fe₂O₃ photocatalysis, not only in heterogeneous phase but also in the homogeneous one since 0.70 mg L⁻¹ of total dissolved iron were detected after 480 min of reaction. Despite the faster OTC removal for Fe₂O₃ photocatalysis, both catalysts showed similar ability to degrade the generated byproducts (Fig. 1b). For both catalysts,

Conclusions

TiO₂ and Fe₂O₃ photocatalysts were successfully supported on the surface of sanded stainless steel Kenics[®] static mixers using spray coating technique. Both catalyst films could be reused in photocatalytic processes with fresh solutions without loss of OTC degradation ability. However, the attachment of TiO₂ to the static mixer surface was stronger compared to Fe₂O₃, for which some iron leaching was noticed. The iron leaching may have contributed to the higher OTC removal achieved for the Fe₂O₃ photocatalyst since hydroxyl radicals were produced from homogenous photo-Fenton reactions. Degradation rates of 0.3 and 0.05 mmol_{OTC} m⁻³_{illuminated volume} s⁻¹ were achieved for Fe₂O₃ and TiO₂ photocatalysis, respectively. The mineralization rate was similar for both photocatalysts. The use of spray coating as TiO₂ deposition method led to faster OTC degradations compared to dip coating technique. Maximum OTC degradation rates were attained for the deposition of 50 mL of TiO₂ suspension and 75 mL of Fe₂O₃ suspension using spray coating technique. The addition of H₂O₂ to the solution dramatically improved the OTC degradation for TiO₂ and Fe₂O₃ photocatalysis, with highest degradation rates achieved for 77 and 154 mg L⁻¹ of H₂O₂, respectively. The increase on the number of static mixing elements from two to six did not improved the OTC degradation rate.

Acknowledgments

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References

- [1] J. Coronado, F. Fresno, M.D. Hernández-Alonso, R. Portela, *Design of Advanced Photocatalytic Materials for Energy and Environmental Applications, Green Energy and Technology*, Springer-Verlag London, United Kingdom, 2013.
- [2] C.-H. Hung, C. Yuan, H.-W. Li, *Journal of Hazardous Materials*, 322 (2017) 243.
- [3] N. Miranda-García, S. Suárez, B. Sánchez, J.M. Coronado, S. Malato, M.I. Maldonado, *Applied Catalysis. B: Environmental*, 103 (2011) 294.
- [4] M.J. Sampaio, C.G. Silva, A.M.T. Silva, V.J.P. Vilar, R.A.R. Boaventura, J.L. Faria, *Chemical Engineering Journal*, 224 (2013) 32.
- [5] R.-a. Doong, C.-Y. Liao, *Separation and Purification Technology*, 179 (2017) 403.
- [6] M.J. Arlos, M.M. Hatat-Fraile, R. Liang, L.M. Bragg, N.Y. Zhou, S.A. Andrews, M.R. Servos, *Water Research*, 101 (2016) 351.
- [7] B.A. Marinho, R.O. Cristóvão, R. Djellabi, J.M. Loureiro, R.A.R. Boaventura, V.J.P. Vilar, *Applied Catalysis B: Environmental*, 203 (2017) 18.
- [8] R.K. Thakur, C. Vial, K.D.P. Nigam, E.B. Nauman, G. Djelveh, *Chemical Engineering Research and Design*, 81 (2003) 787.