

Oxidation by products

The assessment of contaminants disappearance is not enough to ensure the absence of residual products because the photocatalytic treatment may give rise to a variety of organic intermediates which can themselves be toxic, and in some cases, more persistent than the original substrate.

To identify by products formed by photocatalytic treatment is not an easy task, however fragmentation pathways studies are available for several pharmaceuticals as reported in Table 2. Photocatalysis would result in the mineralization of organic carbon and release of nitrogen and chlorides from the molecule. Photocatalytic transformation of the nitrogen moieties to N_2 , NH_4^+ , NO_2^- or NO_3^- depends on the initial oxidation state of nitrogen and on the structure of the organic.

The removal of 50 mg L^{-1} VAN solution yields maximum concentrations of 2.45 and $2.53 \text{ mg N-NH}_3 \text{ L}^{-1}$ after 120 min of photocatalytic oxidation using 0.1 and $0.2 \text{ g TiO}_2 \text{ L}^{-1}$, respectively. When $0.2 \text{ g TiO}_2 \text{ L}^{-1}$ were applied up to 87% of the stoichiometric amount of chloride was reached within 120 min of irradiation, corresponding to $0.087 \text{ mmol L}^{-1}$ (Lofrano et al., 2014). Nitrate formation was not observed throughout the photocatalytic oxidation process, probably due to insufficient irradiation time. Accordingly Elmolla and Chaudhuri (2010) did not detect nitrate ions during the first 6 h of photocatalytic oxidation of AMX, AMP and CLX. No evidence was found by Abellan et al. (2007) about the presence of the anions NO_2^- or NO_3^- within 10 h of photocatalytic treatment of 100 mg L^{-1} SMX solution.

Table 2. Fragmentation pathway studies of photocatalytic treated pharmaceuticals

ACY	Li et al., 2016
AMI	Giancotti et al., 2008
AMX	Klauson et al., 2010
ATL	Ji et al., 2013
B	Giancotti et al., 2008
CAP	Garcia-Segura et al., 2014; Gao et al., 2016
CDN	Kuo et al., 2016

CIP	An et al., 2010
DCF	Calza et al., 2006; Martínez et al., 2011, Michael et al., 2014
ERY	Gao et al., 2016
ERYA	Cai et al., 2014
ETA	Giancotti et al., 2008
F	Giancotti et al., 2008
IBP	Choina et al., 2013, Michael et al., 2014
LNC	Gao et al., 2016
LZP	Sousa et al., 2013
NPX	Kanakaraju et al., 2015
OFL	Jimenez-Villarin et al., 2016
PZQ	Čizmic et al., 2016
RIF	Gao et al., 2016
SMT	Fukahori et al., 2015
TC	Gao et al., 2016

Future challenges

The removal of emerging contaminants from wastewater is urgently required and even more necessary for wastewater reuse. In order to meet this challenge, the future of nano catalysts is to be used in development of green technologies with high levels of removal efficiency of contaminants and energy saving to facilitate direct water reuse.

Knowing that photocatalytic processes are managed by different parameters: pH, irradiance/wavelength, catalyst loading, surface area, surface charge, concentration and nature of substrate/pollutant, reactor geometry, etc , many efforts have been faced by the scientific community trying to correlate catalysts properties with photocatalytic activity, and the resulting outcomes always pointed out a mixed balance between certain surface, electronic and structural properties that seemed to be playing important roles on the overall photocatalytic behaviour, where, simultaneously, a very significant dependence on the photoreactor geometry and the corresponding

operational conditions appeared to be also taking place. Therefore, the photocatalytic activity of every catalyst is essentially specific and related to the chemical nature of pollutant.

Nanomaterials can be immobilized in the form of nanostructured thin films on different substrates in order to evaluate their potential applications in combined membrane-photocatalytic treatments.

In terms of integration of these nanostructured photocatalytic films on membrane, research is still in its beginning and much remains to be done. Judicious engineering of the semiconductor nanostructured materials may significantly enhance to the development of an green technology, energy saving and highly efficient for emerging contaminants removal.

References

- Abellán M.N., Bayarri B., Giménez J., Costa J., (2007) Photocatalytic degradation of sulfamethoxazole in aqueous suspension of TiO₂, *Appl. Catal. B: Environ.* 74 233–241.
- Achilleos, A., Hapeshi, E., Xekoukoulotakis, N. P., Mantzavinos, D., & Fatta-Kassinos, D. (2010). Factors affecting diclofenac decomposition in water by UV-A/TiO₂ photocatalysis. *Chemical Engineering Journal*, 161(1), 53-59.
- Agarwal, S., Tyagi, I., Gupta, V. K., Sohrabi, M., Mohammadi, S., Golikand, A. N., & Fakhri, A. (2017). Iron doped SnO₂/Co₃O₄ nanocomposites synthesized by sol-gel and precipitation method for metronidazole antibiotic degradation. *Materials Science and Engineering: C*, 70, 178-183.
- Akiyama T, Savin MC. (2010) Populations of antibiotic-resistant coliform bacteria change rapidly in a wastewater effluent dominated stream. *Sci Total Environ.* 408:6192-6201.
- An, T., Yang, H., Li, G., Song, W., Cooper, W. J., & Nie, X. (2010). Kinetics and mechanism of advanced oxidation processes (AOPs) in degradation of ciprofloxacin in water. *Applied Catalysis B: Environmental*, 94(3), 288-294.
- Barnes, K. K., Kolpin, D. W., Furlong, E. T., Zaugg, S. D., Meyer, M. T., & Barber, L. B. (2008a). A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States—I) Groundwater. *Science of the Total Environment*, 402(2), 192-200.

Benotti M.J, Trenholm R.A , Vanderford B.J , Holady J.C., Stanford B.D , Snyder S.A. (2009), Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water, 43, 547–603.

Hua-Lin Cai H.L., Feng Wang F., Huan-De Li H.D., Wen-Xing Peng W.X., Rong-Hua Zhu R.H, Deng Y., Jiang P., Yan M., Hu S.M., Lei S.Y., Chen C. (2014) Quantitative analysis of erythromycylamine in human plasma byliquid chromatography-tandem mass spectrometry and its applicationin a bioequivalence study of dirithromycin enteric-coated tablets witha special focus on the fragmentation pattern and carryover effect, Journal of Chromatography B, 947– 948, 156 – 163.

Calza, P., Sakkas, V. A., Medana, C., Baiocchi, C., Dimou, A., Pelizzetti, E., & Albanis, T. (2006). Photocatalytic degradation study of diclofenac over aqueous TiO₂ suspensions. Applied Catalysis B: Environmental, 67(3), 197-205.

Carbajo, J., Jiménez, M., Miralles, S., Malato, S., Faraldo, M., & Bahamonde, A. (2016). Study of application of titania catalysts on solar photocatalysis: Influence of type of pollutants and water matrices. *Chemical Engineering Journal*, 291, 64-73.

Chen, M., & Chu, W. (2012). Degradation of antibiotic norfloxacin in aqueous solution by visible-light-mediated C-TiO₂ photocatalysis. Journal of hazardous materials, 219, 183-189.

Čizmić M., Ljubas D, Ćurković L., Škorić I., Babić S. (2016) Kinetics and degradation pathways of photolytic and photocatalytic oxidation of the antihelmintic drug praziquantel, Journal of Hazardous Materials (in press), <http://dx.doi.org/10.1016/j.jhazmat.2016.04.065>

Choina, J., Kosslick, H., Fischer, C., Flechsig, G. U., Frunza, L., & Schulz, A. (2013). Photocatalytic decomposition of pharmaceutical ibuprofen pollutions in water over titania catalyst. Applied Catalysis B: Environmental, 129, 589-598.

Czech, B., & Buda, W. (2015). Photocatalytic treatment of pharmaceutical wastewater using new multiwall-carbon nanotubes/TiO₂/SiO₂ nanocomposites. Environmental research, 137, 176-184.

Daneshvar N., Salari D., Khataee A.R., (2004) Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂, J. Photochem. Photobiol. A: Chem. 162 317–322.

Elmolla, E. S., & Chaudhuri, M. (2010). Degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution by the UV/ZnO photocatalytic process. *Journal of hazardous materials*, 173(1), 445-449.

El-Sayed, G. O., Dessouki, H. A., Jahin, H. S., & Ibrahem, S. S. (2014). Photocatalytic Degradation of Metronidazole in Aqueous Solutions by Copper oxide nanoparticles. *Journal of Basic and Environmental Sciences*, 1, 102-110.

Fuentefria DB, Ferreira AE, Corcao G. (2011) Antibiotic-resistant *Pseudomonas aeruginosa* from hospital wastewater and superficial water: are they genetically related? *J Environ Manage*. 92:250-255.

Fukahori S., Fujiwara T. (2015) Photocatalytic decomposition behavior and reaction pathway of sulfamethazine antibiotic using TiO₂, *Journal of Environmental Management*, 157 103 – 110

Gao B., Dong S., Liu J., Liu L., Feng Q., Tan N., Liu T., Bo L., Wang L.(2016), Identification of intermediates and transformation pathways derived from photocatalytic degradation of five antibiotics on ZnIn₂S₄, *Chemical Engineering Journal*, 304, 826 – 840.

Garcia-Segura, S., Cavalcanti, E. B., & Brillas, E. (2014). Mineralization of the antibiotic chloramphenicol by solar photoelectro-Fenton: From stirred tank reactor to solar pre-pilot plant. *Applied Catalysis B: Environmental*, 144, 588-598.

Giancotti V., Medana C., Aigotti M., Pazzi M., Baiocchi C. (2008) LC-high-resolution multiple stage spectrometric analysis of diuretic compounds Unusual mass fragmentation pathways, *Journal of Pharmaceutical and Biomedical Analysis*, 48, 462 - 466

Giraldo-Aguirre A.L., Erazo-Erazo E.D., Flórez-Acosta O.A., Serna-Galvis E.A., Torres-Palma R.A. (2015), TiO₂ photocatalysis applied to the degradation and antimicrobial activity removal of oxacillin: Evaluation of matrix components, experimental parameters, degradation pathways and identification of organics by-products, *Journal of Photochemistry and Photobiology A: Chemistry*, 311, 95–103

Gomez-Solís, C., Ballesteros, J.C., Torres-Martínez, L.M., Juarez-Ramírez, I., Torres, L.A.D., Zarazua-Morin, M.E., Lee, S.W., 2015. Rapid synthesis of ZnO nano-corncores from Nital solution and its application in the photodegradation of Methyl Orange. *J. Photochem. Photobiol. A Chem.* 298, 49e54.

Guillard C., Lachheb H., Houas A., Ksibi M., Elaloui E., Herrmann J.M., Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO₂ comparison of the efficiency of powder and supported TiO₂, *J. Photochem. Photobiol. A: Chem.* 158 (2003) 27–36.

Hinojosa-Reyes M., Arriaga S., Diaz-Torres L.A., Rodríguez-González V., Gas-phase photocatalytic decomposition of ethylbenzene over perlite granules coated with indium doped TiO₂, *Chem. Eng. J.* 224 (2013) 106–113, doi:<http://dx.doi.org/10.1016/j.cej.2013.01.066>.

Hu, X., Yang, J., & Zhang, J. (2011). Magnetic loading of TiO₂/SiO₂/Fe₃O₄ nanoparticles on electrode surface for photoelectrocatalytic degradation of diclofenac. *Journal of hazardous materials*, 196, 220-227.

Klauson, D., Babkina, J., Stepanova, K., Krichevskaya, M., & Preis, S. (2010). Aqueous photocatalytic oxidation of amoxicillin. *Catalysis Today*, 151(1), 39-45.

Isidori M., Bellotta M., Cangiano M., Parrella A., (2009) Estrogenic activity of pharmaceuticals in the aquatic environment, *Environ. Int.* 35 826-829.

Ishibashi I., Fujishima A., Watanabe T., Hashimoto K. (2000) Quantum yields of active oxidative species formed on TiO₂ photocatalyst, *J. Photochem. Photobiol. A: Chem.* 134 139–142.

Ji Y., Zhou L., Ferronato C., Yang X., Salvador A., Zeng C., Chovelon J.M. (2013) Photocatalytic degradation of atenolol in aqueous titanium dioxide suspensions: Kinetics, intermediates and degradation pathways, *Journal of Photochemistry and Photobiology A: Chemistry*, 254 35 - 44.

Jimenez-Villarin J., Serra-Clusellas A., Martínez C., Conesa A., Garcia-Montaña J., Moyano E. (2016) Liquid chromatography coupled to tandem and high resolution massspectrometry for the characterisation of ofloxacin transformationproducts after titanium dioxide photocatalysis, *Journal of Chromatography A*, 1443, 201 – 210.

Kanakaraju, D., Kockler, J., Motti, C. A., Glass, B. D., & Oelgemöller, M. (2015). Titanium dioxide/zeolite integrated photocatalytic adsorbents for the degradation of amoxicillin. *Applied Catalysis B: Environmental*, 166, 45-55.

Kanakaraju, D., Motti, C. A., Glass, B. D., & Oelgemöller, M. (2015). TiO₂ photocatalysis of naproxen: effect of the water matrix, anions and diclofenac on degradation rates. *Chemosphere*, 139, 579-588.

Kuo C.S., Lin C.F., Hong P.K.A. (2016) Photocatalytic mineralization of codeine by UV-A/TiO₂ – Kinetics,intermediates, and pathways, *Journal of Hazardous Materials*, 301, 137–144

Lair A., Ferronato C., Chovelon J.M., Herrmann J.M., (2008) Naphthalene degradation in water by heterogeneous photocatalysis: an investigation of the influence of inorganic anions, *J. Photochem. Photobiol. A: Chem.* 193 193–203.

Li G., Nie X., Gao Y., An T. (2016) Can environmental pharmaceuticals be photocatalytically degraded and completely mineralized in water using g-C₃N₄/TiO₂ under visible light irradiation?—Implications of persistent toxic intermediates. *Applied Catalysis B: Environmental* 180, 726 – 732.

X. Lu, J. Jiang, K. Sun, D. Cui, Applied surface science characterization and photocatalytic activity of Zn₂ +_ TiO₂/AC composite photocatalyst, *Appl. Surf. Sci.* 258 (2011) 1656–1661, doi:<http://dx.doi.org/10.1016/j.apsusc.2011.09.042>.

Martínez, C., Fernández, M. I., Santaballa, J. A., & Faria, J. (2011). Aqueous degradation of diclofenac by heterogeneous photocatalysis using nanostructured materials. *Applied Catalysis B: Environmental*, 107(1), 110-118.

F. Méndez-Arriaga, S. Esplugas, J. Giménez, Photocatalytic degradation of nonsteroidal anti-inflammatory drugs with TiO₂ and simulated solar irradiation, *Water Res.* 42 (2008) 585–594.

Mboula, V. M., Hequet, V., Gru, Y., Colin, R., & Andres, Y. (2012). Assessment of the efficiency of photocatalysis on tetracycline biodegradation. *Journal of hazardous materials*, 209, 355-364.

Michael I., Achilleos A., Lambropoulou D., Osorio Torrens V., Pérez S., Petrović M., Barceló D., Fatta-Kassinios D (2014) Proposed transformation pathway and evolution profile of diclofenac and ibuprofen transformation products during (sono)photocatalysis, Applied Catalysis B: Environmental 147, 1015 – 1027.

Mitoraj, D., & Kisch, H. (2008). the nature of nitrogen-modified titanium dioxide photocatalysts active in visible light. Angewandte Chemie International Edition, 47(51), 9975-9978.

Mitoraj, D., & Kisch, H. (2010). On the Mechanism of Urea-Induced Titania Modification. Chemistry—A European Journal, 16(1), 261-269.

Moustakas, N. G., Kontos, A. G., Likodimos, V., Katsaros, F., Boukos, N., Tsoutsou, D., ... & Falaras, P. (2013). Inorganic–organic core–shell titania nanoparticles for efficient visible light activated photocatalysis. Applied Catalysis B: Environmental, 130, 14-24.

Nasuhoglu, D., Rodayan, A., Berk, D., & Yargeau, V. (2012). Removal of the antibiotic levofloxacin (LEVO) in water by ozonation and TiO₂ photocatalysis. Chemical Engineering Journal, 189, 41-48.

Paola A.D., Addamo M., Augugliaro V., García-López E., Loddo V., Marcì G., Palmisano L. (2006) Photodegradation of lincomycin in aqueous solution, Inter. J. Photoenergy 1–6, Article ID 47418.

Palominos R, Freer J, Mondaca MA, Mansilla HD. Evidence for hole participation during the photocatalytic oxidation of the antibiotic flumequine. J Photochem Photobiol Chem. 2008;193:139–145

Paul, T., Dodd, M. C., & Strathmann, T. J. (2010). Photolytic and photocatalytic decomposition of aqueous ciprofloxacin: transformation products and residual antibacterial activity. Water Research, 44(10), 3121-3132.

Pelaez, M., Nolan, N. T., Pillai, S. C., Seery, M. K., Falaras, P., Kontos, A. G., ... & Entezari, M. H. (2012). A review on the visible light active titanium dioxide photocatalysts for environmental applications. Applied Catalysis B: Environmental, 125, 331-349.

Pérez-Estrada, L. A., Maldonado, M. I., Gernjak, W., Agüera, A., Fernández-Alba, A. R., Ballesteros, M. M., & Malato, S. (2005). Decomposition of diclofenac by solar driven photocatalysis at pilot plant scale. *Catalysis Today*, 101(3), 219-226.

Rizzo, L., Meric, S., Kassinos, D., Guida, M., Russo, F., & Belgiorno, V. (2009). Degradation of diclofenac by TiO₂ photocatalysis: UV absorbance kinetics and process evaluation through a set of toxicity bioassays. *Water Research*, 43(4), 979-988.

Xekoukoulotakis N., Xinidis N., Chroni M., Mantzavinos D., Venieri D., Hapeshi E., Fatta-Kassinos D., UV-A/TiO₂ photocatalytic decomposition of erythromycin in water: factors affecting mineralization and antibiotic activity, *Catal. Today* 151 (2010) 29-33.

Sakthivel TS., Neppolian B., Shankar M.V., Arabindoo B., Palanichamy M., Murugesan V. (2011) , Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO₂, *Sol. Energy Mater. Sol. Cells* 77 (2003)

Salaeh, S., Perisic, D. J., Biosic, M., Kusic, H., Babic, S., Stangar, U. L., ... & Bozic, A. L. (2016). Diclofenac removal by simulated solar assisted photocatalysis using TiO₂-based zeolite catalyst; mechanisms, pathways and environmental aspects. *Chemical Engineering Journal*, 304, 289-302.

Sousa M.A., Lacina O., Hrádková P., Pulkrabová J., Vilar V.J.P., Gonçalves C., Boaventura R.A.R., Hajšlová J., Alpendurada M.F. (2013) Lorazepam photofate under photolysis and TiO₂-assisted photocatalysis: Identification and evolution profiles of by-products formed during phototreatment of a WWTP effluent, *Water Research*, 47, 5584 – 5593.

Vilar V.J.P., Boaventura R.A.R., Faria J.L., Photocatalytic activity of TiO₂-coated glass raschig rings on the degradation of phenolic derivatives under simulated solar light irradiation, *Chem. Eng. J.* 224 (2013) 32–38, doi:<http://dx.doi.org/10.1016/j.cej.2012.11.027>.

Yap P.-S., Lim T.-T., M. Srinivasan, Nitrogen-doped TiO₂/AC bi-functional composite prepared by two-stage calcination for enhanced synergistic re-moval of hydrophobic pollutant using solar irradiation, *Catal. Today* 161 (2011) 46–52, doi:<http://dx.doi.org/10.1016/j.cattod.2010.09.024>

Van Doorslaer X., Demeestere K., Heynderickx P.M., Van Langenhove H., Dewulf J. (2011) UV-A and UV-C induced photolytic and photocatalytic degradation of aqueous ciprofloxacin and moxifloxacin: reaction kinetics and role of adsorption, *Appl. Catal.B: Environ.* 101 (2011) 540–547.

Van Doorslaer, X., Haylamicheal, I. D., Dewulf, J., Van Langenhove, H., Janssen, C. R., & Demeestere, K. (2015). Heterogeneous photocatalysis of moxifloxacin in water: Chemical transformation and ecotoxicity. *Chemosphere*, 119, S75-S80.

Yahiat, S., Fourcade, F., Brosillon, S., & Amrane, A. (2011). Removal of antibiotics by an integrated process coupling photocatalysis and biological treatment—case of tetracycline and tylosin. *International Biodeterioration & Biodegradation*, 65(7), 997-1003.

Yang, L., Liya, E. Y., & Ray, M. B. (2008). Degradation of paracetamol in aqueous solutions by TiO₂ photocatalysis. *Water research*, 42(13), 3480-3488.

Zhang, J., Fu, D., Xu, Y., & Liu, C. (2010). Optimization of parameters on photocatalytic degradation of chloramphenicol using TiO₂ as photocatalyst by response surface methodology. *Journal of Environmental Sciences*, 22(8), 1281-1289.

Zhu C., Wang X., Huang Q., Huang L., Xie J., Qing C., et al., Removal of gaseous carbon bisulfide using dielectric barrier discharge plasmas combined with TiO₂ coated attapulgite catalyst, *Chem. Eng. J.* 225 (2013) 567–573, doi:[http:// dx.doi.org/10.1016/j.cej.2013.03.107](http://dx.doi.org/10.1016/j.cej.2013.03.107).