Environ Sci Pollut Res (2017) 24:12556–12561
DOI 10.1007/s11356-016-7640-y

Fast photocatalytic degradation of pharmaceutical micropollutants and ecotoxicological effects

Isabella Natali Sora[1,2] · **Davide Fumagalli**[1]

Received: 1 July 2016 / Accepted: 7 September 2016 / Published online: 17 September 2016

Abstract Aqueous solutions of ciprofloxacin (CP) and ibuprofen (IBP) in the presence of $LaFeO_3$ photocatalyst, of H_2O_2, and of both $LaFeO_3$ and H_2O_2 were irradiated under visible light. The degradation rate in the presence of both $LaFeO_3$ and H_2O_2 after 5 h irradiation was more than 90 % for CP and 40 % for IBP, much higher than that with only H_2O_2 under visible light. For the sake of comparison, the experiments were also carried out in the dark, and both CP and IBP were not significantly converted. The degradation rate was enhanced by the simultaneous presence of small concentration of $LaFeO_3$ (130 mg L^{-1}) and H_2O_2 (0.003 M). However, tests on the aquatic acute toxicity indicate that the degradation products of CP and IBP induce toxic effects on aquatic organisms, consequently indicating incomplete detoxification after 5 h irradiation. The main degradation product of IBP was 4-isobutylacetophenone (4-IBAP), detected in the irradiated solutions by using UV/vis spectrophotometry. 4-IBAP was more toxic and showed a slower photocatalytic degradation than the parent compound. On the contrary, the toxicity of CP degradation products, although not negligible, was comparable to that of CP itself.

Keywords Lanthanum ferrite · Aquatic toxicity tests · Ibuprofen · Ciprofloxacin

Responsible editor: Philippe Garrigues

✉ Isabella Natali Sora
isabella.natali-sora@unibg.it

[1] Department of Engineering and Applied Sciences, University of Bergamo, Viale Marconi 5, 24044 Dalmine, Italy

[2] INSTM R.U. Bergamo, University of Bergamo, 24044 Dalmine, BG, Italy

Introduction

Pharmaceuticals (PhCs) are widespread environmental pollutants. Recent investigations document that PhC production and administration may vary both between countries and over time (Goossens et al. 2007; Kümmerer 2009; Castiglioni et al. 2006), with fluctuations that are observed not only in different seasons. For many of PhCs, only partial removal from wastewater is observed by using traditional degradation treatments, and thus, most PhCs are still found in the effluents of wastewater treatment plants (WWTPs). Moreover, the discharge into surface waters and/or in WWTPs of PhCs may give rise to ecotoxicological effects (Daughton and Ternes 1999), and in case of antibiotics to antibacterial resistance.

PhCs and their metabolites were detected worldwide at ng L^{-1} to μg L^{-1} levels in surface water bodies in different areas (Verlicchi et al. 2012; Kolpin et al. 2002; Calamari et al. 2003; Mompelat et al. 2009; Ashton et al. 2004). Safety threshold values have been defined for a limited number of PhCs. Moreover, the products of drug degradation may also represent an environmental risk, and it was found that some photoproducts are more persistent and toxic than the parent drug (Della Greca et al. 2004).

The traditional primary treatments used in municipal WWTPs are usually inefficient for the removal of most PhCs. This problem was addressed in some studies at the end of last century, and it was put into evidence that the central nervous system (CNS) drug carbamazepine is neither degraded nor adsorbed (Clara et al. 2004), and in the class of lipid regulators, the removal rate of clofibric acid (the main metabolite of clofibrate) reaches 51 %, while 83 % of bezafibrate is removed (Ternes 1998). Presently adopted treatments, such as biological filters and activated sludge, are more efficient for the removal of PhCs but still inadequate especially for some antibiotics (erythromycin, ofloxacin, sulfamethoxazole, clarithromycin, amoxicillin, tetracycline, and azithromycin), CNS drugs (fluoxetine, diazepam), analgesics/antiinflammatories (ibuprofen, mefenamic acid), and lipid regulators (fenofibric acid, fenofibrate, gemfibrozil) (Hirsch et al. 1999). The photocatalytic processes appear to be convenient and green in comparison with the traditional chemical methods. In these processes, a chemical reaction is initiated when a semiconductor photocatalyst is irradiated by light with an energy that matches or exceeds the band gap energy of the semiconductor, resulting in excited electron-hole pairs that can be applied to the production or degradation of a compound (substrate) (Hoffmann et al. 1995). Moreover, a synergistic effect was demonstrated when photocatalysis was coupled with other AOP technologies, such as ozonization, microwave, or ultrasound treatments, although in some cases, cost issues might arise (Selli et al. 2008).

Among conventional photocatalysts, the TiO_2-based materials have dominated in WWTPs, although the use of energy-consuming ultraviolet (UV) lamps as radiation source is an important drawback of their use. The objective of this work is to assess an economical heterogeneous photocatalyst for the decontamination of water from micropollutants under visible light irradiation. The photocatalytic activity was tested on ciprofloxacin (CP), which is an antibiotic that belongs to the class of therapeutic drugs known as quinolones, and on ibuprofen (IBP), one the most prescribed nonsteroidal antiinflammatory drugs. Since IBP is known to be degraded photochemically under UV radiation and sunlight (Packer et al. 2003) and that the toxic compound 4-isobutylacetophenone (4-IBAP) can be formed photochemically from IBP, upon direct photolysis (Ruggeri et al. 2013), we decided to use a visible light catalyst $LaFeO_3$. As far as we know, this is the first time that the photocatalytic efficiency of $LaFeO_3$ was evaluated for the degradation of IBP and CP under visible light irradiation.

Lanthanum ferrite $LaFeO_3$ was proposed as visible light photocatalyst in 2007 (Li et al. 2007), although the first detailed study on the photocatalytic degradation of organic compounds was reported by Su et al. (2010), who observed an excellent photocatalytic performance in Rhodamine B degradation. Successive studies performed by using nanostructured $LaFeO_3$ with different morphologies (Thirumalairajan et al. 2013), or $LaFeO_3$ nanoparticles supported on the surface of montmorillonite (Peng et al. 2016), confirmed this capability for visible light degradation of Rhodamine B. Fenton-like reaction could enhance the photocatalytic degradation of Rhodamine B through a synergistic effect (Peng et al. 2016). However, tests with dyes (or with any substrate absorbing radiation) are not appropriate in photocatalysis, because they do not distinguish between a pure photocatalytic process, a dye sensitization, or both (Barbero and Vione 2016). Little is known about the photocatalytic efficiency of $LaFeO_3$ under visible light for the degradation of molecules other than the organic dyes. Hu et al. (2012) reported that $LaFeO_3$ displayed photocatalytic activity for the degradation of *p*-chlorophenol (49.0 %) after 5 h visible light irradiation.

In this paper, the photocatalytic efficiency of $LaFeO_3$ nanopowder in the presence of H_2O_2 to decontaminate water from micropollutants under visible light irradiation is reported. Moreover, aquatic toxicity tests were also performed in order to test induced toxic effects on aquatic organisms due to the presence of the degradation products of ciprofloxacin and ibuprofen.

Methods

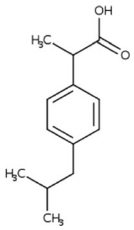
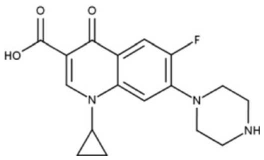
IBP (USP specifications), CP (≥98 % HPLC grade), and H_2O_2 (3 wt%) were from Sigma-Aldrich and were used as purchased. Table 1 shows the structure, the main characteristics, and the occurrence in the aquatic environment of the investigated PhCs.

Lanthanum ferrite $LaFeO_3$ (LF) was prepared by the citrate auto-combustion method (Caronna et al. 2009). LF is a semiconductor with band gap energy in the range of 2.5–2.6 eV (Parrino et al. 2016; Natali Sora et al. 2013). The photocatalytic degradation reactions were carried out by using a Rayonet reactor equipped with eight lamps (8 W, GE lighting 10055-F8T5/D) emitting in the visible region. Irradiation of aqueous suspensions containing 5.0×10^{-5} M (10.0 mg L^{-1}) of IBP, 0.003 M H_2O_2, 130 mg L^{-1} LF or 5.0×10^{-6} M (1.7 mg L^{-1}) of CP, 0.003 M H_2O_2, and 130 mg L^{-1} LF was carried out in magnetically stirred Pyrex glass tubes. The concentrations of IBP and CP were chosen so as to have a significant spectrophotometric signal. The concentration of H_2O_2 corresponded to a mole amount that largely exceeded the mole amount of IBP and CP but was about 1/30 than that used in typical studies on the heterogeneous Fenton-like process. The aqueous samples taken at regular intervals of irradiation were centrifuged for 10 min (Scharlab BL-8). The solutions obtained in centrifuging suspensions after irradiation were denominated IBP_t and CP_t, where *t* was the irradiation time (0, 1, 3.5, 5, 24 h).

The absorption spectra were measured by using an ultraviolet-visible (UV-vis) spectrophotometer (Jasco V-650), with 10-mm light path. Full spectra were taken in order to monitor any spectral interference that may occur. The normalized concentration of CP and IBP was calculated by the formula C_t/C_0, where C_0 and C_t are the total concentrations of the pollutant solution before irradiation and after an irradiation time *t*, respectively.

Acute toxicity of the degradation products of CP and IBP, in terms of the dose (concentration administered) that causes a particular effect in a specified population, was investigated. The *Daphnia magna* (*D. magna* Straus, crustacean cladocera) test was performed following the guidelines UNI EN ISO 6341: 2013 (UNI 2013). Tests were performed at 25 °C, in darkness, for 24 and 48 h, after which immobility was recorded. The *Pseudokirchneriella subcapitata* (*P. subcapitata*, green alga) test was performed according to ISO 8692: 2012 (ISO 2012). Tests were performed in uniform illumination for

Table 1 Main characteristics and occurrence in the aquatic environment of the investigated PhCs

	Ibuprofen	Ciprofloxacin
Structure		
Formula	$C_{13}H_{18}O_2$	$C_{17}H_{18}FN_3O_3$
CAS no.	15687-27-1	85721-33-1
Therapeutic class	Non-steroidal antiinflammatory drug	Antibiotic (fluoroquinolone)
Molecular weight (g mol^{-1})	206.28	331.34
Solubility in water	Slightly soluble	Soluble
Excretion rate in %	1–8 as unchanged, 14 as glucuronide (Ternes 1998)	37 as unchanged (Wagenlehner et al. 2006)
Occurrence in surface water (μg L^{-1})	0.20 in USA (Kolpin et al. 2002)	0–0.04 in Europe (Johnson et al. 2015)
	0.12 in Italy (Zuccato et al. 2005)	0.02 in USA (Kolpin et al. 2002)

72 h, with determination of algal growth. The *Vibrio fischeri* (*V. fischeri*, luminescent bacterium) test was performed according to UNI EN ISO 11348–3: 2009 (UNI 2009), by using a Microtox apparatus. Toxicants influence the metabolism of the bacterium and reduce luminescence, which was measured at 15 and 30 min and compared to control. The toxicity tests were performed on (i) solutions of IBP and of CP which were not irradiated (IBP_0, CP_0); (ii) solutions which were irradiated for 5 h (IBP_5, CP_5); (iii) solutions irradiated for 24 h (IBP_{24}), and, as reference, (iv) a solution of distilled water and H_2O_2. The suspensions containing the catalyst were previously centrifuged to remove LF nanopowders.

Results and discussion

The photocatalytic degradation percentage of IBP with H_2O_2 + LF under visible light irradiation (5 h) was 42 %. As shown in Fig. 1, the degradation after 5 h visible light exposure of only IBP was not significant, while that of IBP with only H_2O_2, or of IBP in the presence of LF alone, was <4 %. A different behavior was found under 24-h visible light irradiation. IBP with only H_2O_2 displayed a degradation percentage of 73 %, which increased to 78 % for IBP with H_2O_2 + LF, while the degradation percentage of IBP itself and IBP with only LF remained <4 %. In Fig. 2, UV-vis absorption spectra of aqueous solutions of IBP with H_2O_2 in the presence of LF irradiated for 0, 3.5, 5, and 24 h are shown. The absorbance peak observed at 220 nm was chosen for the measurement of IBP concentration (Garzón and Martìnez 2004), while the peak at 263 nm was used for the detection of 4-IBAP, which is the main degradation product of IBP (Gasco-Lopez and Izquierdo-Hornillos 1999). The concentration maximum of 4-IBAP was reached after 5 h of irradiation.

The most extensive photocatalytic degradation of CP (92 %) was detected by using H_2O_2 + LF under 5 h visible light irradiation, while degradation under irradiation decreased down to 64 % for CP with only H_2O_2, 38 % for CP

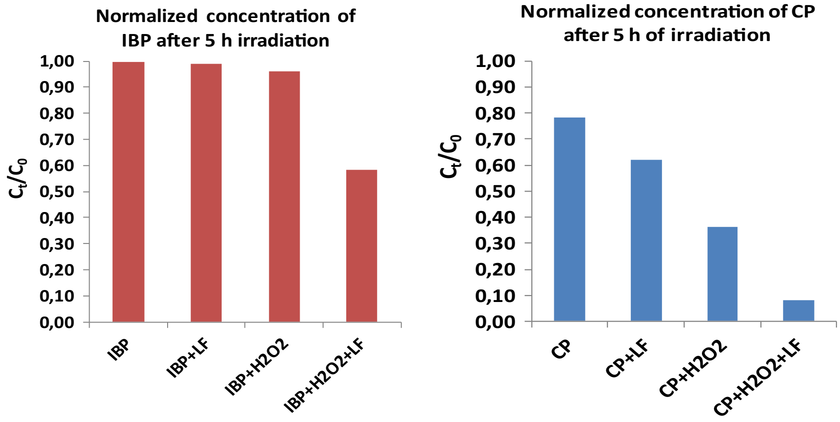


Fig. 1 Normalized concentration of IBP in solutions of IBP alone, IBP + LF, IBP + H_2O_2, and IBP + LF + H_2O_2 after 5 h visible light irradiation. Normalized concentration of CP in solutions of CP alone, CP + LF, CP + H_2O_2, CP + LF + H_2O_2 after 5 h visible light irradiation

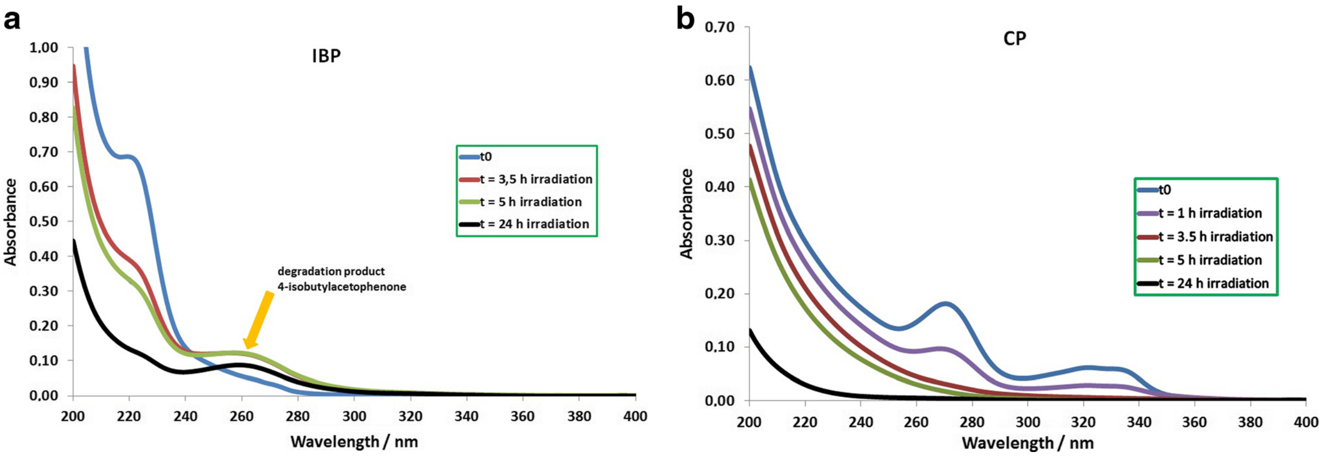


Fig. 2 UV/vis absorption spectra of solution irradiated under visible light: **a** IBP 5 × 10^{-5} M, 130 mg L^{-1} LF, and 0.003 M H_2O_2 for 0, 3.5, 5, and 24 h; **b** CP 5 × 10^{-6} M, 130 mg L^{-1} LF, and 0.003 M H_2O_2 for 0, 1, 3.5, 5, and 24 h

with only LF, and 22 % for CP alone (Fig. 1). The degradation percentage obtained for CP with only LF (38 %) was comparable with the degradation of *p*-chlorophenol (49.0 %) reported by Hu et al. (2012) after 5 h visible light irradiation.

The UV-vis absorption spectra of aqueous solutions of CP with H_2O_2 in the presence of LF irradiated for 0, 1, 3.5, 5, and 24 h showed an absorbance peak at 274 nm and a broad peak at 317 nm, which were used for CP detection (Fig. 2). No other peaks were recorded during the photocatalytic degradation experiments. For the sake of comparison, the experiments were also carried out in the dark, and both CP and IBP were not significantly transformed.

The acute toxicological effects on freshwater organisms of the degradation mixtures of CP and IBP were evaluated, and the results are shown in Table 2. Following the classification related to the chemical toxicity adopted by the Commission of the European Community in 1996, chemicals are highly toxic from 0.1 to 1 mg L^{-1} (expressed by EC_{50} values), toxic from 1 to 10 mg L^{-1}, harmful from 10 to 100 mg L^{-1}, and nontoxic from 100 to 1000 mg L^{-1}. The tests performed on solution IBP_0, which was not irradiated, indicate that IBP_0 was harmful for *P. subcapitata* and *V. fisheri*, while it was toxic to daphnids. Solutions irradiated for 5 h (IBP_5) became highly toxic (*D. magna* and *P. subcapitata*) and toxic to *V. fisheri*. After 24 h irradiation (IBP_{24}), the solutions still displayed a high toxicity. Tests performed on distilled water and H_2O_2 without irradiation displayed no acute toxicity to *P. subcapitata* and to *V. fisheri* and a very slight toxicity to *D. magna* (data not reported in Table 2). Under the described experimental conditions, after 24 h irradiation, the H_2O_2 was fully photolyzed. Moreover, the values of the normalized concentration C_5/C_0 and C_{24}/C_0 of IBP were 0.58 and 0.23, respectively. These results indicate that the toxicity of photoproducts is higher than that of IBP itself and that their degradation rate is smaller. The higher toxicity is most likely due to the presence of 4-IBAP detected in the irradiated solutions by using UV/vis spectrophotometry (Fig. 2). 4-IBAP is known to be a toxic degradation product formed from IBP, when heating is applied or under oxidative conditions (Caviglioli et al. 2002).

Table 2 Dose-effect relationships for acute toxicity to IBP and CP

	IBP_0 (mg L^{-1})	IBP_5 (mg L^{-1})	IBP_{24} (mg L^{-1})	CP_0 (mg L^{-1})	CP_5 (mg L^{-1})
D. magna					
EC_{50} 24 h	10 ± 3	0.4 ± 0.1	0.02 ± 0.01	0.09 ± 0.02	<0.02
EC_{50} 48 h	8 ± 2	0.3 ± 0.1	0.03 ± 0.01	0.07 ± 0.02	<0.02
P. subcapitata					
ECr_{50} 72 h	>10	<0.4	<0.02	<0.17	<0.01
ECr_{20} 72 h	>10	<0.4	1.5 ± 0.5	<0.17	<0.01
V. fischeri					
EC_{50} 15 min	>10	2 ± 1	>1	0.3 ± 0.2	0.06 ± 0.02
EC_{50} 30 min	>10	2 ± 1	0.14 ± 0.02	0.3 ± 0.2	0.07 ± 0.02

The concentration parameters of starting aqueous suspensions were 5.0 × 10^{-5} M (10.0 mg L^{-1}) of IBP, or 5.0 × 10^{-6} M (1.7 mg L^{-1}) of CP, 0.003 M H_2O_2, and 130 mg L^{-1} LF. The solutions that denominated IBP_t and CP_t, where *t* was the irradiation time (0, 5, 24 h), were obtained after centrifuging suspensions of IBP or CP with H_2O_2 + LF

The tests performed on solutions of CP without irradiation (CP_0) and after 5 h irradiation (CP_5) indicated that both solutions were highly toxic for *D. magna*, *P. subcapitata*, and *V. fisheri*. Although the normalized concentration C_5/C_0 of CP_5 was only 0.08, the acute toxicity remained similar to that of CP_0, which suggests that the toxicity of degradation products is comparable to that of CP itself. This result is in agreement with the fact that the antimicrobial activity of fluoroquinolones derives from the quinolone moiety (Dodd et al. 2006), which is preserved under photodegradation (Vasconcelos et al. 2009). In our study, the solutions containing 1.7 mg L^{-1} of CP gave a higher toxicity compared to other studies (Vasconcelos et al. 2009), but it is worth to note that in this case, H_2O_2 was coupled with CP, which may have a synergic toxic effect.

Conclusions

By using visible light irradiation (5 h) and in the presence of LF and aqueous H_2O_2, an extensive photocatalytic degradation of CP (92 %) and IBP (42 %) was observed. However, the degradation products of CP and IBP induced toxic effects on aquatic organisms, which suggests incomplete detoxification after 5 h irradiation. The main degradation product of IBP was 4-IBAP which is more toxic and showed a slower photocatalytic degradation than the parent compound. On the contrary, the toxicity of CP degradation products, although not negligible, was comparable to that of CP itself.

References

Ashton D, Hilton M, Thomas KV (2004) Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom. Sci Total Environ 333:167–184

Barbero N, Vione D (2016) Why dyes should not be used to test the photocatalytic activity of semiconductor oxides. Environ Sci Technol 50:2130–2131

Calamari D, Zuccato E, Castiglioni S, Bagnati R, Fanelli R (2003) Strategic survey of therapeutic drugs in the rivers Po and Lambro in northern Italy. Environ Sci Technol 37:1241–1248

Caronna T, Fontana F, Natali Sora I, Pelosato R (2009) Chemical synthesis and structural characterization of the substitution compound $LaFe_{1-x}Cu_xO_3$ (x = 0-0.40). Mat Chem Phys 116:645–648

Castiglioni S, Bagnati R, Fanelli R, Pomati F, Calamari D, Zuccato E (2006) Removal of pharmaceutical in sewage treatment plants in Italy. Environ Sci Technol 40:357–363

Caviglioli G, Valeria P, Brunella P, Sergio C, Attilia A, Gaetano B (2002) Identification of degradation products of ibuprofen arising from oxidative and thermal treatments. J Pharm Biomed Anal 30:499–509

Clara M, Stren B, Kreuzinger N (2004) Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigations on the behaviour of carbamazepine in wastewater treatment and during groundwater infiltration. Water Res 38:947–954

Daughton CG, Ternes TA (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ Health Perspect 107:907–938

Della Greca M, Brigante M, Isidori M, Nardelli A, Previtera L, Rubino M, Temussi F (2004) Phototransformation and ecotoxicity of the drug naproxen-Na. Environ Chem Lett 1:237–241

Dodd MC, Buffle M-O, Von Gunten U (2006) Oxidation of antibacterial molecules by aqueous ozone: moiety-specific reaction kinetics and application to ozone-based wastewater treatment. Environ Sci and Tech 40:1969–1977

Garzón LC, Martìnez F (2004) Temperature dependence of solubility for ibuprofen in some organic and aqueous solvents. J Solut Chem 33:1379–1395

Gasco-Lopez AI, Izquierdo-Hornillos R (1999) LC method development for ibuprophen and validation in different pharmaceuticals. J Pharm Biomed Anal 21:143–149

Goossens H, Ferech M, Coenen S, Stephens P (2007) Comparison of outpatient systemic antibacterial use in 2004 in the United States and 27 European countries. Clinical Infectious Disease 44:1091–1095

Hirsch R, Ternes T, Haberer K, Krantz K-L (1999) Occurrence of antibiotics in the aquatic environments. Sci Total Environ 225:109–118

Hoffmann M, Martin ST, Choi W, Bahnemann DW (1995) Environmental applications of semiconductor photocatalysis. Chem Rev 95:69–96

Hu R, Li C, Wang X, Sun Y, Jia H, Su H, Zhang Y (2012) Photocatalytic activities of LaFeO3 and La2FeTiO6 in p-chlorophenol degradation under visible light. Catalysis Comm 29:35–39

ISO 8692: 2012 Water quality—fresh water algal growth inhibition test with unicellular green algae. http://www.iso.org

Johnson AC, Keller V, Dumont E, Sumpter JP (2015) Assessing the concentrations and risks of toxicity from the antibiotics ciprofloxacin, sulfamethoxazole, trimethoprim and erythromycin in European rivers. Sci Total Environ 511:747–755

Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. Environ Sci Technol 36:1202–1211

Kümmerer K (2009) Antibiotics in the aquatic environment—a review—part I. Chemosphere 75:417–434

Li S, Jing L, Fu W, Yang L, Xin B, Fu H (2007) Photoinduced charge property of nanosized perovskite-type $LaFeO_3$ and its relationships with photocatalytic activity under visible irradiation. Mater Res Bull 42:203–212

Mompelat S, Le Bot B, Thomas O (2009) Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. Environ Int 35:803–814

Natali Sora I, Fontana F, Passalacqua R, Ampelli C, Perathoner S, Centi G, Parrino F, Palmisano L (2013) Photoelectrochemical properties of doped lanthanum orthoferrites. Electrochim Acta 109:710–715

Packer JL, Werner JJ, Latch DE, McNeill K, Arnold WA (2003) Photochemical fate of pharmaceuticals in the environment: naproxen, diclofenac, clofibric acid, and ibuprofen. Aquat Sci 65:342–351

Parrino F, García-López E, Marcì G, Palmisano L, Felice V, Natali Sora I, Armelao L (2016) Cu-substituted lanthanum ferrite perovskites: preparation, characterization and photocatalytic activity in gas-solid regime under simulated solar light irradiation. J Alloys Comp 682:686–694

Peng K, Fu L, Yang H, Ouyang J (2016) Perovskite $LaFeO_3$/montmorillonite nanocomposites: synthesis, interface characteristics and enhanced photocatalytic activity. Scientific Reports 6:19723

Ruggeri G, Ghigo G, Maurino V, Minero C, Vione D (2013) Photochemical transformation of ibuprofen into harmful 4-isobutylacetophenone: pathways, kinetics, and significance for surface waters. Water Res 47:6109–6121

Selli E, Bianchi CL, Pirola C, Cappelletti G, Ragaini V (2008) Efficiency of 1,4-dichlorobenzene degradation in water under photolysis, photocatalysis on TiO_2 and sonolysis. J Hazard Mater 153:1136–1141

Su H, Jing L, Shi K, Yao C, Fu H (2010) Synthesis of large surface area $LaFeO_3$ nanoparticles by SBA-16 template method as high active visible photocatalysts. J Nanopart Res 12:967–974

Ternes TA (1998) Occurrence of drugs in German sewage treatment plants and rivers. Water Res 32:3245–3260

Thirumalairajan S, Girija K, Hebalkar NY, Mangalaraj D, Viswanathan C, Ponpandian N (2013) Shape evolution of perovskite $LaFeO_3$ nanostructures: a systematic investigation of growth mechanism, properties and morphology dependent photocatalytic activities. RSC Adv 3:7549–7561

UNI EN ISO 11348–3:2009 Water quality—determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri (Luminescent bacteria test)—part 3: method using freeze-dried bacteria. http://www.uni.com

UNI EN ISO 6341:2013 Water quality—determination of the inhibition of the mobility of *Daphnia magna* Straus (Cladocera, Crustacea)—acute toxicity test. http://www.uni.com

Vasconcelos TG, Henriques DM, König A, Martins AF, Kümmerer K (2009) Photo-degradation of the antimicrobial ciprofloxacin at high pH: identification and biodegradability assessment of the primary by-products. Chemosphere 76:487–493

Verlicchi P, Al Aukidy M, Zambello E (2012) Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after secondary treatment—a review. Sci Total Environ 429:123–155

Wagenlehner FME, Kinzig-Schippers M, Sörgel F, Weidner W, Naber KG (2006) Concentrations in plasma, urinary excretion and bactericidal activity of levofloxacin (500 mg) versus ciprofloxacin (500 mg) in healthy volunteers receiving a single oral dose. Int J Antimicrobial Agents 28:551–559

Zuccato E, Castiglioni S, Fanelli R (2005) Identification of the pharmaceuticals for human use contaminating the Italian aquatic environment. J Hazard Mater 122:205–209