Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.769696

51 (2013) 6601–6608
October

Taylor & Francis
Taylor & Francis Group

Sonochemical degradation of twenty-three emerging contaminants in urban wastewater

V. Naddeo*, M. Landi, D. Scannapieco, V. Belgiorno

Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering, University of Salerno, via Ponte don Melillo, 84084 Fisciano (SA), Italy
Tel. +39 089 96 9333; Fax: +39 089 96 9620; email: vnaddeo@unisa.it

Received 9 January 2012; Accepted 14 January 2013

ABSTRACT

The occurrence and fate of pharmaceuticals in the environment, and in aquatic media in particular, have received considerable attention by the scientific community during the last two decades. Pharmaceuticals, which are designed to be biologically active substances, are usually lipophilic and resistant to biodegradation, thus having the potential for accumulation and persistence in the environment. Although they are usually present at relatively low concentrations, ranging between ng/L and μg/L levels, they may cause serious effects on the environment. In this study, the removal efficiency of sonolysis has been tested on a mixture of 23 pharmaceuticals. Diclofenac and carbamazepine degradations were tested at different power densities (100–400 W/L) using low frequency. These compounds were spiked separately in wastewater at high concentrations (mg/L). Subsequently, low-frequency ultrasound-induced degradation of a mixture of 23 emerging contaminants with low concentration (μg/L) in urban wastewater was investigated, working at 100 W/L. It was found that the pharmaceuticals conversion is enhanced at increased applied power densities. The reaction rate for different pharmaceuticals is almost the same in the mixtures and the kinetic regimes are mainly pseudo-first order.

Keywords: Advanced oxidation processes; Emerging compounds; Pharmaceuticals; Sonolysis; Wastewater

1. Introduction

The widespread occurrence of pharmaceuticals and personal care products (PPCPs) in the aquatic environment is a concrete problem of unknown consequences [1–6]. Among the various sources that may be considered responsible for the occurrence of pharmaceuticals in water and soil, the effluents of urban wastewater treatment plants (UWWTPs) are frequently considered as the most important ones [5,7,8]. Over the past few years, pharmaceuticals have been considered as an emerging environmental problem due to their continuous input and persistence into the aquatic ecosystem even at low concentrations (i.e. ng/L).

In the absence of clear answers about the effects, the precautionary principle should be applied in order to prevent pharmaceuticals from entering the environment since their persistence in the environment may pose a critical threat. Once pharmaceuticals enter the aquatic environment, possible fates are listed as it

*Corresponding author.

follows: (a) the compound is ultimately mineralized to carbon dioxide and water; (b) the compound does not degrade readily because of its lipophilic behavior and is partially retained in the sedimentation sludge; and (c) the compound metabolizes to a more hydrophilic molecule, passes through the wastewater treatment plant and ends up in the receiving waters (which are surface waters, mainly rivers) [9].

Recent studies proposed a database in order to quantitatively assess the occurrence and removal efficiency of PPCPs in wastewater treatment plants (WWTPs) [10,11]. In Table 1, some of the most common pharmaceuticals amongst the investigated PPCPs have been summarized and their usual monitored concentrations in WWTPs have been reported. It has to be noted that all the presented concentrations have a magnitude of μg/L.

Aim of this study was to investigate the degradation of the most common drugs in aqueous solution by low-frequency ultrasound to select the optimum operating conditions in terms of density, frequency, and contact time.

1.1. Sonochemical processes: mechanisms and effects of parameters

Sonochemical processes are an interesting option in the field of advanced oxidation processes. This technology consists in the application of ultrasound waves to destroy contaminants or to catalyze oxidation reactions in liquid phase. The technique of sonolysis has been found effective in a number of cases such as cleaning, sterilization in biological and food processes, homogenization, emulsification, disaggregation of powder and catalyst, and biological cell destruction [12]. Ultrasound irradiation, or sonolysis, is a relatively new process in water and wastewater treatment and, therefore, its application for remediation of wastewater is an area of increasing interest. This is also reflected in the small number of publications concerning pharmaceuticals degradation.

Table 1
Mean concentrations of pharmaceuticals in wastewater treatment plants (adapted from Miege et al. [10])

Pharmaceutical compound	Concentration (μg/L)
Atenolol	0.030
Carbamazepine	0.968
Diclofenac	1.340
Erythromycin	0.108
Gemfibrozil	1.630
Ibuprofen	14.60
Iopromide	4.490
Metoprolol	0.160
Naproxen	26.40
Pentoxifylline	/
Propranolol	0.075
Sulfamethoxazole	0.342
Triclosan	0.380
Trimethoprim	0.449

The mechanism of ultrasonic degradation is based on the acoustic cavitation phenomenon, which involves the formation and expansion of micro-bubbles until they reach a critical resonance frequency size: that leads to a subsequent implosive collapse of cavities under the periodic variations of the pressure field. The critical size of the sonolytically induced bubbles depends on the nature of the liquid and irradiation frequency. Therefore, ultrasonic irradiation is a cyclic process of formation (namely, nucleation), growth (expansion), and adiabatic implosion of micro-bubbles [13,14]. In other terms, cavitation plays the role of concentrating the diffusing energy of ultrasound into micro-bubbles.

1.2. Sonochemical treatments of pharmaceutical compounds

Several factors may affect process efficiency in a complex way; the most important ones are the frequency and intensity of ultrasound; reactor geometry; type and nature of contaminant; bulk temperature; and the water matrix characteristics. The latter is of the outmost importance, as the presence of dissolved gases or solids usually improves performance as they serve as extra nucleation centers. This has been demonstrated ina recent study [15] dealing with the degradation of triclosan at 80 kHz in various matrices, i. e. seawater, urban run-off, inlet of a municipal WWTP, pure water, and estuarine water. The authors reported that the first-order kinetic constant of triclosan degradation decreased by about two orders of magnitude from seawater to influent municipal wastewater. Moreover, water sonolysis yields H_2O_2 [16] and the presence of iron ions usually enhances degradation, thus mimicking a sono-Fenton reaction [17]. Nevertheless, only in recent years ultrasound process have been employed to treat PPCPs [16,18–20]. The sonolysis of Diclofenac (DCF) in water was investigated at different ultrasound frequencies (24, 216, 617, and 850 kHz) and in presence of various catalysts (TiO_2, SiO_2, SnO_2, and titanosilicate). Its concentration in an aqueous media decreased using sonolysis from 100% to 16% when ultrasound frequency was modified from 617 to 850 kHz [16]. In

another study, the degradation of DCF by high ultrasound frequency (861 kHz) was shown and the efficiency of elimination was considerably improved by the addition of Fe-species [21]. Recently, the influence of the sonolysis process on the degradation of ibuprofen has also been investigated [22]. The introduction of ultrasound waves increased the degradation of ibuprofen from 30 to 98% in 30 min. Complete removal of ibuprofen was achieved, even though some dissolved organic carbon remained in solution, showing that long-lived intermediates were recalcitrant to ultrasound irradiation. However, chemical oxygen demand and biochemical oxygen demand values indicated that the process oxidized the ibuprofen compound to biodegradable substances, eventually removable in a subsequent biological step [22]. More recent research [23] has evaluated the influence of the ultrasound process on the degradation of l-dopa and paracetamol at different ultrasonic frequencies (574, 860 and 1,134 kHz), using a horn-type sonicator and power values of 9, 17, 22 and 32 W. Authors reported both pollutants conversion and chemical oxygen demand removal rate to decrease with increasing initial solute concentration and decreasing power. The best results were obtained with 574 kHz frequency, but although the results at 574 and 860 kHz are very similar; it is important to remember that lower frequencies are preferred due to the associated drawbacks of the high frequency operation. A recent study [24] focused on the sonolytic degradation of ciprofloxacin. It was found that the production of •OH radicals was maximum at 544 kHz, which was also the most favorable frequency for ciprofloxacin degradation in comparison with 801 and 1,081 kHz. The degradation constant was reported to be strongly dependent on the temperature of the bulk solution: authors reported that the ciprofloxacin degradation constant increased significantly with increasing temperature [24].

2. Materials and methods

The present work is divided into two different phases. The first one, carried out at laboratories of the Sanitary Environmental Engineering of the University of Salerno (Italy), aimed to investigate the effective operating conditions for a low-frequency (20 kHz) ultrasound irradiation in order to degrade two different pharmaceuticals (DCF, Carbamazepine). The second part of the study was performed at the laboratories of the Civil and Environmental Engineering Department at the University of Washington (Seattle, US) and the effective operating conditions of sonolysis in order to degrade the mixture of 23 emerging contaminants were analyzed.

2.1. Chemicals

The 23 emerging compounds (Acetaminophen, Atenolol, Atrazine, Carbamazepine, Diclofenac, Progesterone, Metoprolol, Dilantin, DEET, Pentoxifylline, Oxybenzone, Caffeine, Iopromide, Erythromycin, Fluoxetine, Trimethoprim, Propranolol, Sulfamethoxazole, Ibuprofen, Naproxen, Bisphenol-A, Gemfibrozil, and Triclosan) used in the second step of this work were supplied by Sigma-Aldrich (USA). A Milli-Q water system (Millipore, USA) was used to prepare synthetic solutions.

Wastewater samples were collected from two large UWWTPs (Capaccio, SA, Italy and West Point, WA, USA). A set of samples was collected from the final effluent before disinfection in amber glass bottles prerinsed with ultrapure water and transferred to the laboratory in cooled boxes and then kept at a controlled temperature (+4°C).

2.2. Experimental setup

The initial concentrations of the two investigated pharmaceuticals were equal to 5 mg/L for Carbamazepine (CBZ) and 40 mg/L for DCF; these solutions were spiked into wastewater samples. For DCF solution, the tests were carried out adjusting the original solution (whose inherent pH_0 is 5.3 for DCF concentrations of 40 mg/L) to acidic conditions adding a measured volume of H_2SO_4.

The mixtures of 23 pharmaceuticals were prepared spiking up to 1 μg/L in urban wastewater samples.

A Sonics Vibracell VCX-750 (Sonics & Materials Inc., US) ultrasound generator, operating at a fixed frequency of 20 kHz and equipped with a titanium horn with a 1.3 cm in diameter tip, was employed for the first part of the study. Reactions were carried out in a 300 mL cylindrical Pyrex vessel (Schott Duran, Germany), which was loaded with 200 mL of wastewater spiked at various initial concentrations of pharmaceuticals. The applied electrical power was changed between 100 and 400 W/L, according to what reported elsewhere in scientific literature [12]. During the second phase, an ultrasonic bath (TI-H-5, Elma, Germany) operating at 45 kHz frequency and a variable nominal power, up to 800 W, was employed to carry out tests in 50 mL tubes at different sonication times (from 5 to 180 min).

2.3. Analytical methods

Changes in the pharmaceuticals concentration were monitored using a UV–VIS spectrophotometer (Lambda 12, Perkin Elmer). Sample absorbance was measured at a characteristic peak (DCF at 276 nm and CBZ at 284 nm), which is the wavelength that corresponds to the maximum absorbance and gives a sufficient indication of the drug concentration [19,25]. The assumption that some of the by-products formed during the oxidation could also absorb at the same wavelength should be considered as well. However, in that case, the conversion of the parent compounds obtained in this study would have been even higher [9,19]. Therefore, despite this assumption, UV absorption measurements provide a quick and indicative determination of the conversion [9,26].

In the second part of the study, the analysis of the degradation of emerging contaminants through sonolysis was carried out using a 4,000 Q Trap LC-MS/MS system (Applied Biosystems, Foster City, US) with electrospray ionization (ESI)—positive and negative ionization modes [26,27]. Acetaminophen, atenolol, atrazine, carbamazepine, diclofenac, progesterone, metoprolol, dilantin, DEET, pentoxifylline, oxybenzone, caffeine, iopromide, erythromycin, fluoxetine, trimethoprim, propranolol, and sulfamethoxazole were analyzed in ESI-positive mode [9]. Ibuprofen, naproxen, bisphenol-A, gemfibrozil, and triclosan were analyzed in ESI-negative mode [9]. An Inertsil ODS-3 C_{18} column was used for the separation step [28]. For ESI-positive mode, a mobile phase composed of A: 0.1% formic acid in water and B: acetonitrile–water (1:1 v/v) solution was used. For ESI-negative mode, a mobile phase composed of A: 2 mM ammonium acetate and B: acetonitrile-methanol (1:1 v/v) was used. Absorbance spectrum was measured using a UV–vis spectrophotometer (Lambda 18, Perkin Elmer).

3. Results and conclusions

3.1. DCF and CBZ degradation in separate solutions at high concentrations

The degradation at 20 kHz frequency, for DCF and CBZ in single wastewater solution, is approximately similar. Increasing the ultrasound density, the DCF and CBZ degradation increases vs. time, with about 50% removal for a treatment time of 60 min with 400 W/L.

A set of experiments has been conducted to evaluate the effect of applied power density on the degradation of pharmaceuticals in wastewater samples (Fig. 1). As expected, the enhancement of applied power density resulted in increased cavitational activity, which improved the degradation of DCF and CBZ in wastewater. It is interesting to note that the initial degradation rate increases linearly with increasing power in the tested experimental conditions. This result is supported by previous studies that reported a nearly linear relationship between reaction rates and applied power for the degradation of chlorophenols [17,29], ibuprofen [22], and DCF [18,19].

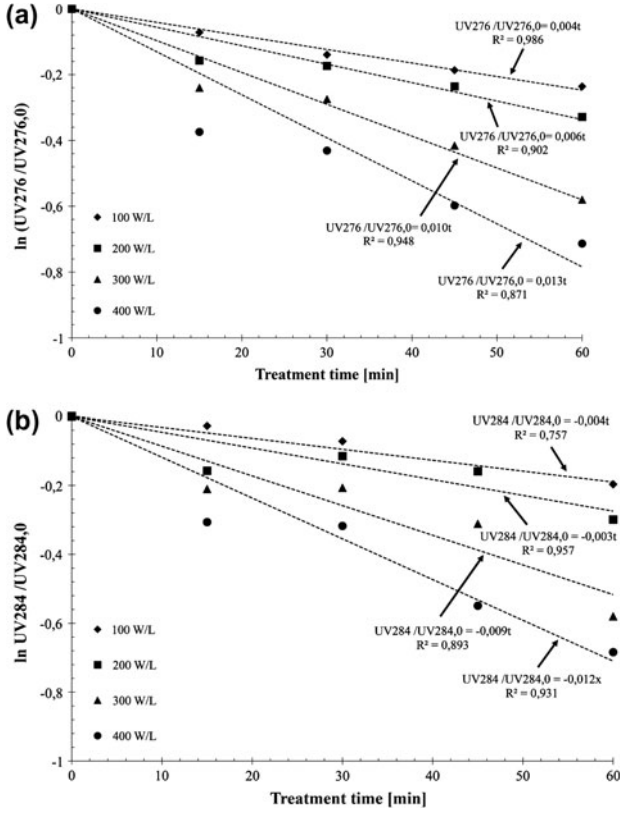

Fig. 1. Variation in content of DCF (a) and CBZ (b) in wastewater treated with different sonication densities.

The removal rates of DCF and CBZ follow first-order kinetics, whereas the reaction rate increases with increasing power density (100 to 400 W/L). Degradation is not controlled by mass transfer. Depending on the ultrasound density, the apparent rate constant (k) and the half-time ($t_{1/2}$) are reported in Table 2.

The illustrated results might be directly connected to the hydrogen peroxide formation, whose concentration increased when high ultrasound densities were applied [18]. The degradation rate coefficient of DCF and CBZ increased with increasing ultrasound intensity. The relationship between degradation rate coefficient and intensity is linear as observed in other studies [30,31]. This is because an increase in intensity leads to larger cavitation bubbles. Above the cavitation threshold, the bubble

Table 2
DCF and CBZ degradation rate constants (k) and half-times ($t_{1/2}$) both for zero- and first-order kinetic referred to sonolysis (ultrasonic horn, 20 kHz) for four different ultrasound densities

	Ultrasound density [W/L]	First order kinetic		
		R^2	$k \times 10^2$ [min^{-1}]	$t_{1/2}$ [min]
DCF	100	0.986	0.4	173.3
	200	0.902	0.6	115.5
	300	0.948	1.0	69.3
	400	0.871	1.3	53.3
CBZ	100	0.957	0.3	231.0
	200	0.757	0.5	138.6
	300	0.893	0.9	77.0
	400	0.931	1.2	57.8

reaches its maximum radius, which is proportional to the square root of intensity [32,33]. The larger cavitation bubbles then collapse and produce high shear, and therefore the molecules degrade faster at higher intensities. More than 55% of DCF was degraded using a 400 W/L power density within 60 min, at initial concentration of 80 mg/L. At 100 W/L, the DCF degradation was quite low, while only small differences between the decomposition rates at 200 and 400 W/L were observed. Results obtained for CBZ are very similar.

3.2. Degradation of a mixture of 23 emerging contaminants

Considering the results obtained during the degradation of the mixture of 23 emerging contaminants, it can be noted that the absorbance of the mixture decreases as the treatment time increases (Fig. 2).

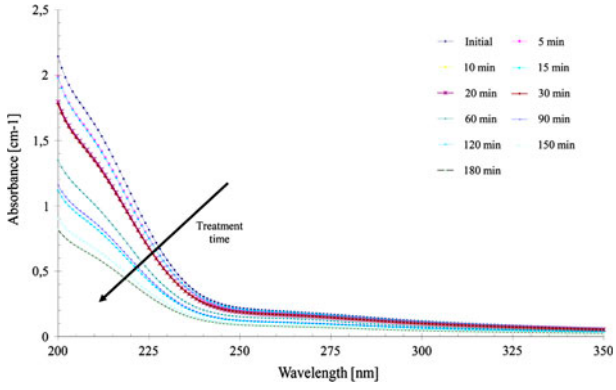

Fig. 2. Absorbance variation during ultrasonic bath treatment (45 kHz) of a mixture of twenty-three emerging contaminants in urban wastewater.

Since the UV_{254} absorbance decreased after sonolysis, it can be inferred that a continuous aromatic bonds breakdown has taken place. It is well established that UV_{254} absorbance represents the aromatic nature of organic compounds and accounts for carbon–carbon double bonds. Hence, the reduction of UV_{254} absorbance during the sonolysis treatment can be explained by the breakdown of the conjugated double bonds.

Fig. 3 shows the normalized plots of the mixture of 23 emerging compounds against time during 180 min sonication at 45 kHz. A strong degradation for all considered emerging contaminants was observed with an average value of 70%. Triclosan degradation was equal to 95%. On the other hand, the lowest degradation rate (50%) was obtained for erythromycin (Fig. 3). The observed results show a marked decrease of both emerging compounds and total organic substance present in the wastewater. Removal rate followed a pseudo-first-order reaction law for quite all

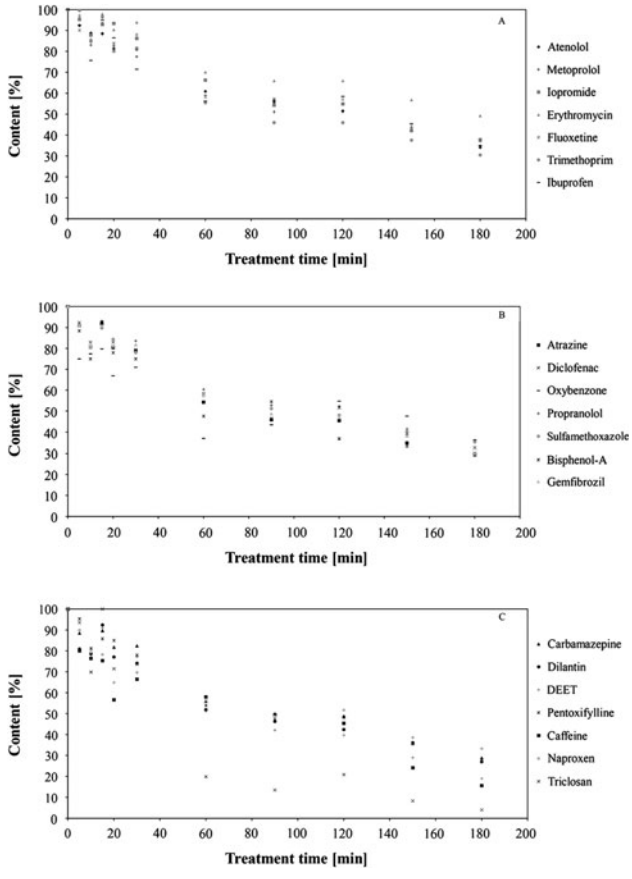

Fig. 3. Variation in content of emerging contaminants in wastewater treated with different sonication time in function of removal at 180 min: compounds showing (A) minimum, (B) medium and (C) maximum degradation.

Table 3
Emerging contaminants degradation rate constants (k) and half-times ($t_{1/2}$) for first-order kinetic referred to sonolysis (ultrasonic bath, 45 kHz, 100 W/L)

Pharmaceutical compound	R^2	$k \times 10^2$ [min^{-1}]	$t_{1/2}$ [min]
Atenolol	0.9747	0.6	115.5
Atrazine	0.9859	0.7	99.0
Carbamazepine	0.9859	0.7	99.0
Diclofenac	0.9836	0.6	115.5
Metoprolol	0.9684	0.6	1155
Dilantin	0.9673	0.7	99.0
DEET	0.9889	0.9	77.0
Pentoxifylline	0.9692	0.7	99.0
Oxybenzone	0.7571	0.6	115.5
Caffeine	0.8892	0.9	77.0
Iopromide	0.9825	0.6	115.5
Erythromycin	0.9739	0.4	173.3
Fluoxetine	0.9674	0.6	115.5
Trimethoprim	0.9750	0.7	99.0
Propranolol	0.9898	0.6	115.5
Sulfamethoxazole	0.9811	0.6	115.5
Ibuprofen	0.9190	0.6	115.5
Naproxen	0.9067	0.7	99.0
Bisphenol-A	0.9429	0.7	99.0
Gemfibrozil	0.9897	0.7	99.0
Triclosan	0.9295	1.7	40.8

analyzed emerging contaminants, even though oxybenzone and caffeine showed the same behavior only at the first reaction stages.

The effect of treatment time was studied on pseudo-first-order plot for the degradation of the emerging contaminants mixture.

As described in Table 3, all the reactions followed pseudo-first-order kinetic model for each contaminant. Results demonstrated that increasing treatment time enhanced the degradation rate by a rate constant varying from $0.4 \times 10^{-2}\,min^{-1}$ to 1.7×10^{-2} min^{-1}, respectively, for erythromycin and triclosan.

Comparing the kinetics of degradation obtained in the two different equipments, the ultrasonic irradiation for CBZ gives a rate constant of 0.7×10^{-2} min^{-1} and 0.3×10^{-2} min^{-1} respectively at 45 kHz (with ultrasonic bath) and 20 kHz (with ultrasonic horn). Similar results were obtained for DCF.

The former setup looks like an attractive option because the ultrasonic horn has a limitation in terms of scale of operation [34]. Thus, it has been also shown on the basis of experiments that use of higher frequencies is beneficial in treating large quantities in an energy efficient way.

4. Conclusions

This work showed that sonolysis can promote degradation of several pharmaceuticals from wastewater. Nevertheless, the specific removal rate depends on chemical structure of the analyzed compound: for instance, after a treatment time of 180 min while triclosan degradation is almost complete (95%), other pharmaceuticals like erythromycin and iopromide are only partially removed (≈50%), using the same ultrasound power at the same frequency. This behavior can be explained considering the complexity of the compound: for instance, erythromycin presents several double bonds which are hardly broken through sonolysis.

The most important findings of this study can be summarized as follows:

(i) sonolysis is an efficient process for the degradation of all the considered emerging contaminants;
(ii) sonolysis performances increase with applied ultrasound power, frequency, and treatment time. The optimum condition in terms of removal rates includes both high frequency and high ultrasound power; and
(iii) the degradation pattern follows a pseudo-first-order kinetic.

The results obtained through this research work can be further enhanced through the investigation of by-products formation by chromatographic techniques, in order to better determine and assess the removal kinetics of the formed compounds. In addition, toxicity bioassays can help to better evaluate the potential impact that these by-products may exhibit; furthermore, additional research may further clarify the potential of combining such methods of advanced chemical oxidation with various bio-treatments that can be established.

Acknowledgments

This research is part of a research project funded by the University of Salerno (FARB). The authors acknowledge the Department of Civil and Environmental Engineering at the University of Washington (Seattle, WA, USA) for their great contribution to the experiments. Assistance provided by P. Napodano, Dr V. Nanaboina, Prof. G. Korshin, and Prof. M.M. Benjamin is deeply appreciated.

List of abbreviations

AOPs	advanced oxidation processes
BOD_5	biochemical oxygen demand
CBZ	carbamazepine
COD	chemical oxygen demand
DCF	diclofenac
DOC	dissolved organic carbon
ESI	electrospray ionization
PPCPs	pharmaceuticals and personal care products
UWWTP	urban wastewater treatment plant
WWTP	wastewater treatment plant

References

[1] F.M. Christensen, Pharmaceuticals in the environment—a human risk? Regul. Toxicol. Pharm. 28 (1998) 212–221. doi: 10.1006/rtph.1998.1253.

[2] B. Halling-Sorensen, S.N. Nielsen, P.F. Lanzky, F. Ingerslev, H.C.H. Lutzhoft, S.E. Jorgensen, Occurrence, fate and effects of pharmaceutical substances in the environment: A review, Chemosphere 36 (1998) 357–394. doi: 10.1016/s0045-6535(97) 00354-8.

[3] V. Naddeo, D. Ricco, D. Scannapieco, V. Belgiorno, Degradation of antibiotics in wastewater during sonolysis, ozonation, and their simultaneous application: Operating conditions effects and processes evaluation. Int. J. Photoenergy (2012), art. ID. 624270, p. 7. doi:10.1155/2012/624270.

[4] T. Heberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data, Toxicol. Lett. 131 (2002) 5–17. doi: Pii s0378-4274(02)00041-310.1016/s0378-4274(02)00041-3.

[5] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK, Water Res. 42 (2008) 3498–3518. doi: 10.1016/j. watres.2008.04.026.

[6] E. Zuccato, S. Castiglioni, R. Fanelli, G. Reitano, R. Bagnati, C. Chiabrando, F. Pomati, C. Rossetti, D. Calamari, Pharmaceuticals in the environment in Italy: Causes, occurrence, effects and control, Environ. Sci. Pollut. Res. 13 (2006) 15–21. doi: 10.1065/espr2006.01.004.

[7] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environ. Health Perspect. 107 (1999) 907–938. doi: 10.2307/ 3434573.

[8] K. Kummerer, Drugs in the environment: emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources: A review, Chemosphere 45 (2001) 957–969. doi: 10.1016/s0045-6535(01)00144-8.

[9] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402–417. doi: 10.1016/j.envint.2008.07.009.

[10] C. Miege, J.M. Choubert, L. Ribeiro, M. Eusebe, M. Coquery, Fate of pharmaceuticals and personal care products in wastewater treatment plants—Conception of a database and first results, Environ. Pollut. 157 (2009) 1721–1726.

[11] V. Belgiorno, L. Rizzo, F. Despo, C. Della Rocca, G. Lofrano, A. Nikolau, V. Naddeo, M. Sureyya, Review on endocrine disrupting-emerging compounds in urban wastewater: Occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse, Desalination 215 (2007) 166–176. doi: 10.1016/j.desal.2006.10.035.

[12] T.J. Mason, Sonochemistry, Oxford University Press, Oxford, 1999.

[13] K. Vinodgopal, J. Peller, Hydroxyl radical-mediated advanced oxidation processes for textile dyes: A comparison of the radiolytic and sonolytic degradation of the monoazo dye acid orange 7, Res. Chem. Intermed. 29 (2003) 307–316.

[14] R.A. Torres, J.I. Nieto, E. Combet, C. Pétrier, C. Pulgarin. Influence of TiO_2 concentration on the synergistic effect between photocatalysis and high-frequency ultrasound for organic pollutant mineralization in water, Appl. Catal., B 80 (2008) 168–175.

[15] L. Sanchez-Prado, R. Barro, C. Garcia-Jares, M. Llompart, M. Lores, C. Petrakis, N. Kalogerakis, D. Mantzavinos, E. Psillakis, Sonochemical degradation of triclosan in water and wastewater, Ultrason. Sonochem. 15 (2008) 689–694.

[16] J. Hartmann, P. Bartels, U. Mau, M. Witter, W.V. Tumpling, J. Hofmann, E. Nietzschmann, Degradation of the drug diclofenac in water by sonolysis in presence of catalysts, Chemosphere 70 (2008) 453–461.

[17] R. Emery, M. Papadakia, L. Freitas dos Santos, D. Mantzavinos, Extent of sonochemical degradation and change of toxicity of a pharmaceutical precursor (triphenylphosphine oxide) in water as a function of treatment conditions, Environ. Int. 31 (2005) 207–211.

[18] V. Naddeo, V. Belgiorno, D. Ricco, D. Kassinos, Degradation of diclofenac during sonolysis, ozonation and their simultaneous application, Ultrason. Sonochem. 16 (2009) 790–794.

[19] V. Naddeo, S. Meric, D. Kassinos, V. Belgiorno, M. Guida, Fate of pharmaceuticals in contaminated urban wastewater effluent under ultrasonic irradiation, Water Res. 43 (2009) 4019–4027.

[20] V. Naddeo, V. Belgiorno, D. Kassinos, D. Mantzavinos, S. Meric, Ultrasonic degradation, mineralization and detoxification of diclofenac in water: Optimization of operating parameters, Ultrason. Sonochem. 17 (2010) 179–185.

[21] G.T. Guyer, N.H. Ince, Degradation of diclofenac in water by homogeneous and heterogeneous sonolysis, Ultrason. Sonochem. 18 (2011) 114–119. doi: 10.1016/j.ultsonch.2010.03.008.

[22] F. Mendez-Arriaga, R.A. Torres-Palma, C. Petriera, S. Esplugas, J. Gimenez, C. Pulgarin, Ultrasonic treatment of water contaminated with ibuprofen, Water Res. 42 (2008) 4243–4248.

[23] Q. Isariebel, J. Carine, J. Ulises-Javier, W. Anne-Marie, D. Henri, Sonolysis of levodopa and paracetamol in aqueous solutions, Ultrason. Sonochem. 16 (2009) 610–616.

[24] E. De Bel, C. Janssen, S. De Smet, H. Van Langenhove, J. Dewulf, Sonolysis of ciprofloxacin in aqueous solution: Influence of operational parameters, Ultrason. Sonochem. 18 (2010) 184–189. doi: 10.1016/j.ultsonch.2010.05.003.

[25] V. Naddeo, V. Belgiorno, R.M.A. Napoli, Behaviour of natural organic matter during ultrasonic irradiation, Desalination 210 (2007) 175–182.

[26] A. Achilleos, E. Hapeshi, N.P. Xekoukoulotakis, D. Mantzavinos, D. Fatta-Kassinos, Factors affecting diclofenac decomposition in water by UV-A/TiO_2 photocatalysis, Chem. Eng. J. 161 (2010) 53–59.

[27] P. Braeutigam, M. Franke, R.J. Schneider, A. Lehmann, A. Stolle, B. Ondruschka, Degradation of carbamazepine in environmentally relevant concentrations in water by Hydrodynamic-Acoustic-Cavitation (HAC), Water Res. 46 (2012) 2469–2477.

[28] G.T. Guyer, N.H. Ince, Degradation of diclofenac in water by homogeneous and heterogeneous sonolysis, Ultrason. Sonochem. 18 (2011) 114–119.

[29] M. Landi, V. Naddeo, V. Belgiorno, Influence of ultrasound on phenol removal by adsorption on granular activated carbon, Desalin. Water Treat. 23 (2010) 181–186. doi: 10.5004/ dwt.2010.1992.

[30] M.A.K. Mostafa, Degradation of addition polymers by ultrasonic waves, J. Polym. Sci. 28 (1958) 519–524.

[31] H.H.G. Jellinek, Degradation of long chain molecules by ultrasonic waves, J. Polym. Sci. 37 (1959) 485–497.

[32] B.E. Notingk, E.A. Neppiras, Cavitations produced by ultrasonics, Proc. Phys. Soc. 63B (1950) 674–685.

[33] N. Daraboina, G. Madras, Kinetics of the ultrasonic degradation of poly (alkyl methacrylates), Ultrason. Sonochem. 16 (2009) 273–279.

[34] P.R. Gogate, Cavitation: An auxiliary technique in wastewater treatment schemes, Adv. Environ. Res. 6 (2002) 335–358.