Electrochemical oxidation of key pharmaceuticals using a Boron Doped Diamond electrode

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Abstract

This study assesses the degradation by electrochemical oxidation via boron doped diamond (BDD) electrodes of the selected pharmaceutical compounds iopromide (IOP), sulfamethoxazole (SMX), 17-alpha-ethinylestradiol (EE2) and diclofenac (DCF) in simulated wastewater and real hospital effluent wastewater. The influence of the flow rate in the electrochemical cell, applied current, initial compound concentration and wastewater matrix (simulated (SWW) versus real effluent (RWW) wastewater) was evaluated. A kinetic evaluation confirmed that the degradation can be described via pseudo first-order reaction kinetics for all experimental conditions tested. It was shown that SMX, EE2 and DCF degraded readily in SWW and RWW. The degradation of IOP was significantly slower, which is in agreement with previously reported slow degradation kinetics using typical advanced oxidation processes. Activation energies for the degradation reactions were calculated. The flow rate in the electrochemical cell had only a moderate effect on the degradation rate of EE2 and DCF. The applied current, however, had a major effect. The BDD electrochemical oxidation was shown to be an effective technique for removing pharmaceutical components from the effluent of a biological hospital wastewater treatment plant. However, the slower degradation of transformation products should be taken into account, when a full mineralization of the pharmaceuticals is pursued.

Keywords:

boron doped diamond; electrochemical oxidation; pharmaceuticals; wastewater

1. Introduction

Preventing, counteracting and remediating wastewater from polluting our environment has been one of the main topics in water research for the last decades. Pollutants that are receiving special attention lately are pharmaceutical products originating from care centers, hospitals and civil use (Wang and Wang, 2016; Rivera-Utrilla et al., 2013). These products enter the environment through sewage systems and wastewater treatment plants causing a wide variety of unwanted effects on organisms that live in surface water and ground water. Some of these products have already been reported in drinking water, thus creating the possibility to affect the human population (Yang et al., 2017).

The possibility to use advanced oxidation processes (AOP) as viable methods for the removal of these substances from wastewater has been reported in the literature (Rivera-Utrilla et al., 2013; Márquez et al., 2014; Mirzaei et al., 2017). One type of AOP is electrochemical oxidation, which has some distinct benefits such as the sole use of electricity for pollutant degradation (without the need to add chemicals), no waste production and operation at ambient temperature (Jardak et al., 2016; Dewil et al., 2017). Initial studies for its use in wastewater treatment have already been reported decades ago. However, an effective degradation has only been achieved when diamond coated anodes were applied (Canizares et al., 2008; Rodrigo et al., 2001). The main advantage of this type of anodes is the high overpotential for water hydrolysis. This property facilitates a highly efficient generation of hydroxyl radicals at the anode's surface, which serve as oxidants for the degradation of the organic compounds (Marselli et al., 2003). Apart from oxidation via these radicals, other mechanisms were shown to take place as well, such as (i) oxidation mediated by other oxidizing species generated from salts present in the wastewater such as hypochlorite and peroxosulphates and (ii) direct oxidation at the anode's surface (Canizares et al, 2005). In contrast, when using typical anode materials such as platinum and carbon, the oxidation mainly takes place at the anode's surface via direct electron transfer after adsorption of the organic compound at the anode or oxidation via physically or chemically adsorbed hydroxyl radicals (depending on the applied voltage) (De Coster et al., 2017). These mechanisms are much slower than the indirect oxidation via free hydroxyl radicals, mainly because these reactions do not only take place at the surface of the anode, but also in the bulk liquid surrounding the anode. Basically, diffusional aspects are the only processes that are limiting the degradation rate at high pollutant concentrations (Canizares et al., 2007). Additionally, these anodes are highly stable, both chemically and electrochemically, resulting in a long lifetime (Canizares et al., 2007). A full overview of the electrochemical degradation technology is provided in Chen (2004). An overview of some recent publications is included in Table 1.

Table 1: Overview of some recent publications on the degradation of pharmaceuticals via BDD

Reference	Substances studied	Main conclusions
Lan et al. (2018)	ciprofloxacin, sulfamethoxazole and salbutamol	- Complete removal of pharmaceuticals observed - No significant impact of common organics in the wastewater - Model developed with excellent correlation with experimental results

Frontistis et al. (2017)	amoxicillin	- Initial COD concentration, current density and treatment time were most important parameters governing amoxicillin degradation - Major transformation products were identified - Degradation pathways were defined
Pérez et al. (2017)	mixed real effluents	- Comparison between Fenton oxidation and BDD was made - For 80% of the effluents studied, BDD degradation was found to be more efficient
Sopaj et al. (2016)	sulfamethazine	- BDD was found to be the best anode material, compared to Ti/RuO_2-IrO_2 and graphite felt - Almost complete mineralisation was achieved
Salazar et al. (2016)	losartan	- Full removal of losartan was achieved - Four aromatic intermediates were identified and short-linear carboxylic acids were determined as degradation products
Zhu et al. (2016)	ciprofloxacin, norfloxacin and ofloxacin	- Eight oxidation products for each parent component were identified and oxidation pathways were proposed - Toxicity after oxidation remained constant for ciprofloxacin and norfloxacin, and increased for ofloxacin (algae inhibition tests) - Oxidation mixture retained antibacterial properties
Brillas et al. (2016)	dopamin	- BDD anodes yielded a faster decomposition of dopamin than Pt anodes due to greater oxidation of OH* generated by BDD - Short-linear carboxylic acids were identified as oxidation products

In this work, the use of a boron doped diamond electrode is evaluated for the degradation of four representative pharmaceuticals: iopromide (IOP), an x-ray contrast agent; sulfamethoxazole (SMX), a sulfonamide based antibacterial agent; 17-alpha-ethinylestradiol (EE2), a steroid derivate used in contraceptives and diclofenac (DCF), a nonsteroidal anti-inflammatory drug. The influence of operating conditions such as flow rate, temperature and current are evaluated. For this purpose, the four pharmaceutical products are dissolved in simulated effluent wastewater (SWW). The results are compared with tests using real effluent wastewater (RWW) originating from a hospital wastewater treatment plant.

2. Materials and methods

2.1. Chemicals

Diclofenac (DCF), sulfamethoxazole (SMX) and 17-alpha-ethinylestradiol (EE2) were purchased from Sigma-Aldrich (Overijse, Belgium). Iopromide (IOP) was purchased from VWR International (Leuven, Belgium). Deionized (DI) water was produced with a reverse osmosis water filtration device (VWR International, Leuven, Belgium) that maintained an electrical conductivity of 5 µS/cm.

SWW was prepared according to the composition provided in Table 2. The chemical oxygen demand (COD) of the SWW was 53.2 mg/L. RWW was taken from the effluent ditch of the University Hospital Leuven, Campus Pellenberg wastewater treatment plant (Pellenberg, Belgium), and had a COD of around 78.4 mg O_2/L. COD was measured using Hach COD test kits and a DR3900 spectrophotometer (Hach, Mechelen, Belgium).

Table 2: Composition of SWW used in the experiments

Substances	Concentration (mg/L)	Supplier
$NaHCO_3$	96	Fisher Scientific (Loughborough, UK)
NaCl	7	Fisher Scientific (Loughborough, UK)
$CaSO_4 \cdot 2H_2O$	60	Merck (Darmstadt, Germany)
Urea	6	S.C. Federa S.V. (Brussels, Belgium)
KCl	4	ChemLab (Zedelgem, Belgium)
$CaCl_2$	3	Sigma-Aldrich (Steinheim, Germany)
Peptone	32	BD Biosciences (Le Pont-de-Claix, France)
$MgSO_4 \cdot 7H_2O$	125	Acros Organics (Geel, Belgium)
$NH_4H_2PO_4$	1.2	Merck (Darmstadt, Germany)
Meat extract	22	Sigma-Aldrich (Steinheim, Germany)

2.2 Electrochemical set-up and experiments

The experimental set-up consisted of a flow-through electrochemical cell, a circulation tank and a centrifugal pump. For each experiment, the buffer tank was filled with 10 L of the experimental solution, which was circulated through the electrochemical cell at a fixed flow rate (controlled via a membrane valve). Electrodes were made of a conductive substrate of silicium, coated with the BDD layer, and yielded a surface area of 189 cm^2. The electrodes were connected to a power source with a maximum voltage of 55 V and a maximum current of 10 A. The conductivity was measured with a WTW Microprocessor Conductivity meter LF537 from VWR (Haasrode, Belgium) while the pH and temperature were monitored with a HI2211 pH meter from Hanna Instruments (Temse, Belgium).

Experimental solutions were prepared by measuring out the appropriate weight of IOP, SMX, EE2 and DCF gravimetrically in concentrations of 0.5 mg/L or 10 mg/L. Complete dissolution of the components was guaranteed by mixing the solution for 2 h on a stir plate before introducing it in the circulation tank. To start the experiment, the circulation pump was activated and the flow rate adjusted using the

valve. Once the flow rate was stable, the BDD cell was turned on. The polarization of the electrodes was switched every 10 min to prevent scaling. Samples were taken at regular time intervals in the circulation tank and analyzed using liquid chromatography (see § 2.3).

2.3. LC-MS experiments

All samples were analyzed on a Dionex Ultimate 3000 HPLC system (ThermoFisher Scientific, Germering, Germany) equipped with an autosampler, a quaternary pump and a variable wavelength detector with a cell volume of 11 µL. The column temperature was controlled at 40 °C with a static air oven compartment (Waters, Bedford, MA, USA). The maximum operating pressure of the system was 400 bar. Peeksil viper tubing (75 µm I.D.) (ThermoFisher Scientific) was used to connect the column to the injector and detector of the system. The tubing was not altered during the experiments to avoid changing the extra-column volume. Analyses were performed using a Poroshell 120 Bonus-RP column (2.1 x 100 mm; 2.7 µm) (Agilent Technologies, Waldbronn, Germany) in gradient mode using 0.5% formic acid in H_2O as mobile phase A and 0.5% formic acid in ACN as mobile phase B. After an equilibration of 7 min at the initial mobile phase condition of 100% A, the mobile phase was changed to 30/70 A/B in 10 min, held for 2 min at 30/70 A/B and returned to 100% A in 1 min. For the identification of the transformation products, the gradient was optimized for each individual compound to minimize co-elution of the different degradation products. The flow rate was 0.3 mL/min and the injection volume 100 µL. The absorbance was measured at wavelengths of 254 nm (IOP) and 280 nm (SMX, EE2 and DCF). For the identification of the transformation products, the HPLC was connected to an LCQ IT mass spectrometer (ThermoFinnigan) with an ESI interface operated in positive ion mode. The ESI needle voltage was set at 4.5 kV and the heated capillary was held at 300°C. Following voltages were applied to obtain an optimal signal: capillary voltage 19.0 V, tube lens offset voltage −15.0 V, octopole 1 offset voltage −3.0 V, octopole 2 offset voltage −10.0 V and interoctopole lens voltage −16.0 V. Nitrogen (Air Liquide, Liege, Belgium) served as sheath and auxiliary gas at flow rates of 100 arb and 60 arb respectively. Helium was used as damping gas. Xcalibur 1.3 software (ThermoFinnigan) was used for instrument control, data acquisition and processing.

2.4. Kinetic evaluation

Because of the very short lifetime of the generated hydroxyl radicals (limited to a few nanoseconds) (Haidar et al., 2013), their concentration can be described via a quasi-stationary state and pseudo first-order reaction kinetics can be considered, following equation (1).

$$-\frac{dC}{dt} = k_{abs} \cdot [OH^*] \cdot C = k \cdot C \qquad (1)$$

where C is the concentration of the organic compound to be degraded, k_{abs} is the absolute reaction rate constant and k the apparent first-order reaction rate constant.

After integration of this reaction rate equation, the corresponding representation of the logarithm vs. time was used to determine the k for the oxidation of the compounds at each experiment.

3. Results and discussion

3.1. Degradation kinetics in simulated wastewater

The kinetics for the degradation of IOP, SMX, EE2 and DCF were first assessed separately in SWW (mono) and then compared to the kinetics of a mixture of the components (mixed). The initial concentration of each component in all tests was 0.5 mg/L. The BDD treatment was carried out at an applied current of 0.9 A and a flow rate in the electrochemical cell of 250 L/h. The results of the degradation experiments are reported in Figure 1.

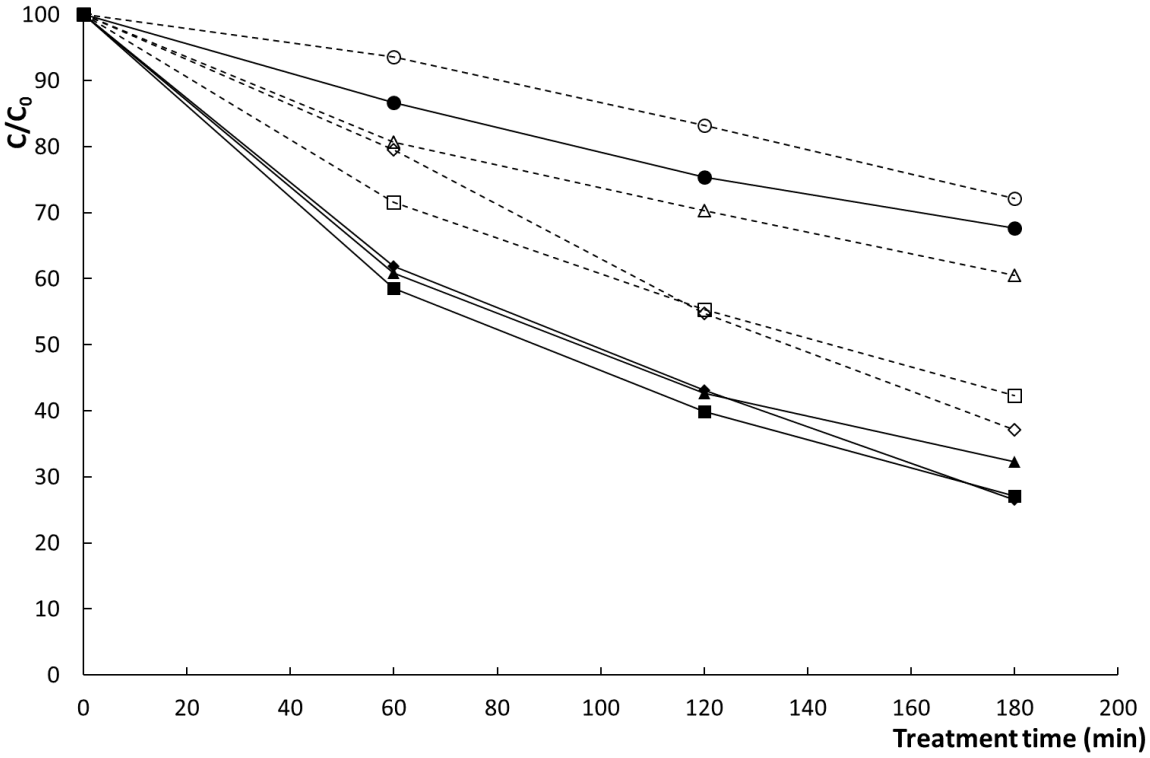


Figure 1: Time course of the compound concentration during BDD treatment for the SWW with each compound individually (mono, closed symbols and full lines) and a mixture of all compounds (mixed, open symbols and dashed lines) (I = 0.9 A; Q = 250 L/h; T = room temperature). Symbols indicate IOP (●/○), SMX (■/□), EE2 (▲/△) and DCF (♦/◊).

Only small differences were observed between the degradation curves of SMX, EE2 and DCF when the compounds were individually added to the SWW, with a degradation of 72.9%, 69.7% and 73.7% after 180 min reaction time, respectively. The IOP degradation occurred much slower. Only 32.3% of the initial IOP concentration was degraded after 180 min. For all components, a considerable decrease in degradation rate was observed when all components were present simultaneously. The degradation after 180 min reaction time was reduced to 27.8%, 67.7%, 39.5% and 66.9% for IOP, SMX, EE2 and DCF, respectively. Especially for EE2, a considerable drop was noticed. For the other components, the decrease was limited.

To quantify these differences in degradation rate, the first order reaction rate constants were determined and are listed in Table 3 for all compounds. The high correlation coefficients (R^2) for the

linear approximation of ln(c) versus t confirms the validity of the assumption that pseudo first-order kinetics are applicable for all degradation curves. Moreover, it confirms the high accuracy of the concentration measurements.

Table 3: Pseudo first-order reaction rate constants for the degradation of IOP, SMX, EE2, DCF in SWW for each individual compound and for the mixture of all compounds (I= 0.9 A; Q= 250 L/h; T= room temperature)

	k (min^{-1})	**R^2**
IOP (mono)	0.0023	0.996
IOP (mixed)	0.0019	0.972
SMX (mono)	0.0074	0.990
SMX (mixed)	0.0050	0.996
EE2 (mono)	0.0064	0.980
EE2 (mixed)	0.0029	0.989
DCF (mono)	0.0075	0.997
DCF (mixed)	0.0058	0.989

The reaction rate constants k are all in the same order of magnitude (10^{-3}), but differences between the exact values are observed. For the individual compounds, the order of reaction rate constants is DCF ≅ SMX > EE2 > IOP. The same order is observed when all compounds are present simultaneously: DCF > SMX > EE2 > IOP. Further, a decrease in k by 17.4%, 32.4%, 54.7% and 22.7% is observed for IOP, SMX, EE2 and DCF, respectively, when the compounds are simultaneously present in the SWW. Especially for EE2, this decrease is significantly higher than for the other components. This observation cannot be explained by the experimental results obtained in this study.

The decrease in k is explained by the competitive degradation of the components. Given a set of process conditions (i.e., I = 0.9 A; Q = 250 L/h and T = room temperature), the amount of hydroxyl radicals generated in the BDD cell is constant. A competitive use of these oxidants for the degradation of the compounds hence occurs if more compounds are added simultaneously. The SWW (without addition of the pharmaceutical compounds) already contains 60 mg/L of organic material (combination of urea, peptone and meat extract that is included in the wastewater). When simultaneously adding all compounds, the total organic matter concentration in the SWW increases from 60.5 mg/L (0.5 mg/L if one pharmaceutical compound is added) to 62.0 mg/L (0.5 mg/L of each of the 4 pharmaceutical compounds when added together), but this increase is limited compared to the overall concentration of organics. The observed decrease in k values is hence induced by only a minor increase of organic matter, suggesting that this type of organics is more prone to oxidative degradation than the organic matter already present in the SWW. In other words, the large decrease in k, for only a limited increase in total organic matter of the SWW suggests that the pharmaceuticals are preferentially targeted by the BDD treatment.

3.2. Influence of flow rate

The influence of the flow rate Q in the electrochemical cell on the observed degradation was tested by measuring the degradation of the pharmaceutical compounds over time at three different flow rates, i.e., 125, 250 and 500 L/h. Tests were carried out in SWW, to which a concentration of 0.5 mg/L of all four pharmaceutical compounds was added simultaneously. The applied current was 0.9 A and all

experiments were performed at room temperature. The results of the degradation tests are shown in Figure 2. The pseudo first-order reaction rate constants are listed in Table 4. Again, high R^2 values confirm the assumption of pseudo first-order reaction kinetics.

Overall, only a limited influence of Q on the degradation kinetics is observed. There is no significant change in k for IOP and SMX. The values of k remain within a 10% margin, irrespective of the flow rate applied. For EE2, an increase from 0.0023 min^{-1} to 0.0029 min^{-1} and 0.0037 min^{-1} is present when Q increases from 125 L/h to 250 L/h and 500 L/h, respectively. This represents a relative increase by 26% and 61%, respectively. The k values for DCF increase from 0.0052 min^{-1} to 0.0058 min^{-1} and 0.0068 min^{-1} for a Q increase from 125 L/h to 250 L/h and 500 L/h, respectively (relative increase by 12% and 31%). It was previously described (Lan et al., 2017; Racaud et al., 2012) that the flow rate in the cell determines the mass transfer coefficient. Racaud et al. (2012) even describe a linear relationship between flow rate and mass transfer coefficient. A limited influence of the flow rate in the cell indicates that the occurring reactions are not mass transfer limited, but rather reaction rate limited (chemical reaction is slower than mass transfer). Hence an improvement of the mass transfer coefficient only influences the overall observed kinetic constant k to a limited extent.

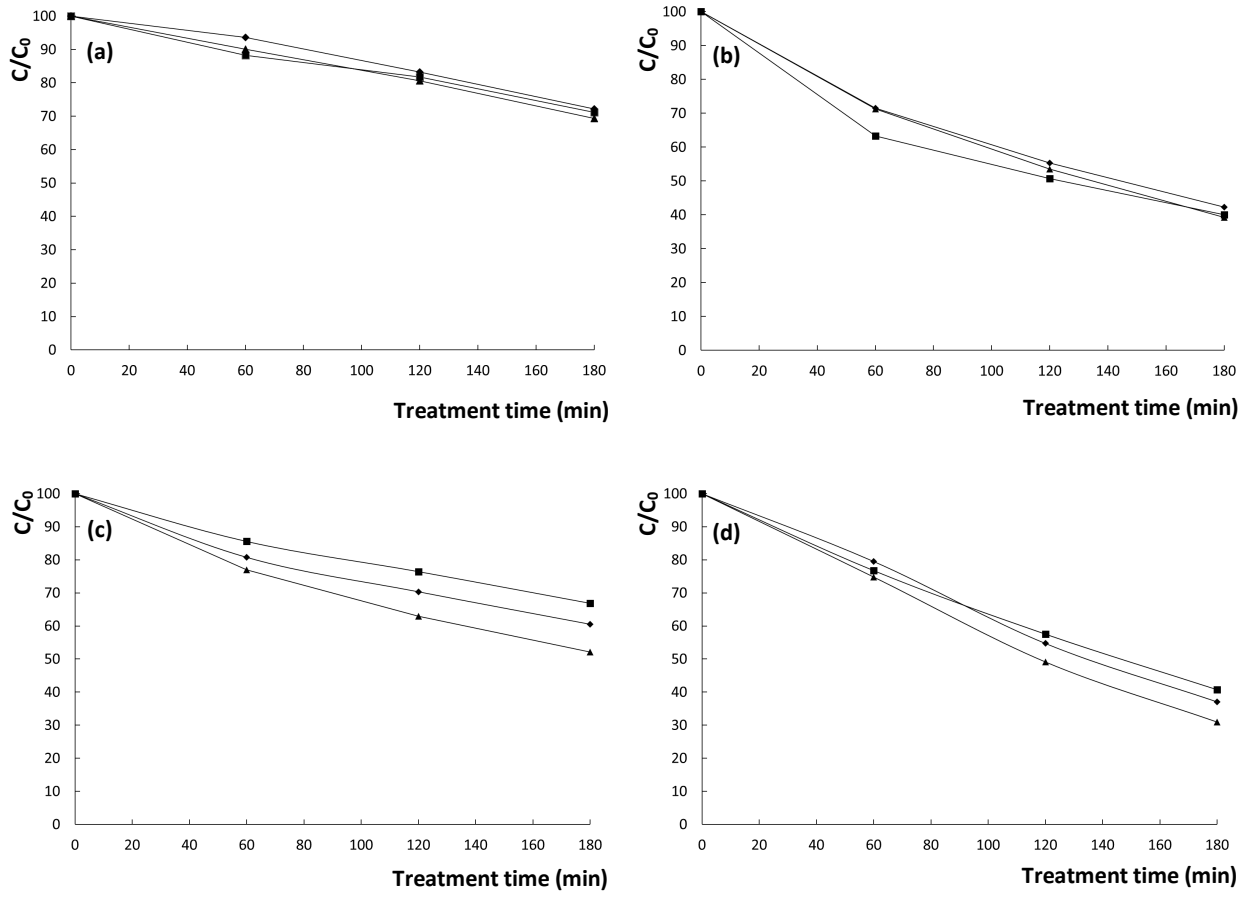


Figure 2: Time course of compound degradation for different flow rates: ■ 125 L/h, ♦ 250 L/h, ▲ 500 L/h for (a) IOP, (b) SMX, (c) EE2 and (d) DCF (I = 0.9 A; T = room temperature).

Table 4: Pseudo first-order reaction rate constants for the degradation of IOP, SMX, EE2, DCF in SWW for different flow rates Q (I= 0.9 A; T= room temperature).

Flow rate Q (L/h)	IOP		SMX		EE2		DCF	
	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
125	0.0019	0.987	0.0052	0.963	0.0023	0.998	0.0052	0.996
250	0.0019	0.972	0.0050	0.996	0.0029	0.989	0.0058	0.989
500	0.0021	0.991	0.0054	0.998	0.0037	0.996	0.0068	0.992

3.3. Temperature dependency

The temperature dependency of the degradation reaction was evaluated by carrying out tests at 18°C, 30°C and 50°C. Tests were carried out on SWW, to which a concentration of 0.5 mg/L of all 4 pharmaceutical compounds was added simultaneously. The applied current was 0.9 A and the flow rate through the electrolysis cell was 500 L/h. The results of the degradation tests are shown in Figure 3. The pseudo first-order reaction rate constants are listed in Table 5.

For all components, the reaction rate increased with increasing temperature. Between 18°C and 50°C, an increase in k was observed of 44%, 168%, 58% and 64% for IOP, SMX, EE2 and DCF, respectively. With an increase of 186%, a prominent increase was observed for SMX when the temperature was elevated. In contrast, the other 3 compounds showed a less pronounced increase in k and a very similar temperature dependency.

The availability of the reaction rate constants at different temperatures further enabled to calculate the activation energy E_a for all degradation reactions. Indeed, as is the case for most chemical reaction systems, the electrochemical degradation is assumed to follow an Arrhenius law:

$$k = A \cdot exp\left(-\frac{E_a}{R \cdot T}\right) \quad (2)$$

with k the reaction rate constant (min^{-1}), A the pre-exponential factor (min^{-1}), E_a the activation energy (J/mol), T the absolute temperature (K) and R the universal gas constant (8.314 J/mol.K).

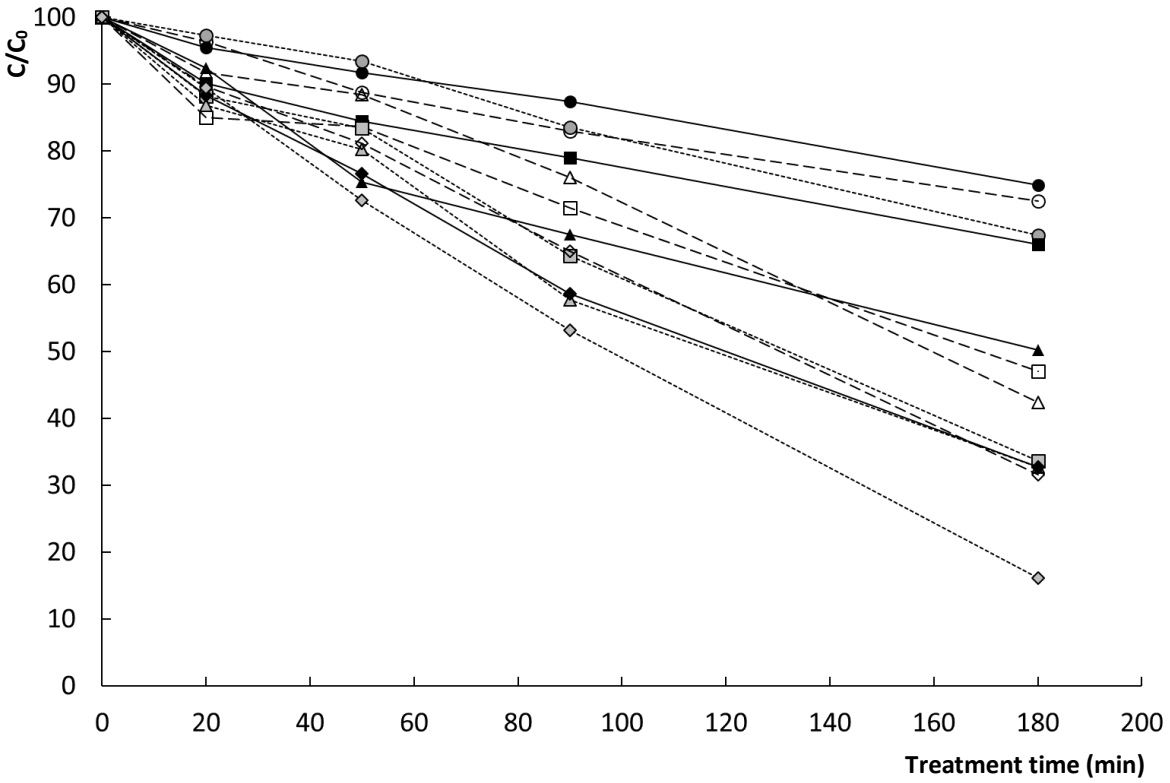


Figure 3: Time course of compound degradation at different temperatures: 18°C (full symbols and full lines), 30°C (open symbols and dashed lines), 50°C (grey symbols and dotted lines) for IOP (●), SMX (■), EE2 (▲) and DCF (♦) at I= 0.9 A and Q= 500 L/h.

Table 5: Pseudo first-order reaction rate constants for the degradation of IOP, SMX, EE2, DCF in SWW at different temperatures (I= 0.9 A; Q= 500 L/h).

Temp	IOP		SMX		EE2		DCF	
(°C)	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
18	0.0016	0.995	0.0021	0.973	0.0039	0.964	0.0062	0.976
30	0.0018	0.986	0.0040	0.976	0.0049	0.977	0.0064	0.998
50	0.0023	0.989	0.0060	0.976	0.0062	0.991	0.0102	0.972

E_a can further be calculated by taking the natural logarithm of both sides of the equation, which recasts it into the form of an equation for a straight line (equation (3)):

$$ln(k) = ln(A) - \frac{E_a}{R} \cdot \frac{1}{T} \quad (3)$$

A plot of ln k vs. 1/T gives a straight line with a slope of $-E_a/R$ and y-intercept of ln(A).

The results of this evaluation are reported in Table 6. The Arrhenius assumption was confirmed by the systematically high R^2 values for the linear fit of the experimental data to equation (3), which were 0.99, 0.94, 0.99 and 0.89 for IOP, SMX, EE2 and DCF, respectively.

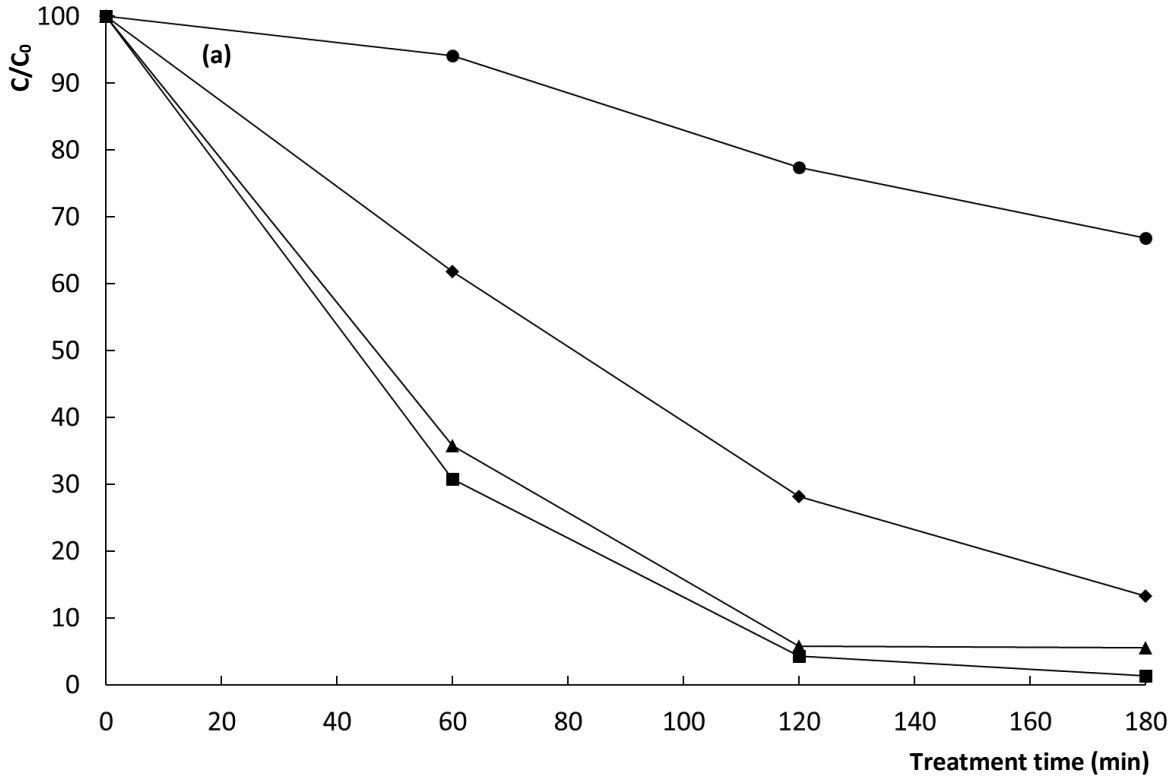
The highest value of E_a was obtained for SMX (24914 J/mol), followed by 12696 J/mol for DCF, 11182 J/mol for SMX and 8950 J/mol for IOP.

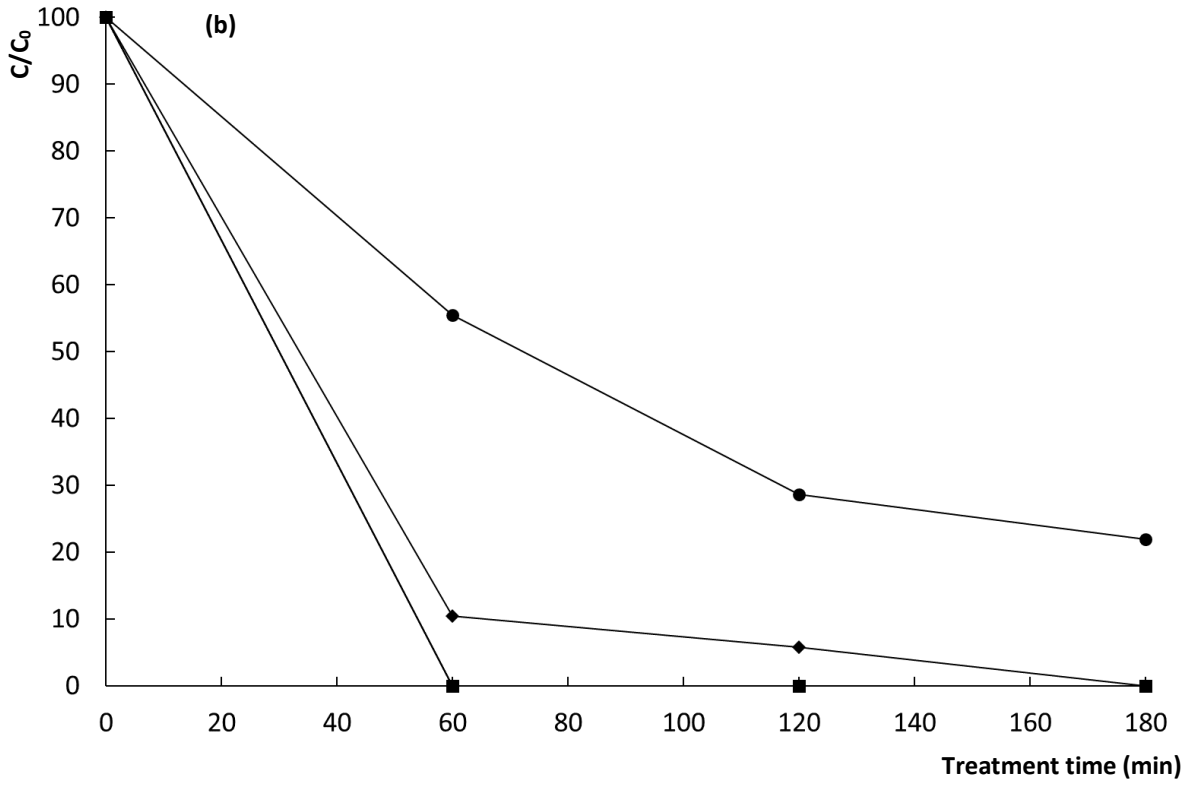
Table 6: Pre-exponential factor A and activation energy E_a for the degradation of IOP, SMX, EE2 and DCF (Q= 500 L/h; T= 50°C).

	IOP	SMX	EE2	DCF
A (min^{-1})	0.0640	68.1	0.403	1.10
E_a (J/mol)	8950	24914	11182	12696

3.4. Degradation in real effluent wastewater

Degradation experiments were also performed using RWW. The wastewater was spiked with the four pharmaceutical compounds simultaneously at concentrations of 0.5 mg/L and 10 mg/L. For the 10 mg/L concentration, the treatment time was extended to 540 min to achieve a sufficient degradation of the compounds. The current I was set at 0.9 and 3.1 A, while the temperature was kept at 50°C. The results of the degradation experiments are presented in Figure 4. The calculated pseudo first-order reaction rate constants k are included in Table 7.





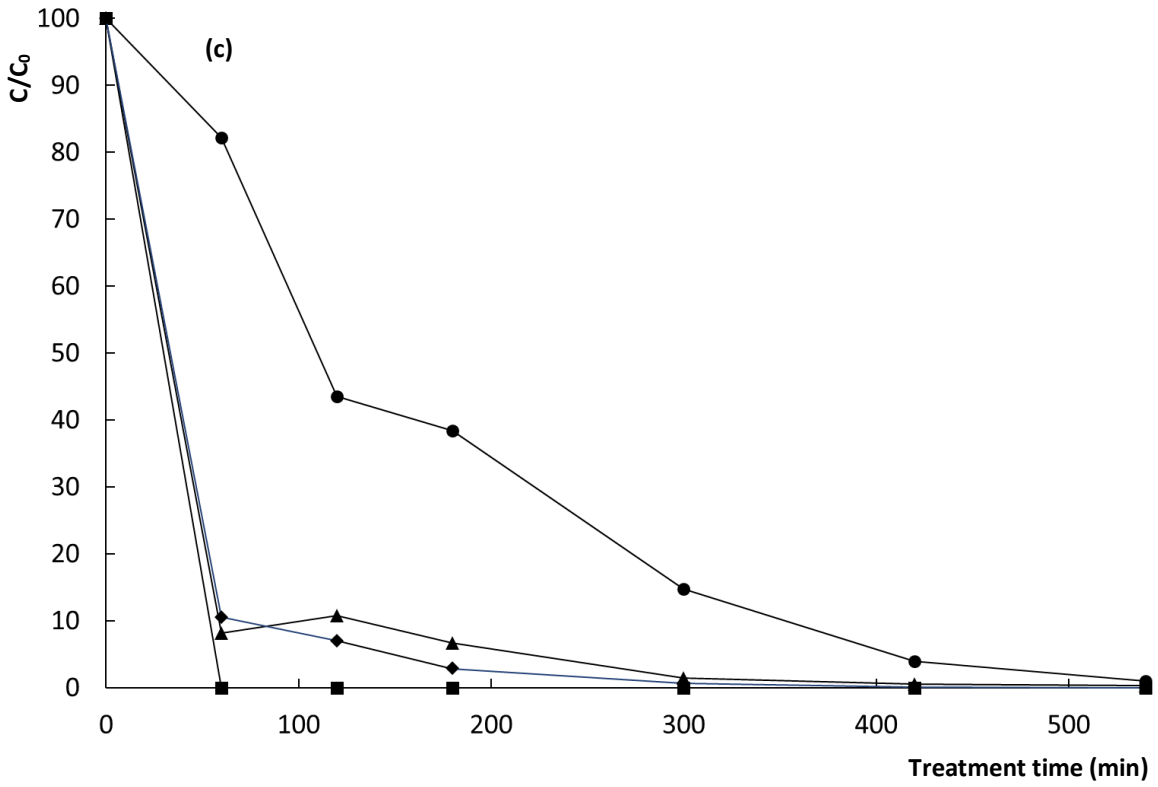


Figure 4: Time course of compound degradation in real effluent wastewater. (a) C_0 = 0.5 mg/L, Q = 500 L/h, I = 0.9 A; (b) C_0 = 0.5 mg/L, Q = 500 L/h, I = 3.1 A; (c) C_0 = 10 mg/L, Q = 500 L/h, I = 3.1 A for IOP (●), SMX (■), EE2 (▲) and DCF (♦).

Table 7: Pseudo first-order reaction rate constants for the degradation of IOP, SMX, EE2, DCF in RWW

	0.5 mg/L, 0.9 A		0.5 mg/L, 3.1 A		10 mg/L, 3.1 A	
	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
IOP	0.0025	0.962	0.0088	0.973	0.0087	0.976
SMX	0.0252	0.990	-	-	-	-
EE2	0.0177	0.908	-	-	0.0095	0.899
DCF	0.0117	0.992	0.0241	0.894	0.0248	0.962

To evaluate the difference in degradation efficiency between SWW and RWW as wastewater matrix, the k-values of the pharmaceutical compounds at the following process conditions were compared: C_0=0.5 mg/L, I = 0.9 A, T = 50°C and Q = 500 L/h. For all four compounds, a significantly higher k was observed in the RWW. However, the relative increase for the different compounds largely differed: k increased with 19%, 367%, 378% and 72% for IOP, SMX, EE2 and DCF, respectively. The systematically higher k for all compounds in the RWW is remarkable since the COD of the RWW (78.4 mg/L) was approximately 50% higher than the COD of the SWW. Similar to the discussion on the selectiveness of the oxidation in section 3.1, it seems that the type of organic matter in the RWW consumes less oxidative species and the selectiveness towards the oxidation of the added pharmaceuticals is higher for the RWW.

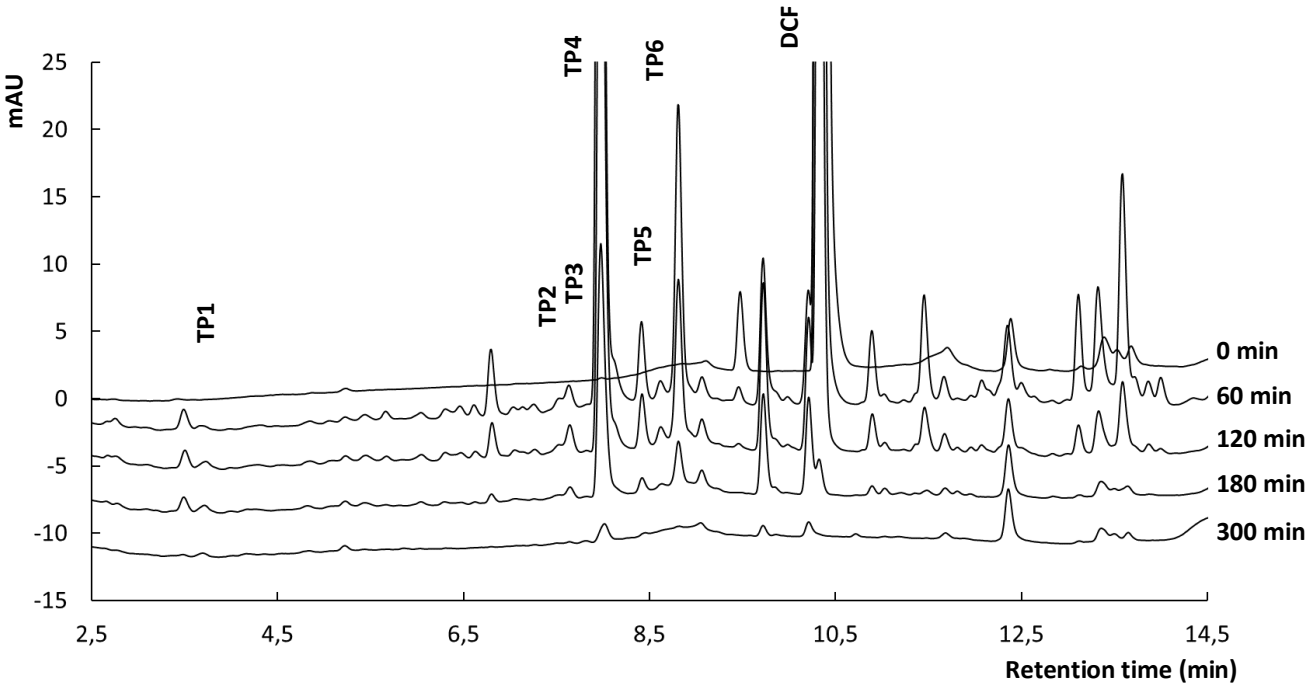
An increase of I to 3.1 A resulted in a significantly faster degradation of all compounds. The concentration of SMX and EE2 already dropped below the detection limit at the first sampling point (at a reaction time of 60 min). Therefore, k could not be determined for these components. For IOP and DCF, k increased by 252% and 106%, respectively. At the same I, increasing the C_0 to 10 mg/L only had a marginal effect on k. Because of the very fast degradation of SMX and EE2 (as mentioned above), no comparison could be made for these compounds. For IOP and DCF, no significant difference in k was observed.

3.5. Fate of the degradation products

So far, only the degradation of the parent compounds has been discussed. However, when oxidation of these pharmaceuticals is conducted, a large number of degradation/transformation products is formed. Figure 5 (a) shows a representative chromatogram obtained for DCF after 0, 60, 120, 180 and 300 min of treatment, using the same experimental conditions as in Figure 4. Note that a number of transformation products (TPs) can clearly be observed in the chromatogram. Some transformation products were tentatively identified based on their *m/z* and literature data (Pérez-Estrada et al., 2005; Yu et al., 2013; Minetto et al., 2012). Their suggested structures are shown in Table 8. Since standard compounds of these TPs were not available, an accurate quantitation of their concentration was not feasible. Therefore, the evolution of their concentration as a function of degradation time is merely represented as the observed area under the curve versus the maximum obtained area under the curve (A/A_{max}) in Figure 5 (b). These results indicate that although DCF is completely removed from the solution after 180 min, it takes two to three times longer to remove all the degradation products from the solution.

Similar results were obtained for SMX, EE2 and IOP (data not shown), where it was also observed that the order wherein the degradation products are removed, is similar to their parent compounds: i.e., the degradation products of DCF are easier to remove than those of SMX, EE2 and IOP.

These observations indicate that monitoring the removal efficiency of the parent compounds is not sufficient when dealing with persistent degradation products, especially when these have a higher toxicity than the parent compound.



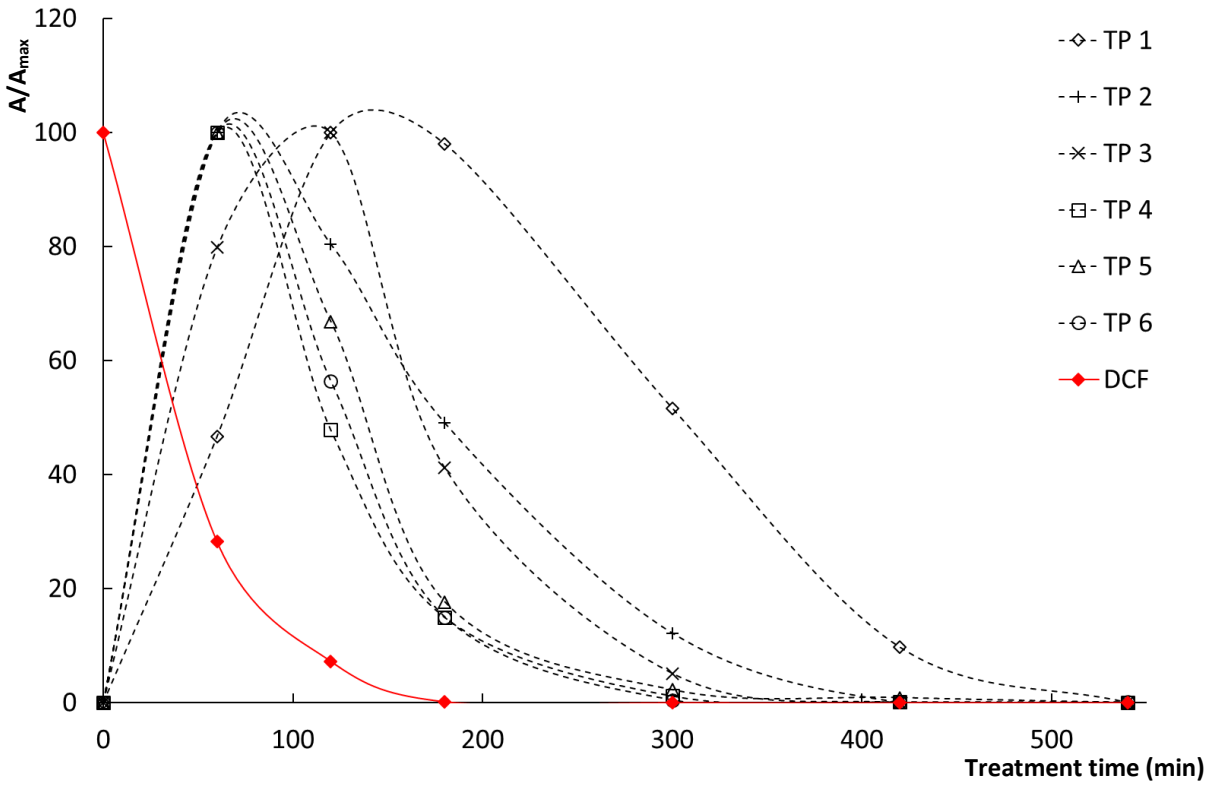
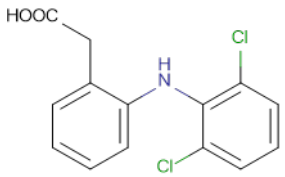
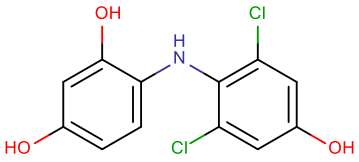
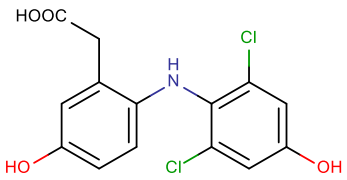
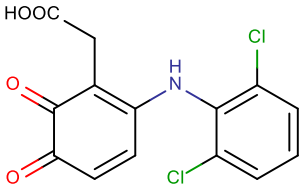
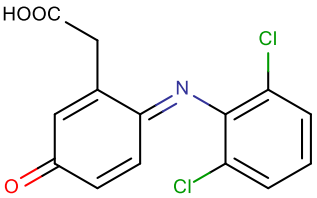
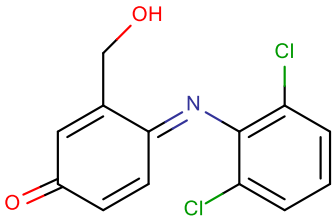
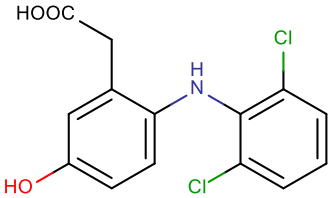


Figure 5: (a) Chromatogram showing DCF and its main transformation products after 0, 60, 120, 180 and 300 minutes of treatment time, (b) Evolution of DCF and its main transformation products as a function of treatment time. The observed area under the curve (A) is plotted as a function of the maximum observed area under the curve (A_{max}) for each compound separately.

Table 8: Tentative structures of the main transformation products of diclofenac, based on their *m/z*.

Compound name	*m/z*	Proposed structure
Diclofenac (DCF)	297	
TP1	286	

TP2	328	
TP3	326	
TP4	310	
TP5	282	
TP6	312	

4. Conclusions

In this study, the degradation by electrochemical oxidation via BDD electrodes was assessed for the selected pharmaceutical compounds IOP, SMX, EE2 and DCF in SWW and real hospital effluent wastewater. The influence of the flow rate in the electrochemical cell, applied current, initial compound concentration and wastewater matrix (SWW versus RWW) was evaluated. A kinetic evaluation confirmed that the degradation can be described via pseudo first-order reaction kinetics for all experimental conditions tested. It was shown that SMX, EE2 and DCF degraded readily in SWW and RWW. The degradation of IOP was significantly slower, which is in agreement with previously reported slow degradation kinetics using typical advanced oxidation processes. Activation energies for the degradation reactions were calculated. The flow rate in the electrochemical cell only had a moderate effect on the degradation rate of EE2 and DCF. The applied current, however, had a major effect. BDD was shown to be an effective technique for removing pharmaceutical components from the effluent of a biological hospital wastewater treatment plant. However, when a full mineralization

of the pharmaceuticals is envisaged, it should be taken into account that the degradation of the transformation products of the parent pharmaceutical compounds can take some 2-3 times longer.

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