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Electrochemical degradation of piroxicam on a boron doped diamond anode: Investigation of operating parameters and ultrasound synergy

Aikaterini Kouskouki^[a], Efthalia Chatzisyseon^[b], Dionissios Mantzavinos^[a] and Zacharias Frontistis^{*[c]}

Abstract: The electrochemical oxidation of piroxicam, a representative nonsteroidal anti-inflammatory drug, was studied using boron-doped diamond (BDD) as the anode. BDD exhibited superior efficiency in comparison with platinum electrodes in terms of PIR degradation. Removal of PIR follows pseudo-first-order kinetics and the apparent kinetic constants decreased from 0.138 to 0.0369 min⁻¹ as the initial PIR concentration increased from 245 to 975 µg L⁻¹. Altering of the pH had little effect on electrolysis of PIR with slightly better removal at pH 9. The presence of 10 g L⁻¹ of tert-butanol inhibited PIR removal indicating that its oxidation is caused by electro-generated hydroxyl radicals. Addition of 200 mg L⁻¹ sodium chloride increased the apparent kinetic constant more than ten times from 0.139 to 1.44 min⁻¹. Similar behavior was observed in the case of bicarbonates and nitrates, possibly due to the generation of selective carbonate radicals and active oxygen species like nitric or nitrous oxides. Experiments were also conducted in various aqueous matrices and it was observed that the presence of humic acid delayed the degradation of PIR, while process efficiency was enhanced in bottled and surface water as well as in wastewater, due to the presence of inorganic ions. Coupling BDD electrolysis with ultrasound (at 14 W L⁻¹, 20 kHz) increased the reaction rate of PIR destruction and the observed synergy was calculated at S=44.6%.

Introduction

In recent years, there is a growing consumption of nonsteroidal anti-inflammatory drugs (NSAIDs). These drugs are used mainly as painkillers, in order to decrease fever and to prevent blood clots [1]. The class of NSAIDs include lots of drugs like ibuprofen, diclofenac naproxen, and piroxicam (PIR). NSAIDs have been extensively detected in surface water and secondary effluents in concentrations ranging from ng L⁻¹ – µg L⁻¹ [1-3]. The use of physical and chemical processes becomes an imperative for the treatment of such persistent pollutants, since conventional biological systems fail to effectively remove NSAIDs [4].

Advanced oxidation processes (AOPs) consist of a group of physicochemical processes based on the in situ production of reactive oxygen species (ROS) [5]. Due to their high oxidation power, ROS can eventually transform organic compounds to carbon dioxide and water [6].

Among several AOPS electrochemical oxidation has stimulated the interest of the scientific community [7-9]. Electrolysis has many advantages: the main reagent is the electron, thus there is no need for additional chemicals while the process control is relatively easy [10-12]. In addition, the synthesis of a new generation of materials like boron-doped diamond (BDD) has improved dramatically the efficiency of the process due to the enhanced production of reactive oxygen species [13-17]. In their pioneering work Guinea, et al. [18] applied both anodic oxidation and electro Fenton process for the treatment of salicylic acid using BDD and platinum electrodes as the anode. Graphite and O₂ diffusion cathodes were used for the electrosynthesis of hydrogen peroxide. Anodic oxidation removed almost 81% of total organic carbon (TOC) after 3 hours with the mineralization current efficiency being 5.4%. The electrogenerated peroxide did not practically improve the process efficiency since there was only 3% and <0.5% increase for TOC removal and mineralization current efficiency, respectively. On the other hand, addition of iron increased significantly the performance of the solar photo-electro Fenton (SPEF) process. The required energy for the total mineralization of 164 mg L⁻¹ salicylic acid reduced almost 4 times from 407 to 93 kWh m⁻³ for anodic oxidation and SPEF, respectively. Ciriako et al. [19] studied the electrooxidation of 1.75 mM of ibuprofen, another NSAID, on a Ti/Pt/PbO₂ and a Si/BDD electrode. They found that while BDD exhibited better performance at 20 mA cm⁻², interestingly both electrodes showed similar efficiency at 30 mA cm⁻². Feng et al. [20] examined the electrochemical decomposition of ketoprofen using platinum or BDD together with carbon felt as the cathode (electro-Fenton process). The apparent kinetic constants for BDD anodic oxidation ranged from 0.035 to 0.214 min⁻¹, when the current increased from 0.1 to 2 A. The use of the hybrid electro Fenton process improved the efficiency of the process. Oxidation of ketoprofen over BDD was also studied by Murugananthan et al. [21] who found, by means of cyclic voltammetry, that ketoprofen is oxidized at 2.0 V due to direct electron transfer. Zhao et al., [22] investigated the use of BDD for the removal of diclofenac and they observed that removal of diclofenac was increased as the voltage increased with mineralization of 30 mg L⁻¹ diclofenac solution approaching 72% after 240 min of electrolysis. Gonzalez et al. [23] used an electrochemical cell consisted of two BDD electrodes in order to decompose naproxen in a semi-batch reactor. The authors concluded that among several operating parameters, namely current, electrolyte, rate flow and pH, the role of current was crucial. Also, when Na₂SO₄ was used they observed total

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removal of naproxen and 38% TOC removal at 194 mA cm^{-2} for $\text{pH}=10.7$ and $Q=4.1 \text{ cm}^3 \text{ min}^{-1}$. Recently, Sivarasan et al. [24] demonstrated that $\text{RuO}_2/\text{IrO}_2/\text{TaO}_2$ coated on titanium dioxide dimensionally stable anode (DSA) was capable of completely removing PIR at 5 mA cm^{-2} after 180 min of treatment with $0.1 \text{ M Na}_2\text{SO}_4$ as the electrolyte, while the mineralization was 56.7% in the same oxidation time.

Organic oxidation reactions are usually carried out on the electrode or on a very thin film (nm) surrounding it [25]. Therefore, a disadvantage of electrolysis is that it requires a large surface area of electrodes. An interesting way to enhance mass transfer on the electrode surface is the simultaneous use of ultrasounds. In addition, the application of ultrasound via the acoustic cavitation can promote the generation of reactive oxygen species [26]. Under this perspective Ren et al. [27] studied the sonoelectrochemical degradation of 10 mg L^{-1} triclosan using 70 W of ultrasound irradiation at 850 kHz , 10 V at $0.82 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$ and different electrodes. For all anode materials tested the simultaneous use of ultrasound was found to increase process efficiency. The synergy observed was 24, 9 and 6% for BDD, silicon carbide, and stainless steel, respectively. The sonoelectrooxidation of methyl paraben, a representative endocrine disruptor was investigated by Steter et al. [28]. The authors found that the observed kinetic constant for the decomposition of 100 mg L^{-1} methyl paraben and 10.8 mA cm^{-2} using BDD anode at 25°C increased from 2.6 to $5.8 \times 10^{-3} \text{ min}^{-1}$ with the application of 523 W cm^{-2} ultrasound at 20 kHz .

The aim of this work was to study the electrochemical oxidation of PIR over a BDD anode. Different operating parameters that influence the conversion of PIR, such as the current intensity, the pH, PIR initial concentration, the water matrix, and the presence of inorganic ions and organic matter were investigated. Finally, the simultaneous use of ultrasounds and BDD anodic oxidation was assessed. As far as we are concerned, this is the first report for the destruction of PIR with the proposed treatment system.

Results and Discussion

Effect of anode material and current density

Preliminary experiments were conducted in order to assess the effect of electrode material on the decomposition of PIR. Boron-doped diamond (BDD) and platinum electrodes were tested and the results are shown in Figure 1. As can be observed the efficacy of BDD was significantly higher than the platinum electrode. Complete electrooxidation of $245 \text{ } \mu\text{g L}^{-1}$ PIR at 26.7 mA cm^{-2} on the BDD anode was achieved in less than 15 minutes of treatment. At the same time, PIR removal in the presence of platinum anode was less than 15%. BDD superiority can be attributed to the larger potential window of BDD than at the platinum electrode. Therefore BDD electrode generates a higher concentration of reactive oxygen species (ROS) before parasitic reactions (i.e. oxygen evolution) occur [29].

In addition, BDD is classified as inert material, thus the ROS are physisorbed on electrodes known as dimensionally stable anodes (DSA), as for example iridium oxide, in which case ROS

are chemically attached on the electrode surface [30,31]. These results are in agreement with the work of Choi et al. [32] who studied the destruction of 1,4-dioxane with BDD, platinum, and stainless steel. They found that under the application of 3.12 mA cm^{-2} the COD removal was 84% and 17% for BDD and platinum electrodes, respectively.

Figure 1. Electrochemical oxidation of PIR over various anode materials. Conditions: $[\text{PIR}]_0=245 \text{ } \mu\text{g L}^{-1}$ in ultrapure water, $[\text{Na}_2\text{SO}_4]=0.1 \text{ M}$, and 26.7 mA cm^{-2} .

Thereafter, the effect of current density for the oxidation of $245 \text{ } \mu\text{g/L}$ of PIR over a BDD and $0.1 \text{ M Na}_2\text{SO}_4$ was investigated and the results are presented in Figure 2. According to equation (1) [30,31], increasing the current density increases the production of ROS and consequently the decomposition of the organic pollutant. The time required for the elimination of PIR was increased from 3 minutes at 80 mA cm^{-2} to 30 minutes for 13.3 mA cm^{-2} , while the apparent kinetic constant decreased almost 5.5 times from 0.782 to 0.138 min^{-1} as shown in Fig 2 (b)

Frontistis et al. [33] observed similar results for the electro-decomposition of $200 \text{ } \mu\text{g/L}$ of the endocrine disruptor ethyl paraben over BDD anode and in the presence of $0.1 \text{ M Na}_2\text{SO}_4$ electrolyte. They observed that when the current density increased from 10 to 70 mA cm^{-2} , the apparent kinetic constant was also increased 3.4 times from 0.05 to 0.17 min^{-1} . Although energy optimization was not the purpose of this work, it should be noted that higher current density leads to higher energy loss due to parasitic reactions like oxygen evolution and therefore lower current efficiency [34].

Figure 2. Effect of current density on (a) the normalized concentration and (b) the apparent kinetic constant for the degradation of 245 $\mu\text{g L}^{-1}$ PIR on BDD anode, 0.1 M Na_2SO_4 , ultrapure water and natural pH.

Effect of initial concentration of PIR

Further experiments were performed to study the effect of the initial concentration of PIR in the range of 245 – 975 $\mu\text{g L}^{-1}$ and the results are shown in Figure 3(a). Figure 3(b) reveals the apparent kinetic constant assuming pseudo first order kinetics. In terms of both % PIR removal and apparent kinetic constant, electrolysis efficiency decreased as the initial concentration of PIR increased. For example, when its initial concentration increased from 245 to 975 $\mu\text{g L}^{-1}$ the observed kinetic constant decreased from 0.138 min^{-1} to 0.0369 min^{-1} . This is a well-known and consistent behavior in several AOPs, such as electrolysis [33] and photocatalysis [35]. Lebig Elhadi et al. [36] studied the electrochemical oxidation of the neonicotinoid pesticide thiamethoxam over a BDD anode. They found that when the initial concentration of thiamethoxam decreased ten times from 10 to 1 mg L^{-1} , the apparent kinetic constant increased almost 14 times, from 0.05 to 0.73 min^{-1} . Similar results were also observed for the destruction of 2-nitrobenzaldehyde on BDD by Bouya et al. [37]. In that study, the observed kinetic constants at 80 mA cm^{-2} and 2% NaCl electrolyte were 0.0045, 0.0083 and 0.0112 min^{-1} for 20, 10 and 5 mg L^{-1} 2-nitrobenzaldehyde, respectively.

Figure 3. Effect of initial PIR concentration on (a) PIR removal, and (b) the apparent kinetic constant for its degradation over a BDD anode, 13.3 mA cm^{-2} , 0.1 M Na_2SO_4 , ultrapure water and natural pH.

Effect of pH

An additional set of experiments was conducted in order to investigate the effect of pH on the elimination of PIR at 13.3 mA cm^{-2} with 0.1 M Na_2SO_4 and the results are presented in Figure 4. Interestingly, altering the pH does not appear to greatly affect the electrooxidation of PIR, at least not at the conditions assayed. A slight increase was observed at alkaline conditions, while the apparent kinetic constants were 0.136, 0.138 and 0.166 min^{-1} for pH 3, 6 and 9, respectively. As with most heterogeneous AOPs, the pH can affect performance primarily in two ways: (i) Favoring the electrostatic attraction or repulsion of PIR to/from the electrode surface. (ii) Altering the rate of the electroproduction of ROS (mainly hydroxyl radicals).

These results are in agreement with the work of Brillas et al. [38] who studied the decomposition of paracetamol over a BDD anode. The effect of pH in the range of 2–12 was almost negligible for the mineralization of paracetamol. According to the authors, this was due to the high concentration of hydroxyl radicals on the BDD surface. The dominant role of hydroxyl radicals was confirmed with additional experiments with an excess of tert butanol, a well-known hydroxyl radical scavenger with a kinetic constant of 6 x

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$10^8 \text{ M}^{-1} \text{ s}^{-1}$ [39] and the results are depicted in Figure 5. Indeed, the presence of tert-butanol significantly delayed the removal of PIR, since its decomposition was 31.5% and 100% in the presence and the absence of 10 g L^{-1} tert-butanol, respectively, and after 30 min of treatment.

Figure 4. Effect of pH on the apparent kinetic constant of the electrooxidation of PIR at 13.3 mA cm^{-2} on a BDD anode, $0.1 \text{ M Na}_2\text{SO}_4$, ultrapure water and natural pH.

Figure 5. Effect of radical scavengers on the electrolysis of PIR at 13.3 mA cm^{-2} on a BDD anode, $0.1 \text{ M Na}_2\text{SO}_4$, ultrapure water (UP) and natural pH.

Effect of inorganic ions and humic acid

In addition, the effect of inorganic water substances like bicarbonates, chlorides and nitrates was investigated. As shown in Figure 6 the presence of bicarbonates enhanced the degradation of PIR. The apparent kinetic constants were 0.624 , 0.301 , and 0.138 min^{-1} for 100 mg L^{-1} , 50 mg L^{-1} bicarbonates and ultrapure water, respectively. It is well known that carbonate ions act as hydroxyl radical scavengers forming carbonate radicals according to equations (2) and (3): [40,41]

Carbonate radicals are one electron oxidant and have reduced oxidation potential (1.78 V Vs NHE) in comparison with hydroxyl radicals. However, they are more selective than hydroxyl radicals and they are characterized by longer lifetime [39], thus they are more likely to diffuse in the bulk solution and to react with PIR. Despite the fact that usually bicarbonates hinder the efficiency of AOPs, there are reports that their presence can increase the performance of processes, such as ultrasound [41] and

photocatalysis [42].

Figure 6. Effect of concentration of inorganic ions on the observed kinetic constant during the electrolysis of PIR at 13.3 mA cm^{-2} on a BDD anode, $0.1 \text{ M Na}_2\text{SO}_4$, ultrapure water and natural pH. BIC: Bicarbonates

On the other hand, the presence of chlorides accelerates the reaction. As shown in Figure 6 the addition of 200 mg L^{-1} of sodium chloride increased almost 10 times the apparent kinetic constant. The effect of chloride in electrolysis is well investigated in several studies since sodium chloride is often used as the electrolyte [33]. It is well known that active chlorine species can diffuse to the bulk solution, thus overcoming mass limitation and enhancing the efficiency of the process [33]. For example, in the work of Lan et al., [43] the presence of 2.25 mmol L^{-1} KCl reduced the time required for the destruction of 22.3 mg L^{-1} ciprofloxacin almost three times from 240 to 80 at mA cm^{-2} . On the other hand, in the same study it was found that the presence of chlorides at high current densities had negative effect on the mineralization of pharmaceuticals due to the increased production of halogenated organic compounds. Recently, Mostafa et al. [44] studied the electro-generation and release of chlorine volatile species using differential electrochemical mass spectrometry (DEMS). They concluded that BDD anode favored the production of $\text{Cl}^{\cdot}$ (2.43 V Vs SHE) due to its large potential window and high over potential of oxygen evolution (2.7 V Vs SHE). In addition, chloride radicals react with the oxygen generated from water splitting according to the following reactions:

Another common ion found in environmental samples, which is usually underestimated in similar studies is the nitrate ion.

Unexpectedly, increasing the concentration of nitrates increased the apparent kinetic constant as shown in Figure 6. When the nitrates increased twenty times from 10 to 200 mg L⁻¹ the observed rate constant increased almost 5.5 times from 0.10 to 0.54 min⁻¹. Recently Villegas-Guzman et al. [45] examined the degradation of fluoroquinolone by electrolysis, electro-Fenton and photo-electro Fenton. They found that process efficiency in the presence of nitrates was comparable (half time lower) with that in the presence of chlorides and significantly higher than using sulfates as the electrolyte. They concluded that this was due to ROS, such as nitric (V = 1.59 V Vs SHE) or nitrous (V = 1.77 V Vs SHE) oxides, generation via reduction. These oxides can also react with hydroxyl radicals according to the reactions:

Effect of organics and water matrix

Humic and fulvic acids are commonly used in order to simulate the natural organic matter (NOM) of environmental water samples or the recalcitrant organic matter, which remains after conventional biological treatment [46]. Experiments were performed with the addition of 5 and 10 mg L⁻¹ of humic acid corresponding to 2.1 and 4.2 mg L⁻¹ of total organic carbon (TOC). As shown in Figure 7 the presence of humic acid decreased the decomposition of PIR. Removal after 30 min of electrolysis at 13.3 mA cm⁻² was 99, 79.6 and 65.1% for 0, 5 and 10 mg L⁻¹ humic

acid, respectively. This inhibition can be explained by the higher organic loading in the case of humic acid since the ratio C_{HA}/C_{PIR} was almost 32.

Further experiments were conducted in different water matrices like surface water (SW), bottled water (BW), and secondary-treated wastewater (WW) and the results are also presented in Figure 7. It was observed that working with real matrices increased the removal of PIR, which is contrary to other studies that applied AOPs, such as photocatalysis [35] Fenton [47] or ultrasounds [48] for the destruction of pharmaceuticals. The apparent kinetic constants were 0.138, 0.288, 0.94 and 1.46 min⁻¹ for UP, SW, BW and WW, respectively. These results are in line with the acceleration observed in the presence of different inorganic anions in this study as discussed in paragraph 3.4 and highlight the potential of the application of electrolysis over BDD electrodes in real effluents.

Figure 7. Electrochemical oxidation of 245 µg L⁻¹ PIR in various water matrices at 13.3 mA cm⁻². BDD anode, 0.1 M Na₂SO₄ and natural pH. UP: ultrapure water, BW: bottled water, SW: surface water, WW: secondary-treated wastewater, HA: humic acid.

Figure 8. Degradation of 245 µg/L PIR using electrochemical oxidation (EO), ultrasound (US) and combined process (EO/US). Dotted line represents the theoretical sum of US and EO. Conditions: 13.3 mA cm⁻² (except US experiment) 0.1 M Na₂SO₄, 14 W L⁻¹ US at 20 kHz, and natural pH.

Effect of ultrasound

In a final set of experiments, the effect of ultrasound radiation with a frequency of 20 kHz and power density of 14 W L⁻¹ was investigated. As seen in Figure 8, ultrasounds alone (i.e. without current) are capable of degrading almost 73% of PIR in 30 min, due to acoustic cavitation and consequently the generation of ROS [48]. At the same treatment time PIR removal, due to

electrolysis, was >98%. The combined sono-electrochemical oxidation was faster than electrolysis or sonodegradation of PIR. However, this increase was only slightly better than the sum of the two individual processes. In Figure 8 the dotted line represents the theoretical sum of ultrasound and electrochemical oxidation. One way to quantify the synergy (S) is to calculate the normalized difference between the kinetic constants obtained under the combined process (k_{combined}) and the sum of those obtained under the individual processes (k_i): [49]

$$S = \frac{k_{\text{EO/US}} - k_{\text{EO}} - k_{\text{US}}}{k_{\text{EO/US}}}$$

$k_{\text{EO/US}}$, k_{EO} , and k_{US} are the apparent kinetic constants for sonoelectrocatalysis, electrolysis and ultrasound, respectively.

$$\text{where } S = \begin{cases} > 0 \text{ synergistic effect} \\ = 0 \text{ cumulative effect} \\ < 0 \text{ antagonistic effect} \end{cases}$$

According to the above equation the S ratio was calculated and was found equal to 46.8%. The ability of ultrasounds to increase the mass transfer inside the (sono) electrochemical reactor is well known. In addition, there are previous studies about the sonogeneration of hydrogen peroxide using low-frequency ultrasound [50]. However, hydrogen peroxide was not detected at the conditions assayed, possibly due to the short treatment time. These results are in line with the work of Tran et al., [51] who investigated the combined oxidation of $10 \mu\text{g L}^{-1}$ of triclosan using Ti/PbO₂ electrodes and ultrasound radiation at 520 kHz. They found that the observed kinetic constants for electrochemical oxidation, sonolysis and sonoelectrocatalysis at 40 W and 2 A were 0.0036 min^{-1} , 0.0004 min^{-1} , and 0.0045 min^{-1} and their synergy was calculated at 11.3%. Despite the observed enhancement for the combined treatment process, the main drawback of sonochemistry is the high energy loss due to heat. Therefore, a complete techno-economic analysis under several operating conditions is needed in order to justify the energy consumed during the use of ultrasounds at large scale.

Conclusions

The main conclusions derived from this work can be summarized as follows:

- Electrochemical oxidation over a BDD anode has the potential to eliminate the concentration of pharmaceuticals like PIR in short treatment times and for concentrations up to hundreds of $\mu\text{g L}^{-1}$ (i.e. less than 30 min for $240 \mu\text{g L}^{-1}$).
- The presence of inorganic ions like bicarbonates, chlorides and nitrates enhanced the decomposition of PIR. On the other

hand, the presence of organic compounds, such as humic acid, hindered the efficiency of the process.

- The simultaneous use of ultrasounds enhanced the efficiency of the process in comparison with electrochemical oxidation alone. Nevertheless, a cost analysis of the optimized process is required in order to promote and justify the use of hybrid sono-electrochemical oxidation process for the removal of such persistent pollutants.

Experimental Section

Materials and methods

Chemicals

Piroxicam (purity $\geq 98\%$, CAS number 36322-90-4), humic acid sodium salt technical grade (CAS number 68131-04-4), sodium chloride (CAS number 7647-14-5), sodium nitrate (CAS number 7631-99-4), sodium bicarbonate (CAS number 144-55-8) were purchased from Sigma Aldrich. Sodium sulfate (CAS number 7757-82-6) was purchased from Scharlau. Acetonitrile HPLC grade (CAS number 75-05-8) was purchased from PanReac AppliChem. Experiments were also performed with different water matrices namely ultrapure water (UP), surface water (SW), bottled water (BW) and secondary-treated wastewater (WW). Table 1 contains the physico-chemical characteristics of the different water matrices used in this work.

Table 1. Characteristics of the water matrices used in this work [52]

Property	Ultrapure Water (UP)	Bottled Water (BW)	Surface Water (SW)	Wastewater effluent (WW)
pH	6	7.5	7.5	8
Conductivity $\mu\text{S cm}^{-1}$	0.056	396	491	311
¹	-	-	2.7	7
TOC, mg L^{-1}	-	211	ND	182
Bicarbonate, mg L^{-1}	-	9.8	5	0.5
Chloride, mg L^{-1}	-	15	274	30
Sulfate, mg L^{-1}	-	3	ND	57
Nitrate, mg L^{-1}	-	-	-	-

Electrochemical experiments

Experiments were conducted in an electrochemical reactor, which is described in detail elsewhere [53]. Briefly, the reactor consists of plexiglass, while the liquid volume was 200 mL. The two electrodes, a BDD purchased from Adamant Technologies SA, Switzerland; B/C 1000 ppm and a stainless steel cathode with a surface area of 8 cm^2 were connected with a programmable power supply unit. In some experiments platinum with a surface area of 8 cm^2 was also served as the anode. The temperature was left uncontrolled during the reaction and never exceeded 33°C . Most

experiments were conducted using 0.1 M Na₂SO₄ as the electrolyte. At specific time intervals, samples of 1.2 mL were collected and analyzed by means of liquid chromatography.

Ultrasound experiments were conducted using a Branson digital sonifier with a nominal power of 450 Watt. The frequency was fixed at 20 kHz, while was transmitted inside the sono (electrochemical) reactor by a titanium horn with a diameter of 1 cm². The actual sonochemical power inside the aqueous medium was calculated by performing calorimetry following the procedure described elsewhere [54]. In this study only low power ultrasounds were applied in order to keep temperature of the water below 35 °C after 15 min of sonoelectrocatalysis.

Liquid Chromatography

PIR was detected by modifying an HPLC method, described in our previous work [48]. The chromatographic system was a Waters Alliance 2695 connected with a Waters 2996 PDA detector. The column was a Kinetex XB-C18 100A column (2.6 µm, 2.1 mm × 150 mm and was connected with a 0.5 µm inline filter (KrudKatcher Ultra) (Phenomenex). The flow rate was 0.2 mL/min and the mobile phase consisted of 75:25 acetonitrile water. The column was thermostated to 45 °C. The injection volume was 100 µL. After the separation, the concentration of PIR was measured using Waters 2996 Photo Diode Array detector at 350 nm.

Keywords: AOPs; Environmental Chemistry; pharmaceuticals; radicals; Water Chemistry

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BDD exhibits superior efficiency in comparison with platinum electrodes in terms of piroxicam degradation. The presence of inorganic anions like chlorides, bicarbonates or nitrates enhances the electrochemical degradation of piroxicam. The coupled sonoelectrochemistry process has a synergy index of 44.6%. (see Figure).

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anode: Investigation
of operating
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