Chapter 12

TREATMENT OF PHARMACEUTICALLY ACTIVE COMPOUNDS BY ELECTROOXIDATION USING BORON DOPED DIAMOND AND PLATINUM ANODES

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ABSTRACT

Clean and hygiene water is a critical environmental issue that touches the life of every human being. In recent years, presence of some pharmaceutical compounds and their metabolites in surface and ground water has become a potential health risk to human beings. Non-steroidal anti-inflammatory drugs (NSAID) are prescribed for muscle pain and inflammatory rheumatic disorders. Ketoprofen one of the NSAIDs, is categorized as a pharmaceutically active compound which resists both the abiotic and biotic degradation. Similarly, β-blockers are a class of drugs used for various indications particularly to control high blood pressure, anti-angina and cardiovascular diseases. One among the β-blockers, atenolol is most toxic to humans and aquatic organisms. The presence of both ketoprofen and atenolol in ground water has been reported at concentrations up to 10 µg/L. A bench scale study was carried out to treat synthetically prepared pharmaceutical compounds (ketoprofen and atenolol) contaminated water in lower concentrations (µg/L) using boron doped diamond (BDD) and platinum anodes. The results were explained in terms of in situ generated of hydroxyl radical (OH), peroxodisulfate (S2O8²⁻), and active chlorine species (ClO2, OCI and HOCI). The physisorbed OH on BDD was observed to trigger the combustion of pollutant molecules in to CO2 and H2O. The BDD anode was found to be effective in the presence of Na2SO4 whereas Pt yields better removal in the presence of NaCl. The influence of electrolyte pH on the mineralization of ketoprofen molecules was found to be insignificant. The

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evolution of chlorine at BDD and Pt with respect to NaCl concentration was studied by means of cyclic voltammetric technique. The poor mineralization at both BDD and Pt anodes in the presence of NaCl as supporting electrolyte was ascribed to the formation of chlorinated organic compounds which are refractory. The complete mineralization was always achieved in the presence of Na₂SO₄ using BDD as anode.

1. INTRODUCTION

1.1. Occurrence

Clean and hygiene water is a critical environmental issue that touches the life of every human being. In the past decade, pharmaceutical compounds and their metabolites in trace quantities in surface and ground water has been detected throughout the world which risks the human’s health and lives [1]. Certain pharmaceutical compounds dissolved in ground water, make their way to pregnant mothers and children via food chain. Generally, ground water source is expected to be polluted by leakage of sewer pipe lines, direct runoff of ground fecal material of pets and livestock, usage of sewage sludge and synthetic fertilizers as manure on agricultural land and recycling the treated (pharmaceutical) wastewater for irrigations. As a consequence, there is an increasing concern on studying the occurrence and fate of pharmaceuticals from various Waste Water Treatment Plants (WWTPs), such as municipal, livestock, hospital, and pharmaceutical drug manufacturing industries. A large spectrum of pharmaceutical compounds is used throughout the world to control variety of diseases. The pharmaceutically active compounds of various classes are analgesics, antibiotics, antiepileptic, Non-steroidal anti-inflammatory drugs (NSAIDs), β-blockers, chemotherapeutics, steroid hormones and X-ray contrast media have been detected in the concentration of µg/L. The consumption per year of analgesic drugs alone is calculated to be 166 tonnes in France during 1998, 128 tonnes in Germany during 2001 and 276 tonnes in Spain during 2003 [2]. The usage of β-blockers in Europe alone is more than 3000 kg per year. The Geological survey of US has found presenting more than 60 pharmaceutical organic pollutants in ground and drinking water sources across the 18 states. A survey in Europe is proved that persistent pharmaceutically active compounds like carbamazepine, ketoprofen and clofibric acid are presented in ground water. Naproxen, Clofibric acid, dichlofenac and gemfibrozil [3] were found to contain in sewage treatment plant effluent and river water. The micro pollutant analysis of wastewater, sludge and leachates shows the variation in concentration levels due to the changes in influent water composition with respect to different seasons and weather conditions. Among the pharmaceutical compounds, NSAIDs and β-blockers are frequently found in ground water with high concentrations [4]. The statistics reveal that the consumption and excretion of these drugs is expected to increase in future. NSAIDs are prescribed for muscle pain and inflammatory rheumatic disorders. They are highly polar compounds because of carboxylic acid moiety. Due to their polar structure, these molecules are easily soluble in ground water instead of remaining adsorbed in subsoil. In the effluent water collected, NSAIDs have been found to the extent of 44%. Ketoprofen one of the NSAIDs, is categorized as a pharmaceutically active compound which resists both the abiotic and biotic degradation. Similarly, β-blockers are a class of drugs used for various indications particularly to control high blood pressure, anti-angina and cardiovascular
diseases. One among the β-blockers, atenolol is most toxic to humans and aquatic organisms. Atenolol was reported to be very stable to UV radiation and its half life in pure water was found to be higher compared to other β-blockers [5]. Also, atenolol is adsorbed by the human body only to the extent of 50% and the remaining is excreted in faeces and urine [6]. The presence of both ketoprofen and atenolol in ground water has been reported up to 10 µg/L [7]. As a matter of fact, these drug compounds escape from sewage treatment plant due to inadequate treatment technique and ultimately reach the ground water bodies either by transportation or percolation [8]. Hence the objective of this work is to address the environmental concern of pharmaceutically active compounds like ketoprofen and atenolol and its removal by electrochemical oxidation method. The molecular structure of ketoprofen and atenolol are as seen in Figure 1.

1.2. Risks and Impacts

Several studies investigated the risk factor of pharmaceutically active compounds to the humans and wild lives. Health protection agencies have fixed the regulations and standards for drinking water quality and permissible levels for the hazardous chemicals in environmental discharges. Also, pharmaceutical concentrations measured in surface waters are well below the concentration levels that are known to cause acute toxicity of aquatic organisms. However, the chronic exposure to pharmaceutical has the potential for numerous subtle effects such as metabolic and reproductive changes in organism. Once the pharmaceutically active compounds enter into the environment, it can produce subtle effects on aquatic and terrestrial organisms. The toxicity of single pharmaceutical will be predominantly due to the specific mode of toxic action. In some cases, the mixture of micropollutants may present environmental hazards that are far greater than those of individual compounds. The presence of micropollutant may also affect the reuse of treated effluent which is generally suggested for a solution of achieving a sustainable water management. These pharmaceutically active compounds may adversely impact human health by endocrine disruption and secretion of antibiotic bacteria which resist the illness [9]. These are not only carcinogenic but also act as inhibitor in biological activity of human body. Hence, the complete removal of pharmaceutically active compounds before entering the aquatic environment and water reclamation plant becomes very essential.

Figure 1. Molecular structure of (a) Ketoprofen, (b) Atenolol.
1.3. Treatment

The available conventional treatment techniques are inadequate to treat low concentration of pharmaceutically active compounds. In Sewage Treatment Plants (STPs), biological methods are extensively adopted for the treatment of water containing pharmaceutically active compounds. The efficiency is very low due to the formation of by-products which are more resistant to oxidation. Moreover, the biological methods are inefficient in the presence of chloride ion (Cl⁻), because it affects the microbial growth. Most of the pharmaceutical compounds are not amenable to biological treatment as they form stable microbial metabolites. In recent years, Adsorption, Nanofiltration and Reverse Osmosis have been adapted to treat the pharmaceutically active compounds instead of conventional biological treatments. However, the treatment is not so effective and not applicable to all pharmaceutically active compounds as they pass through the membrane [10]. The rejection is reported to be influenced by the dipole moment, hydrophobicity and molecular size of the compound [11]. In addition, conventional advanced oxidation process was attempted to remove these compounds but their degradation was observed to be only partial. Since the concentration (µg/l) of the pharmaceutically active compounds in ground and drinking waters is very low, electrooxidation technique was thought to be better choice to destruct them. The removal of NSAIDs from aqueous solution by electrooxidation using dimensionally stable anodes (DSA) and BDD electrode has been reported [12]. However, electrochemical oxidation methods were not explored for the removal of ketoprofen and atenolol. The nature of electrode material is always very crucial since the anodic reactions and its products depend on the anode material employed. The BDD was extensively tried as anode material [12, 13] for the removal of various organics present in wastewater. It has been proved that anodic oxidation of organic pollutants above the water decomposition potential (> 2.3 V) at BDD electrode involve generation of greater quantity of adsorbed hydroxyl radical (OH) which can destroy/mineralize the organic pollutant molecules [14]. The electrooxidation technique was proved to be effective to mineralize the toxic compounds to CO₂ and H₂O. The distinctive features of the BDD electrode [15] are a) it exhibits inert behavior for 'OH adsorption b) better current efficiency c) possessing higher oxygen over voltage with the wide working potential window in aqueous and non-aqueous media that favors the larger generation of more reactive OH d) chemically, electrochemically and physically stable material and corrosion resistant, greater durability e) low and stable background current. The generation of OH by anodic oxidation can be represented as reaction (1)

\[
\text{BDD(H}_2\text{O)} \rightarrow \text{BDD(OH)} + \text{H}^+ + e^- \quad (1)
\]

The hydroxyl radicals generated in situ are expected to react with persistent organic pollutant irrespective of its nature. The conversion of OH to H₂O₂ and molecular O₂ can be represented as

\[
\begin{align*}
2\text{OH} & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \\
\text{OH} + \text{OH} & \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^-
\end{align*}
\]
Treatment of Pharmaceutically Active Compounds ...

\[ 3\text{H}_2\text{O} \rightarrow \text{O}_3 + 6\text{H}^+ + 6\text{e}^- \] (5)

Hence, BDD can be tried to remove pharmaceutically active compound like ketoprofen and atenolol from water. A bench scale simulation study was carried out to treat synthetically prepared pharmaceutically active compounds (ketoprofen and atenolol) contaminated water in lower concentrations (µg/l) using BDD and Pt anodes. Since the natural water sources contain large variety of inorganic salts (Cl\(^-\), SO\(_4^{2-}\), NO\(_3^-\) etc.), the mineralization/oxidation behavior of these compounds was studied in presence of different supporting electrolytes such as NaCl, Na\(_2\)SO\(_4\) and NaNO\(_3\).

2. REMOVAL OF KETOPROFEN

2.1. Cyclic Voltammetric Study of Ketoprofen Oxidation

Cyclic voltammograms were recorded to understand the redox behavior of ketoprofen molecule on BDD electrode at a scan rate of 10 mV s\(^{-1}\) and at a fixed Na\(_2\)SO\(_4\) concentration of 0.1M. Also, the voltammogram was recorded in the absence of ketoprofen. From the results shown in Figure 2, it is apparent that the oxygen evolution potential was observed at around 2.8 V in the case of BDD anode and 2.0 V in the case of Pt anode. The higher oxygen evolution potential of 2.8 V indicates the effectiveness of BDD over Pt. However, in the presence of NaCl as supporting electrolyte, Pt anode was found to be better in accelerating the oxidation reaction (Figure 7b). The reason for this behavior will be discussed extensively in section 2.3. From the anodic sweep of the first cycle (continuous line of Figure 2), the current peak for ketoprofen oxidation was observed between 1.95 V and 2.0 V. The current peak for ibuprofen-BDD system was reported at 2.0 V [12]. The current peak can be attributed to the oxidation of carboxyl group of the ketoprofen molecule. New and well resolved peak observed in the subsequent cycles which was gradually decreased and shifted to less positive potential explains the fouling behavior of the BDD electrode. The fouling phenomenon at BDD surface below water decomposition potential (2.3 V) and its reactivation by anodic polarization process is reported in the literatures [13]. The results confirm the oxidation of ketoprofen around 2.0 V by direct electron transfer and also the deactivation of electrode surface by adsorption of oxidized polymeric product. The reproducibility of each scan was confirmed at least three times. Even though the electron transfer reaction is expected to exhibit reversible character [17] at sp\(^2\) free BDD, irreversible nature of ketoprofen oxidation was confirmed as there was no reduction peak at negative potential window. The oxygen evolution current peak for BDD in Na\(_2\)SO\(_4\) electrolyte is reduced in the presence of ketoprofen which confirms that the activity of the BDD was slightly reduced by direct electron transfer oxidation of ketoprofen molecule on its surface. The oxidation behavior of ketoprofen at Pt electrode in the presence of 0.1 M Na\(_2\)SO\(_4\) was studied (data not shown) and no electron transfer step was noticed between hydrogen and oxygen evolution potential.
Degradation of ketoprofen molecule and its total mineralization was studied at three different applied current densities of 4.4, 8.9 and 13.3 mA cm\(^{-2}\). For every experiment, 5 μM of ketoprofen was taken in 0.1 M Na\(_2\)SO\(_4\) and the results are shown in Figure 3 & 4. The UV-visible spectrum of pure ketoprofen exhibited a peak at 260 nm. This characteristic peak was gradually disappeared over a period of 5 hours of electrolysis at an applied current density of 4.4 mA cm\(^{-2}\). By increasing the current density to 13.3 mA cm\(^{-2}\), the peak was vanished within 120 minutes of electrolysis. Though the peak was disappeared, nearly 50% of the TOC remained in aqueous solution. This clearly indicates that the ketoprofen molecule was totally degraded but part of the degraded molecules remained in aqueous solution. The oxidation of ketoprofen at BDD anode could be explained due to the various oxidants generated according to the reactions mentioned in equations 2-5. It is also apparent that the TOC removal is linear at the lower current density and also at the initial stages of oxidation. The mineralization trend of ketoprofen at BDD suggests current controlled at low current densities and at initial stages. It becomes diffusion controlled at the end of the reaction when the concentration of ketoprofen is very low. By increasing the current density, the rate of oxidation of ketoprofen was found to increase [13-15, 18].
It could be concluded that the complete mineralization of ketoprofen can be achieved by using BDD as anode. The overall mineralization reaction can be represented as

\[
\text{C}_{16}\text{H}_{14}\text{O}_3 + 29\text{H}_2\text{O} \rightarrow 16\text{CO}_2 + 72\text{H}^+ + 72\text{e}^-
\]

(6)

This reaction shows that 72 electrons are involved in incinerating a ketoprofen molecule completely into CO\(_2\). The mineralization current efficiency (MCE) was calculated with respect to the electrolysis time according to the following equation (7).

\[
\text{MCE} = \left[\frac{\Delta(\text{TOC})_{\text{exper}}}{\Delta(\text{TOC})_{\text{theor}}}\right] \times 100
\]

(7)

Where \(\Delta(\text{TOC})_{\text{exper}}\) denotes the experimentally observed TOC removal at time \(t\) and \(\Delta(\text{TOC})_{\text{theor}}\) is the theoretically calculated TOC removal considering that the applied electrical charge (= current \(\times\) time) is consumed to yield the reaction (6). As seen in Figure 5, the MCE was observed to be comparatively better at lower current density of 4.4 mA cm\(^{-2}\) and it is not decreased much with the specific charge passed. At lower current density, the mineralization of ketoprofen was observed to be current control process. In other words, as long as the current employed is below the limiting current density value, secondary reactions such as O\(_2\) evolution are negligible and the electro-energy has been preferably utilized only for mineralization of organic pollutant. Thus, working at low current density is advantageous in terms of the energy consumption. On the other hand, although, the rate of mineralization was found to be comparatively higher at 13.3 mA cm\(^{-2}\), the MCE was observed to be poor. The continuous decrease in MCE with increase in specific charge is attributed to the secondary reaction at higher applied current density. A similar behavior was observed in the mineralization of bisphenol A at BDD anode [13].
The role of initial pH on the oxidation of ketoprofen at BDD surface was also studied at the initial pH of 3.00, 6.00 and 9.00 and the results are presented in Figure 6. It was observed that the influence of pH on mineralization is very marginal. In this case, the acidic condition is slightly favorable because of the higher reactive nature of OH and S\textsubscript{2}O\textsuperscript{2-} [19, 20]. The pH of the aqueous solution was found to shift slightly towards basic pH. It may be due to the formation of carbonate and bicarbonate ions and H\textsubscript{2} liberation from the cathode. Similar trend was observed in the oxidation of phenol using metal oxide coated Ti mesh electrode [21].
Figure 5. Mineralization current efficiency versus specific electric charge for the TOC results shown in Figure 2 (Ketoprofen: 5 µM, Anode: BDD, Na₂SO₄: 0.1 M, (●) 4.4 mA cm⁻², (▲) 8.8 mA cm⁻², (■) 13.3 mA cm⁻², Initial pH: 6.00, T: 25°C) (Adapted from [16]).

Figure 6. TOC removal versus initial pH of the electrolyte using BDD anode at constant applied current density of 8.8 mA cm⁻² (Ketoprofen: 5 µM, Na₂SO₄: 0.1 M, (●) Initial pH: 3.00 (■) Initial pH: 6.00 (▲) Initial pH: 9.00, T: 25°C) (Adapted from [16]).
2.3. Effect of Supporting Electrolyte on Ketoprofen Removal

The effect of supporting electrolytes such as NaCl, Na$_2$SO$_4$ and NaN$_3$ on Ketoprofen oxidation at BDD and Pt was studied at a constant applied current density and the results were shown in Figure 4(b) and Figure 7. The UV-visible spectra indicate that the effective degradation of ketoprofen can only be achieved when SO$_4^{2-}$ is employed as supporting electrolyte. The peak at 260 nm corresponding to the $\lambda_{\text{max}}$ of ketoprofen molecule is completely disappeared within 4 h in the presence of SO$_4^{2-}$ whereas a new peak was appeared around 292 nm for both BDD and Pt electrodes in the presence of NaCl. The new peak around 292 nm could be ascribed to hypochlorite (ClO-) ion [22] and its intensity was increased with electrolysis time. The oxidants such as S$_2$O$_8^{2-}$, SO$_4^-$, Cl$_2$, ClO' can be generated in situ by employing suitable electrolyte. The concentration of active chlorine and chloride ion was measured for both BDD and Pt anodes with NaCl medium. As seen in Figure 8, the SO$_4^{2-}$ strongly influences the rate of mineralization reaction of Ketoprofen molecule. For example, at 12 h electrolysis period, complete TOC removal was achieved using SO$_4^{2-}$ whereas TOC removal is hardly 55 % and 25 % in the presence of NO$_3$ and Cl medium respectively. The in situ generation [23] of S$_2$O$_8^{2-}$ and sulfate radical in the presence of Na$_2$SO$_4$ could be represented as

![Figure 7. UV-vis spectra showing OCT during electrolysis (Ketoprofen: 5 $\mu$M, Applied current density: 8.8 mA cm$^{-2}$, NaCl: 0.1 M, Initial pH: 6.00, T: 25°C) (Adapted from [16]).](image-url)
The oxidants are either consumed for the degradation of ketoprofen molecule or coupled with water molecule to form peroxomonosulfuric acid ($H_2SO_5$) which in turn can produce $H_2O_2$ [20]. Some researchers have pointed out that the ability of $S_2O_8^{2-}$ ($E_0 = 2.01 \text{ V}$) in the oxidation of refractive pollutants is comparatively less [24]. The results obtained using Pt as anode in $SO_4^{2-}$ media show that the mineralization behavior is almost linear with respect to electrolysis time and observed to be poor when compared to BDD. It could be attributed to the poor generation of $OH$, $S_2O_8^{2-}$ and $SO_4^{2-}$ [13, 24].

Using NaCl as supporting electrolyte, active chlorine is formed at anodic surface according to the following reactions.

\[
\begin{align*}
2SO_4^{2-} & \rightarrow S_2O_8^{2-} + 2e^- \\
OH + 2SO_4^{2-} & \rightarrow SO_2^- + OH^- \\
SO_4^{2-} + SO_4^- & \rightarrow S_2O_8^{2-}
\end{align*}
\]

The oxidants are either consumed for the degradation of ketoprofen molecule or coupled with water molecule to form peroxomonosulfuric acid ($H_2SO_5$) which in turn can produce $H_2O_2$ [20]. Some researchers have pointed out that the ability of $S_2O_8^{2-}$ ($E_0 = 2.01 \text{ V}$) in the oxidation of refractive pollutants is comparatively less [24]. The results obtained using Pt as anode in $SO_4^{2-}$ media show that the mineralization behavior is almost linear with respect to electrolysis time and observed to be poor when compared to BDD. It could be attributed to the poor generation of $OH$, $S_2O_8^{2-}$ and $SO_4^{2-}$ [13, 24].

Using NaCl as supporting electrolyte, active chlorine is formed at anodic surface according to the following reactions.

\[
\begin{align*}
\text{BDD} + \text{Cl}^- & \rightarrow \text{BDD} + (\%2)\text{Cl}_2 + \text{OH}^- \\
\text{Cl}^- & \rightarrow \text{Cl}_2 + 2e^-
\end{align*}
\]

While complete mineralization of Ketoprofen was achieved in the presence of Na$_2$SO$_4$, the degradation is only partial in the presence of NaCl as supporting electrolyte. The poor mineralization at BDD and Pt in the presence of NaCl was further substantiated by CV, active chlorine and chloride ion measurement. The CV results shown in Figure 9(a) and 9(b), suggest the evolution of chlorine and formation of ClO$^-$ in the presence of NaCl. In the case of BDD, chlorine evolution peak decreased beyond a critical concentration of Cl$^-$ ion due to the potentiostatic buffering [25]. It is noteworthy that the potential window of BDD has
become narrow due to the active Cl₂ evolution just prior to the potential where OH can be generated. It could be the main reason for the poor efficiency of BDD comparing Pt in presence of NaCl as supporting electrolyte. The active chlorine concentration was measured immediately after 5 h and 20 h of electrolysis time in case of both BDD and Pt anodes at a constant current density of 8.8 mA cm⁻². The active chlorine concentration was found to be 400 ppm at 5 h and 424 ppm at 20 h, whereas in the presence of Pt anode, it was 478 and 547 ppm for 5 h and 20 h, respectively. It can be seen that only a slight variation in electrogenerated active chlorine concentrations was observed between 5 h and 20 h electrolysis period. It was demonstrated that the poly hydroxyl phenol molecules are thoroughly oxidized by active chlorine [26]. In spite of its oxidizing ability, the gaseous Cl₂ would rather be expected to interact quickly with organic pollutant and form stable chlorinated organic intermediates than degrading the same molecule. These compounds are more refractory in nature and probably carcinogenic. As stated, the new peak in the UV-visible spectrum (Figure 7) around 292 nm and well defined anodic oxidation peak at 1.5 V (Figure 9b) indicates the formation of hypochlorite molecule according to the following reaction suggested by Canizares et al [27].

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{HCl}
\]  

Although the active chlorine (Cl₂, ClO⁻) formation was observed in the present study, the overall mineralization efficiency was observed to be poor in the presence of NaCl. It could be due to the formation of refractory intermediates that are more stable towards ClO⁻ attack. The decrease in Cl⁻ concentration during the electrolysis over a period of 30 h at a constant current density of 8.8 mA cm⁻² was observed to be 50 % in the presence of BDD and 80 % while using Pt as anode. These results further confirm that the active chlorine evolution is considerably restricted at BDD as it exhibits a “non-active” behavior. Whereas at Pt anode, the Cl⁻ based oxidants are predominantly formed by direct oxidation of Cl⁻ due to its electrocatalytic activity towards Cl₂ evolution. It is understandable from the anodic evolution peak of Pt electrode that the peak current in SO₄²⁻ media is markedly higher compared to Cl⁻ media, which confirm that the oxidation of chloride at Pt anode becomes a competitive to the oxidation of water molecule since it has lower oxygen evolution overvoltage. In other words, chlorine evolution is predominant at a potential where the oxygen evolution can occur. This fact could be attributed to the overall poor efficiency of Pt anode despite it showed a rapid mineralization rate at initial phase (up to 6 h electrolysis period) in the presence of NaCl. The complex chemistry of Cl⁻ mediated reaction with respect to its concentration and the electrode employed were studied by several authors [26-28]. The mineralization in the presence of NaN₃ is only moderate as the nitrate is an inert supporting electrolyte.

In order to ensure the complete mineralization of atenolol at BDD anode, experiments were carried out at different applied current densities using Na₂SO₄ as supporting electrolyte and the results are shown in Figure 10. The production of OH from water decomposition at BDD is generally believed to be largely responsible for atenolol mineralization. Also, the earlier studies [29] have proved that oxidation of organics involve the in situ generated intermediate oxidants such as SO₄⁻ and S₂O₇²⁻ which are likely to be generated from SO₄²⁻ by consuming the OH as per reactions (8-10). An increase of TOC removal was observed by increasing the applied current density and it is more pronounced at 13.3 mA cm⁻². It indicates that the current densities employed are below the limiting current and the oxidation process is
under the current control regime [30]. Anodic mineralization at higher applied current density is expected to aid the production of OH on surface of the anode which in turn leads to total mineralization. The total mineralization of atenolol could only be accomplished with an electrical charge \((Q)\) consumption of 12 Ah L\(^{-1}\) at a higher applied current density of 13.3 mA cm\(^{-2}\). It is also interesting to note that the \(Q\) required for achieving the same quantity of organic load removal (70% of TOC removal) is 3.0, 2.84 and 2.76 Ah L\(^{-1}\) for 4.44, 8.88 and 13.3 mA cm\(^{-2}\), respectively. The corresponding duration of electrolysis is 15, 7.1 and 4.6 h, respectively. The decrease of \(Q\) values with increasing applied current density is advantageous. The total energy required for atenolol mineralization is calculated to be 57.6 Wh L\(^{-1}\).

Figure 9. Cyclic voltammogram for chlorine evolution peak study at (a) BDD and (b) Pt electrode (Scan rate: 10 mVs\(^{-1}\), Initial pH: 6.00, T: 25°C) (Adapted from [16]).
Figure 10. Effect of current density on the mineralization of atenolol using BDD anode in the presence of Na$_2$SO$_4$ (0.1 M); Atenolol: 2.25 μM, pH 6.0, T: 25 °C; (▲) 4.44 mA cm$^{-2}$; (■) 8.88 mA cm$^{-2}$; (●) 13.3 mA cm$^{-2}$.

Figure 11. Mineralization current efficiency with respect to Q for the TOC removal results shown in Figure 8; (▲) 4.44 mA cm$^{-2}$ (■) 8.88 mA cm$^{-2}$ (●) 13.3 mA cm$^{-2}$. 
Thus, it could be concluded that the complete mineralization of atenolol can be achieved using Na₂SO₄ media with BDD anode. The overall mineralization reaction can be written as:

\[
C_{14}H_{25}N_{2}O_{3} + 31H_2O \rightarrow 14CO_2 + 2NO_3^- + 84H^+ + 82e^- \quad (14)
\]

This reaction shows that 82 electrons are involved in mineralizing a atenolol molecule completely into CO₂. The MCE was calculated for the reaction (14) with respect to the electrolysis time according to the relation (7).

As shown in Figure 11, the MCE for 13.3 mA cm⁻² is very low at the beginning of the electrolysis process compared to other current densities employed. The dramatic decrease of MCE from the starting electrolysis point for 4.44 and 8.88 mA cm⁻², may be attributed to a larger accumulation of pollutants in the vicinity of electrode surface during the initial stage of electrolysis. There is no significant difference in MCE values beyond 2 Ah L⁻¹. It confirms that the coexistence of both sulfate based oxidants (SO₄²⁻, S₂O₇²⁻ etc.) and OH during the mineralization of atenolol. It has been reported that the half life of sulfate based oxidants is longer thereby it diffuses in to the bulk solution and degrades the pollutants [31]. In other words, oxidation reaction is not affected much by the mass transfer limitation as the pollutant concentration is decreased. The earlier researchers [29, 32] observed that the MCE is reduced by extending the duration of electrolysis and also with decrease in pollutant concentration near the electrode surface. Hence, the results reported here clearly shows that the mineralization reaction at BDD could be occurred by both mediated (SO₄²⁻, S₂O₇²⁻ etc.,) and direct oxidation (reactive OH).

### Conclusion

The occurrence, risks and treatment method of some pharmaceutically active compounds were discussed. Degradation of pharmaceutically active compounds like ketoprofen and atenolol by electrochemical oxidation process using BDD and Pt anode was discussed. The cyclic voltammetric studies have revealed that the ketoprofen is oxidized at 2.0 V by direct electron transfer. The rate of oxidation was increased by increasing the current density. The physisorbed OH on BDD was observed to trigger the combustion of pollutant molecules in to CO₂ and H₂O. The mineralization current efficiency was calculated from the TOC abatement and found to be better at lower current density of 4.4 mA cm⁻². The degradation of ketoprofen was found to be current control at initial phase and become diffusion controlled process beyond 80 % of TOC removal. Among the supporting electrolytes reported, sodium sulfate was found to effective for complete mineralization of ketoprofen. In presence of chloride ion, the potential window of BDD electrode was considerably narrowed. The evolution of chlorine at BDD and Pt with respect to NaCl concentration was studied by means of cyclic voltammetric technique. The poor mineralization at both BDD and Pt anodes in the presence of NaCl as supporting electrolyte was ascribed to the formation of chlorinated organic compounds which are refractory. Atenolol is thoroughly mineralized to CO₂ and H₂O at BDD in the presence of SO₄²⁻. The energy required for the same quantity of organic load of atenolol.
contaminated water is interestingly decreased with increasing the applied current. The total mineralization was accomplished at higher applied current of 13.3 mA cm$^{-2}$, with the energy consumption of 57.6 Wh L$^{-1}$. The calculated corresponding mineralization current efficiency value shows that the mediated oxidants play a key role.

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