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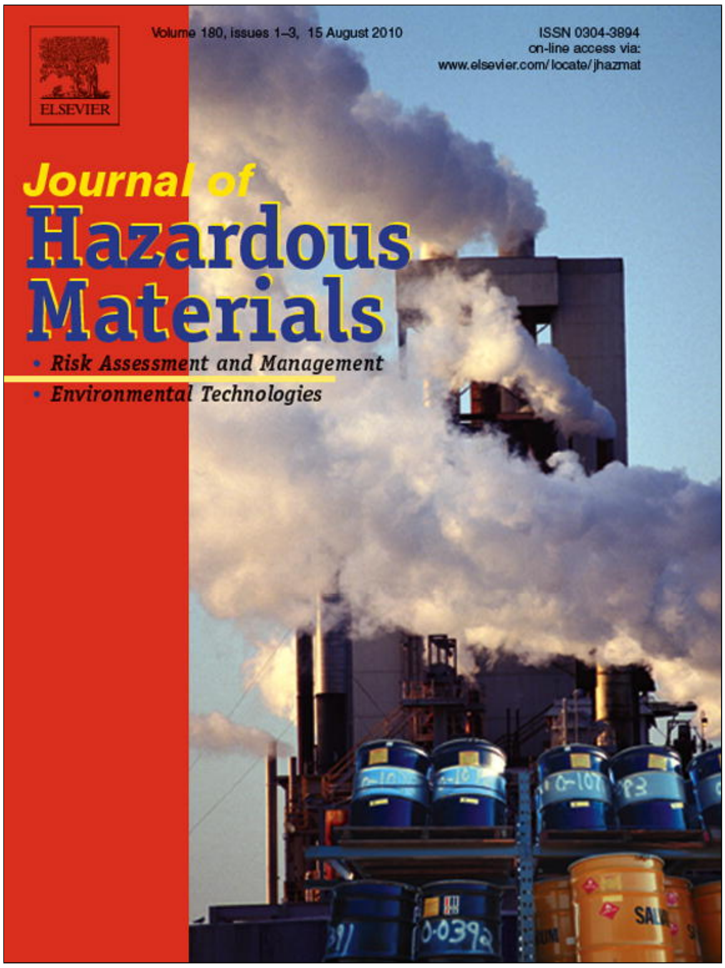
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Anodic oxidation of ketoprofen—An anti-inflammatory drug using boron doped diamond and platinum electrodes

M. Muruganantham[a,*], S.S. Latha[a], G. Bhaskar Raju[a], S. Yoshihara[b]

[a] National Metallurgical Laboratory Madras Centre, CSIR Madras Complex, Taramani, Chennai 600 113, India
[b] Department of Advanced Interdisciplinary Science, Graduate School of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya, Tochigi 321-8585, Japan

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ABSTRACT

The mineralization of ketoprofen (KP) by anodic oxidation was studied by employing boron doped diamond (BDD) and Pt electrodes. The redox behavior of KP molecule, fouling of electrodes, generation of oxygen and active chlorine species were studied by cyclic voltammetry. The effect of electrolyte, pH of aqueous medium and applied current density on the mineralization behavior of KP was also investigated. The degradation and mineralization were monitored by UV–vis spectrophotometer and total organic carbon analyzer, respectively. The results were explained in terms of in situ generation of hydroxyl radical ($^{\bullet}$OH), peroxodisulfate ($S_2O_8{}^{2-}$), and active chlorine species (Cl_2, HOCl, OCl^-). The physisorbed $^{\bullet}$OH on BDD was observed to trigger the combustion of KP in to CO_2 and H_2O. 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. Complete mineralization of KP molecule was achieved using Na_2SO_4 as supporting electrolyte.

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1. Introduction

In recent years, some ingested pharmaceutical compounds and their metabolites were detected in the surface and ground water situated near the sewage water treatment plants (STP) [1]. The non-steroidal anti-inflammatory drugs (NSAID) are special group of pharmaceuticals that are prescribed for muscle pain and inflammatory rheumatic disorders. The usage of these drugs is expected to increase in future [2]. The NSAID drugs are generally 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 [3]. Ketoprofen (KP), one of the non-steroidal anti-inflammatory drugs, is categorized as a pharmaceutically active compound. Its chemical structure is very complex and resists both the abiotic and biotic degradation [4]. The KP was present in the sewage water to the extent of 3.0 $\mu g\,L^{-1}$ [5]. The sample collected from the drinking water treatment plant located near the STP was found to contain several ng L^{-1} of KP [6]. Prolonged exposure to these chemicals is expected to affect the health [7].

Biological methods are extensively adopted for the treatment of wastewater containing pharmaceutically active compounds [8]. Various treatment methods explored by previous investigators have indicated that the option of biological treatment may not be suitable because of the inhibitory effect of chloride on microbial growth [9]. The incomplete removal of KP in STPs was attributed to its stable microbial metabolite [10]. Advanced oxidation process (AOP) was attempted to remove the NSAID compounds but their degradation was observed to be only partial [5]. Thus, there is an urgent need to develop an alternate technology to purify the KP contaminated water. In the present work, the electrochemical oxidation was tried to achieve the complete destruction and removal of KP.

In the past decade, the effectiveness of electrochemical oxidation technique for wastewater treatment was extensively adapted because of its environmental friendliness, amenability to automation and its effectiveness to process wide variety of organic pollutants [11]. The removal of non-steroidal anti-inflammatory drugs from aqueous solution using dimensionally stable anodes (DSA) and boron doped diamond (BDD) electrode was reported [12]. However, electrochemical oxidation methods were not explored for the removal of KP. The nature of electrode material is very crucial since the anodic reactions and its products depend on the anode material employed. The BDD was extensively tried as anode material [12–15] for the removal of various organics present in wastewater. The distinctive features of the BDD electrode [16] are (a) it exhibits inert behavior for $^{\bullet}$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 $^{\bullet}$OH; (d) chemically, electrochemically and physically stable material and corrosion resistant, greater durability and (e) low and stable back-

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* Corresponding author. Tel.: +91 44 22542077; fax: +91 44 22541027.
E-mail address: muruga.chem@gmail.com (M. Muruganantham).

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ground current. The generation of $^{\bullet}$OH by anodic oxidation can be represented as reaction (1):

$$\mathrm{BDD(H_2O)} \rightarrow \mathrm{BDD(^{\bullet}OH)} + \mathrm{H^+} + \mathrm{e^-} \quad (1)$$

The hydroxyl radicals generated in situ are expected to react with persistent organic pollutant irrespective of its nature. The conversion of $^{\bullet}$OH to H_2O_2 and molecular O_2 can be represented as

$$2^{\bullet}\mathrm{OH} \rightarrow \mathrm{H_2O_2} \quad (2)$$

$$\mathrm{H_2O_2} \rightarrow \mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \quad (3)$$

$$^{\bullet}\mathrm{OH} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \quad (4)$$

$$3\mathrm{H_2O} \rightarrow \mathrm{O_3} + 6\mathrm{H^+} + 6\mathrm{e^-} \quad (5)$$

Hence, BDD can be tried to remove pharmaceutically active compound like KP from water. The effectiveness of BDD and Pt anodes for the degradation of ketoprofen was studied in the present investigation.

2. Experimental

2.1. Materials

The ketoprofen (KP) powder obtained from Sigma–Aldrich was used without further purification. KP stock solution with a concentration of 100 µM was prepared in distilled water free from TOC. The working solution of required concentration was obtained by diluting the stock solution. In this study three different supporting electrolytes, viz. Na_2SO_4, $NaNO_3$ and NaCl were tried. The pH of the aqueous solutions was adjusted by dilute H_2SO_4 or NaOH solutions. The other chemicals used were of analytical grade and procured from M/s Merck.

2.2. Preparation of BDD thin film electrode

BDD film was grown on p-Si (1 1 1) substrates by microwave-assisted plasma chemical vapour deposition technique (Model AX2115, AsTeX Corp.). The chemical vapour deposition was carried out at a temperature and pressure of 540 °C and 70 Torr, respectively with a forward power of 1400 W. The details of the fabrication process of BDD electrode was described elsewhere [17]. The carrier gas was ultrapure hydrogen and the carbon source was a mixture of acetone and methanol (9:1, v/v) having B_2O_3 for boron doping with B/C ratio of 10^4 ppm. The deposition was usually carried out for 24 h to obtain an average film thickness of 20 µm. After the deposition, the film was sonicated in ethanol and deionised in water prior to use. The ohmic contact between the electrode and the lead wire was achieved using silver paste. The effective surface area of the plate type electrode covered with BDD film was estimated to be 11.25 cm^2.

2.3. Electrolytic system

Electrochemical experiments were performed using a glass container with a working volume of 250 ml, placed in thermo-regulated water bath attached with a magnetic stirrer. The electrolysis experiments were conducted at a constant temperature of 25 °C using a potentiostat/galvanostat system (Model-KM064, K-Pas Instronics Engineers, India). The BDD/Pt electrode with the effective surface area of 11.25 cm^2 was used as working electrode and the counter electrode was alternative of these two. Both BDD and Pt electrodes were square/rectangle type plate with the inter electrode gap of 10 mm. Cyclic voltammograms were measured in unstirred solution with a computer controlled Gill AC Bi-Stat ACM potentiostat/galvanostat/frequency response analyzer. The reference electrode was Hg/Hg_2 Cl_2 $KCl_{(sat)}$. Prior to every experimental run, the working electrode BDD was polarized anodically for 5 min with 0.1 M H_2SO_4 electrolyte solution at constant current 100 mA while Pt was soaked in concentrated HNO_3 for 10 min to remove any kind of deposition and/or impurities from the surface. The potential difference was measured with respect to SCE. The cell potential was observed to increase up to 0.4 V over a period of 12 h of galvanostatic electrolysis due to continuous decrease in ionic strength.

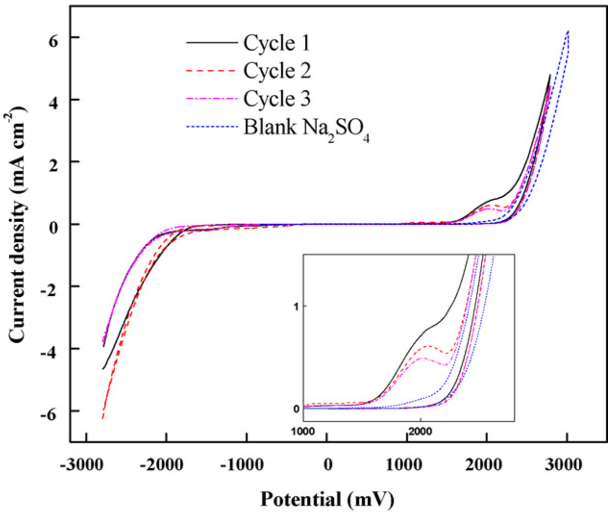

Fig. 1. Cyclic voltammograms of ketoprofen oxidation at BDD electrode (ketoprofen: 5 µM, Na_2SO_4: 0.1 M, scan rate: 10 mV s^{-1}, initial pH: 6.00, *T*: 25 °C). Inset: magnified view of the oxidation peaks.

2.4. Analysis

During the experiment, the samples were drawn at different time intervals and the degradation of KP molecule was monitored by UV–vis spectrophotometer (Model—Shimadzu UV-160A, Japan). The decay of KP molecule was monitored in terms of disappearance of the well-defined peak at 260 nm. The standard method suggested by American Public Health Association was adopted for the analysis of active chlorine (Iodometric) and Cl^- (Argentometric) concentration measurement [18]. The solution pH was measured with pH meter. The mineralization of KP was determined using TOC analyzer (Shimadzu VCSN/CPN Model).

3. Results and discussions

3.1. Cyclic voltammetric study of ketoprofen oxidation

Cyclic voltammograms were recorded to understand the redox behavior of ketoprofen (KP) molecule on BDD electrode at a scan rate of 10 mV s^{-1} and at a fixed Na_2SO_4 concentration of 0.1 M. Also, the voltammogram was recorded in the absence of KP. From the results shown in Figs. 1 and 7(b), 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 as seen in Fig. 7(b). The reason for this behavior will be discussed extensively in Section 3.3. From the anodic sweep of the first cycle (continuous line of Fig. 1), the current peak for KP 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 KP molecule. New and well resolved peak observed in the subsequent cycles which was grad-

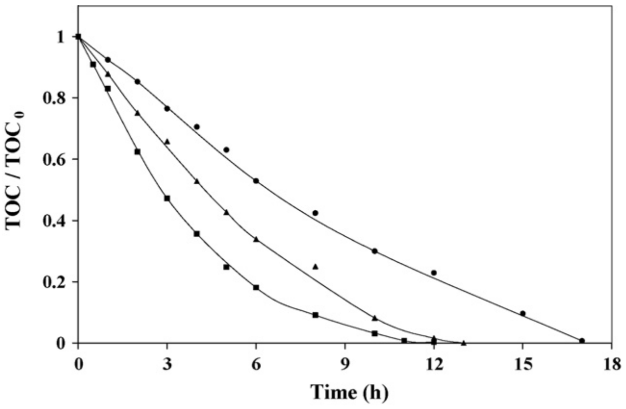

Fig. 2. Kinetics of TOC removal at different current densities (ketoprofen: 5 μM, anode: BDD, Na_2SO_4: 0.1 M, (●) 4.4 mA cm^{-2}, (▲) 8.8 mA cm^{-2}, (■) 13.3 mA cm^{-2}, initial pH: 6.00, *T*: 25 °C).

ually 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 KP 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 [19] at sp^2 free BDD, irreversible nature of KP oxidation was confirmed as there was no reduction peak at negative potential window. The oxygen evolution current peak for BDD in Na_2SO_4 electrolyte is reduced in the presence of KP which confirms that the activity of the BDD was slightly reduced by direct electron transfer oxidation of KP molecule on its surface. The oxidation behavior of KP at Pt electrode in the presence of 0.1 M Na_2SO_4 was studied (data not shown) and no electron transfer step was noticed between hydrogen and oxygen evolution potential.

3.2. Mineralization study of ketoprofen

Degradation of KP 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_2SO_4 and the results are shown in Figs. 2 and 3. The UV–vis spectrum of pure KP exhibited a peak at 260 nm. This characteristic peak was gradually disappeared over a period of 5 h 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 min of electrolysis. Though the peak was disappeared, nearly 50% of the TOC remained in aqueous solution. This clearly indicates that the KP molecule was totally degraded but part of the degraded molecules remained in aqueous solution. The oxidation of KP at BDD anode could be explained due to the various oxidants generated according to the reactions mentioned in Eqs. (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 KP 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 KP is very low. By increasing the current density, the rate of oxidation of KP was found to increase [13,14]. It could be concluded that the complete mineralization of KP can be achieved by using BDD as anode. The overall mineralization reaction can be represented as

$$C_{16}H_{14}O_3 + 29H_2O \rightarrow 16CO_2 + 72H^+ + 72e^- \qquad (6)$$

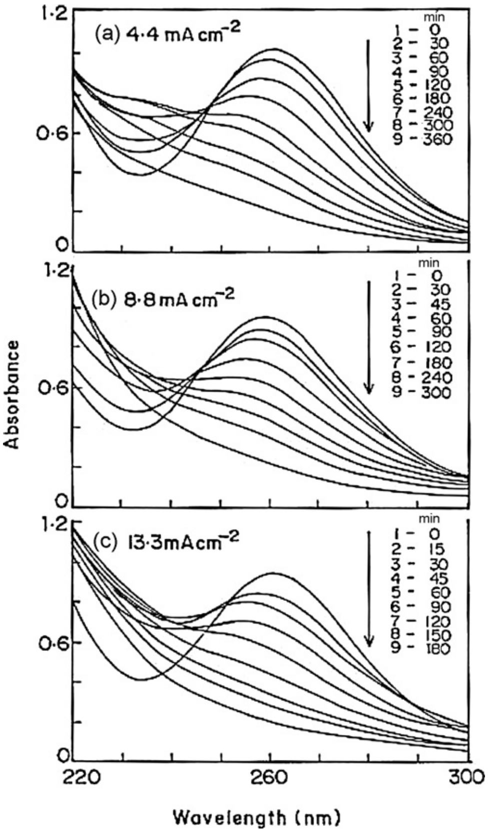

Fig. 3. UV–vis spectra of ketoprofen recorded at different current densities: (a) 4.4 mA cm^{-2}; (b) 8.8 mA cm^{-2}; and (c) 13.3 mA cm^{-2} (ketoprofen: 5 μM, anode: BDD, Na_2SO_4: 0.1 M, initial pH: 6.00, *T*: 25 °C).

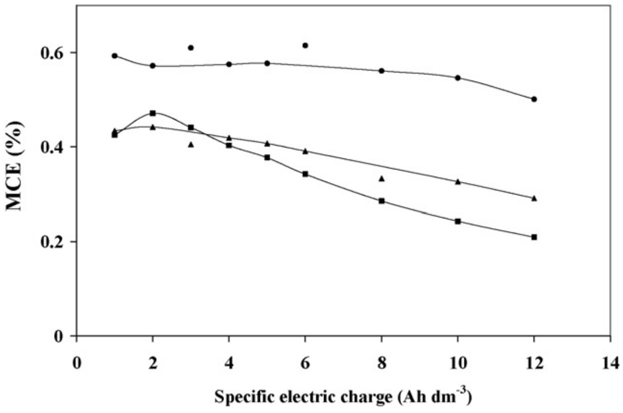

Fig. 4. Mineralization current efficiency versus specific electric charge for the TOC results shown in Fig. 2 (ketoprofen: 5 μM, anode: BDD, Na_2SO_4: 0.1 M, (●) 4.4 mA cm^{-2}, (▲) 8.8 mA cm^{-2}, (■) 13.3 mA cm^{-2}, initial pH: 6.00, *T*: 25 °C).

This reaction shows that 72 electrons are involved in incinerating a KP molecule completely into CO_2. The mineralization current efficiency (MCE) was calculated with respect to the electrolysis time according to Eq. (7).

$$\mathrm{MCE} = \left[\frac{\Delta(\mathrm{TOC})_{\mathrm{exper}}}{\Delta(\mathrm{TOC})_{\mathrm{theor}}}\right] \times 100 \qquad (7)$$

where $\Delta(\mathrm{TOC})_{\mathrm{exper}}$ denotes the experimentally observed TOC removal at time *t* and $\Delta(\mathrm{TOC})_{\mathrm{theor}}$ is the theoretically calculated TOC removal considering that the applied electrical charge (=current × time) is consumed to yield reaction (6). As seen in Fig. 4, the MCE was observed to be comparatively better at lower current

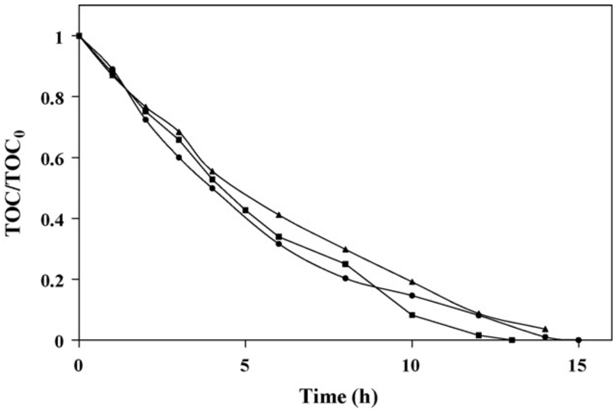

Fig. 5. TOC removal versus initial pH of the electrolyte using BDD anode at constant applied current density of 8.8 mA cm^{-2} (ketoprofen: 5 μM, Na_2SO_4: 0.1 M, (●) initial pH: 3.00, (■) initial pH: 6.00, (▲) initial pH: 9.00, *T*: 25 °C).

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 KP 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 the 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 KP at BDD surface was also studied at the initial pH of 3.00, 6.00 and 9.00 and the results are presented in Fig. 5. 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 $^{\bullet}OH$ and $S_2O_8{}^{2-}$ [20,21]. 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_2 liberation from the cathode. Similar trend was observed in the oxidation of phenol using metal oxide coated Ti mesh electrode [22].

3.3. *Effect of electrolyte*

The effect of supporting electrolytes such as NaCl, Na_2SO_4 and $NaNO_3$ on KP oxidation at BDD and Pt was studied at a constant applied current density and the results were shown in Figs. 3(b) and 6. The UV–vis spectra indicate that the effective degradation of KP can only be achieved when $SO_4{}^{2-}$ is employed as supporting electrolyte. The peak at 260 nm corresponding to the λ_{max} of KP 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 [23] and its intensity was increased with electrolysis time. The oxidants such as $S_2O_8{}^{2-}$, $SO_4{}^-$, 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 Fig. 8, the $SO_4{}^{2-}$ strongly influences the rate of mineralization reaction of KP molecule. For example, at 12 h electrolysis period, complete TOC removal was achieved using $SO_4{}^{2-}$ where as TOC removal is hardly 55% and 25% in the presence of $NO_3{}^-$ and Cl^- media, respectively. The in situ generation [15] of $S_2O_8{}^{2-}$ and sulfate radical in the presence of Na_2SO_4 could be represented as

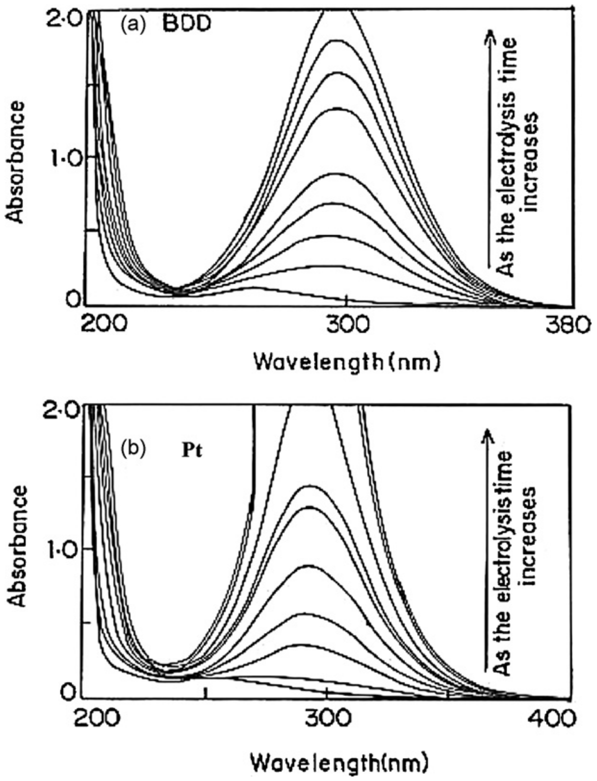

Fig. 6. UV–vis spectra showing OCl^- during electrolysis (ketoprofen: 5 μM, applied current density: 8.8 mA cm^{-2}, NaCl: 0.1 M, initial pH: 6.00, *T*: 25 °C).

$$2SO_4{}^{2-} \rightarrow S_2O_8{}^{2-} + 2e^- \tag{8}$$

$$^{\bullet}OH + 2SO_4{}^{2-} \rightarrow SO_4{}^{-\bullet} + OH^- \tag{9}$$

$$SO_4{}^{-\bullet} + SO_4{}^{-\bullet} \rightarrow S_2O_8{}^{2-} \tag{10}$$

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 [21]. Some researchers have pointed out that the ability of $S_2O_8{}^{2-}$ (E_0 = 2.01 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 $^{\bullet}OH$, $S_2O_8{}^{2-}$ and $SO_4{}^{-\bullet}$ [13,24].

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

$$BDD(^{\bullet}OH) + Cl^- \rightarrow BDD + (1/2)Cl_2 + OH^- \tag{11}$$

$$Cl^- \rightarrow Cl_2 + 2e^- \tag{12}$$

While complete mineralization of KP was achieved in the presence of Na_2SO_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 Fig. 7(a) and (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 Cl_2 evolution just prior to the potential where $^{\bullet}OH$ can be generated. It could be the main reason for the poor efficiency of BDD comparing

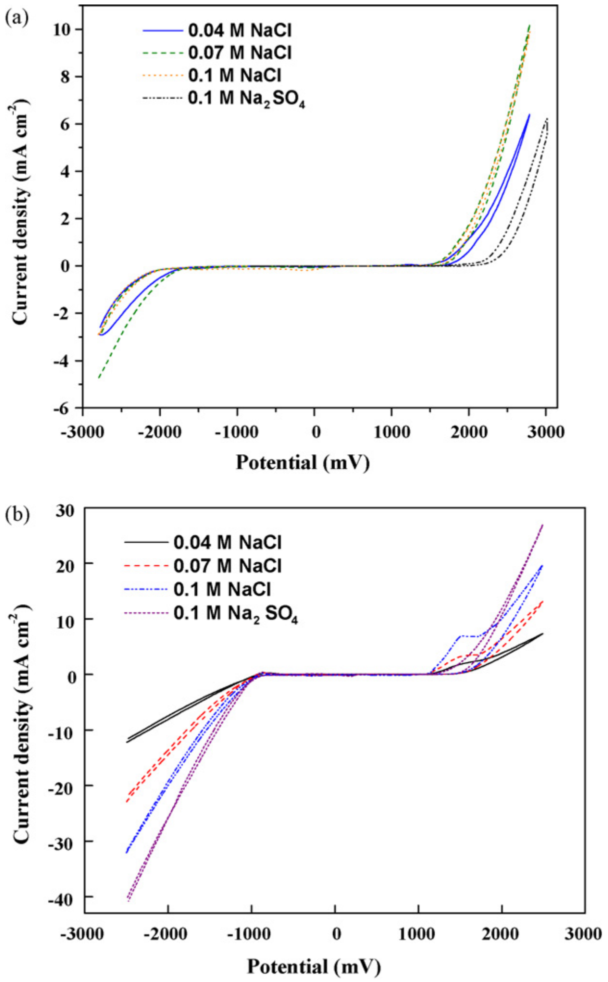

Fig. 7. Cyclic voltammogram for chlorine evolution peak study at (a) BDD and (b) Pt electrode (scan rate: 10 mV s^{-1}, initial pH: 6.00, T: 25 °C).

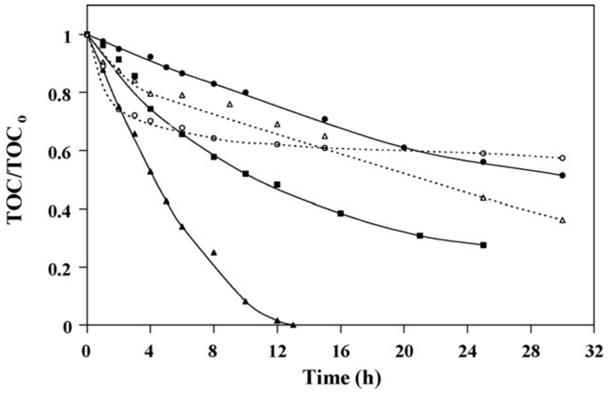

Fig. 8. Effect of supporting electrolyte on TOC removal (electrolyte concentration: 0.1 M, ketoprofen: 5 µM, initial pH: 6.00, T: 25 °C, applied current density: 8.8 mA cm^{-2}, (●) BDD–NaCl, (▲) BDD–Na_2SO_4, (■) BDD–$NaNO_3$, (○) Pt–NaCl, (△) Pt–Na_2SO_4).

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} (Fig. 8). 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 polyhydroxyl phenol molecules are thoroughly oxidized by active chlorine [26]. In spite of its oxidizing ability, the gaseous Cl_2 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–vis spectrum (Fig. 6) around 292 nm and well-defined anodic oxidation peak at 1.5 V (Fig. 7b) indicates the formation of hypochlorite molecule according to the following reaction suggested by Canizares et al. [27].

$$Cl_2 + H_2O \rightarrow HClO + HCl \qquad (13)$$

Although the active chlorine (Cl_2, 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 Cl_2 evolution. It is understandable from the anodic evolution peak of Pt electrode that the peak current in SO_4^{2-} 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 over voltage. 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 $NaNO_3$ is only moderate as the nitrate is an inert supporting electrolyte.

4. Conclusions

Anodic oxidation of ketoprofen at BDD and Pt was studied and the effect of applied current density, pH and nature of the supporting electrolytes on mineralization 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 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 KP was found to be current control at initial phase and become diffusion controlled process beyond 80% of TOC removal. The significance of initial pH on the mineralization of the ketoprofen was observed to be very marginal. Among the supporting electrolytes tried, 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 poor mineralization efficiency in the presence of NaCl may be attributed to the possible formation of refractory chlorinated compounds. The rate of mineralization in the presence of NaCl was found to be better on Pt anode compared to BDD. However, the overall process efficiency was observed to be poor in the presence of NaCl.

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