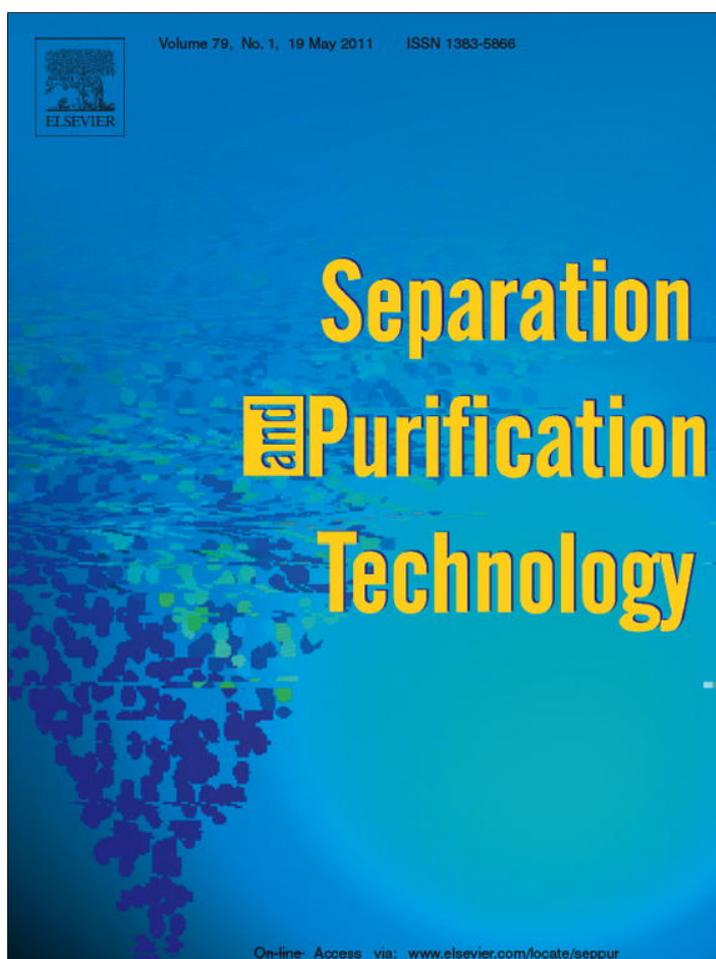


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Role of electrolyte on anodic mineralization of atenolol at boron doped diamond and Pt electrodes

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ABSTRACT

Anodic oxidation of atenolol, known as β -blocker, has been investigated using boron-doped diamond (BDD) and Pt electrodes. The mineralization trend of atenolol in the presence of NaCl, Na₂SO₄ and NaNO₃ was followed using total organic carbon analyzer. The disappearance of chloride ions and generation of active chlorine (Cl₂, HOCl, OCl⁻) were analysed by argentometric and iodometric methods, respectively. The BDD anode was found to be effective in the presence of Na₂SO₄ whereas Pt yields better removal in the presence of NaCl. The initial concentration of NaCl and applied current density on the mineralization of atenolol were found to be significant for both BDD and Pt anodes. These results are explained in terms of electrogenerated oxidants such as \cdot OH, SO₄^{•-}, S₂O₈²⁻, Cl₂, HOCl and OCl⁻. The evolution of chlorine at BDD and Pt with respect to NaCl concentration was studied by means of cyclic voltammetric technique. Though the rate of mineralization was observed to be initially higher in the presence of Pt anode, the overall rate of mineralization is more or less similar beyond 15 h of electrooxidation. The slow degradation at the later stages of electrooxidation was attributed to the presence of residual chlorinated organic compounds which are very refractive. The complete mineralization was achieved in the presence of Na₂SO₄ using BDD as anode.

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1. Introduction

The consumption rate of pharmaceutical compounds by human beings and livestock is increasing day by day. The presence of pharmaceutical compounds and its metabolites in surface and ground drinking water has become potential health risk to human beings [1]. The source of contamination includes excretion of ingested drug and improper disposal of drugs by consumers [2]. Since the sewage treatment plants are ineffective, some pharmaceutical compounds continue to remain in water [3]. The β -blocker compounds are considered to be harmful even in low concentrations (ng L⁻¹ to μ g L⁻¹). Atenolol is the β -blocker group of compound, frequently used for the treatment of high blood pressure, anti-angina and cardiovascular diseases. Its presence was reported in ground water at concentrations up to 10 μ g L⁻¹ [4]. The usage of β -blockers in Europe alone is more than 3000 kg per year. These compounds are present to the extent of 0.84–2.8 μ g L⁻¹ in certain Spanish wastewater [5]. 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 [3,6,7]. Also, atenolol is adsorbed

by the human body only to the extent of 50% and the remaining is excreted in faeces and urine [8]. Hence the degradation and removal of atenolol is very essential. Atenolol removal by anodic oxidation using BDD and electro-Fenton using Pt has been studied and the efficiency of both the processes were compared [9]. However, the working concentration of atenolol studied was relatively higher than the practical applications. Several conventional biological methods have been tried to decontaminate the water containing β -blockers [10]. In general, the biological methods are limited as they require longer treatment time and form the by-products which are more resistant. 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 [11].

Recently, the boron-doped diamond (BDD) is receiving great attention [12] particularly as anode for the oxidation of organic pollutants in lower concentrations (between ng and μ g) [13,14]. 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 (\cdot OH) which can destroy/mineralize the organic pollutant molecules [15]. The electrooxidation technique was proved to be effective to mineralize the toxic compounds to CO₂ and H₂O. However, the complete conversion often depends on operating parameters such as nature

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of the electrolyte [13], applied current density and electrode materials employed. More specifically, the active electrolytes such as NaCl and Na₂SO₄ often influence the mineralization process. This is due to the indirect electrooxidation that occurs in the bulk of the electrolyte. In the presence of Cl⁻ and SO₄²⁻, the oxidants such as hypochlorous acid (HOCl), hypochlorite ion (OCl⁻), chlorine (Cl₂), peroxodisulfate (S₂O₈²⁻) and other free radicals (Cl•, Cl₂•⁻ and SO₄•⁻) are generated in situ. These can act as indirect oxidants for the destruction of organic pollutants. In electrochemical oxidation, the influence of anion is very important. The chlorine based oxidants are considered to be more effective especially for the mineralization of phenol [16] oxalic acid [17] and organic dyes [18]. However, it was observed that the mineralization of Acid black 210 in the presence of NaCl with BDD anode was incomplete mainly due to chlorinated organics generated during the process [19]. In our previous work, it was demonstrated that the chlorinated compounds are formed at BDD anode [13,20], which are even more hazardous than parent compound itself. It may be noted that the chlorinated compounds are more toxic and persistent even with •OH. Nevertheless, the exact role of NaCl and its initial concentration on the degradation of organic compounds is not very clear. It is worthy to note that the formation of active chlorine species varies with respect to the nature of the anode material employed. There are many reports on the anodic degradation of organic pollutants comparing BDD and Pt electrodes [20,21]. Since the Pt exhibits a comparable efficiency with BDD, the mineralization behavior of these electrodes in Cl⁻ medium was studied for better understanding of oxidation. The present study was aimed at the destruction of atenolol by electrooxidation using BDD and Pt anodes in the presence of active electrolytes.

2. Experimental

2.1. Materials

The atenolol powder obtained from Sigma–Aldrich was used without further purification. Atenolol stock solution with a concentration of 100 μM was prepared in distilled water free from total organic carbon (TOC). The working solution of required concentration was obtained by diluting the stock solution. In this study, three different electrolytes viz. NaCl, Na₂SO₄ and NaNO₃ were used. The pH of the aqueous solutions was adjusted by dilute H₂SO₄ 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 [22]. The carrier gas was ultra pure hydrogen and the carbon source was a mixture of acetone and methanol (9:1, v/v) having B₂O₃ for boron doping with B/C ratio of 10⁴ 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 cm².

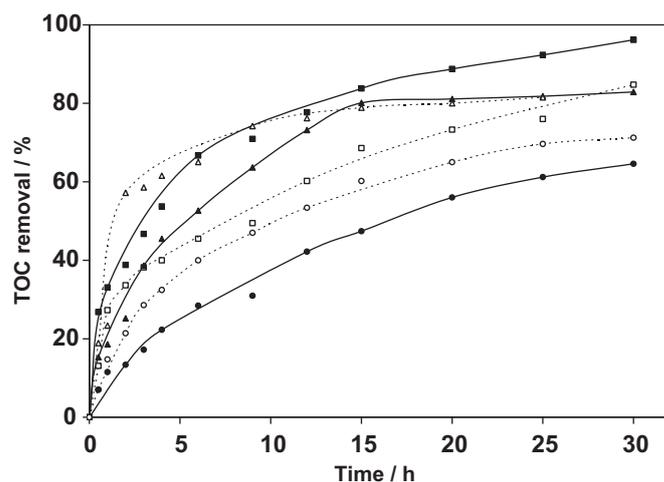


Fig. 1. Influence of electrolytes on TOC abatement at BDD and Pt anodes; BDD: continuous line, Pt: dotted line, atenolol – 2.25 μM, current density: 8.88 mA cm⁻², pH 6.0, and T: 25 °C; (■ □) Na₂SO₄, (▲ △) NaCl, (● ○) NaNO₃.

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 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 electrodes with the effective surface area of 11.25 cm² were used as working electrode and the counter electrode was alternative of these two. Both BDD and Pt electrodes were rectangle plates with an inter electrode gap of 10 mm. Prior to every experimental run, the working electrode BDD was polarized anodically for 5 min with 0.1 M H₂SO₄ electrolyte solution at constant current of 100 mA while Pt was soaked in concentrated HNO₃ for 10 min to remove any kind of deposition and/or impurities from the surface. The potential difference was measured with respect to saturated calomel electrode (SCE). Cyclic voltammetric experiments were carried out in unstirred aqueous solution with a computer controlled Gill AC Bi-Stat ACM potentiostat/galvanostat/frequency response analyzer. The reference electrode was SCE.

2.4. Analysis

During the experiment, the samples were drawn at different time intervals and the mineralization of atenolol was determined using TOC analyzer (Shimadzu VCSN/CPN Model). The standard method suggested by American Public Health Association was adopted for the analysis of active chlorine (iodometric) and Cl⁻ (argentometric) concentration measurement [23]. The solution pH was measured with pH meter.

3. Results and discussion

3.1. Effect of supporting electrolytes on atenolol mineralization with BDD and Pt

Mineralization of atenolol at BDD and Pt electrodes in the presence of NaCl, Na₂SO₄, and NaNO₃ electrolytes was studied at a constant atenolol concentration of 2.25 μM and applied current density of 8.88 mA cm⁻². From the experimental results presented in Fig. 1, it is apparent that both BDD and Pt anodes are effective for the mineralization of atenolol. The rate of TOC removal is better at the initial stages of oxidation i.e., up to 5 h electrolysis time.

In the presence of SO_4^{2-} , around 70 and 50% of TOC was removed within 9 h using BDD and Pt anodes, respectively. Beyond this point, the removal is marginal and it took nearly 20 h to achieve further TOC removal of 25%. The slow rate of mineralization at the later stages may be attributed to mass transfer limitations [14]. Maximum removal of TOC was achieved using BDD in the presence of Na_2SO_4 . About 96 and 84.6% of TOC removal was achieved using Na_2SO_4 as electrolyte with BDD and Pt anodes respectively. Since the BDD has higher oxygen overvoltage than Pt [24], generation of $\cdot\text{OH}$ and $\text{S}_2\text{O}_8^{2-}$ will be in larger quantity. Generation of $\cdot\text{OH}$ at the surface of the electrode can be represented as:



The $\cdot\text{OH}$ thus generated helps in the decomposition [25] of the atenolol molecules. In the case of Na_2SO_4 as electrolyte, $\text{S}_2\text{O}_8^{2-}$ and sulfate radical are generated as represented in the following reactions:



Contrary to above, in some cases SO_4^{2-} was found to play no role on degrading the organic pollutants using BDD anode [26]. In the presence of NaCl, Pt showed a rapid TOC removal rate at initial stage of electrolysis compared to BDD. It clearly shows that no accumulation of intermediate compounds took place using NaCl with Pt anode during the initial electrolysis hours. However, the overall performance of both the anodes is more or less similar by extending the electrolysis periods. In particular, there is no TOC removal beyond 15 h in the presence of NaCl either with BDD or Pt anode. The poor mineralization at a later stage could be attributed to formation of chlorinated organic intermediates. In the presence of NaNO_3 , the performance of both the anodes was observed to be less as there is no oxidants generation from the supporting electrolyte [27]. Also, the mineralization rate of atenolol at BDD is lower compared to Pt in the presence of NaNO_3 . It may be explained due to fouling of electrode. The BDD anode is particularly susceptible for fouling by the nitrate substituted intermediates which in turn reduces the activity of the electrode.

3.2. Effect of NaCl concentration on the oxidation of atenolol

The mineralization of atenolol using BDD and Pt electrodes with different NaCl concentrations was recorded at an applied current density of 8.88 mA cm^{-2} and atenolol concentration of $2.25 \mu\text{M}$. The measured potentials for BDD are 4.9, 4.3 and 3.9 V at 0.01, 0.05 and 0.1 M NaCl respectively. The measured potentials for Pt were found to be slightly less and it was 4.7, 4.2 and 3.85 at 0.01, 0.05 and 0.1 M NaCl concentrations, respectively. A slight increase in the potential was observed during the mineralization of atenolol and a maximum of 0.5 V was found to be increased in the presence of 0.1 M NaCl. It may be due to the depletion in ionic concentration of Cl^- in the bulk of the electrolyte. The results presented in Fig. 2, clearly indicate that the rate of TOC removal was significantly increased by increasing the concentration of NaCl. The oxidation of atenolol in the presence of NaCl could be attributed to the mediated oxidants rather than the direct electron transfer reaction at the surface of the anode. Cl^- is expected to oxidize at anode surface by direct electron transfer reaction or by consuming $\cdot\text{OH}$ which are accumulated in the vicinity of the electrode surface by physisorption at nonactive BDD electrode and by chemisorptions at active Pt electrode. The generation of active chlorine species is represented in Eqs. (5)–(11). The dominance of HOCl and OCl^- depends on the pH

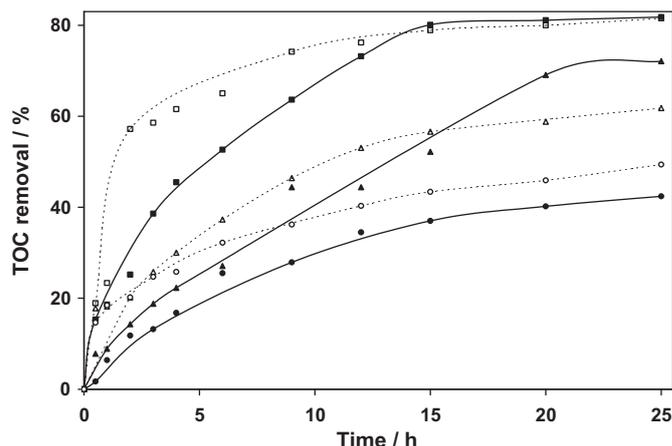


Fig. 2. Effect of initial concentration of NaCl on mineralization of atenolol at BDD and Pt anodes; BDD: continuous line, Pt: dotted line, atenolol – $2.25 \mu\text{M}$, current density: 8.88 mA cm^{-2} , pH 6.0, and $T: 25^\circ\text{C}$; (\blacksquare , \square) 0.1 M, (\blacktriangle , \triangle) 0.05 M, (\bullet , \circ) 0.01 M.

of the electrolyte. The overall results reveal that an increase of Cl^- concentration accelerates the TOC removal



irrespective of the anode materials. The mineralization of atenolol using Pt anode during the initial stage was observed to be better at 0.05 M NaCl concentration. Also, the 60% of TOC removal was achieved within 3 h of electrolysis period using Pt with higher NaCl concentration. On the other hand, the mineralization rate is slower at BDD than Pt with lower NaCl concentration. This trend could be attributed to the better generation of active chlorine at Pt anode. In order to explain the chlorine evolution at BDD and Pt, the cyclic voltammetric experiments were conducted at corresponding NaCl concentrations. From the results shown in Fig. 3, it is evident that the evolution of chlorine on both BDD and Pt was proportionally increased with the NaCl concentration. It is apparent that in the case of BDD electrode, the evolution of current density peaks up to 8 mA cm^{-2} whereas it was increased to 40 mA cm^{-2} in the case of Pt electrode under similar NaCl concentration of 0.1 M. Thus it could be inferred that the chlorine evolution is comparatively high at Pt anode. The appearance of a small shoulder in the presence of Pt at around 1.4 V vs. SCE reflects the Cl^- oxidation at the surface of the electrode [28]. The chlorine evolution behavior is different at BDD as no such oxidation peak was observed in the potential window of -3 to $+3$ V (data shown only from 0 to $+3$ V). The oxygen evolution potential for Si/BDD is 2.8 V [29] and in the presence of NaCl, it was slightly reduced as the chlorine evolution starts at around 1.9 V prior to the water decomposition reaction. It may be noted that by increasing the NaCl concentration, the peak was shifted to less positive potential which further confirms the domination of chlorine evolution rather than $\cdot\text{OH}/\text{O}_2$ formation [29]. Further, the difference of TOC removal rate is markedly higher at 0.1 M. In other words, at the initial stage of electrolysis, the concentration of Cl^- is higher near to the electrode surface. Accordingly the generation of active chlorine and the oxidation is high. However, the TOC removal was hardly improved beyond 15 h. It may be due to the formation of

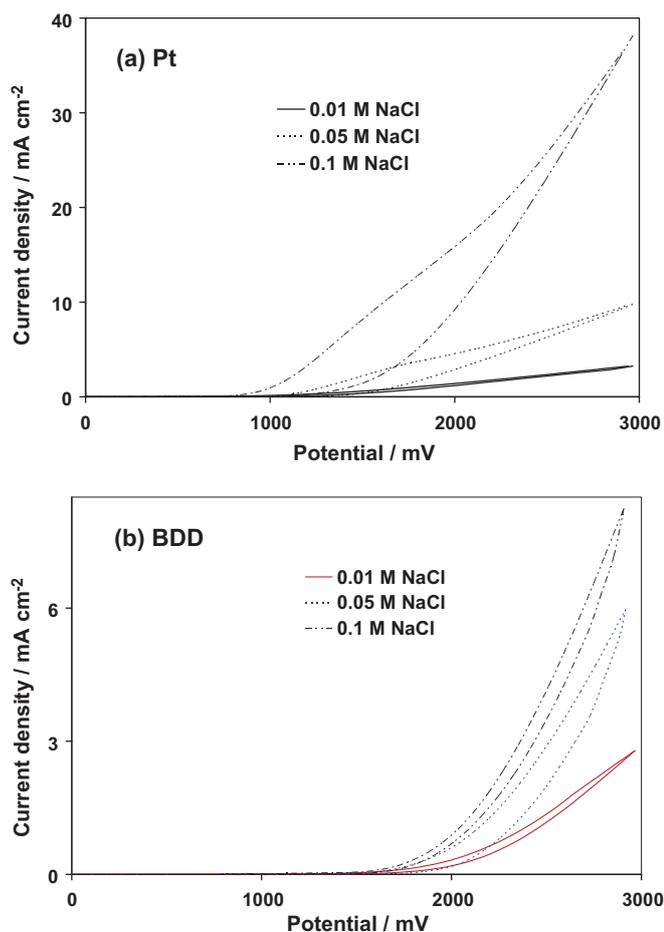


Fig. 3. Cyclic voltammogram for chlorine evolution peak study at (a) Pt and (b) BDD electrode; scan rate: 10 mV s^{-1} , initial pH 6.0, and $T: 25^\circ\text{C}$.

refractory intermediates that resist oxidation. The main drawback of the indirect oxidation mediated by active chlorine is the formation of chlorinated organic pollutants and some of them are more refractive. The changes in the Cl^- concentration were measured and the results are presented in Fig. 4. The Cl^- depletion exactly reflects the quantity of Cl^- oxidized at the anodic surface or with $\bullet\text{OH}$. It is very clear that the Cl^- removal is more effective at Pt than at BDD and a linear one as a function of electrolysis time. Although chlorine based oxidants are continuously generated, the strength of these oxidants is not enough to mineralize chlorinated aliphatic compounds formed at the later stage of electrolysis [30].

3.3. Effect of current density on TOC removal in the presence of NaCl

The effect of current density on TOC removal was studied at three different applied current densities viz. 4.44, 8.88 and 13.3 mA cm^{-2} and the results obtained were plotted in Figs. 5 and 6. The decrease in Cl^- concentration during the electrolysis (Fig. 5) clearly indicates the formation of active chlorine. Results shown in Fig. 6 confirm that the applied current density has marked influence on TOC removal. The TOC removal was found to increase with current density. However, it should be noted that the difference of TOC removal between 8.88 and 13.3 mA cm^{-2} is very marginal particularly with Pt. In general, if the applied current is more than the limiting current, the oxidation will invariably undergo mass transport control. Further, the oxidation of Cl^- is expected to occur by direct electron transfer at the surface of the electrode and also

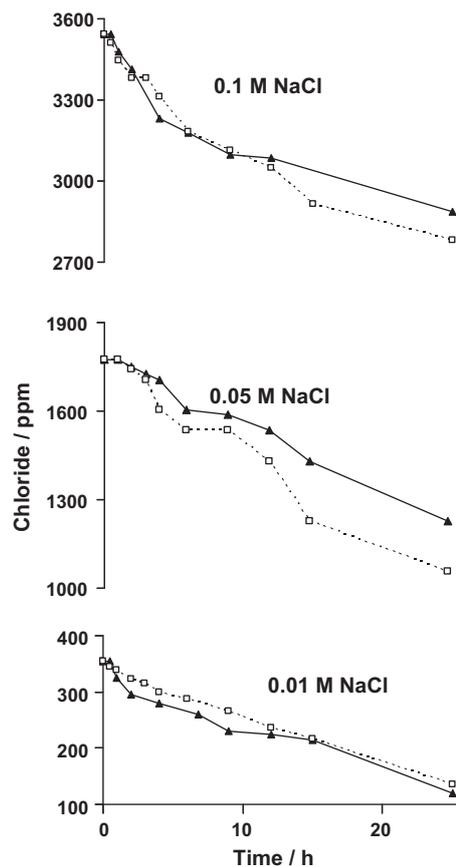


Fig. 4. The change in Cl^- concentration with respect to electrolysis time for the different initial concentration of NaCl; BDD: continuous line (\blacktriangle), Pt: dotted line (\square), atenolol – $2.25 \mu\text{M}$, current density: 8.88 mA cm^{-2} , pH 6.0, and $T: 25^\circ\text{C}$.

by detriment of $\bullet\text{OH}$ formed at the electrode surface from H_2O . The Pt electrode is more favor for the former process because of the lower O_2 overvoltage. Consequently, it promotes the oxidation of Cl^- at its surface. However, at higher applied current, the oxygen evolution dominates the Cl^- oxidation and as a result the decrease in Cl^- concentration is less. From the results shown in Fig. 5, it is evident that the rate of Cl^- oxidation at Pt electrode is considerably reduced at higher applied current compared to BDD.

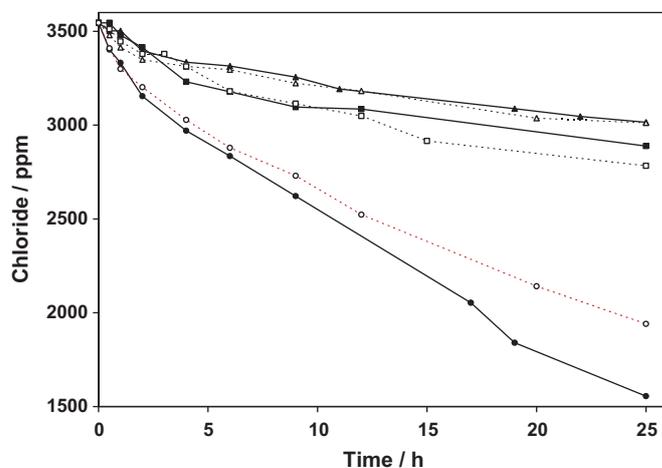


Fig. 5. The change in Cl^- concentration with respect to applied current densities and electrolysis time; BDD: continuous line, Pt: dotted line, atenolol – $2.25 \mu\text{M}$, electrolyte: 0.1 M NaCl , pH 6.0, and $T: 25^\circ\text{C}$; (\blacktriangle) 4.44 mA cm^{-2} , (\blacksquare) 8.88 mA cm^{-2} , (\bullet) 13.3 mA cm^{-2} .

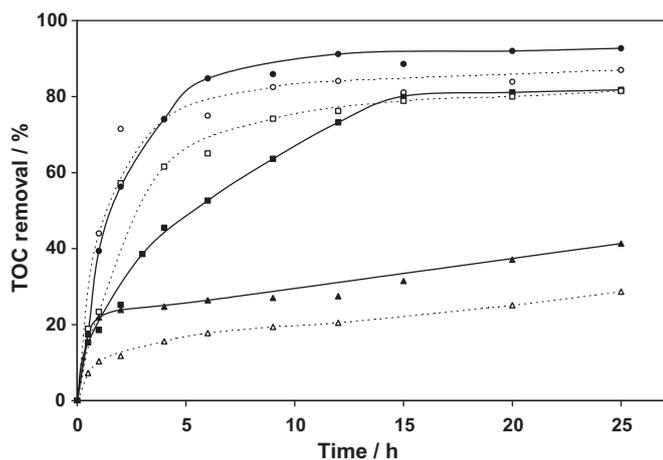


Fig. 6. Effect of applied current density on mineralization trend of atenolol compound using NaCl with BDD and Pt anodes; BDD: continuous line, Pt: dotted line, atenolol – 2.25 μM , electrolyte: 0.1 M NaCl, pH 6.0, and T : 25 $^{\circ}\text{C}$; (Δ , \square , \bullet) 4.44 mA cm^{-2} , (\blacksquare , \blacksquare , \circ) 8.88 mA cm^{-2} , (\bullet , \circ) 13.3 mA cm^{-2} .

This may be the reason for the very marginal TOC removal at Pt between the higher current densities of 8.88 and 13.3 mA cm^{-2} . On the other hand, the proportional disappearance of Cl^- concentration is observed to be enhanced at higher applied current density of 13.3 mA cm^{-2} . At the end of 25 h electrolysis period, the decrease in Cl^- concentration is hardly 700 ppm at an applied current density of 8.88 mA cm^{-2} , whereas it is more than 1600 ppm at 13.3 mA cm^{-2} . At higher applied current, less effective oxidants such as chlorite, chlorate and perchlorate are reported to be formed [31]. As a result, the rate of TOC removal was decreased. Nevertheless, the efficiency of the TOC removal (TOC removal vs. $Q = \text{Ah L}^{-1}$) is increased with increasing applied current density (data not shown). As shown in Table 1, the active chlorine generation was measured for both the anodes at different time intervals. It is evident that the concentration of active chlorine is increased with applied current. The high concentration of active chlorine in the bulk solution results in the effective mineralization of atenolol.

The TOC removal was observed to be better at initial stage of electrolysis irrespective of electrode material and applied current density. It should be noted that the TOC removal beyond 5 h of electrolysis period at a lower applied current density of 4.44 mA cm^{-2} , remain same even after 25 h of electrooxidation. In this case, the rate of TOC removal is expected to be a linear one as the corresponding Cl^- depletion is progressive with electrolysis period. It confirms that the mass transfer limitation is not applicable at lower applied current density. At lower current density, the applied current is utilized to oxidize the Cl^- instead of mineralization process. Also, the aliphatic acid intermediates are expected to form at lower applied current density which are refractory and difficult to oxidize with active chlorine formed. Low mineralization can also be explained due to the formation of chlorinated aliphatic intermediates which resists oxidation by active chlorine and $\bullet\text{OH}$ [30]. Although, the mineralization of organics is slightly better at higher applied current, many studies on the degradation of organic pol-

Table 1
The concentration of active chlorine as a function of electrolysis time for the experiments given in Fig 6.

Electrolysis period (h)	4.44 mA cm^{-2}		8.88 mA cm^{-2}		13.3 mA cm^{-2}	
	Pt	BDD	Pt	BDD	Pt	BDD
6	78.9	87.8	121.2	101.7	188.5	228.3
12	117.1	116.2	228.3	178.4	322.7	376.8
25	242.8	228.3	386.6	325.4	483.3	565.2

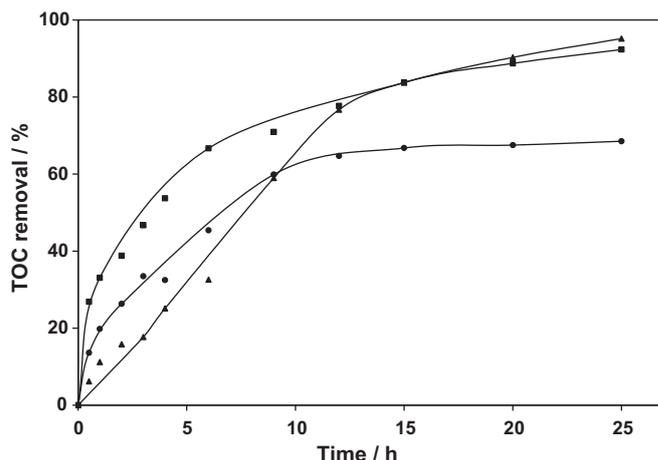


Fig. 7. Mineralization of atenolol with respect to initial pH of the electrolyte at BDD anode; atenolol: 2.25 μM , T : 25 $^{\circ}\text{C}$, electrolyte: Na_2SO_4 (0.1 M), and current density: 8.8 mA cm^{-2} ; (Δ) pH 3.0, (\blacksquare) pH 6.0, (\bullet) pH 9.0.

lutants using NaCl as electrolyte has revealed that the degradation is restricted due to the chlorinated compounds [19,20]. From the results, it could be concluded that the mineralization of atenolol is effective at higher applied current densities when NaCl is present in aqueous solutions.

3.4. Mineralization study of atenolol by BDD

Since the initial pH of the electrolyte is an important variable to achieve the total mineralization, experiments were carried out in three different initial pH conditions viz. pH 3.0, pH 6.0 and pH 9.0. The effect of initial pH on TOC removal during atenolol mineralization at BDD anode in the presence of Na_2SO_4 is shown in Fig. 7. The TOC removal was observed to be relatively faster at pH 6.0. It could be seen that the TOC removal gradually increased with the electrolysis period and reached to a maximum of 95% at pH 3.0. However, the rate of TOC removal was quite slower during the initial stage of electrolysis i.e., up to 9 h. In general, the pH of the electrolyte mostly affects the indirect mediated oxidation and the direct oxidation process remains almost unaffected during the electrolysis. In alkaline condition, the evolution of oxygen is comparatively high which prevents the diffusion of pollutant molecule to the electrode surface [32]. The alkaline pH may favor the formation of inactive hydroperoxide (HO_2^-) anion which act as a $\bullet\text{OH}$ scavenger as per reaction (12).



It was also observed that the change in pH affects the solubility of the oxygen [33] which in turn is expected to affect the generation of free radicals and mediated oxidants in the bulk electrolyte. In the present case, the pH of the electrolyte solution was shifted towards neutral side when the experiment was carried out at alkaline pH 9.0. The final pH was shifted to 3.07, 7.2 and 6.87 from the initial pH of 3.0, 6.0 and 9.0, respectively. It could be explained due to the formation of carbonate and bicarbonate ions during the electrolysis. The similar observation has been reported by Rajkumar et al. [34] during the oxidation of phenol in chloride mediated solutions. In view of the above, further experiments were carried out at an initial pH of 6.0.

The complete mineralization of atenolol was observed at BDD anode with Na_2SO_4 at pH 6.0. Experiments were carried out at different applied current densities and the results are shown in Fig. 8. The production of $\bullet\text{OH}$ from water decomposition at BDD is generally believed to be largely responsible for atenolol mineral-

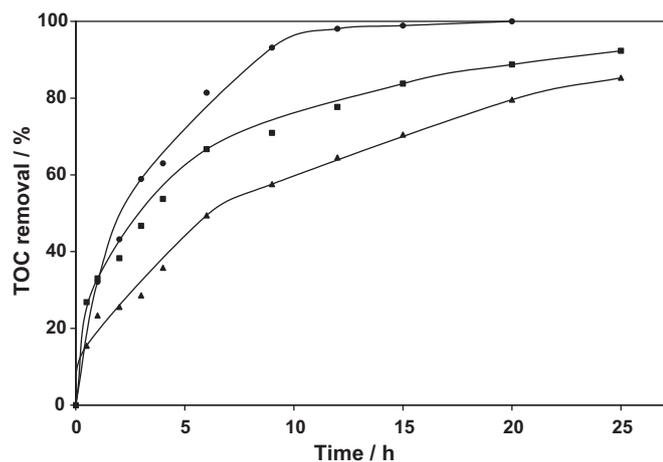
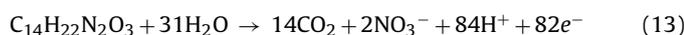


Fig. 8. Effect of current density on the mineralization of atenolol using BDD anode in the presence of Na_2SO_4 (0.1 M); atenolol: $2.25 \mu\text{M}$, pH 6.0, and T : 25°C : (\blacktriangle) 4.44 mA cm^{-2} , (\blacksquare) 8.88 mA cm^{-2} , (\bullet) 13.3 mA cm^{-2} .

ization. Also, the earlier studies [20] have proved that oxidation of organics involve the in situ generated intermediate oxidants such as $\text{SO}_4^{\bullet-}$ and $\text{S}_2\text{O}_8^{2-}$ which are likely to be generated from SO_4^{2-} by consuming the $\bullet\text{OH}$ as per reactions (2)–(4). 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 [35]. Anodic mineralization at higher applied current density is expected to aid the production of $\bullet\text{OH}$ 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} .

Thus, it could be concluded that the complete mineralization of atenolol can be achieved using Na_2SO_4 media with BDD anode. The overall mineralization reaction can be written as:



This reaction shows that 82 electrons are involved in mineralizing a atenolol molecule completely into CO_2 . The mineralization current efficiency (MCE) was calculated with respect to the electrolysis time according to the following relation (14):

$$\text{MCE} = \left[\frac{\Delta(\text{TOC})_{\text{exper}}}{\Delta(\text{TOC})_{\text{theor}}} \right] \times 100 \quad (14)$$

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 ($Q = \text{applied current} \times \text{electrolysis time}$) is consumed to yield the reaction (13). As shown in Fig. 9, 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 ($\text{SO}_4^{\bullet-}$, $\text{S}_2\text{O}_8^{2-}$, etc.) and $\bullet\text{OH}$ during the mineralization of atenolol. It has been reported that the half life of sulfate based oxidants is longer thereby

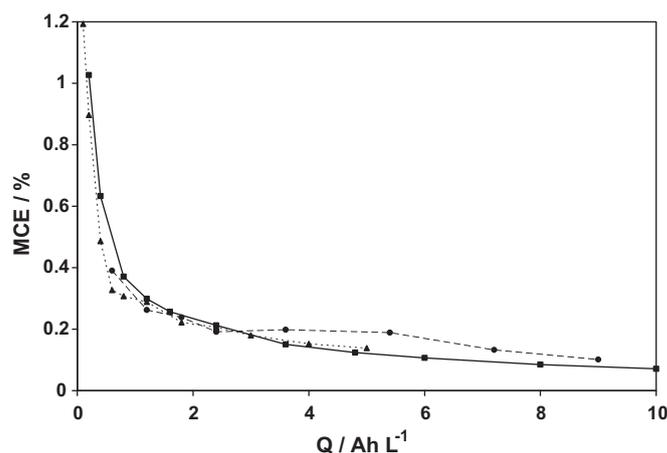


Fig. 9. Mineralization current efficiency with respect to specific electric charge for the TOC removal results shown in Fig. 8; (\blacktriangle) 4.44 mA cm^{-2} (\blacksquare) 8.88 mA cm^{-2} (\bullet) 13.3 mA cm^{-2} .

it diffuses in to the bulk solution and degrades the pollutants [36]. In other words, oxidation reaction is not affected much by the mass transfer limitation as the pollutant concentration is decreased. The earlier researchers [20,21] 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 ($\text{SO}_4^{\bullet-}$, $\text{S}_2\text{O}_8^{2-}$, etc.,) and direct oxidation (reactive $\bullet\text{OH}$).

4. Conclusions

- Mineralization of atenolol by electrooxidation using BDD and Pt electrodes was studied. The nature of the electrolyte strongly influences the anodic oxidation of atenolol. The mineralization of atenolol at BDD with SO_4^{2-} medium is better whereas using Pt was found to be effective in Cl^- medium.
- An increase in the concentration of NaCl , was found to increase the generation of active chlorine, and in turn the mineralization of atenolol. The chlorine evolution is more at Pt electrode than at BDD.
- An increase in applied current increases the generation of active chlorine and in turn the TOC removal. The higher current density was effective when the electrolyte contains Cl^- . Further, at higher current density, the TOC removal was better at BDD than at Pt in the presence of NaCl . The energy required for the same quantity of organic load is interestingly decreased with increasing the applied current.
- Despite Pt anode seem to have promoted the mineralization reaction in presence of NaCl at pH 6.0, the total mineralization could not be achieved due to the formation of residual chlorinated organic compounds. On the other hand, atenolol is thoroughly mineralized to CO_2 and H_2O at BDD in the presence of SO_4^{2-} . 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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