

Research Article

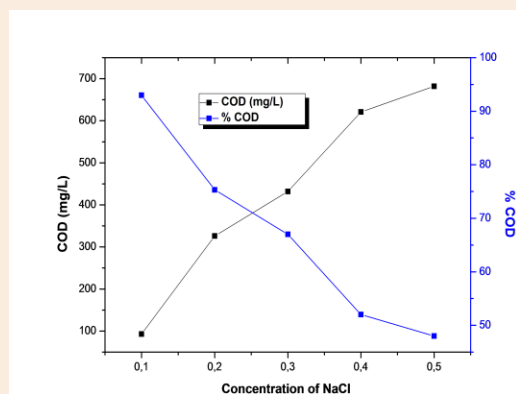
Electrochemical Oxidation of New Pyridazinium-Based Ionic Liquid Derivative using BDD Anode

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Abstract

Eco-friendly ionic liquid 1-(2-ethoxy-2-oxoethyl)pyridazinium chloride (EOPC) newly synthesised has been studied by electrochemical oxidation on boron-doped diamond (BDD) electrodes on basic medium. Through the experimental investigation, to identify the changes closely associated with treatment effect on wastewater containing EOPC, reaction time, pH, temperature, initial concentration of EOPC and current density were analyzed. The EOPC was almost eliminated at a pH value of 13.54, current density of 80mA/cm³, reaction time of 3h and EOPC amount of 15ppm, supporting electrolyte 0.1g/L. The removal ratio of COD is over 90%. EOPC was degraded into H₂O and CO₂ finally.

Keywords: Electrochemical treatment, Boron-doped diamond, pyridazinium



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Introduction

In recent years there has been increasing interest in environmental damage and human injury by industrial pollution, and the relevant legislation is always being made harsher. In this framework electrochemical methods offer a good opportunity to prevent and remedy pollution problems due to the discharge of industrial and sewage effluents. The electrochemical technologies have attracted a great deal of attention because of their versatility, which makes the treatment of liquids, gases and solids possible, and environmental compatibility and it has been proposed as an alternative process for elimination of contaminants in effluents, showing excellent results in various matrices such as textile dyes [1–6], dairy [7,8], herbicides/pesticides [9–13], heavy metals [14], aquaculture [15], landfill leachate [16], pharmaceutical residues [17–21], pulp and paper [22], among others. Moreover, a wide variety of electrode materials have been suggested, such as dimensionally stable anodes, noble metals (e.g. platinum), carbon-based anodes, PbO₂ and BDD; obtaining different removal organic matter efficiencies [23–27] considering that non-active anodes, such as BDD, are useful for direct oxidation of organic material via hydroxyl radicals, while DSA (electrode operates with lower energy consumption and operating cost), such as Ti/IrO₂-Ta₂O₅, are effective for promoting hypochlorite mediated chemistry when chloride is present. In the case of applicability of electrochemical technology for treating wastewaters, dimensionally stable anodes, BDD have been preferentially used as electrode material in this case. In this context, boron-doped diamond anodes allow to directly produce hydroxyl radicals from water electrolysis with very high current efficiencies [28–30]. The chemical structures of the studied pyridanium ionic liquids are given in figure 1.

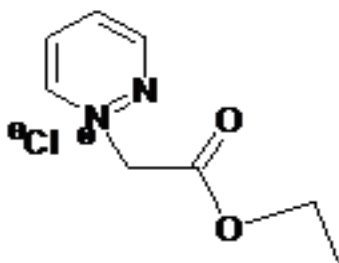


Figure 1 The chemical structure of the studied pyridazinium ionic liquid

Experimental

Electrochemical measurements were performed using a computer controlled by potentiostat/ Galvanostat model PGZ 100 associated to “Volta-Master 4” software. A conventional three-electrode cell (100 cm³) thermoregulated glass cell was used (Tacussel Standard CEC/TH). The anodes were a square plate of BDD and SnO₂ electrodes with effective surface area of 1 cm² for each one, whereas the cathode was a platinum electrode, and the gap between electrodes was 0.5 cm. A saturated calomel electrode was used as a reference. Galvanostatic electrolysis was carried out with a volume of 75 cm³ aqueous solution of 5ppm de pyridazinium. The range of applied current was 10–80 mAcm⁻² and samples were taken, at predetermined intervals during the experiment, and submitted for analysis. All tests were performed at (25 ± 3) °C in magnetically stirred and aerated solutions. In all cases, sodium chloride was added to the electrolytic cell, at different concentrations. The chemical oxygen demand (COD) measurement during the processing permitted the evaluation of the kinetic of organic matter decay and the mineralization efficiency. COD was determined by dichromate method. The appropriate amount of sample was introduced into prepared digestion solution (0-1500 mg O₂.L⁻¹) containing potassium dichromate, sulfuric acid and mercuric sulfate and the mixture was then incubated for 2h at 150°C in COD reactor (WTW CR 3200 thermoreaktor, Germany). COD concentration was measured calorimetrically using AFNOR Method.

Results and Discussion

Effect of electrolyte concentration

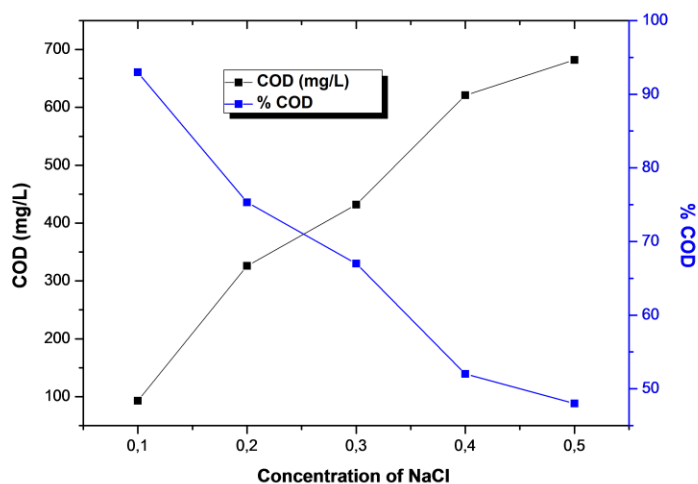


Figure 2 Effect of NaCl concentration on electrochemical degradation of at different time intervals (current density: 80 mA/cm², température: 25°C and pyridazinium concentration: 5ppm)

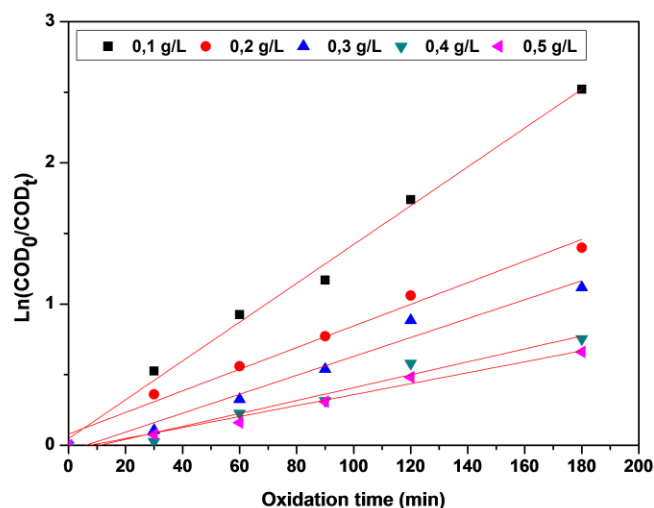


Figure 3 Pseudo first-order plot oxidation of pyridazinium, 25°C, 5 ppm at 80 mA/cm², pH=5.47 for different concentration of NaCl

It could be observed from Fig.2 that, when the concentration of NaCl is over than 0.1 g/L (0.2; 0.3; 0.4). The treatment had little effects. The NaCl concentration was more than enough to oxidize the pollutants in the water. In other hand we found as result that with 0.1g/L we have obtained 93% as COD removal that equal to 106 mg/L of COD (mg/L), after three hour of degradation [34-36]. As a complement we have been calculate kinetics reaction shown in Fig.3. It is shown to be linear to time at each concentration of NaCl. This means that the first order kinetics relative to pyridazinium is operative. The oxidation of pyridazinium solutions at different electrolyte concentrations followed first order with good correlations coefficient (0, 9929) for 0,1g/L during the oxidation process (180 min). The rate constants (k , min⁻¹) as follows:

$$k_{0,1} > k_{0,2} > k_{0,3} > k_{0,4} > k_{0,5}$$

The results showed that the increase in NaCl concentration until 0.5 g/L leads to increase in the oxidation rate of pyridazinium. The concentration of chloride plays an important role in the electrooxidation process via two ways; an increase in the concentration of the supporting electrolyte increases the hypochlorite ions and the cell conductivity. The former enhances the destruction of organics present in the wastewater and the latter can result in a rise of current density at the same voltage which provides more chance for the production of chlorine in the relatively higher current densities [31-32]. It is known that the oxygen evolution is a primary reaction at the anode surface in dilute chloride solutions. 0.1 g/L of NaCl was considered as optimum electrolyte concentration for further studies.

Effect of initial pyridazinium concentration

The influence of the initial pyridazinium concentration on oxidation process was studied at broad range of pyridazinium concentration (5–20 ppm) in the presence of 0.1 g/L NaCl as an electrolyte. Fig.4 shows that the oxidation decreased with increasing pyridazinium concentration, The COD removal decrease from 95% to 27% for 1, 20ppm respectively. The kinetics of disappearance of pyridazinium is represented in Fig.5. First order kinetic. The linear fit between the $\text{Ln}(\text{COD}_0/\text{COD}_t)$ and oxidation time can be approximated as first order kinetics. The parameters k and R (correlation coefficient) of oxidation process are shown in (Table 1). Considering the data in Table 1 reveals that the oxidation of pyridazinium is more functional with lower concentration of pyridazinium [33-34].

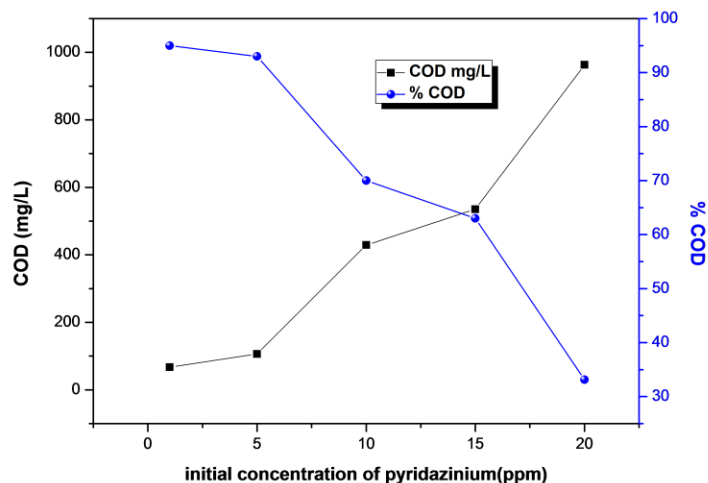


Figure 4 effect of initial concentration of pyridazinium (T: 25 °C, NaCl: 0.1 g/L and current density: 80 mA/cm²)

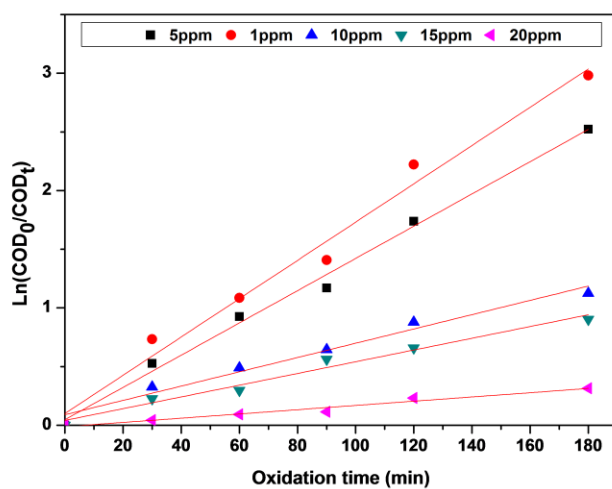


Figure 5 Pseudo first-order plot oxidation 25°C, 0.1g/L of NaCl at 80 mA/cm², pH=5,47 for different concentration of pyridazinium

Table 1 kinetic constant for first order and second order models of dye decolorization (T: 25 °C, NaCl: 0.1 g/L and current density: 80 mA/cm²)

Pyridazinium (ppm)	K (10 ⁻⁴ x min ⁻¹)	R ²
1	163	0.9847
5	137	0.9938
10	61	0.9755
15	50	0.9739
20	18	0.9677

Variation of the pH during the oxidation

The presence of a weak concentration of chloride ions allows to inhibit the water discharge into oxygen, and to favorise hydroxyl or chloride and oxychloride radicals, which are very powerful oxidants. It can be explain why until 0.1g/L of NaCl concentration the COD removal increases with NaCl concentration.

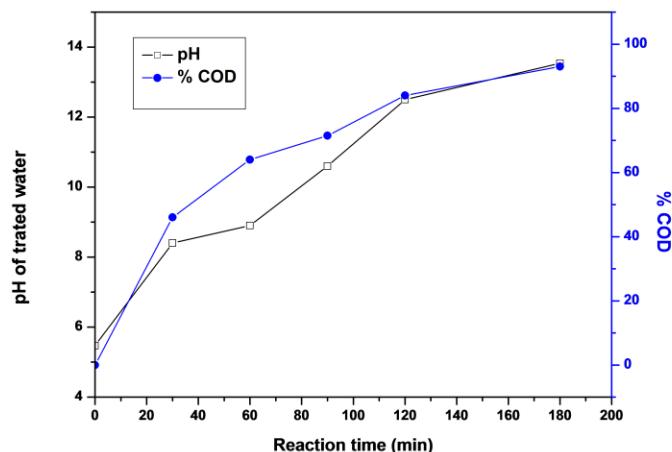


Figure 6 Variation of the pH during the oxidation time

Figure 6 shows that the variation of pH during the electrolysis is significantly increased. Finally the pH in all cases became strongly basic. It is obvious that the continuous addition of high levels of organic matter in the electrolytic cell resulted in the increase of pH. The electrolysis was more effective in terms of %COD reduction when the pH was in the basic rang, The solution pH also changed during the electrolysis process (**Figure 6**). The pH increased from the initial value of 5.47 to below 8.4 can be observed in first minutes as a consequence OH radicals formation, after 180 minutes of electrolyze the pyridazinium was nearly oxidized, the pH of solution approached 13,54 when the COD reduction was 92% after 3h of electrolysis. The increase in pH was caused by the formation of basic substances from the pyridazinium degradation [35].

Influence of applied current density

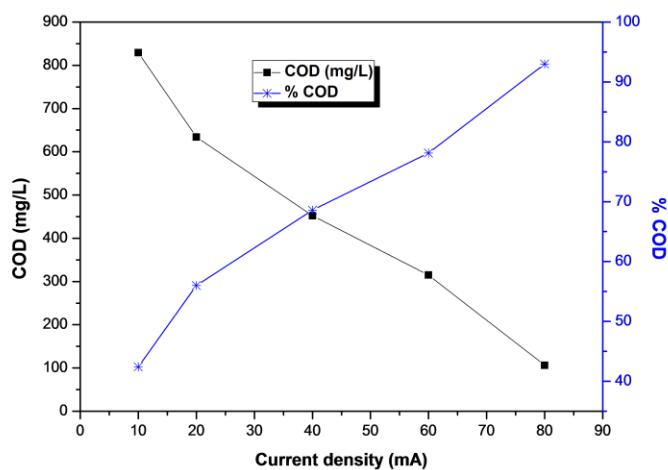


Figure 7 Influence of current density on oxidation of pyridazinium (T: 25 °C, NaCl: 0.1 g/L and pyridazinium: 5 ppm)

Figure 7 presents the influence of applied current density (10, 20, 40, 60 and 80 mA cm⁻²) on pyridazinium oxidation as a function of time for the BDD electrode. Higher COD removal was achieved for the pyridazinium solution (5ppm) in all cases. However, the oxidation time and COD removal rate depended mainly on the applied current density and on the nature of the material (**Figure 2**). Whilst the oxidation time decreased when the applied current density was raised, the elimination rate increased substantially. Although higher COD removal was obtained for BDD anode, the COD removal rate was 106mg/L. This behavior suggests that dye oxidation depends on the increasing of the applied current density, and that it could be carried out by both direct electro-oxidation and mediated oxidation (hydroxyl radicals) [36-39].

Conclusion

This study investigated the treatment of DWW in batch recirculation mode using EO process. BDD is the electrode used at the anode, The EO process is a feasible technology for the treatment of wastewater by high concentrations of COD, The treatment of domestic wastewater by electro-oxidation process was greatly affected by the operating conditions, such as initial concentration of pollutant, concentration of electrolyte support and current density applied. Using BDD at the anode with a current density imposed of 80 mA/cm², the removal COD recorded after 180 min of electrolysis time were 92%. Hence, the electrochemical oxidation process may be a promising technology that can be used as tertiary treatment to remove refractory organic compounds from wastewaters. However, it will be interesting to evaluate the efficiency and the capacity of the EO process to remove microorganisms from wastewater.

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