# **Electrochemical Treatment of Wastewater Industrial Cartons**

M. Errami<sup>1</sup>, R. Salghi<sup>1,\*</sup>, A. Zarrouk<sup>2</sup>, M. Zougagh<sup>3,4</sup>, H. Zarrok<sup>5</sup>, B. Hammouti<sup>2</sup>, S. S. Al-Deyab<sup>6</sup>

<sup>1</sup> Equipe de Génie de l'Environnement et de Biotechnologie, ENSA, Université Ibn Zohr, BP 1136, Agadir, Morocco.

<sup>2</sup> LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, BP 4808, Oujda, Morocco.

<sup>3</sup>Regional Institute for Applied Science Research, IRICA, E-13004 Ciudad Real, Spain

<sup>4</sup>Scientific and Technological Park of Albacete, E-02006 Albacete, Spain

<sup>5</sup> Laboratoire des procèdes de séparation, Faculté des Sciences, Kénitra, Morocco.

<sup>6</sup>Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University,

P.O. Box 2455, Riyadh 11451, Saudi Arabia.

<sup>\*</sup>E-mail: <u>r.salghi@uiz.ac.ma</u>

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In the work described here the technical and economic feasibilities of Advanced Oxidation Processes (AOPs) have been studied: Conductive-Diamond Electrochemical Oxidation, and SnO<sub>2</sub> anode with biological technical. The comparison was made by assessing the two technologies with real example wastewaters polluted with actual wastes industrial cartons in area of Agadir country. That industrial waste contains different types of organic compounds such as (starch, Paraffin's, glue, caustic soda, salt, lubricants, inks, and borax). All two technologies were able to treat the wastes, but very different results were obtained in terms of efficiency and mineralization. Only CDEO could achieve complete mineralization of the pollutants for all the wastes. However, the efficiencies were found to depend on the concentration of pollutant (mass transfer control of the oxidation rate). Results obtained in the oxidation with SnO<sub>2</sub> are lower than boron-doped diamond anodes at 60 mA/cm<sup>2</sup>. The value of COD varies between 2g / L and 3g / L, which correspond to a variation in the costs of the electrochemical oxidation of wastewaters of operation of the cell 945DH / days to 1500 DH / days. The efficiency of the electrochemical process was found to depend mainly on the pollutant concentration present in the waste and on the applied current density. The high efficiency of this technology can be explained in terms of the direct electro-oxidation at the BDD surface and the oxidation carried out by hydroxyl radicals and other electro-generated oxidants.

Keywords: Electro-oxidation; Boron doped diamond, Electro-generated oxidants

# **1. INTRODUCTION**

For the treatment of industrial wastewaters, the combination of chemical oxidation and biodegradation

is a reasonable approach [1,2]. Advanced oxidation technologies as the chemical oxidation step include the following processes applied in this work: (1) ozonation, (2) combination of ozonation with UV-irradiation or hydrogen peroxide (peroxon), (3) combination of hydrogen peroxide with UV irradiation, (4) Fenton's reagent ( $Fe^{2+}/H_2O_2$ ) and the photo-chemically enhanced Fenton process. The main reactant in these processes is the OH<sup>-</sup> radical whose electrochemical potential ( $E^0$ =+1.90V [3]) enables the oxidation of many substances. Biological treatment is suitable for some industrial wastewaters up to a maximum concentration of 140 mg. $l^{-1}$  [4], after which inhibition of the biological treatment process takes over. On the other hand, electrochemical oxidation is becoming a new alternative for industrial wastewater treatment and replacing the traditional processes, because many industrial processes produce toxic wastewaters, which are not easily biodegradable and requiring costly physical or physico-chemical pretreatment [5]. Many researchers had investigated the electrochemical oxidation of various types of wastewater including the phenolic wastewater [6-8]. During the electrochemical destruction of phenol, polymer products deposit on the electrodes as tars, forming a passivating film on the electrode [9, 10]. During the electrochemical conversion of industrial wastewater, an electrolyte is added to the medium to increase conductivity and in return current density. Various electrolytes such as Na<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and their mixtures were used in literature [6-7,11-12] but very few investigators [13-16] made use of NaCl mainly due to toxic intermediates produced such as mono, di and tri substituted chloro-phenols when utilized. In the recent years, electrochemical oxidation with boron-doped diamond (BDD) electrode appears as one of the most promising technology for the treatment of real and synthetic industrial wastewaters in lab and bench-scale plants due to its high efficiency to combust partially or completely organic pollutants [12-19]. The surface of this electrode allows producing large quantity of free hydroxyl radicals from water electrolysis that are well known to be very powerful oxidizing agents [13,18]. The main results are that this technology allows the almost complete mineralization of the organics contained in the wastes with very high current efficiencies. The oxidation mechanisms involved in this technology have also been characterized and include direct electro-degradation, hydroxyl radical mediated oxidation, and oxidation mediated by oxidants generated during the treatment from the salts contained in the waste. Comparison of the utility and treatment costs associated with different technologies is a subject of major importance. Recently, this electrolytic technology has been widely studied with both real [10-23]. The main results are that this technology allows the almost complete mineralization of the organics contained in the wastes with very high current efficiencies. For example, literature data concerning the cost associated with Fenton treatment are in the range 0.2-17.7 € m<sup>-3</sup>. This huge range does not mean that estimations are incorrect, but simply that very different assumptions are made in the cost analysis. The most important of which are equipment amortization cost, raw materials cost, energy cost and labour cost. Hence, in spite of the intense scientific effort carried out by several research groups to study the technical feasibility of a wide variety of treatment techniques, the lack of information on accurate cost estimation (at least under well-defined conditions) complicates any comparisons and, consequently, the choice of the Best Available Technology (BAT) to treat the wastewater generated in industrial processes is more difficult.

The current paper presents the study of a prospective electrochemical treatment system for industrial waste water cartons from CMCP in Big area of Agadir (Morocco) using a boron-doped diamond electrode (BDD).

# 2. EXPERIMENTAL METHODS

#### 2.1. Electrolytic system

Electrochemical measurements were performed using a computer controlled by Potentiostat/Galvanostat model PGZ 100 associated to "Volta-Master 4" software. A conventional three electrodes cell (100 cm<sup>3</sup>) thermo regulated glass cell was used (Tacussel Standard CEC/TH). The anode was a square plate of BDD electrode with effective surface area of 1 cm<sup>2</sup>, whereas the cathode was a platinum electrode, and the gap between electroles was 1.5 cm. A saturated calomel electrode (SCE) was used as a reference. Galvanostatic electrolysis was carried out with a volume of 75 cm<sup>3</sup> aqueous solution of initial COD<sub>0</sub> (2498 mg/L). The range of applied current density was 10 to 70 mA/cm<sup>2</sup> and samples were taken, at predetermined intervals during the experiment, and submitted for analysis. All tests have been performed at different temperature 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) is measured according to the standard methods for examination of wastewater [20]. The Chemical Oxygen Demand (COD) values were of analytical pure grade and used without further purification. The sodium chloride used was of analytical-reagent grade and was obtained from Aldrich (Spain).

#### 2.2. Waste water effluent

A local wastewater cartons CMCP (from a rug industry of cartons in Agadir (Morocco)) provided the cartons effluent, which was sampled at the entrance reservoir of the industry's biological treatment station. This effluent originates from the different waste water units, thus being a complex mixture of and additives whose exact composition is unknown and dependent on the production schedule. Nevertheless, which was characterized by an intense dark yellow color and the presence of a high amount of fibers. Thus, before the electrochemical degradation experiments, the effluent was filtered two times with conventional filtering paper. Furthermore, due to the low conductivity of the effluent, NaClwas added until a 0 - 3 g. L<sup>-1</sup> concentration was reached.

## **3. RESULTS AND DISCUSSION**

### 3.1. Effect of supporting electrolytes

#### 3.1.1. Removal of the chemical oxygen demand

The investigation of the mediator concentration effect has been performed in the range 0-3g/L for NaCl. The presence of chloride ions in surface and groundwater is the principal motivation for

investigating the effect of chloride on electrochemical oxidation of wastewater. During electrolysis, chloride ions are converted into chlorine and subsequently to hypochlorite ions in neutral or slightly alkaline pH. Figure 1 shows the variation of pH for wastewater cartons of electrolysis at 60 mA aunder different concentration of NaCl. Finally the pH in all cases became strong acidic (pH = 4, 2) to basic (pH = 8,9).



Figure 1. Variation of pH for wastewater cartons of electrolysis at 60 mA and 25° C, under different concentration NaCl.

The performance of the BDD anode in the waste effluent degradation was analyzed through the extent of decolorization and COD removal of this waste effluent. In order to compare these performances, the same total value of electric charge per unit volume of the electrolyzed effluent (Qap) was applied in all the experiments (5 kAh.m<sup>-3</sup>). Absorbance (A) were done on 2.5 mL samples of electrolyzed effluent, collected after each 20 min of electro-oxidation times. The waste effluent absorbance was determined from 190 nm to 820 nm in a UV–vis spectrophotometer (UV-1700 Pharmaspec, Shimadzou). After the absorbance determination, the COD of each sample was determined.

The Fig. 2 shown effect of NaCl concentration on the electrooxidation of waste water, carried out at 60mA/cm<sup>2</sup>. We observed that the application of electrolysis in this compound have the ability to reduce considerably the COD [11-14]. For example, 2g/L mass NaCl and 1g/L% NaCl the achieved reduction was 86% and 47% respectively, while for without NaCl was 74%. The presence of a weak concentration of chloride ions allows to inhibit the water discharge into oxygen, and to favorise hydroxyl or chloride and oxycloride radicals, which are very powerful oxidants. It can be explain why until 2 g/L of NaCl concentration the COD removal increases with NaCl concentration.



**Figure 2.** Influence of the concentration NaCl on the trends of %COD electrolysis of waste water cartons ( $COD_0 = 2498 \text{ mgL}^{-1}$ ) using a 1cm<sup>2</sup> BDD anode at T=25°C.

Increasing the chloride concentration more than 3 g/L cause a "potentiostatic buffering" by the chlorine red/ox system and consequently a decrease of the anode potential. Another possibility is the presence of competitive reactions, in particular oxygen and chloride evolution due to recombination of radicals that becomes bigger with the increasing NaCl concentration [12-16].

The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of organic compound on the electrode or indirect via some mediators like chlorinated species or other radicals [11-15]. Since, some oxidant compounds that are produced during oxidation of water (like  $O_2$ ,  $O_3$  or hydroxyl radical) or oxidation of chlorine ions following eq (2) to (4):

Cl- Cl'ads +	e e	(2)
C1- + C1. ads	• Cl <sub>2</sub> + e <sup>-</sup>	(3)
$Cl_2 + H_2O \longrightarrow$	$HC1O + H^+ + C1^-$	(4)

As cited in reference [22]. That at pH higher than 4.5 the complete dismutation of  $Cl_2$  into HClO and  $Cl^-$  is occurred.

The balance of all these phenomena results that there is an optimum of NaCl concentration which is 2 g/L mass of NaCl for the degradation of the waste water cartons.

Fig. 3 illustrates the evolution of concentration COD for oxidation of waste water cartons at different concentration of NaCl as a function of the electrolysis time. The heterogeneous apparent kinetic constants of this waste (kapp) varies from  $1,88 \times 10^{-3}$  min<sup>-1</sup> for without NaCl,  $6.12 \times 10^{-3}$  min<sup>-1</sup> for 3 g/L NaCl,  $7.86 \times 10^{-3}$  min<sup>-1</sup> for 1 g/L NaCl and  $1.53 \times 10^{-2}$  min<sup>-1</sup> for 2 g/L NaCl.



**Figure 3.** Direct electrooxidation at BDD anode: effect of NaCl concentration on the COD (2498mg.L<sup>-1</sup> waste water cartons solution, 60 mA.cm<sup>-2</sup>, pH= 4,3, and T=( $25\pm3$ )°C).

3.1.2. Decolorization of the waste water cartons effluent



Figure 4. Relative absorbance (at 400 nm),  $%A_{rel}$ , as a function of the Qap, under different concentration of NaCl, for the electrochemical degradation of the waste water cartons effluent with the BDD anode.

Fig. 4 show the variation of % A as a function of  $Q_{ap}$  for the different electrolyses carried out with the BDD anode, at 25°C. Clearly, the best conditions for color removal are attained at the 2g/L of electrolyte supporting, when the amount of oxygen evolved at the anode is less significant; hence, a higher fraction of  $Q_{ap}$  is related to the decolorization of the cartons effluent. Under these conditions, % A<sub>rel</sub> becomes less than 30% for a minimum value of concentration of NaCl, this value is about 5 A h, at 25 °C.

# 3.2. Effect of current density

#### 3.2.1. Decolorization of the cartons effluent

Applied current is an important factor affecting the electrolysis kinetics and process economics. Fig. 5 shows the variation of % A as a function of electrooxidation times for the different electrolyses carried out with the BDD anode, at  $(25 \pm 3)$  °C and 2 g/L (NaCl).



Figure 5. Relative absorbance (at 400 nm), %  $A_{rel}$ , as a function of the electrooxidation times, under different current density, for the electrochemical degradation of the waste water cartons effluent with the BDD anode.

Clearly, the best conditions for color removal are attained at the high current densities, when the amount of oxygen evolved at the anode is high significant; hence, a higher fraction of  $Q_{ap}$  is related

conditions % A thecomes less than 70 % f

to the decolorization of the cartons effluent. Under these conditions, %  $A_{rel}$  becomes less than 70 % for a minimum value of  $Q_{ap}$  of about 3 Ah/m<sup>-3</sup>, at 25 °C. On the other hand, for any current density, the higher current density enhances the decolorization rate due to the increased oxidation power of the hydroxyl radicals. Thus, the condition  $i = 60 \text{ mA.cm}^{-2}$  at 2 g/L of NaCl is considered the best one for the decolorization of the effluent due to the lower energy consumption and higher current efficiency involved, as it will be discussed below.

#### 3.2.2. Removal of the chemical oxygen demand

The effect of applied current on the electrochemical process was demonstrated in several studies [19-20]. In Figure 7 the % COD reduction for waste water cartons is presented under different current densities inputs (2g/L of NaCl). Similarly to the decolorization, the best conditions for the COD removal were the higher current density (50 mA cm<sup>-2</sup>) and 2g/L (NaCl) a 97% COD decrease was reached after a value of  $Q_{ap}$  of only 15 kA h m<sup>-3</sup>, and total removal was attained for a  $Q_{ap}$  value of 16 kA h m<sup>-3</sup>. These results are in agreement with the decolorization ones. These studies concluded that applied current increases the rate of electrochemical oxidation process.

The COD of waste cartons was observed to fall with pseudo first-order kinetics (Fig.6), on all the surface studied. This is related to the dependence of the rate of oxidation on the rate of formation of the oxidising species at the electrode surface [15-20].



**Figure 6.** Influence of the applied current density on the trends of % COD electrolysis of cartons effluent ( $COD_0 = 1344 \text{ mg.L}^{-1}$ ) using a 1cm<sup>2</sup> BDD anode. 1% (NaCl) and T=25°C.

The pseudo first-order constant of waste water cartons (k) varies from  $(5,14\times10^{-3})$  min<sup>-1</sup> for 10 mA/cm<sup>2</sup>; (7, 36×10<sup>-3</sup>) min<sup>-1</sup> for 20 mA/cm<sup>2</sup>; (1.11×10<sup>-2</sup>) min<sup>-1</sup> for mA/cm<sup>2</sup> to (1,76×10<sup>-2</sup>) min<sup>-1</sup> for 60 mA/cm<sup>2</sup>. This is exemplified in Fig. 7 where the pseudo first-order plot is presented. From these results it was calculated that the best applied current is 60 mA/cm<sup>2</sup>.



**Figure 7**. Pseudo first-order plot oxidation of waste water cartons 2498 mg/L in 2g/L NaCl at 25°C under different current inputs.

# **4. CONCLUSION**

The results of an investigation of the electrochemical degradation of a real cartons effluent using an BDD anode have been presented, in the absence and presence of chloride ions, for the system's optimized hydrodynamic conditions. The best conditions were attained applying a current density of 60 mA cm<sup>-2</sup>, at 25 °C, with (2 g/L) NaCl addition, when the electrochemical process is under charge transfer control and the BDD anode is stable. The rate of decolorization of the real cartons effluent was increased in the presence of chloride ions (2 g L<sup>-1</sup> NaCl). Thus, using the BDD anode the relative absorbance of the effluent could be reduced to less than 70% using an applied electric charge per unit volume of the electrolyzed effluent of only about 5 kA h m<sup>-3</sup>. This higher decolorization rate has been accounted for by the greater ability of active chlorine to degrade the organic compound of the cartons present in the effluent. On the other hand, the COD removal rate was increased when NaCl was added to the real waste water cartons effluent. Nevertheless, practically total

COD removal was attained with the BDD anode using an applied electric charge per unit volume of the electrolyzed effluent of only 16 kA h m<sup>-3</sup>, with an current density of about 60 mA/cm<sup>2</sup>. This result, which has been accounted for by the high oxidation power of the hydroxyl radicals electrogenerated at the surface of the BDD anode, allows to conclude that anode could be an excellent option for the remediation of waste effluents, specially if its cost is diminished. Finally, if one's goal is simply the decolorization of a that effluent, and especially if one takes into account the cost of BDD anodes and the possible instability of diamond films in the presence of chloride ions.

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