

## RESEARCH PAPER

# Optimizing Electro-oxidation, Electrocoagulation and Electro-Fenton processes for Treating Model Pesticide Wastewater containing Bromuconazole

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### ABSTRACT:

In this work the removal efficiency of Bromuconazole and chemical oxygen demand (COD) from aqueous solution using different electrochemical processes (electro-oxidation process (EOP), electrocoagulation process (ECP) and electro-Fenton process (EFP) were investigated. All experiments were achieved at the natural pH of solution. The effects of some parameters such as current density and H<sub>2</sub>O<sub>2</sub> concentration on COD and pesticide removal efficiency have been carried out at an initial pH of 8.45, current density 5,10,15,20 mA/cm<sup>2</sup>, an initial pesticide concentration of 300 mg/L, 5mM Na<sub>2</sub>SO<sub>4</sub> support electrolyte and temperature of 30°C. The COD decrease at the end of 80 minutes of treatment from 1200 to 167.52 mg/L by EOP, to 248.26 mg/L by ECP, and to 237.94 mg/L by EFP. Results showed that a high COD reduction was obtained by EOP (85.59%), followed by EFP (80.48%) and electrocoagulation at (79.51 %) with a constant current density of 20, 20, 15 mA/cm<sup>2</sup> respectively. The removal of bromuconazole pesticide exhibited a pseudo-second-order reaction with rate constant 0.0009 mg<sup>-1</sup>Lmin<sup>-1</sup>. Moreover, energy consumption, the cost of degradation and sludge formation were also determined.

### KEY WORDS:

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### INTRODUCTION:

During the last years, an increasing concentration on environmental protection and sustainability led to more firm laws that aim to minimizing rate and levels of outflow pollution. On the other hand, research and development has grown into more functional alternative technologies to enhance wastewater treatment processes, without making additional damage to environmental. Industrial wastewater is complex and always consists of inorganic and organic compounds, that make a process of treatments difficult due to the lack of a comprehensive treatment strategy. The water polluted with organic compounds, a best economically feasible alternative process is biological oxidation treatment, although some of toxic molecules do not degrade adequately by such treatment process. (Panizza and Cerisola, 2009).

Electrochemical methods represent an environmentally and economically applicable alternative, in which major reagent is electron, that is efficient, versatile, clean and productive in relation to its cost. (Kapalka, et al., 2010 and Andrade et al.,2007). The electrochemical treatment processes have been greatly used for treatment of wastewater contaminated with pesticides, pharmaceuticals and dyes (Rajeshwar et al.,1994, Silva et al., 2011 and Ciríaco et al., 2009). It has been focused and concentrated on pesticides compounds due to its harmful effect on the human health and the environment (Zaleska and Hupka, 1999 & Wang et al.,2007). Pesticide compounds toxic and harmful to non-target living organisms including humans in which inter the body within the food chain (Chiron *et al.*, 2000). Large number of pesticide compounds are non-

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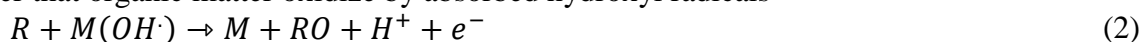
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biodegradable due to its molecular structure that have stable strong bonds. Natural water pollution with pesticide has become a widespread issue. Wastewater originates from pesticide producing industries during cleaning actions after batch operation of the synthesis operation. It usually includes toxic pesticide residues and organics which threatens the quality of ground and surface water (Wang et al.,2007). Wastewater from pesticide manufacturing plants and agricultural industries were evaluated to have pesticide contamination scales of 500 mg/L (Menegola et al., 2005). Among this such class of contaminants, Bromuconazole pesticide take our attention due to their high photochemical stability; its resist to photolysis and hydrolysis is not predicable to be a considerable process in the breakdown of pesticide bromuconazole in aquatic systems.

Bromuconazole compound belongs to the set of triazole fungicides. It is applied as a broad-spectrum fungicide, with curative and preventative action, in order to control the diseases caused by deuteromycetes, basidiomycetes, and ascomycetes (EPA, 2002). Its registered toxicity data include the acute oral LD<sub>50</sub> in rats (365mg/kg) with data

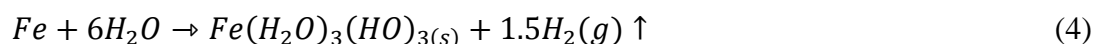
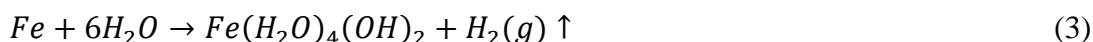


After that organic matter oxidize by absorbed hydroxyl radicals



In which RO indicate oxidizing organic matter and may be further oxidizing by the hydroxyl radicals ( $\cdot OH$ ) formed from water electrolysis.

### 1.2 Theory of EC Process



### 1.3 Theory of EF Process

In EFP, pollutants are break down by the presence of Fenton's reagent in the media together with anodic oxidation at surface of anode



showing that rat's exposure to Bromuconazole produced lesions in all parenchymatous organs including hepatoma and later increase in liver weight (Shchepetkin *et al.*, 2003). Toxicity caused by bromuconazole can be enhance the production of reactive oxygen species in addition to enhancing lipid peroxidation endogenous and antioxidants depression (Cheng et al., 2007).

The using of electrochemical treatment methods for removal of pesticides are of concern. ECP, EOP and EFP are the excellent ways to solve environmental issue produced by the outflow of these effluents. The present work involves removal of Bromuconazole from solutions prepared from the commercially available pesticide by ECP, EOP and EFP. The removal of pesticides by such methods was evaluated with impact of initial pH.

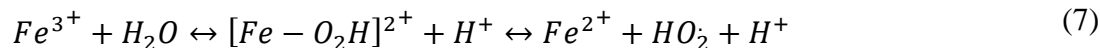
### 1.1 Theory of EO Process

The toxic pollutants are break down by oxidant such as O<sub>3</sub>, ClO<sub>2</sub>, OH, Cl<sub>2</sub>, O, ClOH, H<sub>2</sub>O<sub>2</sub> etc., which are formed from anodic oxidation within the electrolysis (Babuponnusami and Muthukumar., 2012).

ECP is based on in-situ production of coagulants, together, there is a production of hydrogen on a cathode that allows removal of pollutant by sedimentation or floatation. Overall chemical reactions are:

(Greenberg and Clesceri,1992). hydroxyl radical is then generated in the media by a traditional Fenton's reaction between ferrous ion and hydrogen peroxide (Eq. 5):

Renovation of  $Fe^{2+}$  may also be done by the oxidation of the organics with  $H_2O_2$  or by reaction with hydroperoxyl radical ( $HO_2^\bullet$ ) as shown in reaction below:



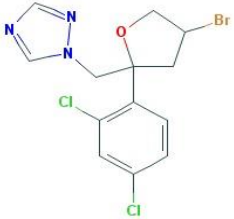
## 2. Materials and methods

### 2.1 Chemicals

Pesticide used in present work was Bromuconazole. Bromuconazole solutions were prepared from the commercially found pesticide solution having a Bromuconazole concentration of 480 g/L. This concentration is similar to that applied by farmers. The property of a

Bromuconazole is shown at Table 1. All solutions were prepared by distilled water. Potassium dichromate ( $K_2Cr_2O_7$ ) Standard solutions, sulfuric acid ( $H_2SO_4$ ) reagent with silver sulphate ( $Ag_2SO_4$ ), has been prepared in order to measure the COD. The COD was determined by a closed reflux colorimetric technique (Chen et al., 2000). All chemicals used were reagent grade.

Table 1. Structure of pesticide present in sample

Name	Structure
Bromuconazole $C_{13}H_{12}BrCl_2N_3O$	
Molecular weight (g/mol)	377.063

### 2.2 Equipment's and Procedures

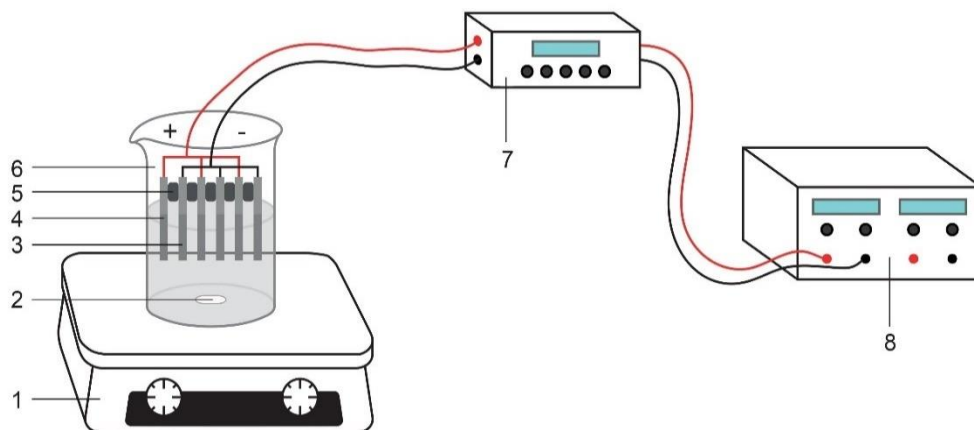
The electrochemical cell consists of a 600 mL glass reactor. Experiments were conducted with 400 mL of the sample and 5 mM of  $Na_2SO_4$  was used as supporting electrolyte. Electrodes were connected to a digital DC power supply Statron 3262.3 model (0-4 A and 0-300 V). The stable stirring speed of 300 rpm with magnetic stirrer was applied along the experiment process. The electrochemical treatment was applied at room temperature and atmospheric pressure. Duration of electrolysis was 80 min. the samples has been drawn at regular intervals of time in order to evaluate the reduction efficiency in COD. All

experiments were repeated duplicate. A constant current density of 5, 10 15, and 20  $mA/cm^2$  has been applied in all the three electrode systems for comparison.

### 2.3 Boron doped diamond electrodes

#### electrode set up

Electrolysis was performed with DC power supplies using two BDD electrodes (one anode and one cathode) with the length of 5 cm and width of 3.7 cm and the distance between two electrodes of 0.5cm. The supporting electrolyte ( $Na_2SO_4$ ) of 5mM and 10mM was added. The samples were withdrawn at a regular time interval of 20 min for 80 min. laboratory scale electrochemical reactor shown in Figure (1).



**Figure 1** Schematic of experimental electrocoagulation system (1. thermostatic magnetic stirrer, 2. magnet, 3. cathode, 4. anode, 5. Rubber Insulator, 6. beaker, 7. polarity changer, 8. DC power supply)

## 2.4 Analytical techniques

During experiments, samples were collected and instantly measured without using any filter. Chemical oxygen demand data were obtained with a procedure shown by TS2789 standard (water

quality-Determination of COD). The samples were titrated with ferric acid ammonium sulphate (FAS) which was previously standardized to determine the amount of potassium dichromate consumed (Yavuz, 2007).

COD removal percentages of obtained samples were calculated as follows:

$$\text{COD removal \%} = \frac{(\text{COD}_o - \text{COD}_t)}{\text{COD}_o} * 100$$

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Where  $\text{COD}_o$  (initial) and  $\text{COD}_t$  (any time) of the pesticide treatment samples and calculated in mg/L.

Remaining pollutants of bromuconazole pesticide were evaluated with the UV-visible spectrophotometer at  $\lambda_{\text{max}} = 230$ .

## 3. Results and Discussion

Despite the used electrochemical processes have their disadvantages and advantages, existing paper aims to understand the extent of pesticide removal in wastewater. Comparison of the methods (EFP, EOP, and ECP) at certain conditions of a current density and time duration aids the identify a point at which best removal of pesticide could be done.

### 3.1 COD removal capacity

It has been noticed that an initial pH of wastewater solution is remarkable operating factor effecting the electrochemical treatment performance (Emanjomeh and Sivakuma, 2009). In order to evaluate its effect during the treatment process, the sample pH was kept at its normal range.

In the case of Electrocoagulation, the higher COD reduction efficiency noted at the end of 80 min was 79.51 %. The current density was  $20 \text{ mA/cm}^2$  and pH 7.79. This is may be due to the fact that the  $\text{Fe}(\text{aq})$  ions formation and then their oxidation to  $\text{Fe}^{3+}(\text{aq})$  led to precipitation of  $\text{Fe}(\text{OH})_3$ ; At higher pH the oxidation by oxygen became higher. During EOP, the generated hydroxide reacts with organic pollutants found in the samples (Yavuz, 2007). At the end of 80 min of

experiment, higher COD removal was 85.59% with a current density of 15 mA/cm<sup>2</sup> and pH 5.32

It may be summarized that at an acidic pH, chlorine is found in the form of a Hypochlorous acid (HOCl) which demonstrate the oxidation process. During EFP, the removal efficiency of COD was 80.48% at the end of 80 min. current density was 15 mA/cm<sup>2</sup> and pH 7.84. When the applied current density is high, COD removal is directly proportional to the

Hydrogen peroxide concentration (Yavuz, 2007). low COD removal was seen during other conditions for all of studied methods.

Although, an optimal pH obtained during treatment process was 7.84 because of organics compound or its intermediate products reactions that might interact with iron species that led to the formation of iron complexes which assist catalytic cycles of iron. The highest COD removal efficiency was determined as shown in the (Fig. 1).

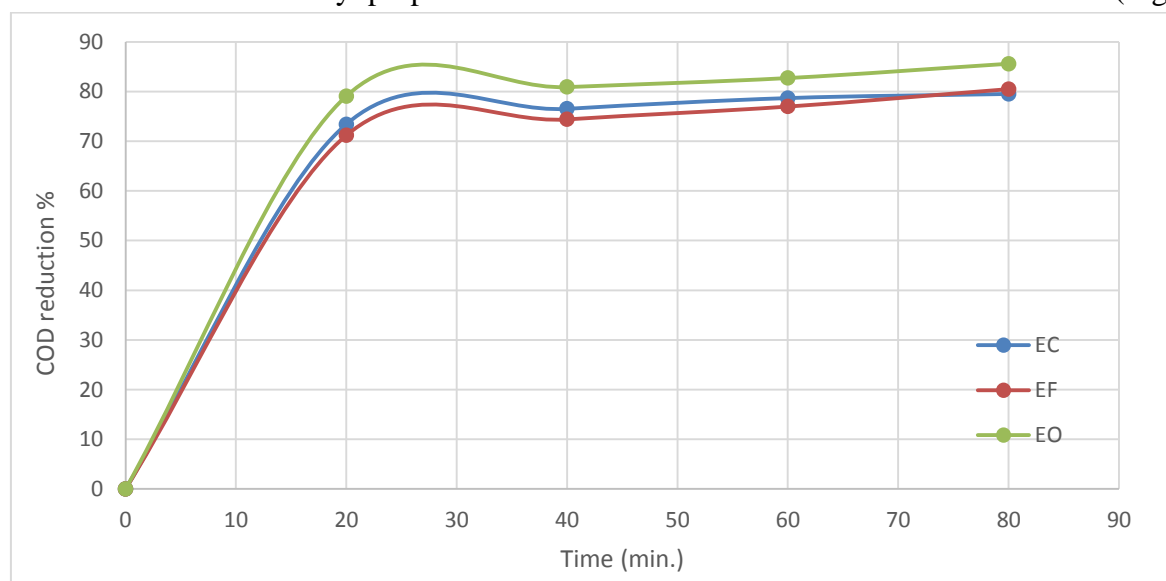


Fig.1. Variation of COD removal efficiency for electrochemical processes (Co=300mg/l, 5mM Na<sub>2</sub>SO<sub>4</sub>, natural pH, i=20mA/cm<sup>2</sup> for EC and 15 mA/cm<sup>2</sup> for EF, EO).

### 3.2 Energy consumption

During electrochemical treatment process, an important economic parameter is energy

$$\text{Energy Consumption (E)} = \frac{I \cdot V \cdot t}{\text{Vol} \cdot 1000} \quad (9)$$

then I, V and t stand for electrical current intensity (A), average voltage of the EC system (v), and reaction time (h), respectively.

From the data of ECP, higher COD reduction percentage of about 79.51% was observed with an energy consumption of about 170.12 kWh/m<sup>3</sup> while, in the EFP and EOP case, the higher COD reduction was 80.48 and 85.59 % with the energy consumption of 96.73 and 54.09 kWh/m<sup>3</sup> respectively. EOP energy consumption is lower than that of the EFP. EFP

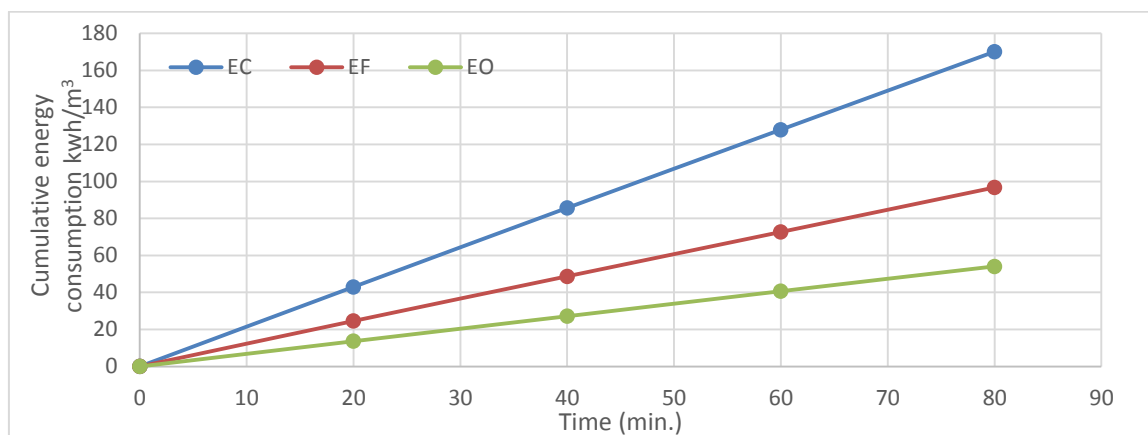
consumption (kWh/m<sup>3</sup>) (Eslami *et al.*, 2013). This parameter is calculated from the bellow equation:

has slightly lower percentage of COD removal (Fig.2) because of higher removal efficiency of BDD.

An experimental result showed that among the used treatment processes, EOP is the best due to high percentage of COD removal and also low energy consumption. Energy consumptions and COD removal efficiency are shown in Table 2.

Table 2. Selected results obtained for degradation of pesticide samples using three different processes

Process	Applied current (mA/cm <sup>2</sup> )	Electrolysis Time (min)	COD removal (%)	Energy Consumption (KWh/m <sup>3</sup> )
Electrooxidation	15	80	85.59	54.09
Electrocoagulation	20	80	79.51	170.12
Electro-Fenton	15	80	80.48	96.73

Fig.2.Variation in energy consumption of different electrochemical processes. (Co=300mg/l, 5mM Na<sub>2</sub>SO<sub>4</sub>, natural pH, i= 20mA/cm<sup>2</sup> for EC and 15 mA/cm<sup>2</sup> for EF, EO)

### 3.3 Energy Cost

The cost of energy (dollar/m<sup>3</sup>) for pesticide removal of each treatment process was

calculated by the following below equation:

$$\text{cumulative energy consumption} \frac{\text{KWh}}{\text{m}^3} * \text{Unit price} \left( \frac{\text{dollar}}{\text{KWh}} \right) \quad (10)$$

Table 3 summarizes energy costs of the pesticide's degradation by different electrochemical treatment processes. within EF, 80.48% COD reduction was carried out with an energy cost of 7.22 dollar/m<sup>3</sup> at 80 min. The EO

has less energy cost, 3.72 dollars/m<sup>3</sup>, and a maximum COD reduction efficiency of 85.59 %. Among these used three treatment processes, ECP has the maximum energy cost (11.71 dollars/m<sup>3</sup>) with reduction efficiency (79.51%).

Table 3. Degradation cost of pesticide for different electrochemical processes

Process	Applied current (A)	Potential different (V)	Cumulative energy consumption KWh / m <sup>3</sup>	Unit price (dollar/kWh)	Energy cost (dollar /m <sup>3</sup> )
EO	1.24	13.0	54.09	0.07	3.72
EC	1.66	30.5	170.12	0.07	11.71
EF	1.24	23.3	96.73	0.07	7.22

### 3.4 Sludge formation

In the ECP and EFP, dissolved ions of ferrous formed at the anode change to ferric ions. there is a fact that ferric ions ( $\text{Fe}^{3+}$ ) are a coagulation material and produce  $\text{Fe}(\text{OH})_3$  contained sludge.

In EC, amount of sludge increased from 2.25 to 2.94 g per 400 ml bromuconazole wastewater by rising the current density from  $5\text{mA}/\text{cm}^2$  to  $20\text{mA}/\text{cm}^2$  within 5mM supporting electrolyte. Flock formations in EC processes became visible after the 3 min. It was investigated that the amount of sludge settled increased directly with the increased of applied electrical power and reaction duration. So, the colour of the sludge was green. This is because of Fe(II) ions settling as  $\text{Fe}(\text{OH})_2$ . In EFP the amount of sludge at the end of 20min of experiments for best removal efficiency is 2.94 g per 400 ml wastewater by increasing the current density in the same manner as EC within 5mM supporting electrolyte. The colour of the settled sludge was brown. In EFP the mineralization of some carbons to carbon dioxide occur, so finally less sludge formed in compare to that formed by ECP. there is a considerable advantage of EOP in terms of sludge, this process does not produce sludge since the hydroxyl radicals formed on anode's surface (Yavuz, 2007).

### 4. Conclusion

The feasibility of electrochemical processes for Bromuconazole pre-treatment are shown, which include EOP, ECP, EFP processes. The effects of parameters such as current density, electrolyte type, and  $\text{H}_2\text{O}_2$  concentration were investigated on COD reduction and removal efficiency of bromuconazole pesticide.

It was seen that these variables remarkably affected Bromuconazole removal efficiency. The obtained Results in the EOP treatment at pH 5.32, indicates a noticeable decrease in COD from 1192.74 to 167.52 mg/L. The EFP treatment gives noticeable removal percentages of COD. Up to 80.48 %, COD lowering was occurred at pH 7.84 with average energy consumption ( $96.73\text{ kWh}/\text{m}^3$ ) and moderate energy cost ( $7.22\text{ dollar}/\text{m}^3$ ). within ECP, the highest COD removal efficiency of 79.51 % was noticed at pH 7.79 with high energy consumption of ( $170.12\text{ kWh}/\text{m}^3$ ) and high energy cost ( $11.71\text{ dollars}/\text{m}^3$ ).

Overall EFP and EOP showed best COD removal efficiency. So EOP is suggested for the treatment of wastewater polluted with pesticide in terms of COD reduction, cost of energy, and energy consumption. The treatment processes must be directly followed by a biological treatment process in order to make it cost-effective and to promote the performance.

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