RESEARCH PAPER

Removal of Bentazone Pesticide from Aqueous Solutions by Electro-oxidation Method

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A B S T R A C T:
  The kinetics of the electro-oxidation degradation of prepared aqueous solutions containing bentazone as a model compound of the thiadiazine group of pesticides was studied in the lab. The oxidation process was conducted under galvanostatic polarization in natural model media using boron-doped diamond (BDD) cathode and anode. Chemical oxygen demand (COD) estimation along the electro-oxidation treatment processing allowed the assessment of kinetic of organic compounds decay as well as the instantaneous current efficiency. The obtained data reflected that the degradation of bentazone pesticide is significantly dependent on initial amount of bentazone pesticide, current density and electrolytes concentration. COD removal follows a pseudo first-order kinetic and the electro-oxidation process was under the control of mass transport within the range studied, regardless the conditions of experimental. The COD removal rate increases with applied current density until 20 mA/cm^2 and decreases for higher values. Two different concentrations supporting electrolyte (5mM, 10mM) were used. The rate of degradation increased significantly with increasing electrolyte concentration. The best obtained conditions for COD removal efficiency on the BDD electrode to degrade bentazone solutions (COD= 91.18 %) include operating at 20 mA/cm^2 and 10 mM Na^2SO^4 as supporting electrolyte. This arrangement and condition allow to approximately complete degradation of bentazone in just 80 min. A decrease in the relative toxicity index value along the electro-oxidation indicate toxic compounds disappearance. The initial toxicity EC50 (5 min) and (15min) were decrease by 81% and 94%

1.INTRODUCTION:

  The conservation of freshwater resources has become a major concern for many countries around the world, and environment protection is an economic and political issue. Among the major sources of water pollution are organic pollutants, particularly pesticides and plant protection products used by farmers to increase crop yields. The widespread use of pesticides in agriculture, as well as excessive pesticide storage and disposal, a re major sources of pollution in rivers, ground wat er, reservoirs, rainwater, soil, and air.

  Pesticides can be removed from water using a variety of advanced technologies. Among these technologies, electrochemical processes are the most recent methods for pesticide degradation. These approaches are safe for the environment and do not generate new radioactive waste. (Kapałka, et al., 2010 and Andrade et al., 2007).
  In electro-oxidation process, the refractory compounds oxidation occurs at very high overpotential, choice of anode material is the most important factor. Electrochemical oxidation with a Boron-Doped Diamond (BDD) anode is well known as a promising treatment technique for the removal of available organic compounds. (Othman, M.A. 2018). Indeed, the high oxidation performance of the BDD by electro generation of

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hydroxyl radical (• OH) from water discharge (Eq. 1).
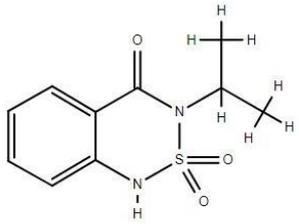
M+H2O-----M(OH.)+H+e   (1)
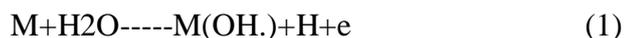
The hydroxyl radicals on the BDD anode are quasi-free on the surface and can react massively with organics close to the anode (Mcbeath et al., 2000). The aim of the current work is to investigate the effect of electrochemical oxidation on bentazone removal in model solutions. Measurements of global parameters such as total organic carbon and chemical oxygen demand have been used to estimate the rate of mineralization. The effect of operating variables such as current density, type of electrolytes on the efficiency of COD and bentazone removal was investigated.

2. EXPERIMENTAL

2.1 Chemicals

All of the solutions in this study were made in the lab as a model solution. Where a concentration of 480g/L of a commercially available bentazone pesticide was chosen for the subsequent works, and deionized water is utilized to prepare the model solution. Bearing in mind that this concentration is identical to what farmers use in agricultural fields. The properties and structural of bentazone is given in table 1. To measure the chemical oxygen demand, sulfuric acid (H_2SO_4) reagent, standard solutions of potassium dichromate ($K_2Cr_2O_7$), and silver sulphate (Ag_2SO_4) were prepared. The value of COD reduction was evaluated using a closed reflux colorimetric method [16]. All chemicals used were reagent grade.

Table 1. Chemical structure of bentazone

Name	Structure
Bentazone Molecular Formula: $C_{10}H_{12}N_2O_3S$	
Molecular weight (g/mol)	240.28 g/mol

2.2 Apparatus and Procedures

In this procedure, an electrochemical cell consists of a 600 mL reactor, and 400 mL of the sample was used as is during the electrooxidation treatment, with 5.0 and 10.0 mM of Na2SO4 added as a supporting electrolyte. The BDD electrodes were connected to a digital power supply Sarton 3262.3 model (0-300 V and 0-4 A). During the experiment, a magnetic stirrer was used to maintain a steady stirring speed of 300 rpm. The electrochemical oxidation reactions were carried out at atmospheric pressure and room temperature and the duration of electro-oxidation process was 80 min. To estimate the COD reduction efficiency, samples were taken at regular intervals. All the experiments were performed in duplicate. A constant current density of 5, 10 15, and 20 mA/cm2 were applied in all experiments.

2.3 Boron doped diamond electrodes set up

The boron-doped diamond electrode was provided by CSEM. Two BDD electrodes were used in electrolysis with DC power supplies (an anode and cathode) with the width of 3.7 cm, length of 5 cm and the distance between two electrodes as 0.5 cm. The supporting electrolyte (Na2SO4) was employed at 5.0 mM and 10.0 mM concentrations. Along the experimental period of 80-minute, the samples were taken at 20-minute intervals for analysis.

2.4 Analytical techniques

Materials were collected and measured without any filtration throughout the experiments. Chemical oxygen demand data were evaluated using the TS2789 (water quality-Determination of COD) standard All samples titrated with ferric acid ammonium sulphate (FAS) which was standardized before each measurement to decide how much potassium dichromate was consumed.

COD removal percentages of taken samples were calculated as follows:

$$COD\ removal = \frac{(COD_o - COD_t)}{COD_o} * 100 \qquad (1)$$

Where CODo indicate the initial concentration and CODt indicate the concentration at given time

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of the pesticide removal and treatment process and calculated in mg/L.

Remaining pollutants of bentazone concentration were measured with the UV-visible spectrophotometer at λmax= 230.

3. Results and Discussion

Despite the fact that the electro-oxidation approach has its own set of advantages and limitations, the current study seeks to determine the level of pesticide removal in wastewater using this method. Several variables in this approach were optimized, including current densities, time duration, support electrolyte concentration, and energy consumption.

3.1 COD removal capacity

The initial pH of the model solution effluent has been found to be an essential element determining the electrochemical process performance (Lepki et al., 2018). To evaluate its effect during the electrochemical treatment process, the sample pH was kept at its range.

The feasibility of using BDD in an electro-oxidation treatment process to remove bentazone pesticide and this by estimation of COD levels in the treated sample. The current density is seen to be the important factor because it controls the reactive oxygen species amounts in addition to other electro-generated oxidants that have the ability of chemical destruction. Pesticide removal has been studied in terms of applied current density and support electrolytes. Figures 1 and 2 show that current density is the most important factor affecting bentazone removal performance. This seen significantly at the 10, 15, and 20 mA/cm2. This can be described by taking into account the formation of the highly reactive hydroxyl radical, which is directly influenced by current density and other oxidizing species including peroxydisulfate (if Na_2SO_4 is applied as in this article) can also be competitively produced with reactive oxygen (Lin et al., 2013).

3.2 Supporting electrolyte

The removal efficiency of bentazone and COD was directly influenced by the addition of support electrolytes as shown in figure (3). In looking at figure 3 and scrutinizing it, it was noticed that COD removal rates were nearly 79% and 82.5 %

for 5.0 mM and 10.0 mM Na2SO4, respectively. please check the results in correct way.

Table 2. COD removal and degradation cost of bentazone at 5 mM electrolyte concentration

Applied current (mA/cm²)	Electrolysis Time (min)	COD removal (%)	Energy Consumption (kWh/m³)	Cumulative energy consumption (KWh / m³)	Energy cost (dollar /m³)
5	80	77.29	2.38	9.58	58.25
10	80	81.03	5.74	23.01	140.51
15	80	83.98	10.63	42.12	260.50
20	80	86.01	16.72	68.54	409.679

Table 3. COD removal and degradation cost of bentazone at 10 mM electrolyte concentration

Applied current (mA/cm²)	Electrolysis Time (min)	COD removal (%)	Energy Consumption (kWh/m³)	Cumulative energy consumption (KWh / m³)	Energy cost (dollar /m³)
5	80	80.91	1.47	5.98	35.98
10	80	85.36	4.15	16.65	101.57
15	80	88.10	8.05	32.62	197.27
20	80	91.18	14.23	57.63	348.74

3.3 Energy consumption

In an electro-oxidation technique, the main economic parameter is an energy consumption E (kWh/m3) (Errami et al.,2014). The energy consumption parameter is calculated from the equation below:

$$Energy\ Consumption\ (E) = \frac{I*V*t}{Vol*1000} \quad (2)$$

Where I, V and t stand for electrical current intensity (I), average voltage of the EC system (V), and reaction time.

The technical feasibility of electrochemical oxidation is normally measured in terms of the percentage of pollutants removed; however, the economic feasibility is measured in terms of energy consumption and supporting electrolyte

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dosage effect of on energy consumptions were investigated and tabulated in table 2 and 3. Because the support electrolytes and current density have an inverse relationship, increasing the Na2SO4 concentration decreases the energy consumption value. At 5mM Na2SO4 supporting electrolyte concentrations and 20mA/cm2 the maximum energy consumption of 68.54 kWh/m3 was observed. (Figure 4).

3.4 Energy Cost

The energy cost (dollar /m^3) for the removal of pesticides for each process was calculated by applying the following equation:

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

However, at the optimal current density of 20 mA/cm^2, the energy cost for the highest removal efficiency by electro-oxidation treatment was (348,74 dollar/m^3). (Table 2&3).

3.5 Toxicity

Toxicity assays based on V. fisheri bioluminescence which are employed as part of more rigorous environmental evaluations or for routine screening and primary evaluation of the bentazone pesticide model solution. To determine toxicity during treatment, the luminescence test was chosen as a sensitive and repeatable screening process. To evaluate the toxicity variation, percentage inhibition data taken from optimum experimental conditions were converted to a relative toxicity index (RTI). The results represented as the RTI values versus a reaction time are illustrated in Figure (6). Any decrease in RTI values during the electro-oxidation process reflects a decrease in concentration of hazardous compounds concentration. Initial toxicity EC50 (5min) was reduced by 81% after 80 minutes of the treatment by EOP. Whereas, the EC50 (15mins) values was declined by 94% for 80 minutes of electrolysis. According to category given by (Yavuz & Koparal, 2006), The EOP was found to have the potential to reduce toxicity to a minor level. This occurred along with COD reduced.

4. CONCLUSION

The electro-oxidation treatment process can efficiently remove pesticides and COD by using boron doped diamond electrode. The studies demonstrated the importance of choosing the best electrolysis parameter in order to achieve best removal rates, which are necessary for any electro-oxidation process application. The current work aimed to evaluate the electro-oxidation technique validity in the treatment of bentazone in model wastewater. The effect of current density and concentration of supporting electrolyte were evaluated on removal efficiency and COD. The current density and concentration of supporting electrolytes had an effect on the removal of bentazone pesticides in aqueous solution. The results of bentazone degradation by electro-oxidation method using BDD indicated that this process gave highest removal efficiency and COD at optimum experimental conditions. At 20mA/cm2 and 10mM supporting electrolyte, the best removal efficiency was 91,18 %. Energy consumption and cost of process at the best obtained result were 57,63 kWh/m^3 and 348,74 Krş/m^3 respectively.
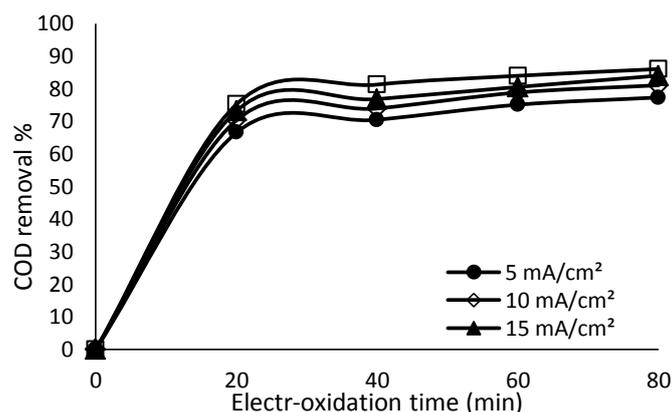

Figure 1. *Variation of COD removal over the time depending on current density (EO, Co= 300 mg/L bentazone, 5mM Na$_2$SO$_4$, pH= 6.43)*

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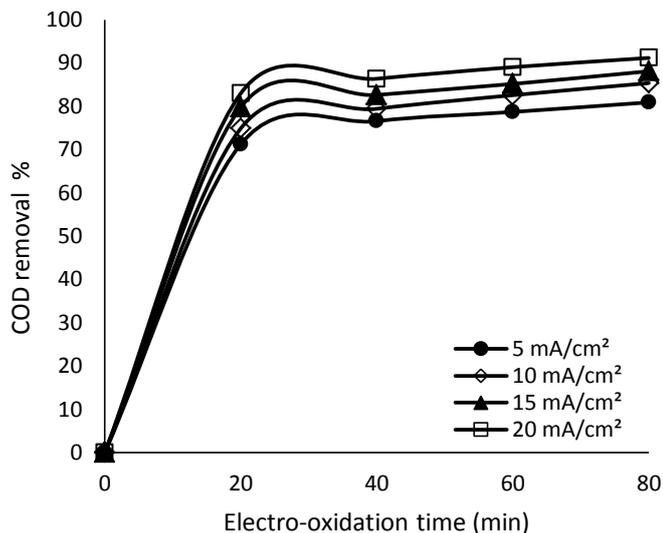
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Figure 2. *Variation of COD removal over the time depending on current density (EO, Co= 300 mg/L bentazone, 10mM Na_2SO_4, pH= 6.31)*
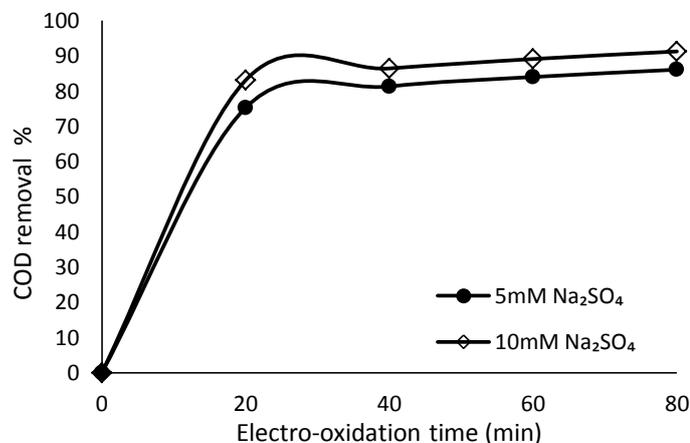

Figure 3. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 300 mg/L bentazone, 20 mA/cm^2)*
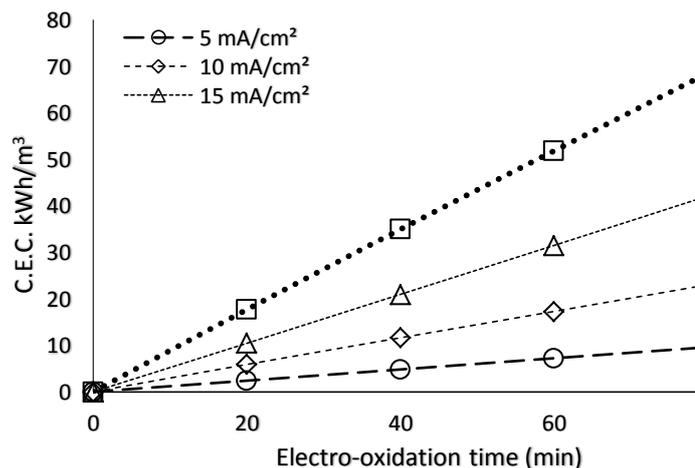

Figure 4. *Variation of energy consumption over the time depending on current density (EO, Co= 300 mg/L bentazone, 5mM Na_2SO_4, pH= 6.43)*
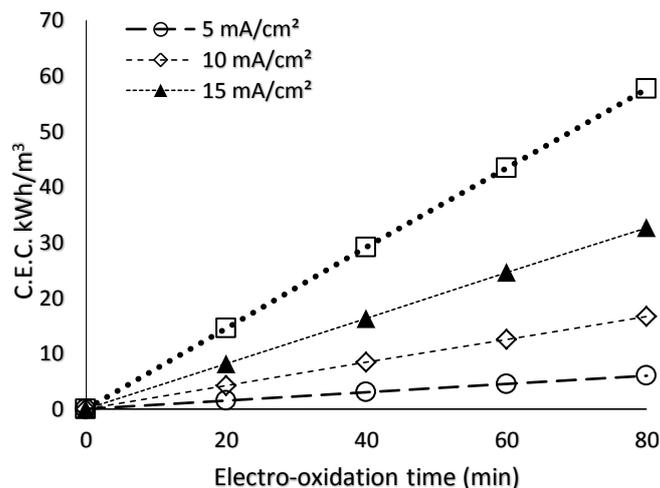

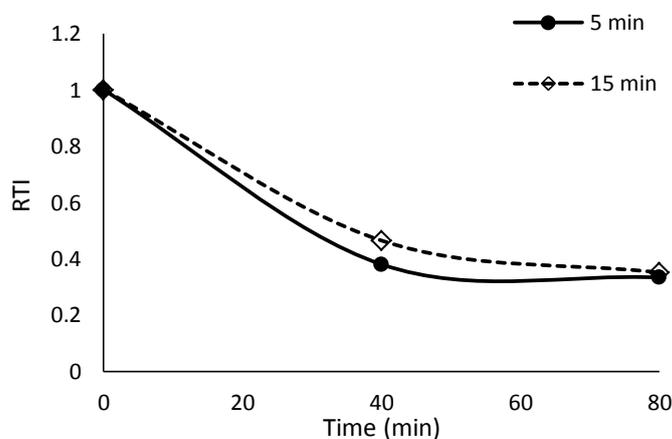**Figure 5.** *Variation of energy consumption over the time depending on current density (EO, Co= 300 mg/L bentazone, 10 mM Na_2SO_4, pH= 6.31)*

Figure 6. *Variation of 5th and 15th mins toxicity of bentazone by electro-oxidation with the time.*

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