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Removal of 2,4-D Isooctyl Ester Herbicide from Model Wastewater by Al-EC

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Abstract— In this study, the removal of 2,4-D Isooctyl ester herbicide, which is used extensively in cereal production, from model wastewater by electrocoagulation (EC) process using aluminium (Al) plate electrodes was investigated. The parameters affecting Al-EC that were studied included the effect of current density, supporting electrolyte concentration and initial pH. The maximum COD removal efficiency was 93.56% and the energy consumption was 202.41 kWh/m^3 at natural pH, applied current density at 50 mA/cm^2, the supporting electrolyte addition of 10 $NaNO_3$ and EC time of 30 minutes. According to the results obtained, it was observed that 2,4-D Isooctyl ester herbicide could be effectively removed from the model wastewater by Al-EC.

Index Terms— Pesticide, Herbicide, 2,4-D Isooctyl ester, Electrocoagulation, COD, Al-Al electrode.

I INTRODUCTION

Reduction of agricultural areas due to increasing world population, developing industry and urbanization bring forward the agricultural applications aimed to obtain product in higher quantities and efficiency [1-3]. Pesticides which are used because of their advantages such as increasing the quality of agricultural products and production efficiency, decreasing and preventing the adverse effects caused by the pests, poses significant problems in terms of environmental and human health [4-5]. The pesticides or pesticide by-products may remain in the water, soil and air as a result of intensive and unconscious usages [6]. During the application of pesticides, some of the pesticide evaporates and is released into the air by regional convection, while another part remains on the plant and soil surface. The pesticides which remain on the soil surface after soil and plant applications may reach to groundwater and other water resources by means of being washed downwards with rain waters [7-8]. The pesticides carried causes pollution of these waters and getting damages of the aquatic life [9]. The pesticides which enter in to food chain by use of the contaminated waters as agricultural irrigation and drinking water causes formation of chronic toxicity in living organisms [10]. Thus, the pesticides give harm also to the other living organisms that live in and have interaction with such environments besides the target organisms [11]. In addition, pesticides applied directly to water and soil accumulate in water and soil for many years, and this cumulative effect adversely affects human health [12]. Recent studies have shown that pesticide exposure is associated with cancer, dementia, Alzheimer's, Parkinson's, amyotrophic lateral sclerosis (ALS), and many psychiatric and neurological diseases [13].

Due to the high chemical stability and low biodegradability of pesticides, the efficient removal methods need to be developed in pesticide removal [14]. Physical, chemical and biological treatment methods are used for pesticide removal from water; however, these types of treatment processes come with some disadvantages, such as high maintenance and operational expenses, the creation of secondary pollutants and lack of effectiveness in remediating wastewater containing different types of

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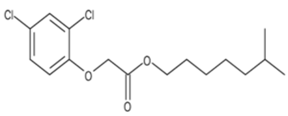
pesticides [15-17]. As a result, electrochemical methods are preferable in the treatment of water and wastewater containing pesticides due to their high removal efficiency, simplicity, the low sample volumes required, the low cost of equipments and the short analysis time [18-19].
In this study, the removal of 2,4-D isooctyl ester herbicide, which is mostly used in cereal production and can be found in groundwater resources, from model wastewater by Al-EC was investigated.

II MATERIALS AND METHODS

A Chemicals and reagents

The herbicide used in the study was 2,4-D Isooctyl ester, which was procured from Hektaş in Turkey. Properties of 2,4-D Isooctyl ester herbicide were given in Table 1. The herbicide solutions used in the present study were obtained through a suitable dilution of a 1 g/L stock solution. All solutions were prepared in distilled water. Sodium nitrate (100%), sodium hydroxide (97%) and hydrochloric acid (37%) were purchased from Merck (Darmstadt, Germany).

TABLE 1
Properties of 2,4-D Isooctyl Ester

Chemical structure	
Molecular Formula	$C_{16}H_{22}Cl_2O_3$
Molecular weight	333,3 g/mol
CAS Number	25168-26-7

B Electrocoagulation experiments

Electrocoagulation studies were performed in a sample volume of 400 mL, at a stirring speed of 200 rpm, using Al-Al electrodes. Characteristic of model wastewater including 2,4-D Isooctyl ester were given in Table 2.

TABLE 2
Characteristic of model wastewater including 2,4-D Isooctyl ester

Initial C_0	500 mg/L
Initial COD	2088 mg/L
$pH_{t=0}$	6±%5

EC studies were carried out in a batch reactor. EC experimental setup consisting of DC power supply (Statron, Type 3262), multimeter (Fluke, 26-III), pH meter (Thermo Scientific, Orion STAR A215) and magnetic stirrer (Heidolph, MR3001) is shown in Figure 1.

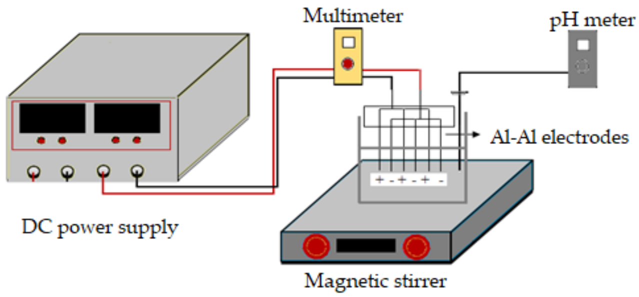


Figure 1. EC experimental setup

The initial pH of the solution was adjusted by using 0,1 M NaOH or 0,1 M HCl.
At the beginning of the study (t=0) and at certain intervals throughout the studies, samples were taken from the reactor and Chemical Oxygen Demand (COD) analysis was performed on these samples. The COD analyzes were carried out according to the Turkish Standard-TS 2789 Water Quality-Determination of Chemical Oxygen Demand. The COD removal was used to evaluate EC efficiency. It was calculated according to the following Equation (1);

$$\text{Removal efficiency }(\%)=\frac{(COD_0\text{-}COD_t)}{COD_0}\times 100 \qquad (1)$$

where, COD_0 is initial COD of herbicide solution (mg/L), COD_t is COD concentration at time t (mg/L).

The energy consumptions in EC process were calculated using Equation. (2);

$$\text{Energy consumption kWh/m}^3 = \frac{V \times I \times t}{v} \qquad (2)$$

where, V is voltage (volt), I is current (ampere), t is EC time (h) and v is volume of the treated wastewater (m^3) [20].

III RESULTS AND DISCUSSION

The parameters affecting Al-EC were evaluated in a batch system. The parameters affecting Al-EC that were studied included the effect of current density, supporting electrolyte concentration and initial pH.

A Effect of current density

The Al-EC processes, current density is the most important parameter for controlling the reaction rate within the EC reactor. It is known that the current density determines the coagulant production rate and bubble production, thus affecting the aggregation of the flocs [21]. The effect of current density on system efficiency in electrocoagulation studies performed with Al-Al electrodes was investigated with the addition of 10 mM $NaNO_3$ supporting electrolyte at 20, 30, 40 and 50 mA/cm^2 current densities. The effect of current density on system efficiency was given in Figure 2 and Figure 3.

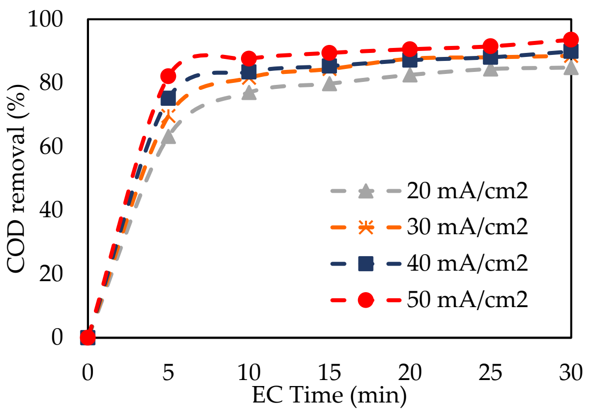


Figure 2. Effect of current density on COD removal (C_0=500 mg/L 2,4-D Isooctyl ester, 10 mM $NaNO_3$, natural pH)

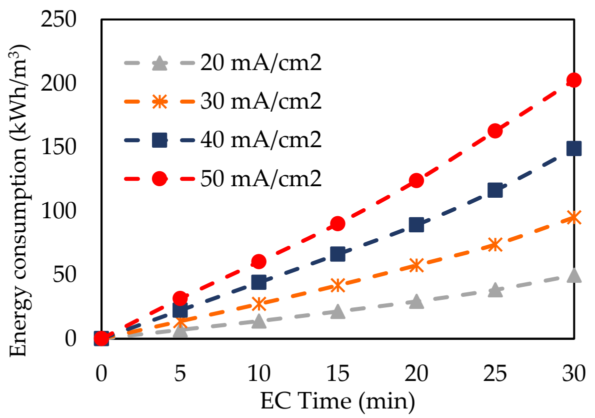


Figure 3. Effect of current density on energy consumption (C_0=500 mg/L 2,4-D Isooctyl ester, 10 mM $NaNO_3$, natural pH)

In the studies carried out at 20, 30, 40 and 50 mA/cm^2 current densities, the COD removal was 84.83%, 88.51%, 89.89% and 93.56% and the energy consumption at these current densities was found to be 49.76, 95.04, 148.82 and 202.41 kWh/m^3, respectively.
Sankar and Sivasubramanian reported similar results for the removal of malathion pesticide from synthetic wastewater by EC, the malathion removal increased with the increase in the voltage applied to the electrode [22].

B Effect of supporting electrolyte concentration

The supporting electrolyte concentration rise the conductivity of the EC solution by enhancing electron transfer in anode dissolution. Accordingly, a larger current can pass through the electrolyte at a smaller voltage, reducing the energy consumption of the EC. The reduction in energy consumption makes the EC process more economical [23].
The effect of supporting electrolyte concentration on system efficiency was investigated by adding 10 mM, 15 mM and 20 mM $NaNO_3$ at 50 mA/cm^2. The effect of supporting electrolyte concentration on system efficiency was given in Figure 4 and Figure 5.

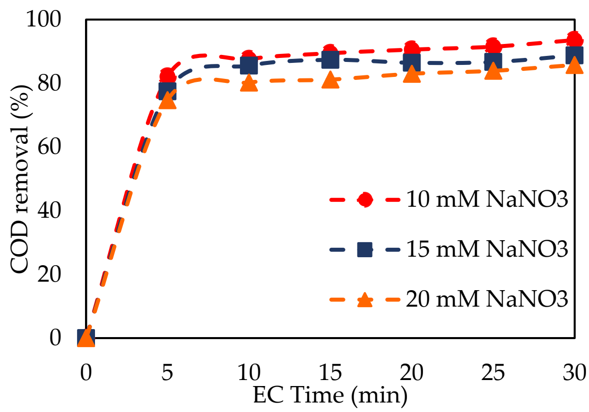


Figure 4. Effect supporting electrolyte concentration on COD removal (C_0=500 mg/L 2,4-D Isooctyl ester, i=50 mA/cm^2, natural pH)

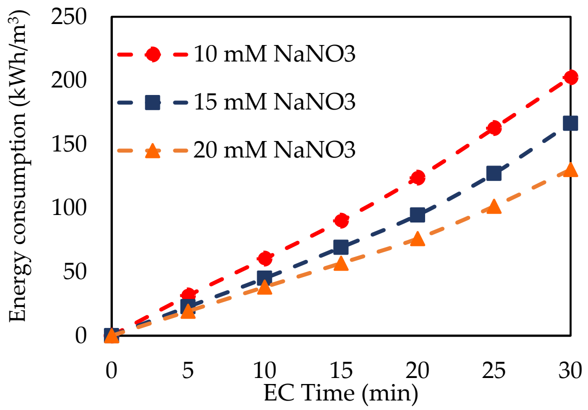


Figure 5. Effect of supporting electrolyte concentration on energy consumption (C_0=500 mg/L 2,4-D Isooctyl ester, i=50 mA/cm^2, natural pH)

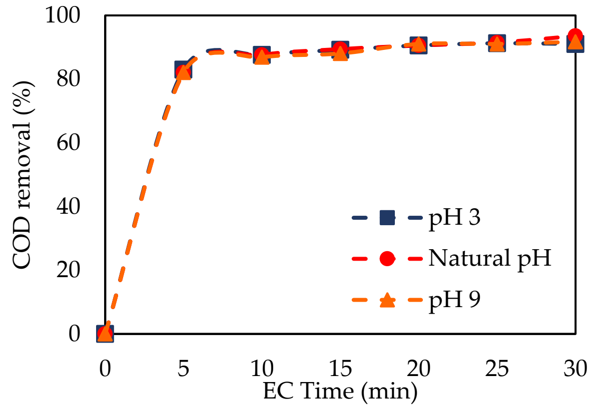


Figure 6. Effect of initial pH on COD removal (C_0=500 mg/L 2,4-D Isooctyl ester, i=50 mA/cm^2, 10 mM $NaNO_3$)

In studies performed at 50 mA/cm^2 with the addition of 10 mM, 15 mM and 20 $NaNO_3$ supporting electrolytes, the COD removal was found to be 93.56%, 88.74% and 85.75% and energy consumption was found to be 202.41, 166.46 and 130.24 kWh/m^3, respectively.
Abdel-Gawad et al. reported that raising the conductivity of the solution has not a considerable effect on the pesticide removal efficieny but it decreases the energy consumption [24].

C Effect of initial pH
The effect of initial pH on Al-EC is reflected by the current efficiency as well as the solubility of metal hydroxides. The efficiency of the treatment depends on the nature of the pollutants where the best removal of the pollutants is close to pH 7. The energy consumption is higher at neutral pH due to the variation of the conductivity. However, the effect of pH is not significant when the conductivity of wastewater is high [25].
The effect of initial pH on system efficiency was investigated at pH 3, natural pH (6±%5) and pH 9 with the addition of 10 mM $NaNO_3$ supporting electrolyte at 50 mA/cm^2. The effect of initial pH on system efficiency was given in Figure 6 and Figure 7.

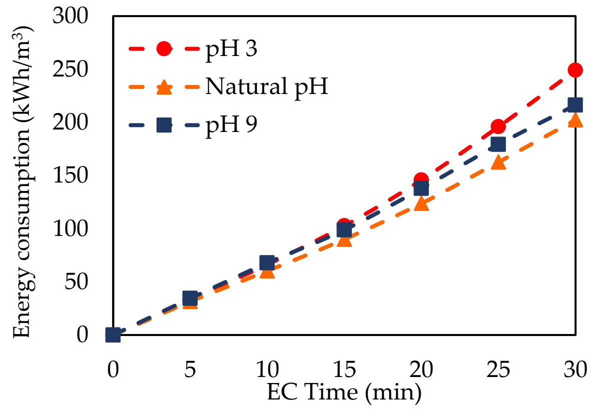


Figure 7. Effect of initial pH on energy consumption (C_0=500 mg/L 2,4-D Isooctyl ester, i=50 mA/cm^2, 10 mM $NaNO_3$)

The effect of the initial pH on the system efficiency, in the studies performed at 50 mA/cm^2 with the addition of 10 mM $NaNO_3$, the COD was found to be 91.03%, 93.56% and 91.72% and the energy consumption was found to be 249.07, 202.41 and 216.31 kWh/m^3, respectively.
In parallel with these presented findings Behloul et al. reported the removal of the pesticide malathion from aqueous solution in batch mode using the EC process. The malathion pesticide removal initial pH increased from 4 to 6, the removal efficiency of malathion increased from 80% to 92%. The maximum removal malathion was observed at neutral pH 6-7.5. This result agreed with the previous studies on EC using aluminum electrodes [26].

IV CONCLUSION

In this study, the Al-EC process was evaluated for the removal of 2,4-D Isooctyl ester herbicide from model wastewater. In considering the effect of current density on system efficiency, it was observed that the COD removal increased with increasing current density. In addition, parallel to the increase in applied voltage, an increase in energy consumption was observed. It has been observed that initial pH and supporting electrolyte concentration did not have a significant effect on system efficiency. The results indicated that Al-EC process is very effective and efficient process for the removal of 2,4-D Isooctyl ester herbicide from model wastewater.

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