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Removal of Diazinon from aqueous solution by electrocoagulation process using aluminum electrodes

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Abstract−Electrocoagulation (EC) is an electrochemical method to treat polluted wastewaters and aqueous solutions. In this paper, the removal of Diazinon was studied by EC on aluminum electrode. The effect of several parameters such as initial concentration of Diazinon, current density, solution conductivity, effect of pH, and electrolysis time were investigated on EC performance. The obtained results showed that the removal efficiency of EC depends on the current density, initial concentration of Diazinon and electrolysis time. The optimum pH is 3 and also the solution conductivity has no significant effect on removal efficiency.

Keywords: Electrocoagulation, Diazinon, Insecticide, Removal Efficiency, Aluminum Hydroxide

INTRODUCTION

Due to their wide application in agriculture and harmful effects, water-containing insecticides like Diazinon can bring about serious environmental problems and also have immediate or even delayed impacts on people's health around the world [1,2].

As a water-containing insecticide, Diazinon is used by many farmers to control pests on fruits, vegetables, and field crops, but excessive concentration of this insecticide has detrimental effect on organisms and blood. Consequently, the amount of usage should be determined cautiously lest the toxicant contaminate ground or sea water [1,2].

There are several methods to remove the toxicant from water, such as treatment by photocatalyst [3] and oxidation [4]. One of the most practical methods is the application of EC which is an electrochemical wastewater treatment technology. The EC process has many advantages like simple equipment requirement, easy operation, no chemical use requirement, rapid sedimentation, sludge stability, low sludge production, and environmental compatibility.

It has successfully been employed for the treatment of different wastewaters such as from hospitals [5], baker's yeast [6], laundries [7], biodiesel [8,9], and slaughter houses [10], wastewaters including surfactants [11], fluoride [12] and heavy metal-containing solutions [13-16].

The EC process is based on in situ production of coagulant by anodic dissolution of aluminum. In this process, iron and aluminum electrodes produce their hydroxides ($Fe(OH)_3$ and $Al(OH)_3$) in the contaminated water. The electrochemical reaction of aluminum electrode in an EC cell can be summarized as follows:

a. Anodic reactions:

$$Al \rightarrow Al^{3+} + 3e^- \quad (1)$$

$$2H_2O \rightarrow O_{2\,(gas)} + 4H^+_{(aq)} + 4e^- \quad (2)$$

b. Cathodic reactions:

$$2H_2O + 2e^- \rightarrow H_{2\,(gas)} + 2OH^-_{(aq)} \quad (3)$$

According to the literature, a few studies have been reported for treatment and removal of Diazinon from aqueous solutions. Daneshvar et al. studied the treatment of Diazinon by ZnO nanocrystals [3]. ZnO nanocrystals with mean diameter size of 14 nm were prepared by precipitation method and examined as photocatalyst in UV induced degradation of insecticide Diazinon. Real et al. investigated the removal of Diazinon via various advanced oxidation processes such as UV radiation, ozone, Fenton's reagent, UV radiation plus hydrogen peroxide, ozone plus hydrogen peroxide and photo Fenton as oxidation process [4]. Wu et al. studied the effect of low-concentration of ozone on removal of Diazinon. Ozone was effective to oxidize and remove 60-99% of 0.1 mg/L aqueous solution of Diazinon [17].

We investigated the removal efficiency of Diazinon in aqueous solution by electrocoagulation. The effect of several parameters such as initial pH, electrolysis time, conductivity, initial concentration of Diazinon and current density on the removal efficiency were measured and studied.

EXPERIMENTS

1. Materials

Diazinon was used to prepare the synthetic wastewater solutions. Initial pH of solutions was adjusted by 0.5 M NaOH and HCl solutions. To adjust the initial solution's conductivity, NaCl was used. Diazinon, HCl, NaOH and NaCl were purchased from Merck.

2. Instrumentation

A double beam UV-Vis spectrophotometer (Braic-2100) was used to determine Diazinon concentration. The electrochemical experiment was carried out by power supply (Sanjesh, Iran, 0-30 V and 0-5 A). The solution conductivity was determined by conductometer (JENWAY, 4020, U.K.).

3. Procedure

The experimental setup is shown in Fig. 1. Experiments were

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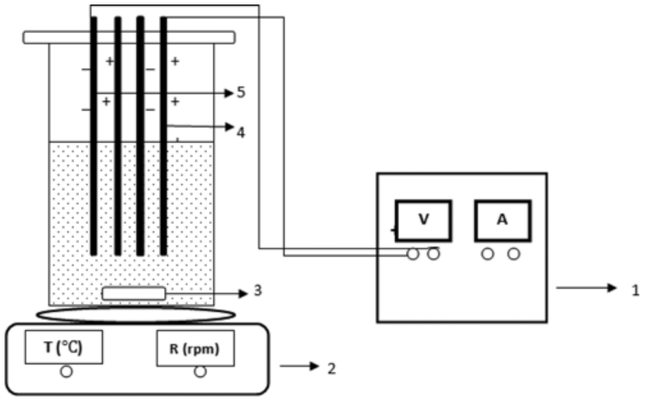

Fig. 1. The schematic diagram of EC instrument.

1. DC power supply
2. Stirrer
3. Magnetic bar
4. Cathode electrode
5. Anode electrode

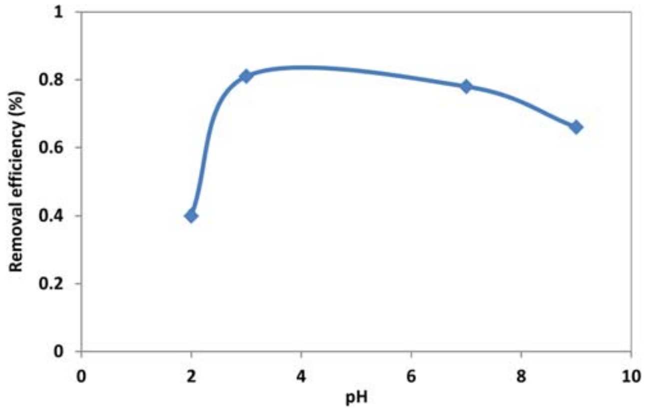

Fig. 2. Effect of pH on Diazinon removal efficiency. Current density (12 mA/cm^2), constant Diazinon concentration (60 mg/L), solution conductivity (6.5 mS/cm) and pH in the range of 3-10.

conducted with four aluminum electrodes connected in bipolar mode and hold through a glass pipe. Dimensions of electrodes were 100×50×2 mm and the distance between two electrodes was 10 mm in all experiments. Only the outer electrodes were connected to the power source. Before each experiment, the electrodes were cleaned by sandpaper and dipped in 0.5 M HCl solution, then rinsed with distilled water, and finally dried for 15 minutes at 75 °C. All experiments were performed at 25±3 °C. The concentration of Diazinon was varied between 10 to 90 mg/L. The applied current density was adjusted in the range of 2.5 to 12 mA/cm^2, whereas voltage changed between 10 to 30 V. The solution's conductivity was variable between 2.62 to 7.7 mS/cm.

In each experiment, 400 ml of Diazinon solution (with specified concentration) was transferred into the EC cell. Then, the current density was adjusted to the desired value. During the process, the solution was agitated at 200 rpm. The solution was sampled at regular time intervals to determine the residual concentration of Diazinon. The total process time was 35 minutes. The Diazinon concentration was analyzed with a UV-Vis spectrophotometer. Absorbance was measured at the wavelength of 248 nm and spectral bandwidth of 0.2 nm.

RESULTS AND DISCUSSION

The removal efficiency (R_e) was calculated according to Eq. (4):

$$R_e = \left(1 - \frac{A}{A_0}\right) \times 100 \tag{4}$$

where A_0 is absorbance of initial solution of Diazinon and A is absorbance of Diazinon at time t.

1. Effect of Initial pH

To examine the effect of initial pH on removal efficiency, a series of experiments were performed on 60 mg/L of Diazinon solution with different initial pH in the range of 3-10. As observed by other authors, the pH of solution changes during the EC process. Vik et al. reported that pH increment occurs when the initial pH is lower than 7 [18]. They observed this increase in pH hydrogen evolution at cathode. However, Chen et al. explained this by the release of CO_2 from wastewater which occurs from H_2 bubble disturbance. Actually, in low pH, CO_2 is released during the H_2 evolution and causes to pH increment [19]. Also, Bazrafshan et al. demonstrated that when pH is higher than 8, the final pH does not vary significantly and only a short drop occurs [12].

Generally, in acidic environment the removal efficiency of Diazinon is better than that of neutral or alkaline solutions. As can be observed in Fig. 2, the optimum efficiency occurred in pH=3. By decreasing pH of the solution, the probability of conversion of aluminum hydroxide into other types of aluminum hydroxide with more charge increases. When pH increases, aluminum hydroxide is converted to the negative aluminum hydroxide complexes according to the following equations:

$$Al\,(OH)_3 + OH^- \rightarrow Al(OH)_4^- \tag{5}$$

$$Al\,(OH)_4^- + OH^- \rightarrow Al(OH)_5^{2-} \tag{6}$$

$$Al\,(OH)_5^- + OH^- \rightarrow Al(OH)_6^{3-} \tag{7}$$

Also, negatively charged aluminate ions may be formed through the following reaction:

$$Al\,(OH)_3 + OH^- \rightarrow AlO_2^- + 2H_2O \tag{8}$$

There is an optimum pH for adequate adsorption of Diazinon and an increase or decrease of pH can affect the removal efficiency of adsorbed Diazinon. In basic media, as a result of the formation of aluminum species, which their acidic sites are filled with hydroxide ions, Diazinon cannot be adsorbed by the precipitate. In high acidic media, the aluminum hydroxide coagulant is solved, so the absorbed Diazinon is released in the solution.

2. Effect of the Initial Concentration of Diazinon

Effect of the initial concentration of Diazinon in EC cell was investigated in the range of 10 mg/L to 90 mg/L. As shown in Fig. 3, by increasing the initial concentration of Diazinon, the removal efficiency is increased. For example, at pH=7 and initial concentrations of 10, 30, 60 and 90 mg/L, about 48.5, 72.9, 78 and 81% of Diazinon was removed from solution, respectively, after 35 minutes. The point of zero charge (PZC) of aluminum is 9.6 [20]. At pH=7, the total charge of sediment is positive. In coagulant with pH lower than PZC, positive ions are created and the precipitate has a positive charge according to the following reactions:

$$Al(OH)_3+H^+\rightarrow Al(OH)_2^++H_2O \qquad (9)$$

$$Al(OH)_2^++H^+\rightarrow Al(OH)^{2+}+H_2O \qquad (10)$$

$$Al(OH)^{2+}+H^+\rightarrow Al^{3+}+H_2O \qquad (11)$$

Diazinon has nitrogen atoms in heterocyclic ring (Fig. 4). Since the non-bonding electrons of nitrogen have donor effect on positive ions, they can react with aluminum or hydroxylated aluminum ions which exist in the sediment. Therefore, Diazinon is adsorbed on sediment and its concentration decreases in the solution. At higher initial concentration of Diazinon, the amount of adsorption and the removal efficiency increase.

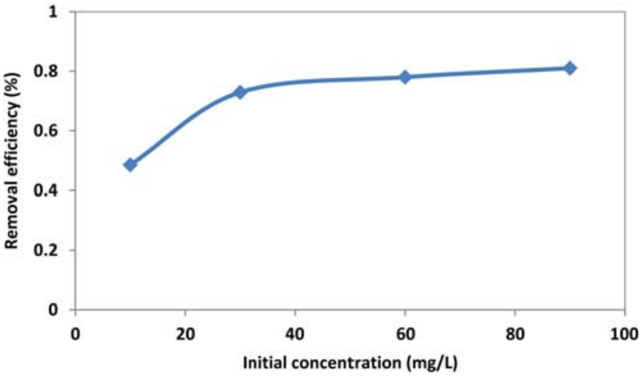

Fig. 3. **Effect of initial concentration of Diazinon on removal efficiency. pH=7, current density (12 mA/cm^2), solution conductivity (6.5 mS/cm) and initial concentrations of 10, 30, 60 and 90 mg/L.**

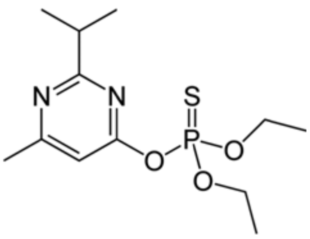

Fig. 4. **The structure of Diazinon.**

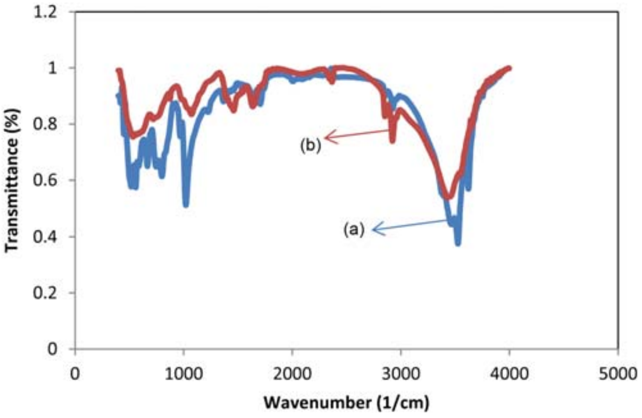

Fig. 5. **The FT-IR spectra of aluminum hydroxide before and after immersing in the Diazinon solution. (a) (Pure Al(OH)$_3$), (b) Al(OH)$_3$ after immersing in the Diazinon solution.**

Fig. 5 shows FT-IR spectra of two samples of aluminum hydroxide before and after immersing in the Diazinon solution. As can be seen, Diazinon can adsorb on the aluminum hydroxide surface.

3. Effect of Current Density

Fig. 6 shows the effect of current density on the removal efficiency of Diazinon. The results show that the removal efficiency of Diazinon depends on aluminum concentration in the EC process. The theoretical amounts of Al dissolution (m_{theo}) in the EC cell can be

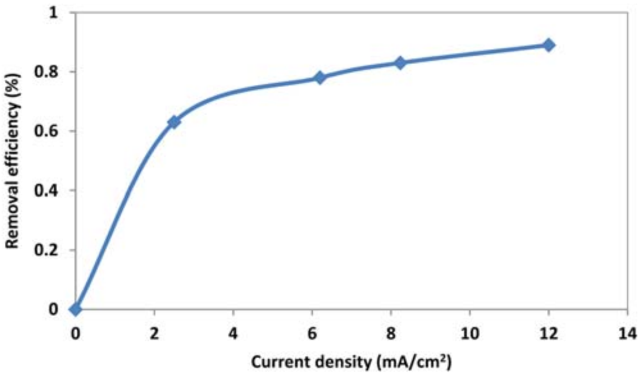

Fig. 6. **Effect of current density on Diazinon removal efficiency. pH=7, constant Diazinon concentration (60 mg/L), solution conductivity (6.5 mS/cm) and current density from 2.5 to 12 mA/cm^2.**

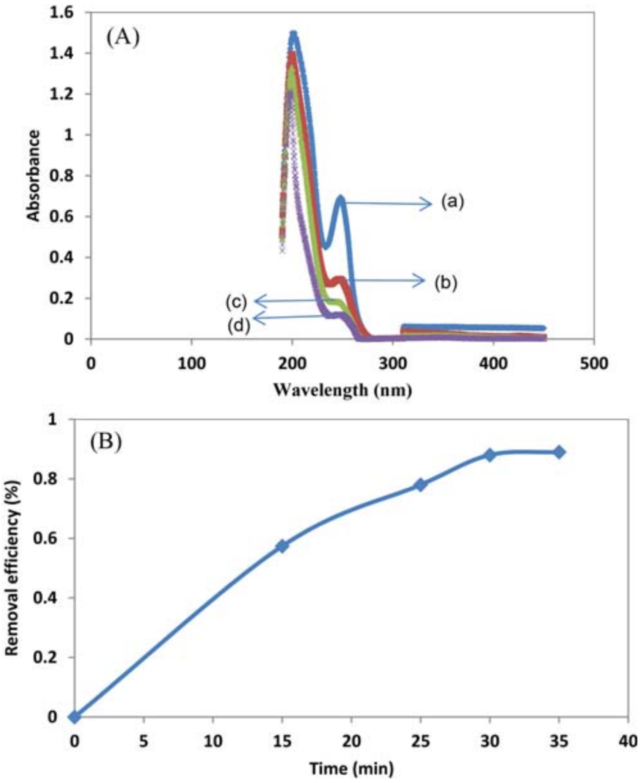

Fig. 7. **(A) UV spectra of Diazinon at different removal time. (a) (at time 0), (b) (after 15 minutes of process), (c) (after 25 minutes of process), (d) (after 35 minutes of process) (B) The removal efficiency of Diazinon. Experiment conditions: pH=7, current density (12 mA/cm^2), constant Diazinon concentration (60 mg/L) and solution conductivity (6.5 mS/cm).**

expressed by Faraday's law as follows [15]:

$$m_{theo}=\frac{ItM}{ZF} \tag{12}$$

where I is the current density (A), t is the time of electrolysis (s), m is the amount of dissolved aluminum (g), M is the atomic weight of the aluminum (g/mol), Z is the metal valance (3 for Al), and F is Faraday's constant (F=96,487 C/mol). By increasing the current density from 2.5 to 12 mA/cm^2, the removal efficiency rises from 63% to 89%. According to Faraday's law, the amount of anodic dissolution of Al grows by increasing the current density. The higher amounts of generated coagulant can enhance the EC removal efficiency. At variance, less aluminum is released from the anode when lower current densities are applied and the removal efficiency of Diazinon is low.

4. Effect of Electrolysis Time

Electrolysis time is an important parameter which affects the removal efficiency and controls the reaction rate. A series of experiments were carried out on solution containing constant Diazinon concentration (60 mg/L) with pH=7 under constant current density (12 mA/cm^2) at different electrolysis times. The UV-Vis spectra (Fig. 7(a)) indicate that by increasing the time of reaction, the absorbance decreases. As shown in Fig. 7(b), the removal efficiency increases from 57.7% after 15 minutes to 89% after 35 minutes of process. According to Faraday's law, the amount of aluminum released from the anode depends on the electrolysis time and current density, so by increasing the time of reaction, more aluminum is released from the anode surface and the Diazinon removal from solution is enhanced.

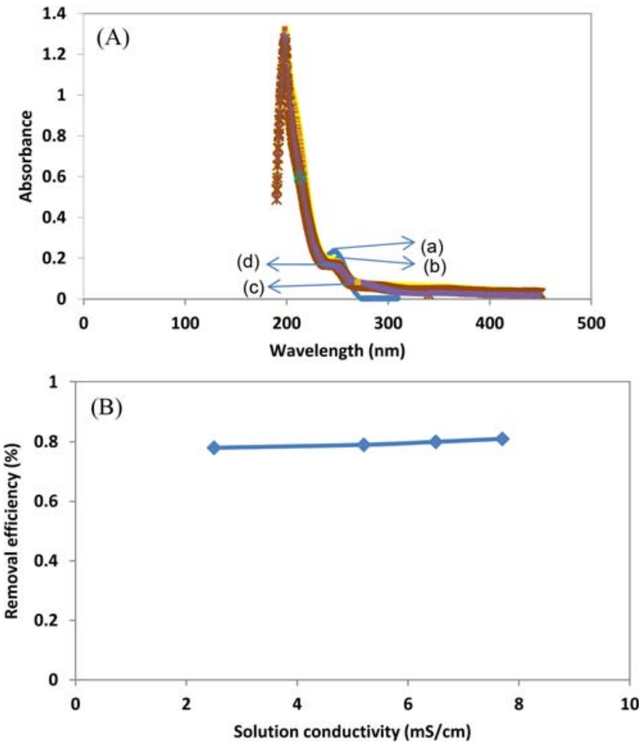

Fig. 8. (A) UV spectra of Diazinon at different solution conductivity. (a) (2.5 mS/cm), (b) (5.2 mS/cm), (c) (6.5 mS/cm), (d) (7.7 mS/cm) (B) Diazinon removal efficiency. Experiment conditions: pH=7, current density (12 mA/cm^2), constant Diazinon concentration (60 mg/L).

5. Effect of Solution Conductivity

To evaluate the influence of solution conductivity on the removal efficiency of Diazinon, the initial solution conductivity of 60 mg/L of Diazinon solution with pH=7 was adjusted by NaCl in the range from of 2.5 to 7.7 mS/cm, whereas the applied current density of 12 mA/cm^2 was applied to electrodes. From Fig. 8(a), no significant change occurred in UV absorbance, and due to that, the removal efficiency of Diazinon remained constant with conductivity increment (Fig. 8(b)).

CONCLUSION

The removal efficiency of Diazinon from aqueous solution was examined by electrocoagulation using aluminum electrodes. The effects of initial concentration of contamination, current density, pH, electrolysis time, and solution conductivity were investigated on removal efficiency. It was observed that an increase in initial concentration of Diazinon caused an increase in removal efficiency. Also, current density and electrolysis time have a significant effect on the removal efficiency. The results revealed that pH=3 is the optimum condition and by increasing the pH of the solution, the removal efficiency decreases.

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