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Removal of Some Pesticides from the Simulated Waste Water by Electrocoagulation Method Using Iron Electrodes.

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This work deals with the possibility of using electrocoagulation method for the removal of some pesticides (malathion, imidacloprid and chlorpyrifos). The effect of various operational parameters of the removal efficiency was investigated and optimized. The removal of pesticides using iron sacrificial oxide was affected by the initial pH, the current density , the amount of NaCl and the initial pesticide concentration. The removal % for pesticides was $\simeq$ 98-99%. When iron used as a sacrificial anode under the operating conditions of initial pH of 6-7, current density of 1mA/cm^2, electrolysis time of 10 min, initial pesticide concentration of 0.5% and NaCl concentration of 1g/L. the obtained results showed that pseudo-second-order equation was found to be in a good agreement with the experimental results.

Keywords: iron electrode, electrocoagulation, pesticides, chemical oxygen demand (COD).

1. INTRODUCTION

One of promising methods for treating hard –to-treat waste water streams is the electrochemically based. Electrochemical processes (electrolysis and electrocoagulation) have been successfully demonstrated for removing pollutants in various industrial wastewaters [1-3]. Removal mechanisms reported in the electrolysis process generally include oxidation, reduction, decomposition, whereas the mechanisms in the electrocoagulation process include coagulation, adsorption, precipitation and flotation [4-6]. Electrocoagulation utilizes iron anode to produce iron hydroxide flocks by reaction at the anode followed by electrolysis.

The electrocoagulation is simple and efficient method for the treatment of many water and wastewater. In recent years, many investigations have been especially focused on the use of electrocoagulation owing to the increase in environmental restrictions on effluent waste water [7-9]. Electrocoagulation has been applied successfully to treat potable water , food and protein waste water [10-12] yeast waste water [13], urban wastewater[14], restaurant wastewater [8,15] tar sand and oil shale waste water [16]. This work aims to study the possibility of using iron electrode for removal of pesticides from simulated waste water by electrocoagulation method.

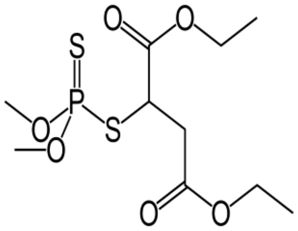
2. MATERIALS AND EXPERIMENTAL METHODS

The pesticides solutions were prepared with deionized water. All chemical reagents used were analytical grade. Batch removal of pesticides from simulated wastewater was performed in an electrolytic cell. The electrocoagulation unit with bipolar electrodes in parallel connection consists of an electrocoagulation cell, a D.C. power and electrodes. The iron cathode and anode consist of pieces of iron electrodes separated by a space of 2 cm and dipped in the simulated wastewater. The electrocoagulation of pesticides was carried out in the reactor (500 ml) using magnetic stirrers to agitate the solutions. There were four electrodes connected in bipolar mode in the electrochemical reactor, each one with dimensions 10 x 5 x 0.2 cm. The total area submerged into the solution of the electrode plates was 20 cm^2. A stirring intensity of 100 rpm was used in order to get a correct homogenization of the wastewater - flocks mixture. The electrocoagulation experiments were carried out at ambient temperature ($\simeq$ 25 °C). The D.C. source was a power supply (0-15V and 0-3A). At the beginning of a run, the pesticide solution was fed into the reactor and the pH and conductivity were adjusted to a desired value. The conductivity of the solution was raised by adding NaCl into the pesticide solution. The pH was adjusted using either 0.1 M NaOH or 0.1 M HCl as necessary. The electrodes were placed into the reactor. The reactor was timed starting when the D. C. power supply was switched on. Samples were periodically taken from the reactor. The particulates of colloidal ferric oxyhydroxides gave yellow-brown color into the solution after electrocoagulation and electrolytic flotation. The sludge was separated by filtration with Whatman filter paper (pore size 11µm). Then the liquid was analyzed for COD determination, which carried out according to Standard Methods for examination of water and wastewater [17].

2.1. Chemicals

Chemicals used for degradation are different types of pesticides; malathion, chlorpyrifos and imidacloprid.

[I] Malathion (Diethyl (dimethoxy thio phosphryl thio) succinate)
[II] Chlorpyrifos (O, O-diethyl O-(3, 5, 6-trichloro-2-pyridyl)-phosphorothioate)
[III] Imidacloprid (1-(6-chloro-3-pyridyemethyl)–N-nitroimidazolidine-2-yliedeneamine)



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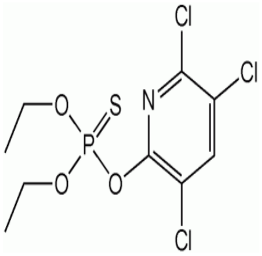

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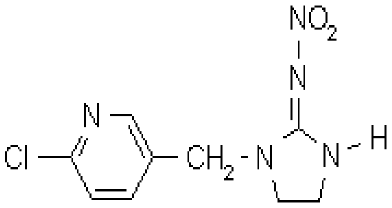

[III]

2.2 Chemical Oxygen Demand COD (mg O_2 /L)

It is a measure of the oxygen equivalent to organic matter content of a sample that is susceptible to the oxidation by strong chemical oxidant. COD can be related empirically to organic matter. COD during the electrolysis was determined by an open reflux (COD reactor, ECO 6, VELP SCIENTIFICA, Italy), dichromate titrimetric method as described in standard methods [18].This method for the determination of COD may be used where sample chloride concentration is known to be less than 2000 mg/l. This means that, in the present investigations the interferences of Cl^- ions present in the solution and the electro-generated species may occur. To eliminate the effect of these interferences, two different methods were taken into considerations [19].The first was carried out by adding sodium bisulphate ($Na_2S_2O_5$) to the organic compound (pesticides) solutions and heating before measurements of COD. The added of sodium bisulphate destroys the hypochlorite with evolution of chlorine gas. The second includes the measurements of COD for blank solutions, which are free from the under test organic compound. These blank solutions were treated under the same operating conditions used in the electro-catalytic oxidation of organic (pesticides) compound solutions. From the measurements of COD values of blank and organic (pesticides) compound solutions after treatment, the value of COD is corresponding to the organic compound present in solution that could be evaluated. The COD values obtained from the two methods were matched with each other. The equation used to calculate the COD removal efficiency in the experiments is:

$$\text{COD Removal \%} = [\text{COD}_{\circ} - \text{COD}_{\text{final}} / \text{COD}_{\circ}] \times 100$$

Where, $\text{COD}_{\circ}$ (initial) and $\text{COD}_{\text{final}}$ of the pesticide solutions are calculated in mg/L

2.3. The optimum operating conditions for the electro catalytic degradation processes:

Several parameters were studied for investigation the optimum conditions for the degradation of synthetic agricultural wastewater (which prepared from pesticides). The studied operating conditions were: effect of the conductivity (NaCl dose), effect of pH, effect of current density, effect of electrolysis time, effect of initial pesticides dose.

3. RESULTS AND DISCUSSION

A series of experiments was carried out in NaCl solution to investigate the effect of different operating factors on the rate of the electrocoagulation method of the investigated pesticides on the iron electrode.

3.1. Effect of the conductivity (NaCl dose):

In general NaCl is used to obtain conductivity in electrocoagulation process. The conductivity of the wastewater is adjusted to the desired levels by adding an appropriate amount of NaCl [15]. The effect of NaCl concentration on the removal % of the pesticides is shown in Fig. (1).

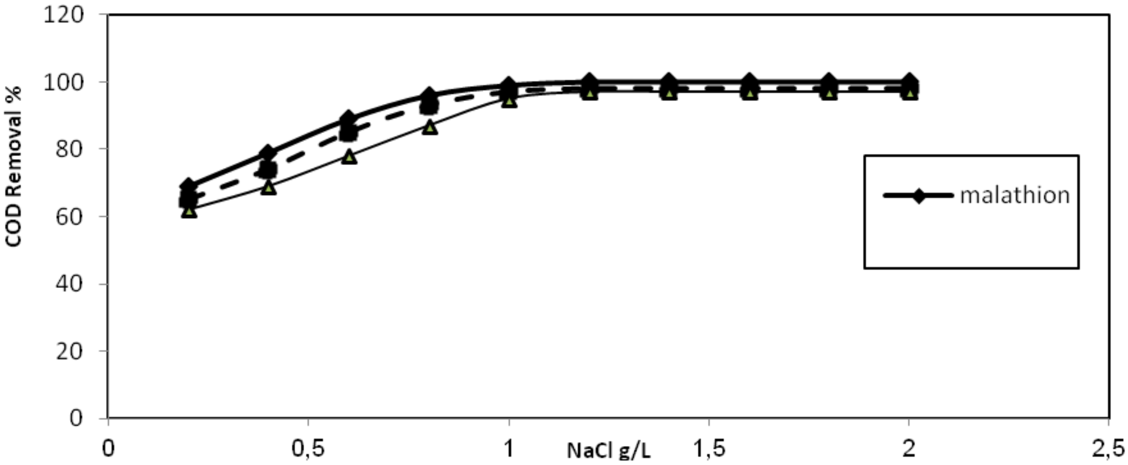

Figure 1. Effect of NaCl concentration change, keeping other variants constant.

When the concentration of NaCl salt in solution increases, conductivity of the solution and the current density increase. The higher ionic strength will generally cause an increase in current density at the same cell voltage or, equivalently, the cell voltage decreases with increasing wastewater conductivity at constant current density. Consequently, the necessary voltage for attaining a certain current density will be diminished and the consumed electrical energy will decrease. According to Vlyssides et al [1, 20] showed that Cl_2 and OCl^- are the products from anodic discharge when chlorides are present in the solution. So, added NaCl not only increases the conductivity but also contributes strong oxidizing agents [20]. It can be seen from Fig. (1) that there is an increase in the removal % of the pesticides up to 98%, 100%, 97% for the pesticides imidacloprid, malathion and chlorpyrifos, respectively when the concentration of NaCl salt in the solution is 1g/L. It was found that raising the conductivity of the solution has not a considerable effect on the removal % but it decreases the energy consumption. According to the obtained results, high removal% with low cell voltages and low energy consumption can be obtained in pesticides solution with NaCl of around 1g/L. In this respect 1g/L was used in the all following experiments.

3.2. Effect of pH on the pesticides removal%

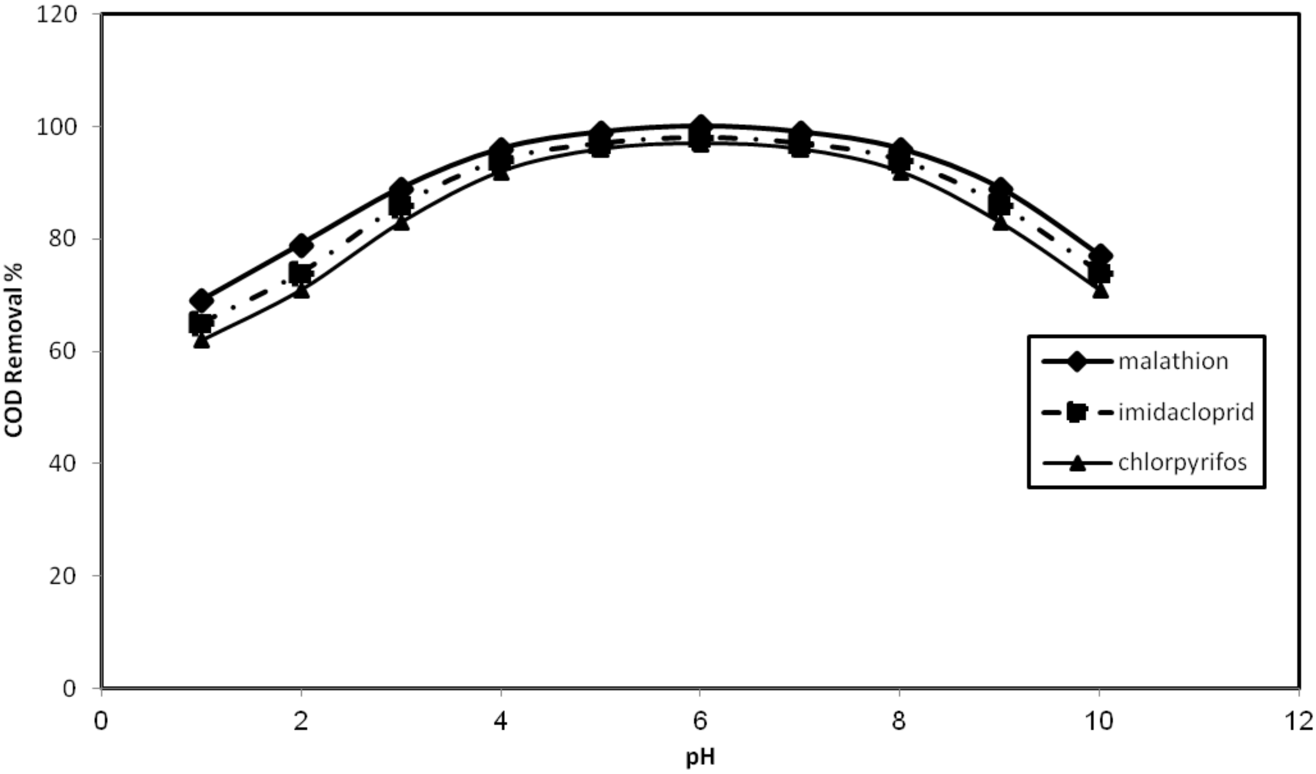

Figure 2. Effect of pH value change, keeping other variants constant

Fig. (2) shows the effect of initial pH value on the removal % of the pesticides under the following conditions: 0.5% initial concentration of the pesticides, current density of 1mA/cm^2, electrolysis time of 10-20 min., temperature of 25˚C. As can be seen from the plot of Fig. (2) that, there was a significant difference in the removal % of pesticides when using iron electrodes at different initial pH values. It seemed that the optimal pH value was ranged from 5-7. The Fe $(OH)_{n\ (S)}$ formed in electrocoagulation remains in the aqueous stream as a gelatinous suspension at $3 < pH < 11$, which can remove the pollutants from the wastewater either by complexation or by electrostatic attraction, followed by coagulation [21].

3.3. Effect of current density

The current density determines the coagulant dosage rate. This parameter should have a significant impact on the removal efficiency of the pesticides. The influence of the current density on the pesticides removal % during the electrolysis with the iron electrodes is reported in Fig. (3). The operating conditions of the electrolysis process was 0.5 % initial dose of the pesticide, pH = 6-7, time of electrolysis = 10-20 min. and temperature of 25 ˚C. The plot of Fig. (3) Indicated that the removal % of the pesticides increased with the increase of the current density up to 1mA/cm^2.

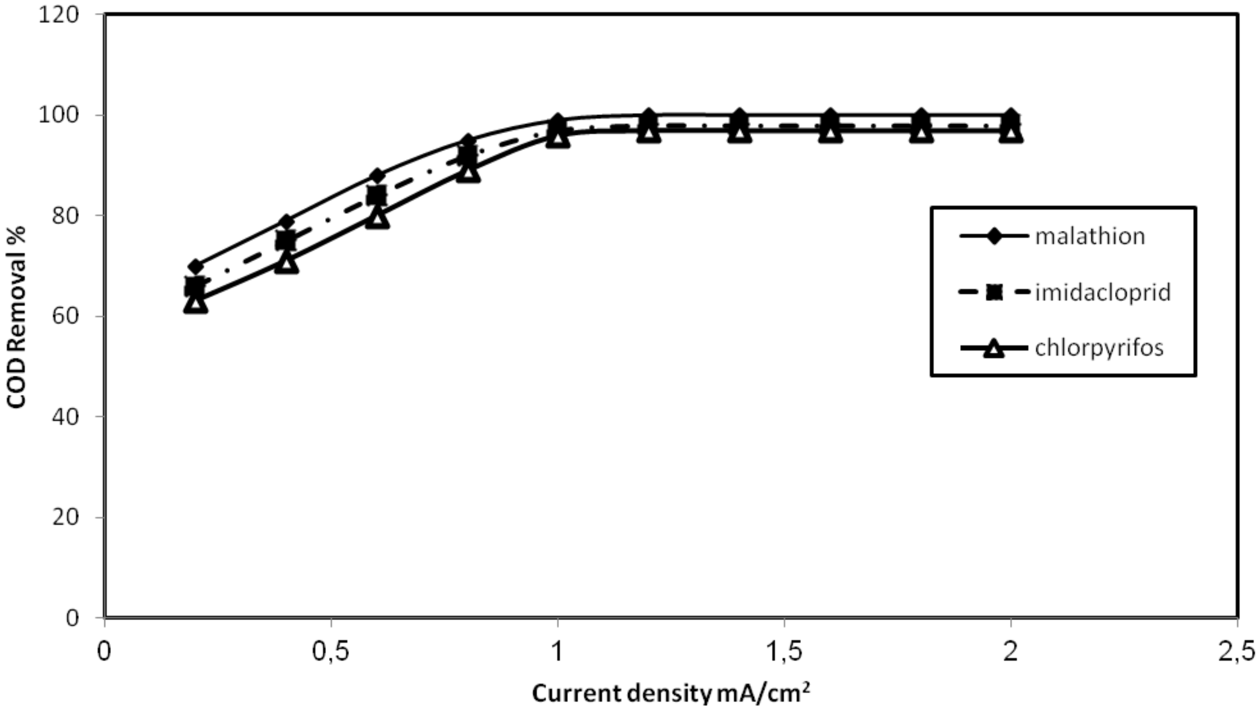

Figure 3. Effect of current density on the removal %, , keeping other variants constant.

The removal of the pesticides at higher current densities than 1mA/cm^2 stayed at the constant value. At a high current density, the extent of anodic dissolution of iron increases, resulting in a greater amount of $Fe(OH)_{n\ (s)}$. Moreover, the rate of bubble- generation increases and the bubble size decreases with increasing current density, both of these trends are beneficial in terms of a high - pollutant removal efficiency by H_2 flotation [22,23]. The minimum energy consumption was 1.5 kWh/kg pesticides at 1mA/cm^2 current density for 10 min. electrolysis time.

3.4. Effect of electrolysis time

Electrolysis time also affects the treatment efficiency of the electrochemical process. Electrolysis time determines the production rate of Fe^{2+} or Fe^{3+} ions. Fig. (4) shows the effect of electrolysis time on the removal % of the pesticides under the following operating conditions: 0.5 % initial dose of pesticides, pH of 6-7, current density of 1mA/cm^2, temperature of 25°C. It is indicated from the plot of Fig. (4) that the removal % increases with the increase of electrolysis time up to 10 minutes. No further increase in the removal % with the increase of the electrolysis time more than 10 minutes.

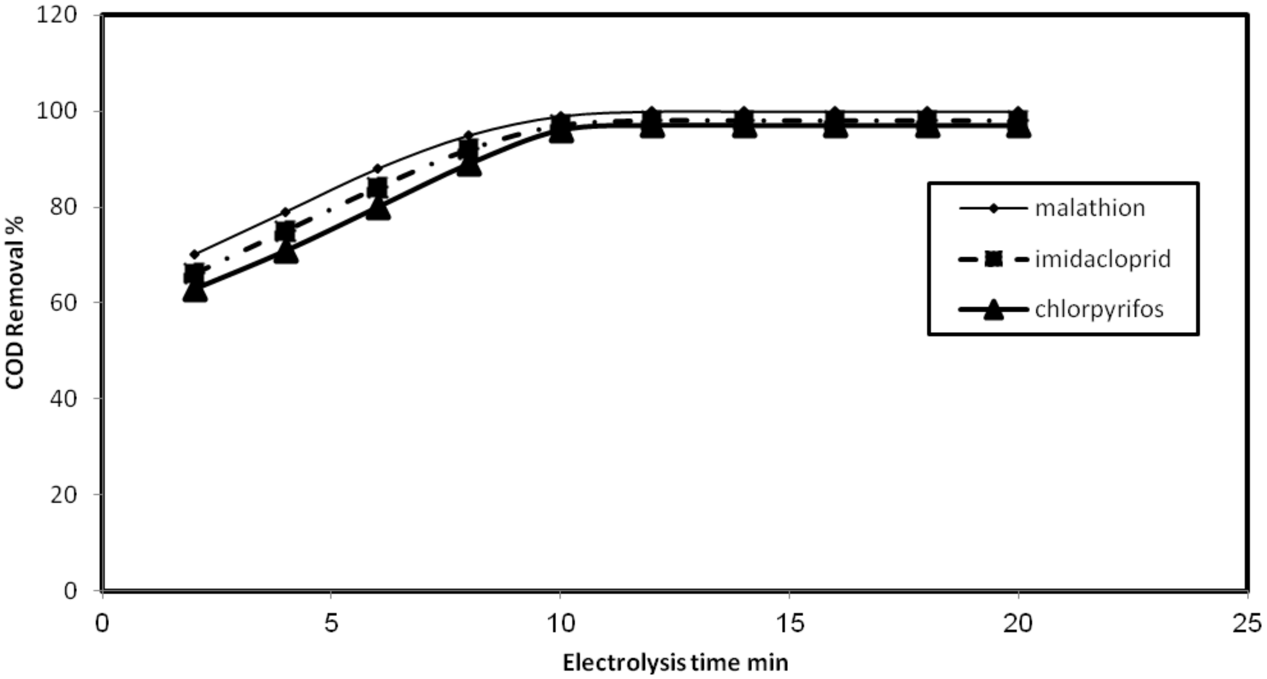

Figure 4. Effect of electrolysis time on the removal %, , keeping other variants constant.

3.5. Kinetic studies of the pesticides removal

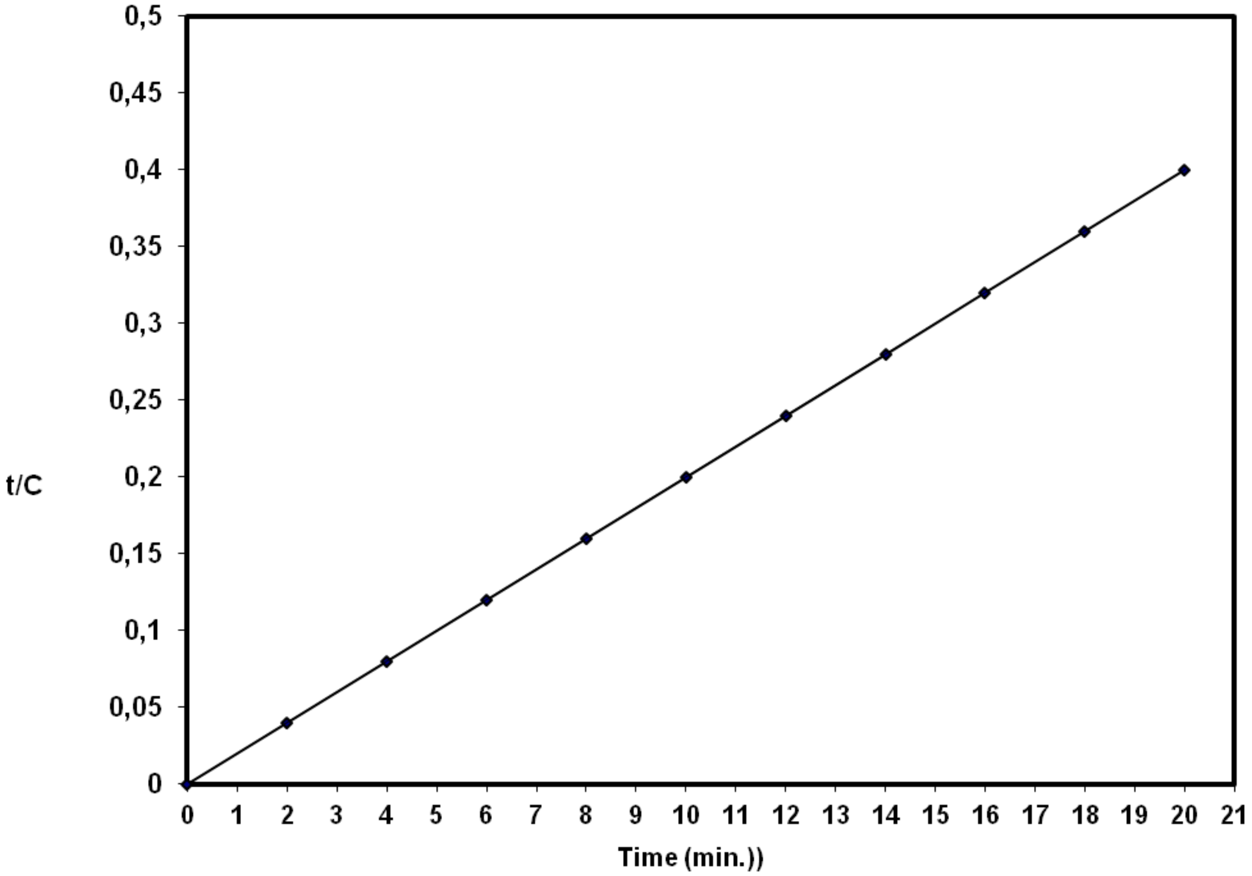

Figure 5. The dependence of the removal rate % of pesticides on time

The removal rate of pesticides can be represented by the following linear- pseudo - second – order equation:

$$\frac{t}{C} = \left[\frac{1}{Cmax}\right] t + (1/k_z)\, C^2_{max}$$

where C = the removal rate % of the pesticide at t time, C_{max} = maximum removal rate % , k_z = the reaction rate coefficient and t = electrolysis time (min).

Fig. (5) shows the plot of pseudo - second – order equation for the pesticide removal " t/C" versus " t". The straight line in plot of linear pseudo - second – order equation shows a good agreement of experimental data with the pseudo - second – order kinetic model for different removal rates. The correlation coefficient (R) for the pseudo - second – order equation was 0.99. The calculated k_z value from the plot (straight line) of Fig. (5) was 0.0156 min $\%^{-1}$. As can be seen from Fig. (5), the calculated C_{max} values from the above mentioned equation also agree very well with the experimental data. This strongly suggests that the pesticides removal rate is most appropriately represented by a pseudo - second – order process.

3.6. Effect of initial pesticides dose

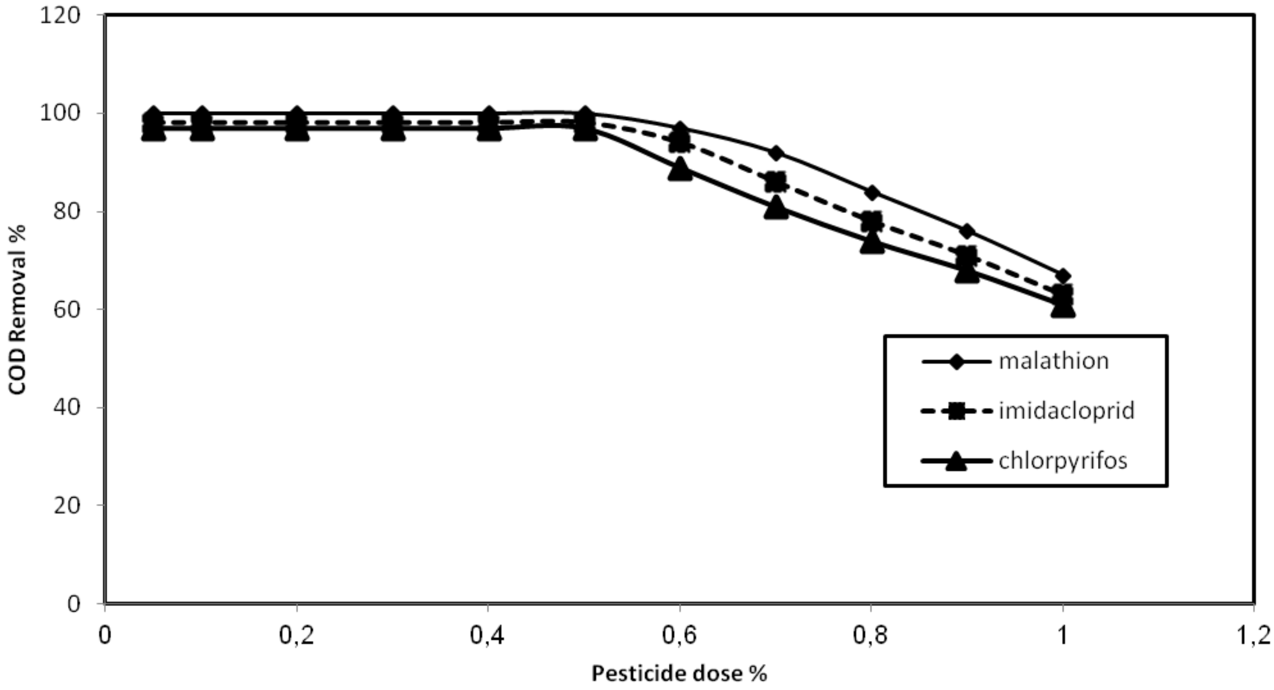

Figure 6. Effect of initial pesticide dose on removal %, keeping other variants constant.

A series of batch experiments with different initial pesticides concentration were carried out to study the effect of initial dose on the removal % during the electrocoagulation process. These experiments were carried out under the following operating conditions: current density of 1mA/cm^2, pH of 6-7, electrolysis time 10-20 min., and temperature of 25˚C. Fig. (6) shows the effect of initial pesticide dose on the removal % of the pesticide from the simulated wastewater. The plot of Fig. (6) indicated that the removal decreased at high initial concentrations of the pesticides. This is possibly due to the formation of insufficient number of iron hydroxide complexes by the electrode for a given conductivity and applied cell voltage to coagulate the excessive number of pesticide molecules at higher concentration. It is therefore, quite clear that under the present experimental conditions the lower is the pesticide concentration, the better is the removal efficiency.

3.7. Electric energy consumption

Electrical energy consumption and current efficiency are very important economical parameters in the electrocoagulation process. Electrical energy consumption was calculated using the equation [24]

$$E = u\, I\, t$$

Where E = electrical energy (Wh)**,** u = cell voltage (volt)**,** I = current in ampere (A) and t = time of electrocoagulation process (hour).

The minimum energy consumption was 1.5 kWh/kg pesticides at 1 mA/cm^2 current density for 10 min. electrolysis time. The current efficiency (C.E.) of the electrocoagulation process was calculated by the following equation [24].

$$\text{C.E.} = \frac{\Delta\, m_{exp}}{\Delta m_{theo}} \times 100$$

This calculation was based on the comparison of experimental weight loss of iron electrodes (Δm_{exp}) during electrocoagulation process with theoretical amount of iron dissolution (Δm_{theo}) according to the Faraday's Law

$$\Delta m_{theo} = \frac{M/t}{nF}$$

Where M is the molar mass of iron, (g.mole^{-1}), t is the applied electrolysis time (second), I is the current in ampere (A), n is the number of electron moles and F is the Faraday constant (F = 95487 C mole^{-1}). As $Fe(OH)_{2\,(s)}$ is supposed to be the formed species, the number of electron moles in dissolution reaction is equal to 2. The specific electrical energy consumption (SEEC) was calculated as a function of iron electrodes weight consumption during electrocoagulation in (kWh/kg Fe) using the equation [24]

$$\textbf{SEEC} = \frac{nFu}{3.6 \times 10^3\ M}$$

These calculations were carried out after optimizing the operational parameters in electrocoagulation process. The calculated values are shown in table (1). A comparison of the various characteristics with those of some other pollutants removal technologies reported in literature is given in table (2) [25-28]. The removal efficiency % of pesticides and operating time of this work are fairly suitable compared with other technologies.

Table 1. The values of specific electrical energy consumption calculated as a function of iron electrodes weight consumption during electrocoagulation in (kWh/kg Fe)

Pesticide Name	**Imidacloprid**	**Malathion**	**Chlorpyrifos**
SEEC	**0.10**	**0.09**	**0.11**

Table 2. A comparison of the various characteristics with those of some other pollutants removal technologies

Pesticides Electrodes	Malthion Removal efficiency %	Chlorpyrifos Removal efficiency %	Imidacloprid Removal efficiency %
Ti/ SnO2-Sb2O3 electrode	97	86	92
Ti/Rh modified electrode	81	69	78
Graphite electrode	95	84	90
Electrocoagulation method	100	97	98

3.8. Discussion

The Fe^{2+} ions in the electrocoagulation reactor are the common ions generated from the solution of iron anodes. In contrast OH^- ions are produced at the cathode. By mixing the solution, hydroxide species are produced which cause the removal of matrices (cations) by adsorption and coprecipitation. In the study of iron anodes, the following mechanism for the production of the metal hydroxides have been proposed [29]:

Anode : Fe(s) → Fe2+ (aq) + 2 e-
Fe2+ (aq) +2OH- (aq) → Fe (OH)2 (s)
Cathode: 2 H2O (l) + 2 e- → H2 (g) +2OH- (aq)
Overall: Fe(s) + 2 H2O (l) → Fe (OH)2 (s) + H2 (g)
Oxidation:

2 Cl- → Cl2 + 2 e-
Cl2 (g) + H2O → HOCl + H+ + Cl-
Fe (OH)2 + HOCl → Fe (OH)3 (s) + Cl-
Fe2+ → Fe3+ + e-
Fe3+ + 3 H2O → Fe (OH)3 + 3 H+

Generally, two main processes occur serially during electrocoagulation: (a) Electrolytic reactions at electrode surfaces. (b)Adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or flotation. Electrogenerated ferric ions may form monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species, depending on the pH range. These are: $FeOH^{2+}$, $Fe(OH)_2^{+}$, $Fe_2(OH)_2^{4+}$, $Fe\ (OH)_4^{-}$ **,** $Fe(H_2O)_2^{3+}$, $Fe(H_2O)_5OH^{2+}$ **,** $Fe(H\ _2O)_4(OH)_2^{+}$, $Fe(H\ _2O)_8\ (OH)_2^{+}$, $Fe_2(H_2O)_6(OH)\ _4^{2+}$, which transform finally into $Fe(OH)_3$ [30-32]. Formation rates of the different species play an important role in the pesticides removal process. Several interaction mechanisms are possible between pesticide and hydrolysis products and the rates of these depend on pH of the medium and types of ions present.

4.CONCLUSIONS

Electrocoagulation process was tested for the removal of pesticides from the simulated waste water. The effect of various operational parameters on the pesticides removal efficiency was investigated and optimized. The removal of pesticides using iron sacrificial anode was affected by the initial pH, the current density, the amount of NaCl and the initial pesticide concentration. The removal % for pesticides was $\simeq$ 98-99%. When iron used as a sacrificial anode under the operating conditions of initial pH of 6-7, current density of 1mA/cm^2, electrolysis time of 10 min, initial pesticide concentration of 0.5% and NaCl concentration of 1g/L. it was found that the removal of pesticides at the same operating conditions employed was 100% for initial pesticide concentration 0-0.5%. At above optimal conditions the electrical energy consumption and SEEC were 1.5 kwh/kg pesticide and 5.2 kwh/kg fe respectively.

The obtained results showed that pseudo-second-order equation model was found to be in a good agreement with the experimental results.

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