Removal of Imidacloprid Pesticide by Electrocoagulation Process using Iron and aluminum Electrodes

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Abstract
The main purpose of this work the removal efficiency of the pesticide imidacloprid and chemical oxygen demand (COD) from aqueous solution using the electrocoagulation process. The effect of several parameters such as initial pH, initial imidacloprid concentration, current density, type of electrolyte, salt concentration, and temperature on the pesticide and COD removal efficiency was investigated on EC performance. The obtained results showed that imidacloprid and COD removal were 95% and 89.5% by using Fe electrodes at 60 min and were 80.8% and 73.1% by using Al electrodes at 90 min. Pesticide removal kinetic followed pseudo second and first order kinetics using Fe and Al electrodes respectively. It can be concluded that electrocoagulation process by Fe electrode is very efficient and clean process for imidacloprid removal and COD from wastewater.

Keywords: Electrocoagulation; Aluminum; Iron; Electrode; Imidacloprid; Pesticide; Water treatment

Introduction
The wide use of pesticides gives rise to serious ecological problems due to their negative environmental effects. The water contamination by pesticides is an important problem that the scientists are dealing with over the year [1,2]. Imidacloprid [1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidenamine] is a widely used insecticide introduced for agricultural use in the 1990s, and it is mainly used at the present to control sucking insects in crops (e.g., aphids, thrips, whiteflies and termites) [3,4]. Imidacloprid belongs to the nicotinoid chemical family. Because of their molecular shape, size, and charge, nicotinoid fit into receptor molecules in the nervous system that normally receive the molecule acetylcholine. Imidacloprid is toxic to some species of aquatic animals at extremely low concentrations [3].

Chemicals
Sodium chloride, potassium chloride, Sodium sulfate, Sodium carbonate, sodium hydroxide, sulfuric acid, potassium dichromate, was of analytical grade and purchased from Merck. Distilled water was used for the preparation of solutions. Standard solutions of potassium dichromate (K2Cr2O7), sulfuric acid (H2SO4) reagent with silver sulfate (Ag2SO4), Mercury sulfate (HgSO4) and were prepared to measure the COD. A stock solution of pesticide (500 mg/L) was prepared by dissolving an accurate quantity of the pesticide in distilled water and suitably diluted to the required initial concentrations. Different standard solutions of pesticide with concentration from 30-150 mg L−1 were prepared to measure its removal at different conditions. The pH of the working solution was adjusted to the desired values with 0.1N HCl or 0.1N NaOH.

Equipments and procedures
The electrocoagulation unit consisted of a 100 ml electrochemical reactor with iron and aluminum electrodes with an effective surface area of 5.4 cm². The electrodes were 17 mm×10 mm and inter electrode distance was 1 cm. The electrodes were positioned vertically and parallel to each other. The current density was maintained constant by means of a precision DC power supply; model (DZ040019) EZ Digital CO. Ltd. (Korea). The pesticide concentration was determined using a double -
beam UV-Vis spectrophotometer, model UV 1601 is from Shimadzu (Japan) at 270 nm. Hot Plate, model (HB502), BIBBY STERILIN LTD. (U.K.). A pH meter model AC28, TOA electronics Ltd., (Japan). Water bath model SB-650, Tokyo Kikakkai CO. Ltd., (Japan). A closed reflux colorimetric unit was used for the COD determination. Chemical Oxygen Demand (COD), HANNA instruments, Thermo reactor, model C9800 in Hungary - Europe.

Analysis

Two main parameters were measured to evaluate the electrochemical treatment efficiency, the remaining pollutant concentration and the COD. Remaining pollutants (imidacloprid) concentration was measured with the double-beam UV-visible spectrophotometer at λ_max=270 nm using calibration curve with standard error ±0.5%. The COD was determined using a closed reflux colorimetric method. The equation used to calculate the pesticide removal efficiency in the treatment experiments was:

\[
\%E = \left( \frac{A_0 - A}{A_0} \right) \times 100
\]  

Where A₀ and A are absorbance values of pesticide solutions before and after treatment with respect to their λ_max [32].

The calculation of COD removal efficiencies after electrocoagulation treatment was performed using the following formula [33].

\[
C_n(\%) = \left[ \left( C_n - C \right) / C_n \right] \times 100
\]

Where C₀ and C are concentrations of wastewater before and after electrocoagulation.

Result and discussion

Mechanism of electrocoagulation process

The mechanism of the electrochemical process in aqueous systems is well known. There are three possible mechanisms involved in the process, i.e. electrocoagulation, electrotallotropation and electro-oxidation. In EC, with electrical current flowing between two electrodes, the coagulant is generated in situ by electrolytic oxidation of the anode material. By using an iron and aluminum anode the Fe(OH)₄ and Al(OH)₃ formation with n = 2 or 3 is released at the anode [32-34].

EC using iron electrodes

Mechanism 1:

At anode:

\[
4 Fe (s) \rightarrow 4 Fe^{2+} (aq) + 8 e^{-}
\]

\[
4 Fe^{2+} (aq) + 10 H_2O l (i) \rightarrow 4 Fe(OH)_{3(aq)} + 8 H^+ (aq)
\]

At cathode:

\[
8 H^+ (aq) + 8 e^{-} \rightarrow 4 H_2 (g)
\]

Overall:

\[
4 Fe(s) + 10 H_2O l (i) + O_2(g) \rightarrow 4 Fe(OH)_{3(aq)} + 4 H_2 (g)
\]

Mechanism 2:

At anode:

\[
Fe^{2+} (aq) \rightarrow Fe^{3+} (aq) + 2 e^{-}
\]

\[
Fe^{3+} (aq) + 2 OH^- (aq) \rightarrow Fe(OH)_{3(aq)}
\]

At cathode:

\[
2 H_2O l (i) + 2 e^{-} \rightarrow H_2 (g) + 2 OH^- (aq)
\]

Overall:

\[
Fe^{2+} (aq) + 2 H_2O l (i) \rightarrow Fe(OH)_{3(aq)} + H_2 (g)
\]

EC using aluminum electrodes

The electrochemical reaction with Al anode can be summarized as follows:

At anode:

\[
Al (s) \rightarrow 2Al^{3+} (aq) + 6 e^{-}
\]

\[
2Al^{3+} (aq) + 6H_2O (l) \rightarrow 2Al(OH)_{3(s)} + 6H^+ (aq)
\]

At cathode:

\[
6H^+ (aq) + 6e^{-} \rightarrow 3H_2 (g)
\]

Overall:

\[
2Al(s) + 6H_2O (l) \rightarrow 2Al(OH)_{3(s)} + 3H_2 (g)
\]

The generation of metal hydroxides (Fe(OH)n and Al(OH)n) are followed by an increase in the concentration of colloids (usually negatively charged) in the region close to the anode [35]. The produced ferrous ions hydrolyze to form monomeric hydroxide ions and polymeric hydroxide complexes that depend on the pH of the solution. The polymeric hydroxides, which are highly charged cations, destabilize the negatively charged colloidal particles allowing the formation of flocks. When the amount of iron in the solution exceeds the solubility of the metal hydroxide, the amorphous metal hydroxide precipitates is formed, which causes sweep flock coagulation [36].

Effect of electrolyte concentration

To evaluate the effect of the salt concentration on imidacloprid removal efficiency and COD, different electrolyte solutions were prepared by the addition of different amounts of NaCl varied from (0.5 - 3 g/L) at a current density of 18.5 mA/cm², initial concentration 50 mg L⁻¹, inter electrode distance of 1 cm, pH of 6.9 and temperature of 20 °C. NaCl was used as a supporting electrolyte to increase the solution conductivity. Figure 1 and Table 2 shows that the pesticide removal efficiency increased from 76.5 to 95% using (Fe) and 67 to 80% using (Al) electrodes, and COD from 65 to 89.5% using (Fe) and 51 to 73% electrodes. As the NaCl concentration increased from 0.5 to 1 g/L. We can see from Figure 1 that increases in the amount of NaCl results in increasing removal efficiency. Therefore, we thought that the EC in the presence of NaCl could improve the imidacloprid removal efficiency by increasing the availability of metal coagulants in the solution and by leading to a reduction of the oxide layer and an enhancement of the anodic dissolution of the electrode material [37].

Effect of current density

Current density is very important parameter that affects the
electrocoagulation process because it directly determines both coagulant dosage and bubble generation rates and strongly influences both solution mixing and mass transfer at the electrodes. So current density is the key operational parameter that affecting the system’s response time and also influencing the dominant pollutant separation mode [38].

To examine the effect of current density on removal efficiency of imidacloprid and COD, a series of experiments were carried out with the current density being varied from 9-55 mA/cm². At initial concentration of 50 mg L⁻¹, inter electrode distance of 1 cm, pH=6.9, inter electrode distance= 1 cm, dimension of the electrodes = 17 mm \times 10 mm and temperature = 20°C. Figure 2 and Table 2 show the effect of current density for the removal of pesticide and COD at a current density of 18.5 mA/cm², NaCl concentration of 1 g L⁻¹ and temperature of 20°C. Figure 4 and Table 3 shows the pesticide removal efficiency and COD after 60 min using (Fe) and 90 min using (Al) electrodes as a function of pH. In (Fe) electrode Figure 4 (a) the removal efficiency of the pesticide and COD is higher in neutral medium (PH6.9), meanwhile, in acidic and alkaline are less. In Al electrodes Figure 4(b) the removal efficiency of the pesticide and COD is low in acidic medium (PH 2.4 and 5.2), meanwhile higher efficiencies were recorded in 6.9-10 pH range which is close to the optimal pH for Al(OH)₃ solid formation. The flocks of Al(OH)₃ have large surface areas, which are useful for a rapid adsorption of soluble organic compounds and trapping of colloidal particles [40].

**Effect of initial concentration of pesticide**

The effect of initial pesticide concentration on the pesticide removal efficiency of anodic dissolution, resulting in a greater pesticide removal rates, showing the pesticide removal efficiency and COD after 60 min using (Fe) and 90 min using (Al) electrodes. Initial concentration of the pesticide 50 mg/L, volume of the solution = 100 ml, NaCl concentration = 1 g/L,a current density of 18.5 mA/cm², pH = 6.9, inter electrode distance = 1 cm, dimension of the electrodes = 17 mm \times 10 mm and temperature = 20°C.

**Table 2: Effect of current density, pH, type of electrolyte, concentration electrolyte, pesticide concentration, and temperature on the efficiency of COD removal for imidacloprid using Fe (a) and Al (b) electrodes.**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Current density (mA/cm²)</th>
<th>pH</th>
<th>NaCl (g/L)</th>
<th>Na2CO3 (g/L)</th>
<th>KCl (g/L)</th>
<th>Electrolyte</th>
<th>Temperature (°C)</th>
<th>COD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>37</td>
<td>18.5</td>
<td>9</td>
<td>NaCl</td>
<td>65.5</td>
<td>COD (%)</td>
<td>55.2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>6.9</td>
<td>5.2</td>
<td>2.4</td>
<td>KCl</td>
<td>pH</td>
<td>Na2CO3 (g/L)</td>
<td></td>
</tr>
<tr>
<td>65.6</td>
<td>67.1</td>
<td>73.1</td>
<td>61.1</td>
<td>32.8</td>
<td>KCl</td>
<td>Electrolyte</td>
<td>Na2CO3 (g/L)</td>
<td></td>
</tr>
<tr>
<td>63.1</td>
<td>73.1</td>
<td>45</td>
<td>60.1</td>
<td>KCl (g/L)</td>
<td>61</td>
<td>2.1</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>52.1</td>
<td>54.3</td>
<td>73.1</td>
<td>50</td>
<td>PESTICIDE [mg/L]</td>
<td>150</td>
<td>50</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>65.6</td>
<td>65.6</td>
<td>73.1</td>
<td>76.1</td>
<td>COD (%)</td>
<td>40</td>
<td>30</td>
<td>20</td>
<td>64.1</td>
</tr>
<tr>
<td>30</td>
<td>40</td>
<td>10</td>
<td>Temperature (°C)</td>
<td>71.6</td>
<td>84</td>
<td>84.2</td>
<td>89.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>70.1</td>
<td>71.6</td>
<td>64.1</td>
<td>COD (%)</td>
<td>85</td>
<td>89.5</td>
<td>89.5</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1: Effect of electrolyte concentration on the efficiency of imidacloprid removal using Fe (a) and Al (b) electrodes.** Initial concentration of the pesticide = 50 mg/L, volume of the solution = 100 ml, current density of 18.5 mA/cm², pH=6.9, inter electrode distance = 1 cm, dimension of the electrodes = 17 mm \times 10 mm and temperature = 20°C.

**Figure 2: Effect of initial pesticide concentration on the efficiency of pesticide removal**

**Figure 3a: Effect of initial pH on the efficiency of pesticide removal**

**Figure 3b: Effect of inter electrode distance on the efficiency of pesticide removal**

**Figure 4a: Effect of electrolyte concentration on the efficiency of imidacloprid removal using Fe (a) and Al (b) electrodes.** Initial concentration of the pesticide = 50 mg/L, volume of the solution = 100 ml, current density of 18.5 mA/cm², NaCl concentration of 1 g L⁻¹ and temperature of 20°C. Figure 4 and Table 3 indicate that increasing temperature has a negative effect on removal efficiency of pesticide and COD, where at 20°C the pesticide removal and COD% reached to maximum. While at higher temperature value (30 and 40°C) the pesticide removal and COD% dropped to low values. In this case, the volume of colloid M (OH)₃ will decrease and pore production on the metal anode well be closed [38].

**Effect of initial pH**

It has been established that the influent pH is an important operating factor influencing the performance of electrochemical process [39]. These experiments were carried out to evaluate the effect of pH, using solutions containing a sample with an initial pH varying in the range (2.4 -10) at initial concentration of 50 mg L⁻¹, inter electrode distance of 1 cm, a current density of 18.5 mA /cm², NaCl concentration of 1 g L⁻¹ and temperature of 20°C. Figure 4 and Table 3 show the effect of initial pH on the efficiency of pesticide and COD. Table 2 indicate that increasing temperature has a negative effect on removal efficiency of pesticide and COD, where at 20°C the pesticide removal and COD% reached to maximum. While at higher temperature value (30 and 40°C) the pesticide removal and COD% dropped to low values. In this case, the volume of colloid M (OH)₃ will decrease and pore production on the metal anode well be closed [38].

**Effect of initial pH**

The effect of initial pH on the efficiency of pesticide removal shows the pesticide removal efficiency and COD after 60 min using (Fe) and 90 min using (Al) electrodes. Initial concentration of the pesticide = 50 mg/L, volume of the solution = 100 ml, NaCl concentration = 1 g/L,a current density of 18.5 mA/cm², pH = 6.9, inter electrode distance = 1 cm, dimension of the electrodes = 17 mm \times 10 mm and temperature = 20°C.
was examined with solutions including pesticide of 30, 50, 100 and 150 mg/L at a current density of 18.5 mA/cm², pH of 6.9, inter electrode distance of 1 cm, NaCl concentration of 1 g L⁻¹ and temperature 20°C. According to the Figure 5 and Table 2, it may be seen that increasing initial pesticide concentration results in decreasing removal efficiency. In fact, when the initial concentration varied from 50 to 150 mg/L, the removal percentage was 95% and 79% using (Fe) and 80% and 66% using (Al). Adsorption on iron and aluminium hydroxide is the main pesticide molecule removal pathway. So, for a constant current intensity, there is obviously the same amount of electrogenerated iron and aluminium cations and hence the same amount of coagulating species. It is more likely that with increasing the initial pesticide concentration, less adsorption sites are available to capture organic pesticide molecules in excess [41,42].

**Effect of type of electrolyte**

Figure 6 and Table 2 explain the effect of electrolyte type on the removal efficiency of imidacloprid and COD at 60 min using Fe and 90 min using Al electrodes in the presence of different supporting electrolytes including NaCl, KCl, Na₂SO₄ and Na₂CO₃, was studied at initial concentration of 50 mg L⁻¹, a current density of 18.5 mA/cm², pH of 6.9, inter electrode distance of 1 cm, NaCl concentration of 1 g L⁻¹ and temperature 20°C. According to Figure 6 and Table 2, pesticide removal at NaCl, is better than KCl, Na₂CO₃ and Na₂SO₄. Higher elimination of pesticide and COD in the presence of NaCl (95%) and (89.5%) using Fe electrodes and (80%) and (73%) using Al electrodes respectively, may be due to higher ionization of this compound. Due to formation of hypochlorite (OCl⁻) and hypochlorous acid (HOCl). It is well known that Cl⁻ anions can destroy the formed passivation layer on electrode and therefore enhance anodic dissolution rate of metal which lead to produce more metal hydroxide [43,44].

**Kinetic studies**

Kinetics studies have important role in determining the rate constant and the order of reaction of this treatment removal [45]. So, rate constant is very significant in the design of wastewater treatment units. It is very essential to know the type of reaction rates for design a wastewater treatment unit. Rate of reaction describes the rates of change in concentration of reactant per unit time. Figures 7 (a) and

### Table 3: Comparison between the Electrocoagulation method for removal of imidacloprid with other methods.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Type of degradation</th>
<th>Reference</th>
<th>Removal %</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidacloprid</td>
<td>Photolysis</td>
<td>P. N. Moza et al. [7]</td>
<td>90%</td>
<td>4 hours</td>
</tr>
<tr>
<td></td>
<td>photo-Fenton oxidation</td>
<td>C. Segura et al. [8]</td>
<td>50%</td>
<td>1 min</td>
</tr>
<tr>
<td></td>
<td>Electro-catalytic oxidation</td>
<td>P. Garrett. [10]</td>
<td>78%</td>
<td>53.2 min</td>
</tr>
<tr>
<td></td>
<td>Electro-Fenton</td>
<td>O. Iglesias et al. [11]</td>
<td>100%</td>
<td>120 min</td>
</tr>
<tr>
<td></td>
<td>Electrocoagulation (Fe electrode)</td>
<td>This study using</td>
<td>95%</td>
<td>60 min</td>
</tr>
<tr>
<td></td>
<td>Electrocoagulation (Al electrode)</td>
<td>This study using</td>
<td>80.8%</td>
<td>90 min</td>
</tr>
</tbody>
</table>

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Figure 4: Effect of pH on the efficiency of imidacloprid removal using Fe (a) and Al (b) electrodes. Initial concentration of the pesticide = 50 mg/L, volume of the solution = 100 ml, NaCl concentration = 1 g/L, current density of 18.5 mA/cm², inter electrode distance = 1 cm, dimension of the electrodes = 17 mm × 10 mm and temperature = 20°C.

Figure 6: Effect of type of electrolyte on the efficiency of imidacloprid removal using Fe (a) and Al (b) electrodes. Initial concentration of the pesticide = 50 mg/L, volume of the solution = 100 ml, current density of 18.5 mA/cm², pH=6.9, inter electrode distance = 1 cm, dimension of the electrodes = 17 mm × 10 mm and temperature = 20°C.

Figure 5: Effect of initial concentration on the efficiency of imidacloprid removal using Fe (a) and Al (b) electrodes. NaCl concentration = 1 g/L, volume of the solution = 100 ml, current density of 18.5 mA/cm², pH=6.9, inter electrode distance = 1 cm, dimension of the electrodes = 17 mm × 10 mm and temperature = 20°C.

Figure 7: Relation between 1/Aₜ and Ln Aₜ against the time for imidacloprid removal using Fe (a) and Al (b) electrodes. Initial concentration of the pesticide = 50 mg/L, volume of the solution = 100 ml, current density of 18.5 mA/cm², pH=6.9, NaCl concentration = 1 g/L, inter electrode distance = 1 cm, dimension of the electrodes 17 mm × 10 mm and temperature = 20°C.
7(b) represent the removal of imidacloprid exhibited pseudo second order with good correlation coefficients (>0.98) using Fe electrodes according to following equation:

$$\frac{1}{A_t} - \frac{1}{A_0} = Kt$$

and exhibited pseudo first order with good correlation coefficients (>0.97) for Al electrodes according to following equation:

$$\ln \frac{A_0}{A_t} = -kt$$

Where $A_t$, $A_0$, t, and k are the pesticide absorbance at initial concentration, pesticide absorbance at each time, time of reaction (min), and reaction rate constant, respectively. Figures 7 (a) and 7(b) explain the plot of pseudo second order and pseudo first order equations for the pesticide removal using Fe and Al electrodes respectively. The straight lines in plot show a good agreement of experimental data with the kinetic models for different removal rates. The calculated k values from the plot (straight line) of Figures 7(a) and 7(b) were 0.0212 mol $^{-1}$ dm$^{-3}$ min$^{-1}$ and 0.0079 min$^{-1}$ using Fe and Al electrodes respectively.

Conclusion

The removal efficiency of imidacloprid from aqueous solution was examined by electrocoagulation using iron (Fe) and aluminum (Al) electrodes. The effects of initial pH, initial abamcent concentration, current density, type electrolyte, salt concentration, and temperature were investigated on removal efficiency and COD. It was observed that these variables significantly affected the imidacloprid pesticide removal efficiency. The optimum imidacloprid pesticide removal was obtained with typical operating conditions: an initial pH of 6.9, an initial pesticide concentration of 50 mg/L, current density 18.5 mA/cm$^2$, salt concentration of 1 g/L and temperature of 20°C, the results showed that imidacloprid and COD removal were 95% and 89.5% by using Fe and were 80.8% and 73.1%, by using Al electrodes. The removal of pesticide was exhibited pseudo second order with rate constant 0.0212 mol $^{-1}$ dm$^{-3}$ min$^{-1}$ for Fe electrode and pseudo first order with rate constant 0.0079 min$^{-1}$ using Al electrodes.

References