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Degradation of Pesticide Monochrotophos from Aqueous Solutions by Electrochemical Methods

*H. Cengiz Yatmaz**, *Yasin Uzman*

Gebze Institute of Technology, Environmental Engineering Department, Gebze 41400 Kocaeli, Turkey
*E-mail: yatmaz@gyte.edu.tr

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The degradation of toxic monochrotophos (MCP) was comparatively studied by electrochemical methods such as direct electrooxidation, indirect electrooxidation, electrocoagulation and electro-Fenton processes. In the direct electrooxidation process using Ti electrodes in electrolyte solutions (6 g/L of NaCl) at two different current densities of 50 and 100 A/m^2, degradation of MCP from aqueous solutions in different initial concentrations (50, 100, 200, 300 mg/L) was investigated to evaluate MCP degradation. It was determined that increases in the initial MCP concentration and current density lead to increase MCP degradation. In this process, considering the effects of different electrolyte concentrations of NaCl (1, 3, 6 g/L) and different electrolyte (6 g/L Na_2SO_4), it was observed that high NaCl concentration increases the MCP degradation and decreases the energy consumption. The degradation and removal of 300 mg/L MCP solution by electrocoagulation using Fe electrodes (pH 8.5, 6 g/L NaCl, 93 A/m^2) was investigated and 78 % removal was achieved. The degradation and mineralization of 300 mg/L MCP solution (6 g/L NaCl, 50 A/m^2) by the indirect electrooxidation processes using Ti electrodes by adding 2 mmol H_2O_2/min was also investigated and 100 % MCP degradation and 20 % TOC removal was obtained. Finally, the degradation and mineralization of 300 mg/L MCP solution (6 g/L NaCl, 93 A/m^2) by the electro-Fenton process using Fe electrodes by adding 2 mmol H_2O_2/min was performed. It was observed that MCP was degraded completely in less than 5 min and was mineralized up to the yields of 66 % efficiency for 90 min.

Keywords: Organophosphorus pesticide, Monochrotophos, electrooxidation, electrocoagulation, electro-Fenton process

1. INTRODUCTION

Food and Agricultural Organization of United Nations estimated that 400.000-500.000 tones of obsolete pesticides are stocked in developing countries [1]. The disposal of such pesticide wastes can cause serious problems due to the chemical nature of the active ingredients in pesticide formulation and due to the large quantities of the unwanted products. Although, those pesticide wastes are not suitable for use, they still contain toxic compounds. On the basis of global estimates totaling 250.000 tones of obsolete pesticides, about 1.25 billion USD would be needed to destroy all stocks [2]. Monochrotophos (MCP) is an organophosphorous insecticide and acaricide. The EPA classifies monochrotophos as a class I toxicity: highly toxic.

Biological degradation of pesticides is generally difficult to their high content in toxic matter. Today the main disposal method of obsolete stock is incineration, an impractical and expensive procedure. High-temperature incineration in dedicated hazardous waste incinerators is currently recommended method for obsolete pesticide treatment. However, sophisticated incinerators do not exist in developing countries and the hazardous wastes incinerating in incinerators change new toxic wastes giving off and into the air [3].

Recently, electrochemical methods have attracted significant attention for treating recalcitrant toxic wastes. The advantages of electrochemical treatment are various and well documented: the catalyst/electrode is immobilized (thus reducing the need to separate the catalyst from the reaction mixture), the variables (i.e. current and potential) are easily controlled and facilitate automation of a process and the cost of equipment is generally not too high. In addition, electrochemical processes are easily adapted for use in flow systems, a fact that is considered important for the feasibility of pesticide treatment systems [4].

In recent studies, many organophosphorus pesticides such as methyl parathion [5], demeton-S-methyl, metamidophos, diazinon, fenthion [6], malathion, parathion ethyl, tetra-ethyl-pyrophosphate (TEPP) [7], phosalone, azinphos-methyl, methidathion [8] have been treated successfully by the electrochemical methods. Good removal rates were observed and it is suggested that electrochemical methods can be used as a pre-treatment step in pesticide waste disposal and pesticide containing waste from aqueous solutions [9-13].

The toxic organic contaminants are usually destroyed by oxidants such as Cl_2, ClO_2, O_3, OH●, ClOH●, H_2O_2 etc. that produced from anodic oxidation during electrolysis [14-16]. The detailed electrochemical reactions taking place during the electrolysis of a brine solution are complicated and not entirely known [16]. In anodic oxidation (AO) organic pollutants are destroyed in an electrolytic cell by absorbed hydroxyl radical formed as intermediate from water oxidation to O_2 at the surface of high O_2-overvoltage anode as follows:

$$M + H_2O \rightarrow M(OH^-) + H^+ + e^- \quad (1)$$

where M(OH●) denotes the absorbed hydroxyl radical are the anode M.

After this the absorbed hydroxyl radicals oxidizes the organic matter:

$$R + M(OH^-) \rightarrow M[\ ] + RO + H^+ + e^- \quad (2)$$

Where RO represents the oxidized organic matter which can be produced continuously by hydroxyl radicals which are also continuously formed [6, 16, 17].

The radicals, OH●, O●, and ClOH●, have very short half-lives due to their high oxidation potential and they either convert to other oxidants (such as Cl_2, O_2, ClO_2, O_3, and H_2O_2) or oxidize organic contaminants (direct oxidation). The primary (Cl_2,O_2) and secondary (ClO_2, O_3,and H_2O_2) oxidants produced from the destruction of radicals have reasonably long half-lives and diffuse into the area away from the electrode, thus continuing the oxidation process (indirect oxidation) [6,16].

The electro-Fenton degradation of some aromatic compounds, mainly herbicides and organophosphorus pesticides, dyes, industrial pollutants and pharmaceuticals as emerging pollutants using different electrolytic cells has also been previously studied [18-21].

Some of the most frequently used AOPs are based on hydroxyl radical production from H_2O_2 decomposition in the presence of ferrous ions at acid pH as Fenton's reaction. In acidic medium, electrochemically produced Fe^{2+} and continuously supplied H_2O_2 are enhanced by the production of OH● from the classical Fenton's reaction (3). These processes are usually carried out at acid pH values in order to keep the iron catalyst soluble and to increase the oxidative activity of the hydroxyl radical [22].

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH\bullet \rightarrow Fe^{3+} + OH\bullet + H_2O \qquad (3)$$

Fe^{2+} production is carried out with a sacrificial Fe anode, which continuously supplies soluble Fe^{2+} to the solution from the following reaction [21]:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (4)$$

A part of Fe^{3+} ions is produced from Fenton's reaction (3) between electrogenerated Fe^{2+} and supplied H_2O_2 and precipitates in the form of $Fe(OH)_3$. In these reactions organic pollutants can be removed by the direct oxidizing action of OH●, as well as by their coagulation with the $Fe(OH)_3$ precipitate [19].

Catalytic reaction is propagated from Fe^{2+} regeneration mainly by reduction of Fe^{3+} with H_2O_2. After addition of H_2O_2 to the initial solution, organics are simultaneously degraded during electrolysis by OH● formed by reaction (3) [23]. The large amount of OH● are generated at the anode from oxidation of water (5) [24].

$$2\ H_2O \rightarrow 2\ OH\bullet_{ads} + 2\ H^+ + 2e^- \qquad (5)$$

In this present study, in order to compare the effect of four different electrochemical processes; direct electrooxidation, indirect electrooxidation, electrocoagulation and electro-Fenton processes of monochrotophos (MCP) degradation and mineralization were performed and process efficiencies were evaluated.

2. MATERIALS AND METHODS

Chemicals

Analytical grades of sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) were used as electrolytes from Merck. pH values were adjusted by 0.1M sulfuric acid (H_2SO_4) and 0.1M sodium hydroxide (NaOH) as required. Hydrogen peroxide (H_2O_2, 30% from Merck) was used for both indirect oxidation and electro-Fenton process. Mobile phase compounds which were acetonitrile (HPLC Grade) and orto-phosphoric acid were obtained from Fluka. Solutions were prepared with high-purity water from Elix Millipore System. Potassium hydrogen phthalate was obtained as a reagent grade from Merck. Analytical Standard Monochrotophos solid (MCP, Dimethyl (E)-1-methyl-2-(methyl-carbamoyl) vinyl phosphate) were obtained from Fluka and the structure of MCP is presented in Figure 1.

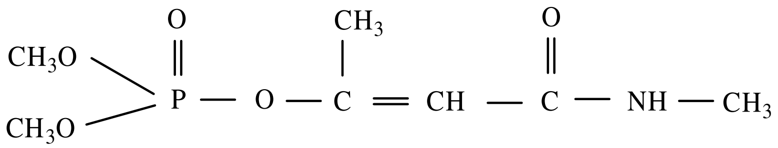

Figure 1. Chemical structure of Monochrotophos (MW: 223.2 g/mol).

Apparatus

A laboratory model DC power supply (Good Will, GPS-3030D) was used for electrolysis. Electrolysis were carried out at room temperature in a cylindrical open glass cell of 500 mL equipped with two electrodes by vigorously stirred with a magnetic bar (500 rpm). The working electrodes were 50 cm^2 titanium electrodes and 27 cm^2 iron electrodes obtained commercially. Electrochemical cell is shown in Figure 2.

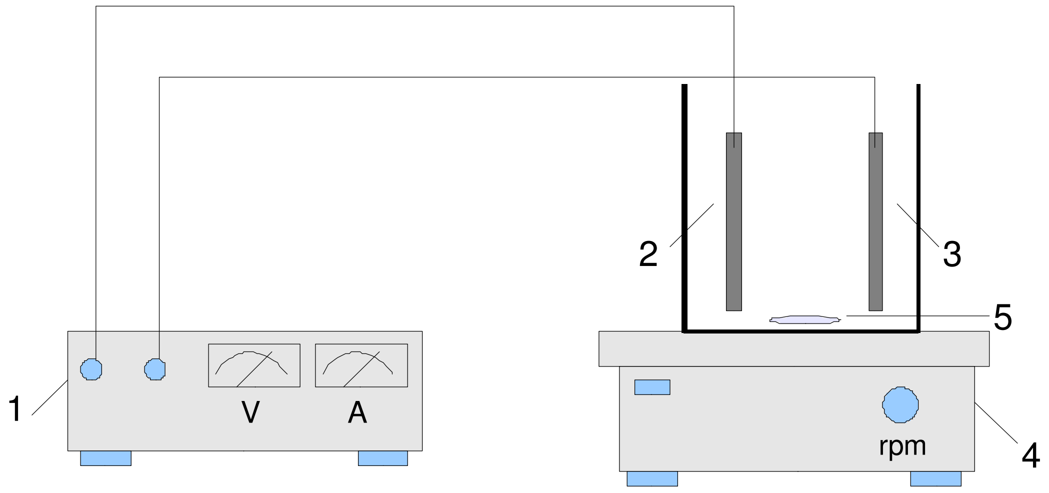

Figure 2. Reactor used in the electrochemical processes: 1. DC power supply; 2. anode electrode; 3. cathode electrode; 4. stirrer; 5. magnetic bar.

Analytical Procedures

The degradation and calibration curve of MCP were monitored by using HPLC (Thermo Lab Alliance, Essence System) with a reverse phase Microsorb MV 100-5, C18, 150x4 column. The column was eluted with a mixture of acetonitrile/water/phopshoric acid at 30:69.5:0.5 (v/v/v). The injection volume was 20 µL. The concentration of MCP was monitored using an UV detector (Lab Alliance, Models 201) at λ=230 nm. TOC calibration curve (using potassium hydrogen phthalate) and total organic carbon content were measured in a model Hach Lange IL 550 TOC with 0.5 mL injection volume. Before the analysis of treated solutions, all samples were filtered through PTFE filters of 0.45 µm purchased from Whatman. The solution pH was measured with a WTW Multi 340i pH meter.

Experimental Procedures

All electrochemical experiments; direct electrooxidation, indirect electrooxidation, electrocoagulation and electro-Fenton were performed in the electrolytic cell (Figure 2). In both indirect electrooxidation and electro-Fenton processes, the hydrogen peroxide solution was added to the cell continuously. At a pre-determined time intervals, samples were collected from the cell for analysis. The current and the amount of charge passed through the solution were maintained constant and displayed continuously throughout electrolysis by means of DC power supply. All the main experimental steps were batch processes.

The aim of the direct electrooxidation by using Ti electrodes was initially to determine the influence of some basic parameters such as current density, initial concentration of MCP, electrolyte concentration and different electrolyte type on the efficiency of degradation of MCP. At the two different current densities of 50A/m^2 and 100A/m^2, the electrochemical cell contained 6 g/L NaCl electrolyte solution with a 5.5 cm distanced Ti electrodes as both anode and cathode was filled with 500 mL solutions of different concentrations of MCP (300, 200, 100 and 50 mg/L) in order to investigate the influence of initial MCP concentration and current density to the degradation. In order to investigate the effect of the NaCl concentration to the degradation and energy consumption, electrochemical cell was filled with 300 mg/L MCP concentration with a volume of 500 mL at a current density of 50 A/m^2. Finally, in the direct electrooxidation process, by using Na_2SO_4 electrolyte at a 50 A/m^2 for 300 mg/L MCP solution, the influence of different electrolyte type to the degradation was investigated.

In the indirect electrooxidation process of MCP, at a constant current density of 50A/m^2, the electrochemical cell contained 6 g/L NaCl electrolyte solution with a 5.5 cm distanced Ti electrodes as both anode and cathode was filled with 500 mL of 300 mg/L MCP solution by adjusting pH to the 3 with H_2SO_4, and H_2O_2 was fed to the cell continuously at a flow rate of 2 mmol/min in order to investigate the degradation and mineralization of MCP for Fenton effect of Ti electrodes.

In another experiment, the removal/degradation of 300 mg/L MCP solution by electrocoagulation using iron electrodes at a current density of 93 A/m^2 in electrolyte solution (6 g/L NaCl) for 90 min was studied by adjusting the solution pH to 8.5.

Finally, the degradation and mineralization of 300 mg/L MCP solution with 500 mL volume in electrolyte solution (6 g/L NaCl) by electro-Fenton process using iron electrodes as both anode and cathode by adjusting pH to the 3 at 93 A/m^2 were also investigated. H_2O_2 was fed to the cell continuously at a flow rate of 2 mmol/min.

3. RESULTS AND DISCUSSION

Degradation of MCP by direct electrooxidation by Titanium electrodes

Effect of initial MCP concentration to the degradation

Initially, the degradation of pesticide monochrotophos (MCP) from aqueous solutions in different initial concentrations (50, 100, 200 and 300 mg/L) was comparatively investigated by direct electro-oxidation process using titanium electrodes as both anode and cathode at a current density of 50 A/m^2 in NaCl electrolyte solution (6 g/L) for 90 min.

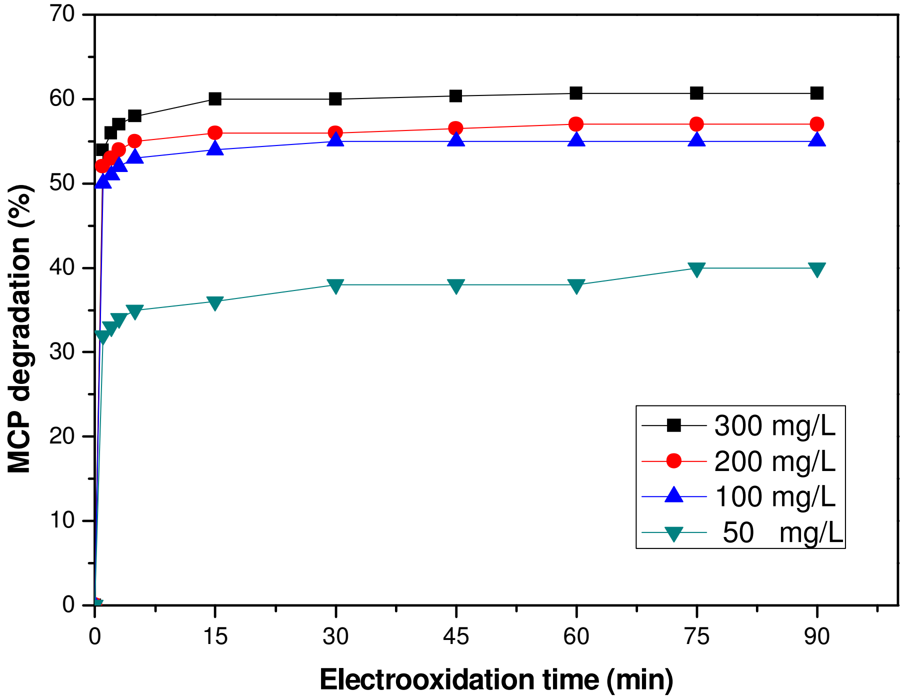

Figure 3. Percentage of MCP degradation by direct electrooxidation using titanium electrodes at a current density of 50 A/m^2.

The effects of initial MCP concentration were shown in Figure 3. As the initial MCP concentration were increased to 50, 100, 200 and 300 mg/L, MCP degradation efficiencies were increased to 40%, 56%, 58% and 62% respectively. However, the electro-oxidation reactions of MCP in all process were stopped in less than 5 minutes. This evidences that the generation of the main oxidant OH● radicals on the Ti surface from reaction (1) was stopped. The degradation of MCP was not efficiently completed in this process. The energy consumptions for all processes were calculated according to:

$$EC = \frac{VIt}{m_i - m_f} \tag{6}$$

where,

EC: energy consumption, kWh/kg MCP reduced
t: time, hour
V: cell potential, Volt
m_i: mass of initial MCP, kg
m_f: mass of final MCP, kg
I: applied current, Amper

In all process, energy consumption for all MCP concentration for five minutes were 54.17, 12.1, 10.12, 6.71 kWh/kg MCP_r respectively. As initial MCP concentration was increased the energy consumption was decreased. The electrooxidation process for 300 mg/L MCP gave the lowest energy consumption and the highest degradation efficiency.

Effect of current density to the degradation

The degradation of pesticide monochrotophos (MCP) from aqueous solutions in different initial concentrations was investigated by direct electro-oxidation process using titanium electrodes as both anode and cathode at a different current density of 100 A/m^2 in NaCl electrolyte solution (6 g/L) for 90 min.

The effect of current density was shown in Figure 4. As the current density was increased to 100 A/m^2, MCP degradation efficiencies of 50 A/m^2 were increased from 40 to 44%, 56 to 57%, 58 to 59%, and 62 to 64% respectively. As observed from different concentrations, the degradation of MCP were increased with the increasing current density, but not at expected level. At higher current density (100 A/m^2), the operating potential was increased and led to an increase in the energy consumption with respect to the 50 A/m^2. The energy consumptions for 50, 100, 200 and 300 mg/L were respectively 90, 40, 12.2, and 10.5 kWh/kg MCPr for 5 minutes. However, the electro-oxidation reactions of MCP in all process were stopped in less than 5 minutes, and the degradation of MCP was not effectively completed either. A disadvantage of direct anodic oxidation is indicated as difficult of achieving a total degradation and mineralization because of the low OH● concentration at the anode [25]

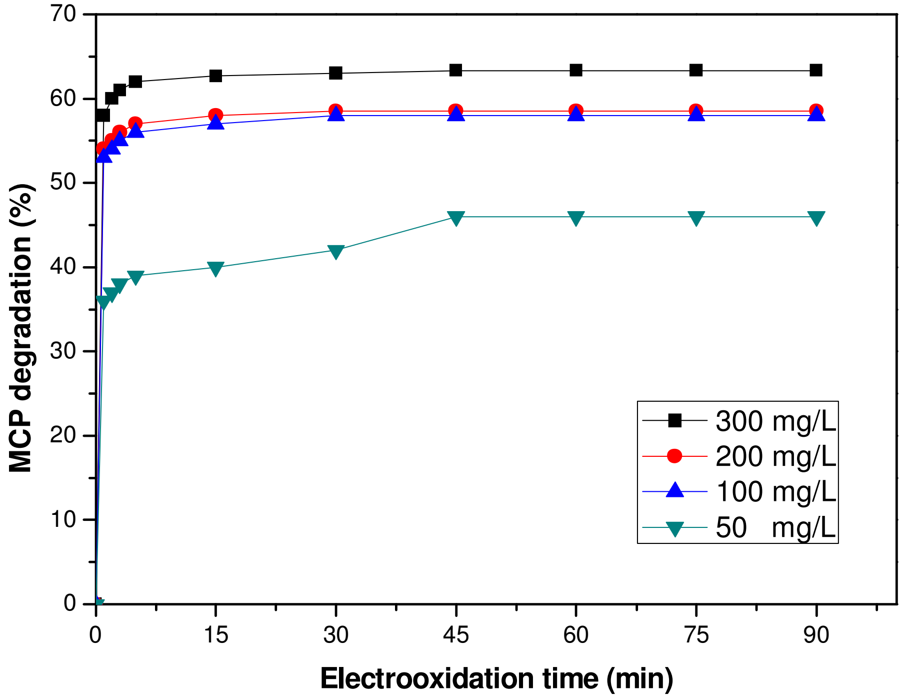

Figure 4. Percentage of MCP degradation by direct electrooxidation using titanium electrodes at a current density of 100 A/m^2.

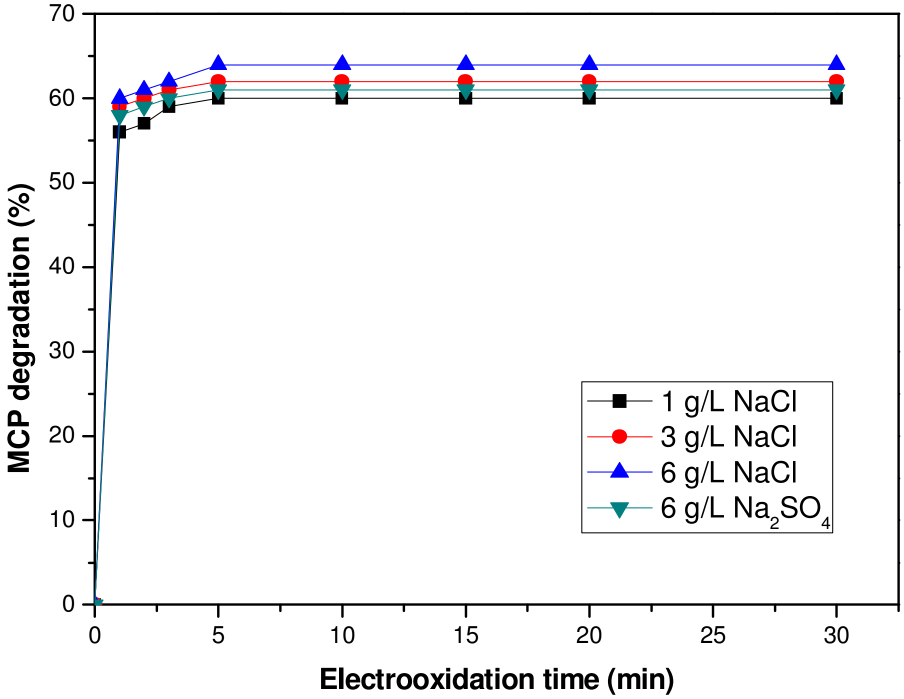

Figure 5. Percentage of 300 mg/L MCP degradation by direct electrooxidation using different NaCl concentration and different electrolyte.

Effect of NaCl concentration and different electrolyte (Na_2SO_4) to the degradation

In the direct electro-oxidation process, finally the effect of different NaCl concentrations (1, 3 and 6 g/L) and the effect of different electrolyte Na_2SO_4 concentration (6 g/L) on the degradation of 300 mg/L MCP were investigated for 30 min at current densities of 50 A/m^2 (Figure 5). The effect of electrolyte NaCl and Na_2SO_4 concentrations was not significant. As the NaCl electrolyte concentration was increased the electrochemical oxidation efficiency was increased. In each electrooxidation process, the reactions were also stopped in less than 5 minutes. The energy consumptions for 1, 3 and 6 g/L of NaCl, and 6 g/L of Na_2SO_4 were calculated as 18.21, 12.95, 6.71 and 15.35 kWh/kgMCP$_r$, respectively. Meanwhile energy consumption was increased with decreasing NaCl concentration. 6 g/L NaCl electrolyte solution gave the lowest energy consumption and the highest degradation efficiency. The results indicated that the use of high concentration of NaCl electrolyte solution would be as economically attractive for the degradation process.

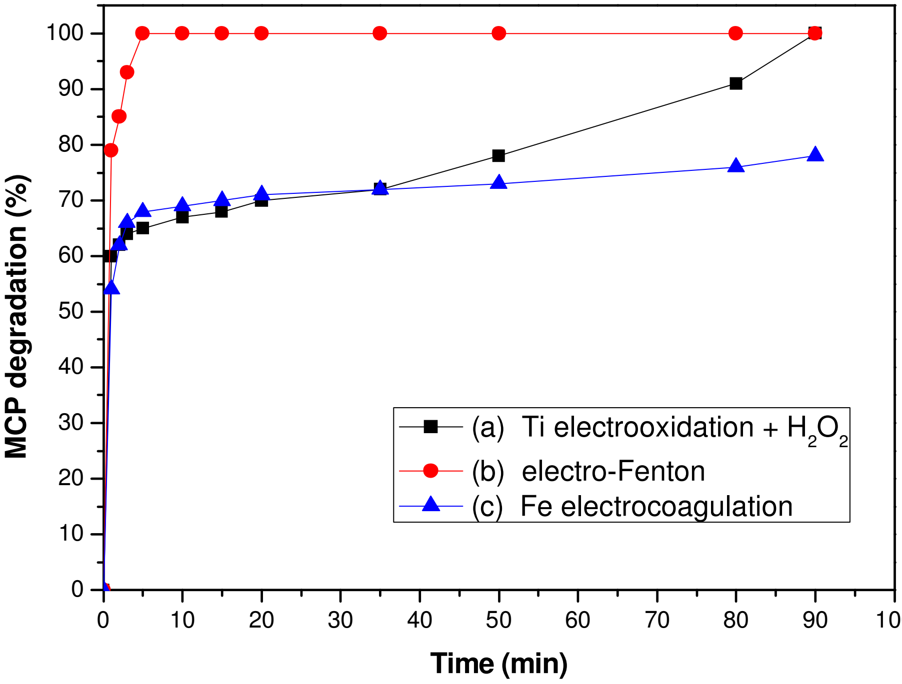

Figure 6. Percentage of 300 mg/L MCP degradation by indirect electrooxidation, electro-Fenton and electrocoagulation.

Degradation and mineralization of MCP by indirect electrooxidation

In the indirect electrooxidation process, by supplying H_2O_2 to the cell, the degradation and mineralization of 300 mg/L MCP in the acidic medium were investigated for 90 min at a current density of 50 A/m^2 in a electrolyte solution of 6 mg/L NaCl as shown in Figures 6 and 7.

Mineralization of MCP was measured as TOC removal % and the degradation of MCP was calculated as MCP degradation %. While in the direct electrooxidation process the MCP degradation was stopped in less than 5 minutes, in the indirect electrooxidation process MCP was completely degraded at 90 minutes (curve (a) of Figure 6). It was indicated in the curve (b) of Figure 7 that TOC removal was attained up to 20% at 90 min in this process. This evidences the generation of the main oxidant OH● with the presence of H_2O_2 was carried out slowly in the indirect electrooxidation process using Ti electrodes [26]. The energy consumption for degradation of MCP for 90 min was 6000 kWh/kg MCP_r which was not efficient.

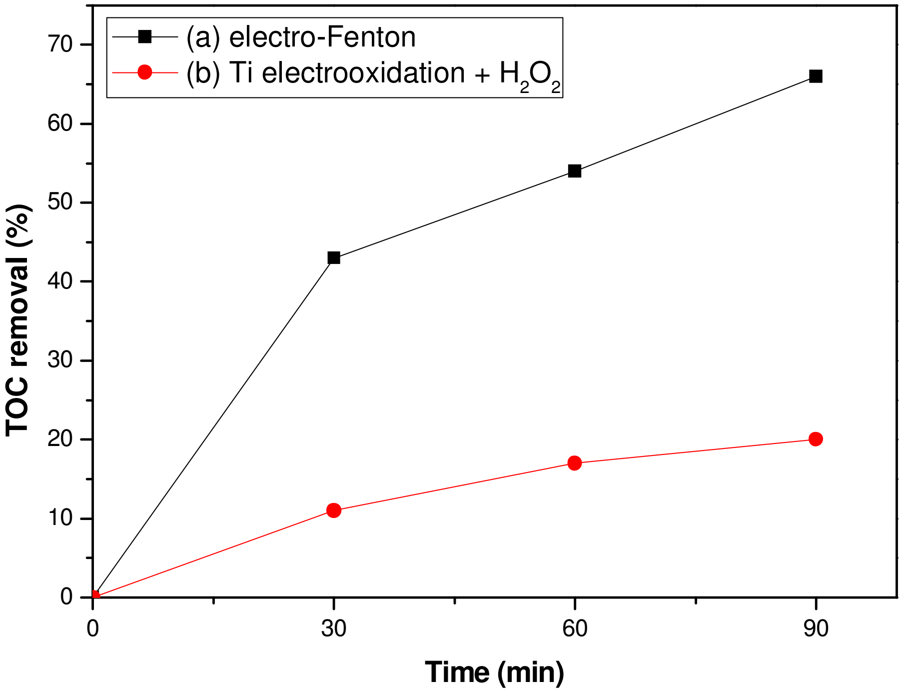

Figure 7. Percentage of TOC removal by electro-Fenton and indirect electrooxidation processes (300 mg/L MCP).

Degradation and removal of MCP by electrocoagulation

The degradation and removal of 300 mg/L MCP was investigated by electrocoagulation process using iron electrodes as both anode and cathode at a current density of 93 A/m^2 in NaCl electrolyte solution (6 g/L) for 90 min. It was shown in the curve (c) of Figure 6 that a very different behavior was observed for the electrocoagulation process where more than 65% of MCP was removed in less than 5 min and after that the removal rate suddenly decreased. This indicates that OH● oxidants also formed by the reaction (5) in the electrocoagulation process and both electrooxidation and electrocoagulation process occurs simultaneously. Thus, MCP was degraded by formed OH● oxidants and removed by the $Fe(OH)_3$ precipitate in the electrocoagulation process. Oxidation of the organic contaminants by the radicals (OH● and O●) and oxidants (O_2, O_3 and H_2O_2) produced from electrolysis could also be responsible for degradation [16]. Similarly in the direct electrooxidation process by Ti electrodes, the oxidation reaction of MCP was slow down, and at longer electrolysis time, the remaining contaminants were slowly removed and precipitated by electrocoagulation. Since it results the relocation of pesticide problem in the precipitate, the electrocoagulation process is not suitable for degradation. Moreover, this process can be used for removal of pesticide from aqueous solutions.

Degradation and mineralization of MCP by electro-Fenton

In this process, the degradation and mineralization of 300 mg/L MCP were investigated by electro-Fenton process with iron electrodes in the acidic medium by supplying H_2O_2 to the solution in order to perform electro-catalytic Fenton reaction.

In contrast to the indirect electrooxidation process, a slightly faster degradation of MCP found for electro-Fenton process as shown in curve (b) of Figure 6. 300 mg/L of MCP was degraded rapidly in less than 5 minutes by electro-Fenton process using iron electrodes. In this process, also the mineralization was measured as TOC removal and it was observed that MCP was mineralized up to the yields of 66% efficiency for 90 min as shown in curve of (a) of Figure 7. The electro-Fenton degradation can be related to the fast reaction of MCP and its oxidation products with OH● generated from reaction (5) at the anode and from the reaction (3) in the medium by the presence of Fe^{2+} in catalytic concentration. Higher TOC removal in the electro-Fenton process could be ascribed to the higher production of OH● by the continuous generation of Fe^{2+} from anode oxidation by reaction (4). Besides, the destruction of soluble TOC is a very complex process because organic indermediates also coagulate with the $Fe(OH)_3$ precipitate [25]. Electro-Fenton process became more efficient method for degradation and mineralization (detoxification) process. Energy consumption of complete degradation of MCP for 5 min was 0.834 kWh/kg MCP_r that means the highest degradation efficiency for MCP degradation process.

4. CONCLUSIONS

In the direct electrooxidation process by using Ti electrodes, increasing the initial MCP and NaCl concentration increases the MCP degradation and decreases the energy consumption. Besides increasing the current density increases the MCP degradation but also increases the energy consumption. The energy efficiency of this method decreases with increasing electrolysis time. Instead of NaCl electrolyte solution, using the same amount of different electrolyte Na_2SO_4 solution has not led to significant degradation efficiency but increased the energy consumption because of higher cell voltage.

Both direct electrooxidation and indirect electrooxidation processes by using Ti electrodes were not efficient methods for degradation of MCP because of higher energy consumption.

The electrocoagulation process by using Fe electrodes is not either effective method for the degradation of MCP. Since it causes the relocation of pesticide problem in the $Fe(OH)_3$ precipitate.

It has been demonstrated that electro-Fenton reaction by using both Fe electrodes with supplying H_2O_2 is the most effecient method for the degradation of monochrotophos in acidic medium. MCP was rapidly degraded within 5 minutes and the energy consumption of complete degradation was 0.834 kWh/kg MCP_r. In this indirect electrooxidation treatment, the MCP was also mineralized and detoxified.

In contrast, the indirect electrooxidation process by using Ti electrodes leads to a lower TOC removal than the electro-Fenton process. The electro-Fenton method may prove to be a feasible process for the detoxification of obsolete monochrotophos.

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