

Pesticides Removal from wastewater by Electrocoagulation Technique Using Stainless Steel (Ss-Ss) Plate Electrodes.

إزالة المبيدات من المياه الملوثة بطريقة التجميع الكهربى باستخدام أقطاب مستوية من الاستانليس

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المخلص:

تعد ادارة المخلفات الخطرة فى الوقت الحالى احدى التحديات التى تواجه هذا العالم التكنولوجى بسبب أطنان المخلفات العضوية التى تحتوى على أنواع كثيرة من المواد المسرطنة والتى لا تعالج بدرجة كافية قبل التخلص منها. وقد أصبحت معالجة المياه الملوثة بالمواد العضوية باستخدام طريقة التجميع الكهروكيميائى (EC) أكثر شيوعاً بسبب تميزها عن مثيلاتها - التجميع بواسطة مواد كيميائية لاسيما عندما تكون هذه الملوثات سامة. ان هذا البحث يهدف الى دراسة تأثير متغيرات العملية وتشمل: شدة التيار المار بالنسبة لمساحة القطب, وقت التفاعل, التركيز الابتدائى للمبيد, نسبة كلوريد الصوديوم المضاف, بالإضافة الى تأثير شدة واتجاه المجال المغناطيسى والتى يؤثر فى اتجاهين مختلفين, على كلا من كفاءة الازالة وكذلك استهلاك الطاقة. هذا من أجل تعين الظروف المثلى للتشغيل. وقد أوضحت النتائج الى أن كثافة التيار (20 mA/cm^2) يعد الأفضل من الناحية الاقتصادية وكذلك تركيز كلوريد الصوديوم (3.5 g/L NaCl). كما أوضحت النتائج الى ان استخدام المجال المغناطيسى فى الاتجاه الموازى للاقطاب له تأثير ايجابى على العكس فى حالة استخدامه فى الاتجاه العمودى حيث أن نسبة ازالة المبيد تصل الى 100% خلال 45 دقيقة عند شدة مجال قيمته 0.041 تسلا مؤثراً فى الاتجاه الموازى.

Abstract

Today hazardous waste management has become one of the most challenging tasks to this technological world because tons of organic pollutants including various carcinogens are being exposed without the sufficient treatment. Electrocoagulation (EC) due to some advantages over chemical coagulation is becoming a popular process to be used for treatment of organic pollutants especially when pollutants are toxic. The aim of this work is to investigate the effect of current density, reaction time, initial concentration, addition of sodium chloride and magnetic field intensity oriented in two different directions on both removal efficiency of methomyl and the energy consumption. Current density 20 mA/cm^2 was recommended from economic point of view as well as 3.5 g/L NaCl concentration. Magnetic field in parallel direction effects positive in contrary of perpendicular direction where the removal efficiency reached to 100% in 45 min when 0.041T was applied in a parallel direction.

Keywords:

Electrocoagulation; Pesticide; Stainless steel electrodes.

1. Introduction

In Egypt like other many countries over the world, the agricultural activity occupies a very important place in the socio-economic domestic context which

led to increase in using of pesticides. Indiscriminate use of pesticides leads to the contamination of our environment (soils, surface and ground waters). Numerous cases of pesticide residue and

ground water contamination have been reported in the literature [1,2]. Pesticides, which indeed seem indispensable for the nutrition of mankind, take a special place among the environmentally problematic substances. Small quantities of pesticides may enter the water environment through drift, leaching and run-off from nearby applications. The contamination of water of ponds, rivers and ground water sources with various insecticides and herbicides is posing a direct threat to human health. Therefore, the removal of pesticides from water is one of the major environmental concerns these days.

The insecticide (methomyl), $C_5H_{10}O_2N_2S$, is a broad spectrum insecticide which belongs to the carbamate family of pesticides. It is used for foliar treatment of vegetable specially tomato, fruit and field crops, cotton, commercial ornamentals, and in an around poultry houses and dairies. It is produced by reacting *S*-methyl-*N*-hydroxylthio acetamidate (MHTA) in methylene chloride with gaseous methyl isocyanate at 30 - 35 °C. It has been classified by the WHO (World Health Organization), EPA (Environmental Protection Agency, USA) and EC (European Commission) as a very toxic and hazardous pesticide [3]. Methomyl pollutant causes environmental concerns because of its high solubility in water (57.9 g/L at 25 °C). Since sorption affinity of methomyl to soils is rather low, it can easily cause contamination of both ground and surface water resources. In addition, various amounts of methomyl have been detected in surface and ground waters not only during actual insecticide application but also after a long period of use [4].

Very important issue in pesticide contamination control is preventing waste water from agricultural or industrial activities. The major sources of pollution by pesticides are waste water from agricultural industries, pesticides formulating and manufacturing plants. Waste water from those sources may

contain pesticides at levels of few $\mu\text{g/L}$ to as high as several hundred mg/L . Suitable treatment is therefore required to prevent it, which is easier than cleaning up the environment afterwards. Several methods are available for pesticides removal such as photocatalytic degradation [5], advanced oxidation processes [6], aerobic degradation [7], nanofiltration [8], ozonation [9] and adsorption [10]. Advanced oxidation processes using hydrogen peroxides are, often ineffective because carbonate and bicarbonate ions, which are abundant in all natural water, react as strong free radical scavengers. In oxidation treatment using ozone which is a powerful oxidant, the total organic carbon removal was no more than 30%. The organic pollutants are almost completely eliminated where removal of total organic carbon still remains a problem in chemical oxidation processes. The use of enzymes to detoxify wastewater failed to attract much attention due to the high cost of enzyme-based systems [11]. Filtration through membranes needs another method such as oxidation reaction catalyzed by enzyme to transform the pesticide into an insoluble product, so that this method is highly expensive.

In recent years increasing attention has been directed towards the application of electrochemical methods for environmental control. It allows flexibility in design and operation and produces aesthetically superior effluents suitable for reuse. The electrochemical process is a very efficient and economic for treatment of wastewater contains toxic and non-biodegradable organic pollutants [12, 13]. Thus by means of electrochemical technologies, which is cost and safety effective, we can help to reduce concentrations of organic pollutants to an extent as minimum as possible and comply the environmental Egyptian law for its limits acceptable of zero COD in case of hazard organic pollutants as pesticides.

In spite of the considerable success of electrocoagulation for the treatment of

temperature ($25 \pm 2^\circ\text{C}$), 250 cm^3 of the methomyl solutions with a known concentration was placed into the electrolytic cell. Magnetic field was applied on a parallel and perpendicular positions to the anode, in order to study the effect of magnetic intensity on removal of methomyl. Different intensities of magnetic field, zero, 0.016, 0.029 and 0.41 Tesla were conducted in this study.

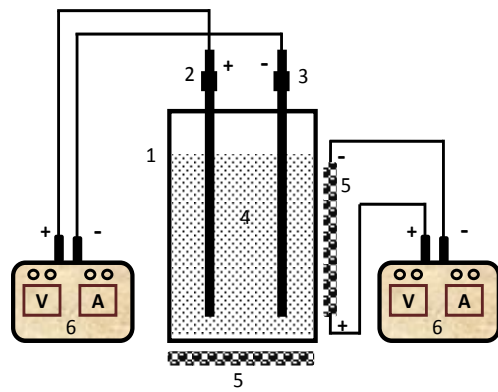


Fig. 1: Schematic diagram of experimental setup:

(1) electrochemical cell; (2) anode; (3) cathode; (4) treated solution; (5) coil to produce magnetic field (6) DC power supply.

Before each run, electrodes were washed by a dilute solution of HCl, then by distilled water in order to remove any adhering scales or oxides and the connected impurities. The efficiency of methomyl removal, % Removal, was calculated as:

$$\% \text{ Removal} = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (1)$$

where COD_i , is the initial chemical oxygen demand and its final value is COD_f .

At the beginning of a run the methomyl solution was fed into the reactor and the pH was adjusted at neutral level, then the electrodes were placed into the reactor. The reaction was timed, starting when the D.C. power supply was switched on. Samples were taken at different time using a pipette, centrifuge at 3000 rpm for

30 min then analyzed. Standard Method for Examination of Water and Wastewater was adopted for quantitative estimation of COD. The COD samples were analyzed using a Shimadzu Model UV-160 double beam spectrophotometer. The effects of current density, initial concentration, conductivity and magnetic field were investigated.

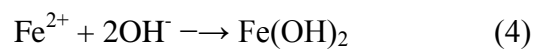
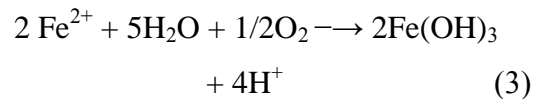
3. Process Mechanism

Electrocoagulation is a complex and interdependent process. A sacrificial metal anode is used to produce coagulating agent to dose the polluted water and electrolytic gases (mainly hydrogen at the cathode) are generated. Electrochemistry, coagulation and hydrodynamics form the basis of electrocoagulation [16].

The most widely used electrode materials in electrocoagulation process are aluminum and iron, sometimes steel. The electrical current causes the dissolution of metal into wastewater. The metal ions, at an appropriate pH value, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants [17].

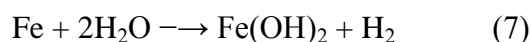
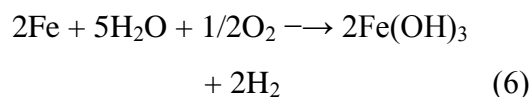
In the case of iron or mild steel electrodes, the mechanisms for the production of metal hydroxide are as [17]:

Anode reactions:



Cathode reactions:



The overall reactions:

During electrocoagulation process, metal hydroxides formation occurs, these flocs have a large surface area, which are beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or flotation.

4. Results and Discussion

The electrocoagulation process is quite complex and may be affected by several operating parameters, such as current density (CD), pollutants concentrations, conductivity of solution, and sometimes magnetic field effect. In order to enhance the process performance, the effects of those parameters have been explored.

4.1 Effect of Current Density

It has been established that cell current is one of the important parameters to control the reaction rate in the electrochemical processes [18]. The current density not only determines the coagulant dosage rate, but also the bubble production rate and size. Thus, this parameter should have a significant impact on pollutants removal efficiencies. To investigate the effect of current density on the removal yield, a series of experiments were carried out on solutions with current density being varied from 5 to 50 mA/cm² where other parameters remain unchanged, 1000 mg/L methomyl concentration, 1g/L NaCl dose without magnetic effect. Fig. 2 shows that an increase in current density from 5 to 50 mA/cm² increases the percentage removal of methomyl from 57 to about 100%. The highest current (50

mA/cm²) produced the quickest removal rate, with a 82% concentration reduction occurring just after 30 min and near 100% during 120 min test run. This expected behaviour is easily explained by the increase of coagulant and bubbles generation rate, resulting in a more efficient and faster removal, when the current is increased [19].

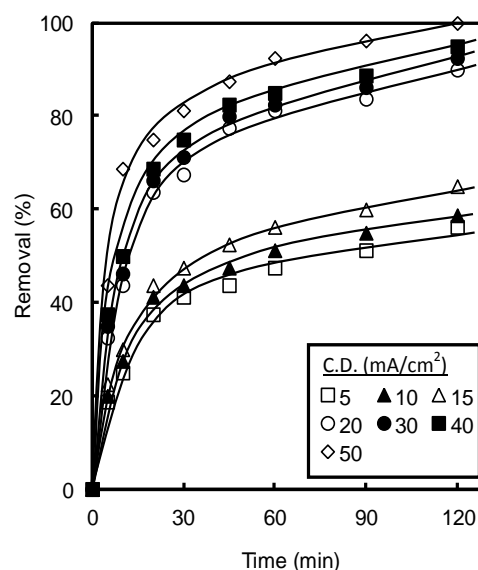


Fig. 2: Effect of current density on the removal efficiency of methomyl ($C_0 = 1\text{g/L}$, $\text{NaCl} = 1\text{g/L}$).

Indeed, the amounts of metal and hydroxide ions generated at a given time, within the electrocoagulation cell are related to the current flow, using Faraday's law:

$$W = \frac{ItM}{ZF} \quad (8)$$

where W is the metal dissolved (g), I is the current intensity (A), t is the contact time (s), M is the molecular weight of iron or hydroxide ion (g/mol), z is the number of electrons transferred in the reaction (2 for iron and 1 for hydroxide) and F is the Faraday's constant (96500 C/mol of electrons).

To assist in assessing the economic feasibility of electrocoagulation in comparison with other techniques, the energy consumption was calculated as follows [19]:

$$\text{Energy consumption (kWh/g methomyl removed)} = \frac{VIt}{(C_0 - C_t) * Q} \quad (9)$$

Where: V is the cell voltage (V), I is the cell current (A), t is the electrolysis time (h), C_0 and C_t are the methomyl initial concentration and its concentration at time t (in mg/L) respectively, Q is the treated volume in liters.

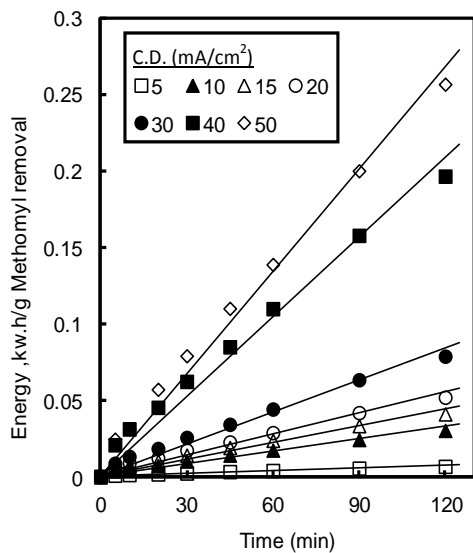


Fig. 3: Energy consumption versus time at different current densities ($C_0 = 1\text{g/L}$, $\text{NaCl} = 1\text{g/L}$).

Figure 3 shows the estimated energy consumption as a function of time for current densities 10, 20, 40 and 50 mA/cm^2 . Exactly for all current densities, power consumption increases with time. The energy consumption is directly proportional with CD. The highest CD gives best removal of methomy but with highest energy consumption. At 60 min, the removal percent was 47.2 and 92.5 while energy consumption was 0.004 and 0.139 kW.h/g for CD 5 and 50 mA/cm^2

respectively. In economic point of view, 20 mA/cm^2 is recommended.

4.2 Effect of Sodium Chloride Concentration

In order to evaluate the effect of sodium chloride concentration on the removal efficiency of methomyl from wastewater, other parameters remain constant ($C_0 = 1000\text{ mg/L}$, $\text{CD} = 20\text{ mA/cm}^2$) where concentration of NaCl was varied from 1 to 7.5 g/L , Fig. 4.

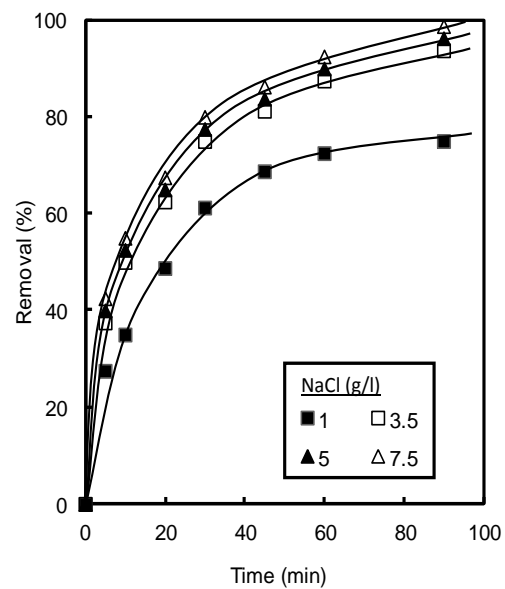


Fig. 4: Effect of NaCl concentration on the removal efficiency of methomyl ($C_0 = 1\text{g/L}$, $\text{CD} = 20\text{ mA/cm}^2$).

Energy consumption versus time at different NaCl concentrations are presented in Fig. 5. As discussed before, increasing of solution conductivity will enhance the removal efficiency and the energy required for removing unit mass of pollutant will be decrease. The energy was decreased from 0.03 to 0.012 kW.h/g methomyl removed when the NaCl concentration increased from 1 to 7.5 g/L .

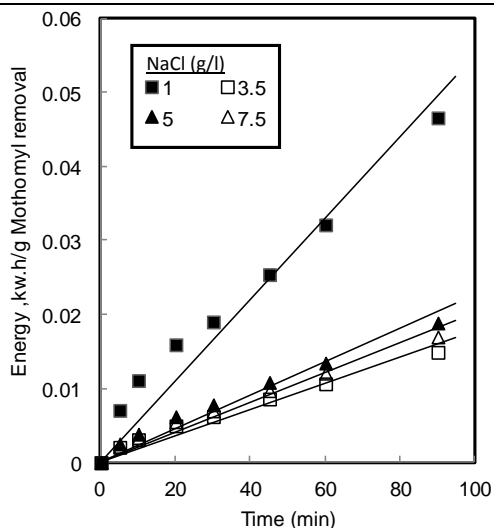


Fig. 5: Energy consumption versus time at different NaCl concentrations ($C_0 = 1\text{g/L}$, $CD = 20\text{ mA/cm}^2$).

4.3 Effect of Initial Methomyl Concentration

In order to examine the effect of pollutant initial concentration on the electrocoagulation performance, a set of experiments with different methomyl initial solutions ranged from 25 to 1000 mg/L. were done where other parameters remain constant at their optimum values, $CD = 20\text{ mA/cm}^2$, and $\text{NaCl} = 3.5\text{ g/L}$. The residual methomyl concentrations were measured at different times of electrolysis.

Fig. 6 shows the removal efficiency versus electrolysis time at different initial concentration. As expected, it appears that the removal rate has decreased upon increasing initial concentration. The percentage removal gradually decreases from 98 to 56.25 as the concentration increases from 25 to 1000 mg/L during 20 min. This is ascribed to the fact that at a constant current density, the same amount of metal ions passes to the solution at different methomyl concentrations.

Consequently, the formed amount of complex metal hydroxides was insufficient to coagulate the greater number of methomyl molecules at higher concentrations, which is consistent with previous studies [20]. Indeed, at high initial concentration (1g/L), methomyl in wastewater was reduced to admissible levels after only 20 min.

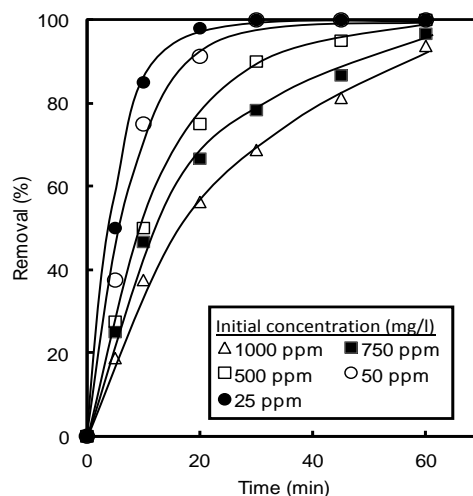


Fig. 6: Effect of methomyl initial concentration on the removal efficiency ($\text{NaCl} = 3.5\text{ g/L}$, $CD = 20\text{ mA/cm}^2$).

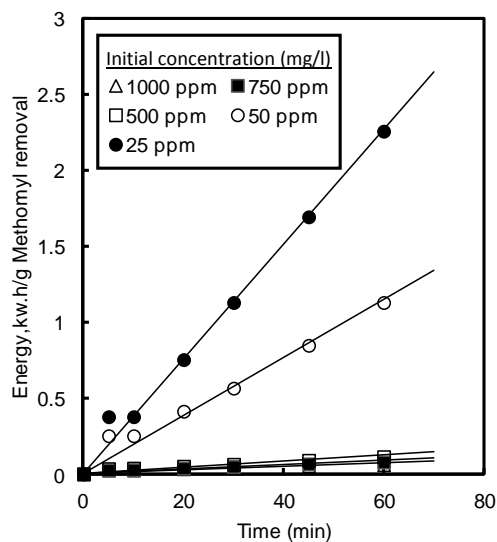


Fig. 7: Energy consumption versus time at different methomyl initial concentrations ($\text{NaCl} = 3.5\text{ g/L}$, $CD = 20\text{ mA/cm}^2$).

Figure 7 represents the energy consumption as a function of electrolysis time for different initial methomyl concentrations. The energy consumption as kW.h/ g methomyl removed has an inverse proportional with concentration, due to the chance to coagulate a greater number of methomyl molecules at higher concentrations for the same metal hydroxide in contrast at lower concentrations.

4.4 Effect of Electromagnetic Field Intensity (EMFI)

Other operating parameter which may be influence the performance of electrocoagulation depending on enhancement mass transfer operation is use of an electromagnetic field (EMF). To study these effect, experiments were carried out at different EMF intensity, 0.016, 0.029 and 0.041 Tesla, with two different positions, parallel and perpendicular anode direction, where other parameters are kept constant ($C_0 = 1\text{g/L}$, $\text{NaCl} = 3.5\text{ g/L}$, $\text{CD} = 20\text{ mA/cm}^2$). The results are shown in Fig 8.

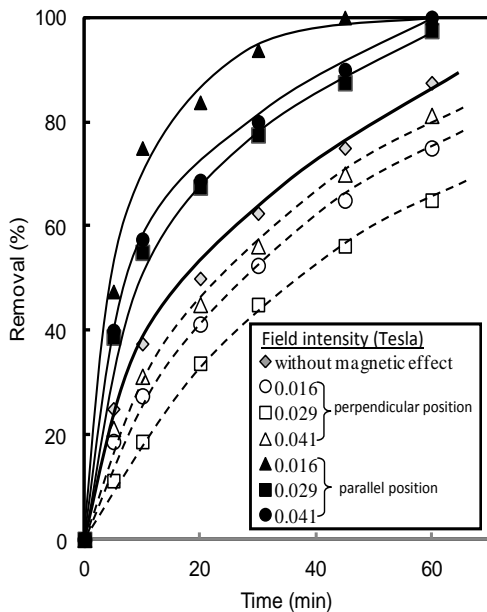


Fig. 8: Effect of EMF intensity on the removal efficiency of methomyl ($C_0 = 1\text{g/L}$, $\text{NaCl} = 3.5\text{ g/L}$, $\text{CD} = 20\text{ mA/cm}^2$).

The data plotted in Fig. 8 demonstrates that, magnetic field in parallel position effects positive in contrary in perpendicular position effects negative when compared with experiments carried in absence of magnetic field. In parallel magnetic field, the removal efficiency was increased with increasing magnetic intensity. The removal efficiency was 87.5, 90 and 100% for intensities of 0.016, 0.029 and 0.041 Tesla respectively compared with 75% when treated without magnetic field for 45 min, and the effect is limited for high intensities. The EMF enhanced the movement of charged ions by Lorenz-force effect, where it has the same direction of ions, this movement decrease the boundary layer thickness, and enhance the mass transfer of ions in bulk solution [21]. In contrast for perpendicular position, the field direction resists the movement of charged ions in the solution and decreases its transfer. The removal efficiency was decreased from 70 to 56.25% when intensity increases from 0.016 to 0.041 Tesla and both are lower than efficiency in case of treatment without magnetic field for 45 min.

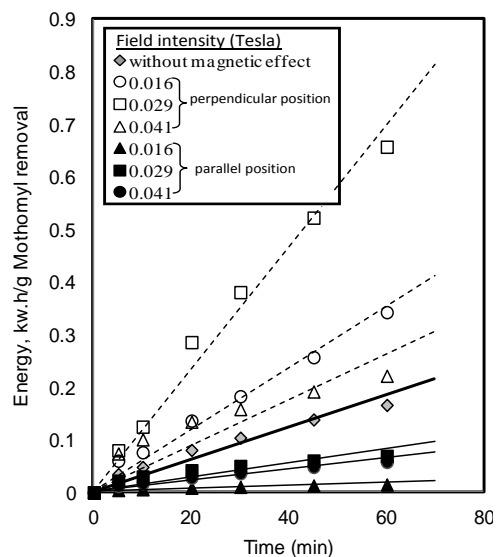


Fig. 9: Energy consumption versus time for two different positions of EMF effect ($\text{NaCl} = 3.5\text{ g/L}$, $\text{CD} = 20\text{ mA/cm}^2$).

The effect of applying EMF on energy consumption during the electrocoagulation process has been studied and presented in Fig. 9. The results illustrate that applying of EMF enhances rate of removal as well as the efficiency but increases energy consumption. The amount of metal dissolved at a given time, is highly affected by the current flow as well as intensity of EMF in parallel position in contrast with perpendicular position due to the lower of ions transfer. Thus application of EMF in electrocoagulation processes must be design in parallel position.

5. Conclusion

The results obtained in this study suggest an opportunity for the application of electrocoagulation technology for treatment of wastewater contaminated with methomyl. The present results have shown that:

1. Performance of methomyl removal by electrocoagulation process using SS electrodes is more efficient at CD = 20 mA/cm², NaCl = 3.5 g/L.
2. The electrocoagulation can achieve percentage removal up to 100% at the optimum conditions.
3. Application of EMF in parallel position has a positive effect while its application in a perpendicular position has a negative effect due to lower mixing efficiency and ions transfer.
4. Energy consumption for electrocoagulation process was found to increase with the increase in current density as well as intensity of magnetic field and decreases with NaCl addition dose and initial concentration.

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