ELECTROCHEMICAL TREATMENT OF WASTEWATER CONTAMINATED BY METHOMYL USING STAINLESS-STEEL FIXED BED ANODE

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ABSTRACT

Today hazardous waste management has become one of the most challenging tasks to this technological world where many tons of organic pollutants including various carcinogens are being exposed without the sufficient treatment. Electrochemical technology is a very efficient and economic method, suitable when the wastewater contains toxic or non-biodegradable organic pollutants. The performance of electrocoagulation using stainless-steel (SS) fixed bed anode in the treatment of wastewater contaminated by a very toxic insecticide (methomyl) has been investigated. A series of batch experiments were conducted in our lab at different operating conditions: current density, initial concentration, sodium chloride dose and the intensity magnetic field oriented in two different directions, as in an attempt to achieve higher removal efficiency. Results showed that both current density and NaCl concentration have positive effect on removal efficiency in contrast with methomyl initial concentration. Concentration of NaCl (3.5g/L) is recommended from economic point of view. Magnetic field in parallel direction effects positive where 100% removal was achieved through 30 min for 0.029T.

Keywords: Wastewater; Electrocoagulation; Insecticide; Fixed bed Anode.

1 INTRODUCTION

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. On the other hand methomyl is a non or poorly biodegradable pollutant. Consequently, it has been frequently detected in water bodies in various regions of the world [1]. 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 [2]. The toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating our environment. Therefore, the removal of pesticides from water is one of the major environmental concerns these days. 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 [3].

Several methods are available for pesticides removal. Most of the past works have focused on the removal of pesticides from water by the more traditional and expensive methods, such as, cation exchange [4], dialysis [5] and adsorption [6]. 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. Pesticides are not completely degraded into inorganic compounds such as CO_2 by ozonation [7]. These findings suggest that the breakdown products of pesticides remain in water after treatment, need complementary operations and are not economical. The use of enzymes to detoxify wastewater failed to attract much attention due to the high cost of enzyme-based systems [8]. Filtration through membranes needs another method, such as oxidation reaction catalyzed by enzyme to transform the pesticide into an insoluble product; so, this method is highly expensive [9]. Compared to the above methods, removal of pesticides by electrocoagulation process has demonstrated efficiency and economic feasibility for removing pesticides that are chemically and biologically stable [10].

The present work aimed to study the removal of a pesticide (methomyl) from aqueous solutions using electrocoagulation process in an electrochemical reactor (EC) with a fixed bed stainless steel (SS) anode. Effect of operational parameters was studied and discussed. Energy consumption as well as anode consumption was calculated under different operating condition.

2 MATERIALS AND METHODS

2.1 Water Sample.

A simulated wastewater contaminated by an insecticide, methomyl, (S-methyl N-[(methylcarbamoyl)oxy] thioacetimidate) was used for all experiments in this study. The physicochemical properties of methomyl are presented in our article published before [10]. The methomyl was supplied by Egyptian Company for commerce and agriculture, Egypt. Synthetic stock solutions were prepared by dissolving accurately weighed amounts methomyl in 1 L of distilled water. Experimental solutions of the desired concentrations were obtained by successive dilution with distilled water. At the end of each experiment- COD of solutions before and during the treatment process ware determined and used for evaluating effective parameters.

2.2 Experimental Setup and Procedure.

An experimental setup was designed and constructed by the teamwork in our lab, a schematic diagram of setup was presented in our published paper [10]. The EC unit consists of an electrochemical reactor with a fixed bed anode made of randomly oriented SS pellets packed in a perforated plastic basket located centrally in the reactor and cathode of stainless steel screen surrounding anode with 2cm apart, D.C. power supply was used to achieves different current densities. Magnetic field was applied on 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. The efficiency of methomyl removal, % Removal, was calculated as:

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

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

In order to study the effect of current density (CD), a series of experiments were carried out with current density being varied from 5 to 50 mA/cm^2 where other parameters remain unchanged, 1000 mg/L methomyl loading, 1g/L NaCl dose without magnetic effect for two different sizes of anode pellets 10mm and 13mm. Same way was used for studying the effect of other parameters, sodium chloride concentration, initial concentration and intensity of electromagnetic field. To assist in assessing the economic feasibility of electrocoagulation in comparison with other techniques, the energy consumption and anode metal consumption were calculated as follows:

$$\text{Energy consumption (kWh/g methomyl removed)} = \frac{VIt}{(C_0 - C_t) * volumetreated\,(L)} \quad (2)$$

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.

The amount of SS anode consumed in electrocoagulation was calculated from Faraday's law,

$$\text{Anode consumption (g-SS/g-methomyl removed)} = ItM/ZFm \quad (3)$$

F is the Faraday's constant (96,500 Columb /mol), M the molecular weight of iron (56 g/mol), z is the number of electron transfer (z_{Fe} = 2) and m is the mass of methomyl removed.

At the beginning of any experimental 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 ELECTROCOAGULATION THEORY

Electrocoagulation is based on the in situ formation of the coagulant as the sacrificial anode corrodes due to an applied current, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation. This technique combines three main interdependent processes, operating synergistically to remove pollutants- electrochemistry, coagulation and hydrodynamics. The reactions occurring in the electrocoagulation process was examined by Yilmaz et al. (2007), Fig. 1 [11].

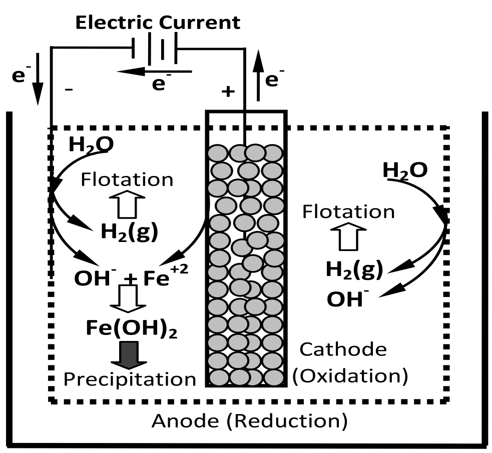

Figure 1. A descriptive diagram for anodic and cathodic reactions.

The main reactions occurring at the electrodes are:

At anode: $Fe == Fe^{2+} + 2e$ (4)

At cathode: $2H_2O + 2e == H_2 + 2OH^-$ (5)

In addition, Fe^{2+} and OH^{-} ions generated at electrode surfaces react in the bulk wastewater to form $Fe(OH)_2$, which favors the coagula precipitation, can be written as

$$Fe^{2+} + 2OH^{-} == Fe(OH)_2 \quad (6)$$

The overall reaction for the electrolytic process from the sequence of reactions (4) - (6) is:

$$Fe + 2\,H_2O \rightarrow Fe(OH)_2(s) + H_2(g) \quad (7)$$

4 RESULTS AND DISCUSSION

4.1 Effect of Current Density

In Fig. 2, the influence of applied current on methomyl degradation was shown as a change of concentration and removal percentage. The increase in current density from 5 to 50 mA/cm^2 increases the percentage removal of methomyl from 85 to 100% during 40 min treating time of 10 mm anode particle diameter. This is ascribed to the fact that at higher current densities the dissolution of anode to Fe^{2+} ions increases according to Faraday's law. Fe^{2+} ions undergo hydrolysis and the resulting hydroxides produce more sludge with a consequent significant removal of methomyl due to its adsorption on $Fe(OH)_2$. Furthermore, more hydrogen bubbles are generated at the cathode with increasing current density; these bubbles improve the degree of mixing of solution that enhances the flotation ability of the cell with a consequent increase in the percentage removal. Also, it was found that the number of H_2 bubbles increases and their size decreases with increasing current density, resulting in a faster removal of methomyl and sludge flotation [12].

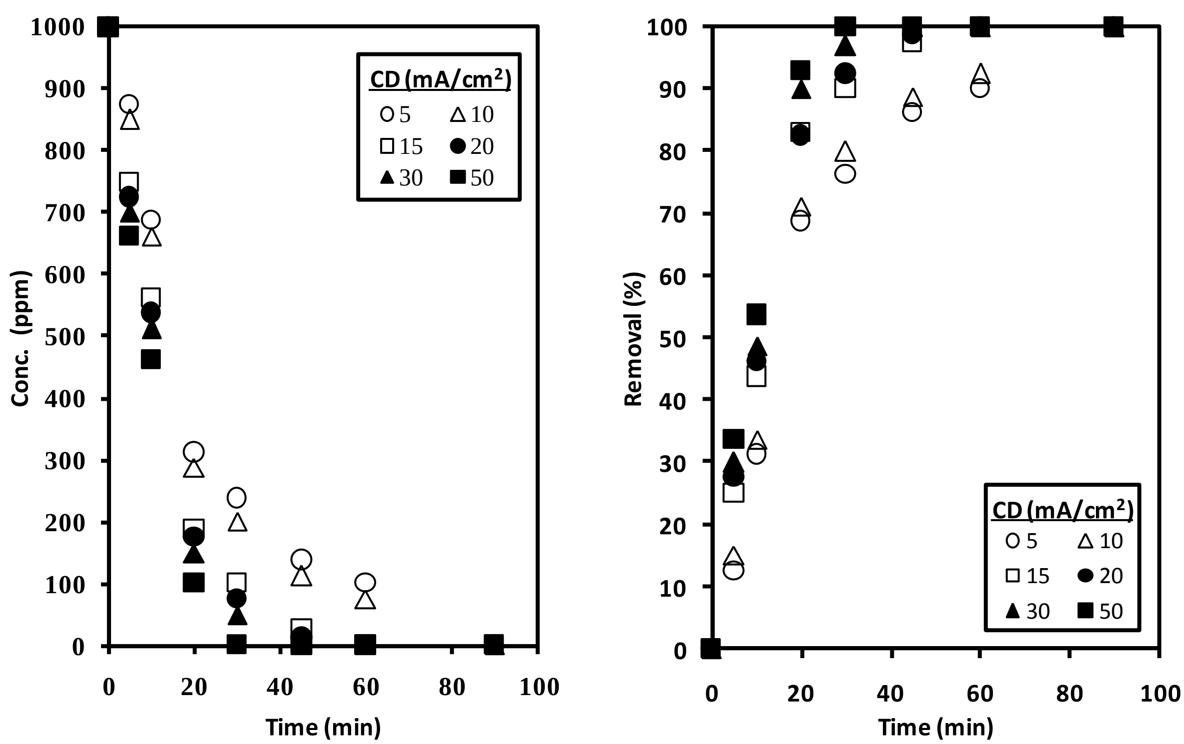

Figure 2. Effect of current density on the removal of methomyl (Co = 1000 mg/L, NaCl = 1 g/L, SS-pellets (dp= 10mm), pH = 7, Temperature = 25°C)

In order to investigate effect of surface area, other experiments were done for 13 mm pellet fixed bed anode for same current densities that have been used before. The same trend was found for anode pellets of 13mm but its efficiency for removal of methomyl is limited comparing with 10 mm pellets where it was increased from 80 to 96% when CD increased from 5 to 50 mA/cm^2 during 40 min treating time, Fig (3). The electrical energy consumed, expressed as kWh/g of methomyl removed as a function of electrolysis time at different applied CD for both 10mm and 13mm anode pellets were calculated and plotted in Fig. 4 while other parameters remain constant. Generally, the energy consumption increases with increasing CD for both small and large pellets but small pellets consumed lower energy may be due to large surface area. The energy was 0.272 kWh/g-removed for small pellet anode compared with 0.305 kWh/g-removed for the large pellet anode during 60 min treating time when 50mA/cm^2 was used in contrast, 0.028 and 0.034 kWh/g-removed when 15mA/cm^2 was used as a current density.

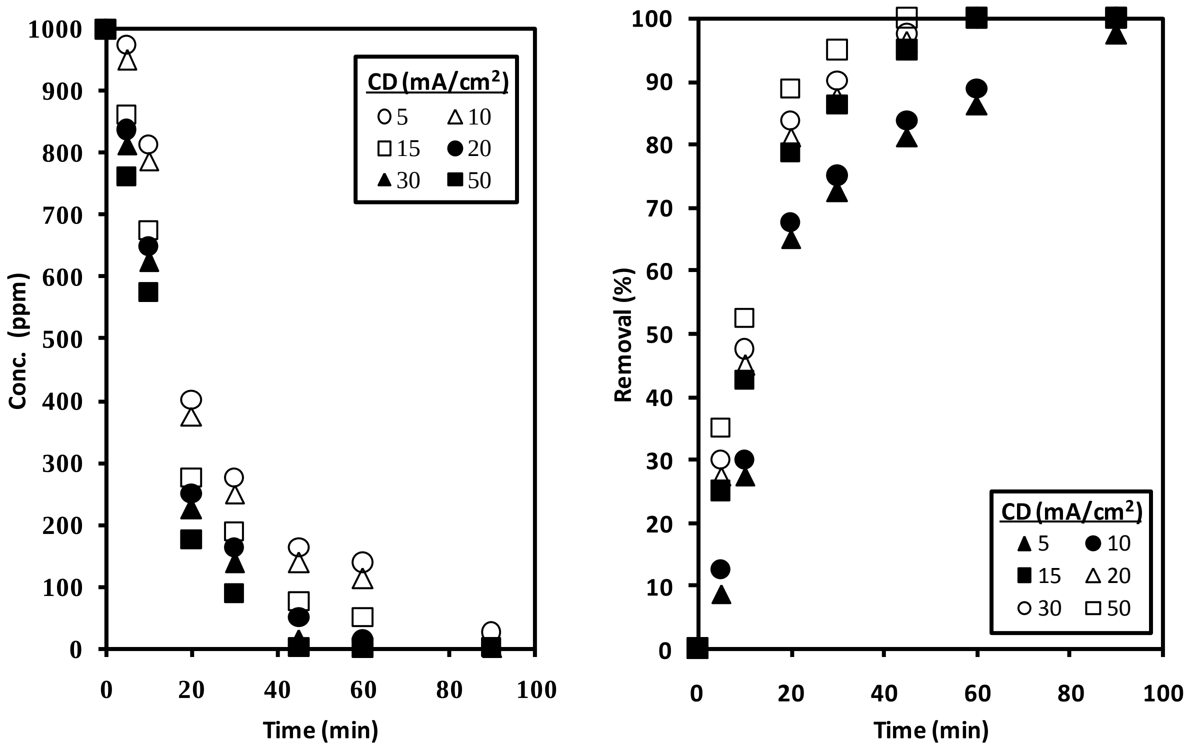

Figure 3. Effect of current density on the removal of methomyl (Co = 1000 mg/L, NaCl = 1 g/L, SS-pellets (dp= 13mm), pH = 7, Temperature = 25°C)

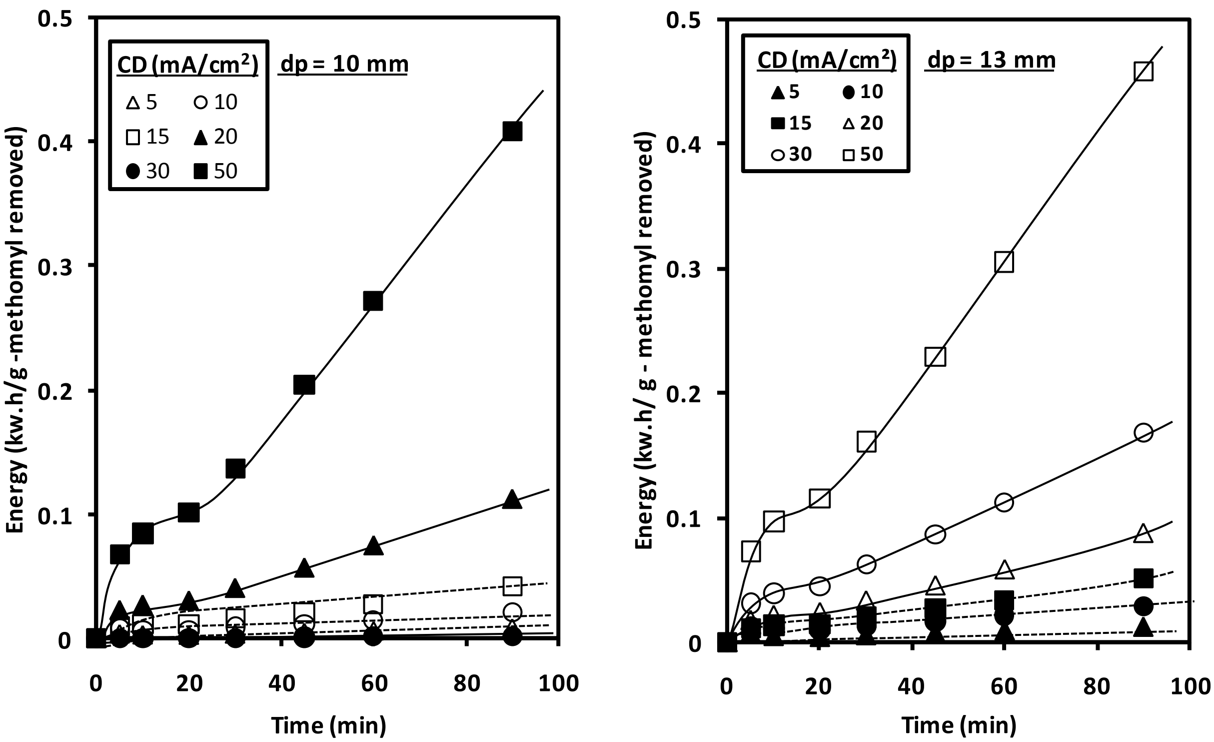

Figure 4. Energy consumption at different current densities for small and large SS-pellet anodes, (Co = 1000 mg/L, NaCl = 1 g/L, pH = 7, Temperature = 25°C).

A comparison between small and large particles anode was studied. It confirms that small particles have a large surface area dissociate more ions and enhances the process. From economic point of view, 15mA/cm^2 at 10 mm pellet diameter is the optimum where it gives highly removal percent with lower energy consumption. Theses optimum conditions were fixed in studying the other operating parameters.

4.2 Effect of Wastewater Conductivity

The conductivity of supporting electrolyte has important effects on the current density in the electrocoagulation process. Therefore it may influence the treatment efficiency significantly. It was recommended that there should be 20% Cl^- to ensure a normal operation of electrocoagulation in water treatment process. The addition of NaCl would lead to the decrease in power consumption with the increase in conductivity [13].

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 mg/L, CD = 15 mA/cm^2) where concentration of NaCl was varied, Fig. 5. It was found that, as sodium chloride concentration increases from 1 to 7.5 g/L, the percentage removal of methomyl increases from 80 to 90% during 20 min. This may be explained by the fact that the higher chloride ion concentration, the higher the ability of chloride ions to destroy any passive oxide film which tends to form on the anode and limit anode dissolution, hence it increases the availability of ferrous hydroxide in the solution and improve the removal efficiency. It is clear that after 3.5 g/L sodium chloride concentration, the salt has a little effect on the percentage removal. The right part of figure illustrates power consumption per unit mass of methomyl removed for different NaCl concentrations the assuring one g/L NaCl not recommended because it needs more power than other concentrations. According to the results, from a economic point of view the optimum sodium chloride concentration is about 3.5 g/L, hence, 3.5 g/L sodium chloride was used in the subsequent experiments.

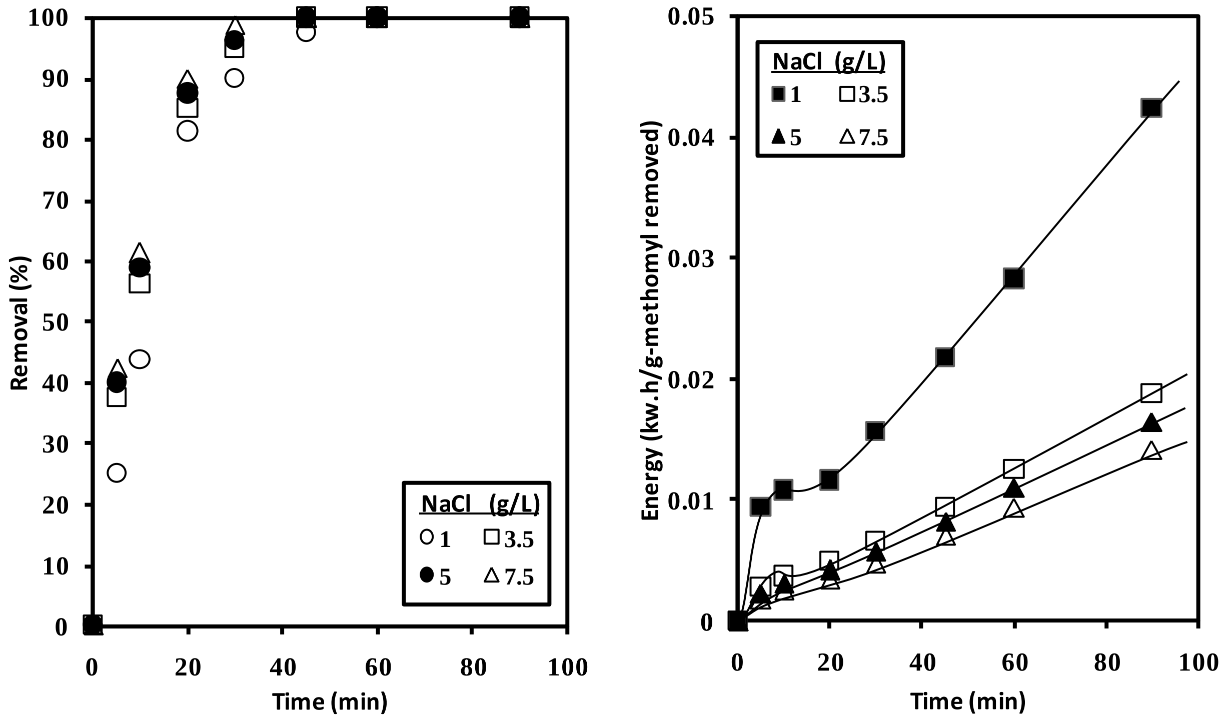

Figure 5. Effect of NaCl dose on the percentage removal and energy consumption (Co = 1000 mg/L, CD = 15 mA/cm^2, SS-pellets = 10mm, pH = 7, Temperature = 25°C).

4.3 Effect of Initial Concentration

The effect of initial concentration on percentage removal of methomyl has been done, figure is not presented. The results indicated that percentage removal gradually decreases from 85 to 62 as the methomyl concentration increases from 25 to 1000 mg/l. during 30 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 concentration. Consequently, the formed amount of complex metal hydroxides was insufficient to coagulate the greater number of methomyl molecules at higher methomyl concentrations, which is consistent with previous studies [14,15].

4.4 Electromagnetic Field (EMF)

In case of electrochemical processes, enhancement of mass transfer of metal ions by utilizing of EMF has been previously demonstrated [14&15]. In the present study, effect of both parallel and perpendicular oriented EMF related the anode was studied at different intensities (EMFI) ranged from 0 to 0.041 Tesla, Fig. 6. It is evident that 95% of methomyl was removed after 20 min when EMF = 0.041Tesla was used in parallel direction compared to 83% removal without utilizing EMF in contrary with the perpendicular direction is 68% . In case of EMF oriented parally with anode, it enhances the mass transfer due to the fact that EMF generated magnetic field induces motion of Fe ions inside the solution. 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. In contrast for perpendicular position, the field direction resists the movement of charged ions in the solution and decreases its transfer.

Energy consumption has a direct proportional with intensity of magnetic field, EMFI. The consumption of energy per gram methomyl removal when parallel filed was used is lower than when using perpendicular field for all intensities but in all cases without using magnetic field it is better from economic point of view.

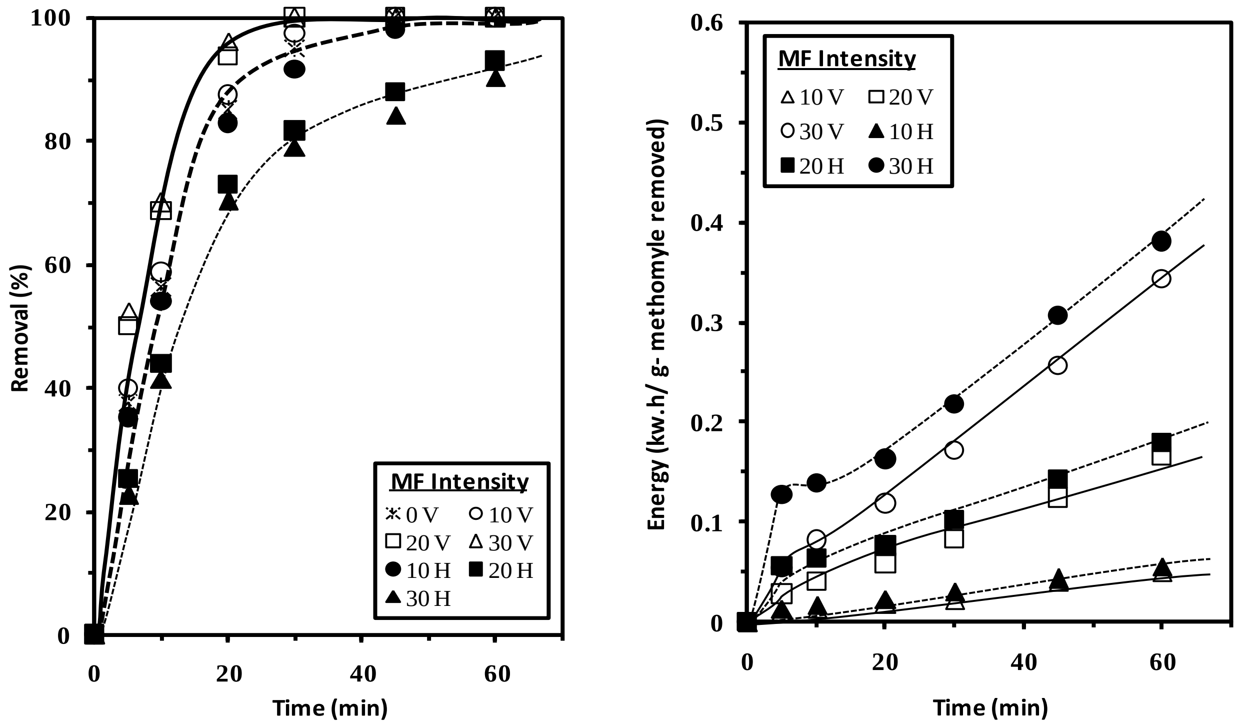

Figure 6. Effect of EMF intensity on the methomyl removal and energy consumption (CD = 15 mA/cm^2, NaCl = 3.5 g/L, SS-pellets = 10mm, pH = 7, Temperature = 25°C).

5 CONCLUSIONS

Electrocoagulation (EC) was assessed as a possible technique for the removal of reduction of methomyl from wastewater. Wastewater samples, prepared in our lab, were treated in a batch electrochemical reactor using stainless steel (SS) electrodes where anode was fixed bed made from two different SS pellets (dp= 10mm or 13mm). The experimental results showed that electrocoagulation can achieve 100% percentage removal for methomyl. The performance of the electrochemical reactor was found to be highly influenced by the anode design, the current density as well as the conductivity of medium. Application of electromagnetic field in parallel direction with anode accelerate the process in contrast of magnetic field perpendicular with anode, it resists the transfer of ions and decreases the process efficiency. The optimum values of operating parameters were 15mA/cm^2, 15 mg/L and without application of EMF based one economic study. All these results give an indisputable evidence that electrocoagulation can effectively reduce methomyl to a very low level from industrial wastewater.

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