FIXED BED ELECTROCHEMICAL REACTORS FOR REMOVAL OF METHOMYL FROM WASTEWATER

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ABSTRACT

Electro coagulation (EC) due to some advantages over chemical coagulation is becoming a popular process to be used for wastewater treatment. Experiments were conducted in our lab to remove a very toxic pesticide (methomyl) using electrochemical reactor with a fixed bed anode made from Al pellets packed randomly in a perforated plastic basket located in stainless steel (SS) screen cathode. Several operating parameters have been studied, such as current density, initial methomyl concentration, addition of sodium chloride, magnetic field intensity oriented in two different directions and retention time in an attempt to achieve higher removal efficiency. It has been shown that the removal efficiency of COD increased with the increasing applied current density and decreasing anode pellets diameter. Increasing NaCl concentration enhances removal efficiency and 3.5 g/L NaCl is recommended from economic point of view. Magnetic field in parallel direction effects positive where around 98% removal was achieved through 45 min for 0.029T magnetic intensity applied in a parallel direction. In order to throw some light on the economics of the process, energy consumption was calculated under different conditions. The new anode design was found to be highly efficient and relatively fast with lower energy consumption compared to conventional cell designs.

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, Tomasevic et al. (2010) and Chang & Lee (2012). 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, Bouzaida et al. (2004). 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.

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 μg/L to as high as several hundred mg/L. Suitable treatments 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, Aungpradit et al. (2007); advanced oxidation processes, Saritha et al. (2007); aerobic degradation, Rajashekara & Manonmani (2007); nanofiltration, Ahmad et al. (2008); ozonation, Maldonado et al. (2006); and adsorption, El-Geundi et al. (2013) & El-Geundi et al. (2014). 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, Bonne et al. (2000). 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. 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 various types of wastewater contains organic pollutants, Bensadok et al. (2008) and Cansares et al. (2008), its application as a possible technique for the treatment of wastewater contains pesticides is rather scarce in the literature.
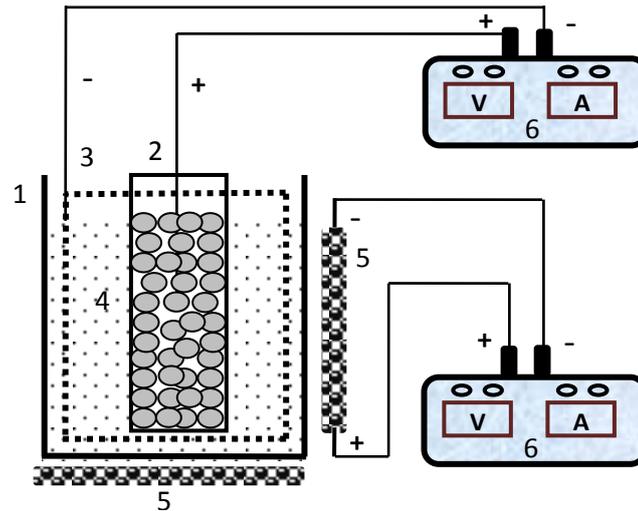
The main objective of the present study, therefore, is to study the removal of a pesticide (methomyl) from aqueous solutions by electrocoagulation process in an electrochemical reactor (EC) with a fixed bed anode. Effect of operational parameters was studied and discussed. Energy consumption as well as anode (Al) 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 shown in Table 1. 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.

Figure 1 represents schematically the experimental setup which designed and constructed by the teamwork in our lab (Faculty of engineering – Minia University). The EC unit consists of an electrochemical reactor with a fixed bed anode made of randomly oriented Al 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. In order to study the influence of pellet diameter, two different sizes of Al pellets were used, 10mm and 13mm. 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:

$$\% \ \text{Removal} = \frac{COD_i - COD_f}{COD_i} \times 100 \tag{1}$$

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

Table 1. Physicochemical properties of methomyl*.

Property	Parameter value
Chemical structure	$CH_3-C=N-O-C-N$ (with O double bond and H, CH_3, $S-CH_3$ substituents)
CAS number	16752 - 77 – 5
Chemical formula	$C_5H_{10}N_2O_2S$
Molecular weight	162.21 g/mol
Molecular volume	179.9 cm^3/mol
Colour	White crystalline solid
Sp.gr at 298.15 K, (-)	1.29
Solubility in water at 298.15 K	58,000 mg/L
Log octanol/water partition coefficient, log K_{ow}	0.60
Log soil organic carbon-water partitioning coefficient	2.6
Melting point, K	351.15 - 316.15
Vapor pressure at 298.15 K, mm Hg	5.4(10^{-6})

* Source: Hazardous Substances Data Bank (HSDB), http://toxnet.nlm.nih.gov/.

Figure 1. Schematic diagram of experimental setup: **(1) electrochemical cell; (2) Fixed bed anode; (3) cathode; (4) treated solution; (5) coil to produce magnetic field (6) DC power supply**.

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 Al metal consumption were calculated as follows:

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

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 Al anode consumed in electrocoagulation was calculated from Faraday's law,

$$\text{Anode consumption (g-Al/g-methomyl removed)} = \frac{ItM}{ZFm} \qquad (3)$$

F is the Faraday's constant (96,500 Columb /mol), M the molecular weight of aluminum (27 g/mol) and z is the number of electron transfer ($z_{Al} = 3$).

At the beginning of an 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   PROCESS MECHANISM

Electro coagulation 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. 2.
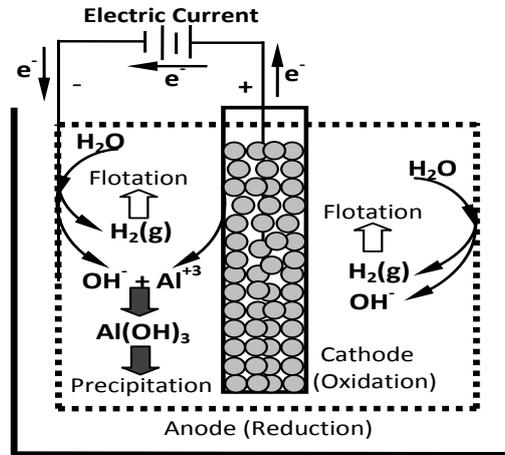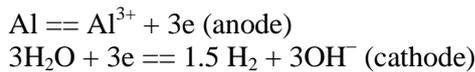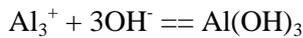

**Figure 2. A descriptive diagram for anodic and cathodic reactions.**

The main reactions occurring at the electrodes are:

$Al == Al^{3+} + 3e$ (anode)
$3H_2O + 3e == 1.5 H_2 + 3OH^-$ (cathode)

In addition, Al^{3+} and OH^- ions generated at electrode surfaces react in the bulk wastewater to form aluminum hydroxide:

$Al_3^+ + 3OH^- == Al(OH)_3$

If the anode potential is sufficiently high, secondary reactions may occur at the anode, such as direct oxidation of organic compounds and of H_2O or Cl^- present in wastewater:

$2Cl^- == Cl_2 + 2e$
$2 H_2O == O_2 + 4H^+ + 4e$
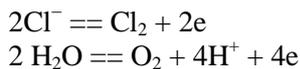
The produced chlorine undergoes a dismutation reaction at pH higher than 3:

$Cl_2 + H_2O == HClO + H^+ + Cl^-$
$HClO == ClO^- + H^+$
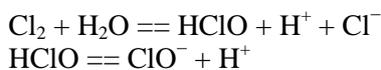
4   RESULTS AND DISCUSSION

The electro coagulation 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   Current Density.

Figure 3 shows the effect of current density (CD) on the removal of methomyl as a change of concentration and removal percentage. That increase in current density from 5 to 50 mA/cm^2 increases the percentage removal of methomyl from 80 to 98% for 40 min treating time. This is ascribed to the fact that at higher current densities the dissolution of anode to Al^{3+} ions increase according to

Faraday's law. Al^{3+} ions undergo hydrolysis and the resulting aluminum hydroxides produce more sludge with a consequent significant removal of methomyl due to its adsorption on Al(OH)$_3$ and its polymeric compounds. Furthermore, more hydrogen bubbles are generated at the cathode with increasing current density; these bubbles improve the degree of mixing of aluminum hydroxides in solution and enhance 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, similar to the work presented in El-Ashtoukhy et al. (2013).
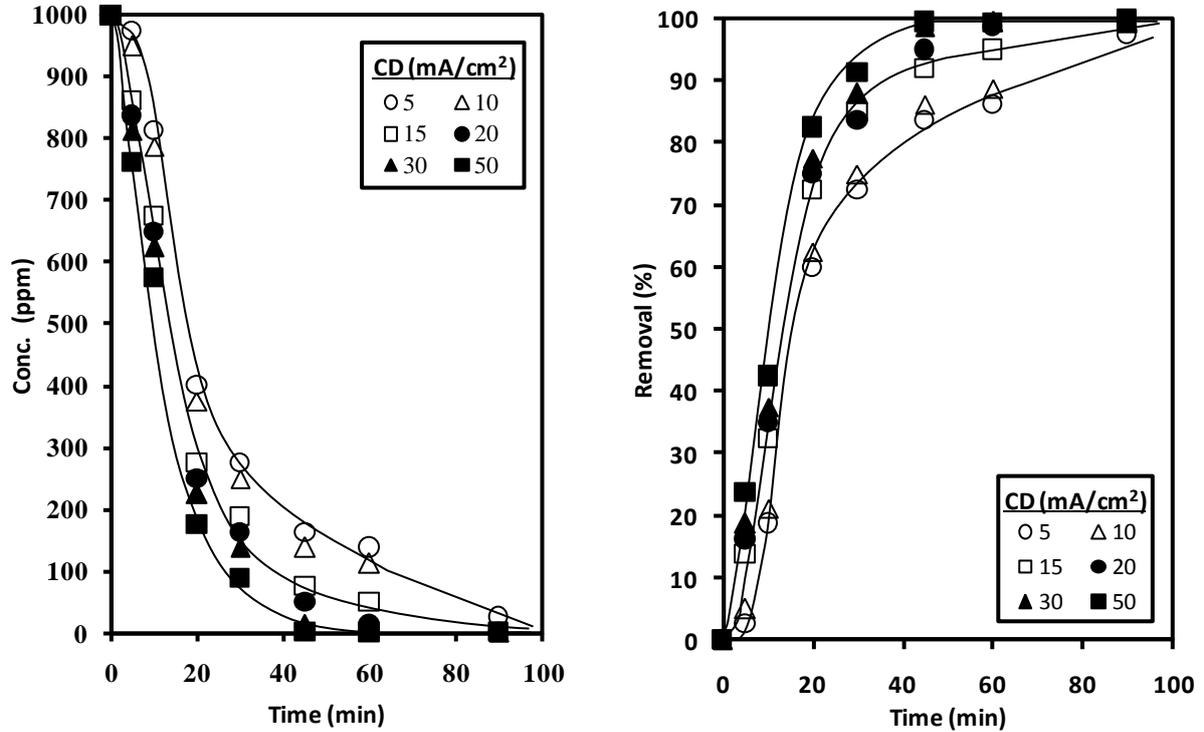
Figure 3. Effect of current density on the removal of methomyl (Co = 1000 mg/L, NaCl = 1 g/L, Al-pellets = 10mm, pH = 7, Temperature = 25°C)

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 75 to 94% when CD increased from 5 to 50 mA/cm^2 during 40 min treating time, the figure is not present. 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 13 mm 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 0.45kW.h/g-removed for small pellet anode compared with 0.53 kW.h/g-removed for the large pellet anode.
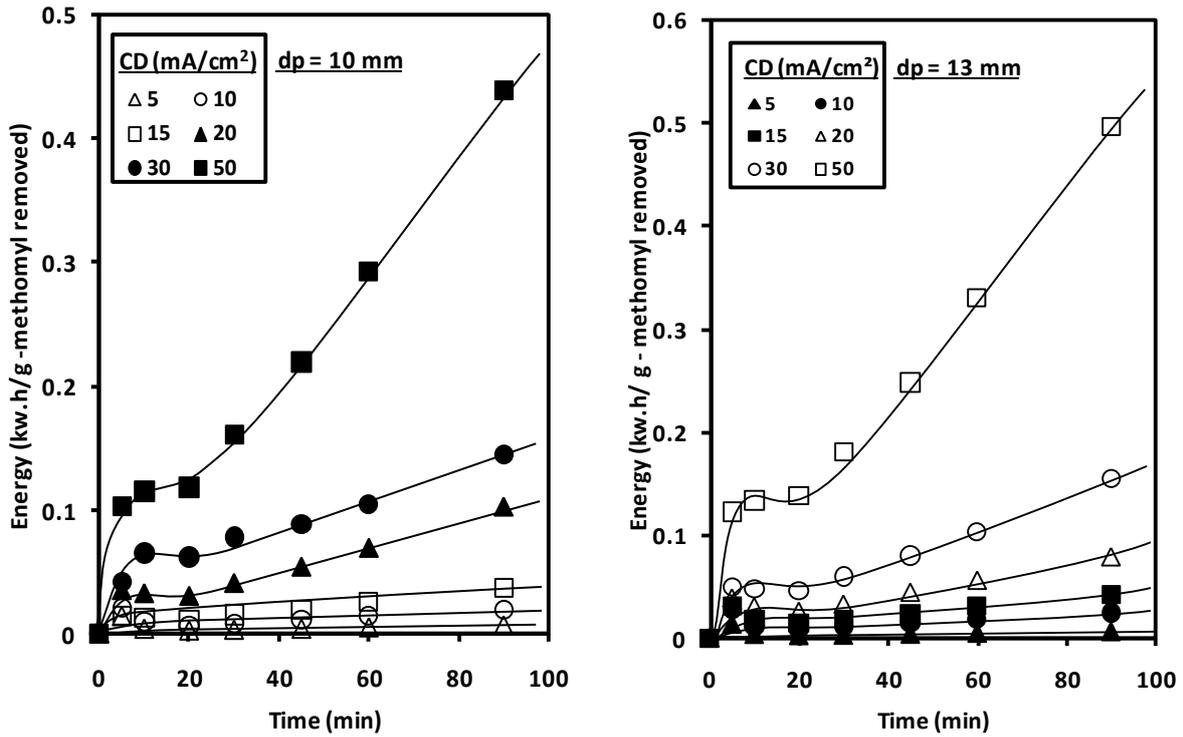
Figure 4. Energy consumption as a function of time at different current density for small and large pellet anodes, (Co = 1000 mg/L, NaCl = 1 g/L, pH = 7, Temperature = 25°C).
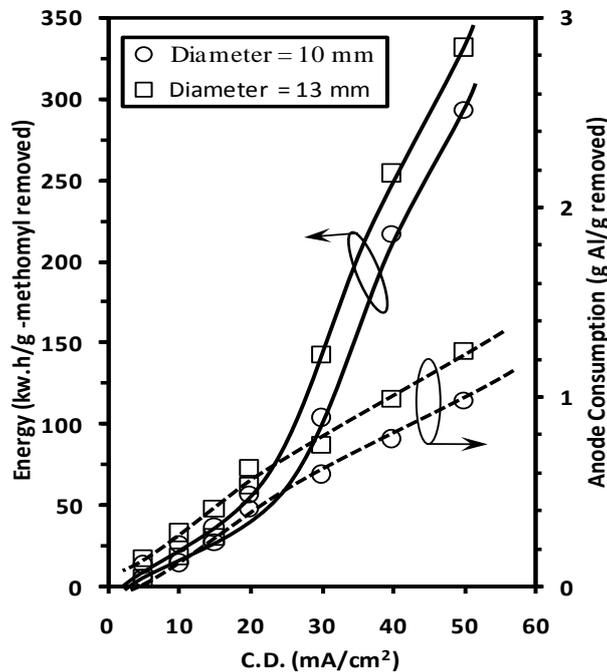

Figure 5. Energy and anode consumption as a function of current density for small and large pellet anodes, (time = 1 h, Co = 1000 mg/L, NaCl = 1 g/L, pH = 7, Temperature = 25°C).

A comparison between small and large particles anode is presented in Fig. 5, where both energy and anode consumption versus CD are illustrated. It confirms that small particles have a large surface area dissociate more ions and enhances the process. From economic point of view, 15 mA/cm^2 at 10mm 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   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 mg/L, CD = 15 mA/cm^2) where concentration of NaCl was varied, Fig. 6. It was found that, as sodium chloride concentration increases from 1 to 7.5 g/L, the percentage removal of methomyl increases from 90 to 99% during 60 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 aluminum hydroxide in the solution and improve the removal efficiency. Also, as the concentration of sodium chloride increase, the activity of the dissolved Al^{+3} in the anode vicinity decreases by virtue of interionic attraction between sodium chloride and the dissolved Al^{+3}, accordingly the potential required to dissolve the aluminum anode (e) decreases according to Nernest equation, El-Ashtoukhy et al. (2013):

$$E = E_0 - \frac{RT}{ZF} \ln a_{Al^{+3}}$$
(3)

where E is the electrode potential, E_0 is the standard electrode potential, T is the absolute temperature, R is the gas constant (R = 8.13 J/mol.K), and $a_{Al^{+3}}$ is the activity of Al^{+3} .

The decrease in the potential required to dissolve the anode reduce the tendency of aluminum to passivate and reduce the tendency of chlorine and oxygen evolution at the expense of aluminum dissolution. Figure 6 shows that after 3.5 g/L sodium chloride concentration, the salt has a little effect on the percentage removal. 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.
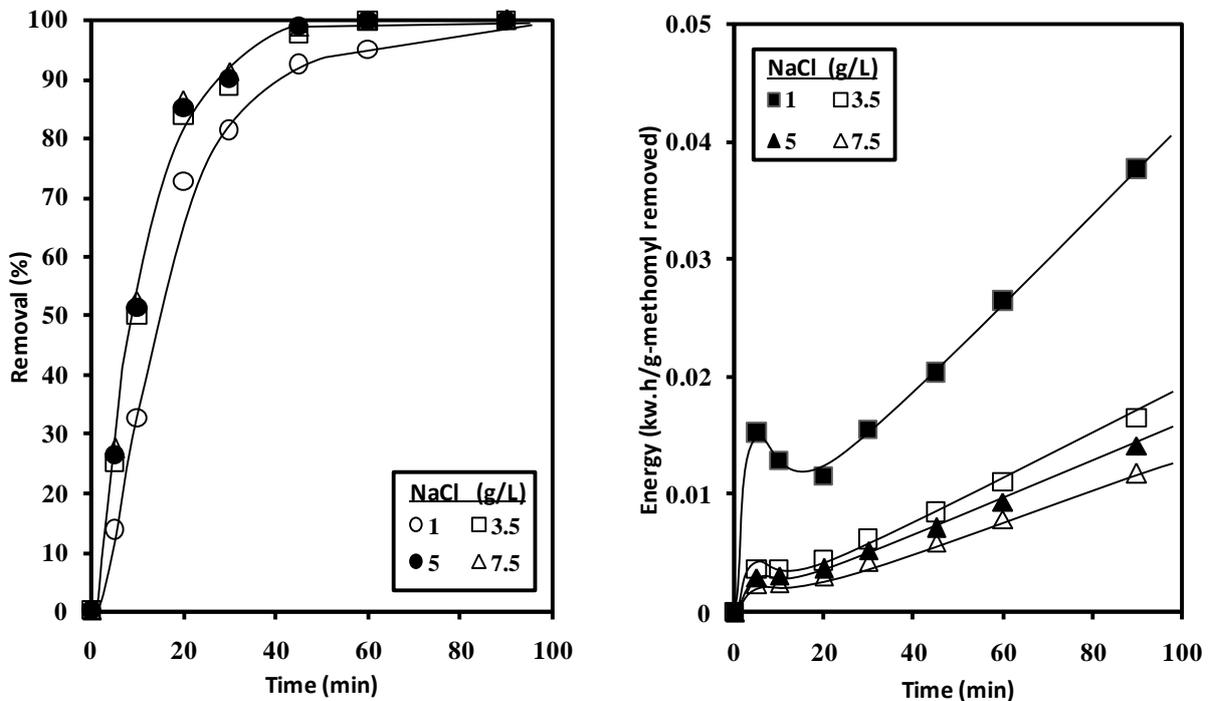

Figure 6. Effect of NaCl dose on the methomy removal and energy consumption (Co = 1000 mg/L, CD = 15 mA/cm^2, Al-pellets = 10mm, pH = 7, Temperature = 25°C).

4.3 Initial Concentration

In order to examine the effect of methomyl concentration, several solutions containing increased concentrations (100-1000 mg/L) of methomyl were treated and the residual concentrations were measured at different times of electrolysis. Figure 7 shows the change in the removal efficiency with initial concentration; it appears that the removal rate has decreased upon increasing initial concentration. The percentage removal gradually decreases from 95 to 75 as the concentration increases from 100 to 1000 mg/L during 30 min treatment. This is ascribed to the fact that at a constant current density, the same amount of aluminum ions passes to the solution at different methomyl concentrations. Consequently, the formed amount of complex aluminum hydroxides was insufficient to coagulate the greater number of methomyl molecules at higher concentrations.
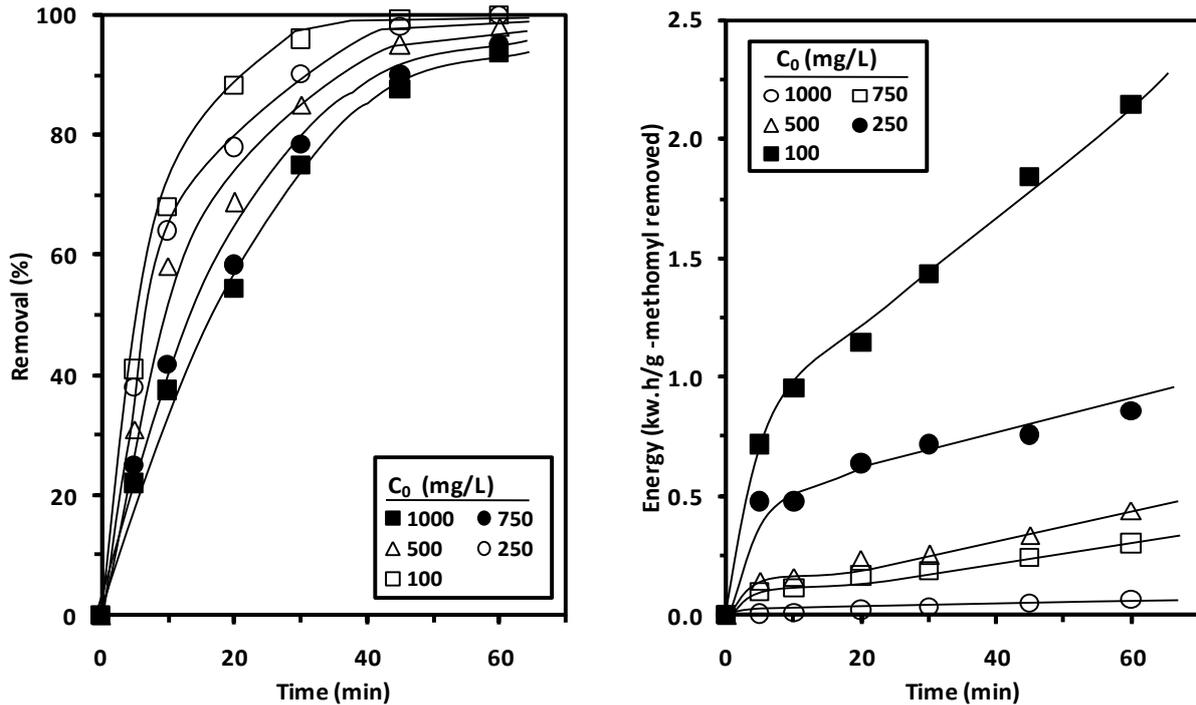

Figure 7. Effect of Initial concentration on the removal and energy consumption (CD = 15 mA/cm^2, NaCl = 3.5 g/L, Al-pellets = 10mm, pH = 7, Temperature = 25°C).

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 by Mahmoud et al. (2013) and Fadali et al. (2013). 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, the results are depicted in Figure 8.

It is evident that 92% of methomyl was removed after 20 min when EMF = 0.041Tesla was used in parallel direction compared to 78% removal without utilizing EMF in contrary with the perpendicular direction is 58% . 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 paramagnetic Al 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. The removal efficiency was decreased from 85 to 68% when intensity increases from 0.016 to 0.041 Tesla and both are lower than efficiency in case of treatment without magnetic field for 30 min.

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.
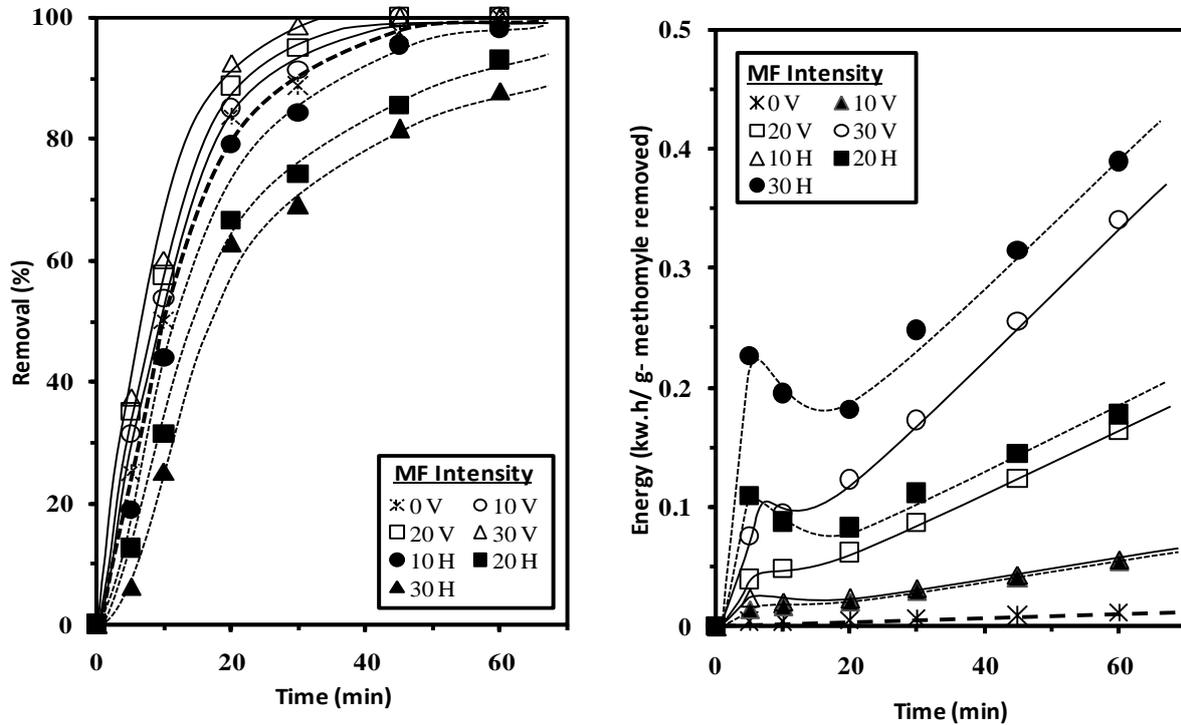

Figure 8. Effect of EMF intensity on the methomyl removal and energy consumption (CD = 15 mA/cm^2, NaCl = 3.5 g/L, Al-pellets = 10mm, pH = 7, Temperature = 25°C).

CONCLUSIONS

Removal of methomyl from aqueous mediums by electrocoagulation (EC) using Al pellets packed together in the form of fixed bed anode seems to be a very efficient method for wastewater treatment as revealed by the this study. Experimental parameters such as, contact time, current density, NaCl concentration, methomyl concentration, anode pellet diameter were investigated. The performance of process was found to be highly influenced by anode pellet diameter where the best is the smallest one. Increasing of current density and NaCl dose enhance the process where the optimum values were found as 15mA/cm^2 and 15 mg/L respectively. The study showed that electrocoagulation can achieve percentage removal up to 100% and 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 application of EMF in parallel direction enhances the mass transfer but not recommended from economic point of view.

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