

## Direct Electrochemical Degradation of Carbamate Pesticide Methomyl Using IrO<sub>x</sub> Anode

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The study's primary goal is to determine carbamate pesticide methomyl's kinetic parameters and degradation efficiency from water solution by direct electrochemical oxidation using IrO<sub>x</sub> anode. Also, define the dependence of the efficiency of methomyl decomposition by direct electrochemical oxidation on the initial concentration of pesticide and electrolyte, applied current, and pH value. The results of methomyl degradation by direct electrochemical oxidation obey the pseudo-first kinetic order. Ultraviolet-visible (UV-Vis) spectroscopy followed the methomyl concentration during the study. The degradation products were studied using the Fourier transform infrared (FT-IR) spectroscopy. Also, this study determines the energy consumption and optimal initial conditions. The phytotoxicity of pesticide and degradation products was studied using mung beans.

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**Keywords:** direct electrochemical degradation; carbamate pesticide; methomyl; IrO<sub>x</sub> anode; sodium sulfate; phytotoxicity.

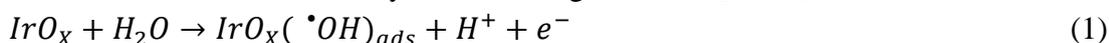
### 1. INTRODUCTION

The population growth necessitates an increase in crop yields in recent decades by using chemical products to provide sufficient food. Primarily, the development of pesticides has contributed to this by protecting crops. Modern trends strive for efficient plant protection and increased yields with as minor damage to human life and ecosystems as possible. A wide range of harmful effects of pesticides, including incredibly toxic, mutagenic, and carcinogenic effects, has been launched through research on

pesticide removal methods from water and soil. In recent years, environmental protection has become one of the most important aspects of modern life. The technological development of human kind has significantly facilitated the way of life by the chemical industry. On the other hand, the ecosystem was disrupted substantially by many realized chemicals. The intensive use of chemicals released into watercourses impairs water quality. The waters with many pesticides have many adverse effects that initiate disorder in the waterway ecosystem. The many studies of the negative effects of pesticides and their residuals on organisms by ingestion besides high toxicity may have carcinogenic, mutagenic, and teratogenic effects [1–3]. Also, the ingestion of water contaminated by pesticides and their residues can increase oxidative stress and cause cellular damage and the generation of toxic metabolites [4,5]. The use of large quantities of pesticides for agricultural product protection initiates contamination of groundwater after dissolution and intake of the parameters of water quality as chemical oxygen demand and total organic carbon [6]. The presence of pesticides and their residuals are highly resistant to degradation by microorganisms and can inhibit conventional biological wastewater treatment and decrease their efficiency [3]. In the last two decades, scientific research has turned to finding solutions for treating wastewater rich in biodegradable particles. Some of the effective methods for pesticide degradation are adsorption [7,8], electrochemical oxidation (direct and indirect) [9–11], and representatives of Advanced Oxidation Processes [12,13].

Electrochemical oxidation processes can be divided in two main groups according to indirect and direct electrochemical oxidation by the oxidizing species generating mechanism. Indirect electrochemical oxidation uses the generated, so-called active chlorine species ( $\text{Cl}_2$ ,  $\text{HOCl}$ , and  $\text{OCl}^-$ ) obtained by the oxidation of chloride ions to degrade pollutants present in the wastewater following the homogeneous reaction. The second category is based on the usage of "active" anodes that directly transfer electrons among organic pollutants and an active surface of the anode. The product of complex reactions onto the anode surface generates the intermediaries (e.g. "active oxygen" and hydroxyl radicals) that are able to oxidize organic compounds.

The mechanism of direct electrochemical oxidation of carbamate pesticide methomyl using the active  $\text{IrO}_x$  anode can be described by the following reactions [14,15]:



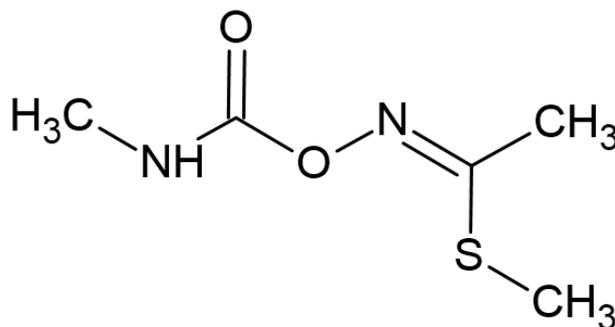
Because the "active" anode interacts fast with hydroxyl radicals, mixed more valence oxides ( $\text{IrO}_x(\text{O})$ ) can be formed after desorption from the anode surface. The formation of more valence oxides is presented by Equation 2:



Additional degradation of the more valence oxides could produce the molecular oxygen according to the reaction (Equation 3):



Due to their high efficiency, carbamate pesticides are widely used to prevent and control pathogenic diseases in agriculture [16]. Also, carbamates can pollute watercourses if they are used intensively on certain land. Studies have shown harmful effects on humans affect endocrine activity and disrupt biological systems [17]. A representative of carbamate pesticides, methomyl (Figure 1), belongs to the group of broad-spectrum neurotoxic pesticides intended to protect agricultural goods from various insects. It can apply it to different crops such as lettuce, tomato, sugar beet, and cotton [18].



**Figure 1.** Structure of carbamate pesticide methomyl

The lethal and sub-lethal effects accompanied by methomyl exposure in aquatic and terrestrial organisms, even in more complex organisms such as rodents, amphipods, and fish, have been described in many studies [19–21]. The high toxicity of the carbamate pesticide methomyl places it in the group of easily accessible chemical compounds that can be used in crises such as terrorist acts or war for water pollution, which is the most crucial resource for survival in addition to food. This study aimed to investigate the efficiency of methomyl in-situ degradation from aqueous solutions by direct electrochemical oxidation (DEO). Tomašević et al. [22] studied the photolytic degradation of the same carbamate pesticide under monochromatic 254 nm ultraviolet light, and efficacy under optimal conditions was approximately 85% after five hours. The photocatalytic degradation of pesticide using the Fe-ZSM5 zeolite, and AlFe-pillared montmorillonite catalysts were investigated by Tomašević et al. [23], and they were determined the complete degradation after four hours. Tamimi et al. [24] were investigated the chemical degradation of methomyl by Fenton and photo-Fenton processes and determined that the used processes highly effective and, after 30 minutes, achieved 100% degradation of methomyl. One of the imperfections of mentioned processes is using of oxidants (mostly H<sub>2</sub>O<sub>2</sub>) which are difficult to store [25].

The kinetics study of the methomyl electrochemical oxidation was only investigated by Grgur and Mijin [10] using the "active" Ti/RuO<sub>2</sub> anode in the presence of "active chlorine". To the best of our knowledge, the efficiency of mineralization of methomyl by DEO using IrO<sub>x</sub> anode was not performed yet. The change of methomyl concentration in a solution was followed via UV/Vis spectrometry and a Fourier Transformation-Infrared spectroscopy was used to determine the changes in the methomyl molecule after the direct electrochemical oxidation process. Also, the phytotoxicity of methomyl and degradation products were studied using the mung bean seeds.

## 2. EXPERIMENTAL PART

### 2.1. Materials and methods

The carbamate pesticide methomyl was purchased from DuPont (USA). Sodium sulfate used as an electrolyte was obtained from Centrohchem (Serbia). Sulfuric acid and sodium hydroxide were

purchased from Fisher Scientific (USA). All chemicals were at least of analytical grade and were used without any further purification treatments. The Arium® Pro Ultrapure Water System (Sartorius, Germany) provided deionized water (18 MΩ). As the current source, a PAR M273 potentiostat/galvanostat in the galvanostatic mode was used. The IrO<sub>x</sub> anode was obtained from De Nora with an area of 5 cm<sup>2</sup> (USA).

The pH measurement was conducted using the Mettler Toledo pH Meter Seven Compact S220 (Switzerland). During the degradation experiments, the electrolytes were stirred by an Ika C-MAG HS (Germany) digital magnetic stirrer. A UV-Vis analysis of reaction solutions was performed using the UV-Vis Shimadzu 3600 spectrophotometer (Japan). The structural analysis of untreated pesticide and degradation products was performed by Fourier-transform infrared spectroscopy. The analogs were fixed on a Nicolet 6700 spectrometer (Thermo Scientific, USA) in attenuated total reflectance (ATR) mode using a one-way 45° F ATR accessory with diamond crystal and electronically cooled DTGS detector. The spectra were co-added to 64 scans at a spectral resolution of 4 cm<sup>-1</sup> and corrected for ATR. The Nicolet 6700 FT-IR spectrometer was equipped with OMNIC software and recorded spectra in the wavelength range 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. A sample of degradation products was prepared by extracting an electrolyte solution, after 120 minutes of reaction, with diethyl ether (Fisher Scientific, USA). The anhydrous sodium sulfate (Kemika, Croatia) was used for drying ether solution and afterward evaporated.

## 2.2. Pesticide degradation by direct electrochemical degradation

The direct electrochemical oxidation of carbamate pesticide was performed in an open reactor ( $V=200\text{ cm}^3$ ) at room temperature ( $\sim 21\text{ }^\circ\text{C}$ ). In the first step, the electrolytes were prepared using medium (deionized water), sodium sulfate, and methomyl. A 10 cm<sup>2</sup> plate made from austenite 18Cr/8Ni stainless steel series 304 was used as the cathode. Electrodes (IrO<sub>x</sub> and stainless steel) were immersed in the electrolyte (at the top of the reactor, with an electrode gap of 3 mm). The reaction is investigated by applying the currents of 300, 400, 500, 600, and 700 mA or at corresponding current densities of 60, 80, 100, 120, and 140 mA cm<sup>-2</sup>. The magnetic stirrer mixed the electrolyte with a constant mixing speed of 700 rpm. The reaction was followed by UV/Vis spectrophotometry. The direct electrochemical oxidation efficiency of pesticide degradation was studied at the pH of pesticide solution (pH 7), pH 3, and 12. The value of pH was adjusted by adding 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> for the acidic state (pH 3) or the same concentration of NaOH solution for the basic state (pH 12).

## 2.3. Degradation efficiency and energy consumption

The pesticide degradation efficiency was calculated using Equation 4:

$$\text{Degradation efficiency} = \frac{(C_0 - C_t)}{C_0} \cdot 100 \quad (4)$$

Where  $C_0$  and  $C_t$  are the methomyl concentration at zero time and at a specified ( $t$ ), respectively.

To determine economic viability, energy consumption is a very important parameter. Energy consumption in kWh m<sup>-3</sup> can be calculated (Equation 5) [26]:

$$\text{Energy consumption} = \frac{U \cdot I \cdot t}{V_s} \quad (5)$$

where  $U$  is the cell voltage,  $I$  is current,  $t$  is an electrolysis time, and  $V_s$  is the solution volume.

#### 2.4. Phytotoxicity study

Phytotoxicity was studied using the Mung bean seeds (*Vigna mungo*) as described before [27]. In brief, the seeds were immersed in 0.5 % NaOCl for 30 min and 10 bean seeds were placed over the filter paper in a sterilized glass Petri plate. The seeds were incubated for one week under ambient conditions and exposed to sunlight. The distilled water was used as control and the samples of the treated pesticide solution were used for soaking the filter paper. In order to examine the effect of the degradation product exclusively, after two hours of treatment of the pesticide solution with direct electrochemical oxidation, the obtained product was isolated from the solution by extraction with diethyl ether. The dry residue after extraction was dissolved in 200 ml of deionized water, and used in this study. The phytotoxicity was calculated using Equation 6:

$$\text{Phytotoxicity (\%)} = \frac{\text{Radicle length of control} - \text{Radicle length of sample}}{\text{Radicle length of control}} \quad (6)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. The reaction kinetics of pesticide degradation

The kinetic parameters obtained by modeling experimental data are necessary to design a wastewater treatment plant. At the beginning of the study, the reaction kinetics of methomyl degradation was established. The influence of initial concentration of pesticide and electrolyte, initial pH value, and applied current on the efficacy of pesticide degradation using direct electrochemical oxidation. Although, most direct electrochemical oxidation degradation processes usually obey the pseudo-first kinetic order (Equation 7):

$$\ln \frac{C_t}{C_0} = -k \cdot t \quad (7)$$

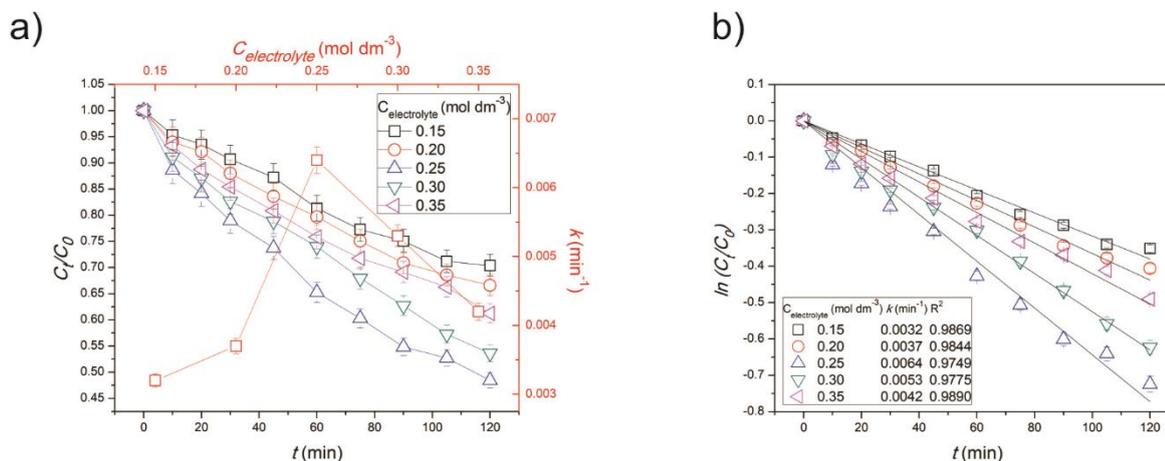
Where  $C/C_0$  represents the relative or normalized concentration.

All results of methomyl degradation by direct electrochemical oxidation show good fitting with the pseudo-kinetic order.

#### 3.2. The influence of electrolyte concentration

Because electrolyte concentration is crucial for direct electrochemical oxidation, the influence of sodium sulfate concentration on the investigated degradation was performed first in the range of 0.15 – 0.35 mol dm<sup>-3</sup> of electrolyte, at pH = 7. Determination of optimal electrolyte concentration is essential since the cost of applied current, sodium sulfate, and degradation efficiency. The increasing of initial electrolyte concentration initiates an increase in conductivity and improves electron transfer during degradation, especially during oxygen evolution [26,28]. Figure 2a displays the dependence of the methomyl relative concentrations on the degradation time at different initial electrolyte concentrations

(black coordinate plane) and the habit of reaction rate on the initial electrolyte concentration (red coordinate plane). In contrast, Figure 2b shows the logarithmic plot of the relative concentrations of methomyl versus the electrolysis time for different electrolyte concentrations.



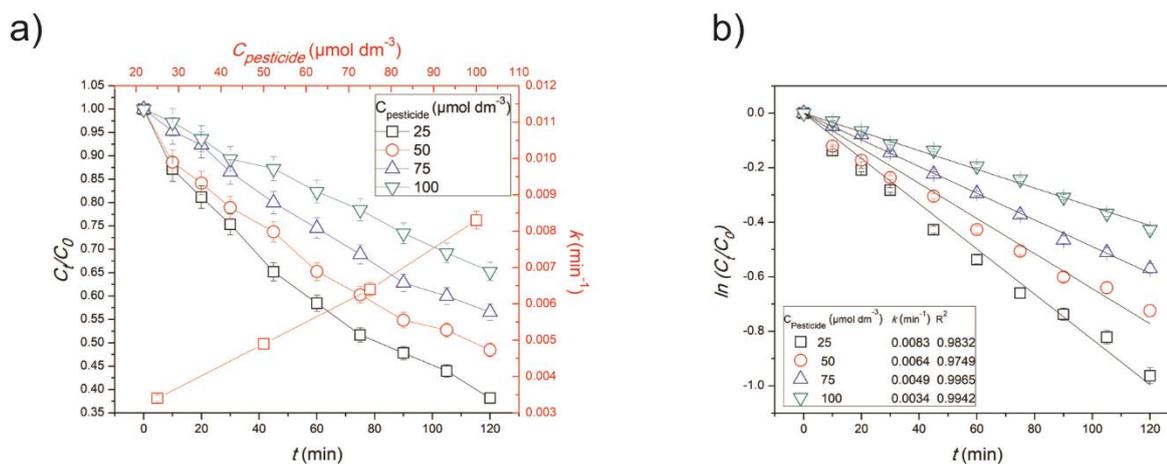
**Figure 2.** The dependence of the methomyl relative concentrations as a function of electrolysis time (black coordinate plane) and dependence of the reaction rate on the initial electrolyte concentration (red coordinate plane) (a). The pseudo-first order kinetics plot and rate constant for methomyl degradation at different initial electrolyte concentrations (b). Conditions:  $C_{\text{Pesticide}} = 50 \mu\text{mol dm}^{-3}$ ,  $pH = 7$ ,  $I = 500 \text{ mA}$ .

According to the results presented in Figure 2, it can be concluded that the increase of the sodium sulfate to concentration  $C_{\text{electrolyte}} = 0.25 \text{ mol dm}^{-3}$  initiated an increase in direct electrochemical oxidation efficiency from 29.7% to 51.6% after 2 hours, and reaction rate from  $k = 0.0032 \text{ min}^{-1}$  to  $k = 0.0064 \text{ min}^{-1}$ . Further increasing of electrolyte concentration to  $C_{\text{electrolyte}} = 0.35 \text{ mol dm}^{-3}$  initiates decreasing of efficiency to 38.8% and reaction rate  $k = 0.0042 \text{ min}^{-1}$ . A decrease in process efficiency and reaction rate value can be caused by scavenging properties of electrochemically generated hydroxyl radicals by  $\text{SO}_4^{2-}$  ions originated by an electrolyte (Equation 8) [27]:



### 3.3. The influence of pesticide concentration

The parameter of pesticide concentration is vital for reactor designing and calculating the time required for treatment and the volume of reservoirs in an effluent treatment plant. The effect of initial pesticide concentration was examined using the different initial pesticide concentrations (25, 50, 75, and  $100 \mu\text{mol dm}^{-3}$ ). Figure 3a shows the dependence of the relative methomyl concentrations on the degradation time at different initial pesticide concentrations (black coordinate plane) and the dependence of reaction rate on the initial pesticide concentration (red coordinate plane). Figure 3b shows the logarithmic plot of the relative concentrations of methomyl versus the electrolysis time for different initial pesticide concentrations.



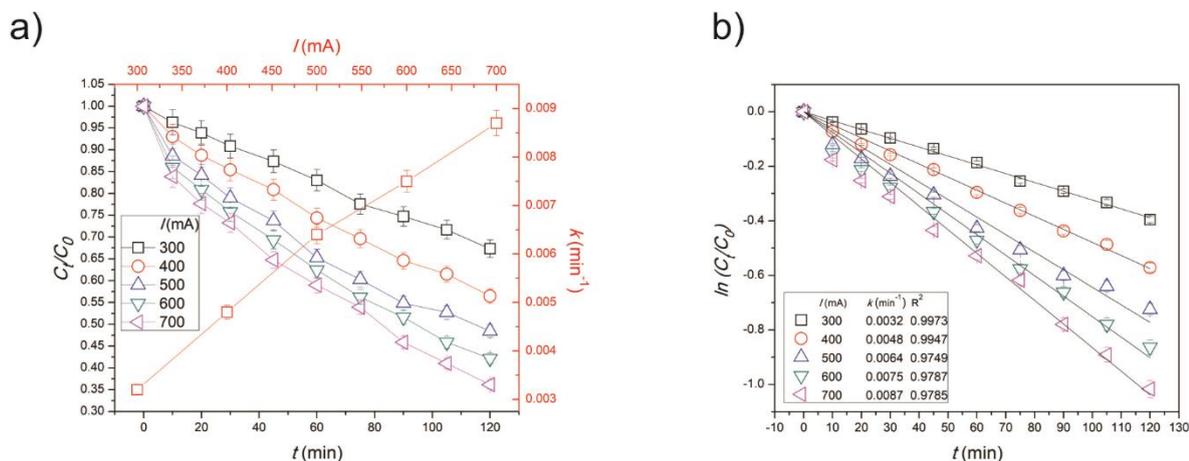
**Figure 3.** The dependence of direct electrochemical oxidation of methomyl as a function of electrolysis time (black coordinate plane) and dependence of reaction rate on the initial pesticide concentration (red coordinate plane) (a). The pseudo-first order kinetics plot and rate constant for methomyl degradation at different initial pesticide concentrations (b). Conditions:  $C_{\text{Electrolyte}} = 0.25 \text{ mol dm}^{-3}$ ,  $\text{pH} = 7$ ,  $I = 500 \text{ mA}$ .

According to the results presented in Figure 3, the carbamate pesticide degradation efficiency by direct electrochemical oxidation decreases with the initial methomyl concentration increase. The increase of initial methomyl concentration from 25 to 100  $\mu\text{mol dm}^{-3}$  initiates the decrease of degradation efficiency from 61.9% to 34.8%, while the reaction rate constant decreases from 0.0083 to 0.0034  $\text{min}^{-1}$ . The determined dependence of degradation efficiency and reaction rate value from initial methomyl concentration results from insufficient adsorption site on the  $\text{IrO}_x$  anode caused by forming the thick film of hydroxyl radicals absorbed onto anode at higher methomyl concentration. The same phenomena were obtained by Zhang et al. [29] using the europium-doped  $\text{PbO}_2$  anode for hydroquinone degradation by the direct electrochemical oxidation process, where after electrolysis for 180 min, the hydroquinone degradation efficiency decreased from 96.33% to 62.59% by increasing of initial concentration from 20 to 200  $\text{mg L}^{-1}$ . Stupar et al. [30] investigated the effect of the same parameter of neonicotinoid pesticide thiamethoxam on pesticide degradation by direct electrochemical oxidation. They defined the same dependence were increasing of initial pesticide concentration is followed by decreasing efficiency from 68.5% ( $C_{\text{pesticide}} = 0.125 \times 10^{-4} \text{ mol dm}^{-3}$ ) to 55.6% ( $C_{\text{pesticide}} = 0.5 \times 10^{-4} \text{ mol dm}^{-3}$ ).

### 3.4. The influence of applied current

The effect of applied current is a significant parameter of every electrochemical oxidation process, and the determination of optimal applied current is essential for process cost-effectiveness [31]. The efficiency of carbamate pesticide methomyl degradation by direct electrochemical oxidation was examined in the values of applied current in the range of 300 to 700 mA. Figure 4a presents the dependence of the methomyl relative concentrations on the degradation time at different applied currents

(black coordinate plane) and the dependence of reaction rate on the applied current (red coordinate plane). Figure 4b shows the logarithmic plot of the relative concentrations of methomyl versus the electrolysis time for the different applied currents.

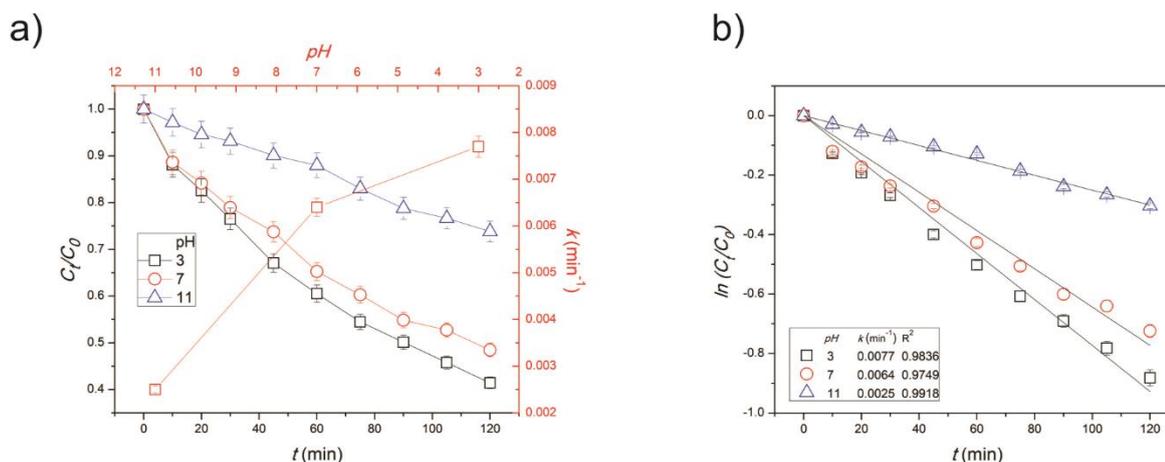


**Figure 4.** The dependence of DEO of methomyl as a function of electrolysis time (black coordinate plane) and dependence of reaction rate on the applied current (red coordinate plane) (a). The pseudo-first order kinetics plot and rate constant for methomyl degradation at different initial pesticide concentrations (b). Conditions:  $C_{\text{Electrolyte}} = 0.25 \text{ mol dm}^{-3}$ ,  $C_{\text{Pesticide}} = 50 \text{ } \mu\text{mol dm}^{-3}$ ,  $pH = 7$ .

According to the results presented in Figure 4, it can be concluded that the increase of the applied current increase the degradation efficiency of pesticide. At the lowest applied current ( $I=300 \text{ mA}$ ), degradation efficiency after 120 minutes is 32.7%, and the reaction rate is  $0.0032 \text{ min}^{-1}$ . The increase of applied current to  $I=700 \text{ mA}$  initiated the rise of degradation efficiency for the same degradation period to 63.9% and the value of reaction rate to  $0.0087 \text{ min}^{-1}$ . According to the presented values, the degradation is almost two times more efficient, and the value of reaction rate at a higher applied current is nearly three times higher than at 300 mA. The same behavior and dependence of degradation efficiency and the reaction rate from applied current are originated by Zhang et al. [29] and Stupar et al. [30], where is determined the increase of the applied current initiates the rise in the degradation of the pollutant using the direct electrochemical oxidation.

### 3.5. The influence of the initial pH value

The last crucial parameter which can affect the degradation efficiency and the reaction rate values is the pH value. The influence of pH value is investigated at acidic ( $pH=3$ ), neutral ( $pH=7$ ) and basic ( $pH=11$ ) conditions. Figure 5a shows the dependence of the methomyl relative concentrations on the degradation time at different initial pH values (black coordinate plane) and the dependence of reaction rate on the different initial pH values (red coordinate plane). Figure 5b shows the logarithmic plot of the relative concentrations of methomyl versus the electrolysis time for different initial pH values.

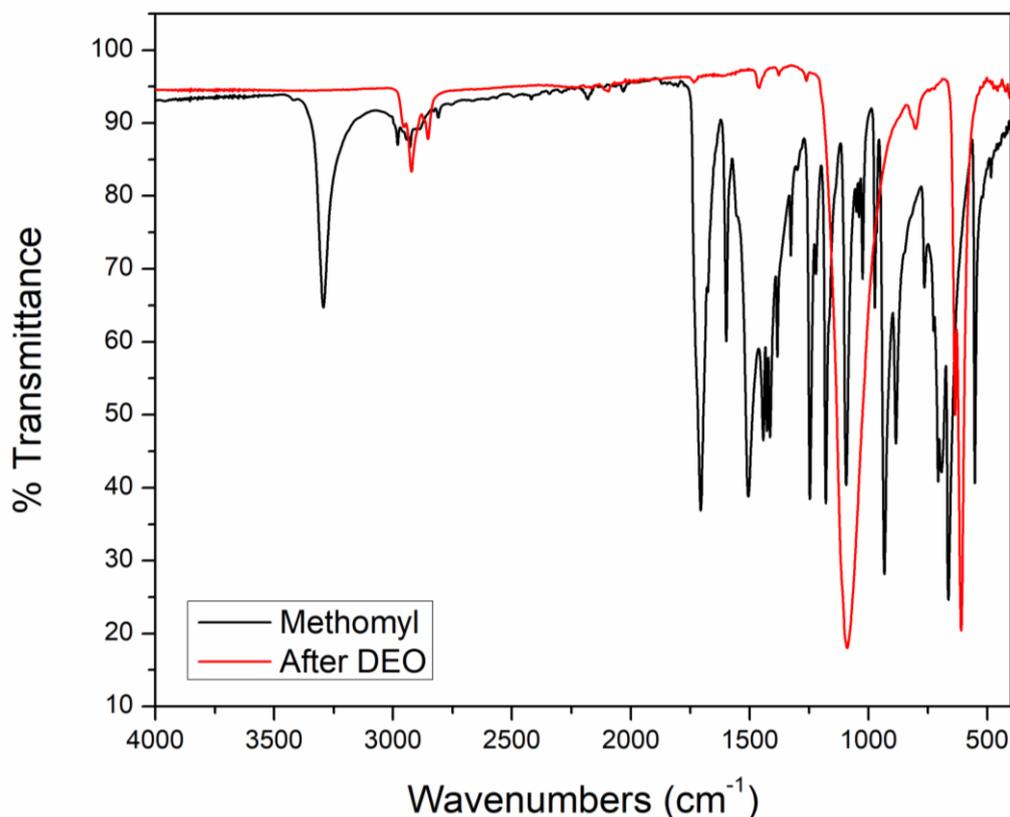


**Figure 5.** The dependence of direct electrochemical oxidation of methomyl as a function of time (black coordinate plane) and dependence of reaction rate on the initial pH value (red coordinate plane) (a). The pseudo-first order kinetics plot and rate constant for methomyl degradation at different initial pH values (b). Conditions:  $C_{\text{Electrolyte}} = 0.25 \text{ mol dm}^{-3}$ ,  $C_{\text{Pesticide}} = 50 \text{ } \mu\text{mol dm}^{-3}$ ,  $I = 500 \text{ mA}$ .

According to the results, the methomyl degradation efficiency by DEO using  $\text{IrO}_x$  anode was higher in the acidic state of the electrolyte. At  $\text{pH}=3$ , after 120 minutes was degraded 68.6% and was determined reaction rate  $k=0.0077 \text{ min}^{-1}$ , increasing pH value to neutral and basic state initiate the efficiency decreasing to 51.6 and 26.2%, respectively. The same trend is determined in values of reaction rates, at neutral and basic states dropped to  $0.0064$  and  $0.0025 \text{ min}^{-1}$ , respectively. The obtained results can be described by enhancement of  $\text{O}_2$  evolution at the anode surface in an alkaline medium which decreases the direct electrochemical oxidation efficiency. The enhancement of  $\text{O}_2$  evolution decreases the diffusion rate of methomyl molecules near the electrode [32]. In addition, at higher pH, more stable and less active  $\text{IrO}_x$  is formed. The same phenomena are obtained in a study of anthraquinone dye Acid Blue 111 by direct electrochemical oxidation where the increasing of initial pH value of the electrolyte initiates the decreasing of degradation efficiency [26].

### 3.6. FT-IR study

The electrochemical degradation of the carbamate pesticide methomyl was also studied using FT-IR spectroscopy. Samples were prepared by extracting the electrolyte solution with diethyl ether as described in the Experimental part. Figure 6 shows the methomyl FT-IR spectra and spectra of extract obtained after the direct electrochemical degradation of the pesticide.



**Figure 6.** The FT-IR spectra of carbamate pesticide methomyl and extract were obtained after the direct electrochemical degradation of the pesticide. Conditions:  $C_{\text{Electrolyte}} = 0.25 \text{ mol dm}^{-3}$ ,  $C_{\text{Pesticide}} = 50 \text{ } \mu\text{mol dm}^{-3}$ ,  $pH = 7.0$ ,  $I = 500 \text{ mA}$

The absorptions in FT-IR spectra of methomyl (Figure 6) at  $3292 \text{ cm}^{-1}$  can be attributed to N–H vibrations, while the intensive peaks at  $1705$  and  $1597 \text{ cm}^{-1}$  originate from C=O vibrations. The absorption peak at  $\sim 1500 \text{ cm}^{-1}$  and peaks in the range  $1413$  to  $1382 \text{ cm}^{-1}$  can be assigned to C–N vibrations. The absorption peaks at  $1325$ ,  $1245$ , and  $1220 \text{ cm}^{-1}$  originated from C–H aliphatic stretching and wagging vibrations. The absorption peak at  $\sim 1900 \text{ cm}^{-1}$  can be attributed to C–O bending. The absorption peak at  $932 \text{ cm}^{-1}$  originated from banding vibrations of secondary amines, while the peak at  $883 \text{ cm}^{-1}$  can be assigned to stretching vibrations of N–O. The moderate peaks at  $706$  and  $692 \text{ cm}^{-1}$  originate from stretching vibrations of C–S.

Unlike the FT-IR spectra of pesticides, and the spectra of electrooxidation residue it is noticeable that the increase of absorption peaks at  $2922$  and  $2852 \text{ cm}^{-1}$  originated from stretching vibrations of C–H. Also, an intensive peak at  $1089 \text{ cm}^{-1}$  can be assigned to stretching vibrations of C–O bending. The absorption peak at  $\sim 800 \text{ cm}^{-1}$  can be assigned to twisting vibrations of C–H. The existence of a peak at  $634 \text{ cm}^{-1}$  belongs to C–S vibrations, while a peak at  $609 \text{ cm}^{-1}$  can be attributed to C–H twisting vibrations. The disappearance of the absorption peaks originating from C–N, N–O, and N–H can prove the possible sensitive positions for electrochemically generated oxidizing agents. Also, the absence of peaks at  $1705$  and  $1597 \text{ cm}^{-1}$  originate C=O indicates the probable cleavage of C=O bonds by direct electrochemical oxidation. The obtained results of FT-IR spectroscopy are complementary to the results

of HPLC-MS analysis of methomyl degradation products generated by reactive oxygen species treatment where were identified N-Methylformamide and Acetamide [33].

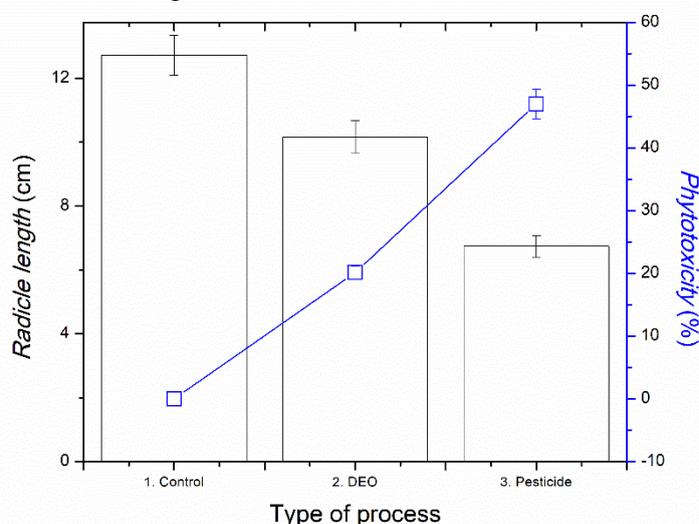
### 3.7. Energy consumption study

The parameter of economic profitability of the process and efficiency are the most important for the design of wastewater treatment plants. The primary data for calculating the economic viability of treatment is energy consumption computed using Equation 5.

The energy consumption was studied on the same applied current values as in the determination of applied current influence on effectiveness. By increasing the applied current from 300 to 700 mA, cell voltage was increased from 3.25 to 4.25 V. By energy consumption calculation, increasing the applied current in the estimated range initiates the increase of energy consumption from 9.75 to 29.75 kWh m<sup>-3</sup>, which is almost three times the increase. By comparing energy consumption values with direct electrochemical effectiveness and reaction rate, at the lowest energy consumption, after two hours was degraded 32.7% and reaction rate was 0.0032 min<sup>-1</sup> and at the highest energy consumption level was degraded 63.9% the value of reaction rate increase to 0.0087 min<sup>-1</sup>. From an economical point of view, optimal conditions for methomyl degradation are  $C_{Electrolyte} = 0.25 \text{ mol dm}^{-3}$ ,  $C_{Pesticide} = 50 \text{ } \mu\text{mol dm}^{-3}$ ,  $I = 500 \text{ mA}$ , and  $pH=3$ , which was efficiently degraded 68.6% and was determined reaction rate  $k=0.0077 \text{ min}^{-1}$ , at this condition, energy consumption was 18.75 kWh m<sup>-3</sup>.

### 3.8. Phytotoxicity study

The untreated wastewaters rich with dissolved pesticides in agricultural ranges can cause multiple harmful effects. One of them is a high rate of phytotoxicity. In the present study, Mung bean seeds were used for phytotoxicological analysis of pesticide and degradation products. The results of the phytotoxicity study are presented in Figure 7.



**Figure 7.** The results of pesticide and degradation product phytotoxicity. Conditions:  $C_{Electrolyte} = 0.25 \text{ mol dm}^{-3}$ ,  $C_{Pesticide} = 50 \text{ } \mu\text{mol dm}^{-3}$ ,  $pH = 7.0$ ,  $I = 500 \text{ mA}$ .

The results presented in the previous Figure 7 show that the untreated solution of carbamate pesticide methomyl had a negative effect on Mung bean seeds germination and determined radicle length was 6.74 cm. Unlike pesticide solution, the radicle length of germinated Mung bean seeds treated with a degradation product solution was 10.16 cm (DEO). The phytotoxicity calculated using Equation 6 of pesticide solution was 47.01 %, and for degradation, product solution was 20.12 %, and these results conclude that direct electrochemical oxidation reduces toxicity.

#### 4. CONCLUSION

The pseudo-first kinetic order can well describe methomyl degradation using direct electrochemical oxidation. The investigation of electrolyte concentration influence shows the determination of the optimal concentration of  $\text{Na}_2\text{SO}_4$  ( $C_{\text{electrolyte}} = 0.25 \text{ mol dm}^{-3}$ ) while the higher concentrations initiate "scavenging" of hydroxyl radicals by sulfate ions. The direct electrochemical degradation in an acidic solution is more efficient. The increased initial concentration of methomyl affects the degradation by direct electrochemical oxidation and decreases the efficiency and reaction rate value. The increase of applied current from 300 to 700 mA causes the growth of degradation efficiency and reaction rate, but this increase makes the process more expensive. The optimal conditions for direct electrochemical oxidation of carbamate pesticide methomyl were found to be  $C_{\text{pesticide}} = 0.25 \text{ mol dm}^{-3}$ ,  $\text{pH} = 3$ ,  $I = 500 \text{ mA}$ .

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