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Research Article

Optimization of Electrocoagulation Conditions in the Degradation Process of Carbofuran Waste (Furadan 3GR) Using Al/Graphite Electrodes

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ABSTRACT

Electrocoagulation is one of the electrochemical methods for treating wastewater and separating pollutants. In this research, the electrocoagulation using Al/Graphite electrodes was applied to artistic wastewater containing carbofuran to see the reduction of its chemical oxygen demand(COD). The electrocoagulation process was chosen in this study based on several advantages, including easy to separate between impurities and the sample and a simple operating system. Several parameters such as electrolysis time, variations in electrolyte concentration, and the effect of pH have been investigated for their impact on the electrocoagulation process. The results showed that the proportion of the best reduction in chemical oxygen demand (COD) was 64.40%. The best conditions were an electrolysis time of 60 minutes, an electrolyte concentration of 0.15 M, and a pH of 10. The results also show that the decrease in chemical oxygen demand (COD) dependson those parameters. These results were investigated further by characterization using UV-Vis spectrophotometry and FTIR spectroscopy. The results of the UV-Vis spectrum showed a decrease in intensity at a wavelength of 275 nm. Analysis of the FTIR spectrum between the initial sample and the results of the electrocoagulation showed that there were similar absorption peaks but with much smaller intensity, indicating that the effluent's pollutants have been deposited.

Keywords: Electrocoagulation, Carbofuran, Al/Graphite, COD

1. Introduction

In agriculture, widespread and sustainable use of pesticides is feared to cause problems of water contamination by pesticides. In addition to having a negative impact on the environment, using pesticides that are not controlled and without following the technical procedures for use also harms users' health. Pesticides are nine of the twelve most potent organic pollutants, according to the Stockholm Convention on Persistent Organic Pollutants. [1]. This is due to pesticides' high mobility and toxicity, whic make these compounds persistent in the environment.

One of the widely used pesticides in agriculture is carbofuran. Carbofuran with the trade name Furadan is a class of insecticides used to eradicate pests in rice and corn plants [2]. Carbofuran is toxic to humans, it has been reported that accumulation of carbofuran in the body can lead to overstimulation of the sensory system by inhibiting acetyl-cholinesterase and causing health problems such as cancer [3]. In addition, carbofuran is degraded in soil for a long time with a half-life of around 30-117 days [4]. The structure of carbofuran can be seen in **Figure 1** [5].

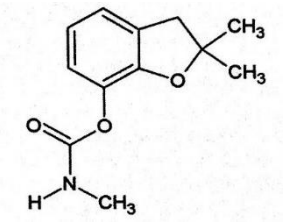

Figure 1 Carbofuran Molecular Structure

One environmentally friendly method widely reported in wastewater treatment is the electrocoagulation method [6]. The electrocoagulation method has several advantages including simple equipment, easy operation, fast sedimentation, sludge/sediment stability, little sludge production and environmental compatibility. In electrochemistry, choosing the right electrode material is very important because it plays a role in determining the reaction that will occur [7]. In this study, Al/Graphite electrodes were used with aluminum as the anode and graphite as the cathode. Several studies have generally proven that Al electrodes improve pollutant removal efficiency better than Fe electrodes. In contrast, graphite has good electrical conductivity, allowing it to be used as an electrode for electrochemistry [8].

In previous studies, herbicide removal from synthetic waste had been carried out using the electrocoagulation method [9]. The results obtained are that the confirmed electrocoagulation method can be applied as a treatment/pre-treatment technique for the removal of pesticides from wastewater, where the clomazone removal efficiency reaches 95-100%, the removal of color and turbidity is 100%, and the percentage of COD reduction reaches 82-94 % [9] [10]. Studies on the ability of the electrocoagulation method to reduce COD carbofuran levels using Al/Graphite electrodes on Furadan 3GR pesticide samples are not too much yet. So this research aimed to determine the effect of the three primary parameters that affect the process of reducing the COD: electrolysis time, the electrolyte concentration of Na_2SO_4, and the initial pH of the solution. From this research, in the future, we can design a more effective electrocoagulation process

2. Materials and Methods

2.1 Tools and Materials

The equipment used in this research were a power supply, analytical balance (Ohaus), a set of glassware (Pyrex Iwaki), vials, spatula, magnetic stirrer, pH indicator, UV-Vis spectrophotometry instrument (Shimadzu) and Fourier Transform Infra Red spectroscopy instrument (FTIR) (Brand Perkin Elmer). Reagents consist of Carbofuran (Furadan 3GR), Na_2SO_4 (Merck), H_2SO_4 (Merck), NaOH (Merck), Aquades, aluminum electrode plates and graphite electrode plates.

2.2 Research Procedure

This research began with preparing a 300 ppm carbofuran solution made from 10 grams of Furadan 3GR pesticide (carbofuran active ingredient) added with 1000 mL of distilled water. The mixture was then stirred at 400 rpm for 30 minutes to dissolve the carbofuran in Furadan 3GR. The mixture was then filtered, yielding a filtrate containing 300 ppm carbofuran. The sample preparation results were then characterized by UV-Vis spectrophotometry to ensure that the Furadan 3GR pesticide sample contained the active ingredient carbofuran. In addition, measurements of the initial COD levels of the samples were also carried out to compare the results of the COD levels before and after the electrolysis process was carried out with the formula [11]:

$$C_R\% = \left(\frac{C_0 - C}{C_0}\right) \times 100\% \quad (1)$$

where C_0 is the waste concentration before, and C is the waste concentration after electrocoagulation.

2.2.1 Determination of Working Potential

1000 mL of an artificial carbofuran sample was added with 0.1 M Na_2SO_4 (14.2 grams). The sample was then electrolyzed with a 0-12 Volt voltage that was increased by 0.5 Volts every 2 minutes. The same treatment was carried out for the blank solution. The electric potential versus electric current curve was made to obtain the electrolysis working area and the minimum potential for electrolyzing the sample.

2.2.2 Determination of the Best Electrolysis Time

1000 ml of 300 mg/L carbofuran solution was put into a beaker. Then 0.05 M Na_2SO_4 (7.1 gram) was added. The anode (Al) was inserted into the electrolysis cell and graphite as the cathode with a distance of 2 cm and connected to a DC current source starting at the application potential used, namely 9 V. Then it was electrolyzed with time variations of 10, 20, 30, 40, 50, and 60 minutes. The time indicating the maximum decrease in COD levels was used in the study.

2.2.3 Determination of Optimum Na_2SO_4 Concentration

1000 ml of 300 mg/L carbofuran solution was put into a beaker. Then 0.05 M Na_2SO_4 (7.1 gram) was added and electrolyzed at the optimum time. The anode (Al) was inserted into the electrolysis cell and graphite acts as the cathode with a distance of 2 cm and is connected to a DC current source starting at the application potential used, which is 9 V.

Furthermore, it was electrolyzed with a variation of concentration 0; 0.1; 0.15; 0.2; 0.25 M. The concentration that showed the maximum decrease in COD levels was used in the study.

2.2.4 Variation of Initial pH Solution

1000 ml of 300 mg/L carbofuran solution was put into a beaker. Then added the optimum Na_2SO_4 and electrolyzed at the optimum time. The anode (Al) was inserted into the electrolysis cell and graphite acts as the cathode with an initial pH of 7 and was connected to a DC current source starting at the optimum time and potential application of 9 Volts. The electrolyzed solution was filtered, and its absorbance was determined using a UV-VIS spectrophotometer. The treatment was repeated for the initial pH of solutions 3; 5; and 10.

2.2.5 Characterization of Results in the Best Conditions

After obtaining the three main parameters with the best conditions, the results were characterized using UV-Vis spectrophotometry and FTIR spectroscopy.

3. Result and Discussion

3.1 Analysis of Initial Sample Characterization Results

The sample was analyzed using a UV-Vis spectrophotometry instrument at a wavelength of 200-700 nm which aims to identify the presence of carbofuran in the 3GR Furadan sample. The results obtained are that the sample has a maximum wavelength absorption of 275 nm. This wavelength value is the same as the maximum wavelength value of carbofuran in previous studies, namely 275 nm [5]. This wavelength is then used to compare the changes that occur before and after the electrocoagulation process. The following sample spectra scan results with a UV-Vis spectrophotometer shown in **Figure 2**.

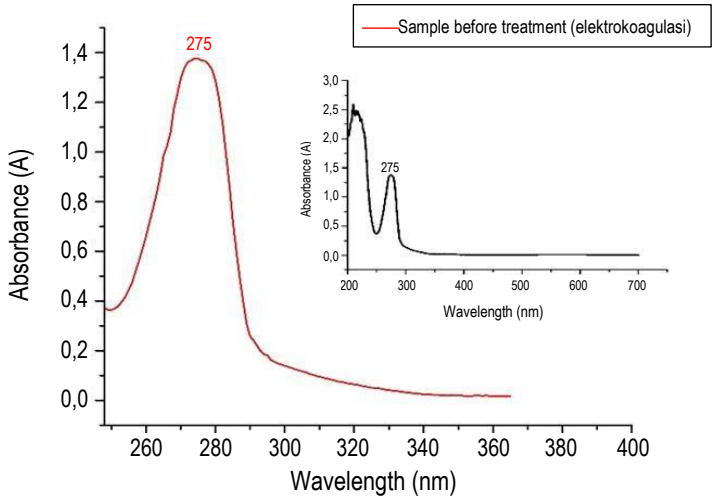

Figure 2. Results of scanning samples using a UV-Vis spectrophotometer

Based on the maximum wavelength absorption results obtained, it can be concluded that the Furadan 3GR pesticide sample positively contained the active ingredient carbofuran. In the sample spectra, the absorption band with a wavelength range of 200-230 nm is the absorption of the inert material present in Furadan 3GR. In general, pesticide formulations include a mixture of active ingredients and inert ingredients including polyacrylic acid at 230 nm xanthan gum; and propylene glycol [12]. Furthermore, analysis of the initial COD content of the sample was carried out using the test method used, namely the closed reflux method using spectrophotometry in accordance with SNI 06-6989.2:2009. The results obtained indicated that the sample had a COD level of 590 ppm (mg/L). This level has exceeded the maximum COD limit of 100 mg/L for pesticide waste that is acceptable to the environment, in accordance with the regulation of the ministry of environment number KEP 51-/MENLH/10/1995 concerning quality standards for liquid waste for industrial activities. [13].

3.2 Determination of Working Potential Range

The working potential used was obtained from sample and solvent electrolysis data by adding 0.1 M Na_2SO_4 at a potential of 0-12 V. The potential was increased by 0.5 Volt every 2 minutes with recorded changes in the flowing current. The data obtained is then described as a potential to current curve. The purpose of determining the working potential is to obtain the working potential range of Al/Graphite electrodes in a carbofuran solution. This is done so that the electrolysis

process is not complicated by reactions that occur in a larger potential area [14].The following potential and current relationship curve is shown in **Figure 3**.

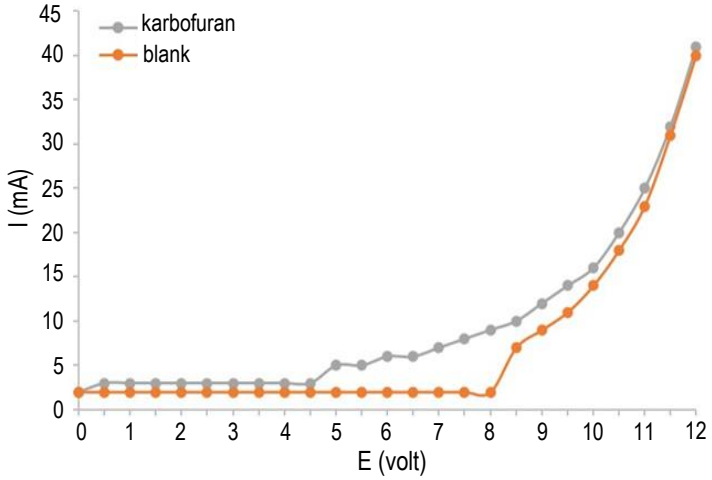

Figure 3. Potential and current relationship curves on carbofuran samples and blank solutions (aquades)

From the curve, the potential range is obtained by determining the inflection point of the curve. The inflection point of the sample electrolysis curve represents the start of the redox process (as the starting point of the working potential area), and the inflection point of the solvent system electrolysis curve is the end point of the working potential range [14]. Based on the curve above, the working potential range is 6.89 V - 9.2 V. Furthermore, the application potential set in this study is 9 V and is kept constant during the work process.

3.3 Electrocoagulation Best Time Optimization

The best time for electrolysis was determined at a fixed working potential with varying electrolysis times, namely 10; 20; 30; 40; 50; and 60 minutes. This time variation range was chosen based on research conducted by John [15] in the range of 0-60 minutes with the best pollutant removal achieved at 97.6% after 60 minutes. Electrolysis was carried out using Al/Graphite electrodes with the same submerged surface area in each process. Next, measurements of the COD concentration were carried out in each sample and the data obtained can be seen in **Table 1**. The time trend data acquired will be used as the best time for the electrocoagulation process at a later stage.

Tabel 1. Data of Electrolysis Time Variation

No	Time(minute)	Initial COD(mg/L)	Final COD (mg/L)	COD reduction
1.	10	590	480	18,64 %
2.	20	590	370	37,28%
3.	30	590	383,33	35%
4.	40	590	346,67	41,24%
5.	50	590	323,33	45,19%
6.	**60**	**590**	**250**	**57,63%**

From the table, the maximum COD value is 250 mg/L at 60 minutes with a percentage reduction of COD of 57.63%. Based on the table above, it can also be seen that the longer the electrolysis time, the COD level tends to decrease. This is in accordance with Daij's research [16], which states that the reaction time also affects the efficiency of COD reduction.

3.4 Determination of Optimum Na_2SO_4 Concentration

The addition of supporting electrolytes is necessary to increase the conductivity of the solution, increase the mobility of ions in the solution and reduce the resistance of the solution. The conductivity of the solution is an important factor that affects the efficiency and energy consumption in electrocoagulation, the lower the energy consumption in electrocoagulation, the more pollutant removal efficiency increases. Therefore, the solution's conductivity increases with adding anions from the salt [17].

The optimum Na_2SO_4 concentration was obtained from electrolyzing the sample at various concentrations, namely 0; 0.05; 0.1; 0.15; 0.2; 0.25 M with a constant working potential of 9 V and at the best electrolysis time (60 minutes). The range

of variations in the concentration of Na_2SO_4 was determined based on previous research by Un [18], with the optimum electrolyte concentration of Na_2SO_4 which is 0.1 M. So, in this study the concentration of Na_2SO_4 was varied at a value less than and greater than 0.1 M to get the best concentration of Na_2SO_4. Next, testing for COD levels was carried out with the data obtained shown in the **Table 2**

Table 2. Data of Electrolyte Concentration Variations

No	Electrolyte concentration (M)	Initial COD (mg/L)	Final COD (mg/L)	COD reduction (%)
1.	0	590	263,33	55,36%
2.	0,05	590	250	57,63%
3.	0,10	590	216,67	63,27%
4.	**0,15**	**590**	**213,33**	**63,84%**
5.	0,20	590	253,33	57,06%
6.	0,25	590	236,67	59,88%

The results obtained were the optimum electrolyte concentration at 0.15 M with a COD value of 213.33 mg/L and a percentage reduction of COD of 63.84%. From the data obtained, it can be seen that the addition of sufficient electrolyte concentration can reduce the COD level of the sample. However, if the electrolyte is added excessively, it can reduce the efficiency of the processing capacity. According to Un [18], excess SO_4^{2-} ions can inhibit the corrosion of aluminum electrodes, leading to lower COD reduction efficiency.

3.5 Effect of Variation in Initial pH of Solution

This study tested the effect of the initial pH of the solution with various pH variations, including 3; 5; 7; and 10. Variation of the initial pH of the solution was carried out to determine the effect of pH that can be applied in the process by adding H_2SO_4 for acid conditioning and NaOH for basic conditioning. Furthermore, COD levels were tested in each sample after the electrolysis process. The data obtained are shown in **Table 3**.

Tabel 3. Data Initial Solution of pH Variation

No	pH	Initial COD (mg/L)	Final COD (mg/L)	COD Reduction (%)
1.	3	590	273,33	53,67%
2.	5	590	290	50,84%
3.	7	590	213,33	63,84%
4.	**10**	**590**	**210**	**64,40%**

Based on the table above, the best results in reducing COD levels were obtained at pH 10, with a sample COD concentration of 210 mg/L and a percentage of COD reduction of 64.40%. These results are according to the research conducted by Ghalwa [11], where the COD and maximum herbicide removal reduction were achieved at pH 10 by the electrocoagulation method using aluminum electrodes. where the reduction of COD and maximum herbicide removal was achieved at pH 10 by the electrocoagulation method using aluminum electrodes.

3.6 Analysis of the Characterization in the Best Condition

From the results of decreasing COD with various variations of parameters, the best conditions were obtained at 60 minutes, electrolyte concentration (Na_2SO_4) of 0.15 M and pH 10 as the initial pH of the optimum solution. The results showed that the COD value of the sample after the electrocoagulation process decreased to 210 mg/L. Based on the equation above, the COD removal percentage is 64.40% in the best conditions. The COD value significantly reduced after treatment indicating that the pollutants present in the pesticide Furadan 3GR including carbofuran had partially precipitated during the electrocoagulation process.

The COD concentration decreased due to the electrocoagulation reactor's oxidation and reduction processes. To be able to indicate the occurrence of changes after the electrolysis process took place, an analysis was carried out using a UV-VIS spectrophotometry instrument. The results obtained are described as sample spectra before and after the electrolysis process. **Figure 4** shows a shift in wavelength and a decrease in peak intensity in the spectra before being electrolyzed with an absorption wavelength of 275 nm. In contrast, the spectra after being electrolyzed with Al/Graphite electrodes, show a decrease in peaks with an absorption wavelength shifted to 279 nm.

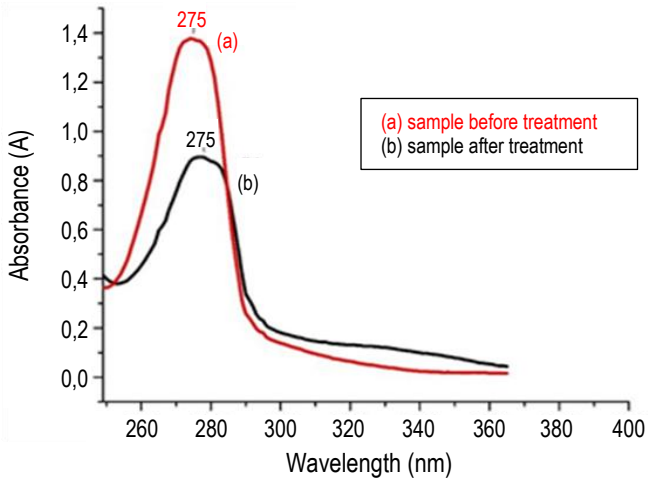

Figure 4. UV-VIS spectra of the sample before the electrocoagulation process and the sample after the electrocoagulation process

FTIR spectroscopy analysis was also carried out to determine the absorption of the sample functional groups shown in **Figure 5**. The FTIR spectra of the sample before processing showed absorption with a broad peak at 3382.96 cm^{-1} indicating the presence of the -OH group of alcohol. The absorption at wave number 1643.36 cm^{-1} indicates the presence of C=O in the aromatic ring, while the absorption band at 1276.39 cm^{-1} indicates the C–O–C group where one carbon atom is attached to the aromatic ring while the other is present. to the aliphatic structure (referring to the carbofuran structure).

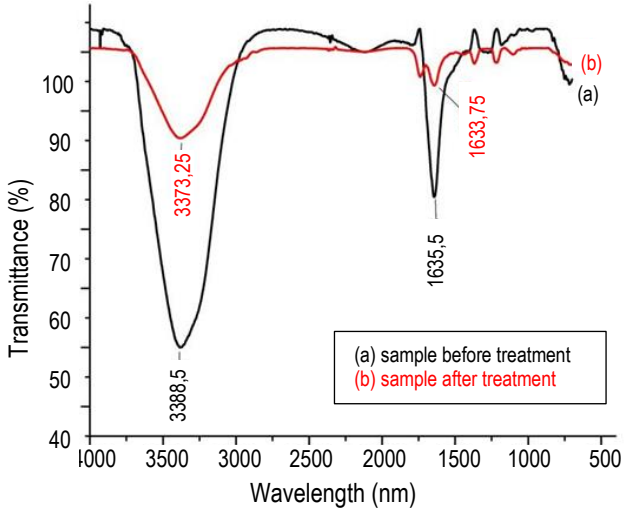

Figure 5 FTIR spectra of samples before electrolysis (a) and sludge produced by electrolysis (b)

In **Figure 5** it can be seen the FTIR spectra of the sample after electrolysis with the assumption that the carbofuran has bonded with the $Al(OH)_3$ floc, this can be shown by the presence of an absorption with a broad peak at 3384.18 cm^{-1} indicating the alcohol OH group. Furthermore, the absorption peak at wave number 1642.94 cm^{-1} indicates the presence of the C=O group. The FTIR spectra above indicate a decrease in peak intensity, indicating that the electrolysis process can reduce the intensity of the existing pollutant concentration (carbofuran). This is also supported by the similarity of the FTIR spectra between the samples before processing and the electrolyzed sludge, so it can be concluded that most of the pollutant substances have been successfully separated from the wastewater through the electrocoagulation method.

4. Conclusion

The electrocoagulation method with Al/Graphite electrodes reduced the COD level of carbofuran by 64.40% under the best conditions. The best condition for COD reduction was 60 minutes of electrolysis time with 0.15 M Na_2SO_4 concentration and pH 10.

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