Electrochemical Degradation of Methanyl Yellow using Carbon/ZnO Electrode

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Abstract

Degradation of methanyl yellowdye by using a voltage source potential and certain current is passed through carbon/ZnO electrodes as anode and silver electrodes as cathode has been developed in this research. Degradation with variation of potential, pH, and time is performed into solution of methanyl yellowcontaining electrolytes support NaCl 0.1 M. Results of this analysis obtained optimum conditions of pH 1 and potential 12 V at degradation time for 15 minutes. In the voltammetryECE reaction occurs on the surface of the electrode, which is irreversible electron transfer, followed by a irreversible chemical reaction. This method can reduce the COD value up to 75.045% and 94.060%degrade methanyl yellowsolution at 25 ppm during 30 minutes. The degradation process in this study follows the first order reaction kinetics.The result of analysis show that methanyl yellowis degraded and produce CO_2.

Keywords: Carbon/ZnO electrodes, Electrochemical degradation, Methanyl yellow, Silver electrodes

1. Introduction

Batik and textile industry is one of the largest waste water originating from the dyeing process. The resulting dye waste from the textile industry is generally a non-biodegradable organic compounds, which can cause environmental pollution, especially the aquatic environment [1]. Methanyl yellow dye is one belonging to the azo, widely used in the textile industry as dye wool, nylon, leather, paper, paint, aluminum, detergents, wood, and fur. Methanyl yellow should not be used for beverages, food, medicines because it can cause skin irritation, cause impaired vision or blurred, by inhalation will cause irritation to the respiratory tract, in large quantities can cause tissue damage and inflammation of the kidneys [2]. Therefore, it is necessary to process wastewater from textile industry further in order to safe for the environment. Methanyl yellow waste treatment meant to eliminate the levels of pollutants contained in the waste in order to qualify to be released into the environment (meet the quality standards specified) [3].

New methods of handling similar cases constantly researched and developed to improve the efficiency and effectiveness of the remediation process water environment [4]. Among the alternative approach is the method of electrolysis, this approach has a good potential in the handling of wastewater containing dye, either of the parameters decrease in the content of pollutants and physical parameters of waters [5]. These advantages can still be improved, for example in terms of the selection electrodes. Selection of electrode materials to support the desired process by improving the performance of the electrode functions as a process of oxidation or reduction takes place. The use of carbon as the anode can answer the problem above [6]. This material has a wide potential range, low currents, cheap, and inert. From this research, it is expected the carbon electrode by doping ZnO can be used to degrade methanyl yellow.

The things that affects the process of electrochemical degradation including, degradation potential, pH and time degradation. To know that methanyl yellow has been degraded CO_2 gas test is performed and to determine the degradation products are safe for the environment tested for Chemical Oxygen Demand (COD), the

measurement of peak current by voltammetry and measuring the absorbance using spectrometry UV-Vis a solution of methanyl yellow before degradation and after degradation.

2. Experimental

2.1. *Materials and research equipment*
Materials used in this research are carbon nanoporous with certain specifications, methanyl yellow dye (Aldrich), paraffin pastilles, paraffin blocks, ZnO powder, wire of silver (Ag), 0.1 M NaCl, 0.1 M NaOH, HCl 0.1 M, $Ba(OH)_2$, distilled water, akuabides, and acetone.

The equipment used in this study aresiglent SPD3303S a DC voltage source, universal indicators, spectrophotometer Shimadzu UV-Vis 1800, voltammeter EDAQ e-corder 410 and controlled by E.Chem software, Mettler AE 200 analytical balance, magnetic stirrer, micropipette tip, hotplate, and some glassware are commonly used.

2.2. *Research procedure*
The procedure of the research are:

2.2.1. *Selection offlow conductor material and optimization composition of carbon paste electrode/ZnO*
Optimization is done with degrading of 10 ppm methanyl yellow solution for 10 minutes using an electrode with variation of nanoporous carbon composition/ZnO, paraffin and current conductor. Electrodes prepared by mixing nanoporouscarbon powder, ZnO powder and paraffin with various proportions [7]. The mixture is heated at a temperature of 40°C using a hotplate. Bodies of electrodeis made from micropipette tip which embedded of current conductor wire (diameter 2 mm) [8]. Then the carbon paste is inserted in the hole of the tip electrode's body (1 cm).

2.2.2. *Optimization of potential degradation, pH, and the optimum time degradation of methanylyellow*
Potential optimizations performed by analyzing 50 mL of 10 ppm methanyl yellow with variations of pH 1 to 9 at optimum potential. Then time optimizations performed by analyzing methanyl yellow solution of 25 ppm on optimum pH and potential. Used variation degradation time5, 10, 15, 20, 25, 30, 35, 40, 45, 60, dan120 minutes [9].

2.2.3. *Analysis methanyl yellow in cyclic voltammetry*
The analysis is performed by measuring 2.5 mL of 1 ppb methanyl yellow with supporting electrolyte NaCl 1 M. The electrodes used areplatinum as a working electrode, Ag/AgCl as a reference electrode and a platinum as auxiliary electrode. The solution is measured atvariation scan rate 50, 100, 200, 250, 400 and 500 mV/s. Analysis is also performed on 1 ppb of methanyl yellow solution result of dilution from the working solution of 25 ppm either before or after degradation in variety of time at optimum scan rate [10].
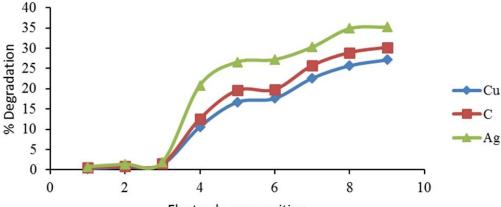
2.2.4. *CO_2 gas analysis*
The gas which formed is passed to a solution of $Ba(OH)_2$ throughU shaped capillary tube.

3. Results and Discussion

3.1. *Results of Selection of Flow Conductor Material and Optimization Composition of Carbon Paste Electrode/ZnO*
Electrode composition ratio of 5:3:4 have highest percent degradation, but in this research is selected electrodes composition of nanoporous carbon/ZnO and paraffin of 5:2:3 by using the current conductor of silver wire (Ag) because this composition have optimum degradation. Optimization results of electrode composition can be seen in Figure 1. From data in Figure 1 above proves that the conductivity of currents conductive greatly affect the percentage of degradation.

3.2. *Results of optimization potential degradation, pH, and the optimum time degradation of methanyl yellow*
Results of optimization potential of methanyl yellow the solution can be seen in Figure 2, which shows the optimal potential at 12 volts with 70.40% percent degradation. pH 1 chosen as the optimum pH because can be degraded methanyl yellow optimally with 94.06% percent degradation.

Figure 1: Curve between electrode composition and percent degradation
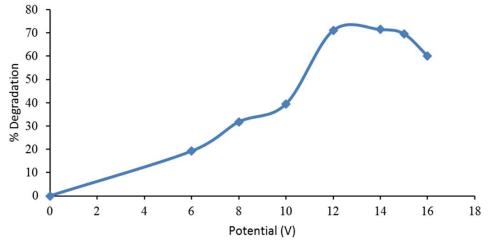

Figure 2: Curve between potential degradation of 10 ppm methanyl yellow and percentage of degraded in the electrolyte solution of 0.1 M NaCl for 15 minutes

At low pH or acidic percent degradation higher due to form neutral molecules in ion methanyl yellow ($C_{18}H_{14}N_3SO_3^-$), with the occurrence protonation (H^+) on a negative charge SO_3^-. The existence of this protonation causes methanyl yellow hydrophobic which causes solubility in water becomes lower and the compound becomes unstable, so methanyl yellow more easily degraded. However, at pH>6 increase in the percentage of degradation but is not significant because the neutralization of the negative charge SO_3^- it is not happening. Methanyl yellow is still in the form of ion ($C_{18}H_{14}N_3SO_3^-$), the absence of protonation (H^+) with ion SO_3^- resulted methanyl yellow more hydrophilic [11]. Results of pH optimization shown in Figure 3.
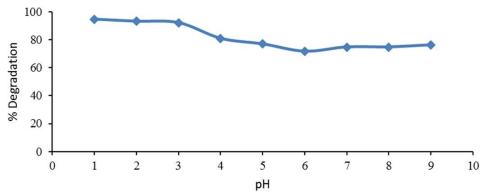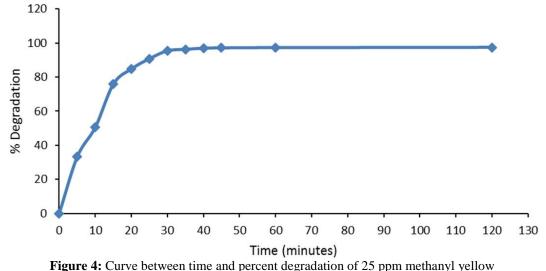

Figure 3: Curve between pH and the percentage degradation of 10 ppm methanyl yellow at potential 12 V for 15 minutes

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Time optimization for degradation of methanyl yellow is performed to determine the time it takes to degrade methanyl yellow optimally. The research shows that the longer time degradation the percent degradation has also increased but began at minute 30 to minute 120 percent degradation is not significant increase (relatively stationary). Curve between time and the percentage degradation of methanyl yellow solution can be seen in Figure 4.

Figure 4: Curve between time and percent degradation of 25 ppm methanyl yellow

The effect of variation electrochemical degradation time qualitatively can be seen in the UV-Vis spectrum shown in Figure 5.UV-Vis spectra show that the longer degradation time, absorption peak at 434 nm decreases this proves that methanyl yellow partially degraded with electrochemistry.
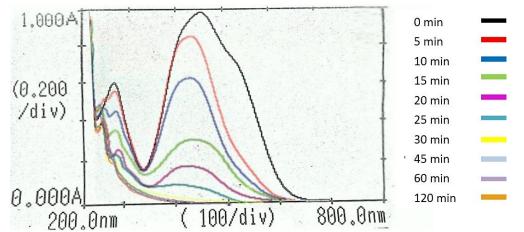

Figure 5: Results of UV-Vis spectra from electrochemical degradation of 25 ppm methanyl yellow at various times

3.3. *Chemical kinetics reaction results*
Reaction kinetics is used to determine the order of the rate for degradation reactions take place. In this study the first order reaction rate approaching that indicates if the initial concentration of methanylyellow enlarged twice the rate of decline in reaction to the degradation process becomes twice as well. At first order reaction curve is created by connecting the value of ln C versus time degradation as in Figure 6.
In this study, the rate of decrease is proportional to the degradation methanyl yellow which left with constant reaction rate 0.1028 ppm/min. Required time for half degradation process of 24.332 ppm methanyl yellow is 6.741 minutes.

3.4. *Analysis results in cyclic voltammetry*
Measurements of methanyl yellow solution using voltammeter aims to determine the effect of scan rate of the anodic and cathodic peak shift. The research shows that the reaction is the reaction of electrochemical-chemical-electrochemical (ECE), the electrochemical reaction that is irreversible electron transfer, followed by a chemical

reaction that is irreversible. This is shown by the oxidation and reduction peaks are not symmetrical, and the larger the scan rate, i_{pa}/i_{pc} also greater [12]. The analysis results of methanyl yellow voltammogram are shown in Figure 7.
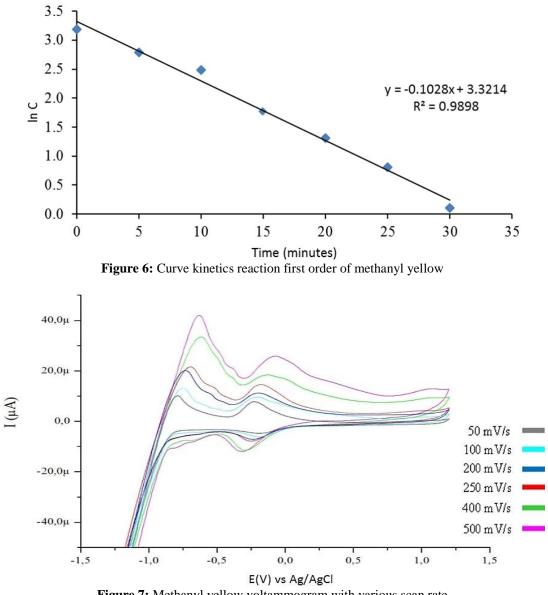

Figure 6: Curve kinetics reaction first order of methanyl yellow

Figure 7: Methanyl yellow voltammogram with various scan rate

Table 1: Results of measurements of the cathodic and anodic peak current in methanyl yellow

v (V/s)	i_{pa} I (µA)	i_{pa} II (µA)	i_{pc} (µA)
0.05	11.910	5.41	2.71
0.10	14.721	6.25	3.29
0.20	19.610	6.41	4.31
0.25	20.830	6.86	4.51
0.40	28.520	7.30	5.97
0.50	37.490	8.80	7.58

The results of measurement of cathodic and anodic peak currentinmethanylyellow shown in Table 1. In this study, the anodic and cathodic peak current decreased with increasing degradation time of methanyl yellow solution. Analysis is performed on methanyl yellow solution with a scan rate of 250 mV/s. Results of comparative analysis voltammogram methanyl yellow before and after degradation can be seen in Figure 8.
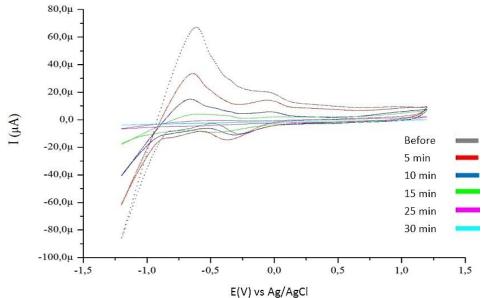
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Figure 8: Voltammogram of methanyl yellow solution before and after degradation in the optimum state

The results of methanyl yellow voltammogram at 25 minutes, peak of anodic and cathodic start ramps. This suggests that time affects the amount of methanyl yellow dye molecule which degraded. Data from measurements of the peak current and the percent degradation of each voltammogram can be seen in Table 2.
Shows that the longer time degradation the percent of reduction in the relative flow also increased. This proves the increased of methanyl yellow degradation. At minute 30 percent reduction in flow as measured by voltammetry has reached 100%, while the measurement of UV-Vis percent degradation amounting to 95.41%. This is because the measurement voltammetry performed 25000 times dilution, so that the resulting concentration is below the detection limit of the measurement from voltammeter.

Table 2: Data from measurements of the peak current and the percent reduction in the relative flow of each voltammogram

Time (minutes)	i_{pa} (μA)	$i_{pa\ 0}$ (μA)	% Relative flow reduction
5	30.750		47.164
10	12.010		79.364
15	4.416	58.200	92.412
25	1.297		97.771
30	0		100

3.5. *Electrical energy needs*
Calculation of electrical energy conducted to determine electricity rates needed to degrade methanyl yellow solution. Demand for electricity which is used to degrade methanyl yellow solution in sharing time on the concentration and the potential installation of 12 V are shown in Table 3.

Table 3: Data of energy and electricity value/kWh required for degradation methanyl yellow in various concentrations and time

Concentrations (ppm)	Mass(mg)	E (Watt.s)	Value/kWh (IDR)
5	0.25	298.296	0.09214
10	0.50	771.900	0.23843
15	0.75	1063.470	0.32849
20	1.00	1320.645	0.40793
25	1.25	1686.120	0.52082

In this study, the higher concentration of solution which degraded the higher electricity rates are needed. This is due to the greater concentration, the number molecules of methanyl yellow which produced also greater so that the energy required to degrade also higher. Curve of methanylyellow between concentration and electric energy (E) (Watt.s) required for the degradation is shown in Figure 9.
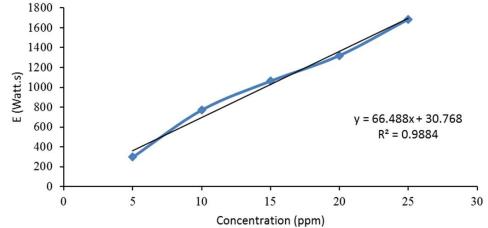

Figure 9: Curve of methanyl yellow between concentration and electric energy (E) (Watt.detik) required for the degradation

3.6. *COD analysis*
COD (Chemical Oxygen Demand) Analysis is performed to determine the amount of oxygen required to degrade pollutants present in water through a chemical reaction. Results of the COD analysis of 25 ppm methanyl yellow and 0.1 M NaCl as shown in Table 4.

Table 4: COD analysis of methanyl yellow and NaCl solution before and after degradation

Solution	COD (mg/L)analysis results		
	Before	After	
		30 minutes	120 minutes
Methanyl yellow 25 ppm	223.781	55.843	49.114
NaCl 0.1 M	32.741	55.391	-

The results show the value of COD decreased in time before and after degradation on 25 ppm methanyl yellow solution within 15 and 120 minutes. While the COD for the reference solution there is an increase in the time before and after degradation due to the concentration of halide ions, especially chloride ions whose levels over 2000 ppm in water samples will result in COD value is greater than it should be [13].

3.7. *CO_2 test results*
CO_2 gas test is intended to prove that one of the degradation products from methanyl yellow dye is CO_2 gas. In this study gave a positive test to test CO_2 gas, shown by the formation of white deposits on the glass beaker. White precipitate formed is $BaCO_3$ compound [14]. Therefore we can conclude one of the degradation products of methanyl yellow is CO_2gas. Reaction that occurs is as follows :

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 \downarrow + H_2O$$
$$\text{white}$$

Conclusion
The optimum conditions of electrochemical degradation from methanyl yellow with carbon electrodes/ZnO is at voltage of 12 Volts, pH 1, and the time of degradation for 30 minutes to degrade of 25 ppm dye solution methanyl yellow 50.0 mL with a percentage of 94.06% degradation. The analysis results of methanyl yellow with electrochemical degradation can be studied by spectrophotometry UV-Vis absorbance shown by decline in

both the visible region and in the ultraviolet region. While the cyclical voltammogram also decline in the anodic and cathodic peak current, the reaction is electrochemical-chemical-electrochemical (ECE), the electrochemical reaction that is irreversible electron transfer, followed by a chemical reaction that is irreversible. COD value of the solution before and after degradation for 30 minutes decreased by 75.045% to 55.843 mg/L as well as the kinetics of chemical reactions following the first order.

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