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Electrochemical Degradation of Malachite Green Dye using Carbon/TiO_2 Electrodes

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Abstract

Degradation of malachite greendye by using a voltage source potential and certain current is passed throughcarbon/ TiO_2 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 malachite greencontaining electrolytes support 0.1 M NaCl. Results of this analysis obtained optimum conditions of pH 7-8 and potential 10 V at degradation time for 15 minutes. Based on the voltammogram, reactions that occur are electrochemical-chemical-electrochemical (E-C-E) and irreversible This method can reduce the COD value up to 81.89% and 100% degrade malachite green solution at 25 ppm during 30 minutes. The result of analysis show that malachite greenis degraded and produce CO_2.

Keywords: Carbon/TiO_2 electrodes, Electrochemical degradation, Malachite green, Silver electrodes

1. Introduction

Organic dye is widely used in the textile industry, ink, paper, leather, plastics and paints. Coloring process will generate waste that seriously affected if dumped into aquatic systems such as rivers and the sea. Direct dye waste will pollute water ecosystems as well as harmful to public health around the region [1]. Malachite green is a dye base belonging to the group trifenil metana, green crystalline powder, when dissolved in water will cause a bluish colored solution greener [2]. Malachite green should not be used for beverages, food, medicines because it can cause skin irritation, blurred vision or cause interference, inhalation will cause irritation to the respiratory tract, in large quantities can cause tissue damage and inflammation of the kidneys [3]. Therefore, it is necessary to waste processing textile industry further that this waste is safe for the environment. Malachite green waste treatment is intended to eliminate the levels of pollutants contained in the waste in order to qualify to be discharged into the environment (meet the quality standards specified) [4].

New methods of handling similar cases constantly researched and developed to improve the efficiency and effectiveness of the remediation process water environment. Waste treatment dye in the water environment is done by physical and chemical processes, namely flocculation combined with flotation, electro-flocculation, filtration membranes [5], electro-kinetic coagulation, ion exchange, radiation, precipitation, and ozonation [6]. However, these methods are generally less effective in the removal of color, expensive and less adaptable to a variety of dyes existing waste [7a]. The potential of using odina wodier bark carbon (OWC) as a low-cost adsorbent to remove malachite green from aqueous solutions, to model the equilibrium and kinetics of the adsorption process was investigated [7b]. So from this statement 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 above problem [8]. This material has a wide potential range, low background currents, cheap, and inert. From this research, it is expected the carbon electrode by doping the TiO_2 can be used to degrade malachite green.

2. Experimental

2.1. *Materials and research equipment*

Materials used in this study are nanopores carbon with certain specifications, malachite green dye (Aldrich), paraffin pastilles, paraffin blocks, TiO_2 powder, wire of silver (Ag), 0.1 M NaCl, 0.1 M NaOH, HCl 0.1 M, $Ba(OH)_2$, distilled water, akuabides.

The equipment used in this study are siglent 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. *Manufacture of carbon paste electrodes with a doping material TiO_2 (C/TiO_2)*

Carbon paste is prepared by mixing 0.6 grams of carbon nanoporous with 0.4 grams of powder TiO_2 and 0.2 grams of paraffin, so that the ratio of carbon:TiO_2:paraffin is 3:2:1. The mixture is heated at a temperature of 40°C using a hotplate. Agency electrode made of a micropipette tip within which pinned the silver wire (diameter 1 mm). Then the carbon paste is inserted in the hole of the tip electrode body (1 cm) [9]. Furthermore, the surface smoothed on clean paper until the surface looks shiny.

2.3. *Optimization of potential degradation, pH, and the optimum time degradation of malachite green*

Potential optimizations performed by analyzing 50 mL of malachite green 10 ppm with variations of the potential of 0 V to 17.5 V to 2.5 V with each intervals of 10 minutes. Optimization of pH 3 to 9 at optimum potential. Further optimization is done by analyzing the time malachite green solution of 25 ppm on optimum pH and potential. Used variation degradation time 5, 10, 15, 20, 25, 30, 35, 40, 45, 60, and 120 minutes [10].

2.4. *Analysis of malachite green in cyclic voltammetry*

The analysis is performed by measuring 2.5 mL of 1 ppb malachite green with supporting electrolyte 1 M NaCl. The electrodes used are glassy carbon as a working electrode, Ag/AgCl as a reference electrode and a platinum as auxiliary electrode. The solution is measured at variation scan rate 50, 100, 200, and 400 mV/s. Analysis is also performed on 1 ppb of malachite green solution result of dilution from the working solution of 25 ppm either before or after degradation with2 Volt potential [11].

2.5. *CO_2gas analysis*

The gas which formed is passed to a solution of $Ba(OH)_2$ through U shaped capillary tube.

3. Results and Discussion

3.1. *Optimal results of potential degradation, pH, and the optimum time degradation potential of optimization results*

Potential degradation is one of the influential factors in the process of electrochemical degradation of malachite green. Potential optimization is performed to determine the optimum potential use in the process of degradation of malachite green. The optimization process of electrochemical degradation of malachite green is done in 50 ml malachite green 10 ppm containing 0.1 M NaCl for 15 minutes with the potential variation. The curve of the relationship between the percentage of potential degradation of malachite green solution can be seen in Figure 1.

From Figure 1 it can be seen that the percentage of degradation of malachite green solution increases with increasing potential. At 10 Volt potential shows a stationary state, where the percent degradation of malachite green value of 93%. So for the next parameter optimization potential use of 10 Volt.

The pH value is one of the factors that influence the speed of the process of degradation reactions malachite green solution. Optimization of pH is done in a way to degrade malachite green solution containing 10 ppm of the electrolyte solution of 0.1 M NaCl at pH 3, 4, 5, 6, 7, 8, and 9 with a potential of 10 volts for 15 minutes. The pH value also affects the color of the solution malachite green, so that measurement of absorbance of the solution at each pH before the degradation process. The curve of the relationship between the pH value of the percentage of degradation of malachite green can be seen in Figure 2. Figure 2 shows that the value of the pH effect on the degradation process, ie the greater the pH, the percentage of degradation of malachite green is increasing. At pH 7 shows a stationary state, where the percent degradation of malachite green is 94%. This shows that the method is applicable to the environment due to the degradation process can be done well without pH adjustment.

Time optimization aims to determine the optimum time of electrochemical degradation of malachite green solution. This process uses 50 ml malachite green 25 ppm so that the degradation process can be observed and studied. The time interval used was 5 minutes performed at the time variation of 0 to 40 minutes and degradation for 120 minutes. The curve of the relationship between the percentage degradation degraded malachite green can be seen in Figure 3.

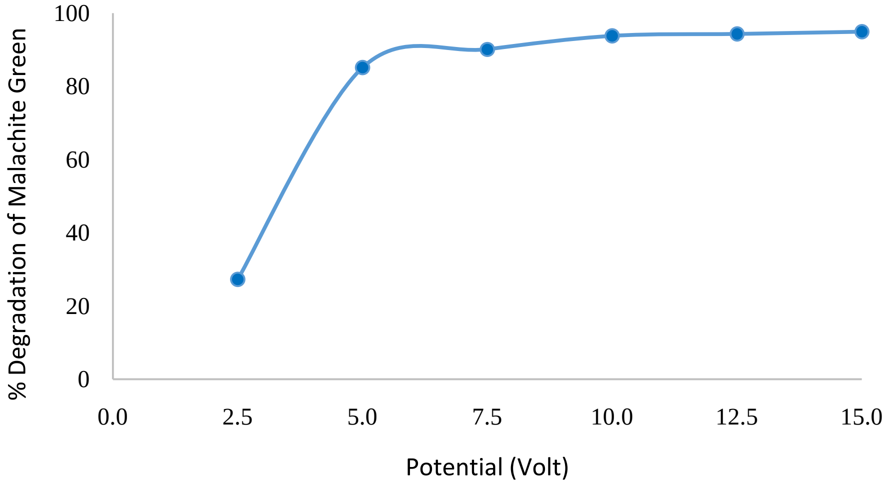

Figure 1: Curve relationship between the potential degradation of the percentage of malachite green 10 ppm degraded in the electrolyte solution of 0.1 M NaCl for 15 minutes

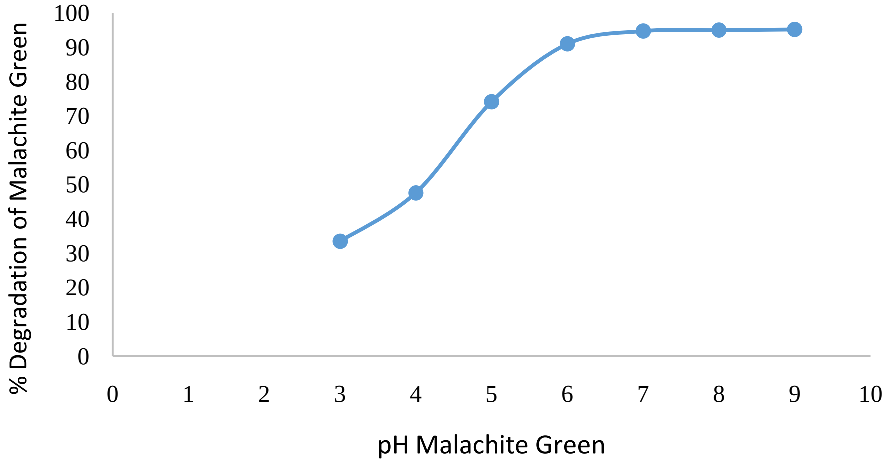

Figure 2: Curve relationship between pH and the percentage of degradation of Malachite green 10 ppm at a potential of 10 V for 15 minutes

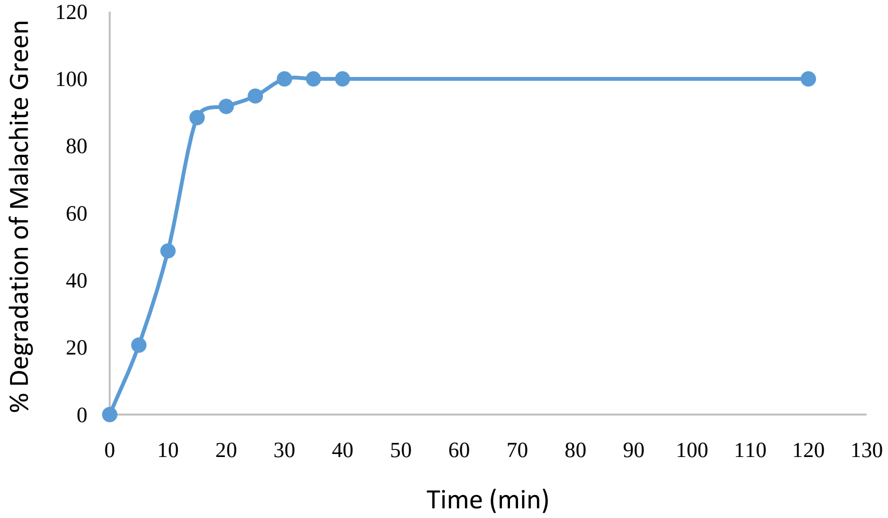

Figure 3: Curve relationship with the percent degradation time malachite green 25 ppm

From the curve of Figure 3 it can be seen that the degradation process continues to increase up to 30 minutes where the percentage value has reached 100%. The best results are shown ranging from 30 minutes to 120 minutes of the degradation process. With these results we can say that this process can be used to reduce waste pollution in aquatic environments.
The degradation process is still being done to 120-minute goal to study the absorption spectra of aromatic compounds from the degradation of malachite green. The degradation process is not carried out more than 120 minutes due to the carbon/TiO_2electrode began to fall out which can cause degradation process was not optimal.

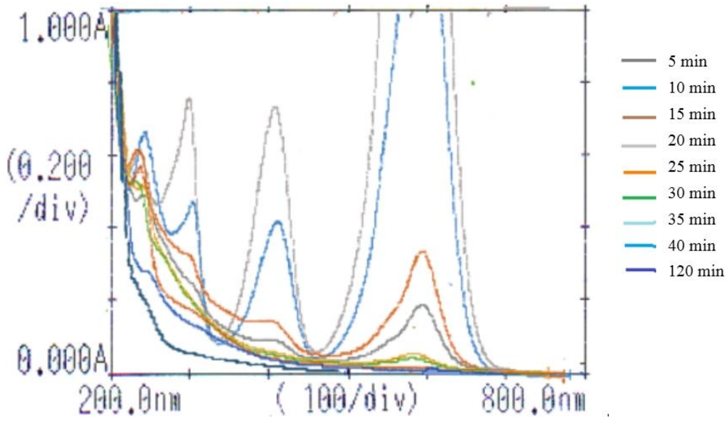

Figure 4: UV-Vis spectra of the sample results of electrochemical degradation of Malachite green 25 ppm at various times

In the UV-Vis spectrum is shown in Figure 4 shows that the longer the time degradation of malachite green, the concentration will decrease. It can be seen from the absorbance at all especially on the absorption peak wavelength of 617.5 nm which is the maximum wavelength of malachite green. Peak absorption decreased with increasing degradation time is reduced due to the intensity of color from blue to green and then colorless. Malachite green solution of 25 ppm have been relegated perfectly demonstrated starting from the 30th minute, because there is no absorption at a wavelength of 617.5 nm. Also in the 30th minute to minute 120 there are no other generated uptake in certain waves. Thus indicating that the byproducts generated in the process of degradation of malachite green solution does not have chromophore groups that can absorb UV light.

3.2. *Chemical reaction kinetics results*

Determination of reaction kinetics is used to determine the order of the rate of degradation reactions take place. Malachite green at the relegation-order reaction rate approaching one and a half because the R value is better than the other reaction order calculation. At first order reaction and a half is a correlation value of 1/Ln C against time degradation as in Figure 5.In this study, the rate of decrease is proportional to the degradation of malachite green are left with a reaction rate constant of 0.0347 min^{-1}.

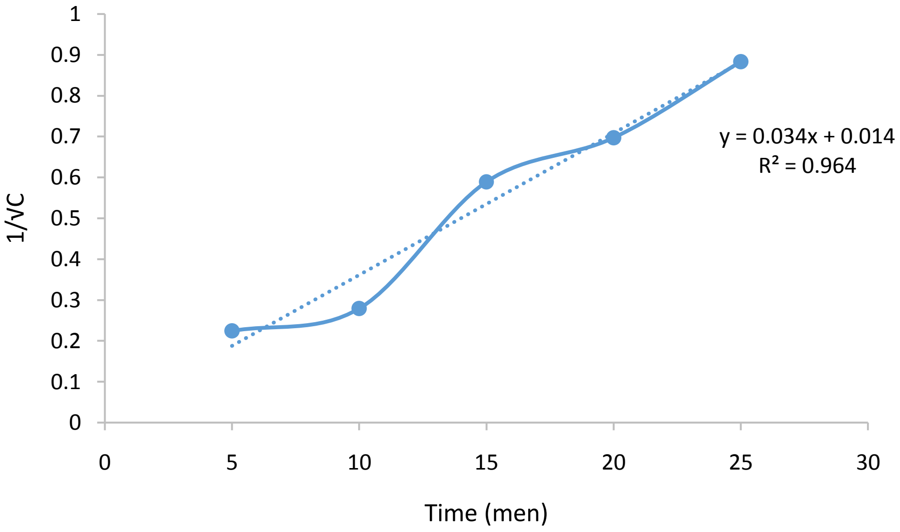

Figure 5: Curve of the half-order reaction kinetics malachite green

3.3. *Results analysis of malachite green in cyclic voltammetry*

Measurement of malachite green solution using voltammeter aims to determine the effect of scan rate of the anodic and cathodic peak shift malachite green. Based on the voltammogram can be seen that the greater the scan rate, the greater the current generated indicating that the reaction is reaction electrochemical - chemical - electrochemical (E-C-E) that is at the beginning of the formation reaction Cl_2 produced by the reaction of Cl on the electrode surface. While the chemical reaction is the formation of HOCl generated from Cl_2 and H_2O followed by degradation reactions malachite green and OCl^- produce CO_2, H_2O and Cl (equation 1). From Figure 6 can also be seen that the reaction occurs irreversible because the separation of the anodic and cathodic potential peaks separated perfectly, so that the two peaks are not mutually overlapping [12].

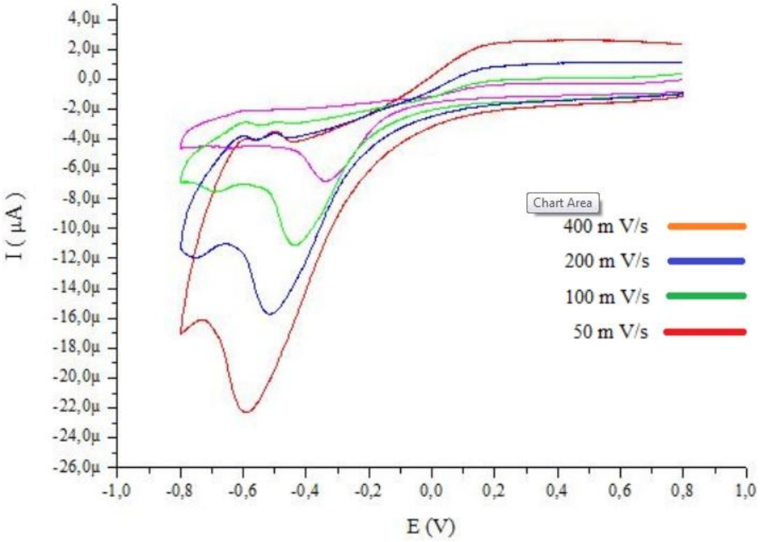

Figure 6: Voltammogram malachite green with various scan rate

To learn the difference voltammogram malachite green before and after degradation, cyclic voltammetry performed the analysis solution of 1 ppb malachite green before and after degradation for 30 minutes at a potential of 2 volts with various scan rate. Results of comparative analysis of malachite green voltammogram after degradation can be seen in Figure 7.

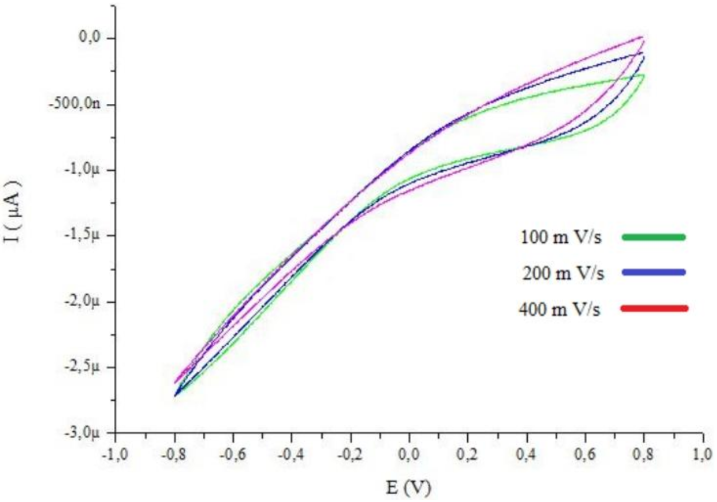

Figure 7: Voltammogram malachite green solution after degradation in optimum condition

Based voltammogram in Figure 7 can be seen that there is no anodic and cathodic peak current after the degradation of malachite green solution for 30 minutes. This shows that the malachite green has been degraded.

3.4. Electrical energy required

Calculation of electrical energy conducted to determine electricity rates needed to degrade malachite green solution. Demand for electricity which is used to degrade malachite green solution in sharing time on the concentration and the potential installation of 10 V are shown in Table 1.

Table 1: Data of energy and electricity fare/kWh required for the degradation of malachite green in various concentrations and time

Concentration (ppm)	Mass (mg)	Average	Price/kWh (IDR)
5	0.25	92.91	0.0287
10	0.50	182.15	0.0563
15	0.75	319.53	0.0987
20	1.00	449.70	0.1389
25	1.25	585.04	0.1807

In this study, the higher the concentration of the solution which degraded the higher electricity rates are needed. This is due to the greater concentration, then the number of molecules produced malachite green is also the more so as the energy required to degrade also higher. Curve relationship between the concentration of malachite green and electric energy (E) (Watt.sec) required for the degradation is shown in Figure 8.

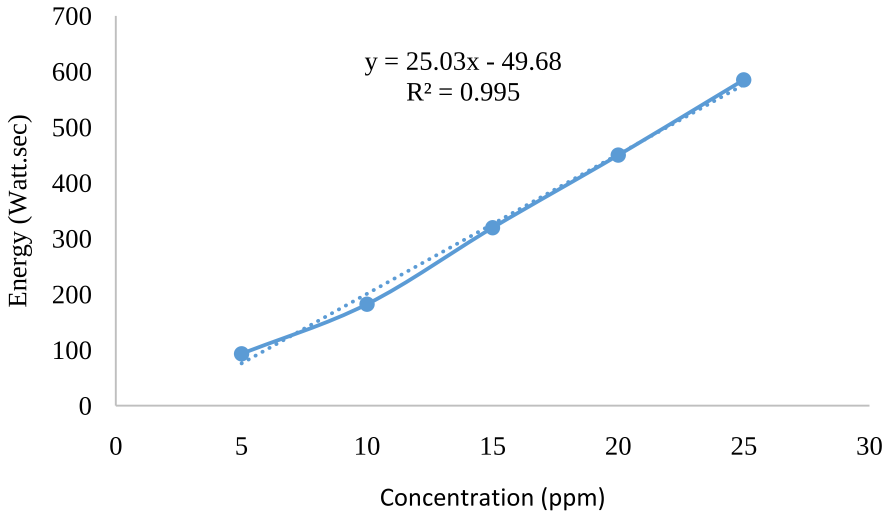

Figure 8: Curve of the relationship between the concentration of malachite green and electric energy (E) (Watt.sec)

3.5. *Analysis COD*

Analysis COD (Chemical Oxygen Demand) is performed to determine the amount of oxygen required to degrade pollutants present in water through a chemical reaction. Results of the analysis of COD malachite green 25 ppm and 0.1 M NaCl as shown in Table 2.

Table 2: Analysis of COD malachite green and NaCl solution before and after degradation

No	Solution	Results of the analysis of COD (mg / L)		
		Before	After (min)	
			30	120
1	NaCl 0,1 M	30,88	57,124	-
2	Malachite green 25 ppm	214,223	38,785	29,221

The results show the value of COD decreased in time before and after degradation of malachite green solution of 25 ppm 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 [13].

3.6. *Compounds CO_2test results*

CO_2 gas test is intended to prove that one of the degradation products malachite green 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. Therefore we can conclude one of the degradation products malachite green is CO_2.Reaction that occurs is as follows.

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

Conclusion

The optimum conditions of electrochemical degradation of malachite green with a carbon/TiO_2electrode is at a potential of 10 Volt, pH 7, and the time of degradation for 30 minutes to degrade 25 ppm solution of the malachite green dye with supporting electrolyte 50.0 mL of 0.1 M NaCl with percentages 100% degradation. Analysis of the results of the electrochemical degradation of malachite green can be studied by spectrophotometry UV-Vis absorbance, degradation shown by both the visible region and in the ultraviolet region. While the cyclic voltammogram there is no anodic and cathodic peak currents. Based the voltammogram electrochemical reactions that occur are electrochemical-chemical-electrochemical (E-C-E) and irreversible. COD value of the solution before and after degradation for 30 minutes decreased by 81.89%.

Reference

1. Moumeni O., Hamdaoui O., *Ultrason. Sonochem*. 19(2011) 404.
2. Dahri M.K., Kooh M.R.R., Lim L.B.L., *J. Environ. Chem. Eng*. 2 (2014) 1434.
3. Wirasto W., Analysis Rhodamine B and Methanyl Yellow in Children Snacks Beverages Elementary in District Laweyan Municipality of Surakarta with Thin Layer Chromatography Method (in Bahasa Indonesia), Faculty of Pharmacy, Universitas Muhammadiyah Surakarta, (2008).
4. Rashed M.N., El-Amin A.A., *Int. J. Phys. Sci*. 2 (2007) 73.
5. Amini M., Arami M., Mahmoodi N.M., Akbari A., *Desalination*, 267 (2011) 107.
6. Asgher M., Bhatti H.N., *Ecol. Eng*. 38 (2012) 79.
7. a) Srinivasan A., Viraraghavan T., *J. Environ. Manage*. 91 (2010) 1915.
   b) Vijayakumaran V., Arivoli S., *J. Mater. Environ. Sci.* 3 (3) (2012) 525-536
8. Lee L., Gyoung-Ja, Pyun, Su-Il. Synthesis and Characterization of Nanoporous Carbon and Its Electrochemical Application to Electrode Material for Supercapacitors, Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, (2007).
9. Lee D.G. Effect of Scale During Electrochemical Degradation of Naphthalene and Salicylic Acid, Department of Civil Engineering, Machigan State University, (2008).
10. Jain R., Sharma N., Radhapyari K. Removal of Hazardous Azo Dye Methanyl Yellow from Industrial Wastewater using Electrochemical Technique, School of Studies in Environmental Chemistry, (2009).
11. Safni, Sari F., Maizatisna, Zulfarman. Degradation of Methanyl Yellow Dyes by Sonolysis and Photolysis with the addition of TiO_2 Anatase (in Bahasa Indonesia), Department of Chemistry, Andalas University Padang, (2007).
12. Gosser D.K. Cyclic Voltammetry Simulation and Analysis of Reaction Mechanisms, VCH Publisher Inc., (1993).
13. Susiana D.E. Parameter Determination of COD and Mercury in Wastewater from Apartment and Hospital (in Bahasa Indonesia), Department of Chemistry, University of Indonesia, (2003).

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