Preparation of Carbon-Chitosan-Polyvinyl Chloride (CC-PVC) Material and its Application to Electrochemical Degradation of Methylene Blue in Sodium Chloride Solution

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Abstract. Electrochemical degradation of methylene blue using Carbon-Chitosan-Polyvinyl Chloride (CC-PVC) electrode in sodium chloride have been done. The aim of this work was to degradation of methylene blue using Carbon-Chitosan-Polyvinyl Chloride (CC-PVC). Carbon chitosan composite electrode was preparing by Carbon and Chitosan powder and PVC in 4 mL tetrahydrofuran (THF) solvent and swirled flatly to homogeneous followed by drying in an oven at 100 °C for 3 h. The mixture was placed in stainless steel mould and pressed at 10 ton/cm². Sodium chloride was used electrolyte solution. The effects of the current and electrolysis time were investigated using spectrophotometer UV-Visible. The experimental results showed that the carbon-chitosan composite electrode have higher effect in the electrochemical degradation of methylene blue in sodium chloride. Based on UV-visible spectra analysis shows current and electrolysis time has high effect to degradation of methylene blue in sodium chloride. Chitosan and polyvinyl chloride can strengthen the bond between the carbons so that the material has the high stability and conductivity. As conclusions is Carbon-Chitosan-Polyvinyl Chloride (CC-PVC) electrode have a high electrochemical activity for degradation of methylene blue in sodium chloride.

1. Introduction
The rapid development of the textile industry, the resulting waste more and more and more complex, such as colour liquid waste due to the textile dyeing process. The colour of the waste water shows the level of pollution of a certain area. Disposal of wastewater into the aquatic environment can lead to environmental pollution problems. Increasing the volume of batik industry is not in line with the knowledge of to process the waste produced in the end of the industry so that the amount of waste generated increases so as to damage, pollute the environment and human health. Waste generated from the batik industry, especially dyestuff waste derived from the batik staining process is often directly discharged into the waters so as to cause environmental pollution [1].

Based on the chemical structure of the dyestuff is divided into various, among others: nitroso dyes, nitro, azo, stilbene, diphenyl methane, triphenyl methane, acridine, quinoline, indigoid, aminokinon, anin and indophenol. While based on the way of dyeing or coloring on the material to be colored are classified into acid dyes, bases, dispersions, direct and others. However, the outline of the dye is classified into two groups namely natural and synthetic dyes. One example of a dye that is widely used in the textile industry is methylene blue. In staining, this compound is only used about 5% while the rest of 95% will be disposed of as waste. This compound is quite stable so it is very difficult to degrade in nature and dangerous to the environment especially in very large concentrations as it can raise COD (Chemical Oxygen Demand) [2].
Methylene blue or basic blue 9 is an alkaline dye commonly used for dyeing paper, hair dye, cotton dyestuff, wool and others. Although methylene blue does not include harmful dyes but after inhalation will cause symptoms of shortness of breath, vomiting, diarrhea and nausea. During this time methylene blue has been used as a model to study the process of adsorption of organic pollutants from aqueous solutions.

Methylene blue is an aromatic heterocyclic chemical compound with the formula C_{16}H_{18}N_{2}S·Cl. Methylene blue has many uses in different fields, such as biology and chemistry. At room temperature, the compound was odorless, dark green powder, which produces blue when dissolved in water. Hydrated forms have 3 water molecules per methylene blue molecule. Methylene blue is a bright blue organic dye belonging to the family of phenothiazines. It is mainly used on tree bark (soft vegetable fibres such as jute, hemp), also silk and wool dyes [3]. The structure of the methylene blue molecule is shown in Figure 1.

![Figure 1. Chemical structure of methylene blue](image)

The dye molecule is a compound of organic substances unsaturated with chromophores as a colour carrier. The unsaturated organic substances found in dyestuff formation are aromatic compounds such as aromatic hydrocarbons and derivatives thereof, phenols and derivatives thereof and nitrogenous hydrocarbon compounds [4].

The electrolysis method often used in treating textile waste is the electro-oxidation method. This method is an effective, selective, economical, pollutant and highly suitable method for organic compounds. The end result is water and carbon dioxide gas [5]. Electrolysis technique does not require oxidizing agent and also catalyst, because electrode (positive pole) can function as a place of oxidation and at the same time can serve as catalyst. Electrodes often used in the electrolysis of organic compounds such as dyes are ruthenium, rhodium, lead and stannum oxide. The use of PbO electrodes as anodes has been widely used for electrolysis [6].

Several studies have applied electrochemical methods to treat batik waste or dyestuff waste such as methylene blue degradation and degradation of textile waste. The success of the electrochemical method is largely determined by the type of electrode [7]. The use of carbon electrodes for the electro-degradation of textile waste has been done [8-9]. To improve the electro-catalytic capability and mechanical strength (mechanical strength) it is necessary to modify the carbon electrode. In addition, the type of electrolyte and concentration is very influential in dyestuff degradation. The most commonly used electrolytes are NaCl and KCl [10, 12, 13, 14].

Modification of carbon electrode has been done a lot. One of which is the modification of the carbon paste electrode by using chitosan for the analysis of Cd^{2+} ions with the interfering ions Mn^{2+} and Ni^{2+} by cyclic stripping voltammetry [11]. With the addition of chitosan to the carbon paste electrode, the modified electrode is capable of detecting Cd^{2+} ions. This is because chitosan is an excellent ionizer, thereby increasing the sensitivity of the carbon paste electrode in holding the Cd metal ion. The ability of chitosan as an adsorbent is based on the presence of two highly reactive active groups when binding to a metal cation. The active groups are an amine group (-NH_{2}) and a hydroxyl group (-OH). Both amine and hydroxyl groups can intercool each other as binders of cation when the concentration of the bonded cations is higher [12].

Chemically, chitosan is a linear polysaccharide in the form of β-(1,4)-2-amino-2-deoxy-D-glucopyranose in which the structure is similar to glycosaminoglycans. In detail chitosan is a heteropolymer of glycosaminoglycans (2-amine-2-deoxy-β-D-glucose) that binds to β-1,4 polymer and contains less n-acetyl-glucosamine. Chitin is consisting of linear chain of acetyl-glucosamine group.
Biologically, chitosan has high biocompatibility, good biodegradability, ability to coat the film (protective layer) and can be well absorbed by the body. Chitosan is also physiologically stable but can still be chemically modified. Chemical structure of chitosan can be seen at Figure 2 [11].

![Chemical structure of chitosan](image)

**Figure 2.** Chemical structure of chitosan

In this study, the modified carbon electrode was analysed by using chitosan and PVC as binder. The carbon-PVC electrode, called C-PVC, has good porosity and good resistance. Carbon chitosan composite electrode was prepared by Carbon and Chitosan powder and PVC in tetrahydrofuran (THF) solvent and pressed. The effects of the current and electrolysis time were investigated using spectrophotometer UV-Visible. The carbon-chitosan composite electrode has higher effect in the electrochemical degradation of methylene blue in sodium chloride. Chitosan and polyvinyl chloride can strengthen the bond between the carbons so that the material has the high stability and conductivity. Porous carbon (porous carbons) are widely used as adsorbents, support catalysts, electronic materials because of their high area and large pore volume [13].

## 2. Methods

### 2.1. Preparation of C-Chitosan-PVC electrode

The C-Chitosan-PVC (CC-PVC) electrode was preparation using 7.5 grams of carbon with a purity of 99.9%, 2.5 grams of chitosan (Merck) with 0.5 gram of polyvinyl chloride (PVC) from Merck to mixing up to homogeneous. The mixture has added 4 mL of tetrahydrofuran (THF) (Merck) as solvent. The mixture was dried by oven at 100°C for 3 hours, then press with pressure 10 ton/cm² for 5 minutes, then electrode called CC-PVC electrode. CC-PVC electrode has preparation is done by connecting CC-PVC material with silver (Ag) wire with glass tube used silver conductive paint and then covered with epoxy.

### 2.2. Preparation of a stock solution of methylene blue of concentration 1000 ppm

The solution of methylene blue (Merck) of concentration 1000 ppm was prepared by dissolving 1000 mg methylene blue powder inserted in a 1000 mL volumetric flask, added distilled water up to the mark, shaken until homogeneous. Methylene blue is the concentration 20 ppm was obtained by dilution a stock solution of methylene blue.

### 2.3. Methylene blue electrochemical degradation procedure

Experiments were performed in an electrochemical cell at a capacity of 250 mL. A total of 50 mL of methylene blue samples were introduced into the electrochemical cell. CC-PVC and Cu is used as an anode and cathode. Each electrode is connected to DC current at power supply. In experiments conducted with variations of the current strength of 6, 7 and 8 V and with electrolysis time of 5, 10, 15, 20, 25, 30 minutes. Magnetic stirrer is used in electrochemical cells as a regulator to keep the homogeneous composition. The solution resulting from electrochemical degradation processing was analyzed using a Spectrophotometer UV-Visible from Hitachi U2010. Methylene blue analysis was performed before and after electrolysis. This analysis was performed using Spectrophotometer UV-Visible in wavelengths between 200-800 nm. This analysis aims to compare the characteristics of methylene blue compounds before and after electrolysis. Experimental set up of electrolysis of methylene blue using CC-PVC and Cu electrode can be seen at Figure 3.
3. Results and discussion

Figure 3. Experimental set up of electrolysis cell for the electrochemical degradation

Figure 4. SEM image for C-PVC (A) C-Chitosan-PVC (B) EDX spectra for C-PVC (C) and C-Chitosan-PVC (D)

Figure 4 shown is the SEM image for C-PVC (Figure 4A) and CC-PVC (Figure 4B). Surface characterization of C-PVC and CC-PVC is significant different. Figure 4B shown is the aggregate form when chitosan added at C-PVC. This condition causes CC-PVC electrodes to be more resistant to erosion than C-PVC electrode. Figure 4A and Figure 4B shown C-PVC and CC-PVC electrodes have
pores so that the solution can enter the pore and have good conductivity. Figure 4C and 4D shown EDX spectra the C-PVC and CC-PVC electrodes. Main element in C-PVC and CC-PVC electrodes is C with amount 99% and another element with less amount are Al, Si, Fe, and S.

The mechanism of the methylene blue redox reaction in sodium chloride can be seen in Figure 5. In the methylene blue redox reactions, most of the focused on the transformation of kinetics into leuco-methylene blue. The reduction-oxidation properties of methylene blue make useful indicators in analytical chemistry. Methylene blue when in an oxidizing environment, but colour less (leuco-methylene blue) when exposed to reducing agent [15].

![Figure 5](image)

**Figure 5.** An oxidation-reduction reaction of methylene blue [15]

![Figure 6](image)

**Figure 6.** UV-Visible spectra of 20 ppm methylene blue 250 mL before and after electrolysis at potential 6 V with different electrolysis time (A) absorbance profile at visible region (B) and ultraviolet region (C)
Figure 6 can be seen that the effect of the electrolysis time to the absorbance in the UV and visible region with a potential of 6 V. It can be concluded that the optimum time obtained electro-degradation 20 ppm methylene blue in 0.5 grams of sodium chloride with potential 6 V at the time of electrolysis 30 minutes. The results of the UV-Visible spectra of methylene blue at a current strength of 6 V are two peaks in the visible region of about 613 and 665 nm. As shown in Figure 6, methylene blue has degradation percent increases with increasing electrolysis time up to 30 minutes. The effect of electrolysis time on methylene blue degradation in sodium chloride was investigated in the range of 5-30 minutes. Figure 6 shown is indicated that the efficiency of methylene blue degradation gradually increases with increasing electrolysis time and strong potential. Electrolysis time and potential can be used to an increase in active chlorine formation and then the increasing the rate of methylene blue oxidation.

Figure 7. UV-Visible spectra of 20 ppm methylene blue 250 mL before and after electrolysis at potential 7 V with different electrolysis time (A) absorbance profile at visible region (B) and ultra violet region (C)

From the results shown in Figure 7, the optimum of electrolysis time of methylene blue can be seen at UV region with potential of 7 A is within 10 minutes is considered as the optimal electrolysis time. The UV-Visible spectra are showing the no peak at the UV region. Figure 7B is shown the absorbance at visible region percentage of degradation 100% at electrolysis time 10 minute. The same at shown in the UV region within 10 minutes methylene blue is degraded perfectly with the value 100% degradation. However, at 15 minutes electrolysis time decreased degradation in methylene blue was the increase of absorbance value in methylene blue until the electrolysis time 30 minutes.
Figure 8. UV-Visible spectra of 20 ppm methylene blue 250 mL before and after electrolysis at potential 8 V with different electrolysis time (A) absorbance profile at visible region (B) and ultra violet region (C)

Figure 8 shows the UV-Visible spectrum of methylene blue at potential 8 V in sodium chloride giving a good result. The effect of high potential and electrolysis to the methylene blue electrochemical degradation in NaCl 0.5 grams is a good result. The UV-Visible spectrum at Figure 8 shows that the UV region does not indicate a peak. Figure 8B, within 5 minutes of methylene blue was electrolyzed with 0.5 grams of sodium chloride capable of degrading of methylene blue. Adding potential gives a significant effect. CC-PVC electrode is a good electrode for electrochemical degradation in 0.5 grams of sodium chloride as an electrolyte, has rapidly and completely degradation in the UV region.
Figure 9. Image of degradation of 20 ppm methylene blue 250 mL before and after electrolysis at potential 7 (A), 8 (B) and 9 (C) V with different electrolysis time (1-7) are 0, 5, 10, 15, 20, 25 and 30 minutes

Figure 9 is a color change occurring in the process of methylene blue degradation. From the Figure 9A with a potential of 7 V in NaCl 0.5 grams can be seen that the color change is not too significant. This can be seen in the variation of electrolysis time 5 to 30 minutes indicating the degradation of methylene blue. This compound is a stable, difficult to decompose, so that high electrolyte and potential are needed.

The effect of the potential can be seen in Figure 9 with a strong current of 9 V at electrolysis time of 10 minutes undergoes a clear color change. From the Figure 9 indicates that at 10 minutes and potential 9 V are good parameters for electrochemical degradation of methylene blue. Figure 9 is shown the electrolysis time at 10 minutes on the percentage of degradation is 100%. Figure 9C is shown the image of degradation of methylene blue with a potential of 9 V. The optimum potential and electrolysis time for electrochemical degradation of methylene blue using C-CPV electrode are at 7 A and 10 minutes. Figure 10 shown the UV-Visible spectra of 20 ppm methylene blue 250 mL before electrolysis and after electrolysis at maximum potential and time are 7 V and 10 minutes, respectively. According to Nordin et al. [4] potential is an important factor in electrolysis. Potential relates to the energy given in electrolysis. The greater the potential, the greater the energy given in the electrolysis cell.

Figure 10. UV-Visible spectra of 20 ppm methylene blue 250 mL before electrolysis (A) and after electrolysis (B) at potential and time are 7 V and 10 minutes, respectively
4. Conclusion
The composite electrode (C-Chitosan-PVC) can degrade the methylene blue dyestuff compound optimally at a current strength of 0.07 A at 10 minutes. The composite electrode (C-Chitosan-PVC) and electrochemical degradation are good techniques for electrochemical oxidation of methylene blue in sodium chloride. This technique uses very simple equipment, easy operation and friendly for the environment.

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