Electrochemical Degradation of Methylen Blue Using Carbon Composite Electrode (C-PVC) in Sodium Chloride

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Abstract: *Electrochemical oxidation of methylene blue using carbon composite electrode in sodium chloride solution have been done. The aim of this work was to degradation of methylen blue using the direct oxidation in undivided electrolysis cell. Carbon composite electrode was prepare by C 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/cm^2. Sodium chloride was used electrolyte solution. The effects of the current and electrolysis time were investigated using cyclic voltammetry, spectrophotometer UV-Visible and gas chromatography mass spectrometry (GC-MS). The experimental results showed that the carbon composite electrode have higher effect in the electrochemical degradation of methylene blue. Based on UV-visible spectra and GC-MS analysis also shows current and electrolysis time for degradation of methylene blue optimum at 1,5 A and 60 minute, respectively. As a conclusions is this method its simple equipment, easy operation and friendly for environmental.*
Keywords: *C-PVC, degradation, electrochemical, methylene blue, sodium chloride*

I. Introduction

There have been many studies focusing on removal of pollutants and organic compounds from wastewater. Various technique have been used for treatment of organic pollutants such as adsorption [1]; coagulation [2]; ozone treatment [3]; electrochemistry [4,5,6]. Paper, dyeing, plastic and textile industries use color for dyeing their products and thus use a huge amount of water which results in the production of a dye-containing wastewater with hazardous effects on the environment [7]. Wastewater from textile industry has a high environmental impact and therefore needs to be treated before being discharged into the environment or reused.

Methylen blue was used as a model day or model cationic dye. It is a heterocyclic aromatic chemical compounds, dye employed by industries such textile industry for variety of purpose. Methylen blue is a hazard and toxic material can cause irritation to the skin, permanent injury to the eyes and also cause irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea [8].

The treatment methods of dyeing wastewater are biological treatment, chemical coagulation, activated carbon adsorption, ultrafiltration, ozonation and electrocoagulation (EC). Several methods have been used for treatment of methylen blue day waste water such as adsorption using poly (vinyl alcohol) [8], TiO_2/UV-C photocatalytic [9], biological and electrochemical methods using SnO_2 anodes [10], SnO_2 and PbO_2 anodes [11]; bismuth doped lead dioxide [12], Ti/Pt and Ti/Pt/Ir electrodes [13], stainless steel net coated with single-walled carbon nanotubes [14], a mixed titanium and ruthenium oxide (Ti/TiRuO$_2$) and a boron-doped diamond [15]. Methylen blue and other day was treatment using various techniques such as Fenton like reaction [16]; absorption using poly vinyl alcohol [8] electrochemistry method [17-21]. Carbon materials have been widely used in both analytical and industrial electrochemistry. The advantages of carbon electrodes are low cost, wide potential window, inert and electrocatalysis activity for a variety of redox reaction. Carbon electrode is superior material of noble metals for oxidation and reduction of organic and biological molecules in both aqueous and nonaqueous media [22].

Other than by direct electrolysis, organic pollutants can also be removed electrochemically by indirect electrolysis, generating in situ chemical reactants that convert them to less harmful products. In this field, the main oxidising agent is active chlorine, in the form of gaseous chlorine, hypochlorous acid or hypochlorite ions, which is anodically produced from chlorides naturally.

The aim of this work was to describe the electrochemical oxidation of methylene blue in sodium chloride solution using carbon composite electrode (C-PVC). C-PVC have been prepared using carbon powder and polyvinyl chloride PVC as a binder material in 4 ml tetrahydrofuran (THF) solvent and swirled flatly to homogeneous followed by drying in an oven at 100°C for 3 hours. The mixture was placed in stainless steel mould and pressed at 10 ton/cm^2. A typical pellet contained approximately amount of Carbon (95%) powder, and approximately 5% of PVC polymer. The effect of current and time electrolysis have been evaluation using

spectrophotometer UV-Vis, High Performance Liquid Chromatography (HPLC) and Gas Chromatography Spectrometry Massa (GC-MS).

II.   Experimental

2.1 Solution
All solutions were prepared by dissolving its analytical grade salt in deionised distilled water. Sodium chloride (NaCl) from Merck was used as the supporting electrolyte. Methylene blue (MB) was prepared from Merck (Darmstadt, Germany).

2.2. Preparation of a carbon composite electrode (C-PVC)
Carbon powder (< 2 micron in size and 99.9% purity, Aldrich Chemical Company) and PVC in 4 ml tetrahydrofuran (THF) solvent and swirled flatly to homogeneous followed by drying in an oven at 100^oC for 3 hours. The mixture was placed in stainless steel mould and pressed at 10 ton/cm^2. A typical pellet contained approximately amount of Carbon (95%) powder, and approximately 5% of PVC polymer.

2.3   Characterization of a carbon composite electrode (C-PVC) using SEM and EDS
Electrode surface was characterized using SEM from JSM 5400 microscope equipped with a microprobe Voyager Noran system.

### 2.4. Experiment procedure of the electrochemical studies
The electrolysis process was performed on a solution of 20 ppm methylen blue in 0,1 M NaCl at room temperature. The electrochemical studies by cyclic voltammetry (CV) were performed in 50 mL capacity glass electrochemical cell. PGSTAT 100 N 100 V/250 mA (Metrohm Autolab) was used for electrochemical behavior measurements; data acquisition was accomplished using the software from Metrohm. Cyclic voltammetry experiments were performed in a three electrodes system using carbon composite electrode (C-PVC) as a working electrode, an Ag/AgCl (saturated KCl) as reference electrode and platinum wire as the counter electrode. All potentials given are with respect to the Ag/AgCl reference electrode.

2.5. Experiment procedure of the electrochemical degradation of methylen blue
Experiments have been conducted in an undivided 1 L capacity electrochemical cell. Carbon composite electrode (C-PVC) was used as anode and cathode. Each electrode was connected to regulated DC power supply. The stirrer was used in electrochemical cell to maintain an unchanged composition. The solutions resulting from electrochemical degradation treatment were analysis using the spectrophotometer UV-Visible, gas chromatography mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC).

III.   Result And Discussion
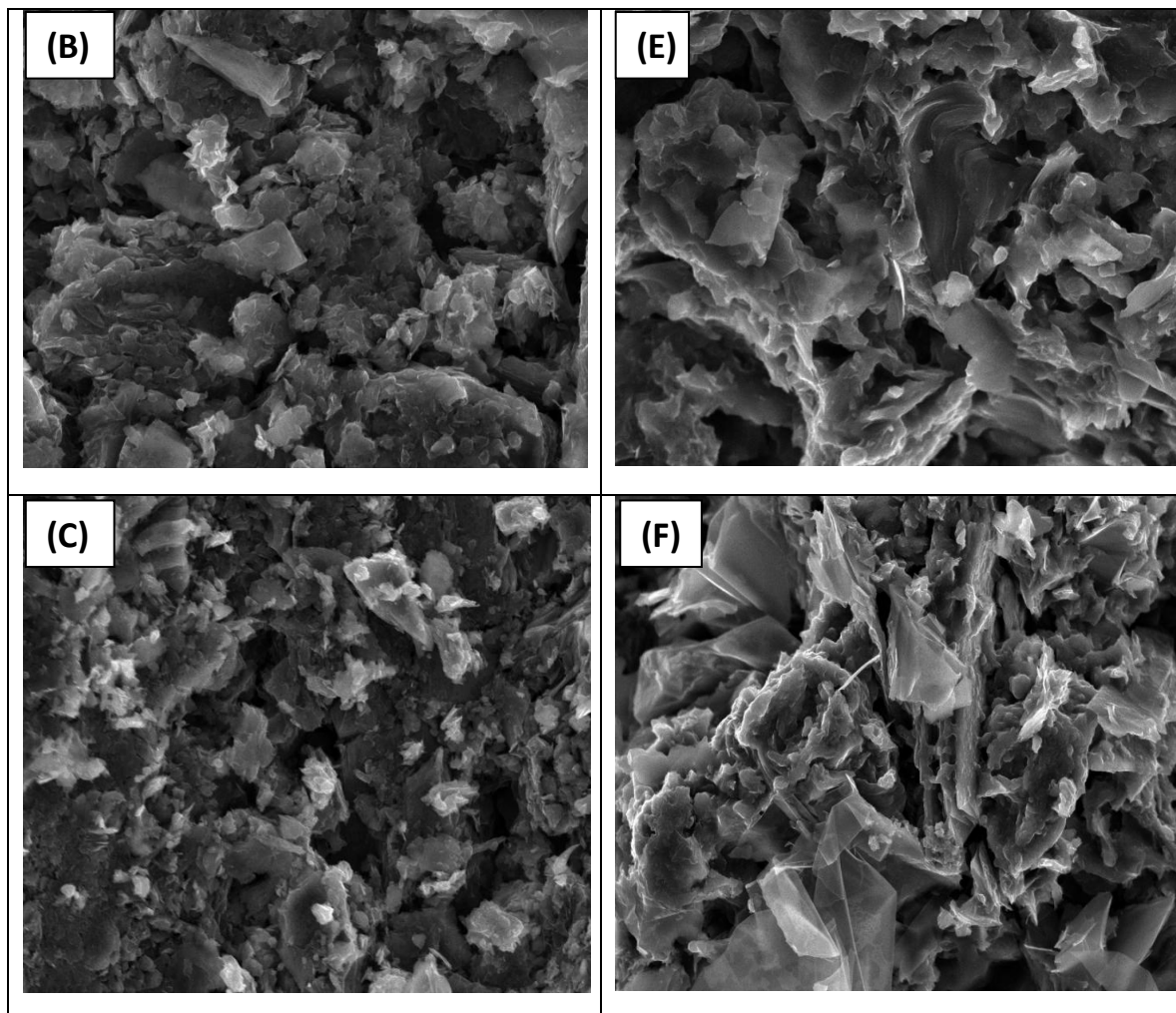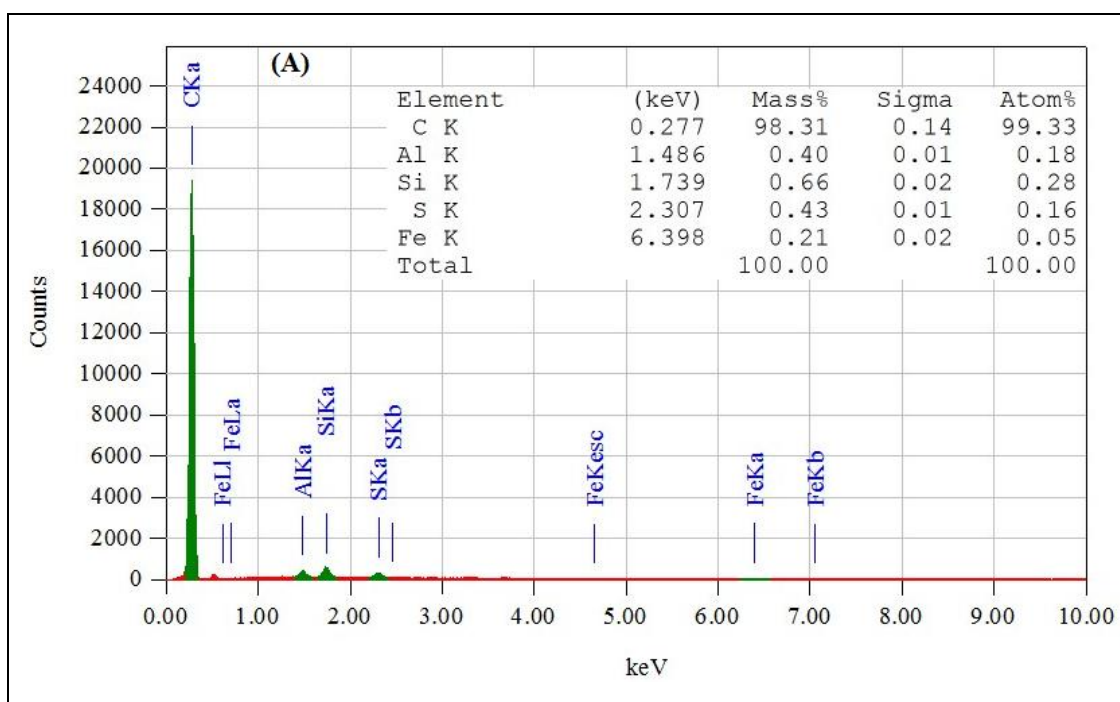
3.1 Characterization using SEM
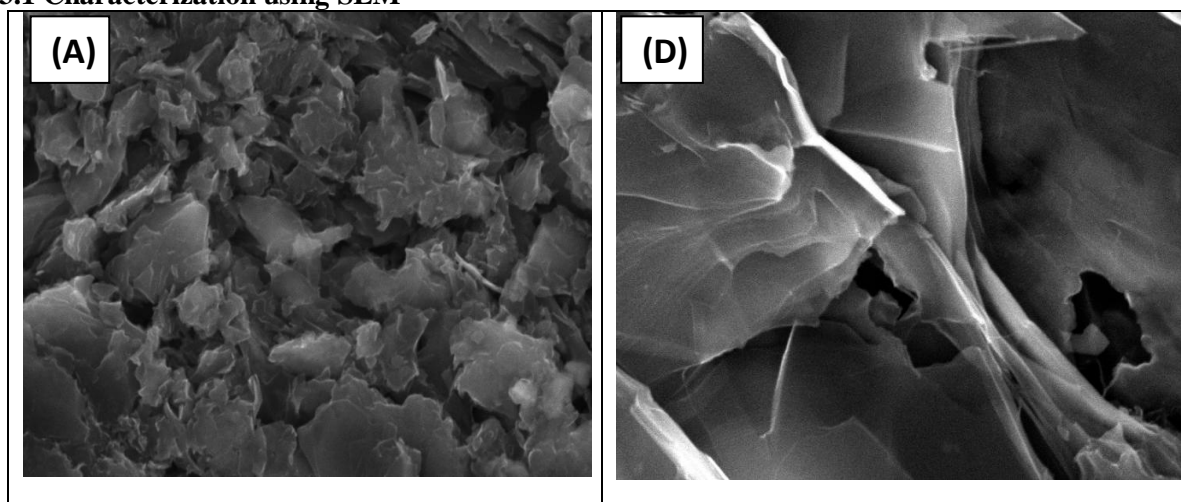
Fig. 1. SEM micrographs at C-PVC cross section (A, B, C) before and (D, E, F) after used for electrolysis of methylen blue 20 ppm (1000 mL) in NaCl 30 g at Current Constant 0.5A. With magnification 1000, 5000 and 3000x.
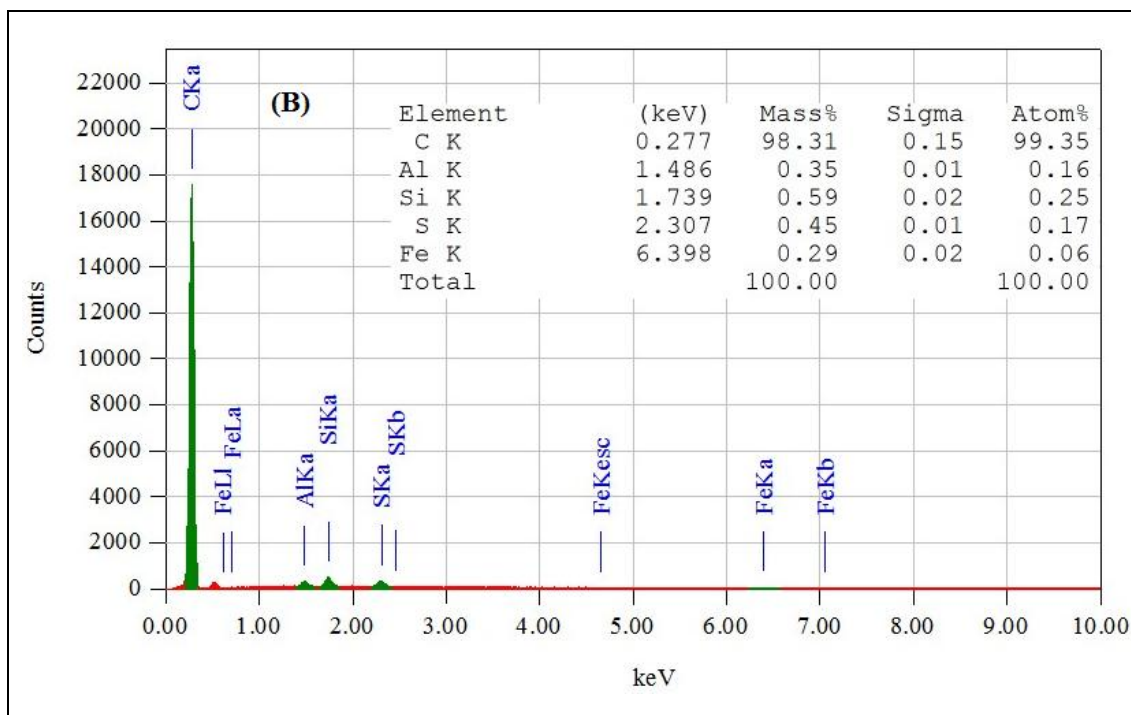
Fig. 2. EDS spectra from C-PVC cross section (A) before and (B) after used for electrolysis of methylen blue 20 ppm (1000 mL) in NaCl 30 g

Fig. 1 showed the morphological study of freshly prepared C-PVC electrodes by SEM. Almost a similar SEM micrograph were displayed by both surface and cross section C-PVC. So in this paper only SEM micrograph almost gave as shown in cross section electrodes (Fig. 1B) were very rough, irregular and having porous characteristic compared to C-PVC electrode surface (Fig. 1A). It has been reported that electrode prepared using powdered C-PVC yielded electrode have surface which is very rough, irregular, and formed a lamellar orientated particles. Fig. 2 shown of EDS spectra from C-PVC cross section (A) before and (B) after used for electrolysis of methylen blue 20 ppm (1000 mL) in NaCl 30 g. Based on EDS spectra, C-PVC electrode have a good stability, because not different chemical composition between before and after use for electrolysis of methylen blue in sodium chloride solution.

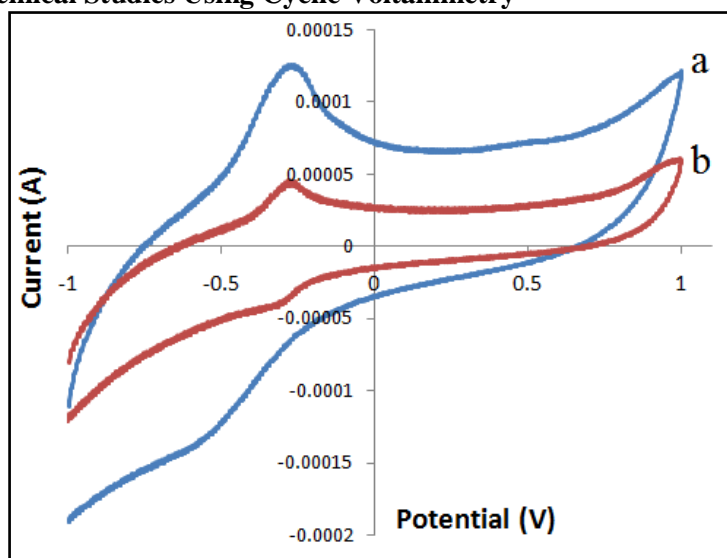### 3.2 The Electrochemical Studies Using Cyclic Voltammetry

Fig. 2. Cyclic voltammograms of 0.1 M NaCl without methylen blue (A) and 20 ppm Methylen Blue in 0.1 M NaCl (B) using carbon composite electrode, scan rate: 100 mV/s.

Fig. 2A and 1B shows the cyclic voltammogram of 0.1 M NaCl without methylen blue (A) and 20 ppm methylen blue in 0.1 M NaCl (B) using carbon composite electrode with scan rate 100 mV/s. The peaks represent the anodic and chatodic peaks at potential -0.25 V. These peaks related to the oxidation of Cl^- to Cl_2 and reduction of Cl_2 to Cl^-. The peaks of the oxidation and reduction of methylen blue not shows at the cyclic voltammogram (Fig. 2) because is very low concentration depending of 0.1 M NaCl. Fig. 3. shown the cyclic voltammogram of 20 ppm NaCl in methylen blue 0-30 ppm using carbon composite electrode with scan rate 100 mV/s. The peaks at 200 mV represent oxidation and reduction of methylen blue.
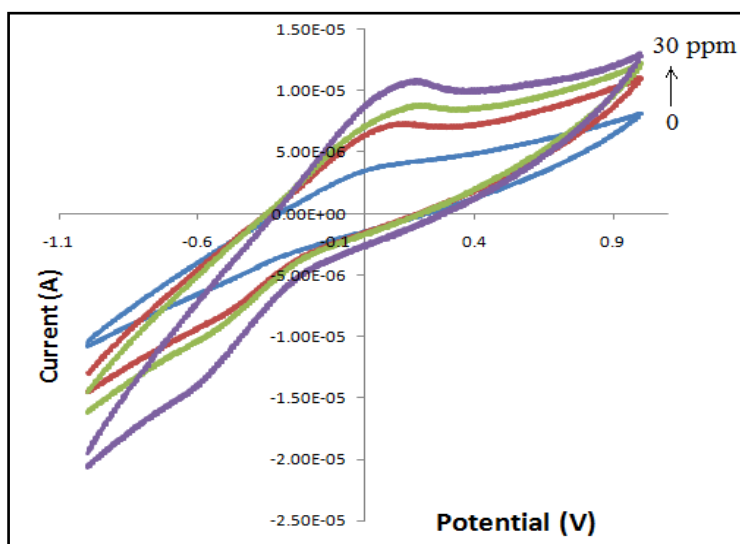
Fig. 3. Cyclic voltammograms of 20 ppm NaCl in methylen blue 0-30 ppm using carbon composite electrode, scan rate 100 mV/s.

Fig. 3 shown effects of sodium chloride electrolyte solutions to methylen blue cyclic voltammetry using carbon composite electrode. Sodium chloride as a electrolyte will be produce of chloride ion. Chloride ions are active species of chlorine, in order to catalyze their reaction of degradation. Mechanism of chloride ions, formation and dissolution of chlorine occurs:

$2Cl^- + 2e \rightarrow Cl_2$ (1)
$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$ (2)
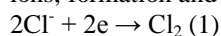
The mechanism redox reaction of methylen blue based in sodium chloride can been see at Fig. 4. Studies on redox reaction of methylene blue are mainly focused on the kinetics of transformation into leucmethylene blue, whereas the kinetics of its reductive decolorization in the presence of transition metal ions have been very scanty. The red-ox properties of methylene blue make a useful indicator in analytical chemistry. Methylene blue is blue when it is in an oxidizing environment, but colorless (leuco methylene blue) if it is exposed to a reducing agent (Fig. 4) [23].
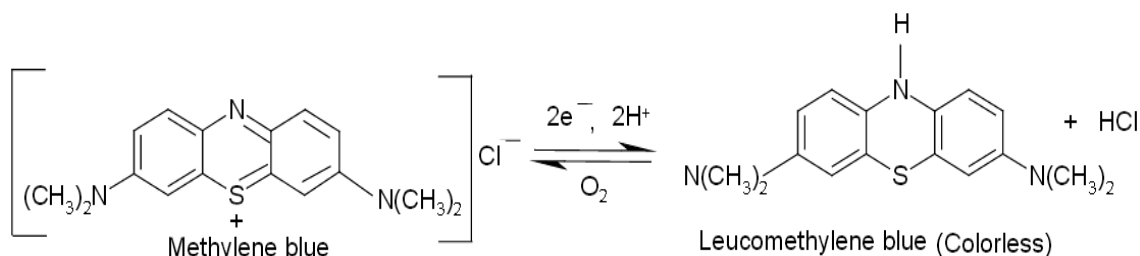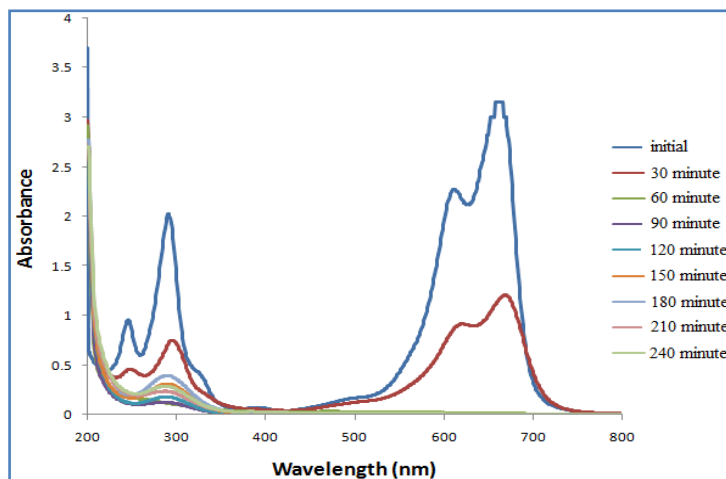
Fig. 4. Proposed redox reaction of methylene blue [23]

Fig. 4. UV-Visible Spectrum of methylen blue 20 ppm (1000 mL) in NaCl 30 g using Carbon Composite Electrode at Current Constant 0.5 A

Effect of electrolysis time on degradation of methylen blue under the optimal conditions was investigated. The degradation of methylen blue during electrolysis was also monitored with spectrophotometry. The UV-Visible spectra of the methylene blue, reported in Fig. 4, present dominant two peaks in the visible region at about 622 and 682 nm. As shown in Fig. 4, the methylen blue degradation rapidly increased with the increased of electrolysis time up to 240 minutes. The effect of electrolysis time on decolorization of methylene blue in the presence sodium chloride was investigated in the range of 30-240 minute. The results in Fig. 4 show that the decolorization efficiency of methelene blue gradually increased with increase in the electrolysis time. The increase in electrolysis time may lead to increasing reduction rate of methylene blue. The methylen blue degradation depends directly on the concentration of electrochemical generated hypochlorite ion in the bulk solution. When the electrolysis time was longer, more hypochlorite ion will be produced in solution under fixed current density. From the results, the electrolysis time at 240 minutes is considered as the optimal electrolysis time.
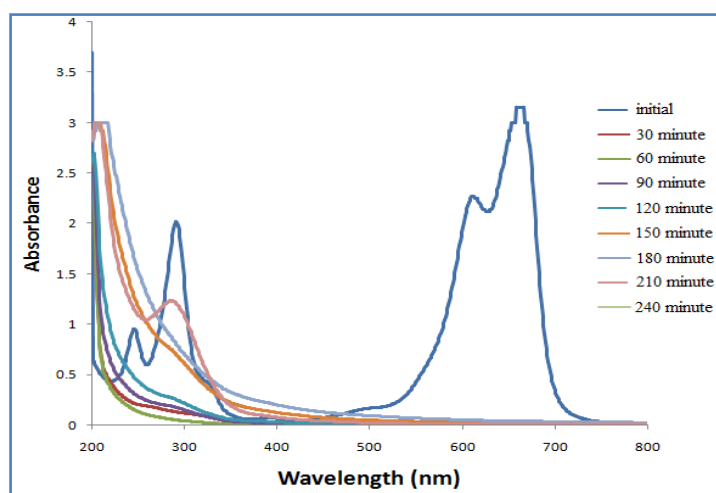

Fig. 5. UV-Visible Spectrum of methylen blue 20 ppm (1000 mL) in NaCl 30 g using Carbon Composite Electrode at Current Constant 1.5 A

Fig. 5 shown UV-visible spectrum of methylen blue 20 ppm (1000 mL) in NaCl 30 g using carbon composite electrode at current constant 1.5 A. Electrolysis of methylen blue 20 ppm (1000 mL) in NaCl using carbon composite electrode with high oxygen evolution over potential, the organic pollutants (methylen blue) are oxidized on the anode surface by the adsorbed hydroxyl radicals electrogenerated by water discharge and therefore the oxidation rate strongly depends on the applied current density and the mass transport in the cell as the pollutants must reach the anode surface. The influence of the current and electrolysis time on the electrochemical oxidation of the methylene blue is shown in Fig. 5. It can also be observed that the oxidation rate was not influenced by the applied current, but an increase in the current caused a increase in the peak at ultra violet region.

Methylen blue is completely degraded after 60 min electrolysis, not shown peak at visible area. This indicates that, chloride ions may change the absorption characteristics of chromospheres during the electrochemical process, the oxidized forms of chlorine certainly appear, catalyzing the reaction of decomposition of methylen blue, leading to complete discoloration of the solution after 60 min. The electrochemical degradation processes of methylen blue, in the presence of chloride ions.
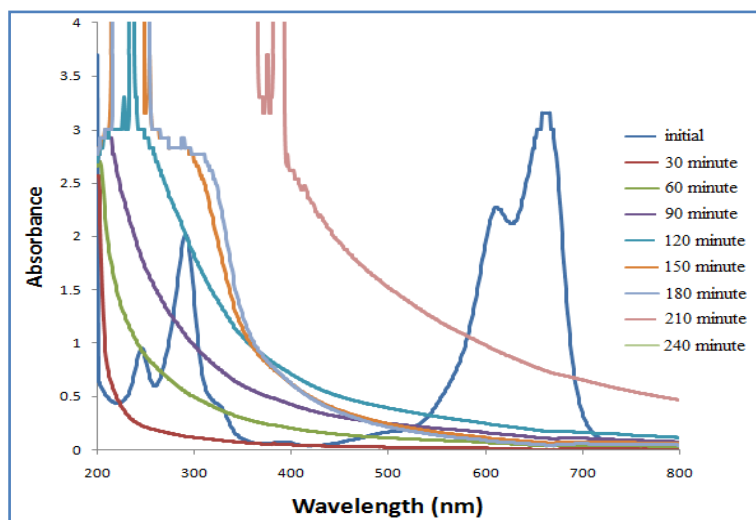

Fig. 6. UV-Visible Spectrum of methylen blue 20 ppm (1000 mL) in NaCl 30 g using Carbon Composite at Current Constant 3.5 A.

Fig. 6 shown UV-Visible spectrum of methylen blue 20 ppm (1000 mL) in NaCl 30 g after electrolysis using carbon composite electrode at high current constant 3.5 A. Electrolysis methylen blue in NaCl at high current constant 3.5 A with short time (30 minute), not shown peak at UV-Visible region. Electrolysis methylen blue in NaCl at high current constant 3.5 A with long time (more than 30 minute) shown high peak at UV-Vis region. This peak is new compounds after electrolysis at high current. This result supported by color change from clear to brown color (Fig. 7c no. 9).
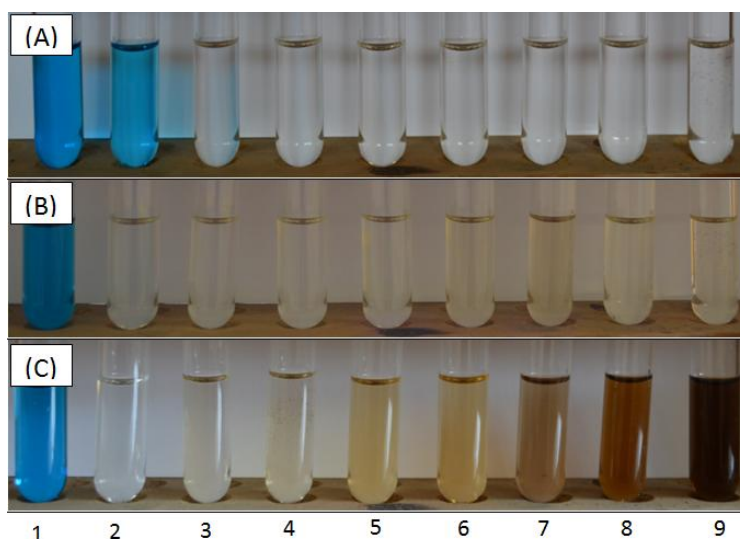

Fig. 7. Visual colour change degradation of methylen blue 20 ppm (1000 mL) in NaCl 30 g using Carbon Composite Electrode at Current Constant (A) 0.5 (B) 1.5 and (C) 3.0 A, with time electrolysis 1-9 are initial (without electrolysis), 30, 60, 90, 120, 150, 180, 210 and 240 minute

Fig. 7A shown is visual color change degradation of 20 ppm methylene blue 1 L in 30 g NaCl using carbon composite electrode with a constant current of 0.5 A. The Effect of the electrolysis time to electrochemical degradation product is the clear solution (Fig. 7A). Based on analysis using spectrophotometer UV-Vis shown the UV region is the new chemical product. Fig. 7B shown the electrolysis of methylene blue 20 ppm (1L) in 30 g NaCl with constant current of 1.5 A. Electrochemical degradation at current 1.5 A shown is

the longer the time of electrolysis increasingly turbid solution formed (Fig. 7B). These results are supported by spectrophotometer UV-Vis in Fig. 5. Fig. 7C shown the electrolysis of methylene blue 20 ppm (1 L) in 30 g NaCl with constant current of 3.5 A. Fig. 7C shown the electrochemical degradation with electrolysis time at 30 minute are a clear solution. The longer of the electrolysis time solution becomes the color changed to brown and C-PVC anode to be destroyed. The good condition for electrochemical degradation of methylene blue are 1.5 A and 60 minute.
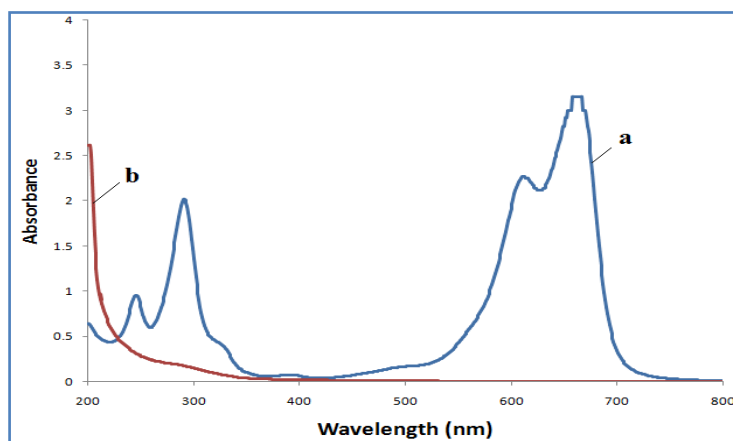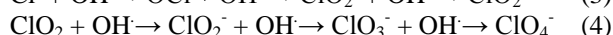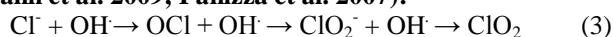

Fig. 8. UV-Visible Spectrum of (A) methylen blue 200 ppm (1000 mL) before electrolysis (initial) and (B) methylen blue 200 ppm (1000 mL) in NaCl 30 g after electrolysis using Carbon Composite Electrode at Current Constant 1.5 A time electrolysis 60 minute

Electrodegradation of methylen blue in sodium chloride (NaCl) activated using chlorine species and OH radicals. Based on **Bergmann et al. (2009) and Panizza et al. (2007)** OH radicals contribution to electrodegradation of methylen blue ini sodium chlorate solution. Indirect electrooxidation by electrogenerated species (active chlorine species, e.g. dissolved chlorine, hypochlorous acid and hypochlorite ions, chlorine dioxide, chlorate, perchlorate; ozone; OH radicals and hydrogen peroxide) is a particularly challenging tool for wastewater treatments. The stepwise oxidation may take place with OH radicals contribution, as shown below **(Bergmann et al. 2009; Panizza et al. 2007):**

$$Cl^- + OH^- \rightarrow OCl^- + OH^- \rightarrow ClO_2^- + OH^- \rightarrow ClO_2 \qquad (3)$$
$$ClO_2 + OH^- \rightarrow ClO_2^- + OH^- \rightarrow ClO_3^- + OH^- \rightarrow ClO_4^- \qquad (4)$$

3.3 Chromatography study
Fig. 9 shows chromatograms from High Performance Liquid Chromatography (HPLC) of the before and after electrolysis of the methylen blue 20 ppm (1L) in NaCl 30 g using the carbon composite electrode. Fig. 9A shows methylen blue 20 ppm before electrolysis with tR 2.885 minute. After 320 minute electrolysis the methylen blue was no more observed peak at tR=2.743 min. The peaks at tR=2.743 min is methylen blue. Fig. 9, there are three new components (tR=5.393; tR=6.444; tR=7.200) in the solution, which presented higher concentration. This indicates the presence of new compounds as intermediate to final degradation (CO_2 and H_2O).
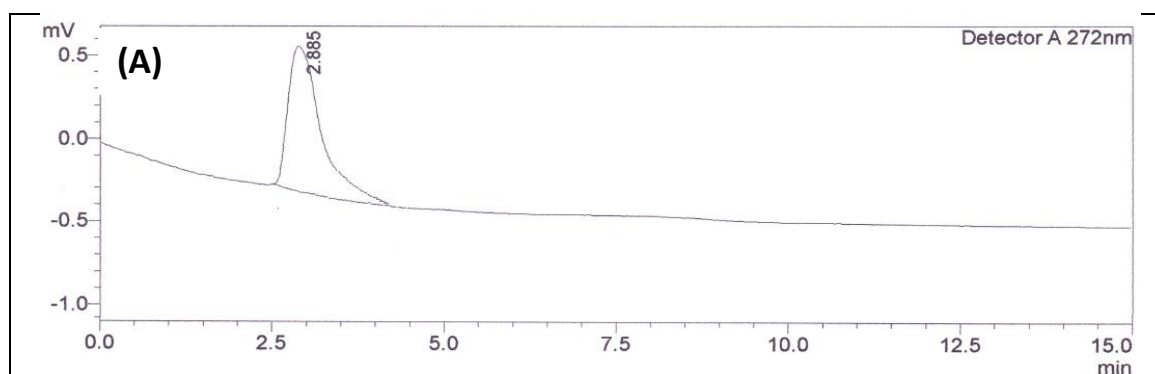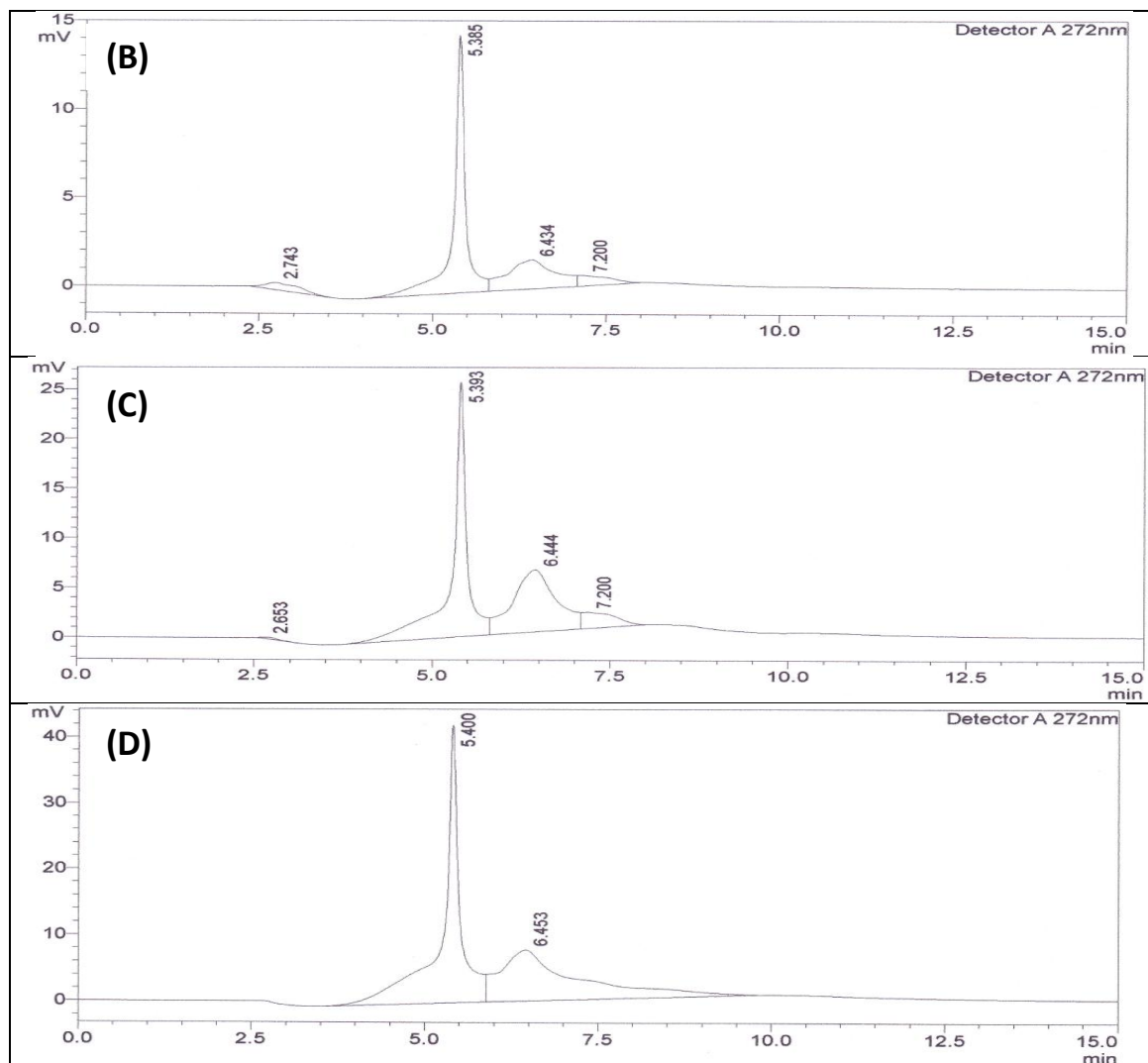
Fig. 9. Chromatograms of the methylen blue 20 ppm solutions (A) and after electrolysis time 60 (B) 150 (C) 320 (D) minute at 1.5 A in NaCl 30 g using Carbon Composite Electrode. Column OCTYL, flow rate 0.8 ml/min, mobile phase: (20:80) aqueous hosphate buffer, pH 5-methanol (2.5 min) and linear gradient buffer–methanol (20:80) to (50:50). Temperature 25°C. Detection wavelength 220 nm.
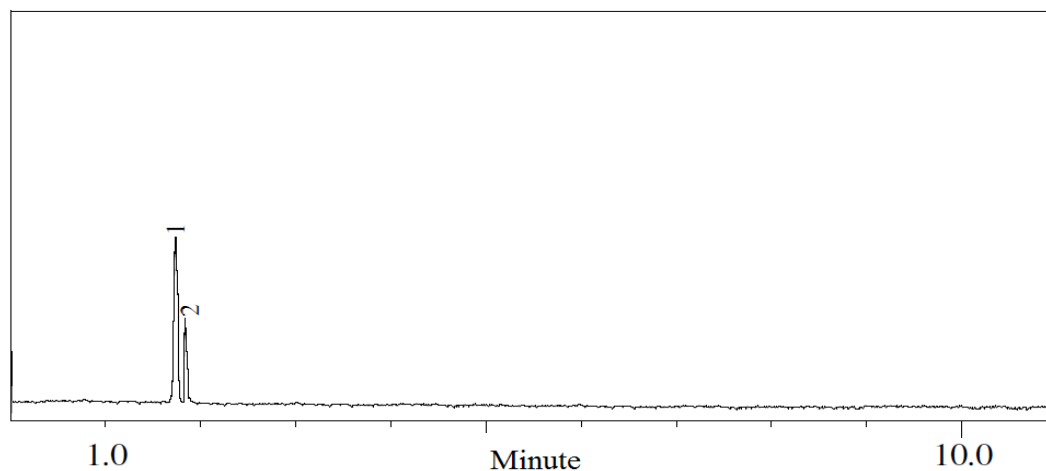

Fig. 10. Chromatogram of Methylen Blue 20 ppm (1L) in NaCl 30 g after Electrolysis using Carbon Composite Electrode at Current Constant 1.5 A time electrolysis 120 minute

Fig. 10 shown the chromatogram from GC-MS the result electrolysis using carbon composite electrode at current constant 1.5 A time electrolysis 120 minute. Base on chromatogram from GC-MS shown two peaks,

this peaks consist of volatile compounds are 2-Pyridinepropanoic acid and 2,4-dichloro-2,4-difluoro-1,3-dithiethane-1,1,3,3-tetraoxide.

IV. Conclusions

In this paper, electrochemical oxidation of methylene blue in sodium chloride was investigated. The results of the electrolysis performed under electrolysis time and current experimental conditions showed that: current and electrolysis time for degradation of methylene blue optimum at 1.5 A and 60 minute, respectively. As a conclusion, carbon composite electrode (C-PVC) and electrochemical degradation is a good technique for electrochemical oxidation of methylene blue in sodium chloride. This technique is a very simple equipment, easy operation and friendly for environmental.

Acknowledgement

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