

Textile Industries Wastewater Treatment by Electrochemical Oxidation Technique Using Metal Plate

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In this study, the optimization of electrochemical oxidation technique for textile wastewater treatment and analysis of the degradation product was experimentally investigated. After some preliminary studies using C.I. Reactive Blue 109, platinum plate electrode (10 mm x 10 mm) and stainless steel (10 mm x 10 mm) were chosen as the best anode and cathode, respectively. The effects of operational parameters such as supporting electrolyte (sodium chloride) concentration, current density, initial pH and electrolysis time on pH changes and percentage of color, chemical oxidation demand (COD), biochemical oxidation demand (BOD), total organic carbon (TOC) and surfactant removal were determined. The optimum range for each of these operating variables was experimentally determined. The results obtained show that the percentage of color, COD, BOD, TOC and surfactant removal in the aqueous phase was removed effectively. Under the optimum operating conditions, sodium chloride concentration of 0.1 M, current density of 20.0 mA/cm², initial pH of 4 and electrolysis time of 75 minutes, the percentage of color and COD removals efficiency reached 96%, while for BOD, TOC and surfactant removals the percentage is slightly lower. UV-visible spectra and Fourier transform infrared spectroscopy (FTIR) analysis also shows the cleavage of chromophore group and degradation of textile wastewater during before and after electrolysis.

Keywords: Electro-oxidation; parameter; COD removal; UV-visible; FTIR

1. INTRODUCTION

Textile industry causes considerable higher impacts to water pollution by discharging their effluents into various receiving bodies includes ponds, rivers and other public sewer. Major pollutants

load from the textile industries are from the several of their wet-processing operations like scouring, bleaching, mercerizing and dyeing [1]. Among these various processes, dyeing process normally uses large amount of water for dyeing, fixing and washing processes [2]. Thus, textile wastewater possess a high COD concentration, large amount of suspended solids, broadly fluctuating pH, strong color, high temperature and low biodegradability caused by varying contaminates within water environment [3].

Nowadays, there is increasing interest in development of innovative for treatments of textile wastewater that contain toxic and non-biodegradable organic pollutants which are traditional method cannot completely oxidize. Based on the previously research, biological treatment of textile wastewater showed low degradation efficiency because of the presence of biologically inert high molecular weight dyestuff [4, 5]. Physical adsorption is effective for removal of non-biodegradable pollutants, but it is quite expensive and difficult for regenerating the adsorbents [6]. Due to the large complexity of the composition in textile wastewater, most of these traditional methods are becoming inadequate.

In recent years, there has been increasing interest in the use of electrochemical technique for the treatment of textile wastewater. In electrooxidation, the main reagent that is used here is electron (clean reagent) where it remove the organics matter in textile wastewater without generating any secondary pollutants and also there is no need for adding extra reagent [7]. The unique features in electrochemical oxidation process such as simplicity and robustness in structure and operation, it is possible that this process can be developed as a cost-effective technology for textile wastewater treatment [8].

In the electrochemical oxidation process, the organic and toxic pollutants present in wastewater such as dye usually destroyed by either the direct or indirect oxidation process [9, 10]. In a direct anodic oxidation process, the pollutants are first absorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In an indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone or hydrogen peroxide can be regenerated by the electrochemical reactions during electrolysis. The pollutants are then destroyed in the bulk solution by oxidation reaction of regenerated oxidants. All the oxidants are generated *in-situ* and are utilized immediately. Among the oxidants, generation of hypochlorite is cheaper as most of the effluents have certain amount of chloride [11].

Many investigations have been successfully employed by using electrochemical oxidation process for textile wastewater treatment such as the electrochemical removal of hazardous dye from industrial effluents [12]. The results show the reduction in COD value and color intensity that has been achieved with high efficiency (90%) after treatment of Rectofix Red 3 BFN dye. The color in wastewater containing Procion Navy and Procion Red dyes was completely removed after 40 minutes of electrolysis at a constant current density of 39 mAcm^{-2} [13]. Decreasing in COD concentration required up to 180 minutes of electrolysis for four different dyes which are Procion Navy, Red, Yellow and the composite. The used of different anode materials for the decolorization of real textile wastewater has been reported before [14]. The best results were obtained when the Ti/Ru_{0.1}Sn_{0.9} electrode is used due to the greater chance of the formation of highly oxidizing hydroxyl radical at this material. It demonstrates that the possibility of total color removal depending on the type of electrode and the nature of the active species generated at the electrode surface.

This paper concerns with the study of parameters optimization for current density, pH, NaCl concentration and electrolysis time that influences the performance of the electrochemical oxidation process of textile wastewater. Analysis using UV-visible spectrophotometer and FTIR was also carried out treated and untreated samples.

2. EXPERIMENT

2.1 Electrochemical cell setup

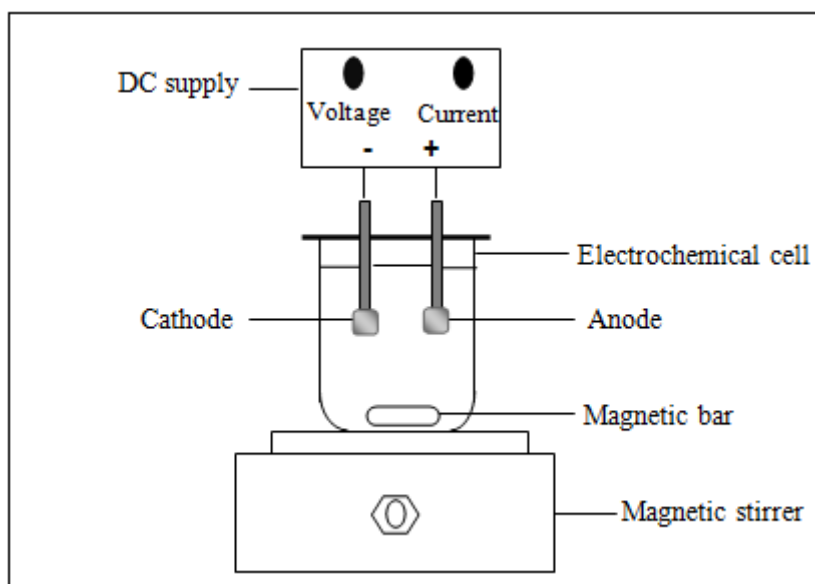


Figure 1. Experimental laboratory set up

Experiments have been conducted in an undivided 50 mL capacity electrochemical cell (Figure 1). Various selected metal plate electrodes (10 mm x 10 mm) and stainless steel (10 mm x 10 mm) were used as anode and cathode respectively. These electrodes were parallel, with the gap between these electrodes was kept constant at 20 mm. Each electrode was connected to regulated DC power supply (CPX 200 Dual 35V 10A Bench Power Supply). The stirrer was used in electrochemical cell to maintain an unchanged composition.

2.2 Electrode Material Selection

The anode was prepared using eight different electrode materials which is platinum (Pt), iridium (Ir), palladium (Pt), nickel (Ni), cobalt (Co), aluminium (Al), silver (Ag) metals plate and carbon rod. In order to select the best metal electrodes, C.I. Reactive Blue 109 (Dylon) was used as a testing colored reagent. All metal plate electrodes were prepared using mechanical alloying technique (MAT) as reported by other author before [15]. Electrolysis was carried out for 1000 mgL⁻¹ C.I.

Reactive Blue 109 in 0.1 M NaCl as a supporting electrolyte using a 10 V power supply. The best electrode was chosen not only based on their decolorization efficiency but also based on their electrochemical stability [16].

2.3 Reagents and wastewater sample

Sodium Chloride (NaCl) which acts as a supporting electrolyte in the electrochemical reaction was purchased from Aldrich. The effluent sample was collected from batik textile factory located in Kelantan and Terengganu, Malaysia.

2.4 Analytical techniques

The wastewater and aqueous solutions resulting from electrochemical treatment were tested for COD and BOD₅ test using established standard methods suggested by American Public Health Association, APHA, while surfactant content was analyzed using a method as reported by several researcher [17 - 19]. TOC was determined using wet chemical method (Shimadzu, model TOC Japan) and pH was analyzed using calibrated pH meter (Metrohm). UV-visible spectrum was obtained for the treated and untreated wastewater using UV-visible spectrophotometer (Shimadzu 2450) in the wavelength range between 200 - 800 nm. Fourier Transform Infrared (FTIR) spectrum of the solution was recorded using FTIR (Perkin Elmer Spectrum One FTIR Spectrometer) before and after electrolysis.

3. RESULTS AND DISCUSSIONS

3.1 Electrode selection

Table 1. Electrochemical oxidation of 1000 mgL⁻¹ C.I. Reactive Blue 109 in 0.1 M NaCl using different type of metal plates as an anode and stain less steel as cathode. Voltage of 10 V was applied

| Anode materials | Decoloring time (min.) | Decoloring percentage (%) | Observation | |
|-----------------|------------------------|---------------------------|----------------------------------|---------------------|
| | | | Electrolysis product | Anode |
| Platinum (Pt) | 30 | 99 | Clear solution | Unchange |
| Palladium (Pd) | 85 | 98 | Clear solution | Unchange |
| Iridium (Ir) | 45 | 99 | Clear solution | Unchange |
| Carbon rod (C) | 60 | 99 | Clear solution | Slightly corroded |
| Silver (Ag) | 70 | 22 | Yellowish solution | Completely corroded |
| Cobalt (Co) | 75 | 97 | Clear solution and precipitation | Completely corroded |
| Nickel (Ni) | 120 | 98 | Clear solution and precipitation | Completely corroded |
| Copper (Cu) | 95 | 93 | Clear solution and precipitation | Completely corroded |

Table 1 summarized the result obtained for selection of the best electrode. Based on Table 1, only four electrodes used (Pt, Pd, Ir and C rod) showing its ability to decolorize 1000 mgL⁻¹ of C.I. Reactive Blue 109 solution without changes in their physical properties. However, Pt was found to be the best electrode based on the time taken to decolorize the colored solution. The electrode used in any electrooxidation work normally should be physically and chemically stable [16]. Pt and Ir were the most stable metals and could be used in the electrooxidation of ethanol in KOH solution and the same results were obtained in these color removal work [16]. A cyclic voltammetry of 1000 mgL⁻¹ of C.I. Reactive Blue 109 was then carried out using those four electrodes in order to obtain their selected electrochemical kinetic parameters. The results obtained were summarized in Table 2.

Table 2. Electrochemical kinetic parameters for electrochemical oxidation of C.I. Reactive Blue 109 in 0.1 M NaCl. Scan rate 1 mVs⁻¹

| Anode | Tafel Area (mV) | Tafel Slope, b (mV/dec) | Reaction Rate Constant, a | Exchange Current Density, i_0 (mA/cm ²) |
|------------|-----------------|-------------------------|---------------------------|---|
| Platinum | 800-1000 | 1114 | 4.483 | 9.464×10^{-2} |
| Palladium | 800-1000 | 419.7 | 2.509 | 1.035×10^{-3} |
| Iridium | 800-1000 | 532.1 | 2.714 | 7.905×10^{-3} |
| Carbon rod | 800-1000 | 702 | 3.258 | 2.279×10^{-2} |

Electrodes with higher exchange current density, i_0 value were normally used in electrochemical oxidation technique, and Pt was found to be as the best electrode. Those four electrodes were later than used in electrochemical oxidation of Reactive Blue 109 for current efficiency, current density, energy usage, COD removal and decolorization efficiency. Formula below based on the COD removal was used to calculate the current efficiency (CE), energy consumption, COD removal and color removal for all electrode used in decolorization process [7, 20, 21].

$$\text{Current efficiency} = 100[(\text{COD}_o - \text{COD}_t)FV/8It]$$

$$\text{Energy consumption} = UIt/3600(\text{COD}_o - \text{COD}_t)V$$

$$\text{COD removal (\%)} = 100(\text{COD}_o - \text{COD}_t)/\text{COD}_o$$

$$\text{Color removal (\%)} = 100(\text{Abs}_{o,\lambda} - \text{Abs}_{t,\lambda})/\text{Abs}_{o,\lambda}$$

Where,

COD_o = COD before electrolysis (g/L)

COD_t = COD after electrolysis (g/L)

U = voltage applied (V)

F = Faraday constant (96487 Cmol⁻¹)

I = current used (A)

t = electrolysis time (sec.)

V = volume (L)

Abs_{o,λ} = initial absorbance at selected wavelength

Abs_{t,λ} = absorbance at time *t* at selected wavelength

Table 3. Current efficiency, COD removal, color removal and energy consumption for electrochemical oxidation of C.I. Reactive Blue 109 in 0.1 M NaCl using different type of electrodes

| Electrode | Current efficiency (%) | COD Removal (%) | Color removal (%) | Energy consumption (kWh/g) |
|------------|------------------------|-----------------|-------------------|----------------------------|
| Platinum | 64 | 94 | 99 | 52 |
| Iridium | 55 | 81 | 99 | 61 |
| Palladium | 50 | 73 | 98 | 67 |
| Carbon rod | 61 | 89 | 99 | 55 |

Results obtained were summarized in Table 3. As a conclusion based on the results in Table 3, Pt was chose as anode material while stainless steel was maintained as cathode for further experiment involving textile industrial wastewater treatment.

3.2 Optimization of electrolysis parameters for electrooxidation of textile industrial wastewater

3.2.1 Effect of supporting electrolyte concentration

Generally, NaCl was used as supporting electrolyte in electrochemical process. NaCl was chosen as supporting electrolyte due to its capability to enhance the degradation efficiency and shortened the reaction times [22, 23].

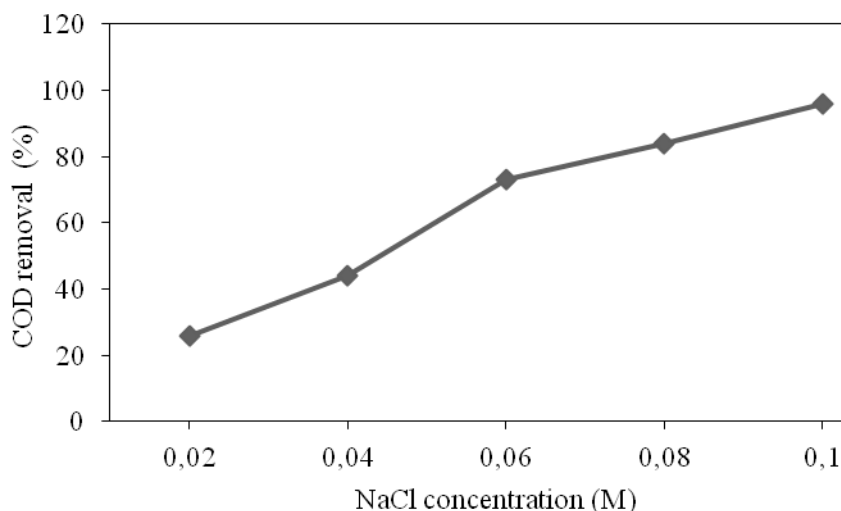


Figure 2. Effect of NaCl concentration on COD removal of textile industrial wastewater

It is apparent that increasing the chloride concentration may increases the COD removal due to the increased mass transport of chloride ions to the anode surface and also increased diffusion in the diffusion layer of the anode (Figure 2). As a result, more amount of hypochlorite ion will be generated

[24]. Thus, higher concentrations of hypochlorite ion were able to oxidize more organic molecules in wastewater [25]. 0.1 M of NaCl was considered as an optimum electrolyte concentration due to highest COD removal in textile industrial wastewater.

3.2.2 Effect of applied current density

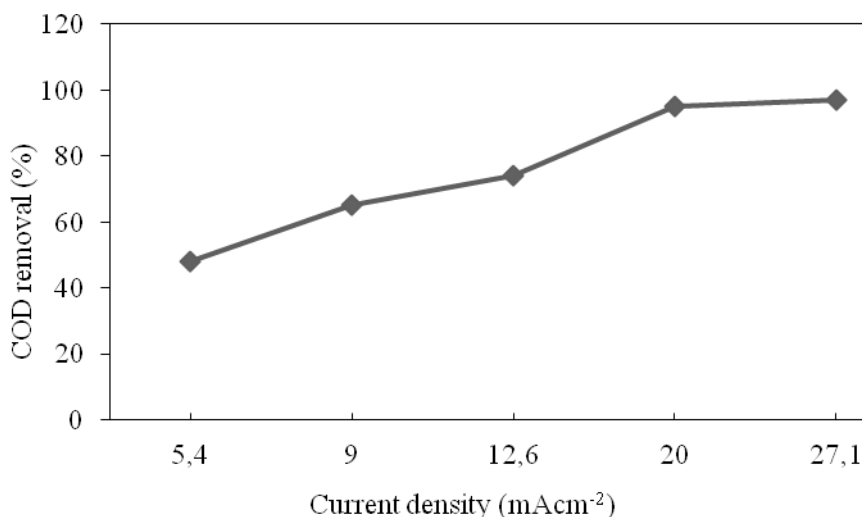


Figure 3. Effect of current density on COD removal of textile industrial wastewater

Electrolysis was conducted using different current density values to investigate the effect of current density on the COD removal of textile industrial wastewater. Figure 3 shows that COD removal percentage was increased with the increasing of current density. This is due to production of oxidant such as hypochlorite ion in solution. Increasing generation of oxidant is proportional to current density, which eventually increases the pollutant degradation [26, 27]. The increase in hypochlorite ion approaches equilibrium with degradation of organics present in the effluent [28]. Increasing the current density of the electrochemical cell followed by the production of more electron, which results in increasing the rate of overall reaction [11]. But at higher current density values, production of extra electrons may contribute to undesirable side-reactions such as parasitic loss reactions leading to the depletion of hypochlorite concentration. From the results, COD removal percentage was almost unchanged at higher current density which is 27.1 mAcm⁻². At the same time, more energy would be consumed at higher current density, so the optimal current density obtained for this study was 20 mAcm⁻².

3.2.3 Effect of pH

Most pollutants in textile wastewater are weak organics acid or base, so the pH value of wastewater can influence the property of pollutants available in wastewater. The effect of pH in the

range of 4 to 11 for treatment of textile industrial wastewater was carried out by using either H_2SO_4 or NaOH to adjust the pH of the solution.

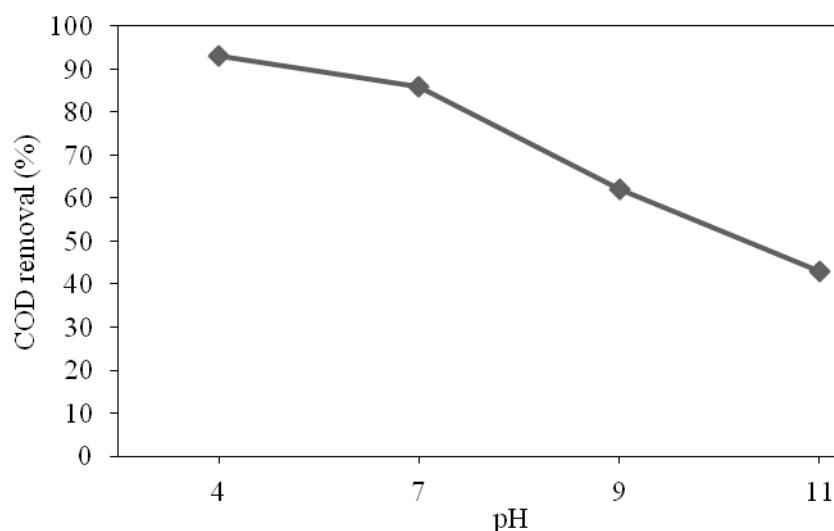


Figure 4. Effect of pH on COD removal of textile industrial wastewater

Figure 4 shows that the COD removal decreased by increasing the pH of the solution. The reason is that less production of chlorine/hypochlorite ion takes place in alkali medium which more favorable to form chlorate or perchlorate instead of chlorine/hypochlorite ion. In acidic medium, COD removal percentage is higher because of the chlorine/chloride that present in the solution is in the form of hypochlorous acid which possesses higher oxidation potential compared to hypochlorite [29]. Therefore, pH 4 is the optimum pH value for treatment of textile industrial wastewater based on Figure 4 with highest COD removal percentage compared to other pH values.

3.2.4 Effect of electrolysis time

Effect of electrolysis time on COD removal under the optimal conditions was investigated. As shown in Figure 5, the COD removal percentage rapidly increased with the increased of electrolysis time up to 75 minutes. After 75 minutes of electrolysis time, COD removal percentage was slowly increased until up to 97%. The COD removal efficiency 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. Therefore, color and COD value in the solution were reduced in higher concentration of hypochlorite. From the results, the electrolysis time at 75 minutes is considered as the optimal electrolysis time due to only slight different in COD removal percentage compared to after 90 and 105 minutes.

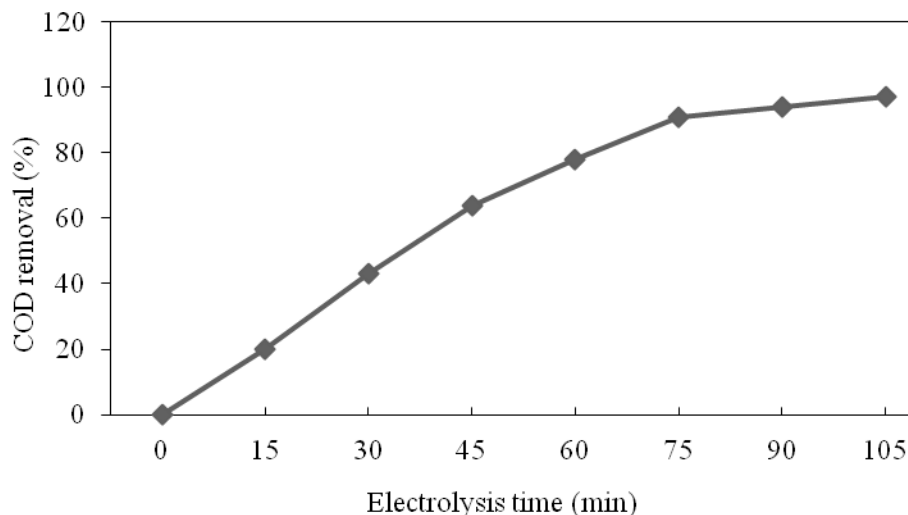


Figure 5. Effect of electrolysis time on COD removal of textile industrial wastewater

Based on the preliminary studies either using standard dye (Reactive Blue 109) or textile industries wastewater, the optimum operating conditions selected for further treatment of textile waster are as summarized in Table 4.

Table 4. Optimum operating conditions for textile industrial wastewater using metal plate electrode

| Electrodes | Working (anode) | Platinum |
|------------------------|-----------------------|-----------------|
| | Counter (cathode) | Stainless steel |
| Supporting electrolyte | 0.1 M NaCl | |
| Current density | 20 mAcm ⁻² | |
| Voltage applied | 10 V | |
| pH | 4 | |
| Electrolysis time | 75 minutes | |

3.3 Characterization of textile wastewater before and after electrolysis

3.3.1 Physico-chemical parameters

Table 5. Wastewater analysis parameters of textile industrial wastewater from four batik industry factories before and after electrochemical treatment

| Sample | COD (mg/L) | | BOD ₅ (mg/L) | | TOC (mg/L) | | Surfactant (μmol/L) | | pH | |
|--------------|------------|-------|-------------------------|-------|------------|-------|---------------------|-------|--------|-------|
| | Before | After | Before | After | Before | After | Before | After | Before | After |
| Wastewater A | 1640 | 104 | 21.4 | 10.5 | 59.3 | 8.48 | 1.61 | 1.06 | 11 | 7 |
| Wastewater B | 1071 | 230 | 15.1 | 9.2 | 37.0 | 10.9 | 1.89 | 1.54 | 11 | 7 |
| Wastewater C | 1358 | 484 | 18.2 | 11.7 | 42.5 | 16.3 | 2.37 | 1.97 | 10 | 7 |
| Wastewater D | 889 | 73 | 13.6 | 7.9 | 19.5 | 8.2 | 1.13 | 0.93 | 12 | 8 |

Note: Electrolysis time; t = 105 minutes; [NaCl] = 0.1 M; Voltage applied = 10 V

Analysis on selected water quality parameters (COD, BOD₅, TOC, surfactant and pH) values on textile wastewater before and after electrolysis were carried out using the optimum operating conditions as previously determined. The results obtained show that the electrochemical oxidation process is able to reduce the COD, BOD₅, TOC and surfactant content values in textile industrial wastewater. From those four parameters, COD, BOD₅ and TOC removal percentage were not less than 65, 39 and 58% respectively, while for surfactant, the removal percentage was not more than 35% (Table 5). The values are different among the factories involved due to the different types of dyes and additives used in the process. The reduction in these parameters value was due to the breaking of large molecule to a small molecule which is easier to be oxidized chemically or biologically by electrochemical oxidation technique [30]. This breaking process was supported by the existence of self-generated hypochlorite ion which is able to reduce the concentration of organic compound available [3]. Measurement of pH on textile wastewater found that all of the samples were in alkaline conditions and change to neutral upon completion of electrochemical oxidation time due to the formation of carbonate buffer through CO₂ produced at the end of electrolysis process [31].

3.3.2 Spectral analysis

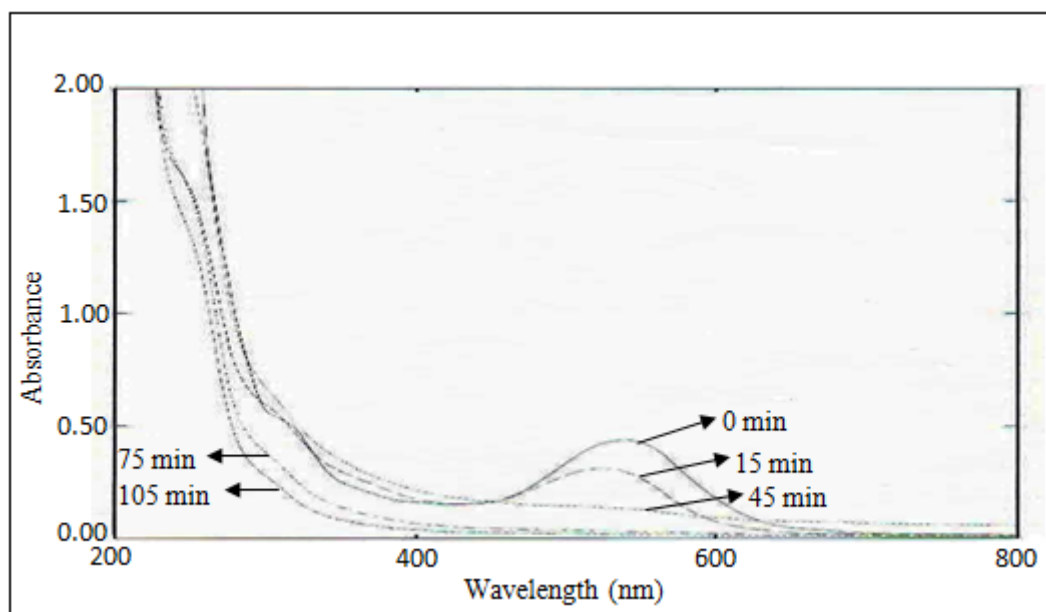


Figure 6. UV-visible spectra during the electrochemical oxidation process of textile industrial wastewater

Textile wastewater obtained from Wastewater A was used extensively for spectral analysis of wastewater before and after electrolysis.

i. UV-vis spectrum analysis: The changes in absorbance characteristics of dye in effluent were investigated over a wide wavelength region during electrochemical oxidation process. As seen in Figure 6, after 15 minutes of electrolysis, considerable decrease in the absorbance of peaks occurred. It might be attributed to decolorization and degradation of chromophore group or higher organic carbon.

The disappearance of all the peaks at the end of the electrolysis time shows that the mineralization of the dye effluent is completely achieved [32, 33]. It is clear that the electrochemical oxidation process for treatment of textile wastewater have completely removed the color of the dye used.

ii. FTIR spectrum analysis: Figure 7(a and b) shows the FTIR spectra of textile wastewater before and after 75 minutes of electrolysis time. It can be seen that some structural changes occurred during electrolysis. In Figure 7(a), the appearance of peak at 3460 cm^{-1} and 2928 cm^{-1} indicates the presence of O-H stretching and C-H stretching respectively.

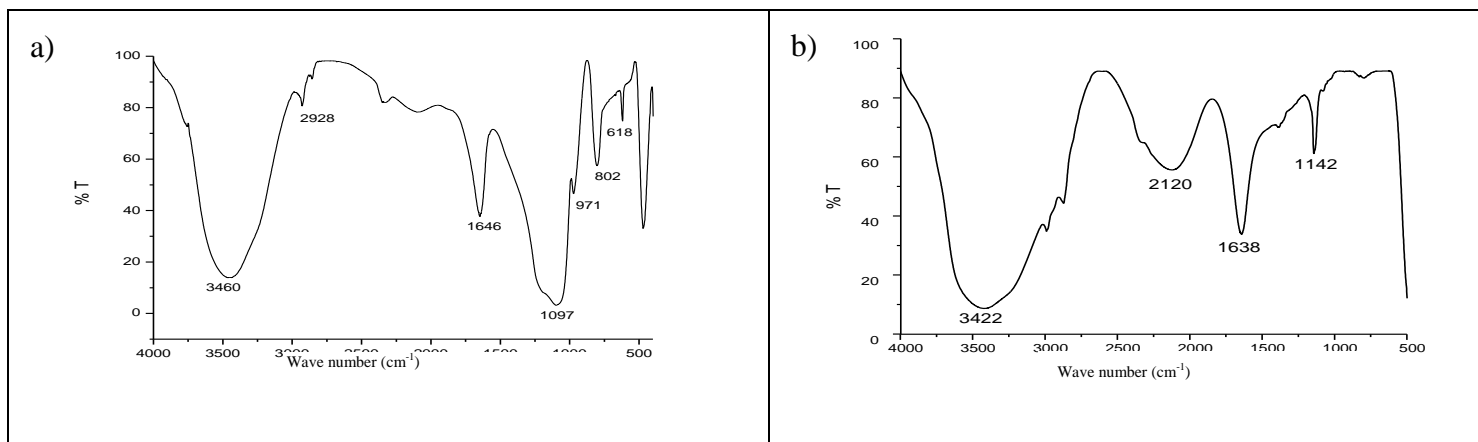


Figure 7. FTIR spectra of textile industrial wastewater a) before (0 min) and b) after electrolysis (75 min)

The peaks at 1646 cm^{-1} , 1097 cm^{-1} and 971 cm^{-1} indicates the bending of primary N-H, C-O and C-N stretching respectively. The peak at 1444 cm^{-1} represents azo groups (C=N) which is a chromophore group that may give colored compound [34]. The formation of peaks at 802 cm^{-1} and 618 cm^{-1} shows *ortho* substitution (out of plane) for aromaticity or benzene ring. Meanwhile in Figure 7(b), only several peaks appeared after electrolysis which are 3422 cm^{-1} , 2120 cm^{-1} , 1638 cm^{-1} and 1142 cm^{-1} . Those peak indicates the O-H, $\text{C}\equiv\text{C}$ (alkyne), C=C (alkene) and C-O stretching respectively. The variations of this band can be explained by the completed degradation of organic compound and formation of new species as intermediate organic compound [35].

4. CONCLUSIONS

In the present work, optimization of operational parameters in electrochemical oxidation process for treatment of textile industrial wastewater using various metal plates and analysis of degradation product was performed successfully. The operational parameters such as supporting electrolyte concentration, current density, pH and electrolysis time were investigated. From all the results, the optimum conditions of each parameters has successfully achieved where the COD removal shows the higher percentage which is 96 %. The results of UV-visible and FTIR spectrum showed that,

the mineralization and degradation of textile wastewater is completely achieved after electrolysis. It can be concluded that under optimized experimental condition, the treatment of textile wastewater by electrochemical oxidation method can be carried out not only for COD removal but also for color removal as well.

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