

Scientific paper

Decolorization of C. I. Reactive Orange 4 and Textile Effluents by Electrochemical Oxidation Technique using Silver-Carbon Composite Electrode

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Abstract

In this study, the electrochemical oxidation of C. I. Reactive Orange 4 (RO4) on a silver-carbon composite (AgC-PVC) electrode was studied using the cyclic voltammetry, potential liner V, and electrolysis methods. The AgC-PVC electrode was used as the working electrode in the electrochemical measurement of RO4 in the presence of NaCl as a supporting electrolyte. The UV-Vis spectra of RO4 after the electrochemical oxidation showed the complete decolorization of the solution. The electrolysis products were characterized using FTIR and GC-MS. The results showed that in the presence of OCl^- as an active oxidant, RO4 molecules are broken down into several lower-molecular-weight molecules by the electrochemical technique. The electrode used was also able to reduce the COD, BOD_5 and surfactant contents in the textile effluents using a pilot scale reactor. This proved that the prepared AgC-PVC electrode was beneficial for removing both the color and other pollutants from textile effluents.

Keywords: Decolorization; electrochemical oxidation; composite electrode; textile effluents; C. I. Reactive Orange 4

1. Introduction

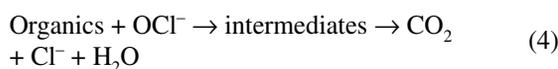
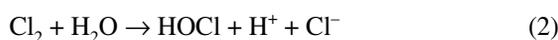
Dyes are a major problem in textile effluent management because dye colors are visible with the naked eye even in small quantities ($<1 \text{ mg L}^{-1}$). Only 60–90% of the dyes used in the textile industries is fixed to textile fibers, with the remaining 10–40% is discharged as effluent.¹ Azo dyes are the most widely used dyes in the textile industry.² These dyes contain the azo chromophore group ($-\text{N}=\text{N}-$), along with an auxochrome such as $-\text{OH}$ or $-\text{SO}_3$.³ Reactive dyes are one example of an azo dyes that contains the azo group in its molecular structure. A special feature of reactive dyes are the formation of covalent bonds between the dyes and textile fibers.⁴ Because of the existence of the azo group in their structures, the presence of reactive dyes in the environment has a negative impact on the environment and human health.⁵ Therefore, the decolorization of

textile industry effluent is very important before releasing it to the environment.

The electrochemical oxidation technique has gained attention in recent years for textile industrial effluent treatment because of its efficiency in removing organic and inorganic pollutants from effluents.³ In addition, no additional chemical is required for electrochemical oxidation, because the electron is the main reagent in the electrochemical reaction.² The non-biodegradable molecules in reactive dyes can be broken into smaller molecules and easily removed using this electrochemical oxidation technique.⁶ The working electrode plays an important role in electrochemical studies because it acts as a site for electrooxidation and electrocatalytic reactions. Therefore, the selection of electrode materials play an important role in obtaining an electrode with the highest efficiencies for an electrochemical reaction and electrocatalytic reactivity.⁷ Among the

electrodes that have been used in the decolorization study of synthetic dyes and textile industry effluents are Pt,^{4,8,9} boron-doped diamond (BDD),^{3,10,11} dimensionally stable anodes (DSA),^{7,12,13} and activated carbon fiber (ACF).^{14,15}

In addition to the electrode materials, the efficiency of the electrochemical oxidation of organics is also dependent on the presence of species that can act as a mediator or oxidant in the bulk solution. The effect of chloride ions in the electrochemical oxidation of dyes and textile industry effluents has been the object of numerous studies.^{8,9,16} The oxidation of chloride ions produced from the addition of sodium chloride as a supporting electrolyte can lead to the formation of active oxidants such as chlorine, hypochlorous acid, and/or hypochlorite, depending on the pH (Eq. 1–3). These active oxidants can oxidize the organics at the anode or/and in the bulk solution (Eq. 4).



In the current study, the electrochemical oxidation of C. I. Reactive Orange 4 (RO4) and textile effluents were carried out using silver–carbon composite (AgC-PVC) electrode. The composite electrode was prepared by mixing two different element powders with polyvinyl chloride (PVC). The existence of two different elements in an electrode will give the synergistic effect^{17,18,19} and active bifunctional catalyst^{20,21} which directly increasing the electrode performance in the electrochemical oxidation and catalytic reaction. As for now, no studies have been done for the treatment of textile effluents by using this electrode. The characterization of the electrolysis products of RO4 and textile effluents were also performed in this study.

2. Experimental

2.1. Chemicals

All the chemicals used were analytical grade without further purification. Silver (Ag) powder with a purity

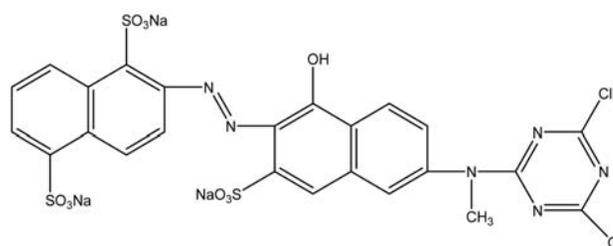


Figure 1. Molecular structure of RO4

of 99.9% was purchased from Aldrich. RO4 (Figure 1), which was used as a synthetic dye in this study, was purchased from Dylon. Polyvinyl chloride (PVC) and graphite powder (C) were obtained from BDH Ltd., whereas tetrahydrofuran (THF) was obtained from System. Sodium chloride (NaCl), which acted as a supporting electrolyte in the electrochemical reaction, was purchased from R & M Chemicals. Dichloromethane (DCM) was purchased from Fischer Scientific.

2.2. Preparation of AgC-PVC Electrode

The AgC-PVC electrode was prepared using a mechanical alloying technique (MAT)^{22,23} by mixing the powder combination of Ag and C (Table 1) with PVC at a ratio of 95% powder mixture to 5% PVC (wt.%). The total weight of the pellet obtained was approximately 1.5 g. Then, 4 mL of THF was added to the mixture to dissolve the PVC. The mixture was then stirred until homogenous and allowed to dry in an oven (100 °C) for 2 h. The mixture was placed in a 1-cm diameter stainless steel mold and pressed at 10 toncm⁻². The pellet obtained was then connected to a silver wire with silver conducting paint (Sigma-Aldrich) and sealed in a glass rod. Subsequently, epoxy resin (Devcon) was applied to cover the silver wire connecting surface. The prepared AgC-PVC electrode was used for electrolysis cell and pilot-scale reactor.

2.3. Electrochemical Measurement and Electrolysis of RO4

Electrochemical measurements were performed using a Radiometer Analytical Voltalab potentiostat (Model PGZ 402), whereas data acquisition was accomplished using the VoltaMaster 4 software. Cyclic voltammetry and

Table 1. Composition ratio and mass of Ag, C and PVC for the preparation of AgC-PVC electrodes

| Electrode | Ag:C ratio (%) | Mass of Ag (g) | Mass of C (g) | Mass of PVC (g) |
|--|----------------|----------------|---------------|-----------------|
| Ag _{0.0} C _{95.0} -PVC ₅ | 0:100 | – | 1.425 | 0.075 |
| Ag _{28.5} C _{66.5} -PVC ₅ | 30:70 | 0.4275 | 0.9975 | 0.075 |
| Ag _{47.5} C _{47.5} -PVC ₅ | 50:50 | 0.7125 | 0.7125 | 0.075 |
| Ag _{66.5} C _{28.5} -PVC ₅ | 70:30 | 0.9975 | 0.4275 | 0.075 |
| Ag _{95.0} C _{0.0} -PVC ₅ | 100:0 | 1.425 | – | 0.075 |

linear potential measurements were carried out in a three-electrode system, which consisted of working (AgC-PVC), counter (Pt wire), and reference electrodes (saturated calomel electrode, SCE). A NaCl solution was used as a supporting electrolyte. An electrolysis study was performed using a two-electrode system, which consisted of a working electrode (AgC-PVC electrode) and counter electrode (Pt plate), with a NaCl solution as a supporting electrolyte. A DC power supply (TTi PSU Bench CPX 400) was used throughout the electrolysis process. The electrochemical cell used for both experiments was a simple and undivided cell with a capacity of 100 mL. Prior to any measurements, the solutions were deoxygenated by bubbling N_2 gas through the solution for 15 min, which was then allowed to flow freely throughout the entire experiment to remove the interfering oxygen gas during measurements.

2. 4. Instrumentation

To observe the level of decolorization of the RO4 and effluents before and after treatment, the sample solution was characterized using an UV-Vis (Shimadzu UV-2450) in the range of 200–900 nm using 10 mm quartz cuvettes. The electrolysis product was characterized using FTIR (Perkin Elmer 1310) in the range of 4000–400 cm^{-1} and GC-MS (Shimadzu QP5050A). The samples were extracted with DCM (HPLC grade) using separatory funnel liquid-liquid extraction method as described by Rajkumar et al (2007).¹³ The operating conditions of GC-MS is provided in Table 2. The Ag concentration in the aqueous solution was measured using ICP-OES (Perkin Elmer Optima 4300DV) using 6 series of standard solutions (0.1, 0.3, 0.5, 1.0, 2.0 and 5.0 ppm) as the calibration method.

Table 2. The operating conditions of GC-MS for the identification of intermediate compounds

| | |
|-----------------------------|--|
| GC Instrument | Shimadzu QP5050A |
| Injection mode | Split |
| Column | HP-5MS |
| Injection volume | 1 mL |
| Carrier gas/Flow | $N_2/1.1 \text{ mL min}^{-1}$ |
| Temperature program | 40 °C (10 min), 100 °C (12 °C/min), 200 °C (5 °C/min), 270 °C (20 °C/min) |
| Injector temperature | 240 °C |

2. 5. Electrochemical Oxidation of Textile Effluents Using $Ag_{28.5}C_{66.5}$ -PVC₅ Electrode

A sample was obtained from the batik industry in Terengganu, Malaysia. A pilot-scale reactor (Figure 2) with a 10-L capacity was equipped with four $Ag_{28.5}C_{66.5}$ -

PVC₅ (30% Ag: 70% C) electrodes (same dimension as stated in Section 2.2) as anodes and four stainless steel electrodes (20 cm long with 1.3 cm diameter) as cathodes. The distance between the electrodes was 3 cm. A small water pump was used to circulate the effluent during electrolysis. Before electrolysis, the untreated textile effluents were characterized to determine the COD, BOD₅, TSS, surfactant contents, and pH. Standard methods 209C, 507, and 508B (Ref. ²⁴) were used for the TSS, BOD₅ and COD analyses, respectively, whereas the surfactant was analyzed using the method described by Rolan et al (2010).²⁵

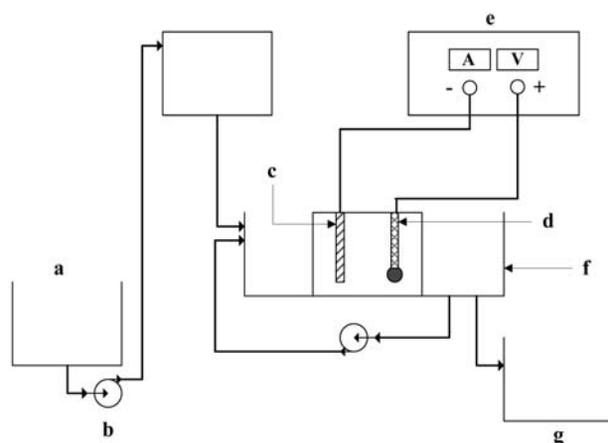


Figure 2. Schematic of pilot-scale reactor for electrochemical oxidation of textile effluents: (a) untreated effluent, (b) peristaltic pump, (c) stainless steel rod, (d) $Ag_{28.5}C_{66.5}$ -PVC₅ electrode, (e) potentiostat, (f) electrolysis cell, and (g) treated effluent. Total volume of effluent = 5 L.

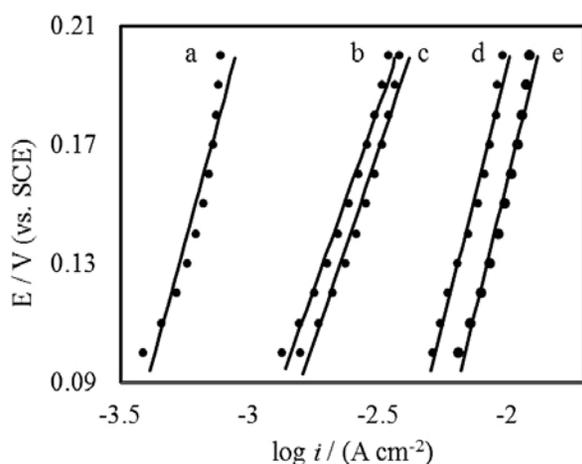
3. Results and Discussion

3. 1. Electrochemical Kinetic Parameter of Electrodes

Previous studies showed that a Tafel plot is a good method for determining the speed of an electrochemical reaction. A Tafel plot can be used to verify the quality of an electrode, based on the previous studies conducted by Tapan et al. (2005).²⁶ Figure 3 shows the Tafel plots for AgC-PVC electrodes with different Ag:C composition ratios (0:100, 30:70, 50:50, 70:30, and 100:0) in a Tafel area of +0.1 V to +0.2 V (vs. SCE). The AgC-PVC electrode with a composition ratio of 30:70 (known as the $Ag_{28.5}C_{66.5}$ -PVC₅ electrode) exhibits the highest value of exchange current density (i_0), which is 3.555 $mA \text{ cm}^{-2}$ (Table 3), compared to other electrodes. This shows that this electrode possesses better electrochemical catalytic properties. Therefore, the $Ag_{28.5}C_{66.5}$ -PVC₅ electrode was selected for further study on the decolorization of the RO4 solution.

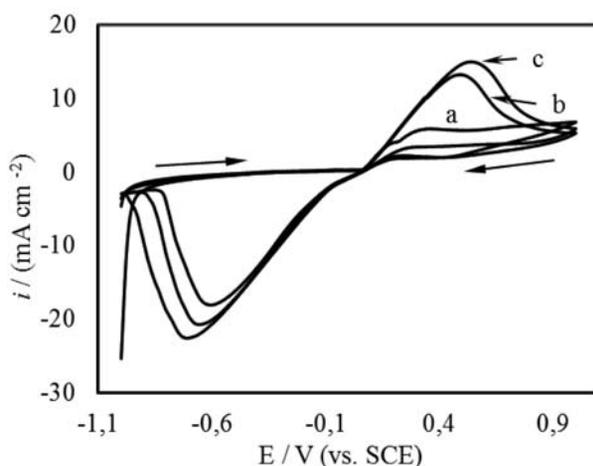
Table 3. Electrochemical kinetic parameters for AgC-PVC electrodes with different composition ratios in 4 mg L⁻¹ of RO4 + 1.0 mol L⁻¹ NaCl

| Electrode | R ² | Tafel slope, b (mV dec ⁻¹) | Reaction rate constant, a | Exchange current density, i ₀ (mA cm ⁻²) |
|--|----------------|--|---------------------------|---|
| Ag _{0.0} C _{95.0} -PVC ₅ | 0.948 | 319 | 1.175 | 0.207 |
| Ag _{28.5} C _{66.5} -PVC ₅ | 0.985 | 354 | 0.867 | 3.555 |
| Ag _{47.5} C _{47.5} -PVC ₅ | 0.987 | 344 | 0.885 | 2.675 |
| Ag _{66.5} C _{28.5} -PVC ₅ | 0.990 | 243 | 0.788 | 0.572 |
| Ag _{95.0} C _{0.0} -PVC ₅ | 0.982 | 259 | 0.815 | 0.713 |

**Figure 3.** Tafel plots of (a) Ag_{0.0}C_{95.0}-PVC₅, (b) Ag_{66.5}C_{28.5}-PVC₅, (c) Ag_{95.0}C_{0.0}-PVC₅, (d) Ag_{47.5}C_{47.5}-PVC₅, and (e) Ag_{28.5}C_{66.5}-PVC₅ in 4 mg L⁻¹ of RO4 + 1.0 mol L⁻¹ NaCl (scan rate = 1 mV s⁻¹)

3. 2. Cyclic Voltammetry of Ag_{28.5}C_{66.5}-PVC₅ Electrode

Cyclic voltammograms of the Ag_{28.5}C_{66.5}-PVC₅ electrode in 1.0 mol L⁻¹ NaCl and RO4 are shown in Figure 4. Curve (a) (Figure 4) is the cyclic voltammogram for the electrolyte background. In the anodic potential sweep for curve (a), an anodic peak appeared at +0.46 V (vs.

**Figure 4.** Cyclic voltammogram of (a) 1.0 mol L⁻¹ NaCl; (b) 1.0 mol L⁻¹ NaCl + 4 mg L⁻¹ RO4; (c) 1.0 mol L⁻¹ NaCl + 12 mg L⁻¹ RO4 using Ag_{28.5}C_{66.5}-PVC₅ electrode (scan rate = 100 mV s⁻¹)

SCE) while cathodic peak appeared at -0.67 (vs. SCE) due to the redox behavior of Ag. After the addition of the RO4 solution, the Ag_{28.5}C_{66.5}-PVC₅ electrode exhibited an anodic peak at +0.5 V (vs. SCE), whereas during a reverse scan, a cathodic peak appeared at -0.65 V (vs. SCE). These anodic and cathodic peaks were both due to the redox behavior of Ag and RO4. The current density increased significantly with a further addition of RO4 (curve b and c). This suggests that the electrochemical oxidation of RO4 is favorable in these media.

3. 3. Effect of Operating Parameters in Electrolysis

Figure 5a shows that the decolorization efficiencies were significantly affected by the applied cell voltage. The satisfaction level for the decolorization when using a lower applied voltage should be considered because the application of a higher voltage in decolorization leads to energy loss, high temperatures, and electrode damage.²⁷ Increasing the applied voltage from 4 V to 10 V increased the percentage of RO4 decolorization from 91.05% to 99.12% after 100 min of electrolysis. This was due to the increased generation of OCl⁻ species. Figure 5b shows that increasing the electrolysis time increased the decolorization level for RO4. A longer electrolysis time increased the generation of OCl⁻ ions, which resulted in a better RO4 decolorization efficiency compared to a shorter electrolysis time. The figure shows that increasing the electrolysis time from 20 min to 100 min increased the level of decolorization from 84.85% to 99.12%, respectively.

Figure 5c shows the effect of the supporting electrolyte concentration on the decolorization of the RO4 solution. The supporting electrolyte that was used in this study was a NaCl solution. The purpose of the NaCl addition during electrolysis was to modify the conductivity of the electrochemical process and facilitate the passage of the electrical current. The solution conductivity in the electrolytic cell influences the cell voltage, current efficiency, and electrical energy consumption.²⁸ As seen in Figure 5c, increasing the concentration of NaCl from 0.05 mol L⁻¹ to 1.0 mol L⁻¹ increased the level of RO4 decolorization after 100 min of electrolysis from 85.69% to 99.12%, respectively. The generation of self-electrogenerated OCl⁻ ions and the cell conductivity increased pro-

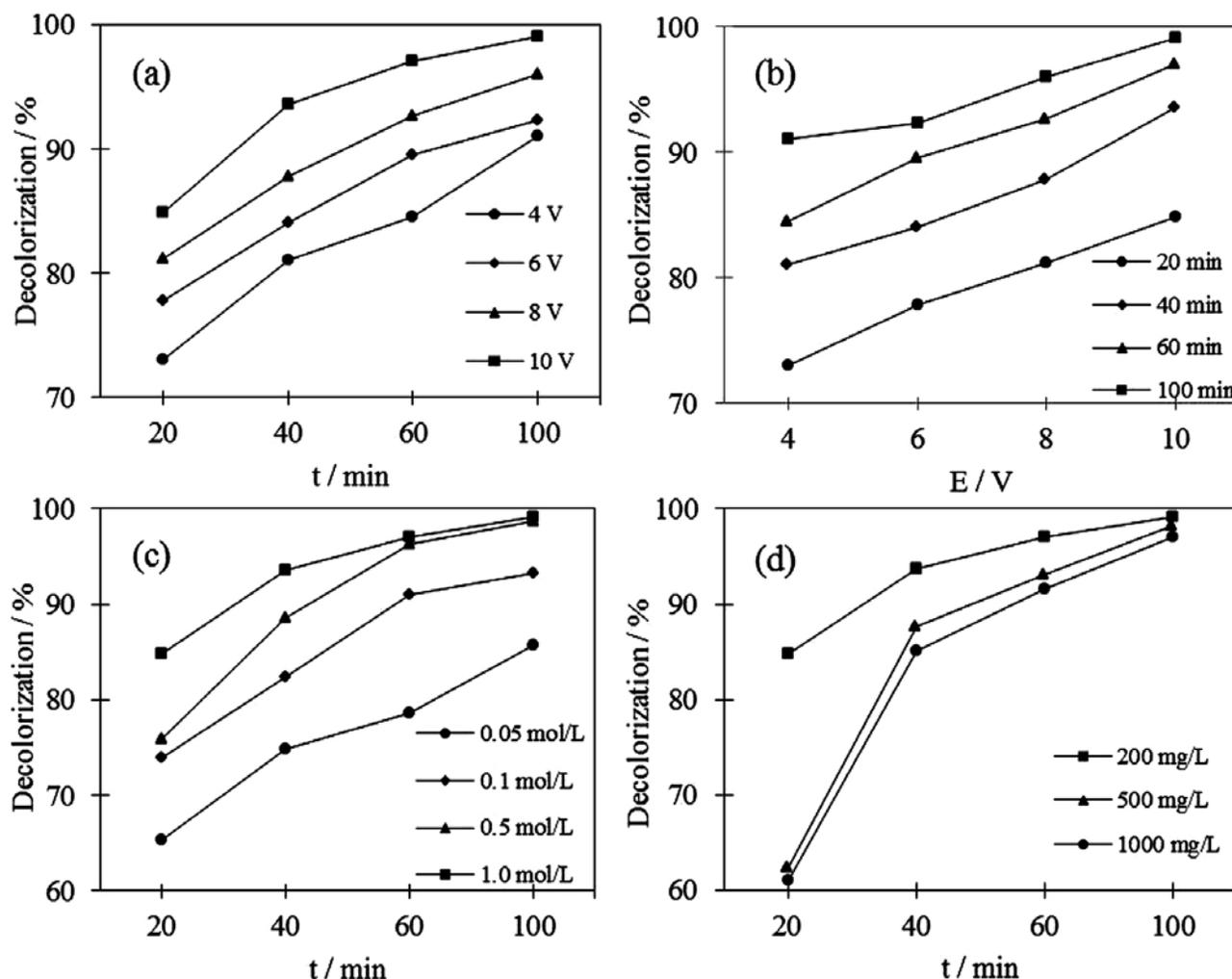


Figure 5. Effects of (a) applied voltage, (b) electrolysis time, (c) concentration of supporting electrolyte, and (d) initial concentration of RO4 on decolorization of RO4 solution

portionally with the concentration of the supporting electrolyte used.¹⁶ Figure 5d shows that the initial concentration of dye played an important role in obtaining a satisfactory level of decolorization. As shown in this figure, the percentage of decolorization decreased from 99.12% to 96.99% when the initial concentration of the dye increased. This was explained by the decrease in the ratio of the OCl^- species to the dye concentration with an increase in the initial dye concentration.

3. 4. Decolorization of RO4 Solution

A UV–Vis spectrophotometer was used to determine the level of RO4 decolorization using the $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode before and after 100 min of electrolysis. Figure 6 shows the UV–Vis spectra obtained for 200 mg L^{-1} of RO4 in 1.0 mol L^{-1} NaCl. The initial spectra (0 min) showed that the wavelength of maximum absorbance (λ_{max}) at 391 nm in the UV region corresponded to the azo

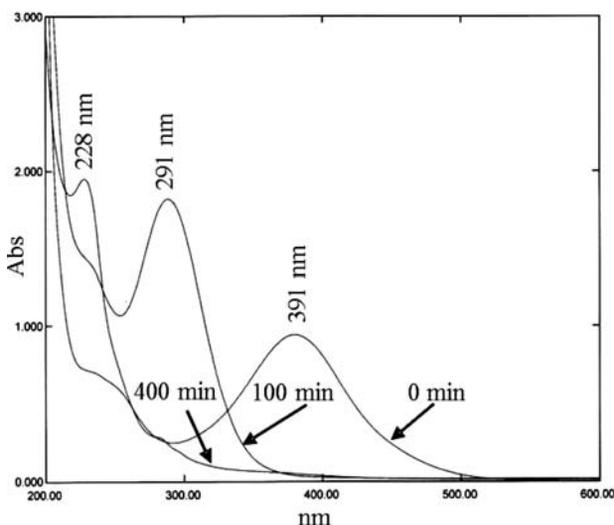
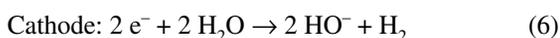
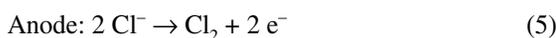


Figure 6. UV–Vis spectra of RO4 solution ($[\text{RO4}]_0 = 200 \text{ mg L}^{-1}$; $[\text{NaCl}] = 1.0 \text{ mol L}^{-1}$; $E = 10 \text{ V}$)

group.¹⁶ In addition, another peak was also observed at 228 nm in the UV region, which corresponded to conjugated aromatic rings.⁴ The spectra obtained after 100 min of electrolysis show the disappearance of the azo group and aromatic ring peaks after the electrolysis process. This suggest that the azo group and conjugated aromatic ring were completely destroyed by the electrochemical process, and a colorless solution was produced by the electrolysis.

The spectra obtained after 100 min of electrolysis also show the presence of a new peak at 291 nm in the UV region. This peak may not be related to an intermediate formation but correspond to the formation of an electrogenerated OCl^- species, which is a powerful oxidant for the oxidation of organic pollutants.³ The electrolysis mechanism is shown below:



The presence of the peak at 291 nm at the end of the electrolysis shows that the mineralization of the dye was not completely achieved.⁸ Therefore, the complete mineralization of an organic compound must be ensured to prevent the formation of OCl^- ions by extending the electrolysis time.²⁹ Figure 6 shows the spectra obtained after 400 min of electrolysis. As can be seen, the OCl^- ion formation peak at 291 nm completely disappeared.

3. 5. Characterization of Electrolysis Products

3. 4. 1. FTIR Study

Figure 7 shows the IR spectra of RO4 before and after the electrolysis process. It can be seen that some structural changes might have occurred during the electrolysis process. In Figure 7 for RO4 spectrum before the electrolysis process, the appearance of peaks at 3442.20 cm^{-1} and 1640.57 cm^{-1} indicates the presence of hydroxyl and azo groups, respectively. Additional peaks can also be noticed at 1553.87 cm^{-1} (secondary amine N-H bend), 1478.90 cm^{-1} (aromatic -C=C- stretching), 1346.83 cm^{-1}

(triazinic group -C-N- stretching), and 1185.34 cm^{-1} (secondary amine C-N stretching). The other peaks at 1026.55 cm^{-1} , 848.63 cm^{-1} , and 626.35 cm^{-1} are thought to belong to C-O-H, aromatic C-H, and C-Cl stretching, respectively. The IR spectra of RO4 after the electrolysis process (Figure 7) show the appearance of peaks at around 3428.79 cm^{-1} and 1644.85 cm^{-1} , which correspond to the hydroxyl and carbonyl groups, respectively. This variation in the IR spectra could be related with the aromatic rings breakage leading to the accumulation of low molecular weight species with hydroxyl and carbonyl groups.

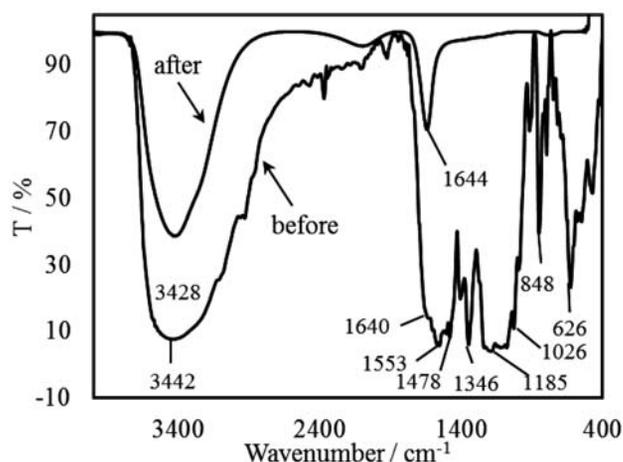


Figure 7. IR spectra of RO4 solution before and after electrolysis of RO4

3. 4. 2. GC-MS Study

The intermediate compounds formed during the degradation of RO4 were identified using GC-MS. Samples were collected at different time intervals during the electrolysis of 200 mg L^{-1} of RO4. Figure 8 shows the proposed mechanism for the electrochemical oxidation of RO4. The retention time for all of the intermediate compounds formed was summarized in Table 4. The 20-min electrolysis results illustrated in Figure 8 shows the formation of compounds (i) to (vi) while the compounds identified after 100 min of electrolysis is compound (iii) and (vii), as showed in Table 4. Compound (iii) is present in the samples at different time intervals. This suggest that this com-

Table 4. Retention time for intermediate compounds formed by GC-MS

| No. | Compound name | Molecular weight (g mol^{-1}) | Molecular formula | Retention time (min) |
|-------|-----------------------------------|--|---|----------------------|
| (i) | (2-(pentyloxy)ethyl)cyclohexane | 198.34 | $\text{C}_{13}\text{H}_{26}\text{O}$ | 14.91 |
| (ii) | 2-methyl benzoic acid | 136.15 | $\text{C}_8\text{H}_8\text{O}_2$ | 47.03 |
| (iii) | 1,3-dichlorocyclopentane | 139.02 | $\text{C}_5\text{H}_8\text{Cl}_2$ | 5.60 |
| (iv) | 1,2-dichlorocyclohexane | 153.05 | $\text{C}_6\text{H}_{10}\text{Cl}_2$ | 10.63 |
| (v) | 1-chloro-2-(2-chloroethoxy)ethane | 143.01 | $\text{C}_4\text{H}_8\text{Cl}_2\text{O}$ | 7.40 |
| (vi) | methyl-2,3-dichlorobutanoate | 171.02 | $\text{C}_5\text{H}_8\text{Cl}_2\text{O}_2$ | 9.96 |
| (vii) | methyl 2,2,3-trichlorobutanoate | 205.47 | $\text{C}_5\text{H}_7\text{Cl}_3\text{O}_2$ | 16.19 |

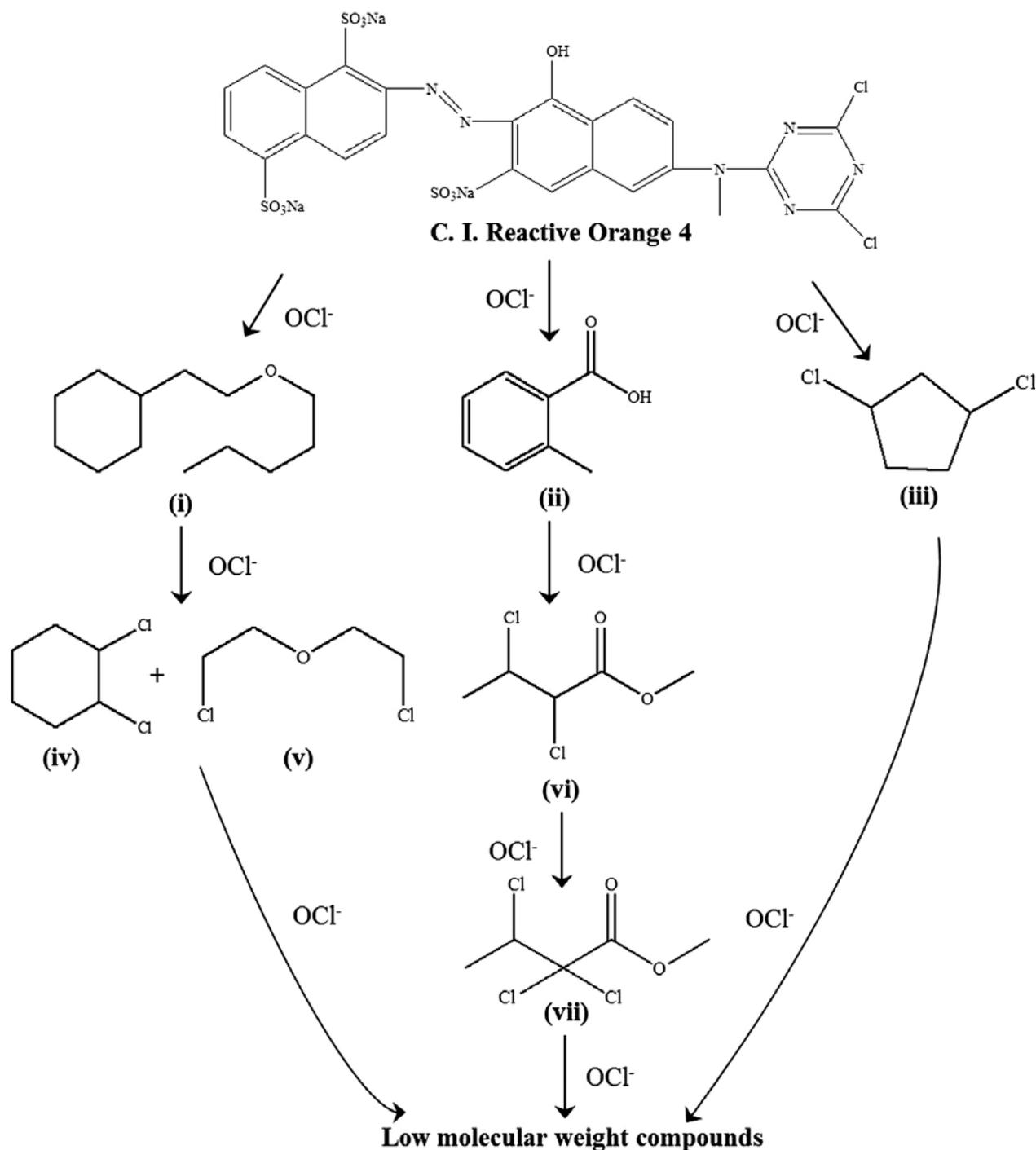


Figure 8. Proposed mechanism for electrochemical oxidation of RO4

compound was formed over the period of the electrolysis process.

The presence of an active oxidant during electrolysis causes the RO4 molecules to be broken down into several small molecules. The active oxidant will continue to break down the molecules that have been formed into other molecules with lower molecular masses at the end of the electrolysis process. Several compounds showed the

presence of carbonyl groups in their molecular structures. This may support the results obtained from the FTIR study (Figure 7), where the figure shows the appearance of the carbonyl group in the molecular structure of RO4 after 100 min of electrolysis.

Most of the compounds produced during the electrolysis of RO4 were undesirable toxic and mutagenic chlorinated by-products. They were produced by the

presence of chloride ions in the solution.^{4,6} This is the main disadvantage of using the electrochemical oxidation technique in the presence of chloride ions. However, the generation of chlorinated by-products can be controlled by two things: (1) the concentration of NaCl (a greater NaCl concentration will result in greater chlorinated by-product generation) and (2) the current density (low current densities produce fewer chlorinated by-products).⁶

3. 6. Stability Analysis of $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ Electrodes

The stability of the prepared electrode was determined by cyclic voltammogram with five cycles as shown in Figure 9. The anodic (A1) and cathodic (C1) peaks shift towards positive and negative potential, respectively in Figure 9 is not really significant between each cycle. It shows better stability of the electrode in the electrochemical oxidation of RO4. The stability of Ag in the $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode after the electrolysis of 200 mg L^{-1} of RO4 was determined using ICP-OES. The result obtained is summarized in Table 5. As can be seen, the percentage of Ag ions in an electrolytic solution was very insignificant, which indicated that the electrodes used were very stable because of the low amount of dissolved Ag in the solution.

3. 7. Surface Morphology of $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ Electrodes

Figure 10 shows the FESEM micrograph obtained from the morphological study of freshly prepared $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ (a) and after (b) electrolysis of 200 mg L^{-1} RO4 using 10 V applied voltage and 100 min elec-

trolysis. The FESEM micrograph in Figure 10a shows that the surface of the electrode was rough and irregular. In addition, the surface of the prepared electrode shows that the existence of voids that are not filled by the element and PVC. The voids formed normally will increase the porosity characteristic of the electrode which allowing electrochemical oxidation occurred within the electrode.

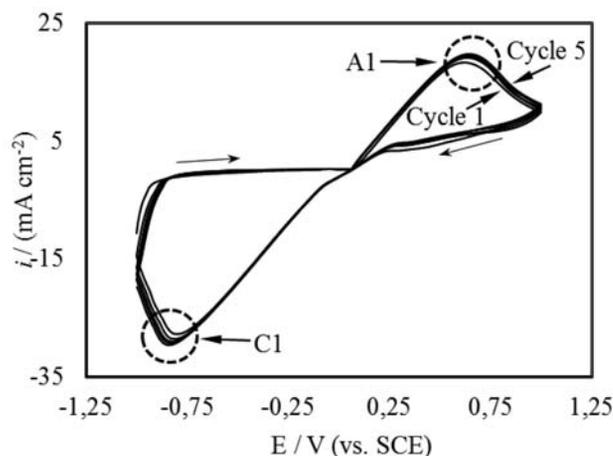


Figure 9. Cyclic voltammogram of $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode in 4 mg L^{-1} of RO4 + 0.1 mol L^{-1} NaCl with five cycles (scan rate = 100 mV s^{-1})

Table 5. Percentage of dissolved Ag in electrolytic solution after electrolysis of 200 mg L^{-1} of RO4 in 1.0 mol L^{-1} NaCl using $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode

| | |
|---|-----------------------|
| Mass of Ag in electrode (g) | 0.4275 |
| Concentration of Ag in electrolytic solution ($\mu\text{g L}^{-1}$) | 164.9 |
| Percentage of dissolved Ag (%) | 1.32×10^{-3} |

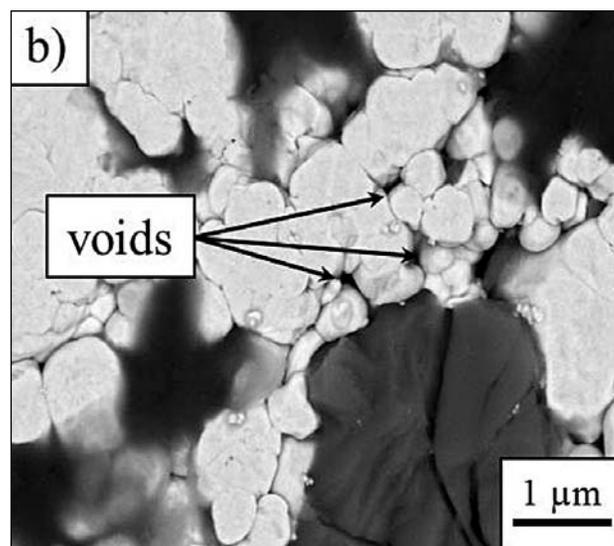
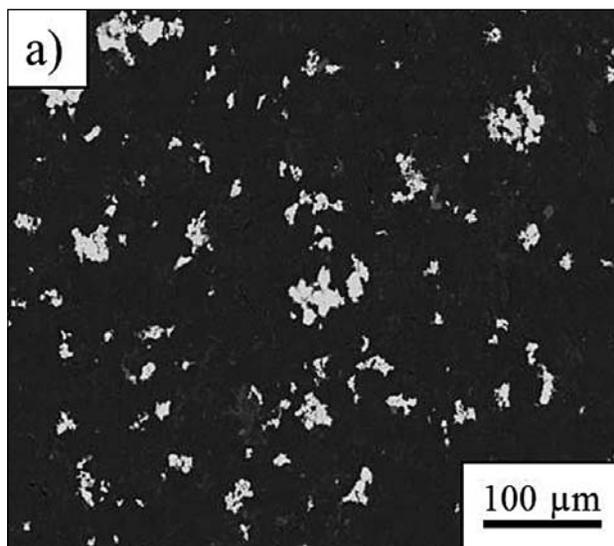


Figure 10. FESEM micrograph of freshly prepared $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode using a) 100x and b) 4000x magnifications.

3. 8. Electrochemical Oxidation of Textile Effluents Using $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ Electrode

Figure 11 shows the UV–Vis spectra for textile effluents before and after treatment with an electrochemical technique using the pilot-scale reactor. For untreated effluents (0 min), two peaks are observed at wavelengths of 478 and 605 nm. The appearance of the peak at 478 nm in the visible region corresponds to the azo group,³⁰ whereas the peak at 605 nm in the visible region corresponds to the anthraquinone group.¹³ After 100 min of electrolysis using the $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode with an applied voltage of 10 V in the presence of 1.0 mol L⁻¹ of NaCl as a supporting electrolyte, the previous peaks completely disappeared, proving that the electrochemical oxidation method was able to decolorize all the colored material in the effluents.

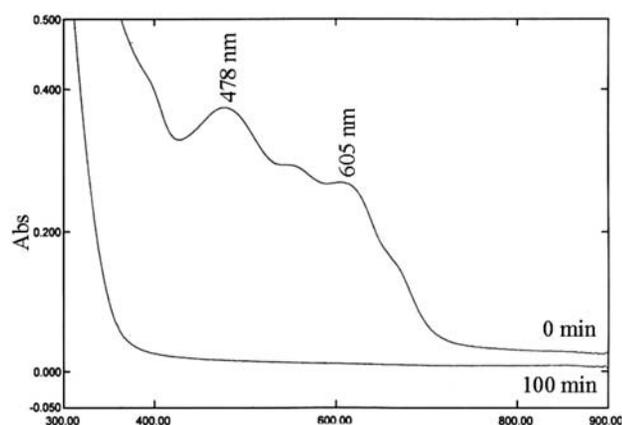


Figure 11. UV–Vis spectra for textile effluents before and after treatment using electrochemical oxidation technique ([NaCl] = 1.0 mol L⁻¹, applied voltage = 10 V, t = 100 min)

3. 9. Characterization of Treated Textile Effluents

Studies on untreated and treated textile effluents using various effluent parameters have been reported by many authors^{31–33} The characterization results for the textile effluents before and after treatment were summarized in Table 6. In addition to the color removal shown in Figure 11, the electrochemical method using the $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode could also significantly reduce the COD, BOD₅, and surfactant content (Table 6). As previously discussed, textile effluents contain, not only colored compounds (e.g., azo compounds), but also numerous oxidizable organic compounds that cannot be oxidized by microorganisms. Therefore, treatment using this technique could not only significantly reduce the existing organic compounds, but could also reduce these compounds to much softer oxidizable organic compounds.

Table 6. Characterization of textile industrial effluents before and after treatment with electrochemical method using $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode (supporting electrolyte = 1.0 mol L⁻¹ NaCl, applied voltage = 10 V, t = 100 min, energy consumption = 2.86 kWh g⁻¹)

| Parameters | Before treatment | After treatment |
|--|------------------|-----------------|
| COD (mg L ⁻¹) | 1728.00 | 448.00 |
| BOD ₅ (mg L ⁻¹) | 51.30 | 22.50 |
| TSS (mg L ⁻¹) | 768.57 | 178.29 |
| Surfactant (mg L ⁻¹) | 25.16 | 14.49 |
| pH | 10.97 | 10.07 |

4. Conclusions

An AgC-PVC electrode composed of 30% Ag and 70% C (known as the $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode) was found to be the best among the prepared electrode because it had the highest value of exchange current density (i_0), which is 3.555 mA cm⁻². This high value of i_0 showed that the electrode possessed better electrochemical catalytic properties. This electrode was applied to the decolorization of RO4 and textile effluents. The results showed that when the $\text{Ag}_{28.5}\text{C}_{66.5}\text{-PVC}_5$ electrode was used with an applied voltage of 10 V in the presence of 1.0 mol L⁻¹ NaCl for 100 min of electrolysis to decolorize RO4 solution and textile effluent, decolorization percentages of more than 95% were obtained for both RO4 and effluent solution. This electrode was also able to reduce the COD, BOD₅, and surfactant contents of a colored solution during the treatment of textile effluents using this electrochemical technique with a pilot treatment plant, which makes it viable at a larger scale.

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Povzetek

Proučevana je bila elektrokemijska oksidacija barvila reaktivno oranžno 4 (RO4) na elektrodi iz kompozitnega materiala srebro-ogljik (AgC-PVC). Omenjena elektroda je služila kot delovna elektroda za merjenje vsebnosti RO4 ob prisotnosti NaCl kot podpornega elektrolita. Po elektrokemijski oksidaciji je UV-Vis spekter pokazal popolno razbarvanje raztopine. Produkti elektrolize, ki so bili okarakterizirani s pomočjo FTIR in GCMS analize, so pokazali, da je molekula RO4 razpadla v manjše molekule ob prisotnosti OCl^- kot aktivnega oksidanta. Uporabljena elektroda je zmanjšala tudi KPK, BPK_5 in vsebnost surfaktantov v odpadnih vodah iz tekstilne industrije v pilotnem reaktorju. Rezultati dokazujejo uporabnost proučevane AgC-PVC elektrode za razbarvanje in odstranjevanje drugih polutantov iz odpadnih voda tekstilne industrije.