

Available online at BCREC website: https://bcrec.id

BCREC

Bulletin of Chemical Reaction Engineering & Catalysis, 16 (4) 2021, 847-856

Research Article

Graphite/NiO/Ni Electrode for Electro-oxidation of the Remazol Black 5 Dye

Ni Made Wiratini^{1,2,*}, T. Triyono¹, Wega Trisunaryanti¹, Agus Kuncaka¹

¹Department of Chemistry, Universitas Gadjah Mada, Yogyakarta, Indonesia. ²Department of Chemistry, Universitas Pendidikan Ganesha, Singaraja, Indonesia.

Received: 9th July 2021; Revised: 9th September 2021; Accepted: 10th September 2021 Available online: 12nd September 2021; Published regularly: December 2021



Abstract

Graphite/NiO/Ni electrode had been fabricated for the electro-oxidation of remazol black 5 dye. The electrode was synthesized by electrodeposition method. Electro-oxidation of 100 ppm remazol black 5 dye was carried out at various concentrations of NaCl, 0.025; 0.05; 0.1; 0.25; and 0.5 M, variations in electro-oxidation time were 15, 30, 45, and 60 minutes, and pH variations were 4, 6, and 8. Cyclic voltammetry test revealed that graphite/NiO/Ni electrode had higher electrocatalytic capability compared to graphite electrode. The X-ray diffraction (XRD) patterns showed the decreasing value of 20 from 44.6° for Ni to 43.5° for NiO. Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) showed that NiO/Ni deposited on the graphite surface in the form of solid grains and cracks, FTIR showed that δ (Ni-O) bond appeared at 582–511 cm⁻¹. The decolorization efficiency of remazol black 5 for graphite/NiO/Ni electrode was 100% for 45 minutes of the electro-oxidation process, while the decolorization efficiency of remazol black 5 for graphite electrode was 99.74% for 60 minutes of the electro-oxidation process.

Copyright © 2021 by Authors, Published by BCREC Group. This is an open access article under the CC BY-SA License (https://creativecommons.org/licenses/by-sa/4.0).

Keywords: graphite/NiO/Ni; electro-oxidation; remazol black 5 dye; textile waste

How to Cite: N.M. Wiratini, T. Triyono, W. Trisunaryanti, A. Kuncaka (2021). Graphite/NiO/Ni Electrode for Electro-oxidation of the Remazol Black 5 Dye. *Bulletin of Chemical Reaction Engineering & Catalysis*, 16(4), 847-856 (doi:10.9767/bcrec.16.4.11702.847-856)

Permalink/DOI: https://doi.org/10.9767/bcrec.16.4.11702.847-856

1. Introduction

Synthetic dyes are widely used in the textile industry, especially in the textile dyeing process. Textile industry activities have a negative impact on aquatic ecosystems. The negative impact is colored liquid waste that comes from the dyeing process. Most of the liquid waste is very stable, resistant to chemical reagent reactions, very difficult to decompose, toxic, and carcinogenic [1]. The synthetic dyes, which are used for textile coloring are remazol black 5, remazol brilliant orange 3R, remazol golden yellow, and

remazol red. The concentration of river water pollution due to textile waste reaches 10–15% (m/v) and 50% of the textile waste contains remazol black 5 compounds [2]. Remazol black 5 is an azo group compound (–N=N) and a sulfonate (–SO₃–) [3]. Remazol black 5 dye waste requires effective and efficient handling so that it does not cause environmental pollution.

Various efforts have been made to reduce textile waste pollution, such as coagulation and flocculation to treat batik waste [4], decolorization and biodegradation of remazol reactive dyes by *Clostridium species* [5], methylene blue adsorption by silica gel from coal fly ash [6], electrochemical oxidation of methylene blue by graphene-modified electrodes [7]. The disad-

^{*} Corresponding Author. Email: ni.made.wiratini@mail.ugm.ac.id (N.M. Wiratini); Telp: +62 85 237 465 122

vantages of chemical coagulation, adsorption, and membrane filtration methods are expensive and there are residual adsorbents or coagulants [8]. Azo dyes are resistant to bacterial and biological activity, and the degradation process takes a long time. Therefore, it is necessary to develop alternative technologies that are able to degrade dyes effectively and efficiently [9].

Electrochemical oxidation or electrooxidation is a textile wastewater treatment technology. This technology attracts attention because it has high efficiency, high degradation speed, easy operation, low cost, does not require a catalyst separation process, does not produce secondary pollutants, and is environmentally friendly [10-15]. Electro-oxidation is a process that produces hydroxyl radicals (•OH). Hydroxyl radicals are highly oxidizing species. They can cause the mineralization of organic matter into carbon dioxide, water, and inorganic ions [16]. The performance of the electro-oxidation process depends on the electrode material, the characteristic/amount of electrolyte, and pH [17].

Various types of electrodes have been used for the electro-oxidation of various dve wastes. Each electrode produces a different efficiency of organic pollutant degradation. The expanded graphite diamond (EG/Diamond) anode electrode has removed 80% of anthraquinonic dye and the expanded graphite (EG) electrode has removed 66% of anthraquinonic dye, at a current of 20 mA/cm², 0.1 M Na₂SO₄ for 4 hours. However, with chlorine mediated electrooxidation (NaCl as the supporting electrolyte), the decolorization is faster, i.e. more than 98% decolorization in 25 minutes [18]. Pt anode electrode has degraded 96% reactive blue 109 (1000 mg/L) at pH 4, current (I) 20 mA/cm², 0.1 M NaCl [19]. Pt/MnO₂ anode electrode has degraded 90% methylene blue (40 mg/L) at pH 8, current (I) 7 mA/cm²; 0.05 M Na₂SO₄ for 2 hours [20]. The anode electrode Ti/Ta₂O₅/SnO₂ has degraded 95% methylene blue (0.025 mM) with a current (I) of 9.1 mA/cm², 0.1 M NaSO₄ for 3 hours [21]. Graphite electrodes on electrofenton have degraded 99.2% rhodamine B with the addition of 10 mg/L Fe²⁺ catalyst, pH 3, voltage 8 V, for 2 hours [22].

Graphite is often used as an anode for textile dye electro-oxidation because it is relatively inexpensive, intensively used on a laboratory scale for investigation of new processes, and gives satisfactory results. However, graphite electrodes also have weaknesses, such as low oxidation activity of organic compounds, high average corrosion rate, and low mineralization

efficiency [21]. The efficiency of the electrooxidation process is highly dependent on the electrode material, dye concentration, and other operating parameters, such as pH; concentration and type of electrolyte solution; and the duration of the electro-oxidation process. Nickel oxide (NiO) and nickel (Ni) are anode materials for the oxidation of organic compounds in alkaline media [23]. NiO is a metal oxide that is a semiconductor, the most promising electrocatalyst, more often used compared to Pt or RuO₂, environmentally friendly, and inexpensive [24]. Ni is used as an electrocatalyst for anodic and cathodic reactions in the organic synthesis and electrolysis of water [25].

The combination of transition metal oxides on graphite is a potential technology to increase catalytic activity [11]. The combination of transition metal oxides on graphite can overcome the disadvantages of graphite electrodes, so it can increase the efficiency of dye degradation. The combination of NiO/Ni on graphite electrodes is carried out by electrodeposition. This study examines graphite electrodes and graphite/NiO/Ni electrodes in the electrodegradation of remazol black dye 5. The effect of the experimental conditions studied is the concentration of NaCl electrolyte solution, the electrooxidation time process, and the pH.

2. Materials and Methods

2.1 Materials

The materials used for the investigation are NiSO₄.6H₂O (Sigma Aldrich, >98%), H_2O_2 (Merck, 30%), TMOS (SCIP, 99%), H3BO3 (Merck, \geq 99.5%), ethanol (Merck, 99.7%), NaCl (Merck, \geq 99.5%), H_2SO_4 (Merck, 98%), graphite electrode (SCIP, 99.9%), and remazol black 5 (Sigma Aldrich, \geq 50%).

2.2 Preparation of the Graphite Electrode

Graphite electrodes were immersed in 50 mL of $0.003~M~H_2SO_4$ and $30\%~H_2O_2$ in a ratio of 1:4 for 15 minutes [2]. The graphite electrodes were heated in the oven at 110 °C for 2 hours. Then, the graphite electrodes were cooled in a desiccator and weighed using a digital analytical balance. The graphite electrode was characterized by XRD-6000 and cyclic voltammetric Autolab type III Metrohm. Cyclic voltammetric characterization was carried out at a scan rate of 10 mV/s in a 0.1 M NaCl solution, Ag/AgCl as a reference electrode, Pt as a counter electrode, and graphite as a working electrode.

2.3 Graphite/NiO/Ni Electrode Synthesis

Graphite/NiO/Ni electrode was synthesized by the electrodeposition method, a modification of the research conducted by Zhang et al. [26]. A total of 100 mL of Ni deposition solution (0.2) M NiSO₄.6H₂O and 0.4 M H₃BO₃) was stirred for 10 minutes at 100 rpm. Electrodeposition was carried out at 9 volts for 120 minutes. The graphite/NiO/Ni electrode formed was heated at 400 °C for 2 hours and weighed on an analytical balance. Graphite/NiO/Ni electrodes were characterized by XRD-6000 SHIMADZU. The graphite/NiO/Ni electrode morphology was characterized by electron microscopy (SEM-EDX, FEI Inspect S50). Its chemical structure was proven by infrared spectroscopy Fourier transformation (FT-IR). Characterization of graphite/NiO/Ni with cyclic voltammetric Autolab type III Metrohm was carried out at a scan rate of 10 mV/s in 0.1 M NaCl solution, Ag/AgCl as a reference electrode, Pt as a counter electrode, and graphite/NiO/Ni as a working electrode.

2.4 Electro-oxidation of Remazol Black 5 Dye

The process of electro-oxidation of remazol black 5 dye was carried out by varying the concentration of sodium chloride solution, electro-oxidation time, and pH. A schematic diagram of remazol black 5 electro-oxidation with graphite electrodes and graphite/NiO/Ni electrodes is shown in Figure 1. Graphite electrodes were used as cathodes and graphite/NiO/Ni electrodes were used as anodes. Electrodes were connected to a DC of 9 volts. The distance between the anode and cathode electrodes was 1 cm.

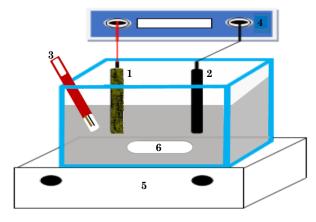


Figure 1. The electro-oxidation schematic cell of remazol black 5 with (1) anode (graphite/NiO/Ni or graphite), (2) cathode (graphite), (3) pH meter, (4) DC power supply, (5) magnetic stirrer, and (6) magnet.

2.4.1 Electro-oxidation of Remazol Black 5 Dye at Various Concentration of NaCl Solution

Electro-oxidation of remazol black 5 dye was carried out at various concentrations of sodium chloride solution. A total of 75 mL of 100 ppm of remazol black 5 dye was added to 50 mL of NaCl solution with a concentration variation of 0.025; 0.05; 0.1; 0.25; and 0.5 M respectively. Electro-oxidation was carried out at 9 volts for 30 minutes. The results of the electro-oxidation were filtered and measured by a UV-vis spectrophotometer.

2.4.2 Electro-oxidation of Remazol Black 5 Dye at Various Electro-oxidation Time

Electro-oxidation of remazol black 5 dye was also carried out at various times. A total of 75 mL of 100 ppm of remazol black 5 dye was added to 50 mL of 0.025 M NaCl solution. The electro-oxidation was carried out at 9 volts for 15, 30, 45, and 60 minutes respectively. The results of the electro-oxidation were filtered and measured using a UV-vis spectrophotometer.

2.4.3 Electro-oxidation of Remazol Black 5 Dye at Various pH

Electro-oxidation of remazol black 5 dye was carried out at various pH. A total of 75 mL of 100 ppm of remazol black 5 dye at pH of 2, 4, 6, and 8 respectively was added with 50 mL of 0.025 M NaCl solution. Electro-oxidation was carried out using 9 volts DC for 30 minutes. The results of electro-oxidation were filtered and measured using a UV-vis spectrophotometer

Determination of the maximum wavelength of remazol black 5 dye was carried out by measuring the absorbance of remazol black 5 dye at the wavelength of 200–800 nm by UV-vis spectrophotometer. The measurement results showed the maximum wavelength of remazol black 5 dye is 595 nm. Therefore, measurement of the results of electro-oxidation by UV-vis spectrophotometer was carried out at 595 nm wavelength. The decolorization efficiency in the electro-oxidation of remazol black 5 dye was calculated by the equation:

$$\%E = \frac{A_i - A_f}{A_i} \times 100 \tag{1}$$

where A_i is the absorbance value of remazol black 5 dye solution before electro-oxidation and A_f is the absorbance value of remazol black 5 dye solution after electro-oxidation.

3. Results and Discussion

3.1 Characterization of Graphite and Graphite/NiO/Ni Electrodes

The gravimetric method was carried out to prove that NiO/Ni was already attached to the graphite electrode. The results showed that the mass of the graphite electrode was 5.721 grams before electrodeposition and 6.103 grams after the electrodeposition process. The addition of

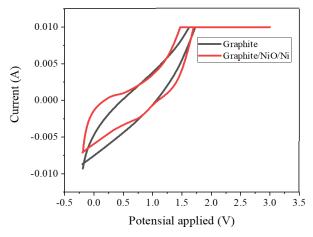


Figure 2. Voltamogram of graphite and graphite/NiO/Ni electrodes at 0.1 M NaCl at a 10 mV.s⁻¹ scan rate.

0.382 grams of mass after electrodeposition had proved that NiO/Ni has been deposited on the graphite as graphite/NiO/Ni.

Electrochemical catalyst electrode characterization was tested by cyclic voltametric. The electroactive capability of the electrode was an important factor to be tested. The electrocatalytic character of an electrode was measured by oxidation reaction which is indicated by the voltammogram data. The high current re-

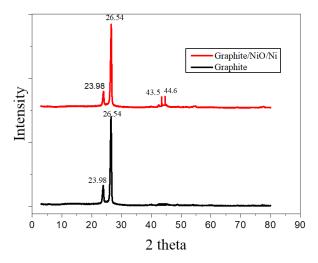


Figure 3. XRD pattern of graphite and graphite/NiO/Ni electrodes.

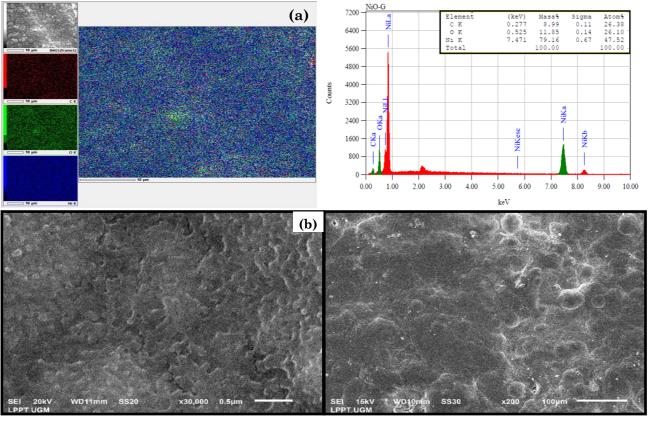


Figure 4. (a) EDX spectrum of graphite/NiO/Ni electrode and (b) SEM images of graphite/NiO/Ni electrode.

sponse of the voltammogram data shows the ease of the Cl⁻ oxidation reaction by the electrode [27]. Graphite electrode and graphite/NiO/Ni voltammograms data are presented in Figure 2. The voltammogram data in Figure 2 shows that the current response of graphite/NiO/Ni electrode was higher than graphite electrode. This indicated that Cl⁻ oxidation reaction by graphite/NiO/Ni electrodes was easier, hence the electrocatalytic ability of graphite/NiO/Ni electrodes was higher than graphite electrodes.

Testing of the phase composition of the electrode surface was carried out using an XRD instrument. The graphite and graphite/NiO/Ni electrode diffractograms are shown in Figure 3. As shown in Figure 3, the characteristic peak of graphite appeared at $2\theta = 26.54^{\circ}$ (002). Characteristics of graphite appeared at 2θ = 26.5° (002), 54.7° (004), and 87.1° (006) [28]. The XRD diffractogram on graphite/NiO/Ni electrode showed the appearance of two new diffraction peaks at $2\theta = 43.5^{\circ}$ and 44.6° . The XRD spectrum characteristic of NiO appeared at $2\theta = 37.2^{\circ}$ (111), 43.3° (200), 62.9° (220), 75.4° (220), and 79.4° (311) [29]. Based on Figure 3, the XRD spectrum of the graphite/NiO/Ni electrode showed that Ni was deposited on graphite as NiO at $2\theta = 43.5^{\circ}$. The diffraction peak at $2\theta = 44.6^{\circ}$ in Figure 3 shows the characteristics of Ni (JCPDS No. 70-0989), this indicated that NiO/Ni catalyst had been deposited on the graphite electrode as graphite/NiO/Ni.

Characterization by SEM-EDX showed that NiO/Ni was deposited on the graphite surface. The results of EDX analysis presented in Figure 4 showed that Ni and O particles scattered on the graphite surface particles were solid

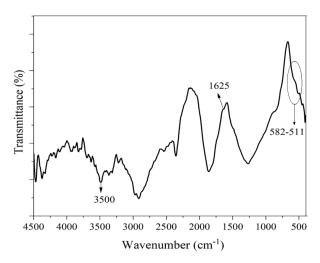


Figure 5. FTIR spectrum of graphite/NiO/Ni electrode.

grains and cracks. The same results were also found for NiO electrodeposits on fluorine doped tin oxide (FTO) glass substrate [23].

FTIR spectra of graphite/NiO/Ni electrodes in 500–4500 cm⁻¹ was shown in Figure 5. Figure 5 shows the appearance of a peak at 3500 cm⁻¹ which indicated stretching (v) (O–H), 1625 cm⁻¹ indicated bending (o) (HO–H), and 582–511 cm⁻¹ showed δ (Ni–O). Previous research stated that δ (Ni–O) occurred between 610 and 480 cm⁻¹ [30], stretching (v) (O–H) occurred at 3500 cm⁻¹ and bending (o) (HO–H) appeared at 1625 cm⁻¹ [31].

3.2 The Electro-oxidation of Remazol Black 5 Dye at Various Concentrations of NaCl Solution

The concentration of NaCl greatly affects the degradation of remazol black 5 dye. Degradation of remazol black 5 dye occurs in the presence of oxidizing agents Cl₂, HClO, and ClO⁻. The number of oxidizing agents Cl₂, HClO, and ClO⁻ are influenced by the concentration of NaCl. The mechanism of electrochemical degradation in presence of NaCl is as follows:

Anode reaction : $2Cl^- \rightarrow Cl_2 + 2e^-$ (2) Cathode reaction : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (3) Bulk solution reaction : $Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$ (4) Bulk solution reaction : $HOCl \rightarrow H^+ + OCl^-$ (5)

Increasing NaCl concentration will clearly increase the quantity of Cl_2 as an oxidizing agent. The quantity of oxidizing agents will be proportional to the degradation rate [15].

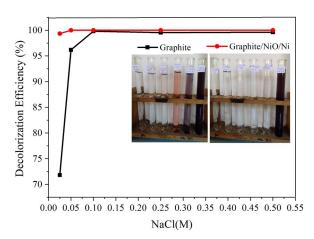


Figure 6. Relation between NaCl concentration and percentage of the decolorization efficiency 100 ppm of remazol black 5 dye. Insert picture: remazol black 5 dye degradation that is caused by NaCl concentration in graphite and graphite/NiO/Ni.

Based on Figure 6, an increase in NaCl solution concentration shows an increase in the decolorization efficiency of remazol black 5 dye. However, at a concentration of 0.1 M NaCl to 0.5 M NaCl, an increase in remazol black 5 dye decolorization efficiency is not significant, since the HOCl formed can already degrade most of remazol black 5 dye. Figure 6 shows that the highest decolorization efficiency of remazol black 5 dye for graphite electrode occurred at 0.1 M NaCl with 99.81% decolorization efficiency, while the highest decolorization efficiency of remazol black 5 dye for graphite/NiO/Ni electrode occurred at 0.05 M NaCl with 100% decolorization efficiency. An increase in NaCl concentration above the best condition did not influence the efficiency of the decolorization, since almost all remazol black 5 had been degraded. When electrolyte concentration in the degradation process had reached the best condition, the addition of electrolyte concentration did not increase the dye degradation [32]. This means an addition of electrolyte concentration above 0.1 M NaCl is not necessary since it does not increase the efficiency of the degradation process.

Figure 6 shows that the decolorization efficiency of the graphite/NiO/Ni electrode was 99.35%, while that of the graphite electrode was 71.81% at 0.025 M NaCl concentration. With 0.05 M NaCl concentration, the decolorization efficiency of the graphite electrode was 96.19%, while the decolorization efficiency of the graphite/NiO/Ni electrode was 100%. The electro-oxidation rate of organic pollutants depends on the catalytic activity of the anode

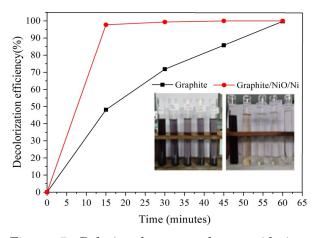


Figure 7. Relation between electro-oxidation time and percentage of the decolorization efficiency 100 ppm of remazol black 5 dye. Insert picture: remazol black 5 dye degradation that is caused by electro-oxidation time in graphite and graphite/NiO/Ni.

[33]. The catalytic activity of the anode can be increased by the addition of a catalyst. Electrocatalysis can improve electrode kinetics by accelerating the half-cell reaction on the electrode surface [34]. Ni is used as an electrocatalyst for anodic and cathodic reactions in organic synthesis and water electrolysis [25]. Based on Figures 2 to 5, NiO/Ni was deposited on the graphite electrode. The NiO/Ni which was deposited on the graphite electrode functioned as an electrocatalyst on the graphite electrode. This caused the decolorization efficiency of graphite/NiO/Ni electrodes to be higher than that of graphite electrodes. Previous research indicated that deposition of oxide ZnO-TiO2 on graphite felt (GrF) can increase the degradation yield of amido black 10B dye. Electrooxidation of Amido Black 10B dye with GrF-ZnO-TiO₂ electrode showed that the degradation results reached 98% after 70 minutes of electro-oxidation process, which was higher than that of the graphite electrode at 35% [2].

3.3 Electro-oxidating Remazol Black 5 Dye at Various Electro-oxidation Time

The electro-oxidation process of remazol black 5 dye by graphite and graphite/NiO/Ni electrodes in NaCl solution occurs through two mechanisms, namely a direct mechanism and an indirect mechanism. Indirect electro-oxidation of remazol black 5 dye was done by the OCl⁻ ion, like Equation 5. The indirect reaction of remazol black 5 dye degradation is as follows:

$$Dye + OCl^{-} \rightarrow CO_2 + H_2O + Cl^{-}$$
 (6)

The mechanism of direct pollutant degradation in the electro-oxidation process has several stages. Pollutant (MOx) in water forms MO_x(HO•) radical (Equation 7). The radical then changes into MO_{x+1} (Equation 8) and releases oxygen (Equation 9). MO_{x+1} undergoes a further reaction and produces oxygen like in Furthermore, Equation 10. the radical MO_x(HO•) and MO_{x+1} oxidize organic pollutants (Equations (11 and 12)). All of the processes occur catalytically on the anode surface according to Equations (9-12).

$$MO_x + H_2O \rightarrow MO_x(HO \cdot) + H^+ + e^-$$
 (7)

$$MO_x(HO \cdot) \to MO_{x+1} + H^+ + e^-$$
 (8)

$$MO_x (HO \cdot) \rightarrow MO_x + H^+ + e^- + \frac{1}{2} O_2$$
 (9)

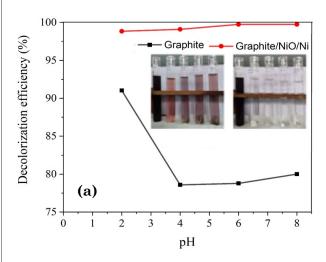
$$MO_{x+1} \to MO_x + \frac{1}{2} O_2$$
 (10)

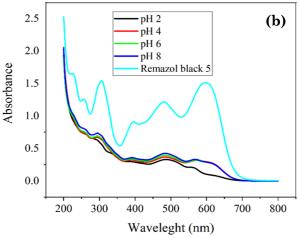
$$MO_x(HO \cdot) + RH \rightarrow MO_x + H_2O + R \cdot$$
 (11)

$$MO_{x+1} + RH \rightarrow MO_x + RHO$$
 (12)

Overall, the electro-oxidation process was directly degraded by the adsorbed hydroxyl radicals generated from the water oxidation reaction [35].

Figure 7 shows that the percentage of remazol black 5 dye decolorization efficiency increases by increasing electro-oxidation time because more hypochlorite ions (OCl-) and hydroxyl radicals (•OH) are formed. The hypochlorite ion and hydroxyl radicals act as the main oxidizing agents in dye degradation [36]. Figure 7 shows that after 15 minutes of electro-oxidation process, the graphite electrode decolorization efficiency was 48.13% and that of graphite/NiO/Ni electrode was 97.75%. The highest decolorization efficiency of remazol black 5 dye using graphite/NiO/Ni electrodes was 100% and the electro-oxidation process lasted for 45 minutes. While at the graphite electrode, the highest decolorization efficiency of remazol black 5 dye was 99.74% and the electrooxidation process lasted for 60 minutes. The de-





colorization efficiency of the graphite/NiO/Ni electrode was higher than the graphite electrode because NiO/Ni electrocatalyst was deposited on the graphite. The NiO/Ni electrocatalyst increased the ability of the electrode to oxidize Cl⁻ to be Cl₂ (Equation 2), hence accelerated the reaction of Equations 4 - 5 and automatically increased the decolorization efficiency of the remazol black 5 dye (Equation 6). A previous study on the electrochemical oxidation of methylene blue (MB) using stainless steel graphene hydroxyl (SS/G-OH) electrode in NaCl electrolyte showed that the MB concentration decreased by >99% after 30 minutes of electrolysis [7].

3.4 Electro-oxidation of Remazol Black 5 Dye at Various pH

The acidity of the solution affects the performance of the electro-oxidation process. In the electro-oxidation process, chloride ions are used as a supporting electrolyte to produce active chlorine (Cl₂, HOCl, and ClO⁻). The active chlorine depends on the pH of the solution. The active chlorine in the pH range of 3-8 is HClO, ClO⁻ in pH > 8, and Cl_{2(aq)} in pH close to 3. The standard potential of each active chlorine are Cl_{2(aq)} (E° = 1.36 V/SHE), HClO (E° = 1.49 V/SHE), and ClO⁻ (E° = 0.89 V/SHE) [11].

Based on Figure 8, the highest decolorization efficiency for graphite electrodes was found 91.03% at pH 2, while for graphite/NiO/Ni electrodes was found 99.74% at pH 6. When the pH is 2, the main active chlorine is Cl₂. The amount of Cl₂ formed exceeds its solubility so that it forms bubbles. It may be partially diffused away from the anode to react

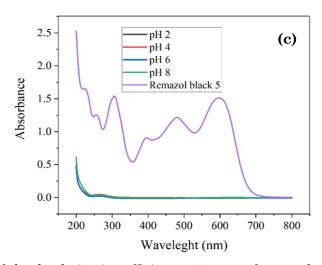


Figure 8. (a) Relation between pH and percentage of the decolorization efficiency 100 ppm of remazol black 5 dye. Insert picture: remazol black 5 dye degradation that is caused by various pH in graphite and graphite/NiO/Ni, (b) the absorbance spectra of the graphite electrode, (c) the absorbance spectra of the graphite/NiO/Ni electrode.

with other chlorides, forming trichloride or hypochlorous acid, and chloride ions [37]. As a result of this incident, not all of the chlorine formed degraded remazol black 5, so the decolorization efficiency of pH 2 was lower than pH 6 even though it had a higher E° Cl2 than E° ClO-. At pH 6 the main active chlorine is HOCl. HOCl is not affected by gas desorption at the anode, so the decolorization efficiency of remazol black 5 dye was higher than pH 2. In addition, the decolorization efficiency of graphite/NiO/Ni electrode was higher than graphite, because there were NiO and Ni deposited on graphite, as shown in Figures 2 to 5. NiO and Ni acted as electrocatalysts that could accelerate the electro-oxidation reaction of remazol black 5. The results of a similar study stated that pH 5.49 was the best for the electrooxidation of textile waste which used Ti/RuO₂ anodes [17] and pH 4 was the best for degrading 96% reactive blue 109 (1000 mg/L) with Pt anode electrode at current (I) 20 mA/cm², 0.1 M NaCl [19].

Figures 8(b) and 8(c) show the spectra of remazol black 5 before and after electrooxidation. The spectra of remazol black 5 before electro-oxidation showed six bands, namely 595, 558, 391, 310, 254, and 229 nm. Two are in the visible region (595 and 558 nm) and the others are in the ultraviolet region (229, 254, 310, and 391 nm). Previous research stated that remazol black 5 spectra showed 5 spectra bands, namely one in the visible region (595) nm) and others in the ultraviolet region (229, 254, 310, and 391 nm) [3]. The peak at 595 nm is the characteristic of the chromophoric azo group (-N=N-), while the peaks at 254 and 310 nm are associated with benzene and naphthalene rings [3,37]. Figure 8 shows all the decreasing peaks during the electro-oxidation process. The decreasing peak at 595 nm indicated that the chomophoric azo group could be easily electro-oxidized. On the other hand, the decrease in absorbance in the UV region was lower, because the aromatic structure was more stable than the chromophoric azo group. The decrease in absorbance spectra for graphite/NiO/Ni electrodes (Figure 8(a)) is greater than that for graphite electrodes (Figure 8(b)); this is caused by the NiO/Ni electrocatalyst. The NiO/Ni electrocatalyst has improved the performance of graphite electrodes in the remazol black 5 dye electro-oxidation process. Remazol black 5 dye electrodes may lead to the formation of intermediates. This intermediate accelerates the decrease in absorbance at 595 nm

by removing the chromophoric azo group before the aliphatic carboxylic acid and carbon dioxide are formed [38].

4. Conclusion

NiO/Ni electrocatalyst has been successfully deposited on graphite electrodes by electrodeposition. NiO/Ni electrocatalyst has improved the performance of graphite electrodes in remazol black 5 electro-oxidation. The best NaCl concentration for remazol black 5 electrooxidation was 0.05 M for graphite/NiO/Ni and 0.1 M for graphite with 100% and 99.81% decolorization efficiency, respectively. The best time for remazol black 5 electro-oxidation was minutes for graphite/NiO/Ni and 60 minutes for graphite with 100% and 99.74% decolorization efficiency, respectively. While, the best pH for the remazol black 5 electrooxidation was pH 6 for graphite/NiO/Ni and pH 2 for graphite with 99.74% and 91.03% decolorefficiency, ization respectively. ite/NiO/Ni electrodes have good prospects to be developed as electrodes to degrade textile waste.

Acknowledgment

This research was supported by the Directorate General of Resources for Science, Technology, and Higher Education under the Ministry of Research and Higher Education through the BPPNDN S3 scholarship; Chemistry Department, FMIPA Universitas Gadjah Mada; and Chemistry Department, FMIPA Universitas Pendidikan Ganesha.

References

- [1] Kenova, T.A., Kornienko, G.V., Golubtsova, O.A., Kornienko, V.L., Maksimov, N.G. (2018). Electrochemical Degradation of Mordant Blue 13 Azo Dye Using Boron Doped Diamond and Dimensionally Stable Anodes: Influence of Experimental Parameters and Water Matrix. Environmental Science and Pollution Research, 25(30), 30425–30440. DOI: 10.1007/s11356-018-2977-z.
- [2] El-Kacemi, S., Zazou, H., Oturan, N., Dietze, M., Hamdani, M., Es-Souni, M., Oturan, M.A. (2017). Nanostructured ZnO-TiO2 Thin Film Oxide as Anode Material in Electrooxidation of Organic Pollutants. Application to The Removal of Dye Amido Black 10B from Water. Environmental Science and Pollution Research, 24(2), 1442-1449. DOI: 10.1007/s11356-016-7920-6.

- [3] Droguett, T., Gomes, J.M., Gabaldon, M.G., Ortega, E., Mestre, S., Cifuentes, G., Herranz, V.P. (2020). Electrochemical Degradation of Reactive Black 5 Using Two-different Reactor Configuration. Scientific Reports, 10(1), 1–11. DOI: 10.1038/s41598-020-61501-5.
- [4] Rahmadyanti, E., Febriyanti, C.P. (2020). Feasibility of Constructed Wetland Using Coagulation Flocculation Technology in Batik Wastewater Treatment. *Journal of Ecological Engineering*, 21(6), 67–77. DOI: 10.12911/22998993/123253.
- [5] Joe, J., Kothari, R.K., Raval, C.M., Kothari, C.R. (2011). Decolorization of Textile Dye Remazol Black B by Pseudomonas Aeruginosa CR-25 Isolated from The Common Effluent Treatment Plant. Journal of Bioremediation & Biodegradation, 02(02), 2-6. DOI: 10.4172/2155-6199.1000118.
- [6] Sulistiyo, Y.A., Andriana, N., Piluharto, B., Zulfikar, Z. (2017). Silica Gels from Coal Fly Ash as Methylene Blue Adsorbent: Isotherm and Kinetic Studies. Bulletin of Chemical Reaction Engineering & Catalysis, 12(2), 263– 272. DOI: 10.9767/bcrec.12.2.766.263-272.
- [7] Yusbarina, Y., Roto, R., Triyana, K. (2021). Hydroxyl Functionalized Graphene As a Superior Anode Material for Electrochemical Oxidation of Methylene Blue. Rasayan Journal of Chemistry, 14(2), 1140-1147. DOI: 10.31788/rjc.2021.1426180.
- [8] Kaur, P., Sangal, V.K., Kushwaha, J.P. (2015). Modeling and Evaluation of Electro-Oxidation of Dye Wastewater Using Artificial Neural Networks. Royal Society of Chemistry Advances, 5(44), 34663–34671. DOI: 10.1039/c4ra14160a.
- [9] Jager, D., Kupka, D., Vaclavikova, M., Ivanicova, L., Gallios, G. (2018). Degradation of Reactive Black 5 by Electrochemical Oxidation. *Chemosphere*, 190, 405–416. DOI: 10.1016/j.chemosphere.2017.09.126.
- [10] Migliorini, F.L., Steter, J.R., Rocha, R.S., Lanza, M.R.V., Baldan M.R., Ferreira, N.G. (2016). Efficiency Study and Mechanistic Aspects in The Brilliant Green Dye Degradation Using BDD/Ti Electrodes. *Diamond & Related Materials*, 65, 5–12. DOI: 10.1016/j.diamond.2015.12.013.
- [11] Brillas, E., Martínez-Huitle, C.A. (2015). Decontamination of Wastewaters Containing Synthetic Organic Dyes by Electrochemical Methods. An Updated Review. *Applied Catalysis B: Environmental*, 166–167, 603–643. DOI: 10.1016/j.apcatb.2014.11.016.

- [12] Sirés, I., Brillas, E., Oturan, M.A., Rodrigo, M.A., Panizza, M. (2014). Electrochemical Advanced Oxidation Processes: Today and Tomorrow. A Review. *Environmental Science* and Polluttion Research, 21(14), 8336–8367. DOI: 10.1007/s11356-014-2783-1.
- [13] Martínez-Huitle, C.A., Dos Santos, E.V., De Araújo, D.M., Panizza, M. (2012). Applicability of Diamond Electrode/Anode to The Electrochemical Treatment of a Real Textile Effluent. Journal of Electroanalytical Chemistry, 674, 103-107. DOI: 10.1016/j.jelechem.2012.02.005.
- [14] Särkkä, H., Bhatnagar, A., Sillanpää, M. (2015). Recent Developments of Electrooxidation in Water Treatment. A Review. *Journal of Electroanalytical Chemistry*, 754, 46–56. DOI: 10.1016/j.jelechem.2015.06.016.
- [15] Moreira, F.C., Boaventura, R.A.R., Brillas, E., Vilar, V.J.P. (2017). Electrochemical Advanced Oxidation Processes: A Review on Their Application to Synthetic and Real Wastewaters. Applied Catalysis B: Environmental, 202, 217-261. DOI: 10.1016/j.apcatb.2016.08.037.
- [16] Oturan, M.A., Aaron, J.J. (2014). Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review. Critical Reviews in Environmental Science and Technology, 44(23), 2577–2641. DOI: 10.1080/10643389.2013.829765.
- [17] Kaur, P., Kushwaha, J.P., Sangal, V.K. (2017). Evaluation and Disposability Study of Actual Textile Wastewater Treatment by Electro-oxidation Method Using Ti/RuO2 Anode. Process Safety and Environmental Protection, 111, 13-22. DOI: 10.1016/j.psep.2017.06.004.
- [18] Peleyeju, M.G., Umukoro, E.H., Babalola, J.O., Arotiba, O.A. (2015). Electrochemical Degradation of an Anthraquinonic Dye on an Expanded Graphite-Diamond Composite Electrode. *Electrocatalysis*, 7(2), 132-139. DOI: 10.1007/s12678-015-0291-9
- [19] Nordin, N., Amir, S.F.M., Riyanto, Othman, M.R. (2013). Textile Industries Wastewater Treatment by Electrochemical Oxidation Technique Using Metal Plate. *International Journal of Electrochemical Science*, 8(9), 11403–11415.
- [20] Alaoui, A., El Kacemi, K., El Ass, K., Kitane, S., El Bouzidi, S. (2015). Activity of Pt/MnO2 Electrode in The Electrochemical Degradation of Methylene Blue in Aqueous Solution. Separation and Purification Technology, 154, 281–289. DOI: 10.1016/j.seppur.2015.09.049.

- [21] Shestakova, M., Sillanpää, M. (2017). Electrode Materials Used for Electrochemical Oxidation of Organic Compounds in Wastewater. Reviews in Environmental Science and Biotechnology, 16(2), 223–238. DOI: 10.1007/s11157-017-9426-1.
- [22] Nidheesh, P.V., Gandhimathi, R. (2014). Removal of Rhodamine B from Aqueous Solution Using Graphite-graphite Electro-Fenton System. Desalination and Water Treatment, 52, 1 0 1 2, 1 8 7 2 1 8 7 7. D O I: 10.1080/19443994.2013.790321.
- [23] Basharat, F., Rana, U.A., Shahid, M., Serwar, M. (2015). Heat Treatment of Electrodeposited NiO Films for Improved Catalytic Water Oxidation. RSC Advances, 5(105), 86713– 86722. DOI: 10.1039/c5ra17041a.
- [24] Dar, F.I., Moonooswamy, K.R., Es-Souni, M. (2013). Morphology and Property Control of NiO Nanostructures for Supercapacitor Applications. *Nanoscale Research Letters*, 8(1), 1–7. DOI: 10.1186/1556-276X-8-363.
- [25] Döner, A., Telli, E., Kardaş, G. (2012). Electrocatalysis of Ni-Promoted Cd Coated Graphite Toward Methanol Oxidation in Alkaline Medium. *Journal of Power Sources*, 205, 71–79. DOI: 10.1016/j.jpowsour.2012.01.020.
- [26] Zhang, J., Zhang, D., Liu, Y. (2019). Ni-SiO2 Nanoporous Composite as an Efficient Electrocatalyst for the Electrooxidation of Hydrogen Peroxide. *Journal of Materials Science: Materials in Electronic*, 30(15), 13895–13909. DOI: 10.1007/s10854-019-01707-0.
- [27] Mukimin, A., Vistanty, H., Zen, N. (2015). Oxidation of Textile Wastewater Using Cylinder Ti/β-PbO₂ Electrode in Electrocatalytic Tube Reactor. Chemical Engineering Journal, 259, 430–437. DOI: 10.1016/j.cej.2014.08.020.
- [28] Popova, A.N. (2017). Crystallographic Analysis of Graphite by X-Ray Diffraction. Coke and Chemistry, 60(9), 361–365. DOI: 10.3103/S1068364X17090058.
- [29] Fan, M., Ren, B., Yang, X., Yu, H., Wang, L. (2019). NiO@NiO and NiO@Co₃O₄ Hollow Core/Shell Composites for High-Performance Supercapacitor Electrodes. *Journal of Nanoscience and Nanotechnology*, 19(12), 7785–7789. DOI: 10.1166/jnn.2019.16857.
- [30] Rebelo, Q.H.F., Ferreira, C.S., Santos, P.L., Bonacin, J.A., Passos, R.R., Pocrifka, L.A., Paula, M.M.S. (2019). Synthesis and Characterization of a Nanocomposite NiO/SiO₂ from a Sustainable Source of SiO₂. *Particulate Science and Technology*, 37(8), 907–911. DOI: 10.1080/02726351.2018.1455781.

- [31] Azaceta, E., Chavhan, S., Rossi, P., Paderi, M., Fantini, S., Ungureanu, M., Miguel, O., Grande, H.J., Tena-Zaera, R. (2012). NiO Cathodic Electrochemical Deposition from an Aprotic Ionic Liquid: Building Metal Oxide N-P Heterojunctions. *Electrochimica Acta*, 71, 39–43. DOI: 10.1016/j.electacta.2012.03.093.
- [32] Kariyajjanavar, P., Jogttappa, N., Nayaka, Y.A. (2011). Studies on Degradation of Reactive Textile Dyes Solution by Electrochemical Method. *Journal of Hazardous Materials*, 1 9 0 (1-3), 9 5 2 9 6 1. D O I: 10.1016/j.jhazmat.2011.04.032.
- [33] Hajji, M., Baddouh, A., Rghuiti, M., Jbara, O., Tara, A., Bazzi, L., Benlhachemi, A., Hilali, M. (2015). Electrochemical Degradation of Some Organic Dyes by Electrochemical Oxidation on a Ti/Cu₂O Electrode. Applied Journal of Environmental Engineering Science, 1(1), 1–8. DOI: 10.5004/dwt.2011.1926
- [34] Patel, P.S., Bandre, N., Saraf, A., Ruparelia, J.P. (2013). Electro-Catalytic Materials (Electrode Materials) in Electrochemical Wastewater Treatment. $Procedia\ Engineerin\ g\ , \quad 5\ 1\ , \quad 4\ 3\ 0\ 4\ 3\ 5\ . \quad D\ O\ I\ : 10.1016/j.proeng.2013.01.060.$
- [35] Nidheesh, P.V., Zhou, M., Oturan, M.A. (2018). An overview on The Removal of Synthetic Dyes from Water by Electrochemical Advanced Oxidation Processes. *Chemosphere*, 1 9 7 , 2 1 0 2 2 7 . D O I : 10.1016/j.chemosphere.2017.12.195.
- [36] Morsi, M.S., Al-Sarawy, A.A., Shehab El-Dein, W.A. (2011). Electrochemical Degradation of Some Organic Dyes by Electrochemical Oxidation on a Pb/PbO2 Electrode. *Desalination and Water Treatment*, 26, 301–308. DOI: 10/5004/dwt.2011.1926.
- [37] Gautam, R.K., Chattopadhyaya, M.C. (2016). Advanced Nanomaterials for Wastewater Remediation. Publisher: CRC Press. DOI: 10.1201/9781315368108-4
- [38] Rivera, M., Pazos, M., Sanromán, M.Á. (2011). Development of an Electrochemical Cell for The Removal of Reactive Black 5. *Desalination*, 274 (1-3), 39–43. DOI: 10.1016/j.desal.2011.01.074.