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Preparation of Polyaniline/Polypyrrole Thin Films as Electrode in Salt Water Dechlorination

Maryanti, Yusmaniar*

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Jakarta,
Jl. Rawamangun Muka, Jakarta 13220, Indonesia

**Corresponding author:* yusmaniar@unj.ac.id

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Abstract

Chlorine is a chemical element that is widely used in daily life that require for dechlorination process to prevent the environment. One method that can be used to treat chlorine waste is through dechlorination. During the dechlorination process, electrodes that chemically stable properties are used. This study aims to test the dechlorination of polyaniline (PANI), polypyrrole (PPy), and various compositions of PANI/PPy composite. FTIR shows related functional groups found in PANI, PPy, and PANI/PPy. XRD shows that the PANI formed was in the semicrystalline phase, while PPy was in the amorphous phase. The conductivity test shows that the PANI sample has the highest conductancy value compared to the PPy or PANI/PPy samples. PANI/PPy with composition ratio of 75/25 had the highest difference in conductance values compared to other composites. The highest dechlorination efficiency value occurred in PANI at a voltage of 1.8 V, which was 1.9%. Meanwhile, in PANI/PPy composite, the highest dechlorination efficiency value came from PANI/PPy 75/25, which was 0.97%.

Keywords: Polyaniline/polypyrrole, oxidative polymerization, dechlorination, conductive polymer

1. Introduction

Chlorine (Cl_2) is one of the rare elements found in free form. Generally, this element is found in the form of bonding to other elements or compounds, forming NaCl salts or chloride ions in seawater. In daily life, chlorine is widely used for disinfectants in bottled water, hydrant tests, and active ingredients in bleach products. Although there are many benefits, the use of chlorine can cause problems due to the waste of chlorine. Incorrect handling of waste such as dumping it directly into the environment without being processed before can give bad impact on ecosystem damage [1]. One solution to overcome the chlorine waste is dechlorination method.

Dechlorination is a method of removing chlorine residues. Electrochemical chlorination technology is called electrocatalytic dehydrohalogenation (ECH). This innovative technology is one of the most prospective because it has many features, such as high efficiency, relatively affordable equipment, harmless reaction conditions, and easy to operate. In the ECH process, the role of electrodes is very important [2]. It takes electrodes that have high conductivity, are good capabilities in storing and releasing electrons slowly, and have a stable chemical structure [3].

Generally, carbon is used as an electrode in the dechlorination process because of its effectiveness in removing chlorine. However, the use of this material is still too expensive to replicate [4]. An alternative material that can be used as an electrode is a conductive polymer. The use of conductive polymers for dechlorination has advantages because of its high conductivity, transparency, affordable price, and easy to synthesize. In addition, in conductive polymers there is a process of charging and discharging. The exchange of ions between polymers and electrolytes known as electrochemically switched ion exchange (ESIE). Ion exchange in conductive polymers occurs not only on the surface, but absorbs up to the electrode [5][6].

Moreover, polyaniline (PANI) and polypirol (PPy) are conductive polymers that have several advantages. PANI has an affordable price, low density, electrical conductivity that can reach 103 S/cm, stable chemical structure, and is easy to synthesize [7]; While PPy can be processed with reaction materials as surfactants to modify its chemical, physical, and even electrical properties. In addition, the properties of PPy surfaces, such as their wetness and charge density can be easily controlled [8]. The manufacture of PANI/PPy composites is expected to improve the physical and chemical properties of pure PANI or PPy, so that these composites can serve as better electrodes in the process of water dechlorination. Based on that background, this study aims to synthesize PANI, PPy, and PANI/PPy films with oxidative polymerization methods as electrodes for the purpose of water dechlorination.

2. Materials and Methods

2.1 Materials

The tools used in the study were eDAQ potentiostat, FTIR spectroscope, XRD, Ag/AgCl as reference electrodes, and Pt as auxiliary electrodes. While the materials used in this experiment are aniline, pyrrole, amonium peroxydisulfate (APS), HCl, NaCl, and aquadest.

2.2 Polyanilin Synthesis

In this study, polyanilin was made through oxidative polymerization using APS oxidants. PANI synthesis is done by mixing 0.92 mL of aniline with 2.5 mL HCl 2 M and a aquadest up to a total volume of 25 mL. Then, the solution is stirred for 15 minutes. In other chemical glasses, APS solution is made by dissolving 1.7114 g of APS in 2.5 mL HCl 2 M and a aquadest up to a total volume of 25 mL. After that, the APS solution is added to the aniline solution drop by drop. The process of testing APS is followed by constant stirring at a temperature of 0-5 °C. After the addition of APS, the solution is left for 2.5 hours in a cooler. After the polymerization process is complete, the formed PANI is filtered, washed with an aquadest, and dried in a desiccator for 7 days. PANI samples that have been synthesized are then characterized, filmed with a mounting press device, and tested for dechlorination of Cl^- ions.

2.3 Polypirol Synthesis

PPy is synthesized through oxidative polymerization using APS oxidants. PPy synthesis is done by mixing 0.71 mL of pyrrole with 2.5 mL HCl 2 M and a aquadest up to a total volume of 25 mL, then stirred for 15 minutes. In other chemical glasses, APS solution is made by mixing 2.5101 g of APS with 2.5 mL HCl and aquadest up to a total volume of 25 mL. Next, an APS solution is added to the pyrol solution drip by drop. The process of testing APS is followed by constant stirring at a temperature of 0-5 °C. After the addition of APS, the solution is left for 2.5 hours in a cooler. After the polymerization process is complete, the PPy sample is filtered, washed with an aquadest, and dried in a desiccator for 7 days. PPy samples that have been synthesized are then characterized and made into film with a press mounting tool.

2.4 Synthesis of Polyaniline/Polypyrolle Composites from Aniline and Pyrrole Monomers

PANI/PPy composites are made through oxidation polymerization methods. First, 0.46 mL aniline is coupled with 2.5 mL HCl 2 M and a aquadest up to a total volume of 15 mL. The solution is then stirred for 15 minutes. In other chemical glasses a solution is made APS solution by mixing 0.8557 g of APS with 2.5 mL HCl 2 M and a aquadest up to a total volume of 15 mL. Once the aniline is stirred for 15 minutes, add the APS. This procedure is done in waterbath at a temperature of 0-5 °C while stirring.

Next, 0.35 mL of pyrole is added to the PANI solution and stirred for 30 minutes. In a 50 mL chemical glass is made APS solution, by mixing 1.2550 g of APS with 19.65 mL of aquadest. After the stirring for 30 minutes is complete, the APS solution is added to the system while stirring. The solution is then let stand while continuing to stir for 3 minutes. Then the sample is left in a cooler for 2.5 hours, the solution is filtered, and the obtained PANI/PPy composite is washed with an aquadest, then dried in a desiccator for 7 days. Furthermore, variations in PPy concentrations in the manufacture of PANI/PPy composites with ratios (75/25; 50/50; and 25/75) with oxidative polymerization methods.

2.5 Polyaniline/Polypyrrole Composite Film Synthesis

First, weigh 0.5 g of PANI/PPy composite powder. Then the powder is put into a template and pressed for 3 minutes with a pressure of 8 tons. The result will be obtained a PANI/PPy composite film with an average thickness of 0.1 cm and a diameter of 2.5 cm. The same procedure is performed on the filming of polyaniline and polypirol.

2.6 Dechlorination test

Dechlorination measurements were conducted in a three-electrode cell using Pt as electrode counter, Ag/AgCl as reference electrode, and PANI, PPy, and PANI/PPy composites as working electrodes. The voltage were controlled in the range of -0.3 - 0.8 V with a scan rate of 25 mV/s. Conductivity of the solution was measured along the dechlorination process.

2.7 Polyaniline Characterization

The synthesized polyaniline is characterized by FTIR and XRD spectroscopy, respectively to determine the existence of the function group and its crystallinity.

3. Results and Discussions

3.1 FTIR Characterization

Figure 1 shows the FTIR spectrum of PANI, PPy, and PANI/PPy composite films recorded at wavenumber 450-4000 cm$^{-1.}$ All the main peaks of PANI can be seen in Figure 1a. The peak of C-H strain, C=C quinoid ring, C=C benzenoid ring, and N-H group are at wavenumber of 2900 cm^{-1}, 1600 cm^{-1}, 1460 cm^{-1}, and 3450 cm^{-1}. The peak at the wavenumber of 1300 cm^{-1} is characteristic of N-H bending are clearly observed. At wavenumber of 1250 cm^{-1} and 1164 cm^{-1} there are peaks that are characteristic of C=N and C-H bending.

The FTIR PPy spectrum is indicated by Figure 1b. Peaks at wavenumber of 3300 cm^{-1} and 1640 cm^{-1} are characteristic of the strains of N-H and C-N in the vibrational plane. The peaks that appear at wavenumber 1540 cm^{-1} and 1460 cm^{-1} are typical locations of C=C and C-N vibration strains in pyrrole rings. The inner-outer vibration bonds of C-H are shown at peaks of 1150 cm^{-1}, 1030 cm^{-1} and 900 cm^{-1} [9][10].

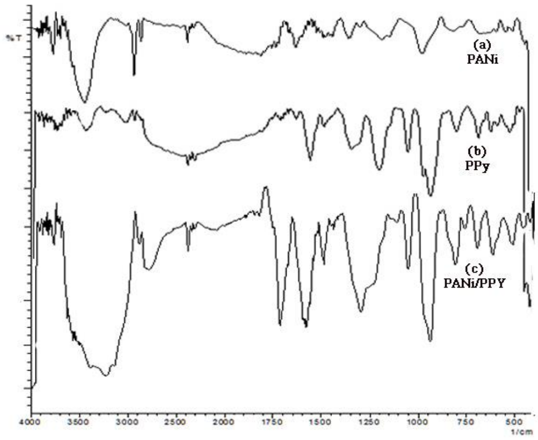

Figure 1. Sample FTIR spectrum (a) PANI, (b) PPy, and (c) PANI/PPy.

The FTIR PANI/PPy spectrum is shown in Figure 1c. There is a slight difference in intensity and the position of the resulting peaks in the composite. Peak shifts occur due to changes in the chemical environment because of the interaction between Ppy and PANI [9]. The absorption peaks at wavenumber 3400 cm^{-1} and 2900 cm^{-1} are suggested as N-H strains polypyrrole and polyaniline. In addition, peak shifts are due to interactions between π bonds in the aromatic rings of polyaniline and polypyrrole [10].

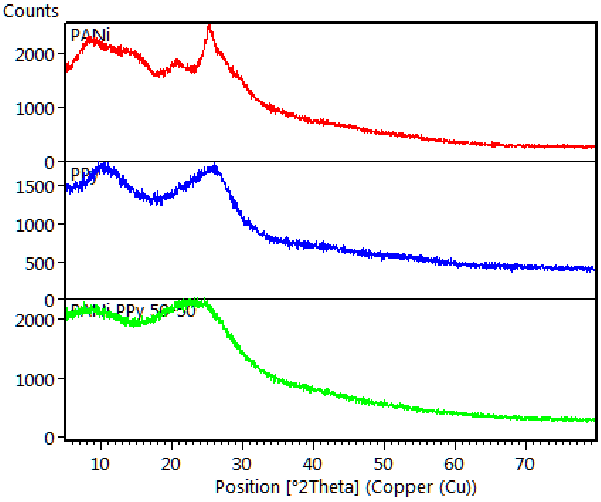

Figure 2. XRD PANI, PPy , and PANI/PPy diffraction patterns.

3.2 XRD Characterization

The XRD characterization results of the PANI, PPy, and PANI/PPy samples are shown by Figure 2. On a PANI difractogram, the appearance of peaks at the positions 2θ 8.35° and 25.2° indicates emeraldine salt polyaniline [11][12]. In the PANI diffraction pattern there is also a rather sharp peak of 2θ, indicating that the phase is semicrystalline. PANI has a crystal lattice field (131) with an overall crystalline form that is monoclinic. While in the pattern of diffraction PPy there is a peak that is in the range of 2θ 10.3° and 25.8°. The peak that hit indicates that PPy is amorphous. The appearance of a peak of 25° in PPy due to the partial interaction of π-π* bonds of the PPy chain. The PANI/PPy diffraction pattern produces a sloping and wide peak. In addition, the peak of 2θ of PANI in the PANI/PPy sample decreased in intensity. This is due to hierarchical superstructures play as impurities to inhibit the growth of PANI crystals and cause more PPy chains to form in PANI/PPy composites [13][11][14].

3.3 Dechlorination Test

Conductance measurements are performed to determine the performance of the sample in the dechlorination process. Anodic oxidation reactions between Cl$^-$ ions and water that take place during the test process follow the following reaction equations [15]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad (2)$$

$$HClO \rightarrow H^+ + ClO^- \quad (3)$$

$$6HClO + 3H_2The \rightarrow 2ClO_3^- + 4Cl^- + 12Cl^- + \frac{3}{2} O_2 + 6e^- \quad (4)$$

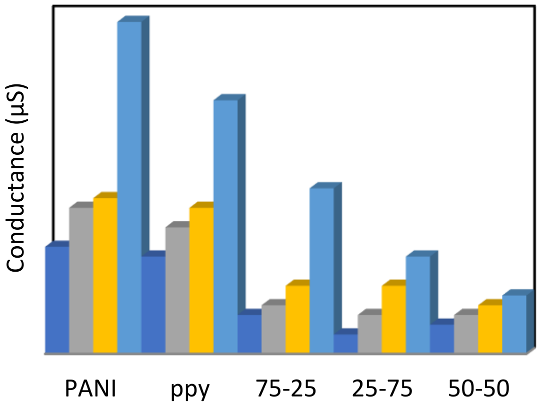

Figure 3. Graph comparison of the difference in conductance values on each voltage variation.

The difference in conductance value in the PANI sample when fed voltage 0.5 V by 11 µS and when fed voltage 1.8 V by 34 µS. The increase in conductance values is due to when the voltage is flowed to the sample, the concentration of the Cl^- ions on the surface of the anode has gradually increased due to the movement of the Cl^- ions to the anode [16].

The data showed that PANI conductance values were higher than PPy and PANI/PPy. Among PANI/PPy composite variations, the composite conductance value with a concentration ratio of 75/25 is higher than composite with a concentration ratio of 25/75. As the voltage increases, the conductance value of all samples also increases, which suggests that its dechlorination efficiency is getting better. This result is indicated by Figure 4.

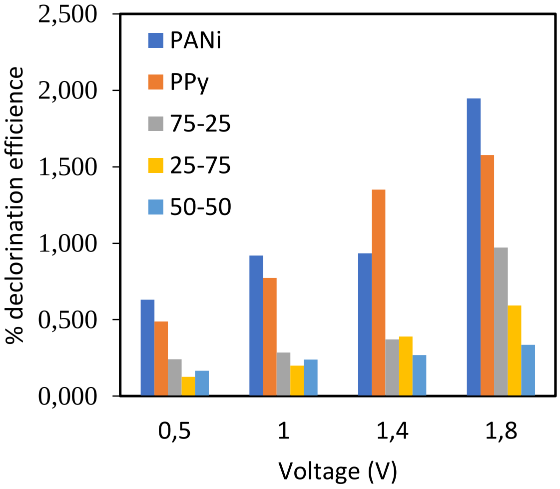

Figure 4. The chlorination efficiency values of PANI, PPy , and PANI/PPy at varying voltages.

The high conductance difference value in PANI at a voltage of 1.8 V is directly proportional to the percentage of chlorination efficiency shown in Figure 4. In addition, the chlorination efficiency of the PANI/PPy 75/25 composite tends to be higher than other PANI/PPy composites, suggesting that the best PANI/PPy composites for the dechlorination process successfully synthesized in this study came from PANI/PPy 75/25. From these results, the dependence value of PANI is 1.94% and the PANI/PPy 75/25 composite is 0.97%.

4. Conclusion

Semicrystalline phase of PANI, amorphous PPy, and PANI/PPy composites were successfully synthesized through oxidative polymerization techniques. The PANI sample had the highest value compared to PPy or PANI/Ppy sample. Among the PANI/Ppy composites, PANI/PPy with a composition of 75/25 had the highest difference in conductance value compared to other composites. The increase of conductance could enhance the efficiency of chlorination. The highest chlorination efficiency values occurs in PANI at a voltage of 1.8 V, which is 1.9%. While in the PANI/Ppy composie, the The highest chlorination efficiency value comes from PANI/Ppy 75/25, which is 0.97%.

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