High photoelectrocatalytic activity of selenium (Se) doped TiO$_2$/Ti electrode for degradation of reactive orange 84

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Abstract. Studies on the synthesis of TiO$_2$/Ti doped Se electrode to degrade reactive orange 84 (RO 84) compounds under UV-Visible irradiation have been successfully carried out. The research objective is to obtain the Se-TiO$_2$/Ti electrodes and test performance in degrading RO 84 under irradiation of UV-Visible light by photoelectrocatalytic. Se-TiO$_2$/Ti electrode were prepared by anodizing and dip coating methods. XRD analysis of TiO$_2$/Ti electrode showed the formation of anatase crystals. The surface morphology of the electrode showed the nanotube structure while the composition of the elements in the electrodes was determined by EDX and the presence of selenium was detected at 0.80%. The characteristics of using Linear Sweep Voltammetry (LSV) show that TiO$_2$/Ti electrodes are active in UV light, while Se-TiO$_2$/Ti electrodes are active in visible light. Electrode activity test in degrading RO 84 showed that the Se-TiO$_2$/Ti photoelectrocatalysis performance with variations in UV and irradiation of visible light was good in integrating RO 84 with a degradation rate of 98%.

1. Introduction

The textile industry is one of the producers of liquid waste, the rest of the coloring process. The handling of textile waste becomes very complicated because the types of dyes used are very diverse and do not consist of one type of dye$^{[1–3]}$. One of the dyes used is reactive orange 84. Reactive orange 84 (RO 84) is a dye derived from the azo class which is soluble in water with the molecular formula $C_{58}H_{38}Cl_2N_{14}O_{26}S_8$ containing chromophore groups$^{[4–7]}$.

Efforts to deal with conventional textile waste have been carried out, but the results are less effective. An alternative method that is more effective and being developed is the photodegradation method using photocatalyst semiconductors such as titanium dioxide (TiO$_2$)$^{[8–11]}$. TiO$_2$ photocatalyst has good properties such as chemical stability in a long period of time, environmentally friendly, has fairly large bandgap energy that is 3.2 eV and has absorption in the UV light region$^{[12–15]}$. However, sunlight reaching the earth only contains 5-7% of UV light, so it needs to be modified from TiO$_2$ to have active absorption in the wavelength region of visible light$^{[16–19]}$.

The doping method is a method of modifying TiO$_2$ which is done by adding another element (dopant) into the TiO$_2$ crystal lattice. Nonmetallic elements are effectively used as doping such as chalcogenic groups have been reported$^{[20–22]}$. The elements classified as chalcogenic are oxygen (O), sulfur (S), selenium (Se), tellurium (Te), vanadium and polonium (Po)$^{[23–25]}$. In this study we are interested in using Se doping as the TiO$_2$ photooxidation doping material to degrade organic pollutants under visible light. Based on the literature that has been described, the research of Selenium doped TiO$_2$/Ti composite (Se-TiO$_2$/Ti) applied in photoelectrocatalytic cells is still underdeveloped, so we study the synthesis of Se-TiO$_2$/Ti electrodes and its application for degradation of RO 84.
2. Experimental Methods
The implementation of this research was carried out in several stages, namely Ti plate preparation (titanium) by growing the TiO$_2$ thin layer on Ti plate by anodizing method[26,27]. The manufacture of Se-TiO$_2$/Ti sol-gel by the sol-gel method which is coated on Ti plates which have been overgrown with TiO$_2$ layers on the surface by dip-coating nanoparticle growth method[28]. The characteristics of Te-TiO$_2$/Ti electrodes with instruments such as XRD (X-Ray Diffractometer), SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-Ray), Fourier Transform Infrared Spectroscopy (FTIR), LSV (Linear Sweep Voltammetry), and Degradation of the reactive orange 84 test using a photoelectrocatalysis Multi Pulse Amperometry (MPA).

3. Results and Discussion

3.1. XRD characterization
Characterization using XRD was carried out to see the structure and size of TiO$_2$ crystal solids formed. Figure 1 shows diffraction patterns in which the spectrum at the peak of 2θ 39.57º (111) and 57.53º (112) shows the anatase peak, which corresponds to (JCPDS No. 21-1272). The diffractogram data is in accordance with the research that has been done [29–31] and provides information that the fabrication of TiO$_2$ on the surface of the Ti plate has been successfully carried out.

![Diffractogram XRD of TiO$_2$/Ti plate](image)

**Figure 1.** Diffractogram XRD of TiO$_2$/Ti plate

3.2. FTIR characterization
Figure 2 shows some of the bonds formed, namely Ti-O, Se-O, O-H. At wave number 3379 cm$^{-1}$ indicates the presence of O-H stretching (strong vibration) with a strong signal. The presence of O-H groups is thought to originate from the titanil group as the terminal Ti-OH from the crystalline phase of TiO$_2$ or from water absorbed on the surface. In the wave absorption of 400-1250 cm$^{-1}$ Ti-O bonds are formed with the peak of absorption in the region of 1085 cm$^{-1}$. The appearance of absorption at the peak of 447 cm$^{-1}$ indicates the presence of Se-O. This spectra matches what has been reported [28]
3.3. SEM-EDX Characterization

Figure 3A shows SEM data on the surface of the Se-TiO$_2$ electrode showing the shape of the crystals scattered on the surface of the electrode indicating the attachment of selenium sol-gel to the surface of the TiO$_2$/Ti electrode. The electrodes contain the desired three elements namely titanium, oxygen and selenium. The peaks indicate the presence of titanium at the energy levels of 0.4 and 4.5 KeV, while the existence of the element selenium at the peaks of 1.4 and 11.2 KeV. The appearance of the Se peak is an indication of the presence of the selenium element on the TiO$_2$/Ti electrodes from the results of the preparation which indicates the success of Se doping by the sol-gel method. The composition of the constituent elements Se-TiO$_2$/Ti electrodes can be seen in Figure 3B.

3.4. Electrode Activity Test Using Linear Sweep Voltametry (LSV)

The photoelectrolysis performance test uses the LSV technique, where the working electrodes of TiO$_2$/Ti and Se-TiO$_2$/Ti counter electrodes Pt and the Ag/AgCl reference electrodes are dipped in a 0.1 M NaNO$_3$ electrolyte solution and then connected to a Portable potentiostat. By using a potential of -1 Volt to 1 Volt to see the oxidation current in the electrolyte solution. Then the scan rate is set at 0.1 V/s to regulate the speed of movement of ions towards the surface of the electrode[32,33]. The voltamogram produced can be seen in Figure 4.
Figure 4. Voltammogram LSV (A) TiO$_2$/Ti electrode (B) Se-TiO$_2$/Ti electrode

Figure 4A shows the LSV TiO$_2$/Ti electrodes produced have the highest activity when irradiated by UV light irradiation. This is consistent with the theory that TiO$_2$ has photoelectrocatalysis activity when irradiated by UV lamps. LSV voltamograms using Se-TiO$_2$ electrodes give good response when irradiated by Visible lamps as shown in Figure 4B. Irradiation using visible light has a good activity compared to when irradiating UV lamps. This is due to the addition of selenium on the surface of TiO$_2$/Ti which can shift the conduction band. Se-TiO$_2$ electrodes can absorb light with greater wavelengths with less energy.

3.5. Photocatalytic degradation test

Figure 5 shows a maximum degradation strength of Se-TiO$_2$/Ti electrodes was obtained at a concentration of 0.5 ppm of 95% under Visible light. The degradation (%) produced for the RO 84 compound under Visible irradiation shown in Figure 6 with the maximum degradation (%) at a concentration of 0.5 ppm of 95%. Modification of TiO$_2$/Ti with selenium dopant can increase the degree of crystallization of the anatase crystal structure on TiO$_2$ itself, besides that it can produce more oxygen so that, it can capture electrons and prevent the recombination of e$^-$ and H$^+$[34–37].

Figure 5. photocatalytic reactive degradation (%) of RO 84 using Se-TiO$_2$/Ti under UV and Visible irradiation
3.6. Photoelectrocatalysis degradation test

Figure 6 shows a decrease in the concentration of the RO 84 compound using Se-TiO$_2$/Ti electrodes in UV and visible light. Se-TiO$_2$/Ti electrodes are able to work actively when illuminated by Visible light. The maximum degradation of Se-TiO$_2$/Ti electrodes to the RO 84 compound under Visible light is shown in Figure 8 with the maximum percent degradation in the 0.5 ppm RO 84 solution by 98%.

![Figure 6. RO 84 degradation (%) using Se-TiO$_2$/Ti by photoelectrocatalysis](image)

4. Conclusion

The surface morphology of the electrodes shows the nanotube structure while the composition of the elements in the electrodes is determined by EDX and the presence of selenium is detected at 0.80%. The characteristics of using LSV show that TiO$_2$/Ti electrodes are active in UV light, while Se-TiO$_2$/Ti electrodes are active in visible light. Se-TiO$_2$/Ti is made using the dip-coating method. Se-TiO$_2$/Ti electrodes by photocatalyst and photoelectrocatalysis are very good in Visible light areas with 95% and 98% degradation, respectively.

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