Photocatalytic Degradation of Organic Waste in Visible light using TiO$_2$ Nanotubes Array

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Abstract. Photocatalytic degradation of organic waste using TiO$_2$ nanotubes array has been investigated. The phenol was used as organic waste in this research. The Titania nanotubes were obtained by anodization method with 98% ethylene glycol and 0.5%wt NH$_4$F as electrolyte solution at 50 V for 2 hours. The prepared catalysts were characterized by different techniques such as electron microscopy (SEM), X-Ray diffraction (XRD), Fourier transform infrared (FTIR) and UV-vis reflectance spectroscopy (UV-DRS). The effect of pH and initial concentration of phenol has been evaluated. The results showed that the best pH for degradation phenol was obtained at pH 5. In this condition, the phenol has been reduced from 40 ppm to 6.9 ppm for 180 min.

1. Introduction
Phenol is a representative contaminant in industrial effluents such as wastewaters from steel industries, pharmaceutical industries, plastic and varnish industries, textile units, pesticide plants, textile and pulp, and paper manufacturing plants [1-2]. The presence of Phenol in the environment represents a serious ecological problem due to its toxicity for human life, aquatic life and others [3]. The conventional technologies are used to eliminate phenol from wastewater such as oxidation, adsorption, coagulation and enzyme oxidation [4]. However, these conventional methods could not completely degrade organic pollutants and could produce secondary pollutants [5-6].

The advanced oxidation process (AOPs) may become an interesting alternative to traditional technologies. Among AOPs, heterogeneous photocatalysis with nanoparticles has shown high efficiency in the removal of a wide range of organic contaminants in wastewater [7-11]. Titania oxide is a well-known effective semiconductor photocatalyst due to generates hydroxyl (OH) radicals, which are more powerful than ozone and other advanced oxidation processes (AOPs) used to degrade organic pollutants. Moreover, TiO$_2$ has high photocatalyst activity, chemical stability relatively low-cost and especially non-toxicity [12]. Furthermore, TiO$_2$ has been applied in photocatalysis such as water purification and decomposition of pollutants, hydrogen generation, air purification and also medical applications, such as drug delivery, orthopaedic and dental implants [9,13-15].

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However, photocatalysts in water purification and decomposition of pollutants are often used in a slurry system which needs separation and recovery of catalyst, moreover, it causes damages to the recirculation pumps. This disadvantage is overcome realizing the photocatalysis thin film. One of the photocatalysts in the form of thin films is TiO$_2$ nanotubes arrays (TNTs) which fabricated by anodization method. In recent years TNTs have received considerable attention due to their large surface area, high photocatalytic activity, and convenient recycling when compared with conventional TiO$_2$ powder [16].

The anodization method is a relatively simple process for the synthesis of the TiO$_2$ nanotube arrays due to the easily controlled synthesis parameters. The different structures of the TiO$_2$ nanotube arrays will be synthesized by adjusting anodization time, the composition of electrolyte and anodization voltage [17-18]. The highly ordered TiO$_2$ nanotube array has synthesized by the anodization method in this study. Anodization voltage was adjusted to control the structure of the TiO$_2$ nanotube. The photocatalytic activity of the TiO$_2$ nanotube arrays was examined for phenol degradation.

2. Materials and Method

2.1. Materials.
All chemicals, used in the synthesis were of analytical grade and used as received. Ethylene glycol, HF, HNO$_3$, and phenol were purchased from Sigma-Aldrich.

2.2. Preparation of Titania nanotubes arrays.
The nanotube arrays were synthesized by anodic oxidation of titanium foils (3 cm x 2 cm) with 99.6% purity and 0.3 mm in thickness. Before anodization, the Ti foils were cleaned by water. Afterward, the samples were chemically etched by immersing in a mixture of 3.2 HF and 5.4 HNO$_3$ for 40 s and immediately rinsed with deionized water in a sonicator for 10 s, dried under air and used immediately. The anodization was performed in a two-electrode configuration bath with the Ti foil as the anode and the platinum (Pt) foil as the cathode. We used an electrolyte solution of ethylene glycol with consisting of NH$_4$F (0.5 wt.%) and H$_2$O (2 wt.%) and placed in a beaker glass for 2 h at different potential (20-60 V) and at room temperature using DC power supply (ESCORT 6030SD). After anodization, the obtained nanotube electrodes were rinsed immediately with deionized water and then dried in air. The prepared samples were annealed at 500°C for 3 h.

2.3. Sample Characterization.
The morphology of the synthesized catalyst was examined using scanning electron microscopy (SEM, JEOL 6390 A). The crystal structure was analyzed using X-ray diffraction (XRD, Analytical type EMPYREAN). Element analysis and the chemical bond of the catalyst were examined using Fourier transform infrared spectrophotometer (FT-IR, Shimadzu IR Prestige-21). The bandgap value was analyzed using UV-Vis diffuse reflectance spectra (UV-Vis DRS, Shimadzu type 2450). The amount of phenol degradation was determined using a UV-Vis spectrophotometer (Genesys 10).

2.4. Degradation of Phenol
The degradation of phenol was performed in a photocatalytic reactor with a mercury lamp as a visible light source in atmospheric pressure for 3 h. PHILIPS HPL-N 250 W mercury lamp is used as a photon source placed in a test box with a distance of 3 cm from the catalyst. This lamp is a mixture of 17.25% UV light and 82.75% visible light. The phenol solution as much 250 ml with a different initial concentration (10 ppm, 20 ppm, and 40 ppm) and different pH values (ph 5, no adjust, ph 8) was used in the degradation process. During the irradiation, samples were taken from the irradiated solutions at different time intervals 30 s.
3. Results and Discussion

3.1. Characterization

In order to investigate the effect of potential anodization on the formation of TiO$_2$ nanotubes, samples were prepared using different potential anodization. The structures of the prepared samples were characterized by SEM. The SEM image of TiO$_2$ TNTs at different voltage are shown in figure 1. Figure 1 shows the potential anodization affecting the formation of the nanotubes in the sample. Anodization with a voltage of 30 V has not produced a perfect nanotubes morphology. TiO$_2$ TNTs have been successfully fabricated on the surface of Ti by potential anodization at 50 V as shown in figure 2(c). The diameter and length of TNTs for various potential anodization could be seen in table 1.

![Figure 1. SEM image of top view (1) and crossed section view (2) of TNTs prepared for (a)30V (b)40V (c)50V](image)

Table 1. indicated the greater potential anodization produced TiO$_2$ nanotubes which are the longer and larger diameter. This result indicated that the formation of TiO$_2$ nanotubes can be influenced by a voltage that was used during the anodization process. Lai C. W. and Sreekantan S. (2011) reported the greater the potential of anodization, produced the longer the tube. It is due to the greater the voltage then the driving force of ions to move through the barrier layer on the bottom of the tube becomes larger, resulting in deeper pores and longer tubes [16].

3.1.1. XRD

The XRD patterns of catalyst TNTs uncalcined and calcined at 500°C and with potential anodization showed in figure 2. It shows that without calcination exhibited an amorphous structure. The phase of TNTs at various voltage was identified to be anatase and had crystallinity were almost the same. Anatase peaks were observed at 25.3° and 48°. The peaks at 38°, 40°, 53° and 63° were identified as the main peak of Ti [19].
3.1.2. \textit{FT-IR} and \textit{UV-Vis} DRS

The FTIR images and \textit{UV-Vis} diffuse reflectance spectra for samples are shown in figure 3. Figure 3 (a) shows visible valleys in the FTIR transmittance spectrum at wavenumbers of about 3800 cm$^{-1}$ and 1500 cm$^{-1}$ show the stretching OH bond of the hydroxyl structure attached to Ti (Ti-OH) and OH bending (TNTAs absorb water molecules) [12]. The valleys observed in the wavenumbers 840 and 520 cm$^{-1}$ are Ti-O-Ti stretching bonds of TiO$_2$ crystals.

The UV-Visible diffuse reflectance spectra for samples are shown in figure 3(b). It shows the value of bandgap energy. The TiO$_2$ catalyst with the anatase crystalline phase has a bandgap energy value of 3.2 eV [12]. The test results performed, the average bandgap energy value for the four catalysts of 3.21 eV. With this value, the catalyst will be active at the wavelength of 387 nm which is included in the visible light spectrum (380-700 nm). Sunlight contains 5% UV rays and 45% visible rays.

3.2. \textit{Photocatalytic activity.}

The photodegradation of phenol was conducted to evaluate the TNTs catalyst. The relationship between potential anodization and degradation of phenol was also investigated, as shown in figure 4.
Figure 4. Effect of differential potential anodization on (a) phenol degradation and (b) initial degradation rate of phenol.

Figure 4 shows the results of phenol degradation using TNTs. It was found that TNTs 50V exhibited higher activities than other samples. The initial degradation rate of this TNTs was 0.380 ppm/min. The crystallinity of all samples was almost the same, therefore the result indicated that the morphology of TiO$_2$ plays an important role in phenol degradation. It was primarily attributed to the morphology of the nanotubes. Khan and Yang (2009) reported tubular structure facilitated fast electrons transfer due to reduced grain boundary and was expected to improve charge separation in photocatalytic reactions [20]. Ghicov et al (2009) reported longer nanotube larger specific area and more active sites which are favorable for the oxygen evolution reaction. Therefore it caused light absorption more efficiently [21].

Figure 5. Effect of the initial concentration of phenol on the performance of TNTAs 50V photocatalyst.

The effect of initial concentration at phenol degradation was also observed and can be seen in figure 5. The pH of this examination was 6. The initial concentration of 40 ppm shows the highest percent removal. It shows the increase in the initial concentration of phenol caused a greater percentage of phenol degradation. It was probably due to the higher initial concentration caused by the increasing phenol adsorption on the surface of TiO$_2$. Therefore the phenol was easily degraded.

The effect of pH on the degradation of phenol can be seen in figure 6. This experiment was carried out at an initial concentration of 40 ppm of waste using a 50-volt catalyst. Figure 7 shows the best phenol degradation percentage at pH 5 with a final concentration of 3 hours to 6.9 ppm. Lian Yu (2016) reported that slightly acidic pH a phenol compound can easily dissolve by releasing H$^+$ ions from its hydroxyl group to form C$_6$H$_5$O-phenoxide. This condition will facilitate radical species to attack phenoxide to produce the final product in the form of CO$_2$ and H$_2$O [6].
Figure 6. Effect of pH conditions on the degradation of phenol waste 40 ppm by using TNTAs 50V photocatalyst.

The results of this research could potentially be applied to the industrial scale that produces phenol waste, so that waste products can be safely discharged into the environment. The catalyst synthesis can also produce hydrogen gas which is useful for industrial needs such as the ammonia-making industry and urea fertilizer. The resulting catalyst has a great potential for repeated use because of its easy separation process with degraded wastes.

4. Conclusions
The effect degradation of phenol was influenced by TiO$_2$ morphology, pH and initial concentration of phenol. The longer nanotubes provide better degradation of phenol. The best pH for degradation phenol was obtained at pH 5. In this condition, the phenol has been reduced from 40 ppm to 6.9 ppm for 180 min.

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