

Phenol Removal in Aqueous Solution through Photodegradation using Titanium Dioxide Nanoparticles Assisted with Hydrogen Peroxide

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Abstract—The removal of phenol in aqueous solution through photodegradation was studied using synthesized titanium dioxide (TiO₂) nanoparticle assisted with hydrogen peroxide (H₂O₂). The results show 62.24 % of 100 ppm phenol was removed after 180 minutes reaction using TiO₂ nanoparticles. The addition of H₂O₂ in a treatment system increases the phenol removal up to 95.45 % due to the presence more hydroxyl radicals (•OH) which plays an important role in degrading phenol molecules. TiO₂ nanoparticles was synthesized using sol-gel method and characterized using X-ray Diffraction (XRD), Transmissions Electron Microscopy (TEM), and Energy Dispersive X-ray Spectroscopy (EDX) to study their physical properties. The SEM micrograph shows that the synthesized TiO₂ had small particles size with irregular shape composed of titanium and oxygen elements as proved by EDX. X-ray diffractogram pattern revealed the existence of anatase phase of TiO₂ with high degree of crystallinity which supports the good performance of TiO₂ nanoparticles for phenol removal.

Keywords—phenol; photodegradation; titanium dioxide; nanomaterials; hydrogen peroxide

I. INTRODUCTION

Phenols and their phenolic compounds have been widely used in various applications even though they have been classified as toxic and hazardous pollutant [1]. Phenol is also a matter of concern in the biological stage of wastewater treatment, due to its bio-resistance and toxicity to microbial population [2]. As they have high toxicity and carcinogenic character, they have caused considerable damage and threat to the ecosystem in water bodies and human health. Therefore, an effective and economical treatment for eliminating phenol in water has been an urgent demand. The conventional treatment methods of phenol and cyanide removal from wastewater such as chemical coagulation, electrochemical oxidation, solvent extraction, and membrane separation are not effective and efficient enough since these methods are costly, time consuming and elaborate. Previously, physical adsorption using granular activated carbon (GAC) is very effective and most versatile methods for the elimination of both phenol and cyanide. They have been widely used by

various researchers for waste water treatment [3,4]. However, due to the regeneration problem use of GAC, it is not appropriate for developing countries.

Recently, advanced oxidation process (AOP) via photodegradation using a titanium dioxide photocatalyst has attracted the public concern due to its ability to convert the pollutants into the harmless substances directly in the wastewater. This type of photodegradation is used by some drinking water and wastewater facilities to destroy pollutants. Photodegradation is a degradation of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, such as infrared irradiation, visible light and ultraviolet light. It includes photodissociation, the breakup of molecules into lower molecular weight fragments by photons through oxidation reaction with the presence of photocatalyst [5]. Titanium dioxide (TiO₂) is considered as one of the most promising photocatalyst materials for the effective degradation of a wide range of organic pollutants as well as for destruction of microorganisms in wastewater. This is due to their unique properties, such as phase composition and structure, surface hydroxyl groups and particle size. In addition, its surface defects play a very important role in the activity of this oxide in photocatalytic reactions [6,7]. It is generally accepted that most of the TiO₂ photocatalyst applications are limited to UV-light irradiation because the light absorption edge is at wavelengths shorter than 420 or 380 nm for the rutile and anatase phases, respectively [8].

II. EXPERIMENTAL

A. Preparation

Titanium dioxide nanoparticles were synthesized using sol-gel method by adding 30 mL of titanium tetraisopropoxide (Ti[OCH(CH₃)₂]₄, Aldrich, A.C.S. Reagent) into 5 mL of isopropyl alcohol dropwise. Then 180 mL of distilled water is added into a solution mixture at pH 1.5 (adjusted with HNO₃). The resulting solution was continuously stirred for 10 hours until a transparent colloid was formed. The colloid solution

was concentrated at 60 °C with a rotary evaporator and then calcined at 400 °C for 17 hours in air to yield TiO₂ nanoparticles.

B. Characterizations

The physical properties of the prepared TiO₂ photocatalyst was studied using various methods including X-ray diffraction with Cu-Kα (λ=1.54Å) radiation. Scans were performed in step of 0.2°/second over the range of 2θ from 10 up to 80°. The morphology was observed using TEM (Philips CM12) coupled with EDX analyzer. Nitrogen (N₂) adsorption-desorption isotherm is recorded using Accelerated Surface Area & Porosity (ASAP) 2010. Prior to the N₂ analysis, the samples were degassed at 200°C for 12h under vacuum conditions. IR spectra were analyzed in a PerkinElmer spectrum 400 FT-IR Spectrometer in the range 4000–400 cm⁻¹. Thermal stability study of the sample was done using thermo-gravimetry SDT Q600.

C. Photocatalytic Studies

Synthesized TiO₂ (0.1 g) was suspended in 100 ppm phenol solution (100 mL) by stirring in a 150 mL pyrex bottle. The bottle was illuminated by a UV lamp (6 W and λ=354 nm) for 3 hours. After that, a small quantity of the suspension was withdrawn and filter through a milipore membrane filter (0.2 μm) to remove the photocatalyst particles. Then, the absorbance of phenol at 270 nm in the samples was analyzed using UV-Visible spectrophotometer. The removal of phenol for the each sample was calculated using the expression in Equation 1.0 [9].

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 \quad (1.0)$$

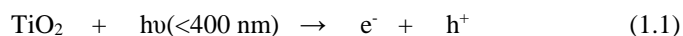
Where η is a percent removal, C₀ the absorbance of the solution at 270 nm wavelength before UV illumination, and C_t is the absorbance of solution at 270 nm wavelength after 3 hours UV illumination. In order to study the present of hydrogen peroxide towards photodegradation and phenol removal, the experiment was repeated with 10 μL of 1M hydrogen peroxide was added into photocatalytic system.

III. RESULTS AND DISCUSSION

Control experiments were conducted to study the stability of phenol solutions towards photolysis (with UV light only) and adsorption (with TiO₂ without UV illumination). It was found that only a minor loss of the phenol (2.41 %) was observed, indicating that phenol is highly stable towards photolysis process (Table 1). Again in non-irradiated suspensions but with the presence of synthesized TiO₂, there was a slight loss of phenol (4.04 %) probably due to adsorption of the substrate onto TiO₂ (Table 1). This can be correlated to the high surface area and acid strength of TiO₂ [10]. On the other hand, in the presence of TiO₂ and irradiated by UV light, a rapid removal

of phenol (62.24 %) occurred through photodegradation process after three hours irradiation (Table 1).

The results indicated that both UV illumination and the TiO₂ photocatalyst were necessary for the photodegradation of the phenol substrates. It was well known that the photodegradation of pollutants in solution is initiated by the formation of an electron-hole pair on the photocatalyst surface when the semiconductor was illuminated with UV light. Illumination of UV light with less than 400 nm wavelength towards TiO₂ generates electrons in the conduction band and leave positive holes in the valence band [11]. The excited electron in the conduction band will react with dissolved oxygen (O₂) in aqueous solution and resulting in the formation of hydroxyl radical (•OH), as shown by a series of reaction below (Equation 1.1 - 1.5) [12].



The •OH radicals are extremely reactive and readily attack phenol molecules and degrading the phenol to CO₂ and H₂O [13]. The production of •OH can be increased with the present of the strong peroxide agent like H₂O₂ through photolysis process (Equation 1.6) [14].



Thus, the addition of H₂O₂ (0.000001 M) in the reaction system increases the photocatalytic degradation with 85.45 % removal of phenol after 180 minutes (Table 1). It was suggested that the function of H₂O₂ in this case is not only as the source of hydroxyl radical (•OH) but also to prevent and reduce the recombination rate of electron and positive hole of the TiO₂ catalyst by the following reaction (Equation 1.7-1.9) [15].

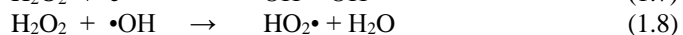


TABLE 1 REMOVAL OF PHENOL USING VARIOUS TREATMENT SYSTEM

Treatment system	Phenol removal (%)
Phenol + UV	2.41
Phenol + TiO ₂	4.04
Phenol + TiO ₂ + UV	62.24
Phenol + TiO ₂ + H ₂ O ₂ + UV	85.45

Photodegradation of phenol was found to increase from 85.45% to 98.20 % as the concentration of H₂O₂ use increased from 0.000001 M to 0.0001 M (Table 2). It is because, when the concentration of H₂O₂ use increase, the number of

hydroxyl radical that can be produce also increase, therefore the rate of photodegradation also will be enhance. Tasseroul *et al.* (2016), in their research also proved that H₂O₂ concentration give significantly effect on the photodegradation of phenol, whereby they stated that through the addition of H₂O₂, a higher OH⁻ concentration and a more effective mineralization can be attained [16]. However, when the concentration of H₂O₂ was increased to 0.001 M and 0.01M, the photodegradation process is decreased with percentage of phenol removal was 88.62 % and 75.20%, respectively. This is attributed to the formation of Ti(O)₂(OH)₂ and Ti(OOH)(OH)₃ complex from the reaction between TiO₂ photocatalyst with the H₂O₂ at higher concentration of H₂O₂ [17]. This complex can hindrance the formation OH radicals which play an important role in photodegradation process, hence decrease the percentage amount of phenol that can be degraded and removed.

TABLE 2: REMOVAL OF PHENOL (%) IN PHENOL + TiO₂ + UV + H₂O₂ TREATMENT SYSTEM AT DIFFERENT CONCENTRATION OF H₂O₂

Concentration of H ₂ O ₂ (M)	Phenol Removal (%)
0.000001	85.45
0.00001	90.60
0.0001	98.20
0.001	88.62
0.01	75.20

In this study, titanium dioxide (TiO₂) nanoparticles was formed by hydrolization of titanium isopropoxide by water in an alkaline medium (Equation 1.10).



After calcination at 400°C for 17 hours, highly crystalline TiO₂ was produced and by-product are completely decomposed and evaporated. X-ray diffraction of TiO₂ was carried out to determine their phase structure. The X-ray diffractogram pattern shows signal with high intensity and sharp peak characteristic of the anatase TiO₂ phase (Fig. 1) [10].

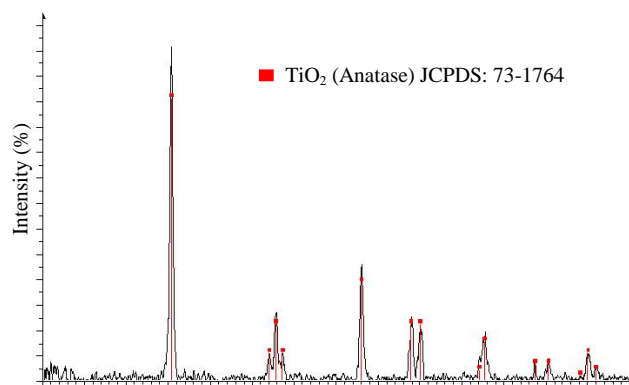


Fig. 1: X-ray diffractogram of synthesized TiO₂ nanoparticles

The existence of anatase phase of TiO₂ contributes to the excellent photocatalytic activity of TiO₂. There are two types of crystal structures in TiO₂ which is the rutile type and the anatase type that has been used a photocatalyst. Both types are expressed using the same chemical formula (TiO₂) however, their crystal structures are different. Apparently, the anatase type exhibits higher photocatalytic activity [18]. One of the reasons for this is the difference in the energy structure between the two types. It is known that the conduction band in the anatase type is closer to the negative position than in the rutile type, therefore, the reducing power of the anatase type is stronger than that of the rutile type. Due to the difference in the position of the conduction band, the anatase type exhibits higher overall photocatalytic activity than the rutile type. Moreover the small size of anatase TiO₂ obtained in this study has contributed to their high photocatalytic activity. The TEM micrograph revealed the particles size of the synthesized TiO₂ is within the range of 30-40 nm with irregular-shaped (Fig. 2) composed of titanium and oxygen elements showed by EDX (Fig. 3).

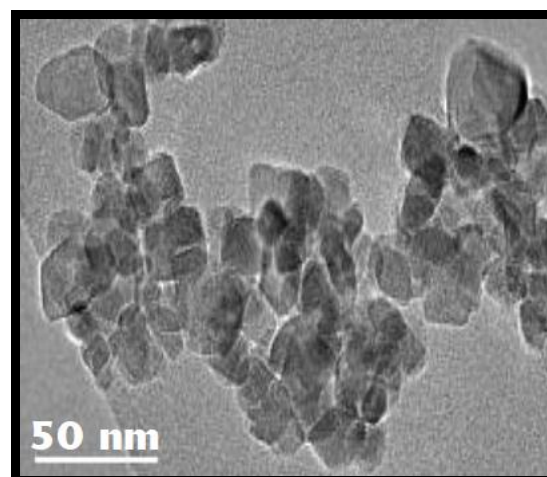


Fig. 2: TEM micrograph of synthesized TiO₂ nanoparticles

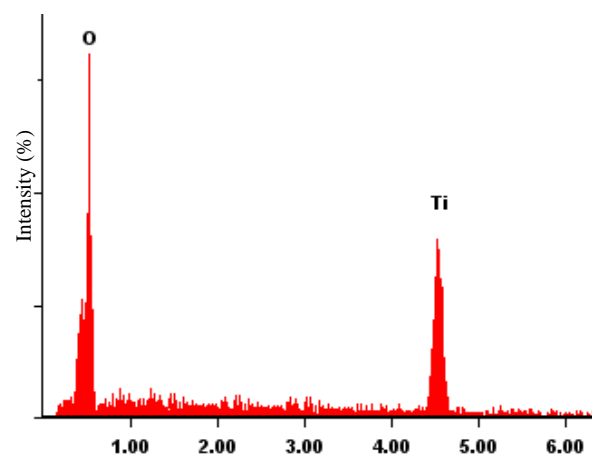


Fig. 3: EDX of synthesized TiO₂ nanoparticles

Fig. 4 show the N₂ adsorption-desorption isotherm plot of synthesized TiO₂ nanoparticles sample. The sample exhibits a typical IV-like isotherm which have one hysteresis loop at relative pressure between 0.6 and 1.0, indicating pore-size distributions in the mesoporous region (2 to 50 nm). The presence of the hysteresis loop is usually associated with the capillary condensation in mesopore structures and classified as type H3 hysteresis according to the IUPAC classification. H3 hysteresis type characteristic for the slit shaped pores. In order to study the thermal stability of the TiO₂ nanoparticles, thermo-gravimetric analysis was carried out. As shown in Fig. 5, the TGA result of TiO₂ nanoparticles showing rapid and large decrease in weight (28%) starting at room temperature till ~100°C. This attributed to the removal of adsorbed water from the TiO₂ nanoparticles surface and decomposition organic residue [19]. Then, 4% weight loss gradually decreased after heating up to 600°C due to the removal of intercalated water molecule such as physisorbed H₂O molecules and chemisorbed H₂O molecules. Subsequently, 12% weight loss in the region of 600 to 700 °C because of the phase structure transformation of anatase TiO₂ into rutile TiO₂ [19]. After 700 °C till maximum temperature studied (900 °C), the thermo-gravimetric curve showed a nearly flat characteristic showing that the material is thermally stable at this temperature.

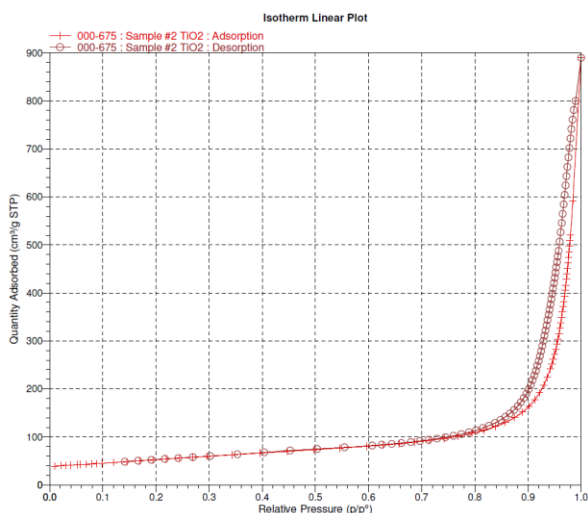


Fig. 4: Isotherms plot of synthesized TiO₂ nanoparticles

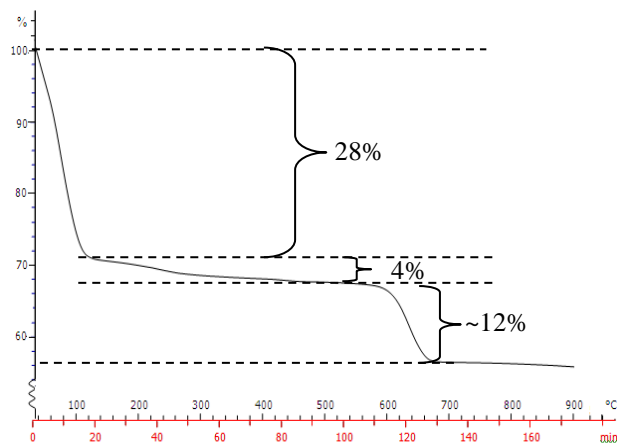


Fig. 5: TGA synthesized TiO₂ nanoparticles

Fig. 6 shows the FTIR spectrum of TiO₂ nanoparticles photocatalyst. Three broad peaks was observed at 3600 to 2800 cm⁻¹, 1700 to 1500 cm⁻¹ and 900 to 400 cm⁻¹ respectively. The first broad peak in the range of 3600-2800 cm⁻¹ is corresponding to the OH stretching mode. On the other hand, the peak at 1700 -1500 cm⁻¹ attributed to the OH deformation mode. The existence of these two broad peaks is due to the presence of water molecule on the surface of TiO₂ photocatalyst since it was used during photocatalyst preparation. Meanwhile, the existence of broad peak with high intensity at ~900 to 400 cm⁻¹ is assigned to M-O (metal oxide) and represents Ti-O-Ti stretching vibrations mode. High intensity of this peak indicated that the sample contains large amount of metal oxide bonding credited to the pure synthesized TiO₂ nanoparticles.

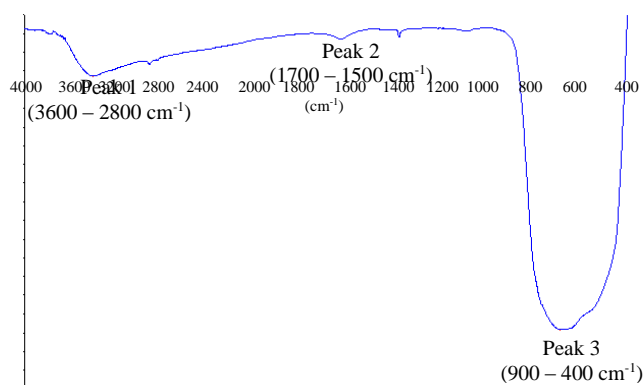


Fig. 6: FTIR spectrum of synthesized TiO₂ nanoparticles

Conclusions

Based on the results obtained, it can be concluded that 62.24% of phenol can be removed through photodegradation process using TiO₂ nanoparticle under UV illumination after 3 hours. The removal of phenol can be increased up to 95.45% with the addition of H₂O₂ at 0.0001 M, due to the presence of

more hydroxyl radicals which can enhanced the photodegradation process initiated by TiO₂ nanoparticles. In this study, TiO₂ nanoparticles was synthesized by sol-gel process involves hydrolysis and condensation reactions of titanium isopropoxide alkoxides.

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