



Research Article

Degradation of Phenol in Pharmaceutical Wastewater using TiO₂/Pumice and O₃/Active Carbon

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Abstract

Phenol is a toxic organic compound that detectable in the pharmaceutical wastewater, and therefore it should be eliminated. This study aims to degrade phenol in the pharmaceutical wastewater treatment using Advanced Oxidation Processes (AOPs) include the photocatalytic process applying Titanium Oxide (TiO₂) that immobilized on pumice stone (PS), as well as ozone process with O₃ and O₃/granulated activated carbon (GAC). Degradation system used two configuration reactors that worked alternately at pH 3 and 9. Photocatalysis was conducted for 4 hours in the photoreactor that equipped with mercury lamp as a photon source, while ozonation was performed for 1 hour in the cylinder glass reactor contained an ozone generator. Phenol degradations were done by photocatalysis, ozonation, photocatalysis followed by ozonation and vice versa. The FESEM-EDS and XRD results depicted that TiO₂ has impregnated on pumice stone and FESEM characterization also indicated that the photocatalyst spread across the surface of the pumice stone. BET analysis results in an increased surface area of the PS-TiO₂ by 3.7 times, whereas bandgap energy down to 3 eV. It can be concluded that ozone process (with O₃/GAC) that followed by photocatalysis at pH 9 could treat the liquid waste with phenol concentration 11.2 down to 1.2 ppm that nearly according to the discharge standards quality (1 ppm). Copyright © 2020 BCREC Group. All rights reserved

Keywords: TiO₂; Pumice stone; Ozonation; O₃/GAC; Pharmaceutical waste; Phenol Degradation

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1. Introduction

The growth of the pharmaceutical industry is increasing year by year since the need for medicine by society is rising. This industry is recognized as one of the most powerful sources of an environmental pollutant, and it mostly comes from various production facilities during manufacturing and maintenance. The sources of

waste are spent fermentation broths, solvents, equipment wash waters, process liquors, and spilled materials [1]. This waste is categorized as toxic and harmful material since it contains high organic complex material indicated by the high concentration of COD, BOD, TDS and phenol. It is difficult to treat with conventional physical/chemical and biological treatment systems or general treatment [2,3]. The former treatment has drawback due to high sludge production and low efficiency of chemical oxygen demand (COD) removal, whereas biological

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treatment has limited success due to expensive and low removal efficiency [3]. Advanced Oxidation Processes (AOPs) using photocatalyst TiO_2 impregnated on pumice (PS- TiO_2) could mineralize most organic pollutant since the presence of pumice as a support material for immobilizing of TiO_2 and therefore, this photocatalyst can degrade the pollutants easily without the problem of filtration for nanosized TiO_2 [4-6]. The high capability of pumice stone to float also play an important role in treating this waste because of the contact photon with TiO_2 and pollutant occur effectively on the surface of liquid waste [7]. Furthermore, the abundance and the low price of PS in Indonesia make it truly applicable for industrial purpose. TiO_2 immobilized on calcium alginate to remove copper from wastewater is also reported by Kanakaraju *et al.* [8]. Waste treatment with TiO_2 proved to degrade many organic compounds such as methyl orange, acetone, toluene, phenol and volatile organic compounds (VOCs) as reported by Slamet *et al.* [6]. Furthermore, TiO_2 can also be extensively used for water disinfection in wastewater treatment and air pollution control [9,10]. Many organic pollutants in wastewater act as electron donors/hole scavengers in the photocatalysis [11]. Furthermore, TiO_2 should be an effective photocatalyst due to thermal stability, low toxicity, noncorrosive and inexpensive [4,5]. Meanwhile, AOPs with ozone and GAC (O_3/GAC) is a well-known technology to treat the industrial wastes since it can mineralize or destruct complex to simple organic compounds. In addition, GAC or carbon nanotube is widely used as an adsorbent of the heavy metal ion from industrial wastes and wastewater [12-14]. GAC is less expensive, abundance, and not necessary to regeneration since the pollutants degraded in the pore of GAC, and therefore it can reduce the consumption of ozone. Many researchers have performed pollutants treatment using O_3/GAC , and they reported that this technology is very effective [15].

The principle of AOPs with PS- TiO_2 (photocatalytic process) utilizes the excitation of an electron from the valence to the conduction band of TiO_2 if it is illuminated by photon more than the band gap energy. The jump of electrons resulted in holes (h^+) in the valence band that can interact with water to form OH radical ($\cdot\text{OH}$). This $\cdot\text{OH}$ and holes are a very reactive compound that can oxidize non-selectively in degrading the waste [5]. On the other hand, ozonation with O_3/GAC utilizes decomposition of ozone to become OH radical ($\cdot\text{OH}$) assisted by GAC as adsorbent and cata-

lyst in promoting ozone decomposition to OH radical [16]. Advanced oxidation processes using O_3/GAC and PS- TiO_2 are efficient methods that use O_3 , $\cdot\text{OH}$, $\cdot\text{O}_2$, $\cdot\text{O}$, holes, and O_2 to accelerate the selective/non-selective oxidation, and therefore, the decomposition of a wide range of organic substances resistant occurred [5,17].

Moreover, TiO_2 is available in the market and easy to use. Unfortunately, there is still the drawback of TiO_2 application due to the difficulty in the filtration of this catalyst after used. These disadvantages can be reduced by immobilizing the photocatalyst on a solid support such as activated carbon, zeolites, and pumice [4,5,18]. Since the pharmaceutical waste contains high organic complex, therefore the combination of photocatalytic process and ozonation should be done in order to treat this pollutant effectively and economically to solve the problem in providing clean water. Since the pharmaceutical wastewater contains relatively high phenol concentration, therefore it is very urgent to study the phenol degradation.

In this paper, the investigation of degradation phenol in the pharmaceutical wastewater using AOPs processes (with PS- TiO_2 and O_3/GAC) was performed using two batch reactors that worked alternately. The characterizations of PS- TiO_2 (FE-SEM/EDX, BET, XRD and UV-Vis DRS) were also performed to evaluate the success of impregnation TiO_2 on pumice. The reduction of phenol concentration was analyzed according to the ASTM standard to evaluate the AOPs process.

2. Materials and Methods

2.1 Materials

Commercial powder of TiO_2 P25 that consists of 79% anatase and 21% rutile with anatase and rutile crystalline size of 20 and 23 nm respectively [19], BET surface area of 53.6 m^2/g [20] was produced by Evonik Industries (Essen, Germany). Tetra Ethyl Ortho Silicate (TEOS) with chemical formula: $\text{Si}(\text{OC}_2\text{H}_5)_4$, purity 98% and all chemicals used in this study were obtained and distributed by Sigma-Aldrich, and O_3 was generated by the ozone generator. Natural pumice was supplied from Bima City, Nusa Tenggara Barat. While the pharmaceutical wastewater was taken from Cikarang.

2.2 Preparation of Photocatalyst

This process was initiated with the preparation of TiO_2 immobilized on pumice stone using the impregnation method. Firstly, pumice

stone (PS) was cut to around 4-5 cm, cleaned ultrasonically for 30 minutes, heated in the furnace at 400 °C for 1 hour, followed by dip coating of PS in sol of TiO₂ (5% w/w of TiO₂ on PS) with TEOS (0.5 mL TEOS for 1 g TiO₂) as an adhesive and Si source and finally the composite PS-TiO₂ was evaporated in the furnace at 350 °C for 1 hour. Subsequently, the PS-TiO₂ underwent characterization and photocatalyst test for degrading phenol in pharmaceutical wastewater.

2.3 Photocatalyst Characterization

The surface morphology of composite PS-TiO₂ was examined using an FE-SEM (FEI-Inspect F50). Energy dispersive X-ray spectroscopy (EDX) that attached to the FESEM is used to determine the elemental composition in the photocatalyst. BET characterization is used to evaluate active surface area, pore volume, and pore size of the PS-TiO₂ (Quantachrome QuadraWin for QuadraSorp SI ©2000-12 version 5.11). To identify the phase of photocatalyst, Shimadzu XRD 7000 X-ray diffractometer operated at 40 kV and 30 mA with scan rate at 2° min⁻¹ over 2θ range of 10-80° was performed. The source of X-ray radiation was Cu. UV-Vis DRS Spectrophotometer Shimadzu 2450 type was used to determine the bandgap energy of the photocatalyst samples. The reflectance and absorbance of the samples was measured in the wavelength range of 200-600 nm.

2.4 Degradation of pollutant measurement

Degradation of phenol was performed on two reactors separately. The photodegradation was carried out in an 1 L Pyrex flask (contains

400 mL of waste with 20 g of PS-TiO₂) equipped with a mercury lamp (HPL-N 250 W/542 E40 HG ISL, Philips, China) as a photon source (17% of UV & 83% of visible light) to trigger the photocatalytic reaction and magnetic stirrer to mix the waste. The amount of 20 g PS-TiO₂ in 400 mL of waste is used since it covered precisely on entire surface of the solution in the 1 L flask. The photoreaction system was placed inside a reflector box, and the lamp was set up 15 cm away from the surface of liquid waste that already contained with PS-TiO₂ as shown in Figure 1a. Photodegradation was started at room temperature 28 °C and stirred for 60 min without irradiation of photon to allow the system to reach an adsorption-desorption equilibrium. After 4 hours irradiation, the phenol concentration was evaluated (the process was denoted as F) by DRS-8000 UV-Vis spectrophotometer on the wavelength of 500 nm with a slight modification of the colorimetric method using 4-aminoantipyrine, as written in the standard method of ASTM D1783-01 (2012).

The ozone processes were carried out with and without GAC at pH 3 and 9. The reactor of ozonation system (with O₃ and O₃/GAC) consists of Pyrex cylinder glass with diameter and height of 4 and 100 cm, respectively. This reactor was equipped with an ozone generator (HS-028, China) with the rate of 0.096 g/h and magnetic stirrer to mix the GAC in the liquid waste a shown in Figure 1b. Prior to ozonation, the reactor has fulfilled with 250 mL of liquid waste with and without 1 g of GAC. The phenol concentrations were analyzed after 1 hour degradation (the process was denoted as O).

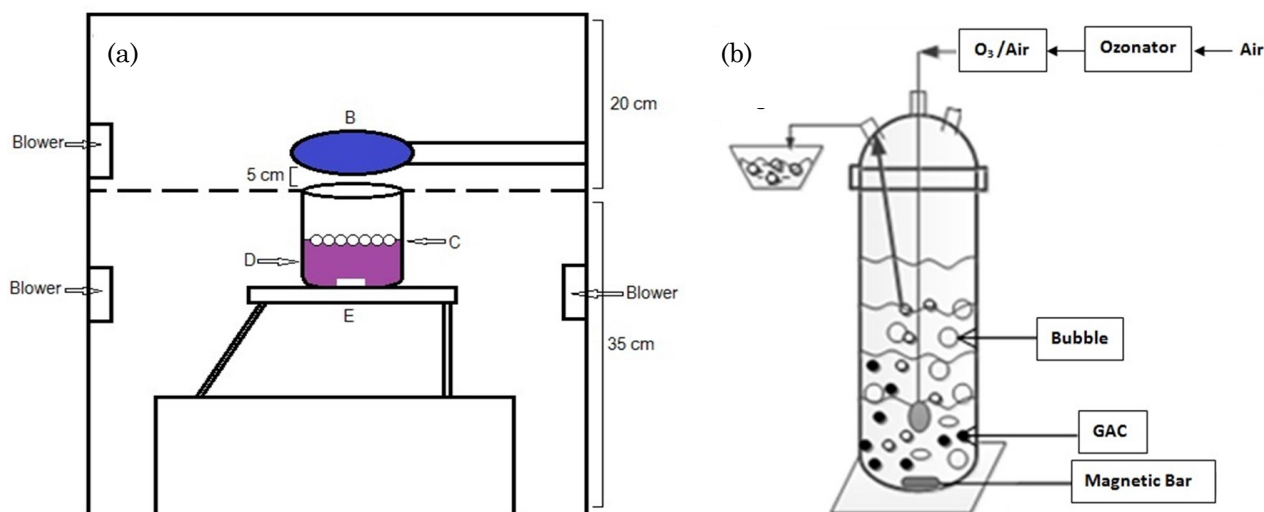


Figure 1. The experimental setup for photoreactor (a) that consists of (A) Reflector box, (B) mercury lamp, (C) PS-TiO₂, (D) pharmaceutical wastewater, (E) magnetic stirrer bar and (b) ozonation reactor.

3. Results and Discussion

3.1 FE-SEM/EDX Characterization

FE-SEM/EDX characterization determines the morphology and elemental composition of the modified photocatalyst surface. Figure 2 depicts the FE-SEM images for PS and PS-TiO₂ samples. From Table 1, elemental composition of PS are Si, Al, Na, K, Fe, Ca, and O that indicates component of the PS are SiO₂, Al₂O₃, Na₂O, K₂O, Fe₂O₃ and CaO [21]. After impregnation process, % mass of O element increased and Ti element was appear. The actual position of the TiO₂ is on the outer surface and in the cavity/hollow space of PS that can be seen in the Figure 2b. This characteristic clearly shows that PS has covered by TiO₂. This phenomenon indicated that PS could be impregnated by TiO₂ and immobilized on the surface of PS as also reported by previous researchers [4,20]. Morphology of TiO₂ is spherical, and it is deposited almost on the surface and hollow space of PS with the same thickness although some aggregates of TiO₂ were also formed. This result is in accordance with the experiment by Chuan *et al.*

[22]. Elemental composition of PS and immobilized TiO₂ on PS that was taken from 3 different places (A, B, and C) are summarized in Table 1, and the spectra of the PS TiO₂ sample has been previously reported [23]. The EDX results of PS-TiO₂ indicated that besides O and Ti, the components, like Si, Na, and Al that contained in PS, were detected and it gave evident the successful of impregnation process. The Fe component was not detected on the PS-TiO₂ since EDX analysis only detects the component on the surface of PS-TiO₂.

3.2. BET Characterization

BET analysis is used to get information about the surface area, pore volume and pore size of the PS and PS-TiO₂ as shown in Table 2. The surface area (SA) of PS is 0.4 m²/g as this material has cavity/hollow space and only has a few pores, whereas TiO₂ is a pores material with surface area of 53.6 m²/g [20]. The small SA of PS could be caused by some impurities that still present on the surface on PS since the PS sample has not been calcinated.

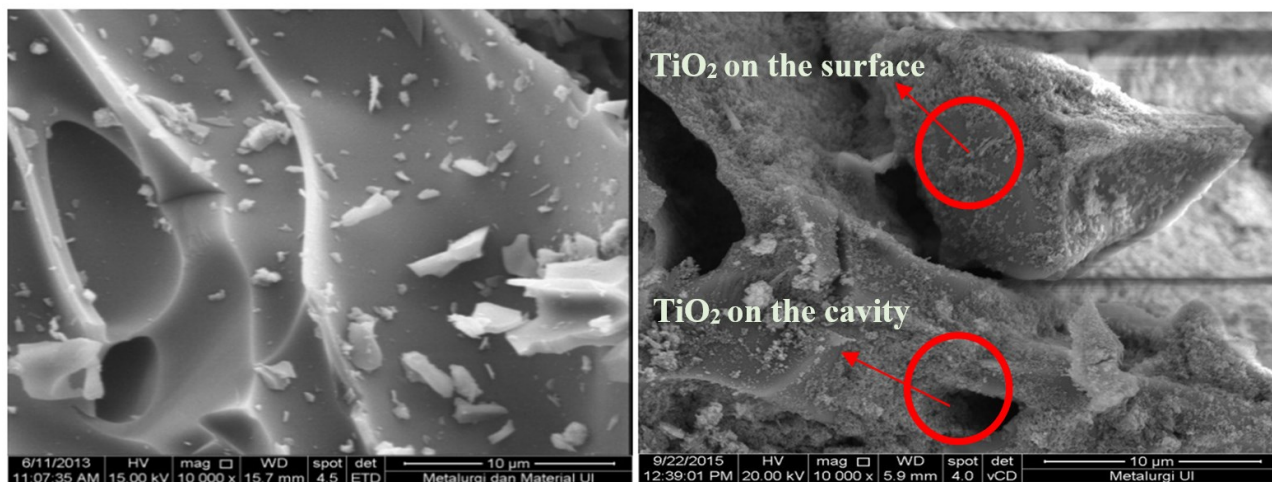


Figure 2. FE-SEM images with magnification of 10000X for (a) Pumice stone/PS; (b) PS-TiO₂.

Table 1. EDX Results for PS and PS-TiO₂

Elements	%Mass					
	PS			PS-TiO ₂		
	A	B	C	A	B	C
O	43.83	44.81	41.39	60.76	61.66	61.47
Na	4.63	4.7	4.28	3.08	2.79	3.41
Al	10.05	9.68	9.71	3.53	4.33	4.33
Si	33.8	34.62	36.39	11.66	11.67	13.95
K	3.08	2.97	3.59	0.69	0.77	0.75
Ca	1.55	0.85	1.29	0.46	0.59	0.39
Fe	3.05	2.36	3.35	-	-	-
Ti	-	-	-	19.82	11.19	15.7

After TiO₂ was coated to the PS, the SA of PS-TiO₂ increased to become 1.48 m²/g (3.7x). Increasing the SA is caused by the availability of pores material TiO₂ film that occupy hollow space/cavity of PS and also it deposited on the outer surface of PS as presented in Figure 2b. The pore volume of PS-TiO₂ increased compare to the PS since the existence of pores material TiO₂ covered on the hollow and outer surface of the PS. The pore volume of TiO₂-P25 was around 0.25 cm³/g as reported by Raj *et al.* [24].

3.3 XRD Characterization

Figure 3 exhibits the X-ray diffraction patterns of the PS and PS-TiO₂. The figure shows that for the PS, the two strongest peaks at 2θ around 23.2° and 27.6° were Fe₂O₃ (JCPDS 39-1346) and Na₂O (JCPDS 03-1074), whereas the weak peak at around 2θ 35.8° and 42.1° were also Fe₂O₃ (JCPDS 39-1346) and Al₂O₃ (JCPDS 26-0031) respectively [25]. The strong broad hump between 2θ 15° and 30° for the PS and PS-TiO₂ indicates that the silica SiO₂ is amorphous [21]. This results indicated that the chemical composition of PS that detectable on XRD analysis are SiO₂, Fe₂O₃, Na₂O, and

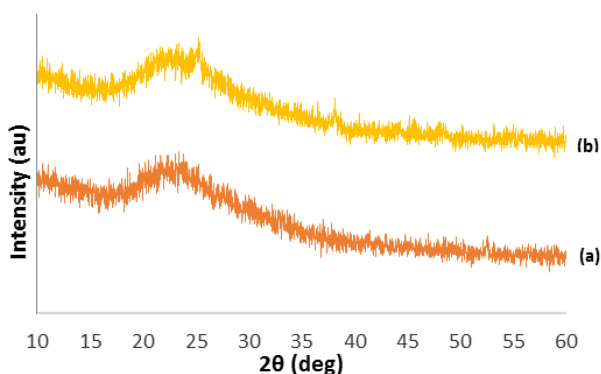


Figure 3. XRD pattern of (a) Pumice stone/PS and (b) PS-TiO₂.

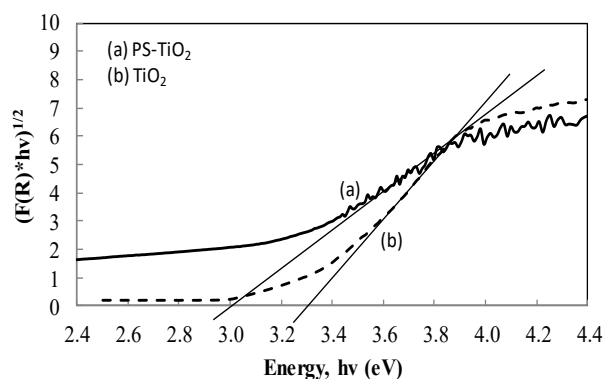


Figure 4. Tauc plot of Kubelka-Munk function vs. Energy ($h\nu$, eV).

Al₂O₃. This result is in accordance with the EDX analysis that previously reported. For The PS-TiO₂, the peaks at around 25.2°, 38.1°, 48.1°, and 54.8° are belong to anatase phase (JCPDS 21-1272), whereas the peaks around 44.1° and 55.8° are belong to rutile phase of TiO₂ (JCPDS 21-1276) [26]. This result indicated that TiO₂ has been impregnated on PS.

3.4 UV-Vis DRS Spectra Analysis

The band gap energy of TiO₂ and PS-TiO₂ is calculated by using Kubelka-Munk function and Tauc plot [27]. The extrapolation of the linear portion of the Tauc plot ($F(R) \cdot h\nu$) to the energy ($h\nu$) axis, result in the band gap energy of the photocatalyst samples as shown in Figure 4, where $F(R) = (1-R)^2/2R$, R = reflectance, $h\nu$ = photon energy. From that Figure, it is clear that PS-TiO₂ undergo lowering band gap until 3.0 eV (410 nm) compare to the pure TiO₂ that has 3.28 eV (380 nm). The reduction of the band gap energy is may caused by small transformation anatase to rutile phase since after impregnation of TiO₂ on PS, it was heated for 1 hour. The bandgap energy of TiO₂ rutile (3 eV) is smaller than anatase phase (3.2 eV) [28]. Another possibility reason is when the PS-TiO₂ was measured using UV-Vis DRS Spectrophotometer, irradiation of UV and visible light penetrated in the PS that contains Si that could also reduce the bandgap [29]. As a result this photocatalyst exhibit enhancement in photoreponse under visible light.

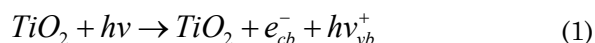
3.5 Photocatalysis and Ozone Process in Degradation of Phenol

Figure 5 presents the degradation of phenol as a function of time irradiation using photocatalytic process with PS-TiO₂ (20 g of PS-TiO₂ in 400 mL of waste). The amount 20 g of PS-TiO₂ in 400 mL of waste is used since that amount precisely covered on entire surface of solution in the 1 L flask. Phenol is an organic substance that mostly in pharmaceutical waste [6]. During the process, the pH values are relatively constant (between 3.17-3.35). It is obvious that increasing the time of photocatalytic process will reduce phenol concentrations.

Table 2. The comparison of BET between PS and PS-TiO₂.

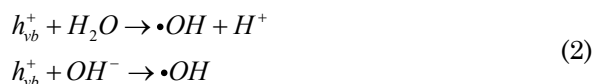
Sample	Surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore size (Å)
PS	0.4	3.4 × 10 ⁻⁴	13.85
PS-TiO ₂	1.48	8.2 × 10 ⁻⁴	8.44

Firstly, phenol in liquid waste was adsorbed by PS and degraded by TiO₂. These two processes occur simultaneously. PS can adsorb waste with high concentration, but it cannot degrade effectively, whereas TiO₂ that has a low capability to adsorb, can degrade relatively high concentration of waste. Furthermore, PS as floating media increases illumination TiO₂ and therefore, an effective process can happen. The availability of O₂ on the surface also assists in the photocatalytic process since it functions as electron scavenger that can reduce the recombination. If TiO₂ is illuminated by a photon, there is an excitation of an electron from the valence band to conduction band and leaves a hole in the valence band according to the reaction Equation (1) as follows [5]:

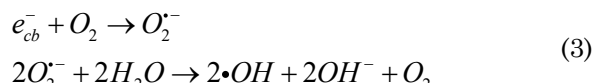


The high oxidation potential of hole causes oxidation of phenol to become CO₂ and H₂O, and therefore, phenol concentration decreased. In addition, hydroxyl radical ($\cdot OH$) which is highly reactive oxidant (with potential oxidation $E_o = 2.86$ V) can be obtained from water

decomposition and the reaction of water with hole according to Equation (2) [5]:



Hydroxyl radicals react non-selectively in the process of phenol degradation. Furthermore, an electron in the conduction band can react with O₂ become superoxide anion that assists in the $\cdot OH$ formation according to the reaction as in Equation (3) [5]:



From Figure 5, it can be stated that after 4 hours illumination the phenol concentrations were constant and still above the standard requirement. This condition could be that other phenol was oxidized since pharmaceutical wastewater consists of complex substances. Another reason is in some cases complete mineralization is slowly for photocatalysis [30].

Comparative study was performed using pure TiO₂ and PS-TiO₂ in degrading phenol. Results indicated that alleviation of phenol concentration was 3.7 times much greater if using pure TiO₂ compare to PS-TiO₂. Phenol degradation using pure TiO₂ could give better result compare to PS-TiO₂ since pure TiO₂ in the slurry have bigger surface area (as mention on the BET analysis) for photodegradation. As a consequence, it could give better yield from kinetic point of few. However, the purpose of impregnation TiO₂ on PS is to avoid the difficulty in separating nanosized TiO₂ photocatalyst from the solution after used as previously reported. In addition, the capability of PS to float increases contact photon to TiO₂.

Figure 6 explains the degradation of phenol in pharmaceutical wastewater as a function variation process at a pH around 3 (actual waste condition). The process of Photocatalysis, Ozonation, Photocatalysis followed by Ozona-

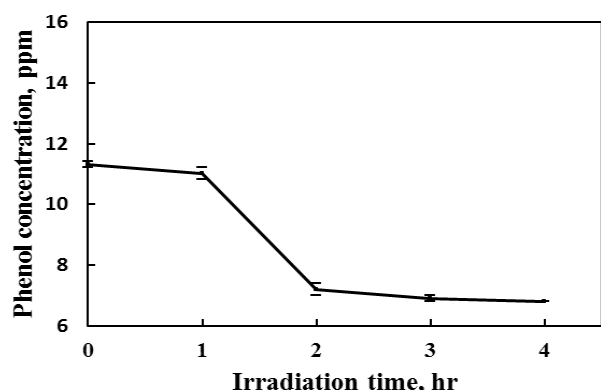


Figure 5. Degradation of phenol as a function of irradiation time.

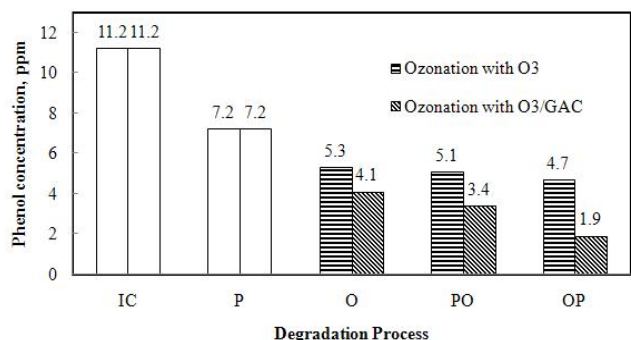


Figure 6. Degradation of phenol as a function of variation process at pH 3.

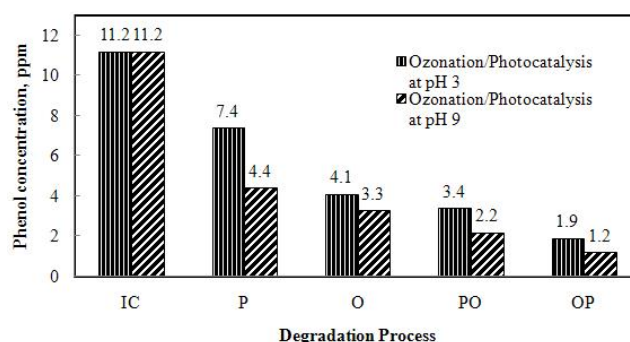
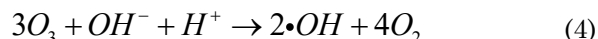
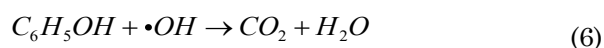
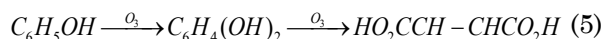


Figure 7. Degradation of phenol as a function of variation process at pH 3 and 9.

tion and Ozonation followed by photocatalysis are denoted as P, O, PO, and PO, respectively. In this experiment, the ozonation was carried out with O₃ and O₃/GAC. The initial concentration of phenol (IC) was 11.2 ppm. It is clear that the elimination of phenol concentration faster at ozone process with GAC compares to the one without GAC. In ozonation with O₃, the phenol degradation was caused by oxidation of phenol with O₃ and •OH. This •OH was obtained by the reaction as presented in Equation (4):



Meanwhile, ozonation with O₃/GAC, the phenol degradation was resulted from oxidation of phenol by O₃, •OH, •O/•O₂ and adsorption of phenol on the surface of GAC. The existence of GAC accelerates the transformation O₃ to •OH and •O/•O₂ which responsible for degrading phenol. Basic electron and oxygen group in the form of chromene and pyrone that exists on the surface of carbon active in the ozone solution can produce OH• dan H₂O₂ [31]. The existence of OH• dan H₂O₂ in the solution act as an initiator in the ozone decomposition to produce •OH. As a result, the degradation rate of phenol with O₃/GAC is better than with O₃. The mechanism of phenol oxidation by O₃ and •OH are presented in Equations (5) and (6) [32,33].



Based on Figure 6, the ozonation process presents better in term of phenol elimination compare to the photocatalysis. This phenomenon may be caused by the amount of the oxidizing agent such as O₃, •OH, •O/•O₂ in ozone process greater than in photocatalysis, while some of the holes that produced by photocatalysis may degrade organic pollutant other than phenol as previously explained. A lot of •OH react with phenol, and most of the holes react with organic pollutant other than phenol. Another possible reason is the limited amount of PS-TiO₂ since some of them sink below a surface, and therefore illumination of some photons could not reach the photocatalyst. In another word, the number of the oxidizing agent in the ozonation process might more than in photocatalysis. Furthermore, photocatalysis has low oxidation rate and suitable for dilute wastewater [30].

Figure 7 shows the degradation of phenol as a function of the variation process at pH 3 and

9. In this process, the ozone process is performed by O₃/GAC. In ozonation at pH 3, phenol degradation is mostly caused by oxidation phenol with O₃ (ozonolysis) since at this pH, ozone is more stable and it is a selective reaction. In contrast, at pH 9, oxidation phenol occurred with •OH, and it is a nonselective reaction [30]. Since •OH with potential oxidation $E_o = 2.86$ V [1] is more powerful oxidant compare with O₃ ($E_o = 2.07$ V), the reduction of phenol was better at pH 9. In photocatalysis point of view, pH also influences the adsorption process. TiO₂ has pH between 6.2-6.8 [7,34]. At pH 9, PS-TiO₂ have a negative charge while phenol has a positive charge. As a result adsorption phenol on PS-TiO₂ taken place easier at pH 9 and resulting higher degradation. Based on Figure 7, it is clear that ozonation process degraded phenol faster than photocatalysis, and based on that figure, it can be concluded that combination process ozonation followed by photocatalysis is considered as the optimum process that can reduce the phenol concentration from 11.2 ppm to 1.2 ppm.

4. Conclusions

Degradation of phenol in pharmaceutical wastewater treatment has been performed by combination photocatalysis with PS-TiO₂ and ozonation with O₃/GAC. The FESEM/EDX and XRD results indicated that TiO₂ was immobilized on the PS. The BET analysis pointed out that immobilized TiO₂ on PS increases the surface area and from the UV-Vis DRS analysis, the band gap energy of PS-TiO₂ down to 3.0 eV. Ozonation with O₃/GAC at pH 9 for 1 hour and followed by photocatalysis with PS-TiO₂ for 4 hours can treat phenol in pharmaceutical wastewater with 90% elimination. This condition was considered as an optimum condition although this value slightly over the maximum quality standard.

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