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PREFACE: The 3rd International Symposium on Applied Chemistry (ISAC) 2017

This proceedings volume contains the written versions of most of the contributions presented during the 3rd International Symposium on Applied Chemistry (ISAC) 2017, which was organized in Balai Kartini Exhibition and Convention Center, Jakarta, Indonesia on October, 23-24, 2017.

ISAC 2017, as the part of Indonesian Sciences Expo 2017, carried a theme "Advances in Sustainable Energy and Chemical Feedstocks". This event was the 3rd international scientific conference organized annually by Research Center for Chemistry, Indonesian Institute of Sciences (LIPI) and Himpunan Kimia Indonesia (HKI, Indonesian Chemical Association).

The symposium was focused on bringing together the scientists and researchers working in the area of applied chemistry to present their work and to discuss the latest trends in technology developments. There were 7 keynote speakers, 48 oral presentations, and 43 poster presentations. Various aspects of chemical related topics were discussed and the presentations were divided into following topics:

- Advanced Materials and Catalysts
- Sustainable Energy
- Food, Natural Products and Pharmaceutical Chemistry
- Environmental Chemistry

We would like to thank all keynote speakers and participants for their contributions to the symposium program and for their contribution for this proceedings volume. We also deeply appreciate all the reviewers who helped to maintain the high publication quality of this volume. We also would like to thank all technical committee for their help and contributions in preparing this proceedings volume.

We are looking forward to the 4th International Symposium on Applied Chemistry that will be held next year. We hope that the symposium will be an excellent platform for all participants and committee to exchange new ideas and application experiences and to find global partners for future collaboration.

Editors

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15.30 - 15.45	**Emrizal M. Tamboesai (OP-19)**	**Sudibyo (OP-20)**
	Geochemistry Characterization, Biomarker and Determination Of Correlation, Maturity Of Petroleum From Bangko-Rohil And Duri Bengkalis, Riau	Application of Taguchi Optimisation of electro metal – electro winning (EMEW) for Nickel Metal from Laterite
15.45 - 16.00	**M. R. Ramachandran, Dr. (OP-21)**	**Dian Angelina (OP-22)**
	Ionic Liquid Loaded Magnetic Nanoparticle Grafted Î'-Cyclodextrin Polymer for the Extraction of Parabens	Synthesis of Carbon Nanotube using Camphor with SS 316 as Catalytic Substrate via Oxidative Heat Treatment Preparation Method
16.00 - 16.15	**Noorfatimah Yahaya, Dr. (OP-23)**	**Nur Nadhirah Binti Mohamad Zain (OP-24)**
	Rapid ultrasound assisted emulsification micro-solid phase extraction based on molecularly imprinted polymer for HPLC-DAD determination of bisphenol A in aqueous matrices	Removal study of phenolic compounds in environmental water samples using non-ionic surfactant and Î²-cyclodextrin modified ionic liquids as a modifier in cloud point extraction

DAY 2, 24 OCTOBER 2017		
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	Moderator: Dian Burhani, M.T.	**Moderator: Dr. Athanasia Amanada S.**
13.00 - 13.15	**Aulia Rahmi Harianti (OP-25)**	**Elza Wijaya (OP-26)**
	Application of Plasma Electrolysis Method for Simultaneous Phenol and Cr(VI) Wastewater Degradation Using Na_2SO_4 Electrolyte	Optimizing The Antioxidant Activity of *Kelakai (Stenochlaena palustris)* Through Multiplestage Extraction Process
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	The Effect Of Adding CTAB Template in ZSM-5 Synthesis	Phytochemical Analysis of Binahong (*Anredera Cordifolia*) Leaves Extract to Inhibit *In Vitro* Growth of *Aeromonas Hydrophila*
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	Degradation of Phenol and Cr (VI) Wastewater with Contact Glow Discharge Electrolysis Method and The Addition of Fe^{2+}	Characterization of Biomasses, Concentrates, and Permeates of Dried Powder of Kombucha Fermentation of Spinach (Amaranthus sp.) and Broccoli (Brassica oleracea) with Membrane Microfiltration and Freeze Drying Techniques for Natural Sources of Folic Acid
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	Combination of Ozonation and Photocatalysis for Pharmaceutical Wastewater Treatment	Effects of Terminal Substitution and Iron Coordination on Antiproliferative Activity of L-Proline-salicylaldehyde Thiosemicarbazone Hybrids
14.30 - 14.45	**Raudina (OP-37)**	**Zatil Afrah Athaillah (OP-38)**
	Degradation of 2,4,6-Trichlorophenol and Hydrogen Production Simultaneously by TiO2Nanotubes/Graphene Composite	Optimization of Carrageenan-based Jelly Products Added with Nutrients for Reducing Osteoporosis Risks

Combination of Ozonation and Photocatalysis for Pharmaceutical Wastewater Treatment

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Abstract. The chemical oxygen demand (COD) and phenol removal from pharmaceutical wastewater were investigated using configuration of two circulation batch reactors in a series with ozonation and photocatalytic processes. The ozonation is conducted with O_3/granulated activated carbon (O_3/GAC), whereas photocatalysis with TiO_2 that immobilized on pumice stone (PS-TiO_2). The effect of circulation flow rate (10; 12; 15 L/min) and the amount PS-TiO_2 (200 g, 250 g, 300 g) were examined. Wastewater of 20 L was circulated pass through the pipe that injected with O_3 by the ozone generator, and subsequently flow through two GAC columns, and finally, go through photoreactor that contains photocatalyst PS-TiO_2 which equipped with mercury lamp as a photon source. At a time interval, COD and phenol concentration were measured to assess the performance of the process. FESEM imaging confirmed that TiO_2 was successfully impregnated on PS, as corroborated by EDX spectra. Meanwhile, degradation process indicated that the combined ozonation and photocatalytic processes (O_3/GAC-TiO_2) is more efficient compared to the ozonation and photocatalysis alone. For combination process with the circulation flow rate of 10 L/min and 300 g of PS-TiO_2,the influent COD of around 1000 ppm are effectively degraded to a final effluent COD of 290 ppm (71% removal) and initial phenol concentration of 4.75 ppm down to 0 ppm for 4 h which this condition fulfill the discharge standards quality. Therefore, this portable prototype reactor is effective that can be used in the pharmaceutical wastewater treatment. For the future, this process condition will be developed for orientation on the industrial applications (portable equipment) since pharmaceutical industries produce wastewater relatively in the small amount.

INTRODUCTION

Nowadays, the environmental problems are faced by countries in the word. The pharmaceutical industry is one of the most significant sectors in the world's economy especially in the countries that have big population. The increasing demand of medicine gives the positive impact on economic. On the other hand, it also creates the negative impact on environmental problems. High concentration pharmaceutical industry wastewater needs the high degree of treatment before it discharged into the environment [1]. Since it categorized as harmful wastewater, conventional treatment such as physical, chemical, and biological methods are not adequate to treat this waste [2]. Recently, Advanced Oxidation Processes (AOPs) such as ozonation [3,4] and photocatalysis [5] are wastewater treatments that provide the high removal of pollutants. In ozone process, the availability of O_3 and OH radicals that have the high oxidative power play an important role in the degradation of pollutants. For instance, high efficiency of ozone process for drinking water system has been studied [6], however, ozone process is relatively expensive due to the consumption of electricity. Meanwhile, photocatalysis with semiconductor TiO_2 is a green technology for degrading wide variety organic pollutants with solar energy [4,5], and other environmental application such as air quality control, CO_2 removal and disinfectant of bacteria [7,8]. Moreover, semiconductor TiO_2 is an effective photocatalyst due to the thermal stability, low toxicity, noncorrosive and inexpensive [9]. Photocatalysis with TiO_2 impregnated on pumice provides some advantages since pumice can act as adsorbent and the capability of pumice to float improves photon absorption. In addition, TiO_2 impregnated on the pumice also reduce the difficulty in the filtration of the photocatalyst since filtration

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can be eliminated by immobilizing TiO_2 on the solid support such as pumice [5,10]. However, photocatalysis still has limitation since its low oxidation rate, only suitable for the dilute wastewater and in some cases the complete mineralization is slowly [4]. In general, a combination of several treatment methods provides the high efficiency removal of pollutants compared with individual method [11]. Therefore, the combination of ozone process and photocatalysis is reasonable for treatment pharmaceutical wastewater that indicated the high concentration of pollutants. This process is required in order to fulfill the discharge standards quality in short time treatment process. Actually, some researchers have investigated this combination, however, they used synthetic and single waste such as formic acids, aniline, pyridine, humic acid etc [4]. To the best of our knowledge, the application of this combination has not been investigated yet for the real wastewater especially pharmaceutical wastewater that consists of hardly degradable substances indicated by the high concentration of COD, BOD, TDS, and phenol.

EXPERIMENTAL

Material and Methods

The pharmaceutical wastewater used in this study was obtained from PT X Indonesia located in Tangerang. The effluent has pH around 5 – 6 with the COD value around 1000 ppm and the initial phenol concentration was 4.75 ppm. The ozone was generated from the air by the ozone generator (Hanaco THS-278 type) with the dosage of 0.1 g/h. This dosage was obtained by Iodometric titration method. Granular activated carbon was purchased and it was applied without any further treatment. Commercial powder of TiO_2 P25 (79% anatase, 21% rutile) was supplied from Evonik Industries. Pumice is supplied from Bima City, Nusa Tenggara Barat, Indonesia. Tetra Ethyl Ortho Silicate (TEOS) or $Si(OC_2H_5)_4$ 98% and all chemicals used in this study were purchased from Sigma-Aldrich.

TiO_2 immobilized on pumice was performed using impregnation method. Pumice (PS) with the size of 4-6 mm was cleaned ultrasonically. Dip coating of PS in the sol of TiO_2 (5 % w/w of TiO_2 on PS) was performed with TEOS as an adhesive and Si source. Finally, the composite PS-TiO_2 was evaporated in the furnace at 350 ^oC for 1 h. The PS-TiO_2 was characterization by FESEM/EDX (FEI inspect F50) and then it underwent photocatalyst test for degrading pharmaceutical wastewater.

Batch-recirculation reactor system and wastewater treatment procedure.

The configuration of two batch circulation reactors with ozonation and photocatalytic processes can be seen in Fig. 1. The waste from the wastewater tank that made of glass with the volume of 30 L (length 30 cm, width 30 cm, and height 34 cm) was firstly pumped through the pipe (ID = 2.1 cm) and it was injected with O_3/O_2 from the ozone generator with the O_3 producing rate 0.1 g/h. Subsequently, the waste went through the two carbon columns and finally, it experienced photodegradation in the 30 L of the photoreactor that equipped with the mercury lamp (HPL-N250 W/542 E40 HGISL) as a photon source (17% of UV and 83% of visible light). For the ozonation, the schematic process was similar to the Figure 1, however, the flow after through GAC was directly recirculation to wastewater tank. For the photocatalysis, the wastewater was allowed to flow directly to photoreactor and back to the wastewater tank. The circulation flow rate of the wastewater was setup and variated (10; 12; 15) L/min, whereas the amount of the PS-TiO_2 also variated (200; 250; 300) g. At a time interval, the COD and phenol concentration were measured according to SNI and ASTM standards.

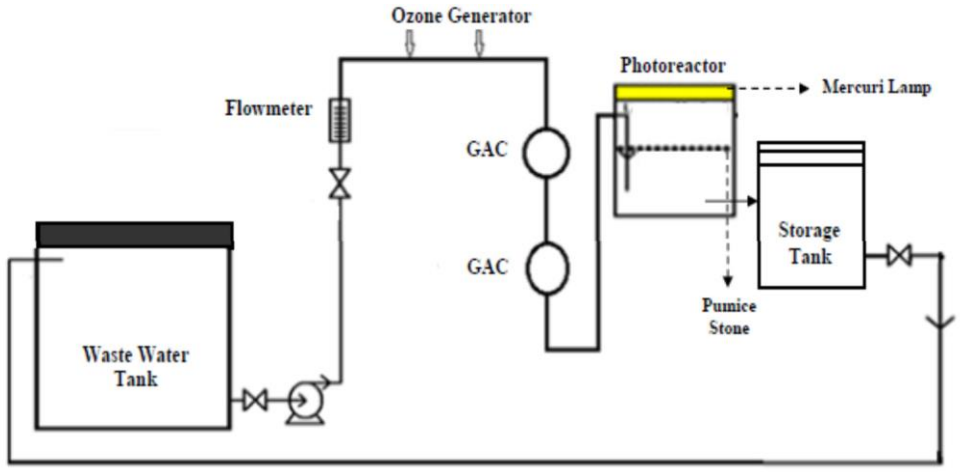

FIGURE 1. The experimental setup for ozone process and photocatalysis

RESULT AND DISCUSSION

Photocatalyst characterization

The FESEM image of PS-TiO_2 indicated that PS has pores and the surface has covered by TiO_2 as shown in Fig. 2.

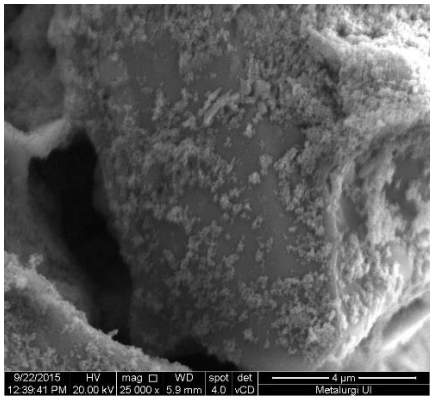

FIGURE 2. FESEM image of PS-TiO_2 (magnification of 25000 X)

The EDX results of PS-TiO_2 (Table 1 and Fig. 3) indicated that besides O and Ti, the components like Na, Al, Si, K, and Ca that contained in PS were detected and it gave evident the successful impregnation of TiO_2 on PS. Similar result also reported by previous researchers [10,12,13]. Table 1 presents the elemental composition of PS-TiO_2.

Table 1. Elemental composition of PS-TiO_2

Elements	%Weight
O	63.1
Na	2.7
Al	3.69
Si	11.91
K	0.63
Ca	0.33
Ti	17.2

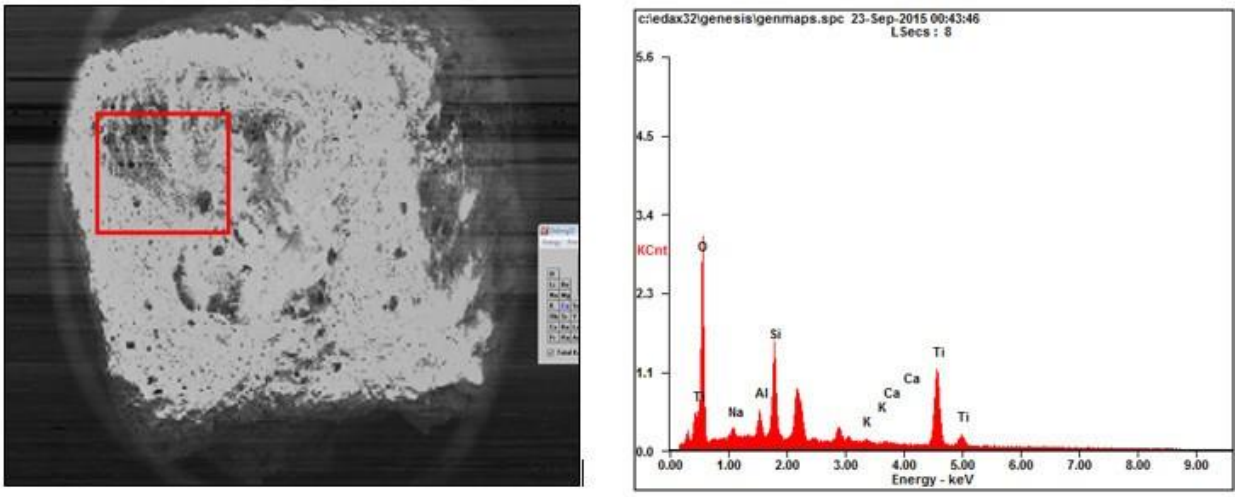

FIGURE 3: EDX analysis of PS-TiO_2

Pollutants degradation by ozone process

Figure 4 shows the reduction of COD from wastewater by O_3/GAC as a function of time with 300 g of PS-TiO_2 at the different circulation flow rate. The reduction of COD is caused by the oxidation of the pollutant with: a). O_3 (ozonolysis), b). with hydroxyl radical ($^{\bullet}OH$) results from the reaction of O_3 with water, and c). the reaction of O_3 in the surface of GAC. The function of GAC is not only as the adsorbent that removes organic carbon, but also accelerate the O_3 transformation into $^{\bullet}OH$ [5]. As a result, ozonation process is very effective in the degradation of pollutant in wastewater. The high performance of ozonation is caused by the high oxidative power of hydroxyl radical and ozone with the redox potential of 2.8 V and 2.07 V respectively [1,4]. There are two reactions through which O_3 decomposes the pollutant. Firstly, direct attack of pollutants by molecular ozone (ozonolysis) that occurs at pH bellow 7 (acidic or neutral condition). This condition is the selective reaction that results in the end product that can't be oxidized further by O_3. Secondly, nonselective decomposition of pollutants by OH radicals at high pH value [4]. It is clear that the circulation flow rate of 10 L/min of the wastewater provides the highest COD removal since at this condition the contact time and the mixing of O_3 and $^{\bullet}OH$ with the pollutant in waste water are sufficient and better compared to others. As a result, pollutant could be degraded effectively. This result is in accordance with the previously reported by Linda Zou et al. (2008) when they studied color removal from reused water with ozone and photocatalytic process [14]. To fulfill the COD standard quality requirement (bellow 300 ppm), this process needs around 12.6 h. For phenol degradation, it diminished from 4.75 ppm to become 0.1 ppm in 6 h ozonation process. On the other hand, at higher circulation flow rate, the contact time of ozone and hydroxyl radical to the pollutant is decreased, which resulted in the slower COD removal. The reduction of COD and phenol concentration due to the oxidation of pollutant in the pharmaceutical wastewater to become degradation product by O_3, $^{\bullet}OH$, and adsorbed by GAC.

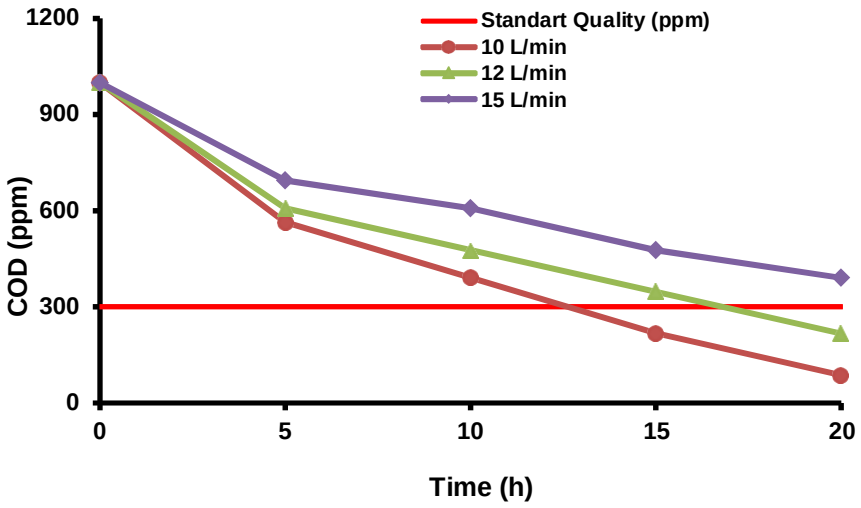

FIGURE 4.The COD reduction as a function of time with ozonation process for various circulation flow rate

Pollutants degradation by photocatalysis

Figure 5 depicts COD removal of pharmaceutical wastewater as a function of time irradiation at 10 L/min circulation flow rate with different amount of photocatalyst. It is clear that the COD rapidly reduced by the photocatalytic process with 300 g of Ps-TiO_2 compared to others. In this process, the hydroxyl radical is considered as the main substance that responsible for degradation of organic matters [11, 14]. In photocatalysis, when TiO_2 absorbs photon greater than its bandgap energy, there is excitation electrons from valence band (vb) to conduction band (cb) and therefore, resulting electrons in the conduction band and holes in the valence band according to Eq. 1. The holes react with water to produce $^{\bullet}OH$ (Eq. 2), and this $^{\bullet}OH$ and the holes itself oxidizes the pollutants to become CO_2 and H_2O [4,15]. Hole is the highly oxidizing agent (+2.53 eV versus standard hydrogen electrode, SHE) that effectively degrade the pollutant [16]. Meanwhile, the electrons can act as the reducing agent to remove heavy metals such as mercury, arsenic, and chromium [17] or reacts with the adsorbed oxygen on the surface of PS-TiO_2 to form hydroxyl radical according to Eq. 3 through various pathways, [4,11]. The reactions in the photocatalysis are as follow.

$$TiO_2 + h\nu \rightarrow TiO_2 (e^-_{cb} + h^+_{vb}) \quad (1)$$

$$h^+_{vb} + H_2O \rightarrow {}^{\bullet}OH + H^+$$
$$h_{vb} + OH^- \rightarrow {}^{\bullet}OH \quad (2)$$

+

$$e^-_{cb} + O_2 \rightarrow O_2^{\bullet -} \quad (3)$$

$$2O_2^{\bullet -} + 2H_2O \rightarrow 2{}^{\bullet}OH + 2OH^- + O_2$$

The pollutants (P) that adsorbed in the surface of PS-TiO_2 plays an important role in the photocatalytic oxidation via successive attacks by $^{\bullet}OH$ or hole as follows [14].

$$P + {}^{\bullet}OH \rightarrow P^{\bullet} + H_2O \quad (4)$$
$$P + h_{vb}^+ \rightarrow P^{\bullet +} \rightarrow \textit{degradation product} \quad (5)$$

From Fig.5 it can be stated that the amount of PS-TiO_2 significantly affects the COD removal. The more the amount ofPS-TiO_2, the higher the COD removal and 300 g of the photocatalyst in this process result in the highest COD removal. This condition is considered as the optimum process. It meant that more $^{\bullet}OH$ and hole are responsible in degrading pollutant. This photocatalysis needs 12 h to fulfill bellow the COD standard quality requirement (290 ppm) that allowed to discharge in the environment. In this condition, the percentage COD removal was 71 %. To reduce the time of the process, the combination of ozonation and photocatalysis was performed.

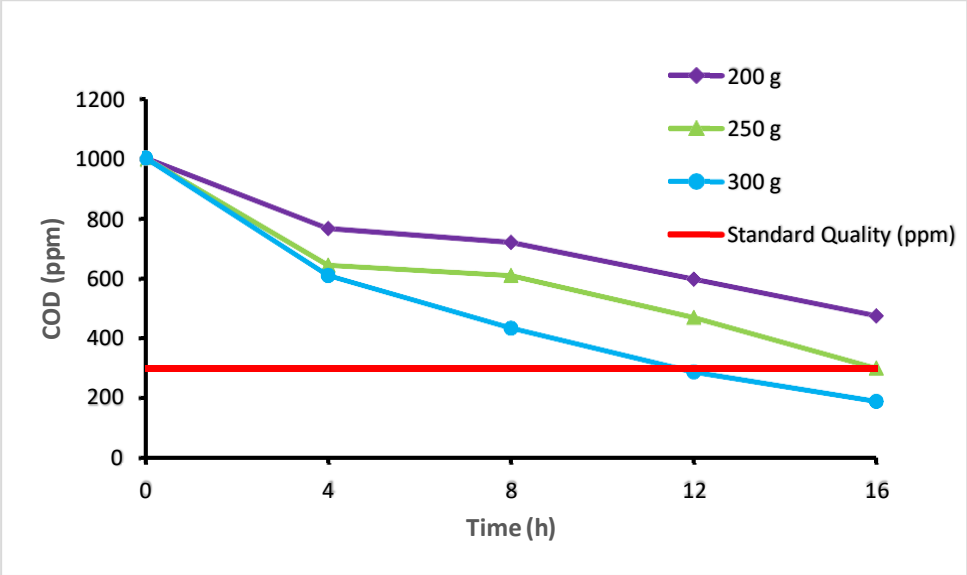

FIGURE 5. The COD removal as a function of time with photocatalytic process for various PS loading

Pollutants degradation by combination of ozone process and photocatalysis

The combination of ozonation followed by photocatalysis processes with batch circulation reactors was performed with the equipment that can be seen in Fig. 2 at the flow rate of 10 L/min and 300 g of the photocatalyst. The PS-TiO_2 covered the surface of the liquid waste in the photoreactor. From Fig. 6, it is clear that the COD removal was rapidly degraded by the combination of the two methods compared to the degradation by the photocatalysis or ozonation alone. The result indicated that after 4 h circulation, the initial COD and phenol concentration of around 1000 and 4.75 ppm declined to 290 and 0 ppm, respectively. On the other hand, the photocatalysis or ozonation alone only reduces the COD to 609 and 651 ppm, respectively. This result is in a good agreement with the study that previously reported [11,14]. In ozone process, O_3 and hydroxyl radicals are responsible for pollutant decomposition. However, electrons generation by photocatalytic also could react with ozone to product $^{\bullet}OH$ via several pathways [14] as follows.

$$O_3 + e_{cb}^- \rightarrow O_3^{\bullet -} \rightarrow \rightarrow {}^{\bullet}OH \qquad (6)$$

The availability of O_2 introduced via ozone generator also can react with the electron to become •OH as final products (Eq. 3). As a consequence, a larger number of $^{\bullet}OH$ (powerful oxidant species) can be produced by the combination of those two processes. In another word, the rapid degradation using this combination process due to not only the role of O_3, $^{\bullet}OH$, GAC in ozonation and the influence of $^{\bullet}OH$ and hole that resulted from photocatalysis process, but also the increasing the number of radical hydroxyls. As a result, the combination process results in more powerful oxidant that responsible for degrading pollutant. The use of combined ozonation and photocatalysis is an attractive route because of the enhancement of the hydroxyl radical generation, a powerful oxidant agent that can oxidize completely the organic matter present in the aqueous system. Ozone process is reported to be efficient for highly contaminated wastewater such as pharmaceutical waste, meanwhile, photocatalysis can completely decompose the intermediate product that resulted from ozone process. Moreover, photocatalysis also found to be efficient to degrade the dilute solution.

Compared to the ozone process, the photocatalytic process indicated slightly higher COD removal. It has been reported that, most of the organic matters could not completely decompose by ozone alone [14]. Moreover, the pH of this treatment was around 5 – 6, and therefore, pollutant was decomposed mainly by direct attack of O_3 and it is a selective reaction that resulted in intermediate product. Since this intermediate product cannot be oxidized further, the COD value was slightly higher [4].

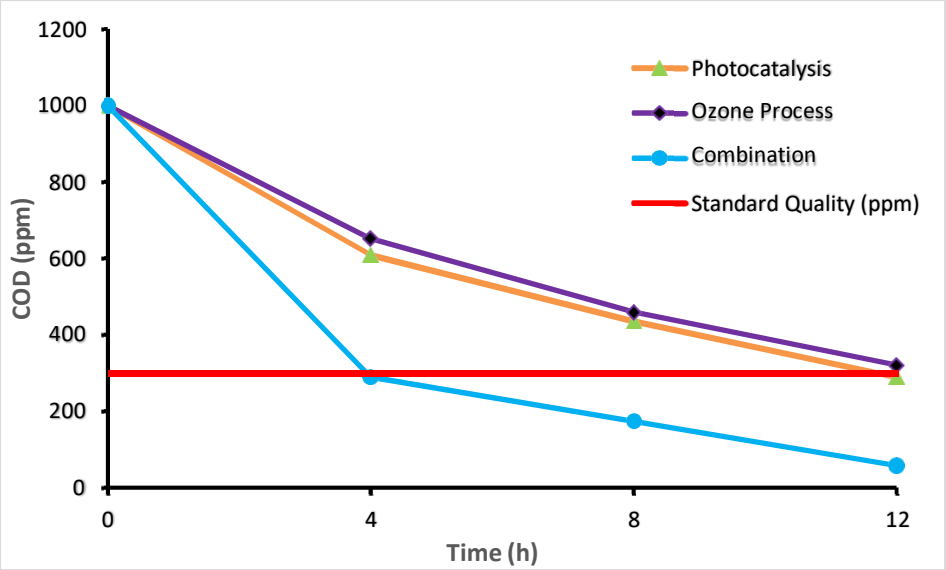

FIGURE 6. The COD removal as a function of time with variation process

CONCLUSION

The combination of ozone process and photocatalysis in a batch reactor with circulation shows as an effective method for pharmaceutical wastewater treatment with relatively high contaminated wastewater indicated by the COD value of 1000 ppm. This process can treat 20 L of pharmaceutical wastewater with the initial COD of 1000 ppm and phenol concentration of 4.75 ppm decrease to 290 ppm and 0 ppm, respectively for 4 h with the circulation flow rate of 10 L/min and 300 g PS-TiO_2. This condition meets the standard quality of effluent and it is considered as an optimum process. Ozone and photocatalytic processes could be an effective and alternative treatment for pharmaceutical wastewater with high concentration of pollutants.

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