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INVESTIGATING THE EFFECT OF HYDROGEN PEROXIDE ON PHOTOCATALYTIC DEGRADATION OF COMMERCIAL PARACETAMOL USING TiO_2

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ABSTRACT

The role of hydrogen peroxide on paracetamol degradation was investigated. Photocatalysis system contains UV radiation and commercial titania (TiO_2) as catalyst. The parameters studied for optimal photocatalysis conditions were catalyst dose (0.05 - 0.2 g), initial concentration of paracetamol (5 - 20 mg L^{-1}), and irradiation times (0 - 210 min). Optimal condition obtained by determining the changes of paracetamol concentration converted to be degradation percentage. The influence of hydrogen peroxide concentrations (1 % - 7 %) on photocatalysis TiO_2 system was studied. The highest paracetamol degradation was obtained at addition of 3 %. It gives positive effect on degradation process. Thus, hybrid process (UV / TiO_2 / H_2O_2) is more effective in comparison to the process UV/TiO_2 and UV/H_2O_2. Paracetamol (5 mg L^{-1}) was degraded about 90.80 % using 0.1 g TiO_2, 3 % H_2O_2 addition for 180 min. According to the GC-MS analysis results, paracetamol degradation forms new less toxic by-products. The hybrid process is an alternative technique for degradation of wastewater containing paracetamol.

Keywords: degradation, paracetamol, photocatalysis, hydrogen peroxide, hybrid process.

INTRODUCTION

Paracetamol is known as analgesic and antipyretic drug and is widely used for managing pain and fever. It is purchased commercially. World production estimated at around 145 000 tons per year [1]. The high amount of market demand increases the paracetamol production. It causes more paracetamol residues generated in Environmental. Koagouw found paracetamol concentration out of Indonesian Standard Quality of Seawater limits in coastal waters around Indonesia reaching 610 ng L^{-1} [2]. Chinnaiyan et al. Reported that paracetamol is one of the highest contaminant in India [3]. The sources of paracetamol in environmental are from human use, hospital effluents, pharmaceutical industries, run-off from aquacultures, fish farming, and concentrated animals feeding operations [4]. Moreover, it is easily accumulative in aquatic environment [5]. The presence of paracetamol declines water quality and be a potential risk for non-target organisms. The Environment Agency of England and Wales proposed paracetamol have been classified in 5th place as potential risk of pollutants to the aquatic environment [6]. Paracetamol was harmful to the aquatic organisms at EC_{50} concentration 11 - 100 mg L^{-1} and very toxic at EC_{50} concentration < 1 mg L^{-1} after long-term exposure as reported by the previous EU Directive 93/67/EEC (Commission of the European Communities 1996) [7].

Photocatalysis is an effective and a simple technique for water pollution treatment [8]. Moreover, this technique is applicable at room temperature, low energy consumption, and environmental clean-up. The common pho-active metal oxide as catalysts used in this technique were ZnO [9, 10], TiO_2 [11], ZnS, WO_3, Bi_2O_3 [12], ZrO [13], and biochar-TiO_2 composite [14]. Among those semiconductor materials, Titanium dioxide (TiO_2) is selected as a catalyst because of stabilization in aqueous media, effectively employed in the abatement of aqueous pollution, high performance, stable towards photo-corrosion, biologically and chemically inert, nontoxic, and low cost [15]. Combination of Advanced Oxidation Processes (AOPs) was proved increases pollutants degradation such as solar/Ag-g-C_3N_4/O_3 process [16], visible/C,N-codoped TiO_2/O_3 [17], UV/TiO_2 coated Zeolite/ H_2O_2 [18], sono-photocatalysis in presence of Fe-doped TiO_2 and H_2O_2 [19], Periodate/UV/US [20], and Visible/Ag_3PO_4/H_2O_2 [21]. It is reported effective because the process has more oxidative species for organic pollutants degradation.

The aim of this study is the investigation of hydrogen peroxide effect on the paracetamol degradation by photocatalysis process using TiO_2 as a catalyst. Commercial paracetamol form was selected as a sample because of its extensive pharmaceutical application. To the best of the knowledge, this system process has not been applied on commercial paracetamol treatment and there is no research reported the paracetamol mechanism degradation by this system. Several parameters namely; catalyst dose, the concentration of paracetamol, irradiation time, H_2O_2 concentration and combination process on paracetamol degradation were studied.

EXPERIMENTAL

Materials and Equipment

The materials used in this study are commercial paracetamol 500 mg tablets (Indofarma production, Bekasi-Indonesia), calcined-commercial Titania (TiO_2, low grade), and hydrogen peroxide (30 %, Sigma). The tools used include ultraviolet-visible Spectrophotometer (SHIMADZU, Japan), GC-MS (Agilent 19091S-433) packed with DB-5MS UI 5 % Phenyl Methyl Silox column (30 m x 250 µm x 0.25 µm), analytical balance (AA-200, Denver Instrument Company), X-ray diffractometer (model: PANalytical EMPYREAN), UV-C Lamp 8 watt (Evaco with λ = 254 nm), centrifuge (NASCO with speed 9000 rpm), and glasses equipment.

Characterization of Catalyst

Low-grade Titanium Dioxide was used as a catalyst. It was calcined under 500°C for 2 hours to get anatase phase of Titanium Dioxide as reported by our previous work [22]. The phase of catalyst was analyzed by X-ray diffractometer (model: PANalytical EMPYREAN) with Cu Kα-ray (λ = 1.54056 Å) as a target source, the tube voltage of 40 kV and current of 30 mA. The powder of calcined TiO_2 was also measured by Diffuse Reflectance Spectrophotometer (DRS UV-Vis) to investigate the band gap. The morphology was observed by Field Emission-Scanning electron microscope (FE-SEM, JEOL JIB 4610F).

Methods

Photocatalytic degradation was conducted at room temperature in reactor containing paracetamol solution 5 mg L^{-1} using 0.1 mg calcined-Titania (TiO_2) under 8 W UV-light irradiation with stirring constantly. The distance between reactor and light source (UV-lamp) was 10 cm. The irradiated paracetamol solution was centrifuged under 10.000 rpm for 5 minutes to separate the catalyst. Filtrate was measured by UV-Visible spectrophotometer at wavelength of 254 nm to measure the changing paracetamol concentration and removal percentage as represented in Eq. 1. Some parameters studied during photocatalysis process were catalyst dose (0.05; 0.1; 0.15; and 0.2 g), initial concentration of paracetamol (5, 10, 15, and 20 ppm), H_2O_2 concentration (1, 3, 5 and 7 %) and irradiation times (0, 30, 60, 90, 120, 180, and 210 min). Paracetamol by-product was extracted by ethyl acetate. The water from aqueous phase was removed by passing through anhydrous sodium and condensing using vacuum rotary evaporator [23]. The collected extract (1µL) was injected to gas chromatograph mass spectrometer (GC-MS) for by-product qualitative analysis. The analysis was carried out with a GC-MS (Agilent 19091S-433) packed by DB-5MS UI 5 % Phenyl Methyl Silox column (30 m x 250 µm x 0.25 µm). A constant flow rate of Helium used as a carrier gas was at of 1 mL min^{-1}. The oven temperature program was set as follows: Initial temperature 60 °C, held for 2 min, ramped to 300 °C at 10 °C min^{-1}.

$$\% \text{ Removal} = \frac{Ci - Cf}{Ci} \qquad (1)$$

RESULTS AND DISCUSSION

Characterization of Catalyst

The structure and crystal size of the calcined TiO_2 catalyst were analyzed by XRD. Based on the results obtained, TiO_2 has a mixed phase containing of anatase and rutile phases as shown in Fig. 1(a) which was detected at the Miller index at (101), (200), (211), and (204) for anatase and 220 for the rutile phase. The optical band gap of calcined-low grade TiO_2 was carried out by Diffuse reflection spectroscopy (DRS). The resulted data was used to calculate the band gap energy (Eg) by Kubelka-Munk function. Fig. 1(b) data shows that catalyst can active in UV-light with band gap energy (Eg) of 3.3 eV. While the morphology of catalyst was observed by FE-SEM. TiO_2 is an irregular spherical and cubical shape and tend to form agglomeration as performed in Fig. 1 (c).

The effect of catalyst dose on Paracetamol degradation

Catalyst dose on paracetamol degradation was investigated to reach an optimal photocatalysis condition. The amount of titania (0.05; 0.1; 0.15; and 0.2 g) was added into 5 ppm paracetamol solution. The research was also conducted under direct UV photolysis without TiO_2 as comparison. Paracetamol was removed 7.06 % for 180 min irradiation times which indicates the sole-photolysis not effective. The degradation of paracetamol increases from 41.12 % to 56.5 % in addition of 0.05 g until 0.1 g TiO_2 as shown in Fig. 2. This data explained by the higher catalyst increases Titania surface area and active site for photon adsorption to produce oxidative species such as hydroxyl radical (HO•) which acts as paracetamol oxidant [17]. Moreover, in presence of 0.15 - 0.2 g catalyst decreases paracetamol degradation to be 50.65 % caused by the higher turbidity, light scattering, lower light penetration, and forming agglomeration [10, 24]. This condition inhibits active site for oxidation processes. The same phenomena is also reported by Vaiano on paracetamol degradation using TiO_2-graphite composites [25]. Therefore, the optimal catalyst dose used for next work is 0.1 g TiO_2.

The effect of initial concentration Paracetamol on degradation

Initial concentration of pollutant is one of important factor influencing the degradation percentage by

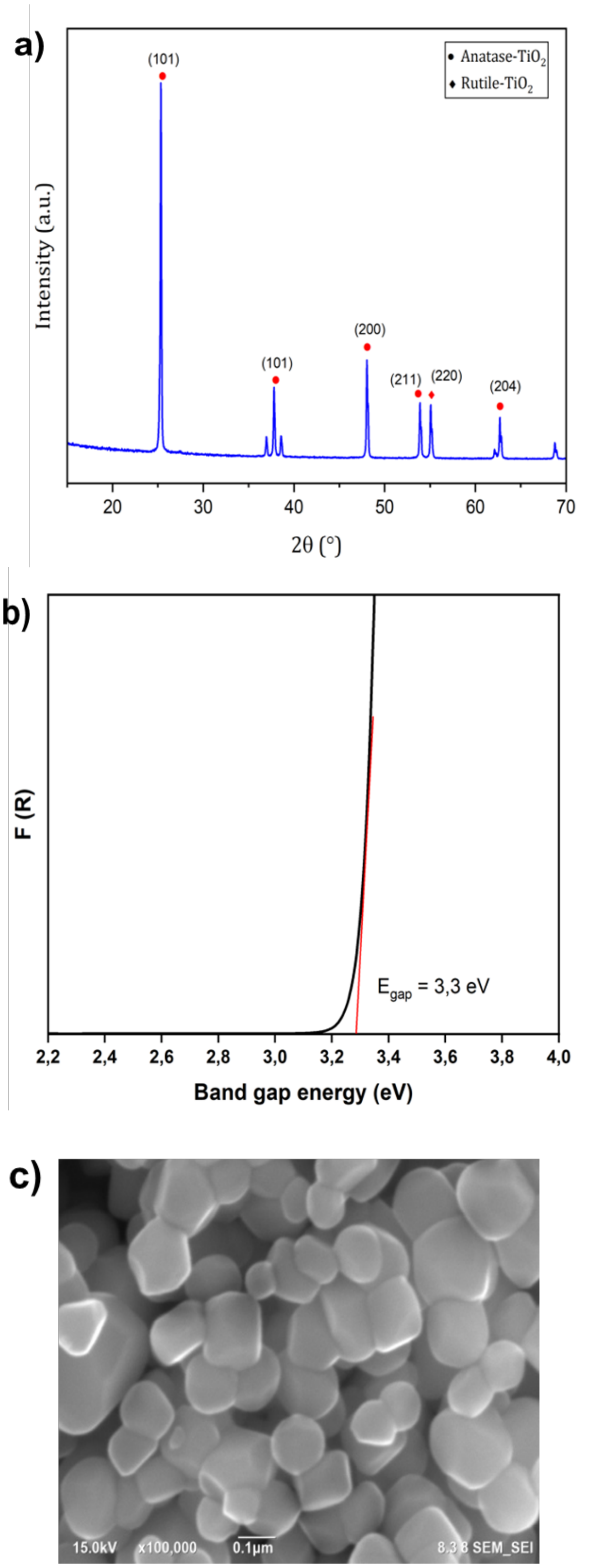

Fig.1. Characterization of calcined-low grade TiO_2 (a) XRD pattern, (b) band gap value, (c) SEM micrograph with 100 000 magnifications.

photocatalysis process. Paracetamol was varied 5 ppm, 10 ppm, 15 ppm and 20 ppm with constant catalyst dose (0.1 g) for 180 min irradiation. The degradation percentage decreases from 56.5 % to 15.58 % at higher paracetamol concentration as presented in Fig. 3. The probability reason of declining paracetamol degradation at higher concentration are blocking active sites of catalyst by more molecules reactant which decreasing the catalyst active sites [17] and decreasing light-penetration to the solution [25, 26]. The same trend is also obtained by Soremo on degradation of insecticide chlorpyrifos by photocatalysis ZrO_2-ZnO nanocomposite [13].

The effect of H_2O_2 concentration addition on paracetamol degradation

The addition of H_2O_2 concentration was 1 %, 3 %, 5 %, and 7 % to investigate the effect of H_2O_2 addition on paracetamol degradation efficiency under optimal photocatalysis TiO_2 process. Fig. 4(a) shows that the presence of H_2O_2 gives a positive effect on the paracetamol degradation for 30 - 180 min. photocatalysis. Paracetamol is degraded 56.5 % without H_2O_2 and increases remarkably to be 90.81 % at 3 % H_2O_2 addition. However, the degradation efficiency decreases at the higher H_2O_2 concentration addition and found the optimal H_2O_2 concentration is at 3 % addition. A similar observation was obtained in other organic pollutants [27 - 32].

The H_2O_2 functioned as electron acceptor to oxygen at optimal condition which prevents the recombination process in photocatalysis TiO_2 [18, 33]. While, it could be a powerful scavenger of hydroxyl radical (HO•) and forms a weaker oxidant (HO_2•) formation at excessive addition on photocatalysis system which results the reduction of paracetamol degradation [17, 28, 30, 34, 35] as exhibited in reaction 1 - 2.

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (1)$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2 \quad (2)$$

The effect of hydrogen peroxide addition on photocatalysis process was plotted to first order model. All kinetic parameters are shown in Table 1. The linearity value is near to 1 that indicates the process well fitted with the first-order model (Fig. 4(b)). The rate constant of 3 % H_2O_2 addition is the biggest value about

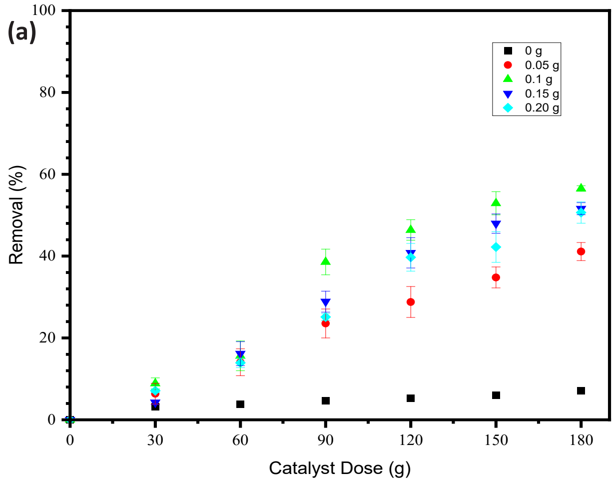

Fig. 2. The effect of catalyst dose on degradation [paracetamol = 5 mg L^{-1}, catalyst = 0.05 g - 0.20 g, t = 180 min, n = 3].

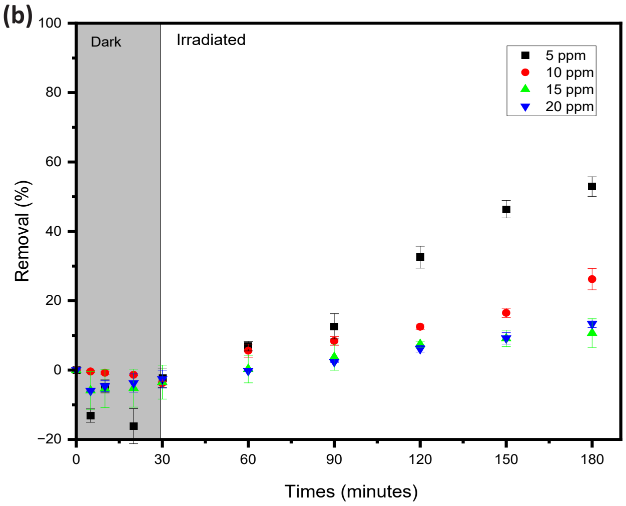

Fig. 3. The effect initial concentration of paracetamol on degradation [paracetamol = 5 - 20 mg L^{-1}, catalyst = 0.1 g, t = 180 min, n = 3].

Table 1. The kinetic rate of H_2O_2 concentration on paracetamol degradation.

H_2O_2 concentration (%)	k_{obs} (min^{-1})	SDV	(R^2)
1	0.0065	0.00035	0.9856
3	0.0143	0.00084	0.9828
5	0.0035	0.00058	0.8752
7	0.0003	0.00060	0.0004

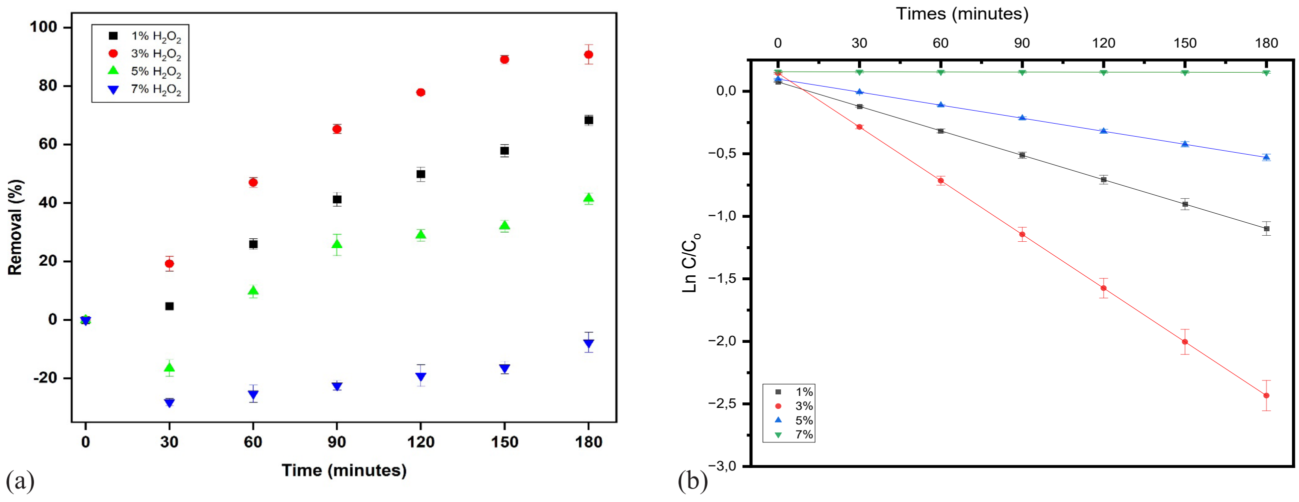

Fig. 4. (a) The effect of H_2O_2 concentration (b) first order model on degradation [paracetamol = 5 mg L^{-1}, catalyst = 0.1 mg, H_2O_2 = 1 % - 7 %, t = 180 min, n = 3].

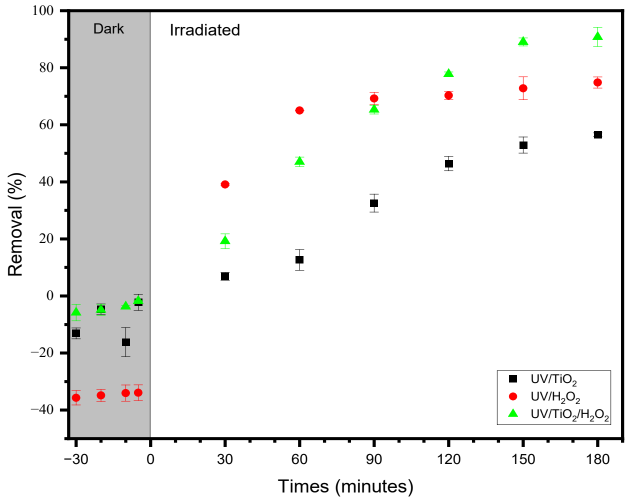

Fig. 5. The effect of hybrid process on degradation [paracetamol = 5 mg L^{-1}, catalyst = 0.1 mg, H_2O_2 = 3 %, t = 210 min, n = 3].

0.0143 min^{-1} and the shortest half-time ($t_{½}$ = 48.4718 min). This result proves that the optimal H_2O_2 addition gives positive effect on paracetamol degradation under photocatalysis process. The excessive H_2O_2 (5 % - 7 %) concentration retards the degradation rate with k_{obs} value about 0.0035-0.0003 min^{-1}.

The effect of hybrid process on paracetamol degradation

Fig. 5 shows a comparison of three processes namely; photocatalysis TiO_2 (UV/TiO_2), photolysis H_2O_2 (UV/H_2O_2), and hybrid process (UV/TiO_2/H_2O_2) on paracetamol degradation. The degraded paracetamol was 6.88 % - 56.5 % under photocatalysis TiO_2, 39.08 % - 74.83 % under photolysis H_2O_2, and 19.21 % - 90.81 % under hybrid process for 30 - 180 minutes irradiation. Based on the obtained results, the photocatalysis H_2O_2 process is better than photocatalysis TiO_2. The result explained by photocatalysis H_2O_2 process has a shorter reaction path than photocatalysis TiO_2 in producing hydroxyl radicals (HO•) as depicted in reaction 3. The same trend is reported by Song in diethyl phthalate oxidation [36]. In addition, peroxide is also an oxidizing agent. However, the paracetamol degradation efficiency increases insignificantly and remained constant (Fig. 5).

H_2O_2 + UV-irradiation → 2 HO•
(direct photolysis) (3)

The combination of the two processes was able to notably enhance paracetamol degradation even though the first 30 - 120 minutes was lower than photocatalysis H_2O_2 (Fig. 5). This is due to the combination system provides a synergistic effect in the formation of hydroxyl radicals. Peroxide will act as an electron catcher (in conduction band) of excited TiO_2 after irradiated by UV light. That condition is needed for preventing the electron-hole recombination process which leads to continuously produce the number of hydroxyl radicals and greater numbers of paracetamol are degraded. The source of HO• radicals in UV/TiO_2 / H_2O_2 system are (a) photocatalysis TiO_2; (b) hydrogen peroxide as an electron acceptor; (c) reaction of superoxide radicals and hydrogen peroxide; and (d) direct UV photolysis of H_2O_2 [19]. These results are consistent with those reported by Affam in pesticides degradation [37].

Kinetic of Paracetamol degradation by hybrid process

The kinetic rate of each processes on paracetamol degradation was determined by plotting to pseudo-first-order model as reported by Putri [26]. The kinetic parameters such as coefficient correlation (R^2), pseudo first orde rate (k_{obs}) and half-time (t½) are given in Table 2. All processes are well fitted with the first order which the coefficient correlation value is near 1 as illustrated in Table 2 and Fig. 6. The rate constant for UV/TiO_2/ H_2O_2 process is approximately 2.75 and 20.43-fold larger than the value obtained for UV/TiO_2 and UV/H_2O_2. This data demonstrates that the hybrid process gives synergy effect and accelerate the paracetamol degradation rate with the smallest half-time value (48.47 min).

Table 2. The kinetic rate of hybrid process on paracetamol degradation.

Process	k_{obs} (min)	SDV	(R^2)
UV/TiO_2	0.0052	0.0004	0.9653
UV/H_2O_2	0.0070	0.0015	0.8066
UV/TiO_2/ H_2O_2	0.0143	0.0008	0.9829

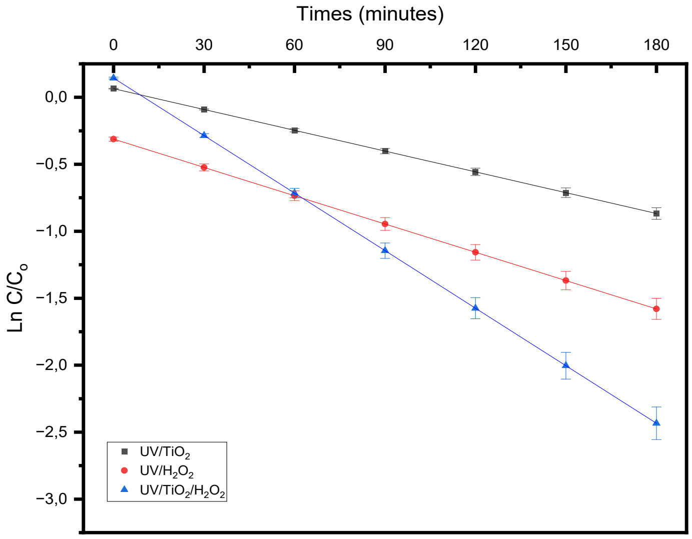

Fig. 6. The kinetic rate of hybrid process on paracetamol degradation [paracetamol = 5 - 20 mg L^{-1}, catalyst = 0.1 g, t = 180 min, n = 3].

Table 3. By-product of degraded paracetamol.

Retention Time (min)	Name of compound	Mr (g mol^{-1})
5.95	Butanamide	87.12
6.04	Isopropyl acrylate	114.14
6.04	2,4-dimethylpentane-3-ol	116.20
6.04	Glutaraldehyde	100.11
6.14	3-methoxybutan-1-ol	104.15
6.14	Octanamide	143.23
6.2	Propanol, oxime	73.09

By-product formed of degraded paracetamol

The formed by-products of the commercial paracetamol degradation are identified by GC-MS analysis and are represented in Table 3. The new by-products in this study are detected namely; butanamide, isopropyl acrylate 2,4-dimethylpentane-3-ol, glutaraldehyde, 3-methoxybutan-1-ol, octanamide, and propanol oxime. In general, this hybrid process degrades paracetamol and transformed by breaking the benzene ring to be simpler and less toxic compounds than paracetamol. The previous report describes the common by-product paracetamol formed by AOPs such as hydroquinone, 1,4-benzoquinone, 4-aminophenol, acetamide, oxalic acid, formic acid, acetic acid, 1,2,4-trihydroxybenzene, and maleic acid [38, 39]. Vogna found some by-products namely; 1,4-hydroquinone/1,4-benzoquinone, 4-acetylaminocatechol and 4-acetylaminoresorcine under direct photolysis H_2O_2 [40]. On the other hand, the compounds formed under photocatalysis TiO_2 were hydroquinone, monohydroxy paracetamol, dihydroxy paracetamol, fumaric and malic acid [41].

The different produced by-product is based on the process system, equipment used for detecting, the pH of solution and the sample condition. Ghanbari found the UV/ H_2O_2 and UV/Chlorine system produce different intermediates on paracetamol degradation [42]. The sample used in this study was in a commercial tablet form containing some components such as polyethylene glycol, propylene glycol, calcium stearate/magnesium stearate, starch, cellulose, sodium benzoate/sodium lauryl sulphate, hydroxypropyl methylcellulose, docusate sodium, and sodium starch glycolate [43] which also possibly contributes to form the different by-product paracetamol.

CONCLUSIONS

The effect of hydrogen peroxide on the TiO_2 photocatalytic system in the degradation of paracetamol has been studied. Optimal conditions were obtained when using 0.1 g TiO_2, 5 mg L^{-1} paracetamol concentration, addition of 3 % hydrogen peroxide with a total degradation percentage of paracetamol 90.81 % for 180 minutes irradiation under UV light. The presence of hydrogen peroxide to the photocatalytic system provides a synergistic effect and a positive impact. The photocatalytic H_2O_2 process produces a higher percentage of paracetamol degradation than photocatalysis TiO_2 and be constant at 90 - 180 min. The combined process (UV/ TiO_2/ H_2O_2) outperformed the highest values at longer degradation times. These data prove that the combined process produces more hydroxyl radicals which act as paracetamol oxidant. The GC-MS data verified that the hybrid process was able to remove paracetamol and form by-products.

Acknowledgments

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