Photo Degradation of Ketoprofen Using Titanium Dioxide as Catalyst

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Abstract

Research on the degradation of pure ketoprofen and tablets by means of photolysis using ultraviolet light and titanium dioxide catalysts has been performed. Ketoprofen and its degradation results were analyzed by ultraviolet spectrophotometers at 260 nm and high performance liquid chromatography. Degradation of ketoprofen is done by photolysis using ultraviolet A (366 nm) and ultraviolet C (254 nm) lamps using titanium dioxide (TiO_2) as catalysts at various concentrations, mass and time. The percentage degradation of pure ketoprofen and tablets using UV A photolysis method and TiO_2 15 mg as catalyst was 51.04 % and 48.11 %, respectively, after 180 min. The percentage degradation of pure ketoprofen and tablets using UV C photolysis method and TiO_2 15 mg as catalyst was 91.08 % and 89.11 %, respectively, after 120 min. The results showed that photolysis method with UV C was better to degrade ketoprofen than UV A with the addition of TiO2 as catalyst. The residual analysis of ketoprofen was performed by high performance liquid chromatography using C18 column (150 mm x 4.6 mm), the mobile phase was acetonitrile: 0.2 % acetic acid (45: 55), the flow rate was 1.2 mL / min. Chromatogram showed a decrease in peak ketoprofen and the emergence of new peaks during ketoprofen degradation process.

Keywords: ketoprofen, photolysis, ultraviolet A, ultraviolet C, titanium dioxide

1. Introduction

Pharmaceutical residue has been identified as potential contaminants in aquatic environments with a variety of water pollutants worldwide (Sacher *et al.*, 2008; Richardson *et al.*, 2005; Kolpin *et al*., 2002; Yang *et al*., 2010). Pollution by drugs increases sharply with continuous drug use over the years. Drug consumption rates are rising in the United States, Japan, France, Spain, Britain and Italy by 11.9 % annually. About 3000 compounds used as anti-inflammatory/analgesic drugs and antibiotics are the most commonly used drugs for therapy (Richardson *et al*., 2011).

The pharmaceutical industry uses active pharmaceutical ingredients (API) for the production of the desired drug. These drugs are pharmacologically active, but toxic in nature, resistant to degradation, chemically resistant to water media, harmful in water bodies and affecting living things (Chelliapan *et al.*, 2006). The drug compounds enter the stream of water from a number of sources such as the pharmaceutical industry, personal care products, hospital waste, therapeutic drugs, sewerage systems and the excretion of livestock (Deegan *et al.*, 2011). The presence of pharmaceutical compounds and their metabolites pose risks to the environment and humans (Kaur *et al*., 2016). Approximately 50 percent of pharmaceutical waste water produced worldwide is released into the environment without proper processing (Monteagudo *et al.*, 2013).

Lack of effectiveness of pharmaceutical waste treatment in the waters can pollute the environment. This fact has led to concerns about the safety of drinking water and the acoustic ecosystem. Therefore, active pharmaceutical ingredients (API) must be degraded so as not to pollute the aquatic environment. Many technologies for the degradation of organic wastes have been carried out among them advanced oxidation processes (AOPs) (Shah *et al*., 2013; Aguinaco *et al*., 2012).

Ketoprofen is an active pharmaceutical compound widely used as a pain medication. This compound is difficult to dissolve in water because it has hydrophobic properties. It causes ketoprofen difficult to degrade in the aquatic bodies so that it will pollute the environment (Feng *et al*., 2014).

Degradation methods of ketoprofen ever performed include electro-Fenton method (Feng *et al*., 2014), UV/H_2O_2, O_3 and O_3/UV processes (Kim *et al*., 2009). Degradation methods with UV light have been done to degrade paracetamol and Direct Red 23-Direct Violet (Safni *et al.*, 2015). This degradation method shows that UV light can degrade organic compounds. Therefore, UV light degradation method is estimated to be used to degrade ketoprofen. In this study the degradation of ketoprofen is carried out using UV-A and UV-C with the addition of titanium dioxide as catalyst.

2. Material and Method

2.1 Material

The chemicals used are pure ketoprofen (Merck), Ketoprofen Tablet (Dexa Medica), distilled water (Brataco), acetic acid (Brataco), acetonitrile HPLC grade (Merck), 96 % ethanol (Brataco), titanium dioxide catalyst.

2.2 Equipment

Double Beam Spectrophotometer (Shimadzu UV 1800), High Performance Liquid Chromatography (Hitachi-Trimaide), Sonication Devices (Bronson 1800), Analytical Scales (Precisa XB 220A), Centrifuge (Centrifuge 80-2), UV Betracher 3 Lamp (Camag) λ = 366 nm and λ = 254 nm 10 watts. Pulse pipette, magnetic stirrer, vortex and other glassware.

2.3 Procedure

2.3.1 Measurement of ketoprofen absorption spectra

The pure ketoprofen substance was weighed as much as 0.0250 g and dissolved in 25 mL of mixture comprising distilled water and ethanol (1: 5) to obtain 1000 mg/L ketoprofen solution. The mother ketoprofen 1000 mg/L solution was diluted to 100 mg/L. The ketoprofen 100 mg/L solution was diluted to 10 mg/L and measured its absorbance by an ultraviolet spectrophotometer.

2.3.2 Degradation of ketoprofen without catalyst

2.3.2.1 The effect of duration of irradiation with UV-A and UV-C on ketoprofen degradation

A total of 10 mL of each ketoprofen solution of 4, 6, 8, 10 and 12 mg/L were fed into 5 petridish. These solutions are irradiated with UV A and UV C rays for 30, 60, 90, and 120 min. The absorption of each solution was measured by an ultraviolet spectrophotometer at a wavelength of 260 nm.

2.3.2.2 Determination of optimum concentration of ketoprofen degradation

The ketoprofen solution of concentrations of 2, 4, 6, 8 and 10 mg / L was degraded using UV-A and UV-C light during degradation time. Absorption is measured at a wavelength of 260 nm. The optimum concentration is determined from the concentration having the greatest percentage of degradation.

2.3.3 Degradation of ketoprofen by the addition of titanium dioxide as catalyst

2.3.3.1 Determination of the maximum number of catalysts

The 10 mg/L ketoprofen solution was added each 10 mL in 5 petridish and added titanium dioxide catalysts to each solution of 5, 10, 15, 20, and 25 mg. Each solution was degraded and centrifuged for 15 minutes at a rate of 1000 rpm. The absorption of each solution was measured by an ultraviolet spectrophotometer at a wavelength of 260 nm.

2.3.3.2 The effect of duration of irradiation with UV-A on ketoprofen degradation

A total of 10 mL of 10 mg / L ketoprofen solution was incorporated into 5 petridish and each of these solutions added 15 mg of titanium dioxide catalyst. This solution was degraded with UV light (λ = 366 nm) for 30, 60, 90, 120, 150 and 180 min, then centrifuged for 15 min. The absorption of each solution was measured by an ultraviolet spectrophotometer at a wavelength of 260 nm.

2.3.3.3 The effect of duration of irradiation with UV-C on ketoprofen degradation

A total of 10 mL of 10 mg/L ketoprofen solution was incorporated into 5 petridish and each of these solutions added 15 mg of titanium dioxide catalyst. This solution was degraded with UV light (λ = 254 nm) for 30, 60, 90, 120, 150 and 180 min, then centrifuged for 15 min. The absorption of each solution was measured by an ultraviolet spectrophotometer at a wavelength of 260 nm.

2.3.4 Analysis of residual solution with HPLC

Pure ketoprofen and tablet ketoprofen were degraded with UV-A and UV-C light and with the addition of titanium dioxide as catalyst. The remaining solution was analyzed by HPLC. This solution was piped 5 mL, filtered with 0.2 µm polytetrafluoroethylene (PTFE) membrane and injected into HPLC 20 µL. The column used was C18 (150 mm x 4.6 mm), the mobile phase was acetonitrile: 0.2 % acetic acid (45: 55), flow rate 1.2 mL/min, injection volume 20 µL, wavelength 260 nm , and at room temperature (Illés et al., 2012)

3. Results and Discussion

3.1 Spectrum of Ketoprofen Absorption

The ketoprofen solution was prepared with a concentration of 10 mg/L in distilled water. The measurement of the absorption spectrum was performed using a double beam spectrophotometer at wavelengths between 200 - 400 nm. Figure 1 shows that the ketoprofen

absorption spectrum has a maximum absorption peak at 260 nm wavelength and absorbance of 0.493.

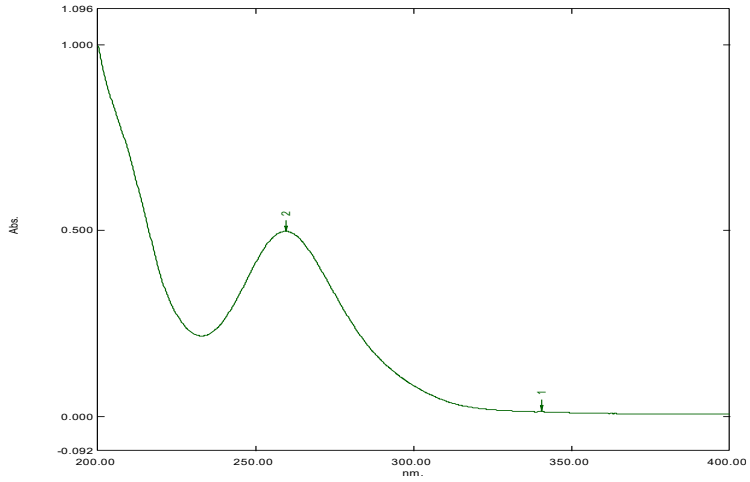

Figure 1: The ketoprofen absorption spectrum at a concentration of 10 mg/L

3.2 The optimum concentration of ketoprofen in the degradation process

Determination of ketoprofen optimum concentration was done at 4, 6, 8, 10 and 12 mg/L concentrations using UV A (366 nm) and UV C (254 nm) photolysis method respectively 120 min. The optimum concentration is determined from the concentration having the greatest percentage of degradation. The results can be seen in Figure 2.

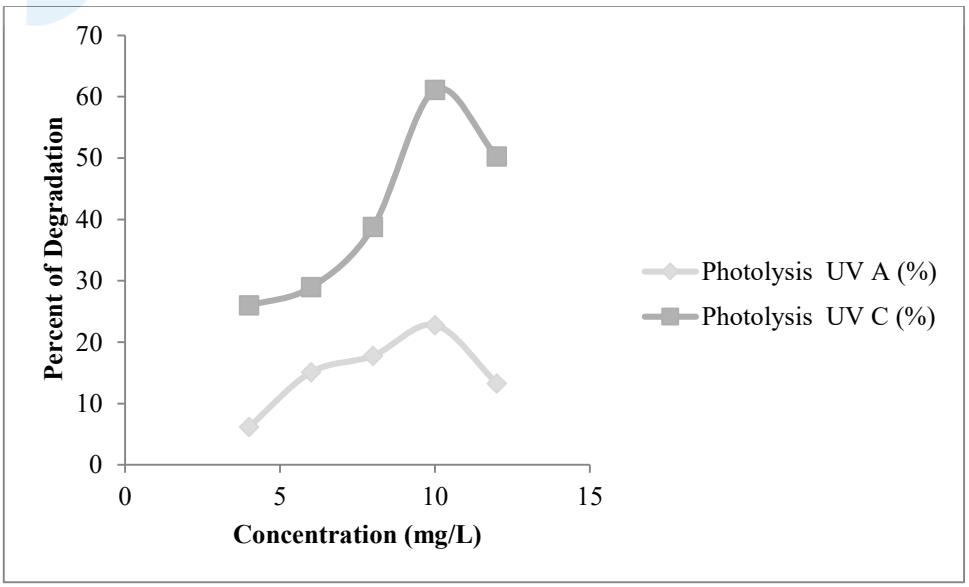

Figure 2: Effect of concentration on ketoprofen degradation percentage

Both methods showed the largest percentage of degradation at concentrations of 10 mg/L. The percentage of photolytic degradation of ketoprofen with UV-A light was 22.75 % and with UV-C was 61.12 %.

3.3 Determination of the number of optimum titanium dioxide catalysts

Determination of optimum catalyst amount was done with UV-A and UV-C light photolysis for 120 min. Each 10 mg/L ketoprofen solution of 10 ml was added catalysts of 5, 10, 15, 20 and 25 mg, and then degraded by photolysis. The results can be seen in Figure 3.

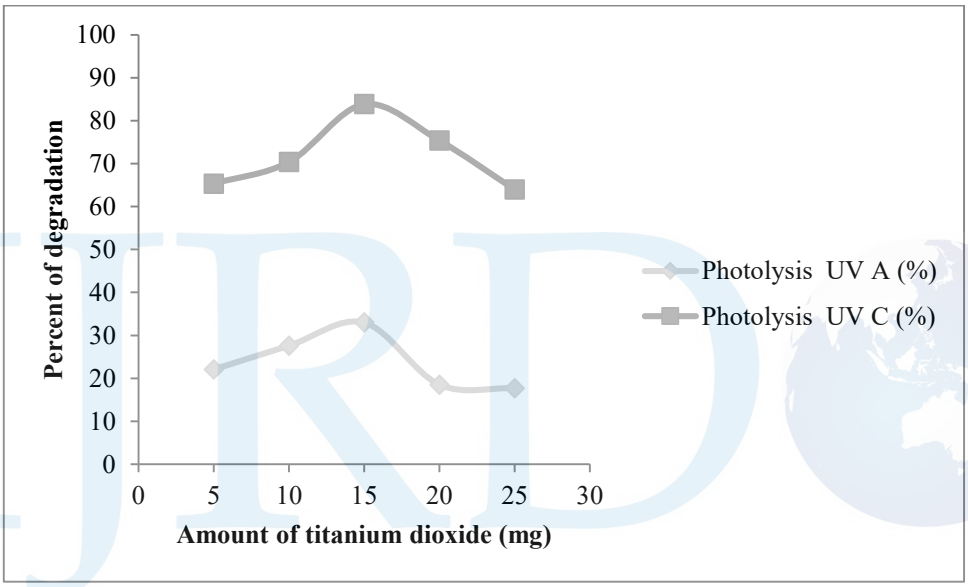

Figure 3: Effect of amount of titanium dioxide catalyst on percentage degradation of 10 mg/L ketoprofen solution by photolysis of UV-A and UV-C light for 120 minutes

Figure 3 shows that the percentage of degradation increases with the increase in the amount of catalysts, as the amount of ketoprofen absorbed more and more on the surface of the catalyst. The optimum amount of catalysts was shown at 15 mg, and there was a decrease at the time of addition of 20 mg of catalyst. Decreasing the percentage of degradation due to the catalysts administered in large quantities will make the solution become saturated and turbid, thereby decreasing the efficiency of degradation. This is due to the increase in the number of catalysts so that the turbidity of the solution is increased thereby reducing the

continued light for the degradation process (Neppolion et al., 2003). The percentage of ketoprofen degradation with the addition of 15 mg catalyst on UV-A light photolysis was 32.99 % and UV-C was 82.49 %.

3.4 The effect of duration of irradiation with UV-A on ketoprofen degradation

Degradation by UV-A irradiation was performed using a 366 nm UV lamp source. The effect of duration of UV-A irradiation on the degradation of ketoprofen without and with the addition of titanium dioxide catalyst can be seen in Figure 4.

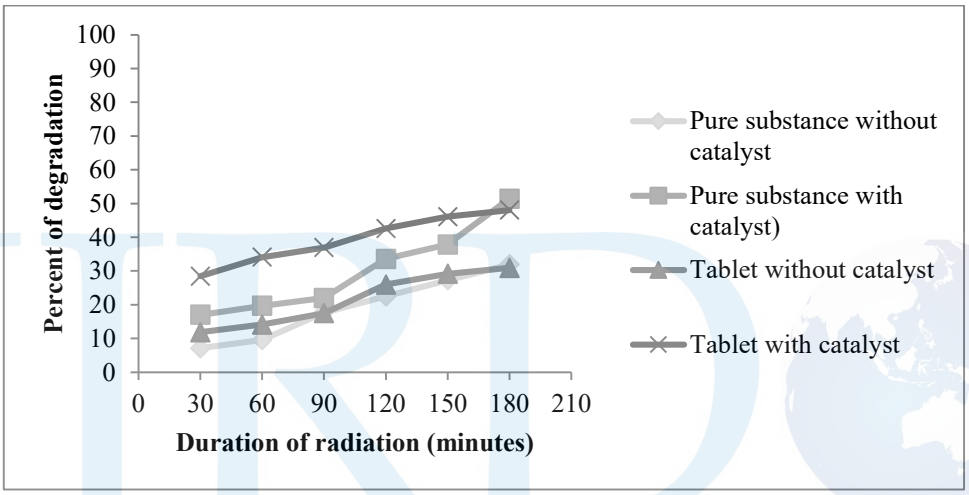

Figure 4. Effect of duration of irradiation with UV-A on persent degradation of pure ketoprofen solution and tablet ketoprofen without catalyst and with titanium dioxide catalyst

Figure 4 shows that the longer the irradiation times the greater the percentage degradation of ketoprofen tablets as the number of ·OH is formed more and more. Percentage degradation of pure substance without catalyst and with catalyst was 31.90 % and 51.40 % for 180 min, respectively. The percentage degradation of ketoprofen tablets without catalyst and with catalyst were 30.92 % and 48.06 % for 180 min, respectively.

3.5 The effect of duration of irradiation with UV-C on ketoprofen degradation

Degradation by UV-C irradiation was performed using a 254 nm UV lamp source. The effect of the duration of radiation on the degradation of ketoprofen with and without titanium dioxide catalyst is shown in Figure 5 below.

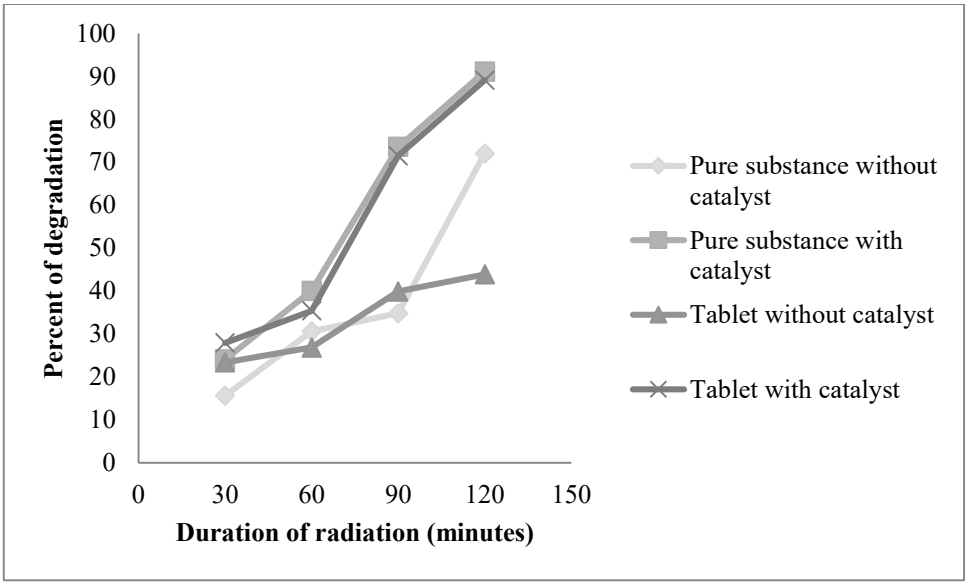

Figure 5. Effect of duration of irradiation with UV-C on the percentage of degradation

Figure 5 shows that the longer the irradiation time the greater the percentage degradation of ketoprofen tablet compound because the amount of ·OH is formed more and more. Percentage degradation of pure substance without catalyst and with catalyst addition was 72.05 % and 91.08 % for 120 min, respectively. The percentage degradation of ketoprofen tablets without catalyst and with catalyst were 43.92 % and 89.11 % for 120 min, respectively.

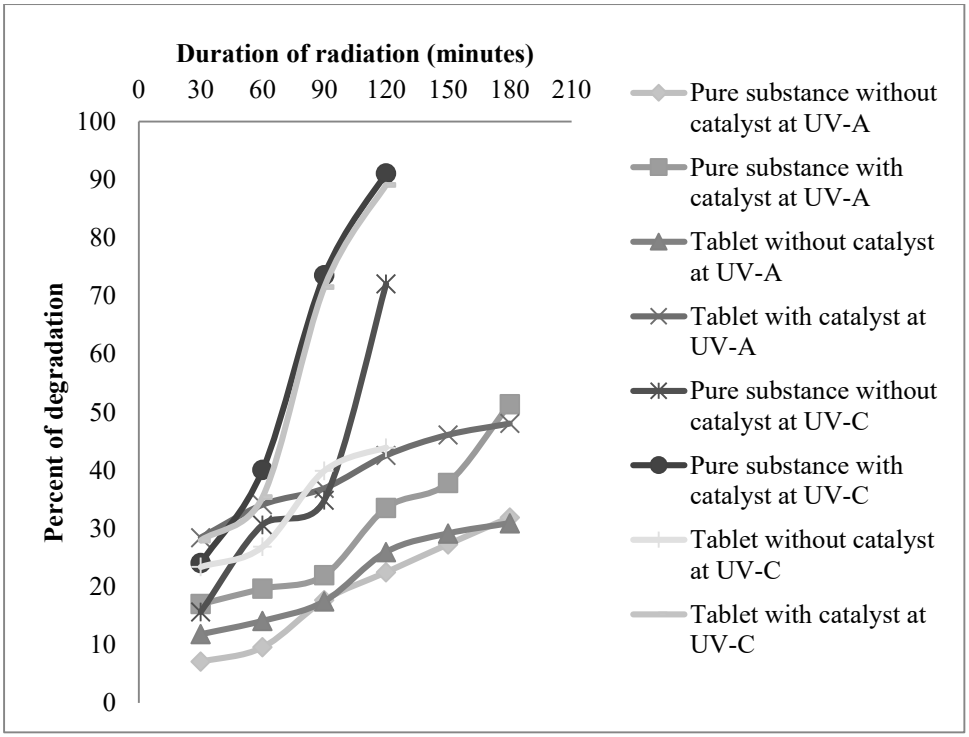

Figure 6: Comparison of percentage degradation with UV-A and UV-C light for pure substances and ketoprofen tablets with and without titanium dioxide catalyst

Figure 6 shows that the largest percentage of degradation in UV-C light photolysis with a 254 nm light source is greater than that of UV-A light photolysis with a 366 nm light source. This is because the wavelength of UV-C is shorter than the wavelength of UV-A so that its energy is bigger. Greater energy will speed up the degradation process.

The ability to degrade pure ketoprofen and tablets with the addition of titanium dioxide catalyst reached 51.40 % and 48.06 % in UV-A and 91.03 % and 89.11 % in UV-C. The degrading ability of pure ketoprofen is greater than that of tablet ketoprofen. This is because ketoprofen tablets contain other substances such as polymers that will inhibit the degradation process.

3.6 Analysis of residual solution with HPLC

Pure ketoprofen and tablets degraded with UV-A and UV-C light using titanium dioxide catalyst were analyzed with High Performance Liquid Chromatography (HPLC) before and after degradation.

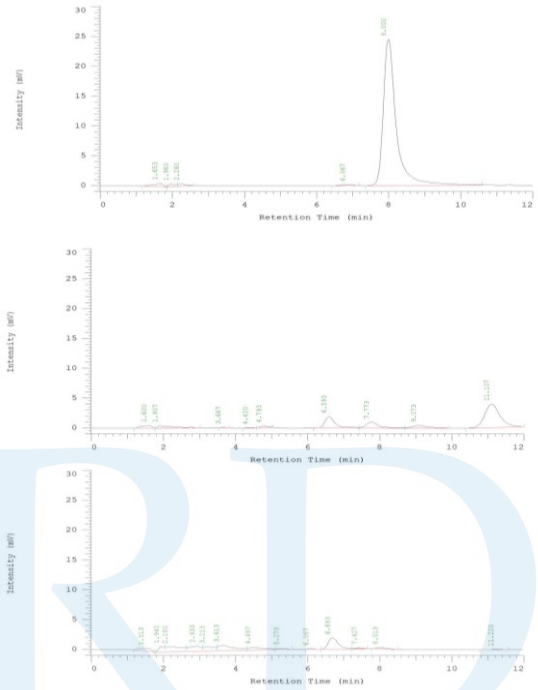

Figure 7: Chromatogram of residual solution of pure ketoprofen degradation with UV-A and UV-C light

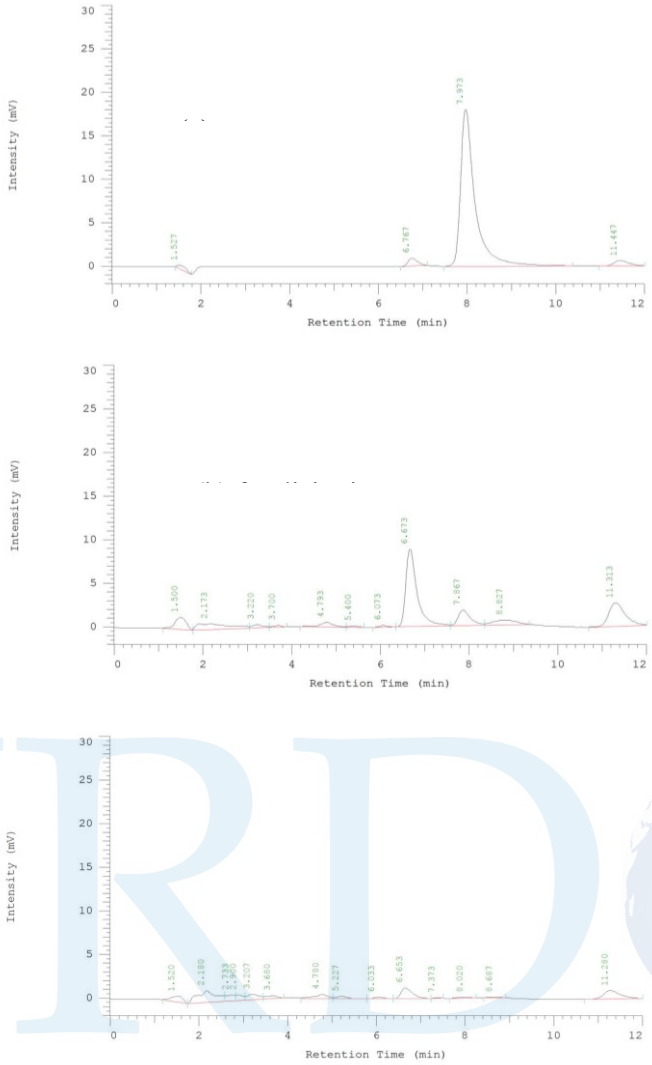

Figure 8: Chromatogram of residual solution of ketoprofen tablet degradation with UV-A and UV-C light

The chromatograms in Figs 7 and 8 show a decrease in peak area due to increased degradation time. There is one peak in the initial solution of ketoprofen at the time of retention (tR) 6 minutes. The presence of a peak in a pure solution of ketoprofen signifies that in ketoprofen solution there is no mixture of other substances. Residual solution on photolysis with UV-A light at 6th and 9th minutes showed some new compounds marked by the appearance of a new peak. Residual solution on photolysis with UV-C light also shows a new

peak at different retention times. Peaks that appear in the 2nd minute and the 7th minute indicate the presence of new compounds formed during the degradation process.

From the above data it can be concluded that percent degradation of ketoprofen by the addition of titanium oxide catalyst is better than without catalyst. This occurs because of the excitation, so that the UV rays on titanium dioxide cause the electrons in the excited catalyst from the valence band to the conduction band to produce a hole in the valence band and the conduction band. This catalyst reacts with oxygen to produce superoxide ions ($O_2^{\bullet -}$), then reacts with water to form OH• which breaks the bond and produces a simpler compound (Attia et al., 2008).

4. Conclusion

Based on this research, it can be concluded that photolysis method with UV-C light is better used to degrade ketoprofen than photolysis method with UV-A light. The percentage degradation of pure ketoprofen and tablets by UV-C light photolysis using titanium dioxide catalyst was 91.08 % and 89.11 %, respectively, after 120 min, while photolysis with UV-A ray was 31.90 % and 51.40 %, respectively, after 180 minute. Chromatogram shows the decrease of peak and the emergence of new compounds during ketoprofen degradation process.

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