

# The Study of Semiconductor Photocatalyzed Oxidation of Beta-Hydroxypropanoic Acid is Bening a Mediator of Variety of Industrial Chemicals

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**Abstract:** Utilising semiconductor photocatalysis, a "green" method, has been widely used to remove environmental contaminants, including organic pollutants found inside and soluble hazardous materials found in waste water<sup>1,3</sup>. Due to its low cost, photo stability, chemical and biological inertness, and resistance to both chemical and photo corrosion, TiO<sub>2</sub> is the most widely used photocatalyst. It is known that organic contaminants in waste water can degrade into CO<sub>2</sub> and H<sub>2</sub>O in aqueous conditions, but that the organic compounds can also be selectively oxidised into fine chemical products rather than completely mineralized in aqueous conditions, dry organic solvent, controlled pH, irradiation time, by using visible or UV light, etc.<sup>4,5</sup>. 3-Hydroxypropanoic acid (3-HPA) is an organic molecule with three carbons and two functions. It is categorised as an  $\omega$ -hydroxyl-aliphatic carboxylic acid and has been found to be a powerful new generation chemical intermediate. In terms of the primary strategic building blocks derived from biological resources, it is ranked third<sup>6</sup>. Because of its dual activity, it can be transformed into a variety of high-value compounds, such as polyesters, acrylic acid, propiolactone, and poly-3-HPA<sup>7</sup>. Through straightforward chemical reactions, these are used in the creation of adhesives, fibres, and resins. It can then selectively oxidise 3-HPA to produce malonic acid (MA) and its byproducts, which together account for a sizable market. Three-hydroxypropionic acid, the polymer used in polyester, degrades biologically<sup>9</sup>. Therefore, research on the photocatalytic action of TiO<sub>2</sub> sensitised on 3-hydroxypropionic acid is planned. The generated photo-product was separated into its derivatives, which were then examined using the proper spectral or other methodologies. Thus, this portion of the published work may stimulate chemists' and chemists' interest in multidisciplinary research.

**Keywords:** Beta hydroxypropanoic acid (BHP), Titanium dioxide, Semiconductor, Photo-oxidation

## 1. Introduction

Semiconductor photocatalytic process has been widely applied as a "green" technology in treating environmental contaminants, such as the removal of the indoor organic pollutants and degradation of the soluble hazardous material in waste water<sup>1,3</sup>. Due to its low cost, photo stability, chemical and biological inertness, and resistance to both chemical and photo corrosion, TiO<sub>2</sub> is the most widely used photocatalyst. It is known that organic contaminants in waste water can degrade into CO<sub>2</sub> and H<sub>2</sub>O in aqueous conditions, but that the organic compounds can also be selectively oxidised into fine chemical products rather than completely mineralized in aqueous conditions, dry organic solvent, controlled pH, irradiation time, by using visible or UV light, etc.<sup>4,5</sup>.

3-Hydroxypropanoic acid (3-HPA) is a bifunctional, three-carbon organic molecule that has been identified as a potent new generation chemical intermediate. It is classed as  $\omega$ -hydroxyl-aliphatic carboxylic acid. In terms of the primary strategic building blocks derived from biological resources, it is ranked third<sup>6</sup>. Its dual purpose allows it to be transformed into a variety of high-value compounds, such as polyesters, acrylic acid, propiolactone, and poly-3-HPA<sup>7</sup>, they are used in the straightforward chemical processes that create adhesives, fibres, and resins. It can then selectively oxidise 3-HPA to produce malonic acid (MA) and its byproducts, which together account for a sizable market. 3-Acrylic acid can be hydrated by a base and then reacidified to produce hydroxypropionic acid. In a different process, ethylene

chlorohydrin is first cyanated, and then the resultant nitrile is hydrolyzed. Another method is propiolactone hydrolysis<sup>8</sup>. As a  $\beta$ -hydroxy acid, 3-hydroxypropanoic acid (3-HP) is biochemically synthesised and utilised in the production of several industrial chemicals, particularly acrylic acid, its esters, and their polymers. Three-hydroxypropionic acid, the polymer used in polyester, degrades biologically<sup>9</sup>.

3-HPA is still an uncommon and expensive chemical that is only sold as an aqueous solution by a few number of providers, despite significant research efforts. Through biological processes, 3-hydroxypropanaldehyde, glucose, and glycerol have been converted into 3-HPA<sup>10,11</sup>. Through a specific oxidation and hydration process, allyl alcohol can benefit 3-HPA<sup>12,13</sup>. The synthesis of 3-HPA has also been documented in patent literature derived from vinyl acetate<sup>16</sup>, 3-hydroxypropanaldehyde<sup>15</sup>, and  $\beta$ -propiolactone<sup>14</sup>. Another patent demonstrates that acrylic acid can react with water to produce 3-HPA through hydration<sup>17</sup>. Using a lot of NaOH and high O<sub>2</sub> pressures, Behr et al. demonstrated an intriguing process for producing 3-HPA from 1,3-propanediol (1,3-PD), an aliphatic diol, by selectively oxidizing it over bi- and tri-metallic catalysts based on Pt and Pd<sup>18</sup>. When using such a "non-green" chemical method, products such as sodium salts are formed, and extra energy is needed to get 3-HPA in a Na-free form. For the purpose of producing 3-HPA, a new green strategy must be developed.

A  $\beta$ -hydroxy acid, 3-hydroxypropanoic acid (3-HP) is biochemically synthesized and is a common building block for several industrial compounds, most notably acrylic acid,

its esters, and related polymers. 3-hydroxypropionic acid, the polymer used in polyester, degrades biologically<sup>19</sup>.

The technique combines the commercially available beta hydroxy acid 3-hydroxypropionic acid (3-HPA), with the high molecular weight and control characteristics of ring-opening polymerization. Because 3-hydroxypropionic acid, or Poly (3-HPA), may be obtained from biological sources, the resultant substance is bio-renewable. With a hydroxyl group on its third carbon atom, 3-hydroxypropionic acid (3-HP) is a non-chiral carboxylic acid with great potential as a platform compound to generate a wide range of other compounds, including 1,3-propanediol (Kim, Kim, Park, & Seo, 2014). The US Department of Energy recognized 3-HP as one of the top value-added compounds made from biomass in 2010 (Bozell & Petersen, 2010).

We consume a lot of organic compounds in many aspects of our daily lives without realizing the negative effects they have on life and the environment. Although this is a pretty generic study, it does indicate that we should be mindful of these negative effects. This endeavor might lead us to adopt an interdisciplinary approach when it comes to pertinent researchers, such as nutritionists, dermatologists, chemists, and chemists. For chemists to gain a deeper understanding of these novel advanced oxidation processes, they should find the mechanistic aspect of photochemical reactions useful. Additionally, this study will make it possible for other researchers' previously reported work.

Malonic acid<sup>20</sup> is the photoproduct of in this study and it is a naturally occurring substance found in many fruits and vegetables.<sup>21</sup> There is a suggestion that citrus fruits produced in organic farming contain higher levels of malonic acid than fruits produced in conventional agriculture.<sup>22</sup> Malonic acid reacts as a typical carboxylic acid: forming amide, ester, anhydride, and chloride derivatives<sup>23</sup>. Malonic anhydride can be used as an intermediate to mono-ester or amide derivatives, while malonyl chloride is most useful to obtain diesters or diamides. In a well-known reaction, malonic acid condenses with urea to form barbituric acid. Meldrum's acid, a flexible intermediate in subsequent transformations, can also be formed by condensing malonic acid with acetone. In the synthesis of malonic ester, the esters of malonic acid are also employed as a -CH<sub>2</sub>COOH synthon.

Under mild circumstances, malonic acid is utilized to introduce an acetic acid moiety through Knoevenagel condensation and subsequent decarboxylation. Examples include the creation of 3,4,5-trimethoxycinnamic acid, the essential intermediary of the vasodilators cinpezat and cinpezide, and cinnamic acid, which is used to produce the anti-inflammatory cinmetacin. Knoevenagel condensation of malonic acid with heptaldehyde and ring closure yields the scent gamma-nonanoic lactone<sup>24</sup>.

To enhance the mechanical qualities of potato and maize starches, malonic acid can be utilized as a cross-linking agent<sup>25</sup>. Usually, the hydrolysis of cyanoacetic acid or the acid saponification of malonates yield malonic acid. The ozonolysis of cyclopentadiene, the air oxidation of 1,3-propanediol catalysed by palladium, the oxidation of 3-

hydroxypropanoic acid by platinum group metals, and the use of malanonitrile as a substrate for a nitrilase are other, more recently reported methods for the preparation of malonic acid.

It has been noted that green wheat plants and lucerne leaves both contain malonic acid. This acid has been widely used in studies on the tricarboxylic acid cycle and is well known for being a competitive inhibitor of succinic dehydrogenase<sup>26</sup>. It is employed in the scent business as well as in flavors. To improve the mechanical qualities of corn flour and potato starch, it is utilized as a cross-linking agent. The diethyl ester of malonic acid (HOOCCH<sub>2</sub>COOH), a dibasic organic acid, is utilized in the synthesis of barbiturates, vitamins B1 and B6, and many other important substances. Malonic acid itself has few uses and is rather unstable. Beetroot has its calcium salt, however the acid is often made by hydrolyzing diethyl malonate. It easily splits into acetic acid and carbon dioxide in addition to going through the typical processes that carboxylic acids go through.

Ethyl alcohol and cyanoacetic acid combine to produce diethyl malonate, or CH<sub>2</sub>(COOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, commonly known as malonic ester. The reactivity of its methylene (CH<sub>2</sub>) group makes it useful in synthesis; a hydrogen atom can be removed from it with ease using sodium ethoxide or another strong base, and the resultant derivative reacts easily with an alkyl halide to generate a diethyl alkylmalonate. In a similar manner, a second alkyl group might be added. Barbiturates are created by reacting the diethyl dialkylmalonates with urea. At 181.4°C, diethyl malonate boils as a fragrant, colorless liquid.

## 2. Experimental

The organic components include ninhydrin, titanium oxide, tungsten oxide, iron oxide, zinc oxide, cadmium sulphide, stannic oxide, copper oxide, 3-hydroxypropionic acid, Silica gel-G, and Resublimed Iodine (sm).

Thin layer chromatography and paper chromatography kits for determining the progress of reaction, pH meter (Eutech pH 510), conductivity meter (Systronic), spectrophotometer (Systronic), tungsten filament lamps 2 X200 W (Philips) for visible light, 450 W Hg-arc lamp, water shell to filter out IR radiations and to avoid any thermal reaction, and I.R. spectrometer (Perkin-Elmer Grating-377) was utilised together with a UV chamber with UV tube (30 W) (Philips).

The 3-hydroxypropionic acid solutions are prepared in water as the required concentrations as mentioned in the Tables. The required concentration of semiconductor or mixed semiconductors has been added to the reaction mixture for heterogeneous photocatalytic reactions. Variations were made to obtain the optimum yield of photoproducts.

Thin layer chromatography, using ninhydrin or resublimed iodine (sm) chamber as the eluent for spot test detection and silica gel-G as an adsorbent, was employed to track the reaction's progress at various time intervals. A slide spot detector with a UV chamber (Chino's) was used to identify colourless spots. After the reaction or process was completed, the photoproducts were separated as their salts,

and by making the right derivatives, they could be recognized using spectrophotometers, IR spectrometers, and NMR spectrometers. By waiting for the right amount of calcium salt malonic acid, the best yield is achieved.

### 3. Results and Discussion

#### 1) The effect of substrate

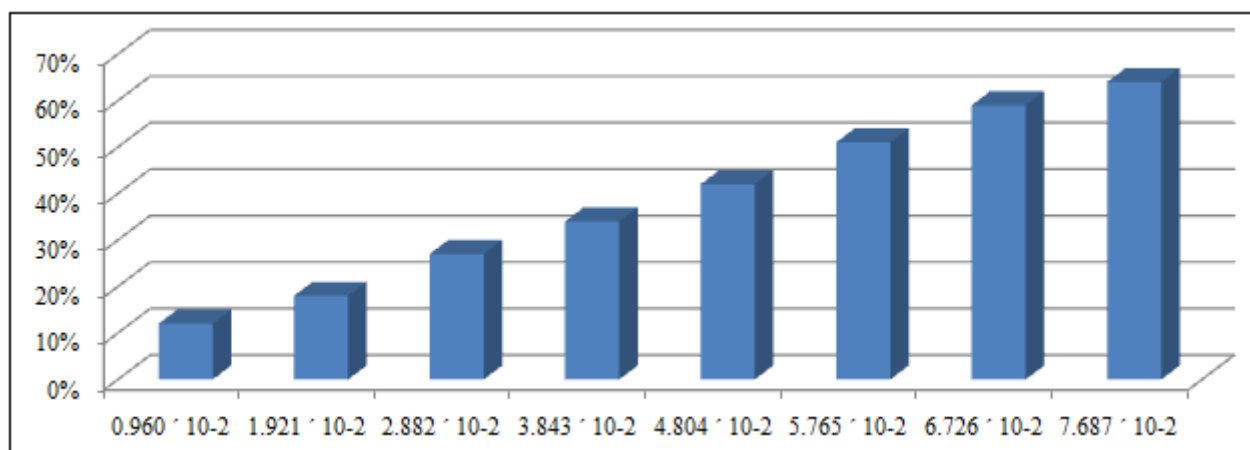
Effect of amount of substrate on the oxidation of 3-Hydroxypropandioic acid was studied at different

concentrations varying from  $0.960 \times 10^{-2}$  M to  $7.687 \times 10^{-2}$  M at fixed amount  $\text{TiO}_2$  ( $1.872 \times 10^{-2}$  M). The total volume of reaction mixture is 50 ml and the results are reported in the Table 1 and shown in Plot 1.

1. Solvent : Water
2.  $\text{TiO}_2$  :  $1.872 \times 10^{-2}$  M (1.50 g/L)
3. Irradiation time: 120 min
4. Visible light :  $2 \times 200$  W Tungsten lamps

**Table 1**

S. No.	Conc. Of Substrate (Beta-Hydroxy propandioic acid)	Percent yield of product (Malonic acid)
1	$0.960 \times 10^{-2}$	12%
2	$1.921 \times 10^{-2}$	18%
3	$2.882 \times 10^{-2}$	27%
4	$3.843 \times 10^{-2}$	34%
5	$4.804 \times 10^{-2}$	42%
6	$5.765 \times 10^{-2}$	51%
7	$6.726 \times 10^{-2}$	59%
8	$7.687 \times 10^{-2}$	64%



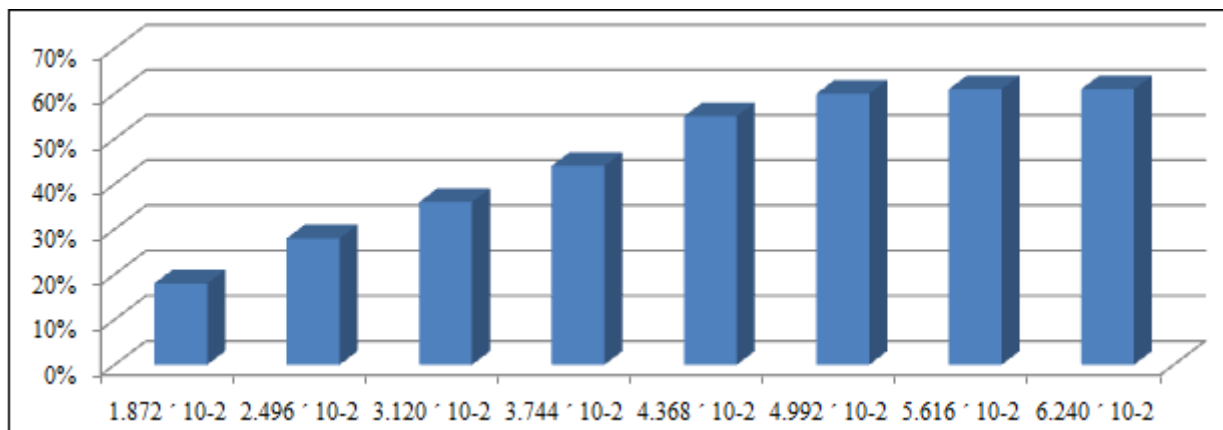
#### 2) The effect of Photocatalyst

Keeping all other factors identical the effect of amount of  $\text{TiO}_2$  has also been observed which were varied from 1.5 gms to 5.0 gms. The total volume of reaction mixture is 50 ml and the results are reported in the Table 2 and shown in Plot 2.

1. Solvent : Water
2. Beta-Hydroxypropandioic acid:  $4.804 \times 10^{-2}$  M (5.00 gm/Lt)
3. Irradiation time : 120 min
4. Visible light :  $2 \times 200$  W Tungsten lamps

**Table 2**

S. No.	Conc. Of Photocatalyst ( $\text{TiO}_2$ )	Percent yield of product (Malonic acid)
1	$1.872 \times 10^{-2}$	18%
2	$2.496 \times 10^{-2}$	28%
3	$3.120 \times 10^{-2}$	36%
4	$3.744 \times 10^{-2}$	44%
5	$4.368 \times 10^{-2}$	55%
6	$4.992 \times 10^{-2}$	60%
7	$5.616 \times 10^{-2}$	61%
8	$6.240 \times 10^{-2}$	61%



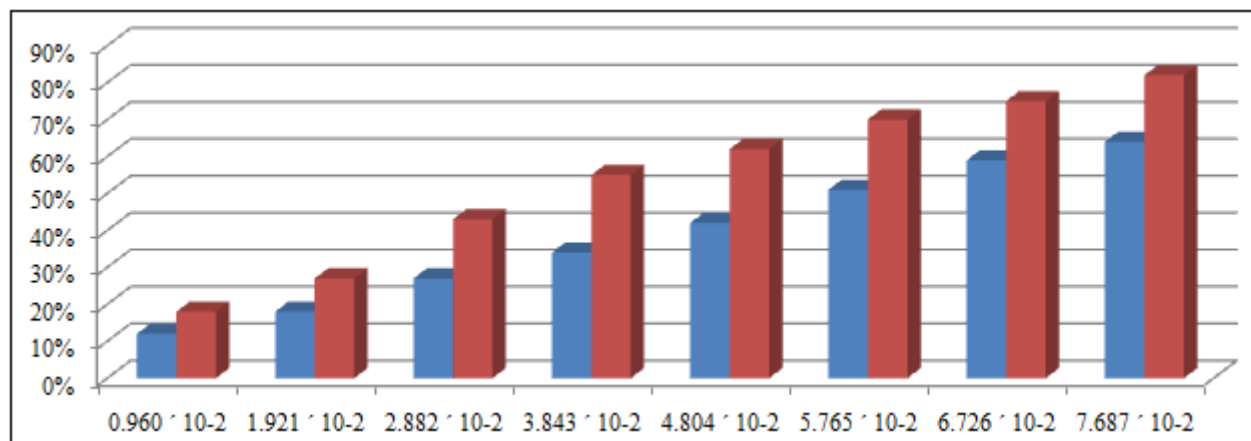
**3) The effect of type of Radiations**

The effect of type of radiations on photocatalytic reaction was studied in visible light and ultraviolet light keeping all other factors identical. The total volume of reaction mixture is 50 ml and the results are reported in the Table 3 and shown in Plot 3

1. Solvent : Water
2.  $\text{TiO}_2$  :  $1.872 \times 10^{-2}$  M (1.50 g/L)
3. Irradiation time : 120 min
4. Visible light :  $2 \times 200$  W Tungsten lamps
5. UV Light : UV Chamber 30 W (Philips Tube)

**Table 3**

S. No.	Conc. of Substrate (Beta-Hydroxypropandioic acid)	Percent yield of product (In visible light)	Percent yield of product (In UV light)
1	$0.960 \times 10^{-2}$	12%	18%
2	$1.921 \times 10^{-2}$	18%	27%
3	$2.882 \times 10^{-2}$	27%	43%
4	$3.843 \times 10^{-2}$	34%	55%
5	$4.804 \times 10^{-2}$	42%	62%
6	$5.765 \times 10^{-2}$	51%	70%
7	$6.726 \times 10^{-2}$	59%	75%
8	$7.687 \times 10^{-2}$	64%	82%



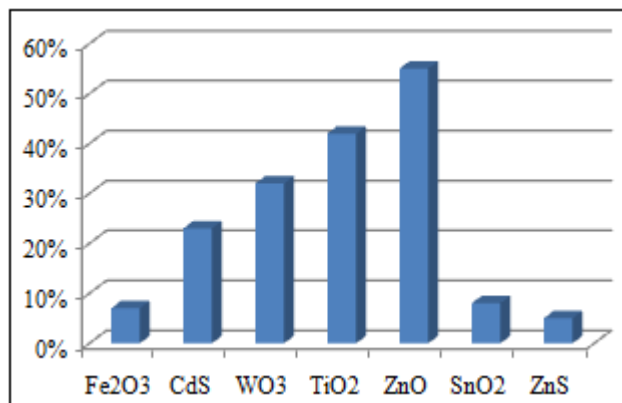
**4) The effect of Nature of Photocatalyst**

The effect of the nature of photocatalyst on photocatalytic reaction was studied by different photocatalysts, which are Ferric oxide, Cadmium sulphide, Tungsten oxide, Titanium oxide, Stannic oxide and Zinc sulphide. The total volume of reaction mixture is 50 ml and the results are reported in the Table 4 and shown in Plot 4

1. Solvent : Water
2. Beta-Hydroxypropandioic acid:  $4.804 \times 10^{-2}$  M (5.00 gm/l)
3. Irradiation Time : 120 min.
4. Visible Light :  $2 \times 200$  W Tungsten Lamps.

**Table 4**

S. No.	Photocatalyst	Band gap (eV)	Wavelength (nm)	Yield of Photoproduct
1	$\text{Fe}_2\text{O}_3$	2.2	564	07%
2	CdS	2.4	516	23%
3	$\text{WO}_3$	2.6	477	32%
4	$\text{TiO}_2$	3.1	400	42%
5	ZnO	3.2	388	55%
6	$\text{SnO}_2$	3.5	354	08%
7	ZnS	3.6	345	05%



The effect of amount of on the oxidation of Beta-Hydroxypropandioic acid (3-HPA) was studied by using variable amount of substrate, as reported in Table 1 and Plot 1. The highest efficiency was observed at optimum concentration. It may be explained on the basis that as the concentration of substrate increases, more substrate molecules are available for photocatalytic reaction and hence an enhancement on the rate was observed with increasing concentration of substrate.

The amount of photocatalyst on oxidation of Beta-Hydroxypropandioic acid (3-HPA) was investigated employing different concentrations of the TiO<sub>2</sub> as reported in Table 2 and Plot 2. It was observed that the yield of photo-product increasing with increasing catalyst level up to  $4.992 \times 10^{-2}$  M and beyond this, the yield of photo-product is constant. This observation may be explained on the basis that on the initial stage, even a small addition of photocatalyst will increase the yield of photoproduct as the surface area of photocatalyst increases, but after a certain amount  $4.992 \times 10^{-2}$  M, addition of photocatalyst do not affect the yield of product because of the fact that at this limiting amount, the surface at the bottom of the reaction vessel become completely covered with photocatalyst. Now increase in the amount of photocatalyst will only increase the thickness of the layer at the bottom. Keeping all the factors identical the effect of the nature of photocatalyst on the photo-oxidation of Beta-Hydroxypropandioic acid (3-HPA) was studied by using visible and UV light as shown in the Table 3 and Plot 3. As we know that the low band gap is more suitable for visible light and this property quite resembles the observed data as the table reported as more yield in UV light.

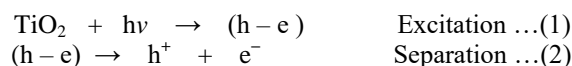
Titanium dioxide (TiO<sub>2</sub>) is the most common photocatalyst and comparably little research has been conducted on zinc oxide, ZnO, which could be a viable alternative for some applications. The effect of other semiconductor particle e.g. Fe<sub>2</sub>O<sub>3</sub>, CdS, WO<sub>3</sub> (having low band gap than TiO<sub>2</sub> semiconductor) on the TiO<sub>2</sub> catalyst photocatalytic reactions have also been studied. TiO<sub>2</sub> is the most frequently used photo catalyst because of its photo stability and low cost, combined with its biological and chemical inertness and resistant to photo and chemical corrosion. On the other hand, binary metal sulfide semiconductors such as CdS and PbS are regarded as insufficiently stable for catalysis and are toxic. ZnO is also unstable in illuminated aqueous solutions while WO<sub>3</sub> has been investigated as a potential photo catalyst, but it is generally less active catalytically than TiO<sub>2</sub>. However, these can be combined (Doping) with other

semiconductors including TiO<sub>2</sub> to achieve greater photo catalytic efficiency or stability. Keeping all the factors identical the effect of the nature of photocatalyst on the photo-oxidation of Beta-Hydroxypropandioic acid (3-HPA) was studied by using different photocatalysts as shown in the Table 4 and Plot 4

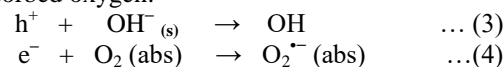
#### Mechanism

The following potential mechanistic portion has been suggested for the photocatalytic oxidation of beta-hydroxypropanoic acid based on the results and discussion, collaborating with the results previously reported for other researched compounds.

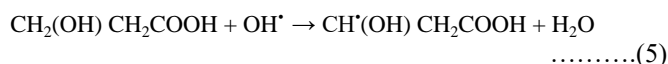
When it comes to a semiconductor oxide like TiO<sub>2</sub>, photocatalytic reactions start when light is absorbed that has an energy that is at least as great as the semiconductor's band gap. A positive hole is left in the valence band when an electron is promoted from the valence band to the conduction band in a titanium oxide solution exposed to visible light.



As previously mentioned, subsets of hydroxyls are retained on the high surface area of TiO<sub>2</sub>, where the net surface density is 4-5 hydroxyl per nm. Furthermore, a surface hydroxide ion is produced when TiO<sub>2</sub> is suspended in a solution of beta-hydroxypropanoic acid, which serves as a site for first photo-oxidation reactions. Photo holes are trapped by surface hydroxyl groups, whereas electrons are trapped by adsorbed oxygen:



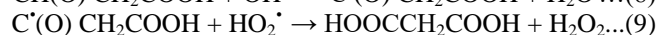
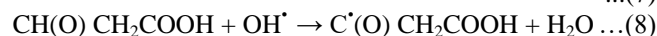
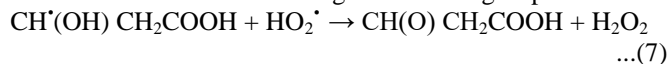
The formed OH<sup>•</sup> radicals are reacted with adsorbed on the surface, is reacted with the Beta-Hydroxypropanoic acid water to generate Beta-Hydroxypropanoic acid radical and water molecule, as follows:



The formed radicals are reacted with adsorbed on the surface, is reacted with the formed water to regenerate hydroxyl group on the surface of the catalyst:



Malonic acid formed according the following steps:



#### 4. Conclusion and Suggestions

Only the research of TiO<sub>2</sub>'s sensitized photocatalytic action on diluted beta-hydroxypropanoic acid in the presence of light and air is presented in this paper. The purpose of this study could be to draw attention to the potential reasons of the side effects that photoproducts may have, which could lead to a shared area of interest for relevant researchers such as chemists and chemists.

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