Study of Semiconductor Photocatalyzed Oxidation of Influential Chemical Gluconic Acid

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Abstract: ***The central point of this work is the metal catalyzed liquid phase photooxidation of gluconic acid in vary natural and normal conductions. Gluconic acid is a fine chemical which finds many industrial applications, mainly as water soluble cleansing agent, as food additive and beverages. Since it imparts a refreshing sour taste in many food items such as wine, fruit juices, etc. Similarly, sodium gluconate has a high sequestering power and it has a unique property of inhibiting bitterness in foodstuffs. Gluconic acid is also widely used in pharmaceutical industry particularly for the preparation of skin - care products, as an antioxidant, it is used precursor for the biosynthesis of ascorbic acid (Vitamin C), and medicinal chemistry for the synthesis of modified drugs. It is a highly valuable chemical and one of the organic building blocks of hyaluronic acid whose current worldwide market is estimated to be over $1 billion. Because of its potential application in environmental treatment and fine chemical synthesis photocatalysis has received enormous attention in recent few decades. Strong oxidation and reduction power of photo excited titanium oxide (TiO2) was realized with the discovery of Honda - Fujishima effect as in 1972, Fujishima et al. reported photo induced decomposition of water on TiO2 electrodes. In wasted water, under aqueous conditions, organic contaminants can be degraded into CO2 and H2O, whereas under dry organic solvent or controlled pH, irradiation time, by using visible or UV light etc.; the organic compounds may also be selectively oxidized into fine chemical products rather than complete mineralization. TiO2 P25 (70% anatase, 30% rutile) is the most employed photocatalytic semiconductor because of its chemical inertness, photostability, low cost, and non - toxicity. It is utilized as a desiccant, brightener, or reactive mediator in commercial products such as foods, paints, pharmaceuticals, drugs, and solar cells. Most of metal oxide which are being used as semiconductors in this study like titanium oxide, zinc oxides etc. are used as the base for these materials. As a food additive, TiO2 is approved for use in the EU, USA, Australia and New Zealand; it is listed by its INS number 270 or as E number E - 270. The US Food and Drug Administration permits up to 1% TiO2 as an inactive ingredient in food products. In this study it is believed that the gluconic acid may come in contact with titanium oxide or other metal oxide in the presence of sunlight and photooxidation may occur where the photo products can impact the human health.***

Keywords: Gluconic acid, Semiconductor, Photooxidation, Titanium Oxide

1. Introduction

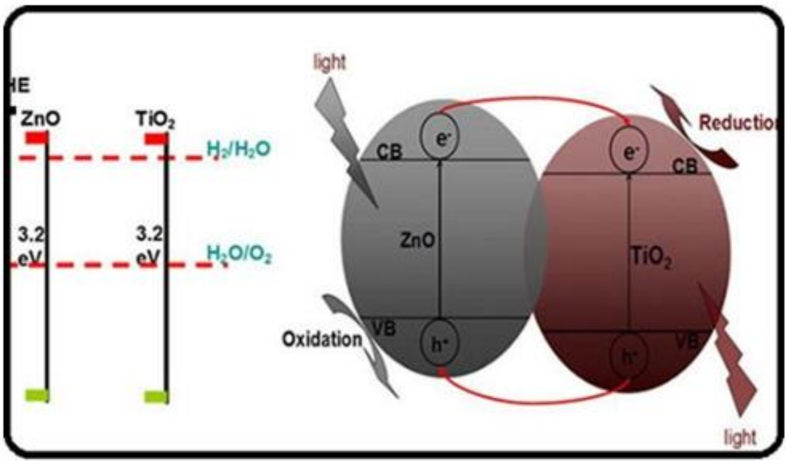
Photocatalysis has received enormous attention in recent years because of its potential application in environmental treatment and fine chemical synthesis. Strong oxidation and reduction power of photo excited titanium oxide (TiO_2) was realized from the discovery of Honda - Fujishima effect. In 1972, Fujishima et. al [1] reported photo induced decomposition of water on TiO_2 electrodes. Since Frank and Bard [2] first examined the possibilities of using TiO_2 to decompose cyanide in water, there has been an increasing interest in environmental applications. It is known under aqueous conditions, organic contaminants in wasted water can be degraded into CO_2 and H_2O, whereas under dry organic solvent or controlled pH, irradiation time, by using visible or UV light etc; the organic compounds may also be selectively oxidized into fine chemical products rather than complete mineralization [3 - 9]. Due to its long - term photo - stability and inertness to chemicals, titanium dioxide (TiO_2) is a valuable material in a wide range of practical applications. It is utilized as a desiccant, brightener, or reactive mediator in commercial products such as foods, paints, pharmaceuticals, drugs, and solar cells. Conversely, binary metal sulphide semiconductors, like PbS and CdS, are thought to be poisonous and insufficiently stable for catalysis. While WO_3 has been studied as a possible photocatalyst, it is typically less active than TiO_2, ZnO is also unstable in lit aqueous solutions.

TiO_2 P25 is the most commonly used photocatalytical semiconductor because it is chemically inert, photostable, low cost and non - toxic [10]. Anatase form has been used for photo - catalytic treatment of contaminants because of its rapid electron transfer when subjected to UV radiation. Heterogeneous photocatalysis is a common example of an AOP for the degradation of Pharmaceuticals and other organic Pollutants in water [11 - 14]. When TiO_2 is subjected to UV light, the electrons in the topmost valence band jump to the lower conduction band and form conduction band holes. In most instances, the valence band holes and conduction band electrons simply recombine liberating heat or light, a process known as recombination.

Most of metal oxide which are being used as semiconductors in this study like titanium oxide, zinc oxides etc. are used as the base for these materials. As a food additive, TiO_2 is approved for use in the EU [15], USA [16], Australia and New Zealand [17]; it is listed by its INS number 270 or as E number E270. TiO_2.

About 1% TiO_2 permits as an inactive ingredient in food products by the US Food and Drug Administration. While, there is no known health effects associated with the use of TiO_2, a recent study found that 3–6 - year - old children are the most affected group of people who consume TiO_2 particles from food products [18, 19]. So that the probable side effects of the photoproducts may be a common field of interest for the relevant researchers like dermatologists, pharmacists as well as the chemists. Similarly, the gluconic acid is an ingredient in various food products as stated above. While, there is no known health effects associated with the use of TiO_2, a recent study found that 3–6 - year - old children are the most affected group of people who consume TiO_2 particles from food products [18, 19].

Similarly, the several aspects concerning the mechanism of semiconductor sensitization reactions are still unknown. In addition; although many remarkable organic methodologies were developed in the last century, but toxic properties and other side effects of many reagents and solvents were not known. It is therefore planned to investigate photo - oxidation of Gluconic acid by semiconductors.



Gluconic acid is a fine chemical that has many industrial applications, primarily as a water - soluble cleansing agent. It is also used as an additive in food and beverages and gives a refreshing sour taste to many food items, such as wine and fruit juices. Gluconate (Sodium gluconate) has a high sequestering power and has an interesting property that it can inhibit bitterness in food. Glucuronic acid is noncorrosive, mildly acidic, not very irritating, non - odorous, nontoxic, easily biodegradable, nonvolatile organic acid widely used in pharmaceutical and medicinal chemistry for the synthesis of modified drugs. It is also largely used as an additive in the food industry, as an active compound in the pharmaceutical industry particularly for the preparation of skin - care products, as an antioxidant, and as a precursor for the biosynthesis of ascorbic acid (Vitamin C) [20].
Gluconic acid is abundantly available in plants, fruits and other foodstuffs such as rice, meat, dairy products, wine (up to 0.25 %), honey (up to 1 %), and vinegar. It is produced by different microorganisms as well, which include bacteria. Molecular mass of gluconic acid is 196.16, chemical formula $C_6H_{12}O7$.

Synonym 2, 3, 4, 5, 6 - pentahydroxyhexanoic acid pKa 3.7 Melting point (50 % solution) Lower than 12°C Boiling point (50 % solution) Higher than 100 °C Density 1.24 g/mL Appearance Clear to brown Solubility Soluble in water Sourness Degree of sourness (sourness of citric acid is regarded as 100) Mild, soft, refreshing taste. It is a highly valuable chemical and one of the organic building blocks of hyaluronic acid whose current worldwide market is estimated to be over $1 billion [20].

It is a natural constituent in fruit juices and honey and is used in the pickling of foods. It is used in meat and dairy products, particularly in baked goods as a component of leavening agent for pre leavened products. It is used as a flavoring agent (for example, in sherbets) and it also finds application in reducing fat absorption in doughnuts and cones. Foodstuffs containing D - glucono - d - lactone include bean curd, yoghurt, cottage cheese, bread, confectionery and meat. Generally speaking, gluconic acid and its salts are used in the formulation of food, pharmaceutical and hygienic products. They are also used as mineral supplements to prevent the deficiency of calcium, iron, etc. and as buffer salts. Different salts of gluconic acid find various applications based on their properties. Sodium salt of gluconic acid has the outstanding property to chelate calcium and other di - and trivalent metal ions. It is used in the bottle washing preparations, where it helps in the prevention of scale formation and its removal from glass. It is well suited for removing calcareous deposits from metals and other surfaces, including milk or beer scale on galvanized iron or stainless steel. Its property of sequestering iron over a wide range of pH is exploited in the textile industry, where it prevents the deposition of iron and for desizing polyester and polyamide fabrics. It is also used in metallurgy for alkaline derusting, as well as in the washing of painted walls and removal of metal carbonate precipitates without causing corrosion. It also finds application as an additive to cement, controlling the setting time and increasing the strength and water resistance of the cement. It helps in the manufacture of frost and crack resistant concretes. It is also used in the household cleaning compounds such as mouthwashes. Calcium gluconate is used in pharmaceutical industry as a source of calcium for treating calcium deficiency by oral or intravenous administration. It also finds a place in animal nutrition. Iron gluconate and iron phosphogluconate are used in iron therapy. Zinc gluconate is used as an ingredient for treating common cold, wound healing and various diseases caused by zinc deficiencies such as delayed sexual maturation, mental lethargy, skin changes, and susceptibility to infections.

The concentrated gluconic acid solution contains certain lactone structures (neutral cyclic ester) showing antiseptic property. In the European Parliament and Council Directive No.95/2/EC, gluconic acid is listed as a generally permitted food additive (E 574). The US FDA (Food and Drug Administration) has assigned sodium gluconate a GRAS (generally recognized as safe) status and its use in foodstuff is permitted without limitation [21].

There are several methods for the determination of D -

gluconic acid and D - glucono - d - lactone. Among them, isotachophoretic method [22] and hydroxamate method [23] are the most commonly used ones for the determination of gluconic acid. The concentration of gluconic acid is also determined by gas chromatography of their trimethylsilyl (TMS) derivatives prepared according to Laker and Mount [24] with inositol as internal standard.

Manufacturers of gluconic acid and its salt in the United States are Pfizer Inc., New York, Bristol - Meyers Co., New York, Premier Malt Products Inc., Wisconsin. European gluconate producers include Roquette Frères in France, Pfizer in Ireland, Benckiser in Germany. Fujisawa and Kyowa Hakko are the manufacturers of gluconate in Japan. Calcium gluconate is also an important product among the derivatives of gluconic acid and it is available as tablets, powder, and liquid for dietary supplements.

In this study it is believed that the gluconic acid may come in contact with titanium oxide or other metal oxide in the presence of sunlight and photooxidation may occur where the photo products can impact the human health.

2. Experimental

The organic compounds i. e. Gluconic acid, Silica gel - G, ninhydrin, Resublimed Iodine (sm), titanium oxide, iron oxide, zinc oxide, tungsten oxide, stannic oxide, copper oxide, some other semiconductors and other analytical chemicals are used directly as purchased.

UV chamber with UV tube 30 W (Philips), spectrophotometer (Systronic), tungsten filament lamps 2 □ 200 W (Philips) for visible light, 450 W Hg - arc lamp, water shell to filter out IR radiations and to avoid any thermal reaction, necessary glass wares, thin layer chromatography and paper chromatography kits for to determine the progress of reaction, conductivity meter (Systronic), pH meter (Eutech pH 510), spectrophotometer (Systronic) and I. R. spectrometer (Perkin - Elmer Grating - 377) was used.

The Gluconic acid solutions are prepared in water solvent 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 and variations were made to obtain the optimum yield of photoproducts.

The progress of reaction was monitored by running thin layer chromatography at different time intervals, where silica gel - G was used as an adsorbent and ninhydrin or resublimed iodine (sm) chamber was used as eluent for spot test detection. For colorless spot detection a slide spot detector; UV chamber (Chino's) was used. At the end of reaction or the process the photoproducts has been isolated as its salts and by preparing appropriate derivatives were identified by spectrophotometer, IR - spectrometer, NMR - spectrometer. The optimum yield was measured by hydroxamate method [23] and conductivity measurements. Various probable variations like the role of different semiconductors, mixed semiconductors, visible and UV - light etc., was studied. Some sets of experiments are also made in controlled conditions such as in absence of UV or visible light, semiconductors and stirring etc.

3. Results and Discussion

In this photooxidation reaction of Gluconic acid by titanium oxide and other metal oxides, there may be saccharic acid, acetic acid, formic acid etc are photo products. Presence of these photo products are identified by TLC methods but quantitative tests are not made in this study. We don't know for sure, but there might be other unknown photoproducts. The overall reaction is believed as follows -

CH2 (OH) - (CHOH) 4 - COOH → HOOC - (CHOH) 4 - COOH + CH3COOH + HCOOH
[Gluconic acid] [Saccharic acid] [Acetic acid] [Formic acid]

1) The Effect of Substrate

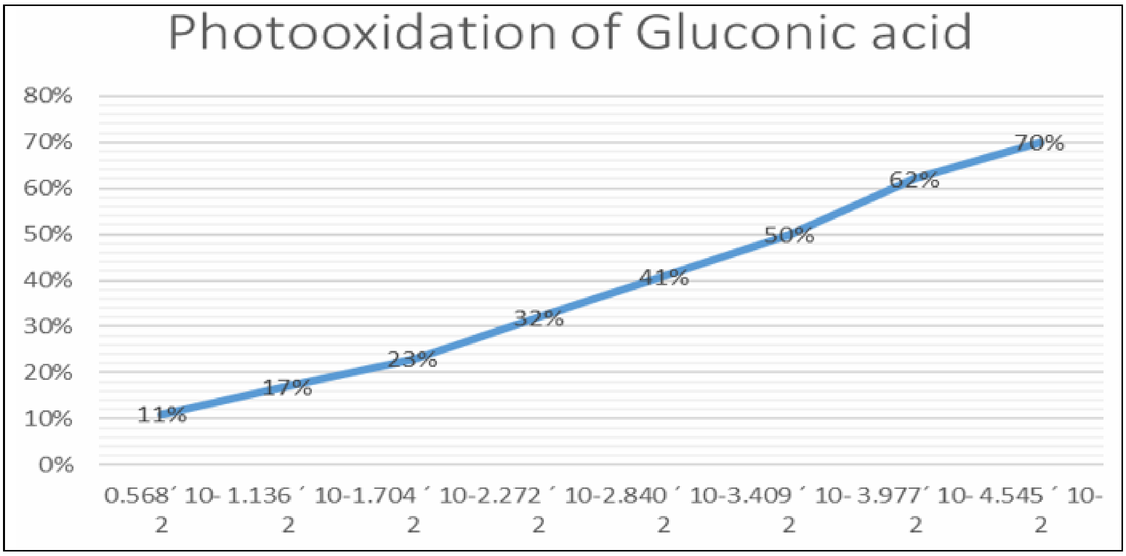
Effect of amount of substrate on the oxidation of Gluconic acid was studied at different concentrations varying from 0.509 × 10 - 2 M to 4.078 × 10 - 2 M at fixed amount TiO_2 (4.382× 10 - 2 M). The total volume of reaction mixture is 50 ml and the results are reported in the Table 1 and shown in Plot 1.

a) Solvent: Water
b) TiO_2: 4.382×10^{-2} M (3.50 g/L)
c) Irradiation time: 120 min
d) Visible light: 2 × 200 W Tungsten lamps

Table 1

S. No.	Conc. Of Substrate Gluconic acid	Percent Yield of Photoproducts
1	0.568×10^{-2}	11%
2	1.136×10^{-2}	17%
3	1.704×10^{-2}	23%
4	2.272×10^{-2}	32%
5	2.840×10^{-2}	41%
6	3.409×10^{-2}	50%
7	3.977×10^{-2}	62%
8	4.545×10^{-2}	70%

Paper ID: SR24325123655 DOI: https://dx.doi.org/10.21275/SR24325123655



Plot 1: The Effect of Substrate

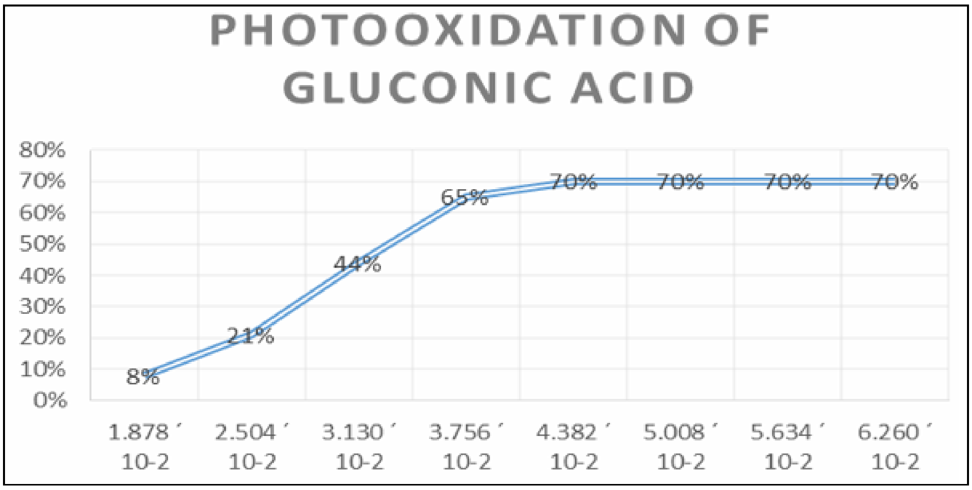
2) The Effect of Photocatalyst

Keeping all other factors identical the effect of amount of TiO_2 has also been observed. The total volume of reaction mixture is 50 ml and the results are reported in the Table 2 and shown in Plot 2.

a) Solvent: Water
b) Gluconic acid: 4.545× 10 - 2 M (8.00 gm/Lt)
c) Irradiation time: 120 min
d) Visible light: 2 × 200 W Tungsten lamps

Table 2

S. No.	Conc. Of Photocatalyst (TiO_2)	Percent Yield of Photoproducts
1	1.878×10^{-2}	08%
2	2.504×10^{-2}	21%
3	3.130×10^{-2}	44%
4	3.756×10^{-2}	65%
5	4.382×10^{-2}	70%
6	5.008×10^{-2}	70%
7	5.634×10^{-2}	70%
8	6.260×10^{-2}	70%



Plot 2: The Effect of Photocatalyst

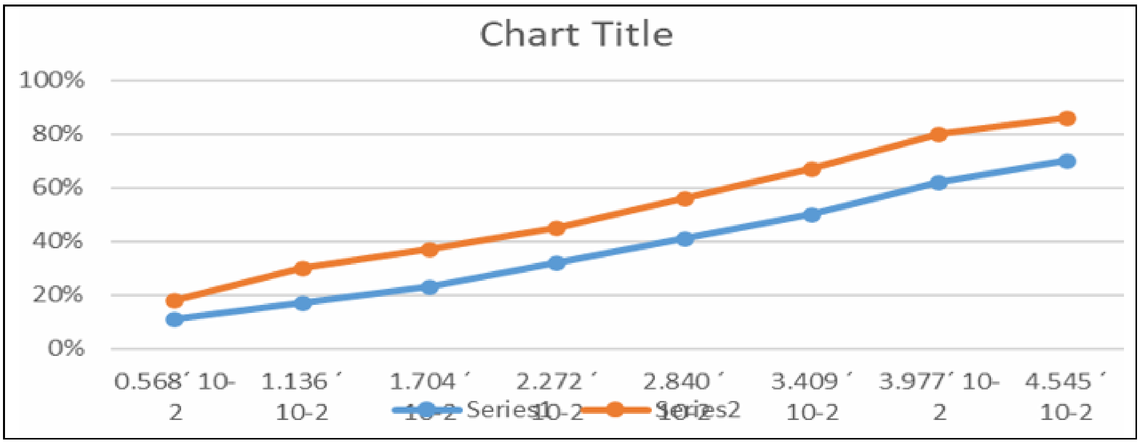
3) The Effect of Type of Radiations

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

a) Solvent: Water
b) TiO_2: 4.382×10^{-2} M (3.50 g/L)
c) Irradiation time: 120 min
d) Visible light: 2 × 200 W Tungsten lamps
e) UV Light: UV Chamber 30 W (Philips Tube)

Table 3

S. No.	Conc. of Substrate Gluconic acid	Percent Yield of Product (In visible light)	Percent Yield of Product (In UV light)
1	0.568×10^{-2}	11%	18%
2	1.136×10^{-2}	17%	30%
3	1.704×10^{-2}	23%	37%
4	2.272×10^{-2}	32%	45%
5	2.840×10^{-2}	41%	56%
6	3.409×10^{-2}	50%	67%
7	3.977×10^{-2}	62%	80%
8	4.545×10^{-2}	70%	86%



Plot 3: The Effect of Light

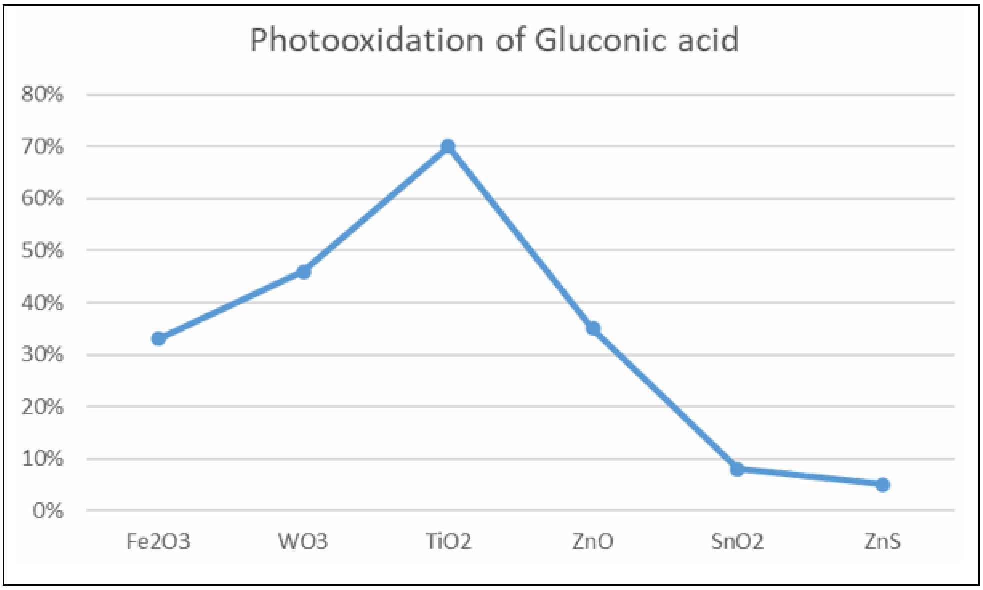
4) The Effect of Nature of Photocatalyst

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

a) Solvent: Water
b) Gluconic acid: $4.078 \times 10^{-2} \times \times 10^{-2}$M (8.00 gm/lt)
c) Irradiation Time: 120 min.
d) Visible Light: 2 × 200 W Tungsten Lamps.

Table 4

S. No.	Photocatalyst	Band gap (eV)	Wavelength (nm)	Yield of Photoproduct
1	Fe_2O_3	2.2	564	33%
2	WO_3	2.6	477	46%
3	TiO_2	3.1	400	70%
4	ZnO	3.2	388	35%
5	SnO_2	3.5	354	08%
6	ZnS	3.6	345	05%



Plot 4: The effect of nature of photocatalyst

The effect of amount of on the oxidation of Gluconic acid 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 Gluconic acid was investigated employing different concentrations of the TiO_2 as reported in Table 2 and Plot 2. It was observed that the yield of photo - product increasing with increasing catalyst level up to 5.008×10^{-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 5.008×10^{-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 Gluconic acid 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

Paper ID: SR24325123655 DOI: https://dx.doi.org/10.21275/SR24325123655

quite resembles the observed data as the table reported as more yield in UV light.

The effect of other semiconductor particle e. g. Fe_2O_3, WO_3 (having low band gap than TiO_2 semiconductor) on the TiO_2 catalyst photocatalytic reactions have also been studied. TiO_2 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_3 has been investigated as a potential photo catalyst, but it is generally less active catalytically than TiO_2. However, these can be combined (Doping) with other semiconductors including TiO_2 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 Gluconic acid was studied by using different photocatalysts as shown in the Table 4 and Plot 4

It is now well established that the photocatalytic oxidation of several organic compounds by optically excited semiconductor oxides is thermodynamically allowed in presence of oxygen at room temperature.

4. Mechanism

On the basis of results and discussion the following tentative mechanistic part has discussed for photocatalytic oxidation of Gluconic acid, with collaborating the results already reported for other studied compounds.

With respect to a semiconductor oxide such as TiO_2, photocatalytic reactions are initiated by the absorption of illumination with energy equal to or greater than the band gap of the semiconductor. When the suspension of titanium oxide irradiated with visible light electron will be promoted from valence band to conduction band leaving a positive hole in the valence band:

$$TiO_2 + h\nu \rightarrow (h - e) \text{ Excitation} \ldots (1)$$

$$(h - e) \rightarrow h^+ + e^- \text{ Separation} \ldots (2)$$

It was explained before, that the surface of TiO_2 with high surface area retains subsets of hydroxyls, where the net surface density is 4 - 5 hydroxyl per nm. In addition, suspension of TiO_2 in solution of Gluconic acid gives a surface hydroxide ion as locations for primary photo - oxidation processes. Photo holes are trapped by surface hydroxyl groups, whereas electrons are trapped by adsorbed oxygen:

$$h^+ + OH^- \mathbf{(s)} \rightarrow OH\bullet \ldots (3)$$

$$e^- + O_2 \text{ (abs)} \rightarrow O_2 \text{ (abs)} \ldots (4)$$

The formed OH• radicals are reacted with adsorbed on the surface, is reacted with the Gluconic acid to generate its radical and water molecule, as follows:

$$Y - OH + OH\bullet \rightarrow Y\bullet - OH + H_2O \ldots (5)$$

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:

$$O_2 \text{ (abs)} + H_2O \rightarrow OH \mathbf{(s)} + HO_2 \ldots (6)$$

The oxidized products of Gluconic acid formed according the following steps:

$$Y\bullet - OH + HO2 \rightarrow Y (O) + H2O2 \ldots (7)$$

5. Conclusion and Suggestions

The work reported is only the study of sensitized photocatalytic action of TiO_2 on Gluconic acid as dilute solution in the presence of light. Gluconic acid is an influential chemical as stated above. This study may have importance to attract the attentions of the researchers about the causes of the probable side effects of the photoproducts and this may arise a common field of interest for chemists, pharmacists as well as industrialists.

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