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Study of Semiconductor Photocatalysed Oxidation of Indispensable Nutrient Vitamin C

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Abstract: ***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. 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. 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. Ascorbic acid (vitamin C) is an essential micronutrient that performs important metabolic functions. It is sensitive to air and light and is degraded by chemical and photochemical oxidation. Ascorbic acid is an ingredient of anti - aging cosmetic products and exerts several functions on the skin as collagen synthesis, depigmentation, and antioxidant activity. As an antioxidant it protects skin by neutralizing reactive oxygen species generated on exposure to sunlight. In biological systems it reduces both oxygen - and nitrogen - based free radicals and thus delays the aging process. In view of the instability of ascorbic acid in skin care formulations, it is often used in combination with another redox partner such as alpha - tocopherol (vitamin E) to retard its oxidation. The methods of testing the photostability of dermal preparations have been described by Thoma and Spilgies. The produced photo - product has been isolated as its derivatives and then analyzed them by appropriate spectral or other suitable methods. Hence, this part of reported work may help to arouse the interdisciplinary interest for chemists as well as pharmacists.***

Keywords: Semiconductor, Photocatalysis, Titanium dioxide, Ascorbic acid, Photo – oxidation

1. Introduction

One of the most important micronutrients, ascorbic acid (L - enantiomer) or vitamin C, is the aldono - 1, 4 - lactone of a hexonic acid. It is essential for preserving the body's equilibrium and regular metabolic functions. Due to the absence of L - gulono - 1, 4 - lactone oxidase, an enzyme required for ascorbic acid synthesis, mammalian cells are unable to produce ascorbic acid1. Fruits and vegetables are good natural sources of vitamin C; however, not all plants are high in this nutrient. Light, heat, transition metal ions, and an alkaline pH cause ascorbic acid to oxidise reversibly into dehydroascorbic acid (DHA), which then hydrolyzes irreversibly to produce 2, 3 - diketogulonic acid.

The number of patents related to ascorbic acid from 1992 to 2021; there have been a stable and relatively high number of applications since 1997. From 2010 to 2013, the patents were even more than 1200 per year, shown in following plot. It can be found that the importance of ascorbic acid has aroused widespread interest in the consumer market.

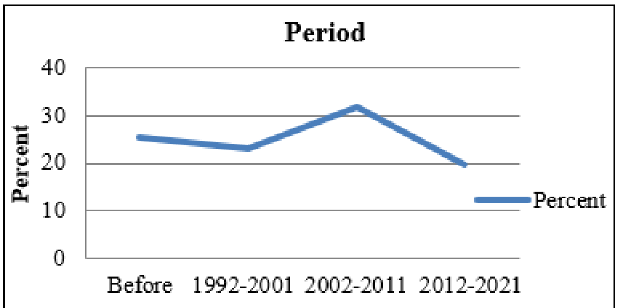


Figure: Shows the number of patents related to ascorbic acid

Reactive oxygen species (ROS) can cause oxidative damage to cells, while ascorbic acid can scavenge free radicals and other oxygen species. Ascorbic acid functions as an antioxidant in food and biological systems, and antiradical capability frequently reflects antioxidant potential. Ascorbic acid, the most potent and natural antioxidant with the fewest adverse effects, helps prevent a number of illnesses brought on by oxidative stress in the body, including cancer, heart disease, ageing, and cataracts[2]. As an antioxidant, ascorbic acid is also utilized to preserve the flavor and nutritional value of food. It works as an anti - browning agent, preventing oxidation - induced browning of fruits and vegetables. Through a mechanism known as the "deactivation reaction, " ascorbic acid prevents browning by converting the o - quinone that polyphenol oxidase produces to the original diphenol[3].

Ascorbic acid is a commonly utilized natural color retention ingredient in meat products that can prevent lipid oxidation and preserve color stability[4]. Ascorbic acid was a good component for cured meat products and had the best protective effect on the quality of cured meat when compared to other organic acids like malic, citric, and tartaric acids[5]. After being frozen, the pork surface treated with ascorbic acid and a combination of it and rosemary extract showed good colour, water content, and pH stability[6].

Pro - oxidant activity is defined as the ability of antioxidants to reduce transition metal ions to a lower oxidation state, which refers to the Fenton reaction[7]. In the Fenton reaction, transition metal ions such as Fe^{3+} are reduced by ascorbic acid and then Fe^{2+} further react with oxygen and hydrogen peroxide to form highly active and destructive hydroxyl radicals[8].

A particular spectrophotometric approach with a repeatability of ±5% has been used to study the kinetics of ascorbic acid photolysis in cream formulations under UV irradiation. The cream compositions result in the formation of photoproducts such as 2, 3 - diketogulonic acid and dehydroascorbic acid[9].

From the 1972 study of Fujishima and Honda on the photocatalytic splitting of water on TiO_2 electrodes, titanium dioxide (TiO_2) as a semiconductor photocatalyst has been the subject of extensive research.1[0] Since then, a great deal of study has been done to improve the photocatalytic efficiency of TiO_2 and comprehend the underlying mechanisms. When titanium dioxide is subjected to ultraviolet light, electrons from the topmost valence band go to the conduction band, where they produce valence band holes and conduction band electrons. Recombination is the process by which heat or light is released when valence band holes and conduction band electrons simply recombine. It is recombination that causes the low quantum yields.1[1–13]

Photoelectron trapping has long been regarded as an effective mechanism to reduce the charge recombination on semiconductor photo catalysts. Many successful efforts have made to enhance the catalytic efficiency of TiO_2 by doping with metals (like Ag) and various non metal doping agents like N, P, S.1[4 - 16]

The objective of this work is to examine the photo - oxidation of ascorbic acid by a semiconductor that is fully mineralized when exposed to visible light. When titanium dioxide is subjected to ultraviolet light, electrons from the topmost valence band go to the conduction band, where they produce valence band holes and conduction band electrons. Recombination is the process by which heat or light is released when valence band holes and conduction band electrons simply recombine. The poor quantum yield of photoproducts is caused by recombination, which is dependent on the semiconductor's band gap. Here, the type of metal oxide (semiconductor) determines the band gap.

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.

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 planed to investigate photo - oxidation of Ascorbic acid by semiconductors.

2. Experimental

The organic compounds i. e. Ascorbic acid (Vitamin C), Silica gel - G, Resublimed Iodine (sm), ninhydrin, titanium oxide, tungsten oxide, iron oxide, zinc oxide, cadmium sulphide, stannic oxide, copper oxide, some other semiconductors and other analytical chemicals.

UV chamber with UV tube 30 W (Philips), spectrophotometer (Systronic), spectrometer (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, pH meter (Eutech pH 510), conductivity meter (Systronic), spectrophotometer (Systronic) and I. R. spectrometer (Perkin - Elmer Grating - 377) was used.

The Ascorbic acid (Vitamin C) solutions are prepared in water and acetonitrile 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. 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 of obtained 2, 4 - DNP [with 0.50gm and 84 ml HCl in 500 ml aqueous solution] was measured by using spectrophotometers and conductivity meter. 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

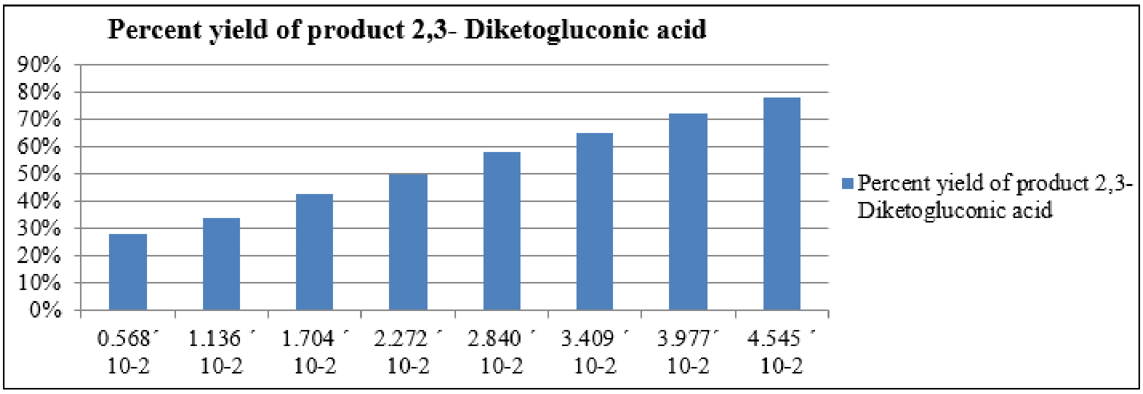
1) The effect of substrate

Effect of amount of substrate on the oxidation of Ascorbic acid (Vitamin C) was studied at different concentrations varying from 0.850×10^{-2} M to 2.840×10^{-2} M at fixed amount TiO_2 (1.872×10^{-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 Ascorbic acid (Vitamin C)	Percent yield of product 2, 3 - Diketogluconic acid
1	0.568×10^{-2}	28%
2	1.136×10^{-2}	34%
3	1.704×10^{-2}	43%
4	2.272×10^{-2}	50%
5	2.840×10^{-2}	58%
6	3.409×10^{-2}	65%
7	3.977×10^{-2}	72%
8	4.545×10^{-2}	78%



Plot 1: The effect of substrate

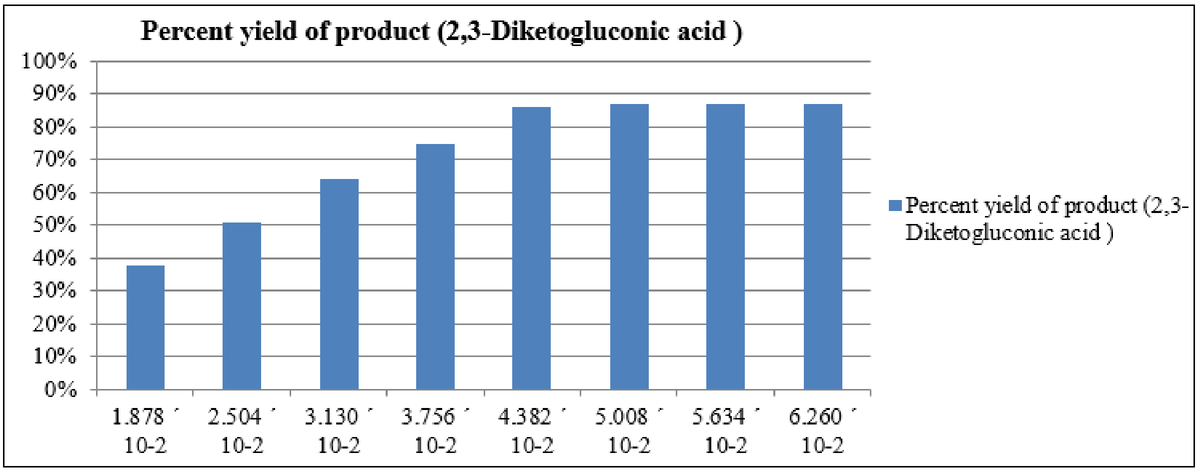
2) The Effect of Photocatalyst -

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) Ascorbic acid (Vitamin C): 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 product (2, 3 - Diketogluconic acid)
1	1.878×10^{-2}	38%
2	2.504×10^{-2}	51%
3	3.130×10^{-2}	64%
4	3.756×10^{-2}	75%
5	4.382×10^{-2}	86%
6	5.008×10^{-2}	87%
7	5.634×10^{-2}	87%
8	6.260×10^{-2}	87%



Plot 2 The Effect of Photocatalyst

3) The Effect of Type of Radiations

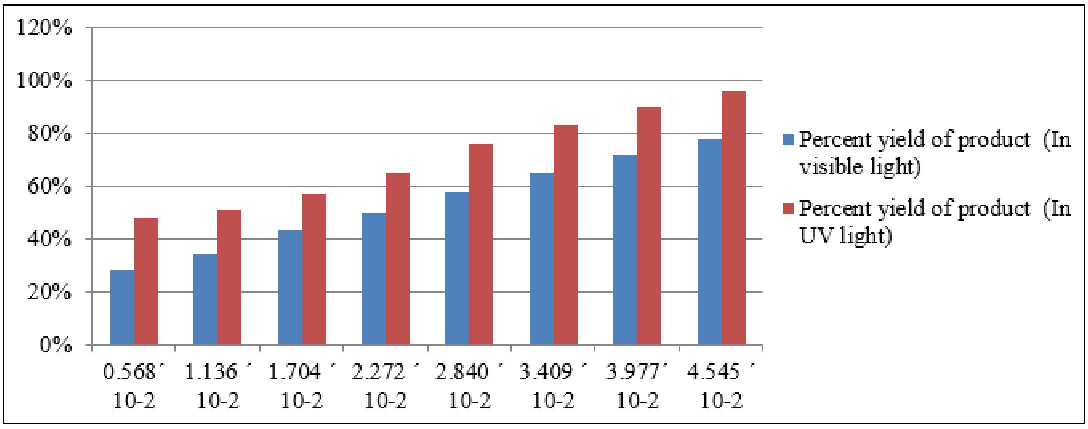
The effect of type of radiations on photocatalytic reaction was studied in visible light and ultraviolet light keeping all other factors identical. The total volume of reaction mixture is 50 ml and the results are reported in the Table 3 and shown in Plot 3

a) Solvent: Water
b) TiO_2: 1.66×10^{-2} M (1.33 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 Ascorbic acid (Vitamin C)	Percent yield of product (In visible light)	Percent yield of product (In UV light)
1	0.568×10^{-2}	28%	48%
2	1.136×10^{-2}	34%	51%
3	1.704×10^{-2}	43%	57%
4	2.272×10^{-2}	50%	65%
5	2.840×10^{-2}	58%	76%
6	3.409×10^{-2}	65%	83%
7	3.977×10^{-2}	72%	90%
8	4.545×10^{-2}	78%	96%



Plot 3: The Effect of Light

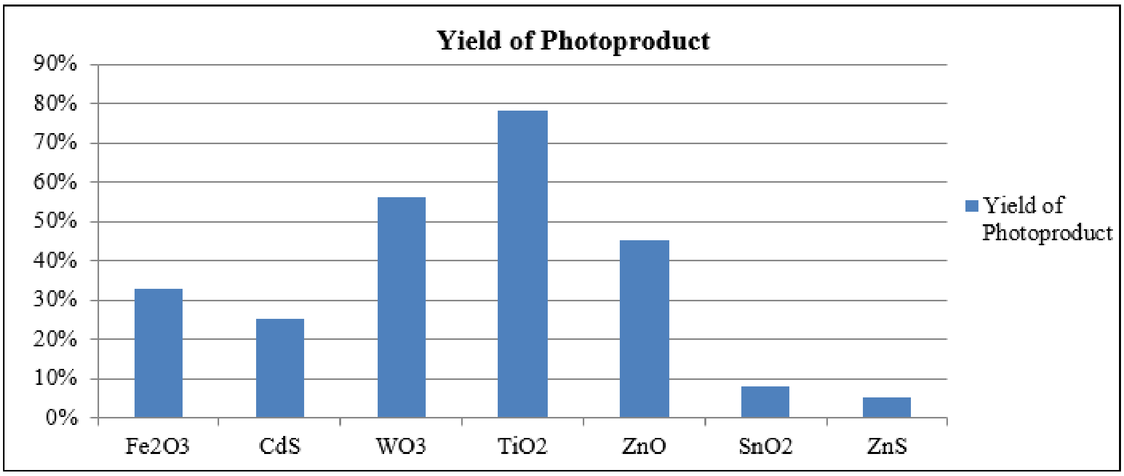
4) The Effect of Nature of Photocatalyst

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) Ascorbic acid (Vitamin C): $4.545 \times 10^{-2} \times 10^{-2}$ 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	CdS	2.4	516	25%
3	WO_3	2.6	477	56%
4	TiO_2	3.1	400	78%
5	ZnO	3.2	388	45%
6	SnO_2	3.5	354	08%
7	ZnS	3.6	345	05%



Plot 4: The effect of nature of photocatalyst

The effect of amount of on the oxidation of Ascorbic acid (Vitamin C) 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 Ascorbic acid (Vitamin C) 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 Ascorbic acid (Vitamin C) 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_2) 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_2O_3, CdS, 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 Ascorbic acid (Vitamin C) 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. On the basis of analytical, chemical and spectral data the product was characterized 2, 3 - Diketogluconic acid.

After completion of photocatalytic reaction the photoproduct was characterized by usual qualitative tests treatment by making its derivatives, spectral studies, chromatographic studied, s and chemical analysis. The yield of photoproduct was determined by spectrophotometric (Colorimetric) study of 2, 4 - DNP derivatives of photoproduct.

4. Mechanism

On the basis of results and discussion the following tentative mechanistic part has discussed for photocatalytic oxidation of Ascorbic acid (Vitamin C), 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 Ascorbic acid (Vitamin C) 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:

$$h^+ + OH^-_{(s)} \rightarrow OH^\bullet \ldots (3)$$
$$e^- + O_2 \text{ (abs)} \rightarrow O_2^{\bullet -} \text{ (abs)} \ldots (4)$$

The formed $OH^\bullet$ radicals are reacted with adsorbed on the surface, is reacted with the malic acid water to generate Ascorbic acid radical and water molecule, as follows:

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

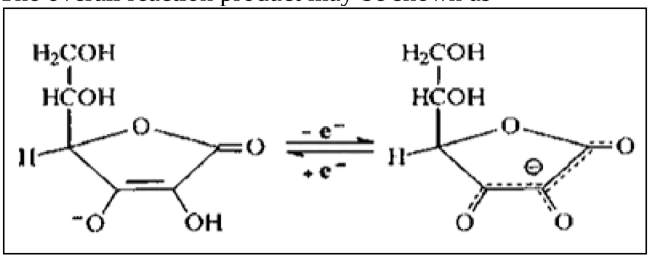
The formed radicals are reacted with adsorbed on the surface, is reacted with the formed water to regenerate hydroxyl group on the surface of the catalyst:

$$O_2^{\bullet -} \text{ (abs)} + H_2O \rightarrow OH^-_{(s)} + HO_2^\bullet \ldots (6)$$

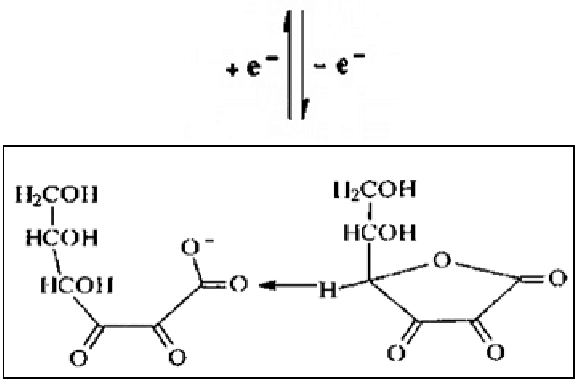
Ascorbic acid (Vitamin C) formed according the following steps:

$$Y^\bullet - OH + HO_2^\bullet \rightarrow Y(O) + H_2O_2 \ldots (7)$$

The overall reaction product may be shown as –



Ascorbic Acid Ascorbate Free Radical



2, 3 - DIKETO - 1 - GLUCONIC ACID DEHYDROASCORBIC ACID

5. Conclusion and Suggestions

The work reported is only the study of sensitized photocatalytic action of TiO_2 on Ascorbic acid (Vitamin C) as dilute solution in the presence of light and air. Ascorbic acid otherwise known as Vitamic C is indispensable nutrient and is present in citrus fruits, gooseberry, bittergourd etc. in high amount. Generally it is present in all fresh vegetables and fruits. This study may have importance to attract the attentions of the researchers about the causes of the probable side effects of the photoproducts.

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