

## ORIGINAL ARTICLE

# Study of Semiconductor Photocatalyzed Oxidation of Mandelic Acid Used In Cosmetic Pharmaceutical Industries

P. R. Meena\*, K. S. Meena and R. K. Khandelwal

H.O.D. Chemistry, P. S. B. Govt. College-SHAHPURA, BHILWARA (Raj.) INDIA\*

Email: meenapushkarraj@gmail.com

### ABSTRACT

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. reported photo induced decomposition of water on  $TiO_2$  electrodes. Since Frank and Bard first examined the possibilities of using  $TiO_2$  to decompose cyanide in water, there has been an increasing interest in environmental applications.  $TiO_2$  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. The alpha hydroxy acids (like Mandelic acid) is being used in a variety of skin care products, peeling agents including moisturizers, cleansers, eye cream, sunscreen and foundations etc.; simultaneously the titanium oxide, zinc oxides etc. are used as the base for these materials. Mandelic acid has a long history of use in the medical community as an antibacterial; particularly in the treatment of urinary tract infections. It has also been used as an oral antibiotic. It is therefore, planned to investigate photo-oxidation of mandelic acid by semiconductors. 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 about the side effects of photo-products, where these are being used. Hence, this part of reported work may help to arouse the interdisciplinary interest about the side effects of photoproducts, where these are being used as cosmetic and pharmaceutical industries.

**Key words:** Mandelic acid, Titanium dioxide, Semiconductor, Photo-oxidation.

Received 29.03.2016 Accepted 18.05.2016

© 2016 AELS, INDIA

### 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].

Inertness to chemical environment and long-term photo-stability has made  $TiO_2$  an important material in many practical applications, and, in commercial products ranging from drugs to foods, cosmetics to catalysts, paints to pharmaceuticals, and sunscreens to solar cells in which  $TiO_2$  is used as a desiccant, brightener, or reactive mediator [10]. 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  $TiO_2$  [11].

Mandelic acid can be found in a variety of cosmetic and skin care products including cleansers, toners, moisturizers, eye creams, acne treatment products, skin lighteners and anti-aging treatment products. It appears to be safe in the quantities found in cosmetic and personal care products. The Environmental Working Group's Skin Deep Cosmetics Database classifies it as a low risk cosmetic ingredient. Mandelic

acid has similar anti-aging benefits to other alpha hydroxy acids. It lightens darkly pigmented areas like sunspots and melasma, while reducing the appearance of fine lines and wrinkles. At the same time, it gives skin a smoother texture and more youthful appearance [12-14].

Mandelic acid peels have proven to be less irritating and penetrating because the molecules of this acid are larger as compared to that of lactic and glycolic acid. This is one of the reasons why people have discovered that mandelic acid peels are excellent for the treatment of damaged skin. When people are looking for a chemical peel for the first time, this one can turn out to be a great choice. People with acne-prone skin can also reap the benefits of mandelic acid peel because they have antibacterial properties. Chemical peeling with mandelic acid, when compared with glycolic acid peels, produced less erythema, and was less likely to result in crusting or blistering or other adverse effects on the epidermis. The onset of erythema is more predictable and gradual, and there is less likelihood that "hotspots" will develop in dry areas of the face [15-16].

It increases skin cells turnover by dissolving the tiny bonds that hold skin cells together, allowing dead skin cells on the surface of the skin to be sloughed off more quickly to reveal healthier cells underneath. This increased rate of sloughing thins the outermost layer of the skin called the stratum corneum. A thinner stratum corneum reflects light better and makes skin look smoother and more youthful. Mandelic acid and other alpha hydroxy acids also soften the appearance of fine lines and wrinkles and improve skin texture. At the same time, they lighten areas that have darkened in response to skin damage and sun exposure. Some alpha hydroxy acids also boost collagen production in the dermis of the skin. Collagen is a protein that gives skin its support and youthful firmness. Due to its anti-inflammatory properties, mandelic acid may also be beneficial for treating rosacea [17-20]. The primary difference between AHAs and BHAs is that AHAs are water-soluble, while BHAs are lipid-(oil) soluble. This unique property of BHA allows it to penetrate the oil in the pores and exfoliate accumulated skin cells inside the oil gland that can clog pores. BHAs are best used where blackheads and blemishes are the issue and make them ideal for skin conditions that may be a result of bacteria. AHAs are best for sun-damaged, thickened, dry skin where breakouts are not a problem.

Although there are no specific side effects are warnings found for Mandelic Acid, it should be noted that as an AHA, caution should be taken when using products containing Mandelic Acid and going into the sun. Sunscreen should always be worn, ideally with an SPF of 30 or higher. The FDA issued a statement asking that all users of products containing AHAs, including Mandelic Acid by default, consider the heightened risks of UV exposure after applying AHA products. However, alpha hydroxy acids are known to cause redness, flaking and skin irritation as the side effects about which nothing is known or very little information's are available.

The alpha hydroxy acids (like Mandelic acid) is being used in a variety of skin care products, peeling agents including moisturizers, cleansers, eye cream, sunscreen and foundations etc.; simultaneously the titanium oxide, zinc oxides etc. are used as the base for these materials. As a food additive TiO<sub>2</sub> is approved for use in the EU, USA and Australia and New Zealand; it is listed by its INS number 270 or as E number E270. The side effects most frequently experienced include redness, swollen skin and itching [21-23].

Similarly the several aspects concerning the mechanism of action of alpha hydroxy acids are still unknown. In addition; although many remarkable organic methodologies were developed in the last century, but toxic properties of many reagents and solvents were not known. It is therefore planed to investigate photo-oxidation of Mandelic acid by semiconductors [24-26].

Mandelic acid has a long history of use in the medical community as an antibacterial; particularly in the treatment of urinary tract infections [27]. It has also been used as an oral antibiotic. Hence, this part of reported work may help to arouse the interdisciplinary interest about the side effects of photoproducts, where these are being used as cosmetic and pharmaceutical industries.

## EXPERIMENTAL

The organic compounds i.e. Mandelic acid, Silica gel-G, Resublimed Iodine (sm), ninhydrine, titanium oxide, tungsten oxide, iron oxide, zinc oxide, cadmium sulphide, stannic oxide, copper oxide, some other semiconductors and other analytical chemicals are purchased by SD Fine or E Merck chemical suppliers.

UV chamber with UV tube 30 W (Philips), spectrophotometer (Systronic), spectrometer (Systronic), tungsten filament lamps 2 x 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) to determine the optimum yields of photoproducts, magnetic stirrer, pH meter (Eutech pH 510), spectrophotometer (Systronic) and I.R. spectrometer (Perkin-Elmer Grating-377) was used.

The mandelic acid 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 in the given practical conditions.

The progress of reaction was monitored by running thin layer chromatography at different time intervals, where silica gel-G was used as an adsorbent. 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.

## RESULTS AND DISCUSSION

### (1)-The effect of substrate

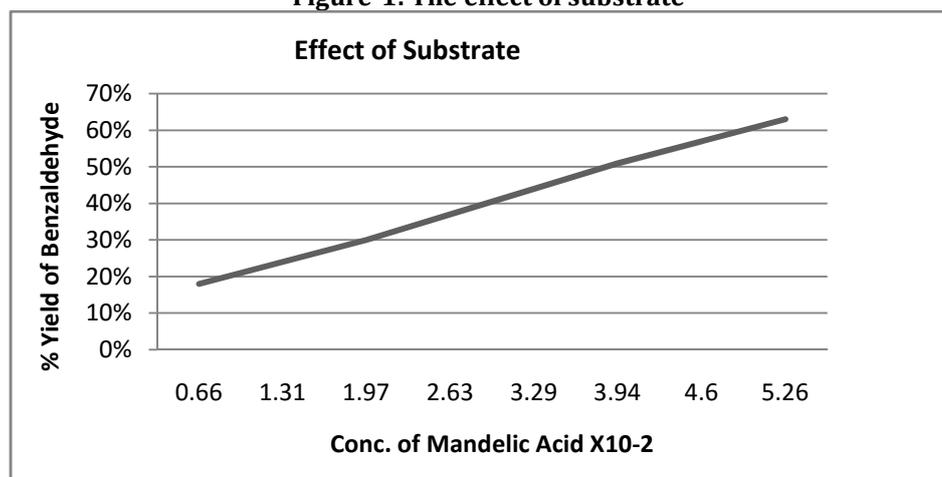
The effect of amount of substrate on the oxidation of mandelic acid was studied at different concentrations varying from  $0.66 \times 10^{-2}$  M to  $5.26 \times 10^{-2}$  M (1gm to 8 gms per litre) at fixed amount  $\text{TiO}_2$  ( $1.66 \times 10^{-2}$  M). The total volume of reaction mixture is 50 ml and the results are reported in the following Table-1 and shown in Figure-1.

1. Solvent : Water
2.  $\text{TiO}_2$  :  $3.79 \times 10^{-2}$  M (3 gm/lt)
3. Irradiation Time : 180 min
4. Visible Light :  $2 \times 200$  W Tungsten Lamps

**Table-1 : The effect of substrate**

S.No.	Conc. of Substrate (Mandelic acid)	Percent Yield of Product (Benzaldehyde)
1	$0.66 \times 10^{-2}$ M	18%
2	$1.31 \times 10^{-2}$ M	24%
3	$1.97 \times 10^{-2}$ M	30%
4	$2.63 \times 10^{-2}$ M	37%
5	$3.29 \times 10^{-2}$ M	44%
6	$3.94 \times 10^{-2}$ M	51%
7	$4.60 \times 10^{-2}$ M	57%
8	$5.26 \times 10^{-2}$ M	63%

**Figure-1: The effect of substrate**



### (2)-The effect of photocatalyst

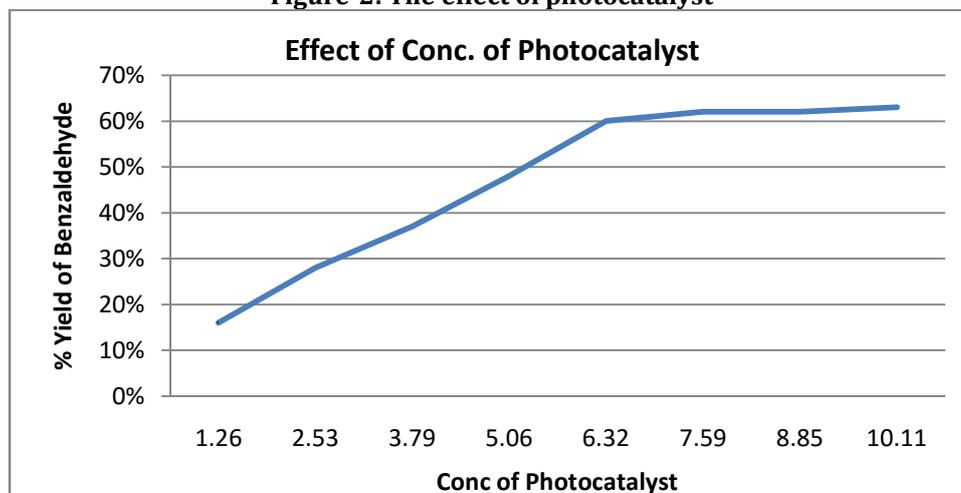
Keeping all other factors identical the effect of amount of  $\text{TiO}_2$  has also been observed. The total volume of reaction mixture is 50 ml and the results are reported in the following Table-2 and shown in Figure -2.

1. Solvent : Water

2. Mandelic Acid :  $3.29 \times 10^{-2}$  M (5.00 gms/Lt)
3. Irradiation Time : 180 min

**Table-2 : The effect of photocatalyst**

S.No.	Conc. of Photocatalyst (TiO <sub>2</sub> )	Percent Yield of Product (Benzaldehyde)
1	$1.26 \times 10^{-2}$ M	16%
2	$2.53 \times 10^{-2}$ M	28%
3	$3.79 \times 10^{-2}$ M	37%
4	$5.06 \times 10^{-2}$ M	48%
5	$6.32 \times 10^{-2}$ M	60%
6	$7.59 \times 10^{-2}$ M	62%
7	$8.85 \times 10^{-2}$ M	62%
8	$10.11 \times 10^{-2}$ M	63%

**Figure-2: The effect of photocatalyst****(3)-The effect of type of Radiations**

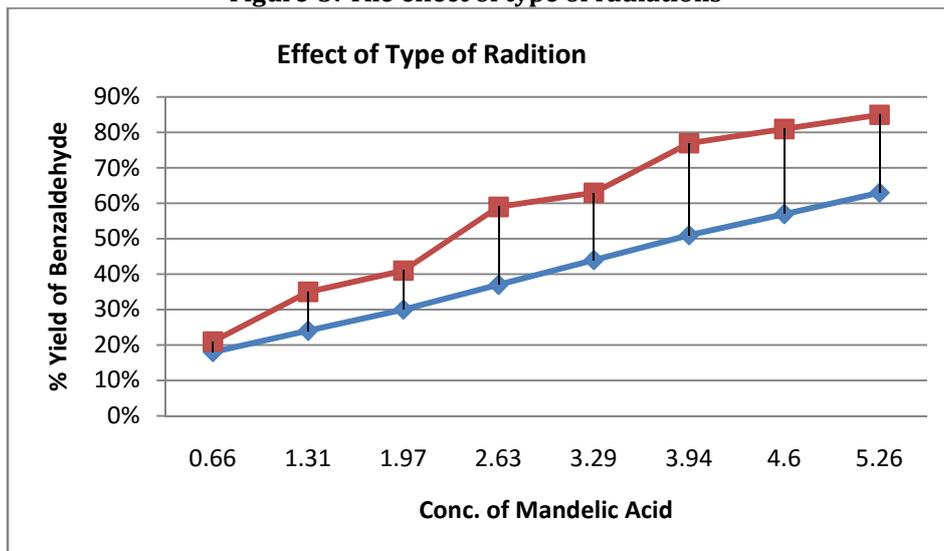
The effect of type of radiations on photocatalytic reaction was studied in visible light and ultraviolet light keeping all other factors identical. The total volume of reaction mixture is 50 ml and the results are reported in the following Table-3 and shown in Figure -3.

- Solvent : Water
2. TiO<sub>2</sub> :  $1.26 \times 10^{-2}$  M (1gm/lit)
3. Irradiation Time : 180 min
4. Visible Light : 2 × 200 W Tungsten Lamps
5. UV Light : UV Chamber 30 W (Philips Tube)

**Table-3 : The effect of type of radiations**

S.No.	Conc. of Substrate (Mandelic acid)	Percent Yield of Product (Visible Light)	Percent Yield of Product (U.V. Light)
1	$0.66 \times 10^{-2}$ M	18%	21%
2	$1.31 \times 10^{-2}$ M	24%	35%
3	$1.97 \times 10^{-2}$ M	30%	41%
4	$2.63 \times 10^{-2}$ M	37%	59%
5	$3.29 \times 10^{-2}$ M	44%	63%
6	$3.94 \times 10^{-2}$ M	51%	77%
7	$4.60 \times 10^{-2}$ M	57%	81%
8	$5.26 \times 10^{-2}$ M	63%	85%

Figure-3: The effect of type of radiations

**(4)-The effect of nature of photocatalyst**

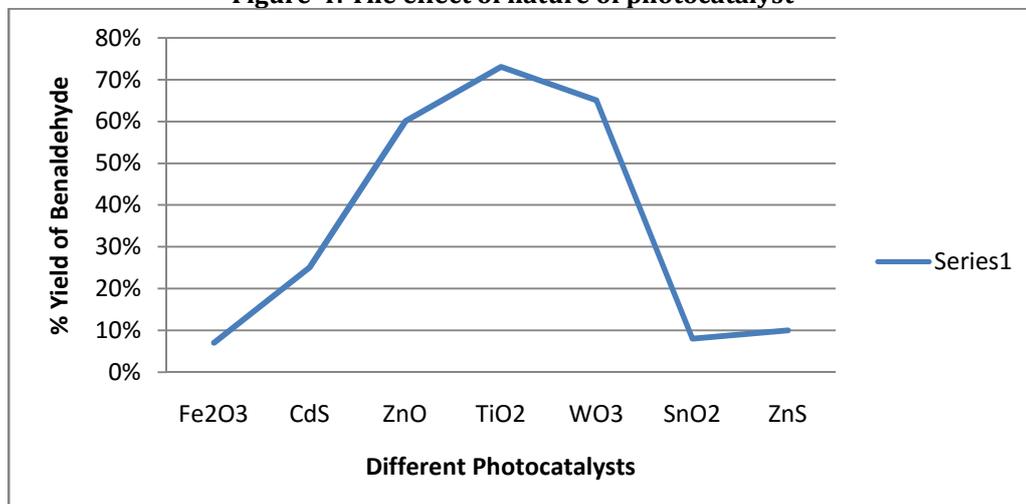
The effect of the nature of photocatalyst on photocatalytic reaction was studied by different photocatalysts, which are Ferric oxide, Cadmium sulphide, Tungsten oxide, Titanium oxide, Stannic oxide and Zinc sulphide. The total volume of reaction mixture is 50 ml and the results are reported in the following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

1. Solvent : Water
2. Mandelic Acid :  $3.29 \times 10^{-2}$  M (5.00 gm/lt)
3. Irradiation Time : 180 min.
4. Visible Light :  $2 \times 200$  W Tungsten Lamps.

Table-4 : The Effect of Nature of Photocatalyst

S.No.	Photocatalyst	Band Gap (eV)	Wavelength (nm)	Percent Yield of Product (Benzaldehyde)
1	Fe <sub>2</sub> O <sub>3</sub>	2.2	564	07%
2	CdS	2.4	516	25%
3	ZnO	3.2	388	60%
4	TiO <sub>2</sub>	3.1	400	73%
5	WO <sub>3</sub>	2.6	477	65%
6	SnO <sub>2</sub>	3.5	354	08%
7	ZnS	3.6	345	10%

Figure-4: The effect of nature of photocatalyst



The effect of amount of on the oxidation of mandelic acid was studied by using variable amount of substrate, as reported in Table 1 and Fig. 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 mandelic acid was investigated employing different concentrations of the  $\text{TiO}_2$  as reported in Table 2 and Fig. 2. It was observed that the yield of photo-product increasing with increasing catalyst level up to  $6.32 \times 10^{-2}$  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  $6.32 \times 10^{-2}$  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 mandelic acid was studied by using different photocatalysts as shown in the Table 3 and Fig. 3. As we know that the band gap for the formation of benzaldehyde is more suitable for UV light and this property quite resembles the observed data as the table reported.

Titanium dioxide ( $\text{TiO}_2$ ) 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.  $\text{Fe}_2\text{O}_3$ , CdS,  $\text{WO}_3$  (having low band gap than  $\text{TiO}_2$  semiconductor) on the  $\text{TiO}_2$  catalyst photocatalytic reactions have also been studied.  $\text{TiO}_2$  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  $\text{WO}_3$  has been investigated as a potential photo catalyst, but it is generally less active catalytically than  $\text{TiO}_2$ . However, these can be combined with other semiconductors including  $\text{TiO}_2$  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 mandelic acid was studied by using different photocatalysts as shown in the Table 4 and Fig. 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 benzaldehyde.

After completion of photocatalytic reaction the photoproduct benzaldehyde was characterized by usual qualitative tests treatment with (1) Semicarbazide; m.pt-224°C (2) Hydroxylamine hydrochloride, (3) 2, 4-Dinitrophenyl phenyl hydrazones m.pt-237°C shows that photoproduct is benzaldehyde. The confirmatory test for phenylpyruvic acid is carried out as following method:

#### **Test for benzaldehyde:-**

Since it is very easy to identify the benzaldehyde by applying the following general tests:-

- 1-A layer of colorless liquid, having a characteristic order of bitter almond appears.
- 2-The photoproduct reduces the Tollen's reagent and does not reduces Fehling solution.
- 3-Few drops of benzaldehyde added into equal amount of dimethyl aniline and a very small pinch of fused  $\text{ZnCl}_2$ ; then heated the content. A deep green colored ppt is obtained.
- 4-In a dry test tube mixed the photoproduct with equal amount of melted phenol and concentrated sulphuric acid respectively. Now 4-5 ml diluted sodium hydroxide solution is added the resultant solution. A violet-red colored solution is produced.

#### **Separation of 2, 4-DNP and Yield Calculations**

In the case of poor yield of photoproduct the visible amount of 2,4-DNP precipitate may or may not appear, according to the amount of hydrazone substances present. The whole is now shaken with 20 ml of ethyl acetate in a glass stopper 50 ml separating funnel. After separation, the aqueous layer, which is nearly colorless, is extracted with further 10 ml of ethyl acetate; as soon as the aqueous layer is colorless, as usually is the case after two extractions, it is discarded. The united ethyl acetate extracts now contain all the unchanged 2, 4-dinitrophenyl hydrazine together with the hydrazones which have been formed. The liquid is also acid, owing to the extraction of certain amount of hydrochloric acid; these must be neutralized by shaking with solid calcium carbonate (1, 2). The solution is decanted into a glass evaporating basin, washing the calcium carbonate with further ethyl acetate until it is colorless. The washing is added to the main bulk of fluid. The substances in solution must now be transferred to toluene (3). This is accomplished by evaporating the contents of the dish on a water bath to 1-2 ml and then, after removal from the bath, adding about 20 ml of toluene. The slightly cloudy orange-yellow solution is again transferred to the separating funnel and is thoroughly shaken with 5 ml of cold 25% sodium carbonate

solution (4). If benzaldehyde was originally present as its hydrazone dissolves in the aqueous layer, coloring it brown. This extraction is repeated with fresh  $\text{Na}_2\text{CO}_3$  solution until the latter remains colorless; two or three repetitions usually sufficient. The united sodium carbonate layers are now acidified by adding concentrated HCl drop by drop. The 2, 4-DNP of benzaldehyde is precipitated and orange- yellow suspension results. This extracted in a separating funnel with successive 10 ml portions of ethyl acetate until the aqueous layer is colorless (5). It is now usually to employ more than 20 ml of ethyl acetate to achieve this. The ethyl acetate solution now contains all the benzaldehyde hydrazone which was present, and is, evaporated to dryness in a glass basin on a water bath. The orange-yellow residue is dissolved when cool in 5% alcoholic KOH (6), giving a deep red solution which is made up in a graduated vessel with further alcoholic KOH to a volume such that the color is suitable for reading in colorimeter. In practice it is found that the total volume at this stage should be about 50 ml for every mg of benzaldehyde that was originally present in the reaction mixture.

(1)-If neutralization be omitted, the subsequent heating of the solution leads to the formation of small quantities of compounds other than the benzaldehyde derivative which are extracted by the sodium carbonate, coloring it brown, and which are afterwards precipitated upon acidification, giving a reddish color in the final treatment with alcoholic potash. When the neutralization is properly carried out, the sodium carbonate always remains colorless in blank determinations, i.e. when no benzaldehyde is present.

(2)- It was that first the practice of neutralize the acid solution before extracting with ethyl acetate, but if this be done it is found that extraction has to be repeated a much larger number of times before the aqueous layer is colorless.

(3)-The solubility of benzaldehyde derivative in ethyl acetate is so great that it is not completely removed by sodium carbonate solution. Moreover, shaking the ethyl acetate solution with sodium carbonate solution to lead to a small amount of saponification, with the result that separation into layers is imperfect. The substitution of toluene for the ethyl acetate overcome both of these difficulties, but it cannot be used for extraction at the outset because the hydrazine and hydrazones are not sufficiently soluble in to render the process efficient.

(4)-The toluene extract and the sodium carbonate solution must both be at room temperature. Warm  $\text{Na}_2\text{CO}_3$  react with other 2, 4-DNPs besides that of benzaldehyde.

(5)-A good deal of care must be taken at this stage that the effervescence produced by the liberated  $\text{CO}_2$  does not leads to loss by splashing.

### Mechanism

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

With respect to a semiconductor oxide such as  $\text{TiO}_2$ , 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:



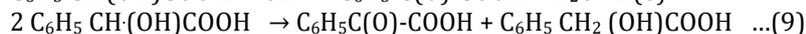
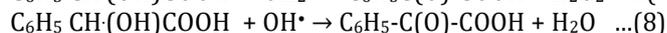
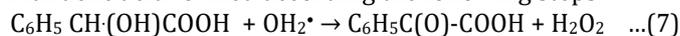
It was explained before, that the surface of  $\text{TiO}_2$  with high surface area retains subsets of hydroxyls, where the net surface density is 4-5 hydroxyl per nm. In addition, suspension of  $\text{TiO}_2$  in solution of lactic acid gives a surface hydroxide ion as locations for primary photo-oxidation processes. Photo holes are trapped by surface hydroxyl groups, whereas electrons are trapped by adsorbed oxygen:



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:



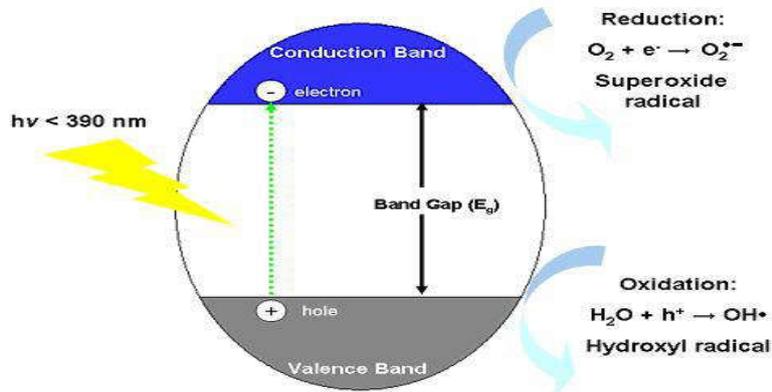
Mandelic acid formed according the following steps:



The elementary photoproduct phenylglyoxalic acid may does not have stability in these circumstances and undergoes to release CO<sub>2</sub> and the final photoproduct benzaldehyde is produced which was well identified by the simple chemical as well as spectral tests. The evolution of CO<sub>2</sub> was also checked during the reaction under controlled conditions.



The whole process can be summarized in the following Fig. 5.



By the observations of photoproducts, it is very important to discuss the characteristic and nature (specially the toxic natures) of photoproduct as the photo reactants are being used in chemical peels, a variety of skin care products including moisturizers, cleansers, eye cream, sunscreen and foundations etc. The U.S. Food and Drug Administration permits up to 1% TiO<sub>2</sub> as an inactive ingredient in food products. While there is no known health effects associated with the use of TiO<sub>2</sub>, a recent study found that 3–6 year old children are the most affected group of people that consume TiO<sub>2</sub> particles from food products. So that the probable side effects of the photoproducts may be the common field of interest for the relevant researchers like dermatologists, pharmacists as well as the chemists. Similarly the side effects of materials in the products where these are being used, may be due these type of oxidative products as the phenylglyoxalic acid and then benzaldehyde may further oxidized into the next successive oxidative product. However, benzaldehyde is used as a flavoring and fragrance in food, cosmetics, pharmaceuticals, and soap and is "generally regarded as safe" (GRAS) by the US FDA [28]. This status was reaffirmed after a review in 2005. It is accepted in the European Union as a flavoring agent. Toxicology studies indicate that it is safe and non-carcinogenic in the concentrations used for foods and cosmetics. It may have carcinostatic (anti-cancer) properties [29].

The mechanistic part of the photochemical transformations is also helpful for chemists to understand more about these new advanced oxidation processes. Hence, this part of reported manuscript may help to arouse the interdisciplinary interest about the side effects of photoproducts, where these are being used.

#### ACKNOWLEDGEMENT

Authors are thankful to Dr. S. K. Sharma, Head, Department of Chemistry, M. L. V. Govt. College, Bhilwara, for providing necessary facility and Author\* is thankful to Dr. B. V. Kabra, Department of Chemistry, M. L. V. Govt. College, Bhilwara for valuable suggestions.

#### REFERENCES

1. Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 1972; 283: 37-38.
2. Frank SN, Bard AJ. Heterogeneous Photocatalytic oxidation of cyanide ions in aqueous solution at titanium dioxide powder. *J Am Chem Soc* 1977; 99: 303-304.
3. R.W. Matthews, *J. Chem. Soc. Faraday Trans. I* 80 (1984) 457.
4. M.A. Fox, *Acc. Chem. Res.* 16 (1983) 314.
5. T. Ohno, K. Nakabeya and M. Matsumura, *J. Catal.* 176 (1998) 76.
6. T. Ohno, K. Tokieda, S. Higashida and M. Matsumura, *Appl. Catal. A* 244 (2003) 383.
7. T. Ohno, T. Mitsui and M. Matsumura, *J. Photochem. Photobiol. A* 160 (2003) 3.
8. Takahara Y. K., Hanada Y., Ohna T., Ushiroda S., Ikeda S., Matsumura M.; Photooxidation of organic compounds in a solution containing hydrogen peroxide and TiO<sub>2</sub> particles under visible light. *Journal of Applied Electrochemistry* (2005) 35:793–797. Springer 2005.
9. Sabin F., Tiirk T. and Vogler A.; Photo-oxidation of organic compounds in the presence of titanium dioxide: determination of the efficiency. *J. Photochem. Photobiol. A: Chem.*, 63 (1992) 99-106 99
10. B. Ohtani, K. Iwai, H. Kominami, T. Matsuura, Y. Kera S. Nishimoto, *Chem. Phys. Lett.* 242 (1995) 315.
11. B. Ohtani, K. Iwai, S. Nishimoto and S. Sato, *J. Phys. Chem. B* 101 (1997) 3349.

12. W. F. Bergfeld, Cosmetic use of Alpha-hydroxy Acids, *Cleveland Clin. J. Med.*, 64, 327-329 (1997).
13. Bernstein E. F., Lee J., Brown D. B., Yu R. J., Van Scott E., *Dermatol Surg.*, 27(5), 429-33 (2001).
14. Van Scott E. J. and Yu R. J., Control of Keratinization with Alpha Hydroxyl Acids and Related Compounds 1, Topical Treatment of Ichthyotic Disorders, *Arch Dermatol*, 100, 586-590 (1974).
15. Deprez P., *Textbook of Chemical Peels: Superficial, Medium and Deep Peels in Cosmetic Practice*, London: Informa Healthcare (2007).
16. Rullan P. and Karam A. M., Chemical Peel for Darker Skin Types, *Facial Plast Surg Clin North Am.*, 18(1), 111-131 (2010) (Pub. Med.).
17. Garg V. K., Sarkar R. and Agarwal, Comparative Evaluation of Beneficiary Effects of Priming Agents in the Treatment of Melasma with Glycolic Acid Peels, *Dermatol Surg.*, 34(8), 1032-1039 (2008). Discussion 1340 (Pub. Med.).
18. Shukichi Sakuraba, and Royoka, Matsushima, *Bulletin of the Chemical Society of Japan*, 43, 2363 (1970).
19. Sarkar R, Bansal S, VK. Chemical Peels for Melasma in Dark-Skinned Patients. *J Cutan Aesthet Surg.* 2012; 5(4): 247-253.
20. Shishira.R.Jartarkar, Mallikarjun.M, Bugude.Gangadhar, Manjunatha.P "Mandelic acid chemical peel in Acne vulgaris: A boon or a bane?" *IOSR Journal of Dental and Medical Sciences (IOSR-JDMS).Volume 14, Issue 5 Ver. VII (May. 2015), PP 32-35*
21. UK Food Standards Agency: "Current EU approved additives and their E Numbers". Retrieved 2011-10-27.
22. US Food and Drug Administration: "Listing of Food Additives Status Part II". Retrieved 2011-10-27.
23. Australia New Zealand Food Standards Code"Standard 1.2.4 - Labelling of ingredients". Retrieved 2011-10-27.
24. Aerobic photo-decarboxylation of  $\alpha$ -hydroxy carboxylic acid derivatives under visible light irradiation in the presence of catalytic iodine. *Tetrahedron Letters* Volume 49, Issue 17, 21 April 2008, Pages 2792-2794
25. van Beek H. C. A., Heertjes P. M.; The Mechanism of the Photoreduction of Azo Dyes in the Presence of DL-Mandelic Acid and in the Absence of Oxygen. *J. Phys. Chem.*, 1966, 70 (6), pp 1704-1711
26. Shinkai S., Nakao H., Ueda K., Manabe O., Ohnishi M.; Selective Photooxidation of Alkali Mandelates by a Flavin Bearing a Crown Ring as a Metal Recognition Site. *Bulletin of the Chemical Society of Japan* Vol. 59 (1986) No. 5 P 1632-1634
27. Putten, P. L. (1979). "Mandelic acid and urinary tract infections". *Antonie van Leeuwenhoek* 45 (4): 622.
28. B. Friedric; W. Elaine; "Benzaldehyde", *Ullmann's Encyclopedia of Industrial Chemistry* (7th ed.), Wiley, (2007), p. 11
29. T. B. Adams, S. M. Cohen, J. Doull, V. J. Feron, J. I. Goodman, L. J. Marnett, I. C. Munro, P. S. Portoghese, R. L. Smith; "The FEMA GRAS assessment of benzyl derivatives used as flavor ingredients". *Food and Chemical Toxicology* (2005). 43 (8): 1207-1240.

**CITE THIS ARTICLE**

P. R. Meena, K. S. Meena and R. K. Khandelwal. Study of Semiconductor Photocatalyzed Oxidation of Mandelic Acid Used In Cosmetic Pharmaceutical Industries. *Res. J. Chem. Env. Sci.* Vol 4 [3] June 2016. 38-46