Photocatalytic oxidation of different carbohydrates by bare and Ag-deposited TiO_2 under UV light irradiation

A

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partial fulfillment for the award for the

Degree of

Master of Science in Biotechnology

By

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Candidate's Declaration

I hereby declare that the work which is being presented in the dissertation entitled "Photocatalytic oxidation of carbohydrates by bare and Ag-deposited TiO_2 under UV light irradiation" in partial fulfillment of requirements for the award of the degree of Master in Science in Biotechnology, Department of Biotechnology Thapar University, Patiala is authentic record to my work during a period of Jan to July 2014 under the supervision of Dr. Bonamali Pal and Dr. Niranjan Das. My thesis has not previously formed the basis for award of any degree, diploma or similar little or recognition.

Patiala

Date- July 18, 2014

Kirandeep Kaur

Kirandeep Kaur

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CERTIFICATE

This is certify that the project entitled "Photocatalytic oxidation of different carbohydrates by bare and Ag-deposited TiO_2 under UV light irradiation" being submitted by Kirandeep kaur in partial fulfillment of requirement for the award of degree for the Master of Science in the Department of Biotechnology Thapar university Patiala, is a record of student's own work carried out by her under our supervision and guidance. The report has not been submitted for the award of any other degree or certificate in this or any other university or institute.

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KIRANDEEP KAUR

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ABSTRACT

In this work we investigated the comparative optical activity and photo degradation properties of different carbohydrates such as glucose, sucrose, starch and carboxymethylcellulose by titanium and metal loaded titanium oxide (Ag loaded titanium oxide prepared by photodeposition and impregnation hydrogen reduction method). The degradation rate of carbohydrates was detected by polariometer and HPLC and its complete mineralization was confirmed by GC. The starch and carboxymethylcellulose (polysaccharide) because of their structural complexity showed slow degradation rate as compare to sucrose (disaccharide) and glucose (monosaccharide). The mechanism involves the production of electron-hole (e^-- h^+) pair by photo excited semiconductor particle (TiO_2), which is responsible for oxidation and reduction reaction of adsorbed species on the TiO_2 surface. Holes oxidize water to hydroxyl radical, which are responsible for degradation of carbohydrates. Silver loaded showed the better degradation activity as compare to bare TiO_2 because metal loaded TiO_2 inhibit the recombination of electrons and holes and enhance photocatalytic activity. After five hour photocatalytic reaction with the metal loaded TiO_2 complete degradation of glucose and sucrose was observed and some industrially value added compound was detected. However polysaccharides were showed slow degradation at same reaction time.

CHAPTER 1

INTRODUCTION

Photo means light and catalysis is the process of increasing the rate of reaction in the presence of a substance without involving it. So, photocatalysis is a process which uses light to activate the rate of reaction in presence of substance called photocatalyst and photocatlyst creates strong oxidation agents to breakdown any organic matter to carbon dioxide and water in presence of photocatalyst, light and water. The different semiconductors (e.g. ZnS, CdS, ZnO, PbS, CdSe and TiO2) are mainly used as artificial photocatalyst for photocatalytic degradation of wide variety of environmental contaminants (Rajh et al. 2011). Fujishima et al. (1969) discovered the photocatalytic water splitting on TiO_2 electrodes and extensive research was carried out regarding TiO_2 and credited TiO_2 as a most promising photocatalyst due to its characteristic properties like chemical stability, nontoxicity, low cost and easily availability etc. (Linsebigler et al. 1995). When photocatalyst like TiO_2 absorbs ultra-violet (UV) radiation with energy equal to or less than the band gap energy, the electron is photo-excited to the conduction band (C_b) from the valence band (V_b), thereby creating the negative-electron (e^-) and positive hole (h^+) pair in the C_b and V_b, respectively as shown in Scheme 1. After that, the photo-generated charge carriers in the bulk diffuse to the surface of photo catalysts and takes part in oxidation-reduction reactions of the surface adsorbed species. The highly oxidizing positive hole breaks apart the water molecule to form hydroxyl radicals and photoelectron takes part in reducing action.

$$TiO_2 + hv \longrightarrow e^- + h^+$$

$$e^- + h \longrightarrow heat$$

$$e- + O_2 \longrightarrow O_2^{\bullet -}$$

$$h^+ + H_2O \longrightarrow OH + H+$$

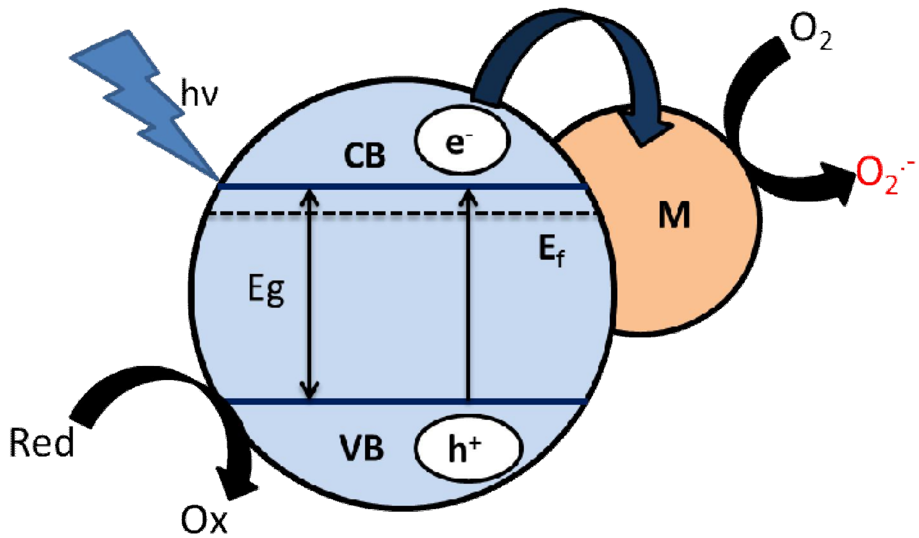
$$R\text{-}H + OH^{\bullet} \longrightarrow R^{\bullet} + H_2O$$

$$R^{\bullet} + h^+ \longrightarrow R^{\bullet -} \longrightarrow \text{Degradation product}$$

$$O_2^{\bullet -} + H^+ \longrightarrow HOO^{\bullet}$$

$$HOO^{\bullet} + e- \longrightarrow HO_2^-$$

$$HOO^- + H^+ \longrightarrow H_2O_2$$



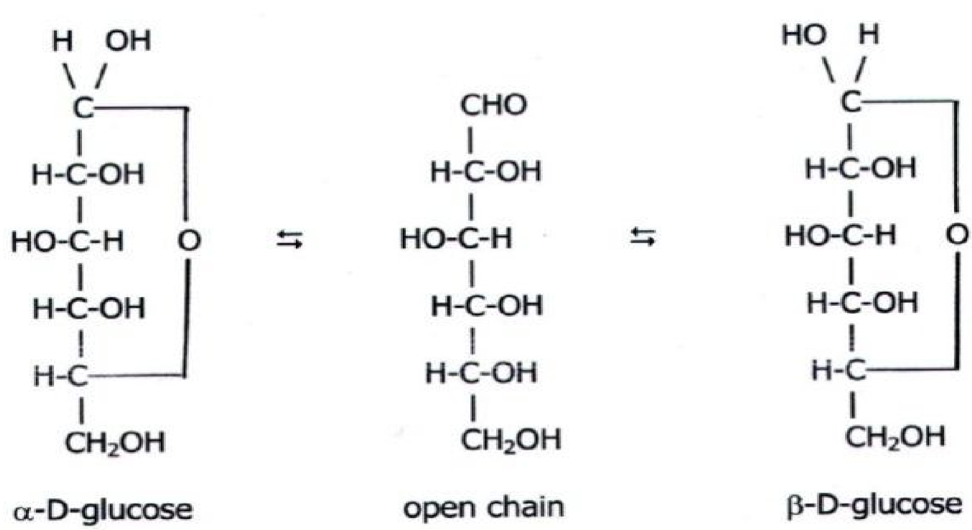
Scheme 1 Mechanism of photocatalysis

The electrons can be adsorbed by oxygen to form superoxide radical or it can react with oxygen along with hydrogen to create hydroxyl radicals and ions. All the species produced are very reactive. The electrons when combined with oxygen are stopped from dropping back and thus recombination is prevented .This means they are more reactive to react with reactant species. Reactivity of TiO_2 can be further be increased by adding metal ion on it which prevent electron-hole recombination as discussed below.

The large band gap (3.2 eV) and a high rate of recombination between electrons and holes results in low quantum efficiency and therefore, prevents it from practical application. So, metallization of TiO_2 surface with noble metals such as Cu, Ag, and Au has been investigated from the early times of photocatalysis to increase the photocatalytic activity. The noble metals act as electron trapper and slow down the recombination rate of electron hole pair. The metal ion or metal doped semiconductor composites exhibit shifts in the Fermi level to more negative potentials and has the mediating role in storing and shuttling photogenerated electrons from the semiconductor to an acceptor. This shift enhances the efficiency in the interfacial charge transfer process and improves the energetics of the composite system.

Food industry constitutes one of most important parts of the world economy. It gives huge amount of solid and liquid wastes containing water soluble carbohydrates which is the main ingredient of plants and plant food. Carbohydrates are aldehyde or ketone compound with multiple hydroxyl groups and is represented by general formula, $C_x(H_2O)_y$. The physical properties of carbohydrates such as solublity, viscosity, crystallinity, stability and optical activity and chemical properties depend primarily on monosaccharide composition, glycosidic linkage, molecular size, branching and functional group present. The presence of asymmetric carbon atoms in carbohydrates makes possible the formation of structural isomers, geometrical isomers, stereoisomers and optical isomers in them. The number of possible isomers of any given compound depends upon the number of asymmetric carbon atoms present in molecules.

Optical isomer (enantiomers) are those isomer differ from each other in deposition of various atoms or groups of atoms in a space around the asymmetric carbon atom. All carbohydrates contain multiple chiral centers are thus optical active. Optical isomers are mirror images of each other. Most of reducing sugar such as glucose exhibit mutarotation when dissolved in water. The specific rotation for two anomer forms of glucose and for the aqueous equilibrium mixture is:



Scheme 2: Mutarotation of glucose

112.2º ⟶ 52.7º ⟵ 18.7º

Alpha D-glucose) Mutarotation (Beta D- glucose)

Photocatalysis by TiO_2 disturb the formation of mutarotation and cause changes in its optical activity. The carbohydrates are mainly classified into three groups-monosaccharide, disaccharide and polysaccharide These monosaccharide and oligosaccharide can serve as food for many harmful microorganisms and cause serious threat for other aqueous livings, both for water plants and animals and therefore, needs to be removed from the environment. Carbohyrates are highly oxidized molecules and except for specific functional groups are relatively insensitive to oxidation. Until now different oxidant like chromic acid, fehling reagent and metal hydroxide $Cu(OH)_2$, Ag(OH) and $Bi(OH)_3$ and biological methods are used. Sewage from food industry are purified using mainly biological methods. The biological processes are based on special metabolisms of some bacteria, transforming organics containing water into mineral compounds. Recently, a research has been undertaken on practical application of Advanced Oxidation Process for purification of industry sewage. The processes such as photocatalysis on semiconductors, H_2O_2 action, ozonation, Fenton-photon reactions, electrochemical oxidation and also their combinations are good examples of the Advanced Oxidation Processes (AOP). Among the AOP, photocatalysis on semiconductors seems to be most promising. The process needs only a photoactive semiconductor and appropriate light UV part of solar for the excitation of semiconductor electrons. Many compounds such as carboxylic acids, organic dyes, phenols, pesticides, surfactants, carbohydrates, some inorganic compounds and many others are fully mineralized by photocatalysis on TiO_2.

The photocatalysis is preferred over conventional method as it does not require toxic solvent as in conventional method and it is a single step reaction. Photo catalysis occurred at ambient temperature and pressure so is relatively cheap process. It does not leave any toxic byproducts also. It is studied that photocatalytic effect of TiO_2 is enhanced by loading of noble metal such as silver. It has been found that photocatalytic oxidation of organic compound by TiO_2 completely degraded to CO_2 and H_2O via many intermediate compounds during longer exposure of light irradiation. By changing experimental parameter such as light exposure time, solvent, surface modified TiO_2 and metal additives we may get the desired products of high selectively and yield. Therefore, in this work, the effect of molecular structures and sizes of carbohydrates such as glucose, sucrose, starch and carboxymethylcellulose on their photo-degradation under UV-irradiation by TiO_2 using various techniques have been studied.

LITERATURE REVIEW

TiO_2 as a photo- catalyst have many applications, because of its chemical stability, non-toxicity, antibacterial, non-corrosive properties (Sunada et al. 2003). TiO_2 can photo catalytically degrade the environmental pollutants like organic and inorganic materials to CO_2, H_2O and harmless inorganic anions and its super hydrophilicity nature leads to self-cleaning property and also resulted in development of anti-fogging glasses (Heller 1995). Doping with noble metal like silver, gold and platinum used as co-catalyst to enhance the photo-catalytic properties of semiconductor. A number of processes like stream gasification, fast pyrolysis and supercritical conversion have been developed for hydrogen gas from biomass. (E.g.cellulose, dead insects and wastes materials). However these processes require harsh conditions including high temperature and high pressure and consequently imply high cost. Compared to these extensive thermochemical processes, photo catalytic reforming process which processes at room temperature is a good approach. Kawai and Sakata (1980) reported that hydrogen could be generated from carbohydrates on $RuO_2/TiO_2/Pt$ photo catalyst under 500 W Xe lamp irradiation.

$$(C_6H_{12}O_6)_n + 6n\ H_2O \longrightarrow 6n\ CO_2 + 12n\ H_2.$$

Moser et al. (1985) reported efficient, rapid and one electron photo-oxidation of chemisorbed polyhydroxyl alcohols and carbohydrates by TiO_2 nanoparticles in an aqueous. It is shown that nanoparticles surface contain the specific binding site for polyhydroxylated aliphatic compounds and it is suggested that octahedral co-ordinated Ti atom is chelated by neighboring hydroxyl of ligand. This binding account for depletion of penta-coordinated Ti atoms of that was observed in the XANES spectra of coated TiO_2.
Glucose is the most accessible hexose as it can be obtained from the most abundant and renewable biomass on Earth. Lecomte et al. (2002) reported that glucose can be catalytically transformed into furan derivate such as hydroxymethyl furfural (HMF) and furan carboxylic acid (FDCA) which is potential compounds to prepare polymeric materials and biofuels by titanium oxide catalysts. Based on this, glucose conversion was

studied with a TiO_2 catalyst obtained by a sol-gel method. The catalytic results showed that higher temperature and reaction time increases the HMF yield.

Photocatalytic oxidation of cyclohexanol**,** cyclopentanol, and cycloheptanol was considered by using titanium dioxide (Degussa P25) as a semiconductor photocatalyst (Palmisano et al 2007). The effect of different operational parameters such as the catalyst, the solvent, time, and oxidant was also studied. Results showed a high percentage of conversion for (71.6%, 94.2%, and 100%, resp.) and that the primary photocatalytic oxidation products are the corresponding cycloalkanone .GC and GC-MS technique were used to identify the several products. The photocatalytic activity is explained by a photo induced electron transfer mechanism through the formation of electron-hole pair at the surface of the semiconductor particles.

The quantum efficiencies of the photocatalytic mineralization of organic pollutants on commercial bare titanium is very low (<1%) owing to the rapid recombination of photo generated electrons and holes created within semiconductor particles. There have been extensive studies to improve the TiO_2 photocatalytic activity including deposition of noble metals (*e.g.* Ag or Pt) on theTiO_2 surface. Metallization of TiO_2 with silver was reported to significantly increase the photocatalytic degradation/oxidation rates of oxalic acid (Szabo et al. 2003), sucrose **(**Vamathevan et al. 2002), methyl orange (Bernard et al. 2003) **,** 2-chlorophenol (Pichat et al. 2004) and phenol, ranging from 50 to 500%. Tade et al. (2003) studied 0.24% wt. of Ag noble metal on nanoparticles TiO_2 improved the photocatalytic activity due to decrease in active catalytic improvement in charge separation. It was observed that photo decay rate is more than double than the uncoated TiO_2. When the amount of loaded Ag increase above this value then photodecay rate will decrease because in this case loss of active photo catalytic surface are play dominant role. The morphology of sample was characterized by ultra-high resolution field emission scanning electron microscope. The crystalline structure and optical properties of samples were investigated by X-Ray diffraction and by UV-Vis spectrophotometer. The effect of metal loading on photo catalytic activity depends upon the type of origin of titiaum, metal and metal precursor concentration. It was reported that the highest photoactivity was observed for TiO_2 loaded with silver (2%Ag on P25) , gold (1%Au on P25) (Orlov et al.2004) and platinum (0.5% Pt. on ST-01) (Kitano et al.2007) clusters cause degradation of phenol 91%,49% and 91% respectively after 60 minutes irradiation under UV light.

Absorption by photocatalyst in visible range can be significantly increase by combination of metal ions. Photocatalyst depend upon chemical nature and concentration of metal doping ions and on method of preparation. Liu et al. (2007) attained an Ag-TiO2/montmorillonite composite by hydrolysis of $TiCl_4$ and, due to the large specific surface area and the effect of silver content to improve light absorption; they observed an increased photooxidation activity as compared to the bare TiO_2.

Photocatalyst TiO_2 degrades and mineralizes a large variety of environmental contaminations, including organic and inorganic anions. Up to now, polychlorobiphenyl (Carey et al. 1976), cyanide ions (Frank S.N.1977), organo chlorides (Hsiao et al. 1983) such as chloromethane and trichloroethylene in soils and ground waters using TiO_2 catalyst.

RELEVANCE OF PRESENT STUDY

Carbohydrates which contain asymmetric carbon atom are considered as optical active. There is no such report available regarding the effect of isomerization of carbohydrates by TiO_2 photooxidation.

The wastes of carbohydrates are usually non toxic, they are widely utilized as animal food and they are also serves as raw material for food and other industries. These non-toxic wastes become very harmful for their natural environment if their concentration exceeds after a certain value. These carbohydrates wastes can serve as food for many micro-organisms. Many bacteria use glucose and they possess the enzymes need for oxidation and degradation of sugar. A few bacteria are able to use oligosaccharide (lactose and sucrose) and polysaccharide (starch) because they possess those enzymes (e.g. lactase and alpha amylase for lactose and starch breakage) requires for cleavage of glycosidic bond and produce simple sugar which can be easily transported into cell. Some microorganisms which are usually present in the waste water, utilize carbohydrates as a carbon source are, *Staphylococcus aureus, Enterobacter aerogenes, Shigella flexneri, Pesudomonas aeruginosa, Bacillus sutilis, Klebsellia pneumonia*. These pathogenic microorganisms are responsible for various infection, including lower respiratory tract infections, skin and soft tissue infection, diarrhea and pneumonia on the human health. The excess amount of carbohydrates present in waste water are broken down by aerobic bacteria resulting in decrease of oxygen for fish and other insects which cause threats to aquatic habitat organisms. So there is need to remove this excessive amount of carbohydrates from sewage water. There are many reports available regarding the photooxidation of carboxylic acids, phenols, pesticides, surfactants, organic dyes and some of inorganic compounds by using TiO2 .There are no such reports available on complete degradation of carbohydrates. So this research mainly focuses on the degradation of carbohydrates by photocatalytic $TiO_{2.}$

OBJECTIVES

- To study the comparative effect on optical isomerization of different carbohydrates glucose, sucrose, starch and carboxymethylcellulose by photooxidation of TiO_2 and metal loaded TiO_2

- To study photocatalytic degradation and complete mineralization of carbohydrates into CO_2 and H_2O by photooxidation using bare and metal loaded TiO_2

MATERIALS AND METHODS

4.1 Materials

Materials used in various experiments were purchased from commercial companies and were used without any further purification. Glucose ($C_6H_{12}O_6$), Sucrose ($C_{12}H_{22}O_{11}$), Starch ($(C_6H_{10}O_5)_n$), Carboxyl methyl cellulose ($C_8H_{15}NaO_8$) were purchased from sigma chemise. Silver nitrates ($AgNO_3$), methanol (CH_3OH), Isopropanol alcohol (C_3H_8O), Sulfuric acid (H_2SO_4) were purchased from Loba Chemie. P25TiO_2 was obtained as a gift from Degussa Company from Germany.

4.2 *Metal loading on TiO_2 by photodeposition*: Photodeposition of Ag on TiO_2 nanoparticles was carried out by photocatalytic reactions. Metal like Ag was loaded on TiO2 by irradiating (2h) test tube containing 10 ml (50 vol %) isopropyl alcohol along with the requisite amount of $AgNO_3$ (0.935 ml of 1 wt. %) in a purged solution with constant stirring. Metal loaded TiO_2 was washed with methanol and dried.

4.3 Characterization: Carbohydrates samples of concentration 55 mM (5 ml) were photo oxidized in the tube having 5 ml of these compounds with bare TiO_2 (50 mg) of TiO_2 and metal loaded TiO_2 in UV exposure under magnetic stirrer for different time periods. Clear solution of these carbohydrates were obtained by centrifugation at 10000 rpm and then filtered by cellulose paper. To predict the degradation rate, reaction samples were analyzed by HPLC (Agilent 1120 compact LC equipped with a Qualisil BDSC -18 column) with flow rate 1ml per minutes and 100% water as solvent system). Reaction samples were diluted ten times prior to HPLC analysis of starch and carboxymethylcellulose. Mineralization level of these reaction samples were analyzed by GC. Same reaction samples were analyzed by LC-MS (Diode Array 295) for identification of the intermediates that were formed during photooxidation by TiO_2.

The different carbohydrate samples at the concentration 0.5 mM were prepared. Photocatalytic oxidation of carbohydrates compounds were carried out in a test tube containing 15 ml of these compounds at concentration 0.5 mM and with bare TiO_2 and metal loaded TiO_2 (10 mg), irradiated with UV light under constant stirring for different time intervals. The reaction samples were centrifuged at 10,000 rpm and filtered with cellulose filter paper. The bare and TiO_2 treated reaction samples were analyzed by polariometer (Automatic Polari meter Optical Activity Limited).

CHAPTER 5

RESLUTS AND DISCUSSION

Carbohydrates are complicated molecules. They slowly change into different isomer in solution. In water they slowly change from one to another form quickly. They are described as being equilibrium with different structure. Carbohydrates solution has the power of rotating the plane of polarized light through certain angles and hence these are said to be optical active. The presence of asymmetric carbon atoms in the compound confers optical activity to it. When a beam of polarized light is passed through an optical active solution, it may be rotated either to right or to left, depending upon the type of optical isomer present. If compound that rotate plane of polarized light to right is called dextrorotary and if compound rotate plane of polarized light to left, then it is called levorotatory. The instrument used for measuring angles of rotation is called polariometer.

From the optical rotation we can calculate the optical activity of carbohydrates solution by using following formula-

$$opticalactivity = \frac{100 \times opticalrotation}{lengthofpolariometertube \times concentrationofsolution}$$

5.1 Effect on optical activity of carbohydrates with photooxidation of TiO_2

Optical activity depends upon the type of substrate. This is because of different substrate contains different number of chiral carbon. Optical activity depends upon the chirality of carbon molecules. It was observed that, starch and carboxymethylcellulose because of having more number of chiral carbon showed higher optical activity as compared to sucrose and glucose which is shown in Fig. 1(a). There was a continuously decrease in optical activity when carbohydrates solution (0.5 mM) treated with TiO_2 in presence of UV light and at a particular time interval its optical activity became zero. All the substances had different treatment time at which their optical activities became zero. Optical activity zero means there is no chiral carbon now solution becomes optical inactive. When carbohydrates solution treated with Ag loaded TiO_2 it attained zero optical activity sooner as compared with bare $TiO_{2.}$ Glucose, sucrose, starch and carboxymethylcellulose became achiral in 90, 180, 240 and 300 min, respectively with the treatment of bare TiO_2 as shown in Fig1 (b). It was because of starch and carboxymethylcellulose had more chiral carbon atoms so they took longer time to become achiral during photooxidation as compared with glucose and sucrose.

Photooxidation with metal loaded TiO_2 of glucose, sucrose, starch and carboxymethylcellulose attained achiral in 30, 90 and 180 min, respectively as shown in Fig1 (c). This was because metal loaded TiO_2 enhanced the photocatalytic properties. So photocatalysis with the Ag loaded TiO_2 carbohydrates became achiral (optical inactive) in less time.

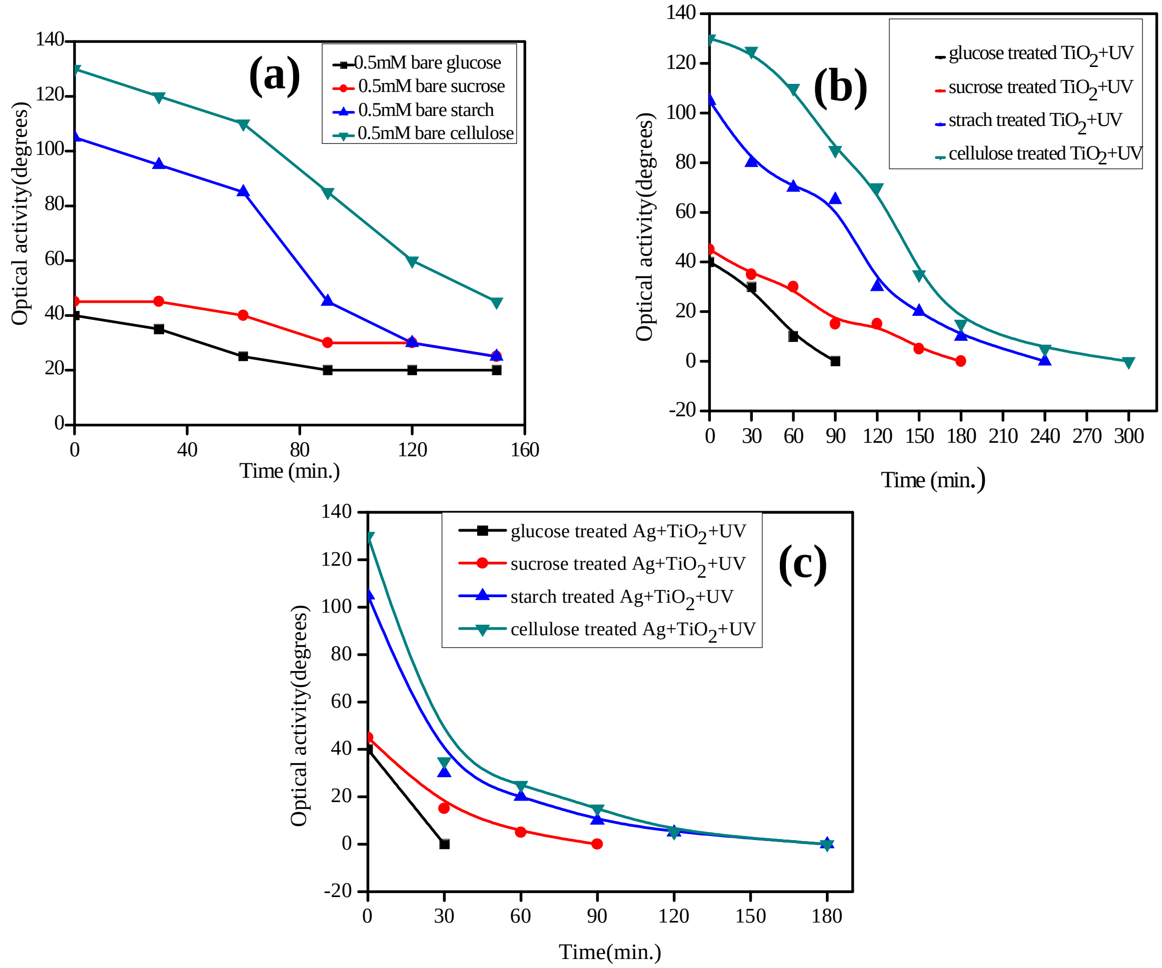
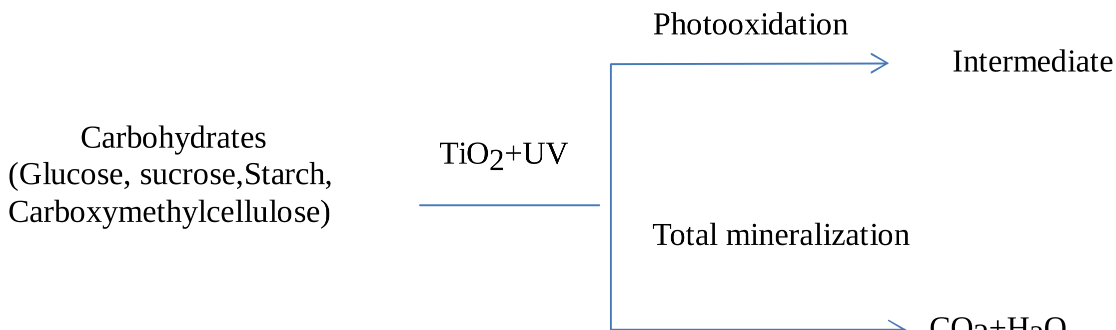


Fig.1:Change in optical activity of carbohydrates at different concentration and time
(a) Authentic carbohydrates (b) treated bare TiO_2+UV (c) treated Ag-TiO_2 +UV

5.2 Degradation of carbohydrates by TiO_2 mediated photooxidation

Photooxidation process of an aqueous phase is based primarily on the attack of hydroxyl radical, resulting in destruction of organic compounds such as carbohydrates. Photocatalytic nature of TiO_2 causes the degradation of carbohydrates and minerlization of carbohydrates into CO_2 and H_2O.



5.2.1 Degradation of glucose

HPLC chromatogram of authentic, after 5 hours photooxidized with bare TiO_2 and Ag-TiO_2 of glucose of concentration 50 mM at retention time 1.793 min shown in Fig.2. In this the peak height represented the concentration of glucose.The peak height decreased with photo oxidation of glucose by TiO_2 and Ag- TiO_2.There was more decreased in peak height with photooxidation of Ag- TiO_2 than bare TiO_2 because metal loading enhanced the photo oxidation activity.

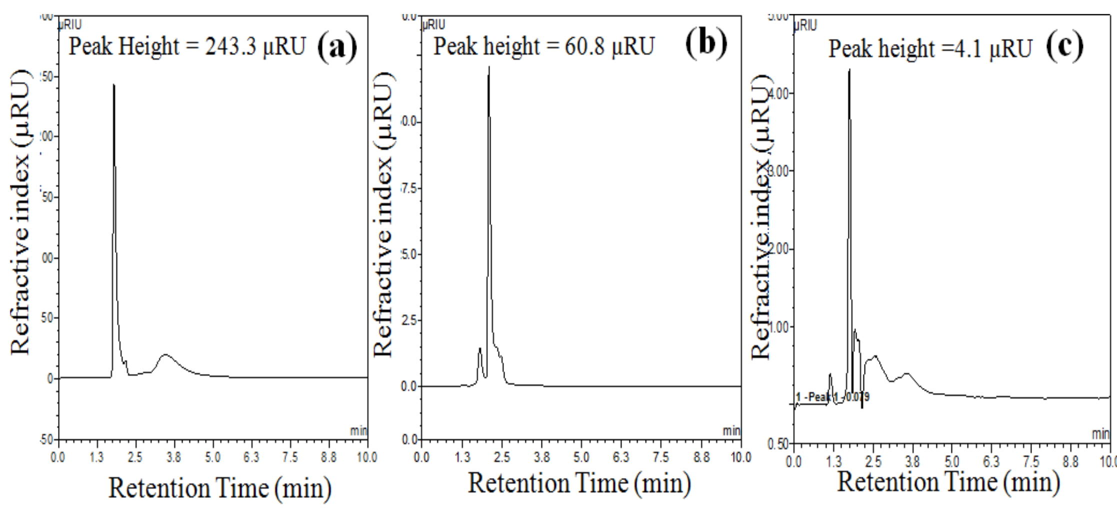


Fig. 2. HPLC chromatograph of glucose: **(a)** authentic **(b)** treated bare TiO_2+UV **(c)** treated Ag-TiO_2+UV

There is gradual decreased in concentration of glucose and increase in amount of CO_2 with photooxidation of glucose with bare TiO_2 and Ag- TiO_2 at different time interval as shown in Fig.3. Glucose is monosaccharide so it was easily degraded. After 5 hours photooxidation the glucose, concentration reduced from 2500 µmol to 82.23 µmol with bare TiO_2 and it was completely degraded with Ag- TiO_2

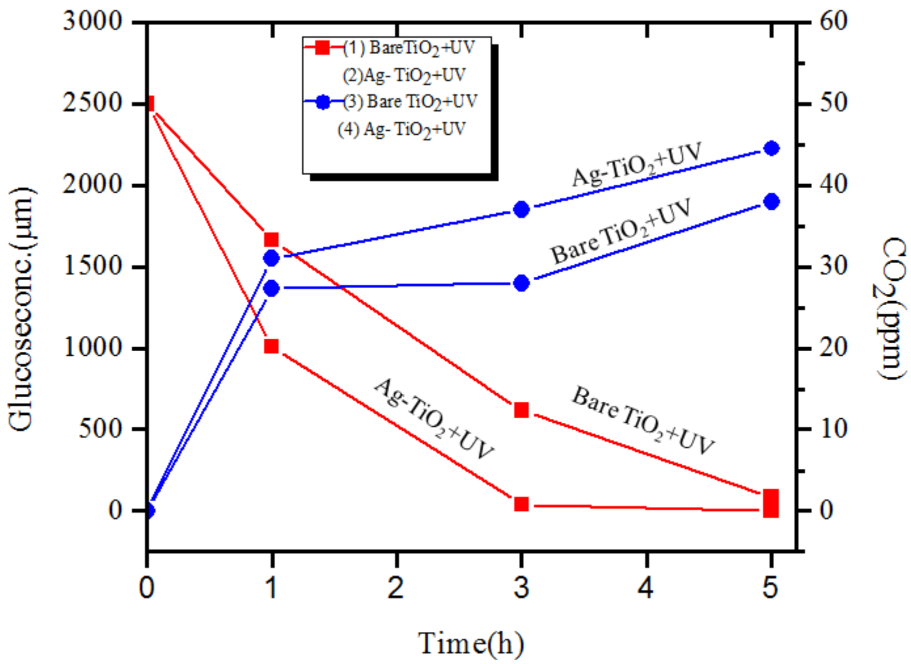


Fig.3: Change in concentration of glucose and amount of CO_2 produced with bare TiO_2 and Ag- TiO_2 nanoparticles

During photo oxidation of glucose various intermediate compounds were formed which ware analyzed through LC-MS as shown in Fig.4.

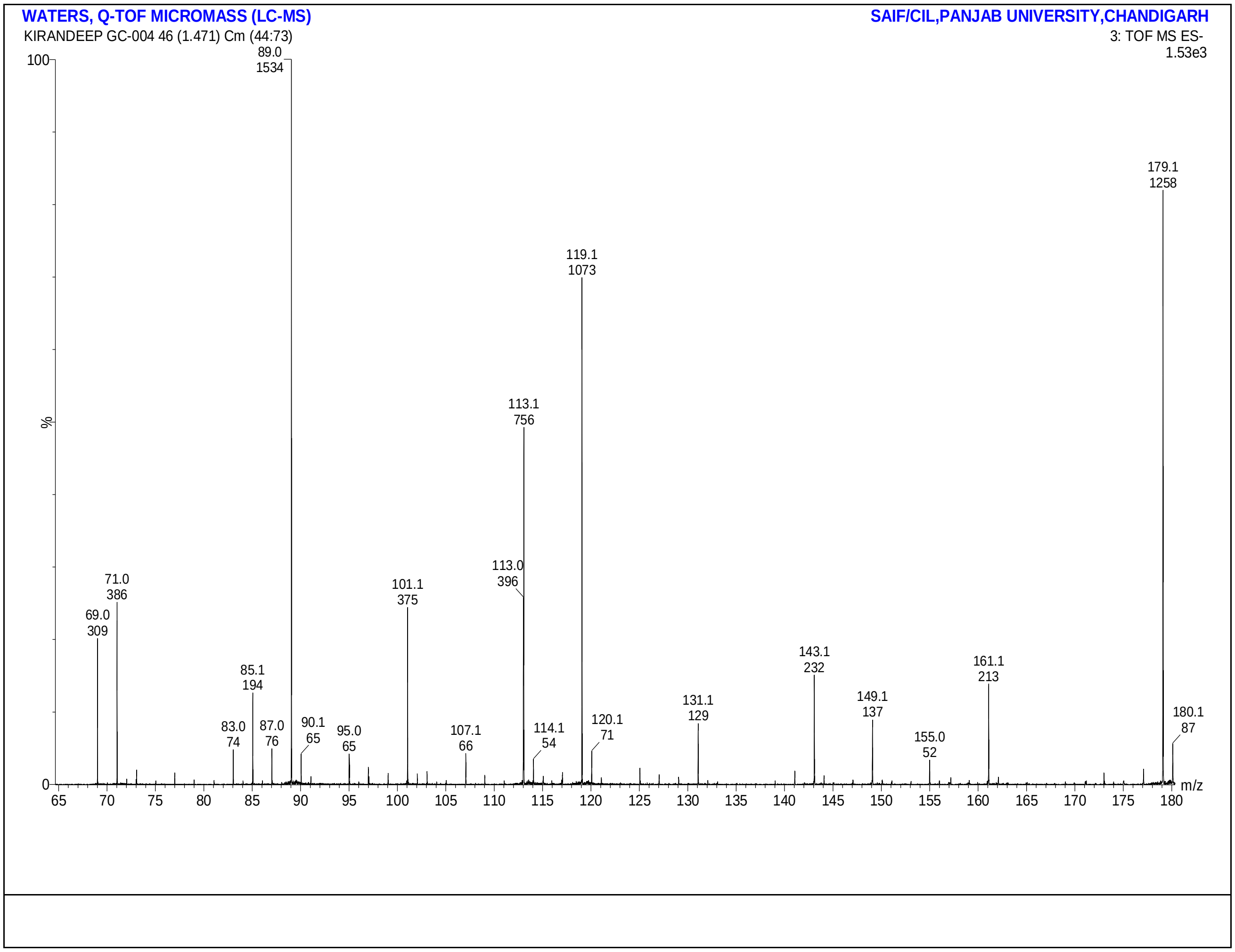
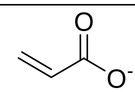
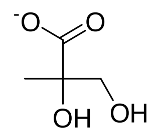
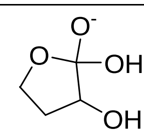
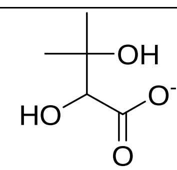
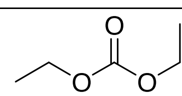


Fig.4 Shows the intermediate products of glucose after 5 hour treatment with TiO_2. Different peaks indicates the various intermediate compounds

Different intermediates formed during photooxidation of glucose are shown in Table1.which indicates structure of intermediate compound with their molecular mass.

Table1. Different intermediates of glucose after 5 hours photooxidation with bare TiO_2

Molecular mass	Compound name	Compound structure
71	Acrylate	
85	Methyl glycerate	
119	Dihydroxyterahydro furan 2-olate	
121.1	2-3 dihyroxy3-methyl butanate	
161	Diethyldicarbonate	

5.2.2 Degradation of sucrose

HPLC chromatogram of authentic, treated with bare TiO_2 and treated with Ag- TiO_2 of sucrose at 50 mM concentration with retention time 1.83 min as shown in Fig. 5.The peak height of sucrose decreases by photooxidation with bare TiO_2 and Ag- TiO_2.

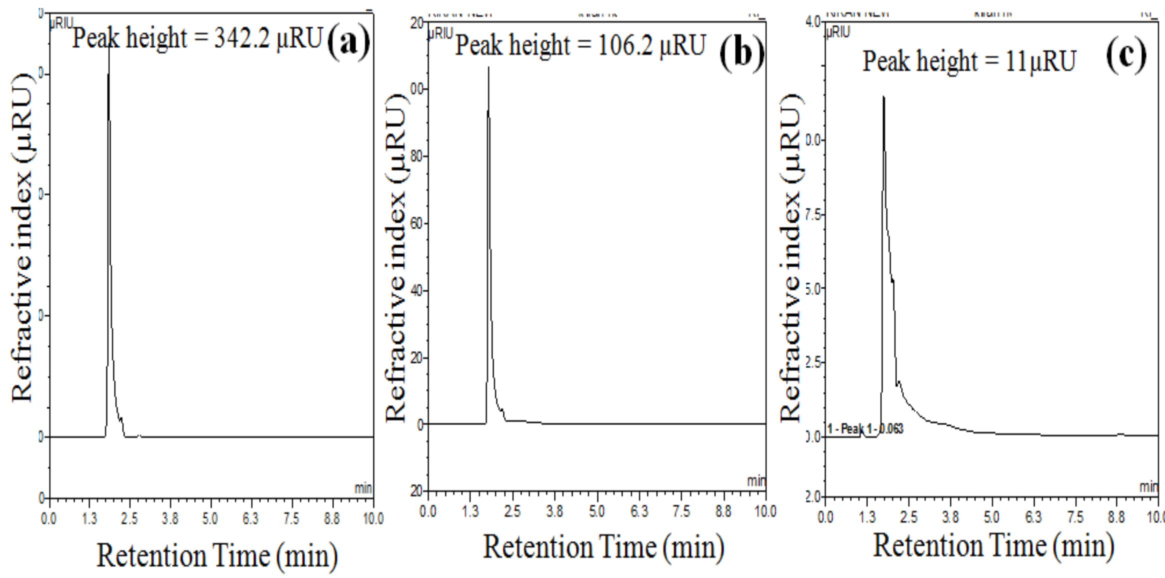


Fig. 5: HPLC chromatogram of sucrose: **(a)** Authentic **(b)** treated with bareTiO_2 +UV **(c)** treated with Ag-TiO_2 +UV

Sucose is diasaccharide it contain glycosidic bond so it takes longer time for degradation and complete minerlization as compared to monosaccharides. At the different reaction time concentration of sucrose was decreased and the amount of CO_2 increased with photooxidation by bare TiO_2 and metal loaded TiO_2. Concentration of sucrose decreased from 2500 µmol to 185.03 µmol with phtooxidation by bare TiO_2 and it was completely degraded by Ag- TiO_2 because metal loading inhibit the recombination process as shown in Fig. 6

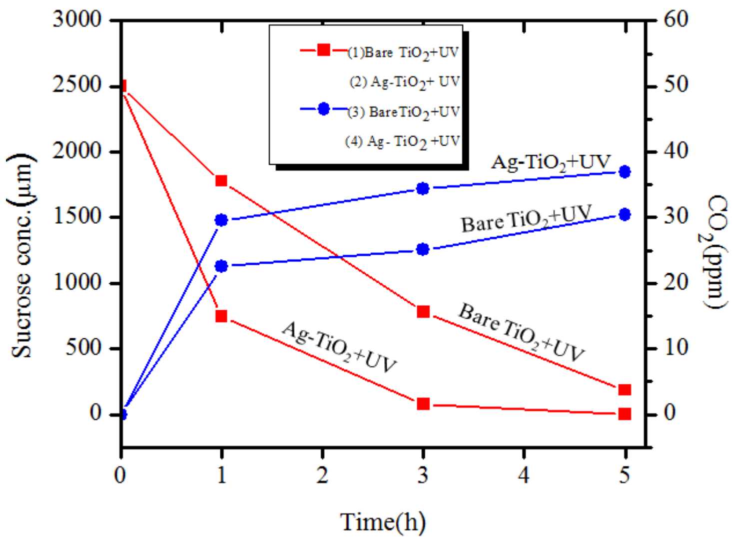


Fig 6: Change in concentration of sucrose and amount of CO_2 produced by bare TiO_2 and Ag- TiO_2 nanoparticles

The different intermediates formed during photooxidation of sucrose were analyzed by LC –MS as shown in Fig.7. Each peak represents the intermediate formed during photooxidation of sucrose.

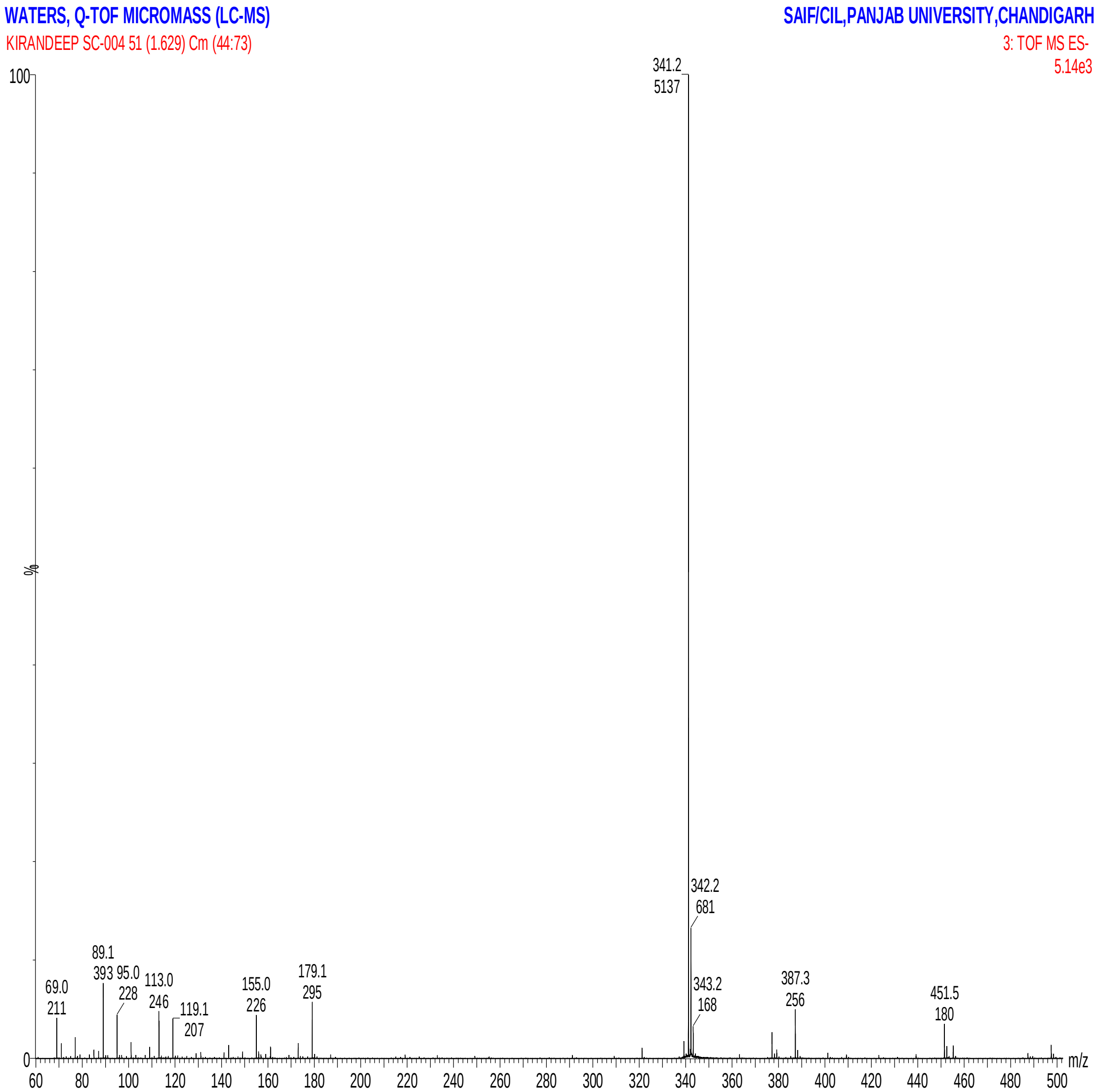
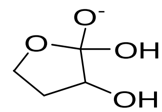
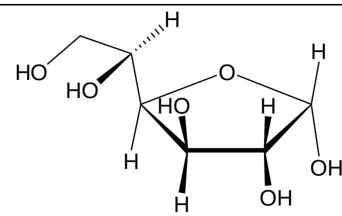


Fig. 7 shows the different intermediate products of sucrose after 5 hour treatment with TiO_2. Different peaks indicate the various intermediate compounds formed during photo oxidation of sucrose.

Intermediates formed during photo oxidation of sucrose are shown in Table 2 with their structure and molecular mass.

Table 2 Different intermediates of sucrose after 5 hours photo oxidation with bare TiO_2

Molecular mass	Compound name	Compound structure
119	Dihydroxyterahydro-furan 2-olate	
180	Glucose	

5.2.3 Degradation of starch

HPLC chromatogram of authentic, treated with bare TiO_2 and treated with Ag- TiO_2 of starch at 50 mM concentration at retention time 2.7 min as shown in Fig. 8. Peak height of starch decreased with photooxidation by bare TiO_2 and Ag- TiO_2

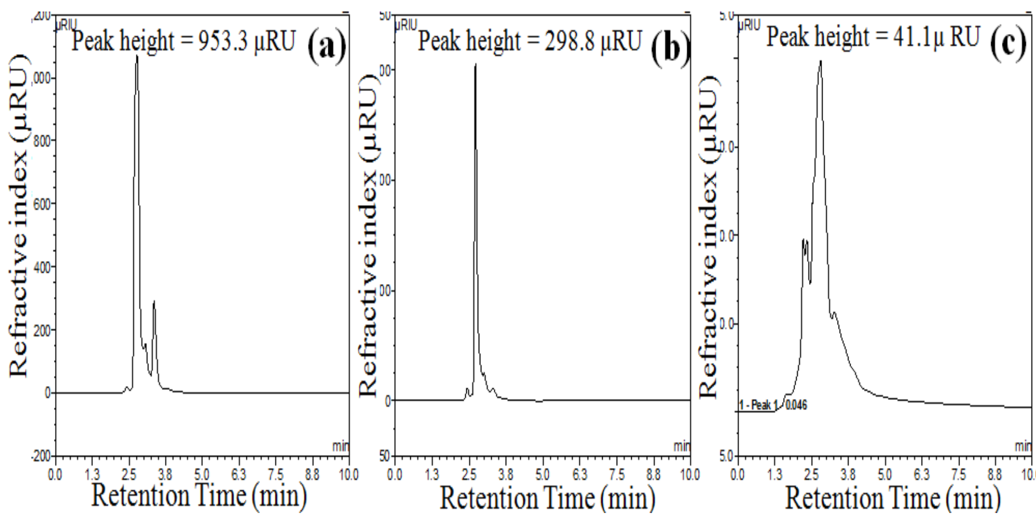


Fig.8: HPLC chromatogram of starch: **(a)** authentic **(b)** treated bare TiO_2+UV **(c)** treated Ag-TiO_2+UV

Starch is a polysaccharide which contains α1-4 glycosidic bond and α1-6 glycosidic bond which create complexity in structure so photooxidation of starch take much longer time for degradation and mineralization into CO_2 and H_2O. There was reduction in concentration from 2500 to 107.52 μmol after 5 hour photo oxidation treatment by bare TiO_2 and it became 45 μmol after 5 hour photo oxidation treatment by Ag- TiO_2 as shown in Fig.9

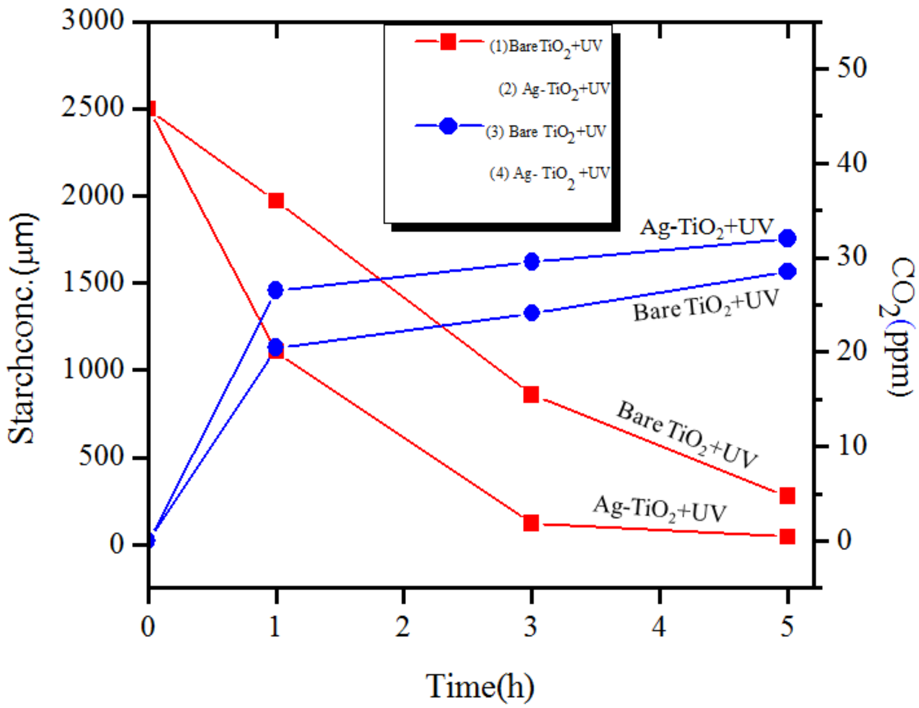


Fig. 9: Change in concentration of starch and amount of CO_2 produced by bare TiO_2 and Ag- TiO_2 nanoparticles

5.2.4 Degradation of carboxymethylcellulose

HPLC chromatogram of carboxymethylcellulose of authentic, bare TiO_2 and metal loaded TiO_2 at retention time 2.3 min was recorded as shown in fig.10. Peak height of carboxymethylcellulose decreased with photo oxidation of carboxymethylcellulose by bare TiO_2 and Ag-TiO_2 which corresponded to concentration of substrates.

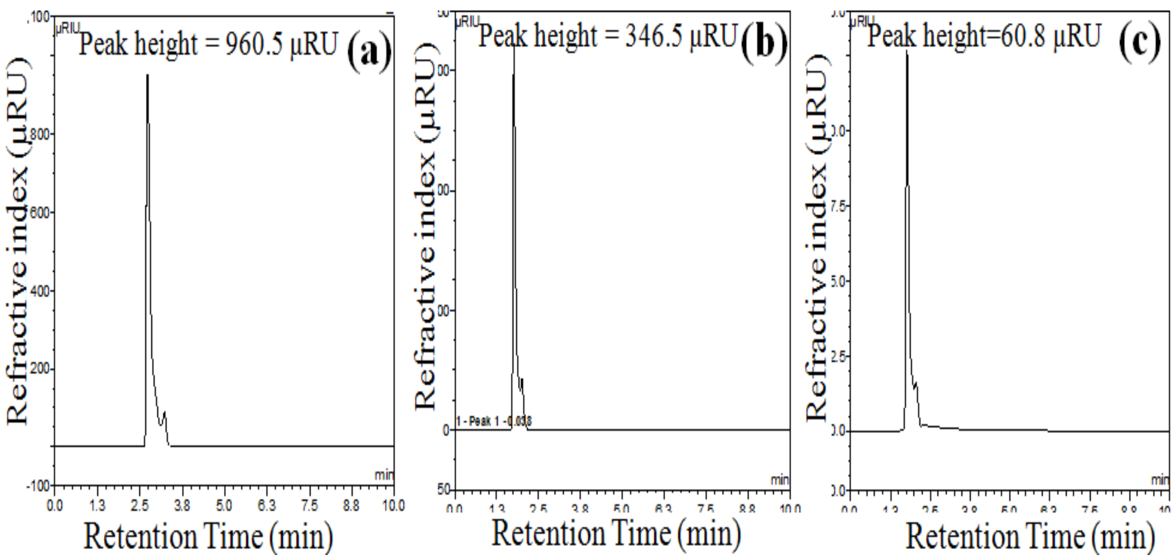


Fig. 10: HPLC chromatogram of CMC: **(a)** authentic **(b)** treated bare TiO_2+UV **(c)** treated Ag- TiO_2 + UV

Concentration of carboxymethylcellulose decreased from 2500 to 278.5 µmol with photooxidation by bare TiO_2 and it became 60.2 µmol after photooxidation with Ag-TiO_2 because metal loading increase the photocatalytic efficiency of bare TiO_2 as shown in Fig.11

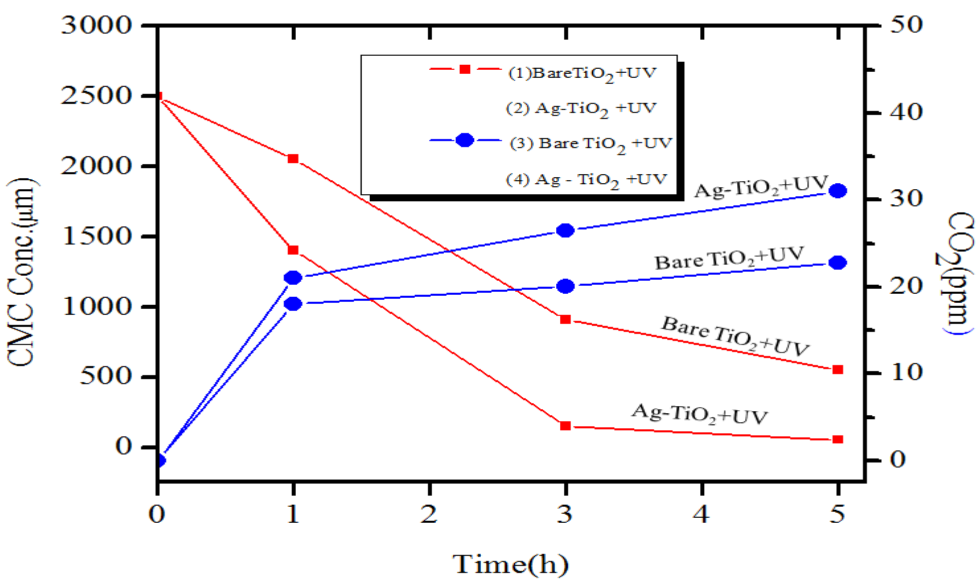


Fig. 11: Change in concentration of CMC and amount of produced CO_2 by bare TiO_2 and Ag-TiO_2 nanoparticles

5.3 Comparative degradation of carbohydrates with bare TiO_2

Degradation of carbohydrates depends upon structural complexity. Glucose concentration reduced from 2500µmol to 41µmol and polysaccharides like starch 2500 µmol to 485 µmol, as shown in Fig.12 (a) CO_2 produce by monosaccharide molecules was 45 ppm and by polysaccharide like starch CO_2 production was 21 ppm as shown in Fig.12 (b) during photo-oxidation by bare TiO_2.

Because Glucose is a monosaccharide so it degraded easily during photooxidation with TiO_2. Sucrose is a disaccharide which contains the glycosidic bond between C-1of glucose and C-4 of fructose residues. So degradation of sucrose takes more time than glucose. Starch is a polysaccharide, contains two components amylose and amylopectin. Amylose possesses a chain of alpha 1- 4 glycosidic bond and amylopectin contain a basic chain of alpha 1- 4 glycosidic linkage with addition of side chains attached to basic by alpha 1-6 glycosidic linkage. Carboxymethylcellulose contains a chain of beta 1- 4 glycosidic bonds. These glycosidic bonds create complexity in polysaccharide structure which required more photooxidation time for degradation as well as mineralization.

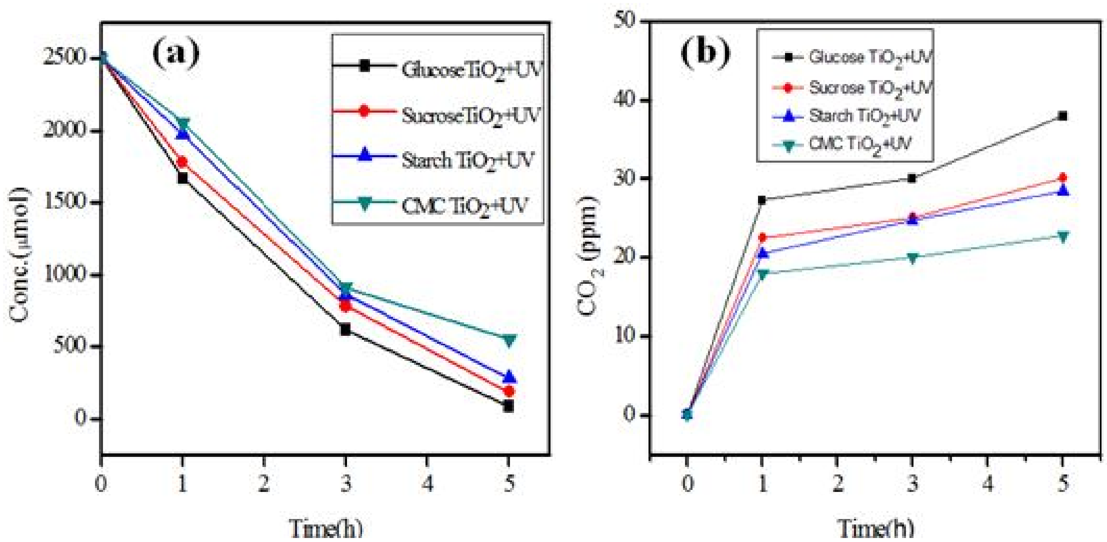


Fig. 12: Comparative degradation of different carbohydrates and CO_2 production by bare TiO_2 **(a)** Comparative degradation, **(b)** CO_2 production

CONCLUSION

The aim of the present study was to degrade the different carbohydrates such as glucose, sucrose, starch and carboxymethylcellulose by photocatalytic activity of titanium oxide (TiO_2). Some research papers reported on photocatalytic degradation of glucose. We have done this research work with the aim to degrade the usually found carbohydrates in different industrially sewage water with the TiO_2 and surface-modified TiO_2 with various metal loading. Metal loaded with silver enhances the photocatalytic degradation of these carbohydrates. Probably the metal acts as the electron trapper, and allows the holes to combine to react with the water molecules adsorbed on the TiO_2 surface. So there could be more formation of hydroxyl radicals ($OH^{\bullet}$) which cause the increase in degradation rate. As starch and carboxymethylcellulose contain glycosidic bonds so they need long time for degradation. After long time exposure with TiO_2 photooxidation, mineralization of compounds occurs. Monosaccharides are simpler structures so that will be mineralized in less time in comparison to the polysaccharides. Therefore, selective photooxidation with TiO_2 and metal loaded TiO_2 not only remove the excessive amount of carbohydrates but also simultaneously can provide high value compounds in the intermediates. Keeping in view with the above-mentioned points, the experimental data of this study were quite consistent. Therefore, this study will find practical applications both in industries and environmental aspects.

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