

Photocatalytic Conversion of Xylose to Xylitol over Copper Doped Zinc Oxide Catalyst

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Abstract

In the present investigation, photocatalytic conversion of xylose by Copper (Cu) doped Zinc oxide (ZnO) was investigated under Ultraviolet Light emitting diode (UVA-LED) illumination. Photocatalysts were synthesized successfully by chemical precipitation method. The synergistic effect of 5 wt% Cu doped ZnO and addition of glycerol as oxygen scavenger improved conversion. The results from our study showed that %conversion of xylose, glycerol are 33.72%, 33.61% respectively and % product yield of 88.79% of Dihydroxyacetone(DHA), 19.87% of xylitol and 13.29% of erythritol were achieved when 1.66 g/L of catalyst were used in ambient conditions under 7 h of UVA-LED illumination. The varied temperature to 50 ± 2 °C had decreased effect on the product yield when compared to that of the reaction carried out at 30 ± 2 °C. High Resolution Mass spectrometry results confirmed the presence of the products xylitol, erythritol and DHA formed during the course of the photocatalytic reaction.

Graphic Abstract



Keywords Biomass conversion · Photocatalysis · UVA-LED · Xylose · Cu doped ZnO · Glycerol · Xylitol

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1 Introduction

Biomass valorisation for the production of valuable chemicals have paved the way to combat depletion of fossil resources. The utilisation of naturally occurring sugar such as xylose for producing ethanol, furfural, and xylitol through catalytic conversion processes has been the topic of current research [1]. About 20-30 wt% of lignocellulosic biomass consists of hemicellulose, which mainly comprising of D-xylose residues [2]. Xylose is a pentose sugar (C_5) with molecular formula $C_5H_{10}O_5$ is often used as a food sweetener [3]. Xylose dehydrates to furfural in the presence of different types of acid catalyst, either Brønsted or Lewis catalyst under high temperature conditions generally between 140 and 240 °C [4]. However, the above process uses high-pressure conditions or microwave radiations, which causes structural instability in catalysts and also its leaching, resulting in lower recovery for reuse [5]. Industrially, Xylitol is produced by catalytic hydrogenation in the presence of a noble metal-free catalyst, RANEY® nickel at 80–130 °C under 40–70 bar of hydrogen (H₂). Xylose reduces to xylitol between 100 and 125 °C (lower than the melting point of xylose) in the presence of the noble metal based catalyst such as ruthenium (Ru), rhodium (Rh) and platinum (Pt) [6–9]. Another study [10] reported that Ru appeared as the most efficient catalyst for selectively converting xylose to xylitol in the presence of rutile phase TiO₂ supported Ru (1 wt%).

Nevertheless, in comparison with the use of Ni based catalyst, use of highly precious noble metals may not be the desirable choice for large scale applications. An activated carbon (AC) supported Ni-Re bimetallic catalysts (Ni-Re/ AC) were used to hydrogenate xylose and hemicellulosic hydrolysate into xylitol under mild reaction conditions [11]. Also, Ru decorated carbon foam (Ru/CF) was used as a catalyst to convert xylose to xylitol in the presence of external hydrogen gas at 40-60 bar and high temperature of 100–120 °C to obtain maximum yield. The studies discussed above involves the processes that requires high temperature, H₂ atmosphere which is energy consuming, costly, tedious and not so environmental friendly [12]. Photocatalysis is reported to be one such technology which offers sustainable route for the production of valuable compounds. Photocatalysis has been considered as a promising alternative by carrying out the reactions in ambient and mild conditions [13]. "Photocatalysis" is the term to describe the acceleration of chemical reactions by photo-induced electron/hole, in the presence of a photocatalyst. The process is considered as clean, energy-saving, technologically simple, ecologically benign and low cost offering the possibility of extending the spectrum of applications to a variety of processes, including oxidations and oxidative cleavages, reductions, isomerizations, substitutions, condensations, and polymerizations [14]. Photocatalysis has been extensively studied for contaminants remediation, fine chemical synthesis, proton reduction, carbon dioxide (CO₂) reduction [15]. In recent decades, Photocatalysis finds its application in the conversion of biomass to high value-added products by replacing the conventional method of production [16]. Currently, the

photocatalytic semiconductor based particles have found its application in the field of biomass conversion. ZnO is an n-type wide band gap semiconductor with high photocatalytic activity, high thermal and mechanical stability, and non-toxic nature. Numerous nanoscale morphologies including nanoparticles, thin films, dumbbell-shaped crystals, micro-/nano-rods, nanowires, and nanopetals have been used to assess the photocatalytic properties of ZnO [17]. However, the use of ZnO particles as a photocatalyst has some limitations such as fast recombination of electron-hole pairs and its susceptibility to deterioration upon exposure to UV irradiation in aqueous solution, a phenomenon usually referred to as photocorrosion [18]. In order to suppress the photocorrosion effect and to increase its photocatalytic activity, various techniques such as coating with noble metals, doping with metals and creating composites with other semiconductors have been practiced [19]. ZnO particles have been doped with different metals such as Cu, Al, Ag, Sn, Ga for improving photocatalytic activity [20]. Cu–ZnO composites have wide applications in catalytic conversion of CO₂ or CO to methanol, hydrogenation/dehydroxylation of biomass (fructose, sorbitol, glycerol or furfural) to diols, photocatalytic H₂ production, and methanol steam reforming [21]. These catalytic hydrogenation reactions require highly flammable molecular hydrogen gas that is obtained from petrochemical sources. The present challenge is to replace hazardous hydrogen gas with an alternative safer, cleaner source for hydrogenation reactions. This could be achieved through utilisation of solvents such as glycerol and isopropanol as hydrogen donors. Studies conducted by Vaiano et al. [22], Díaz-Alvarez and Cadierno [23] and Natarajan et al. [24] prove that hydrogenation reactions can be carried out with the use of greener solvents by reducing the need of petroleum based hydrogen source. Also, most of the existing photocatalytic studies and applications have used Xenon lamps, mercury lamps, and Iron-halide lamps as light source. However, the use of these light sources has limits due to lack of achieving the path of sustainability and eco-friendly sources [25]. Light-emitting diodes (LEDs) recently became a promising alternative light source for photocatalytic applications for their high energy efficiency, long lifetime, compact size and DC power supply availability [3, 26].

Considering the growing interest in the area of valorisation of biomass and important findings in recent years on photocatalytic conversions, an attempt has been made to investigate photocatalytic conversion of xylose. Cu doped ZnO nanoparticles, activated using UVA-LED are used as photocatalyst. The reactions are carried out under ambient conditions and by utilizing glycerol as hydrogen donor to avoid usage of petroleum based hydrogen gas. The study is focused on analysing the effect of varying catalyst load, addition of glycerol and reaction temperature on efficiency of conversion of xylose.

2 Materials and Methods

2.1 Chemicals

Zinc acetate dihydrate $(Zn(CH_3 \cdot COO)_2 \cdot 2H_2O)$, copper chloride $(CuCl_2 \cdot 2H_2O)$, diethylene glycol, sodium hydroxide (NaOH) were purchased from Merck Private Ltd. (Mumbai, India). D-xylose (99%), xylitol (99%), glycerol anhydrous $(C_3H_8O_3)$, dihydroxyacetone (DHA), and erythritol (99%), solvents for UHPLC analysis such as acetonitrile, water, Triethylamine (TEA) were purchased from Sisco Research Laboratories Pvt. Ltd. (Mumbai, India). UVA-LED strip were purchased from Probots Techno Solutions (Bengaluru, India).

3 Methods

3.1 Photocatalyst Preparation

Pure Zinc oxide (ZnO) nanoparticles were purchased commercially from Sisco Research Laboratories Pvt. Ltd. (Mumbai, India). Copper (Cu) doped ZnO nanoparticles were synthesized by wet chemical precipitation method as described by Rahmati et al. [27]. Briefly, Zn (CH₃·COO)₂·2H₂O and CuCl₂·2H₂O were mixed stoichimetrically to obtain 5 wt% Cu doped ZnO. The solution was stirred for 10-15 min to which NaOH solution was added drop wise to obtain the precipitate. Then to the precipitated solution diethylene glycol was added and continued stirring for 10-15 min. Bluishwhite sol-gel precipitated particles were separated by centrifugation @7500 rpm for 15 min. The collected particles were washed with distilled water 3-4 times followed by washing with ethanol for 2-3 times to remove any impurities. The particles were dried in hot air oven @ 100 °C for 4 h and further subjected to calcination in a programmed muffle furnace @ 500 °C for 1 h. The obtained particles were used for further studies.

3.2 Development of Lab Scale Photocatalytic Reactor

A laboratory scale experimental set-up was developed from three necked glass rectangular flat bottom flask of 500 mL capacity and are shown in Fig. 1a. UVA-LED strip was used as light source for illumination. The wavelength emission range of UVA-LED strip used in our study were analysed using Spectral radiometer (Spectral Evolution SR-3500, Department of Earth Science, University of Mysore). To achieve uniform illumination and as much effective as possible, the LED strip was rolled up around the external surface of the reactor. The reactor contained port for purging nitrogen gas used to remove dissolved oxygen inside the reactor and a sampling port fixed with self-sealing septa to withdraw the sample from the syringe. To prevent loss of illumination, the reactor was covered with aluminum foil. The reactor is placed on the magnetic stirrer to achieve uniform mixing up of the solution.

3.3 Photocatalyst Characterization

3.3.1 UV–Vis Spectroscopy

The UV–visible optical absorption spectrum of the undoped ZnO and Cu doped ZnO have been carried out at room temperature using UV–Vis spectrophotometer (model Shimadzu UV 1601, Japan) by measuring the wavelength from 200 to 700 nm. The energy band gap for both undoped ZnO and Cu doped ZnO has been calculated using the Tauc relation [28].

$$\alpha(E) = \frac{A(E - Eg)^p}{E} \tag{1}$$

where 'A' is a constant, ' E_g ' is optical energy band gap of the material, 'p' is exponent which depends upon the kind of transition (1/2, 2, 3/2) for direct, indirect and direct forbidden transitions.

3.3.2 X-Ray Diffraction (XRD) Analysis

The crystalline structure of undoped and Cu doped ZnO particles were investigated using X-ray diffractometer (Rigaku, Japan). The X-ray diffraction spectrum was recorded from Cu-k α radiation at a wavelength of 1.54 Å. The diffractogram was collected in reflection mode by scanning the 2theta range from 1° to 80° with a step size of 1°/min at room temperature. The average crystallite size is estimated by the following Debye-Scherer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{2}$$

where, 'D' is the crystallite size (nm), ' λ ' is wavelength of X-ray used (nm), ' β ' is full width half maximum (FWHM in radians), ' θ ' is Bragg's diffraction angle (in degree).

3.3.3 Scanning Electron Microscopy with Energy Dispersive Spectrum (SEM–EDS)

The structure and morphology of undoped ZnO and Cu doped ZnO nanoparticles were examined through Scanning Electron Microscope (SEM) (Leo 435 VP, Leo Electronic systems, Cambridge, UK). Also, the elemental compositions of the nanoparticles were analyzed using SEM equipped with Energy Dispersive Spectrum (EDS/EDAX).



Fig. 1 a Schematic representation of photocatalytic reactor; b the wavelength range of UVA-LED strip measured from spectral radiometer

3.3.4 FTIR Studies

FTIR spectra of particles were recorded in the range 4000–400 cm⁻¹, using FTIR-8400S spectrometer (Shimadzu, IR solution 1.30, Shimadzu Corporation, Japan).

3.4 Photocatalytic Reaction Studies

The reactions were carried out using 5 g/L of initial xylose concentration, 1.66 g/L of catalyst, 300 mL of reaction volume, UVA-LED illumination. The reactor was purged with nitrogen gas for 10–15 min before the start of the reaction and the solution was kept under constant stirring condition @ 300 rpm for about 7 h. The liquid samples were drawn hourly and filtered through 0.22 μ m syringe filter to remove the catalyst from the liquid sample and subjected for further analysis. Photocatalytic reactions were performed to evaluate the conversion of xylose into value-added products such as xylitol, erythritol. The degree of conversion of xylose and glycerol were calculated as below and presented as percentage conversion

Conversion of Xylose (%) = $\frac{(initial xylose - xylose at time t)}{initial xylose} \times 100$

 $Conversion \ of \ Glycerol \ (\%) = \frac{(initial \ glycerol - glycerol \ at \ time \ t)}{initial \ glycerol} \times 100$

Product yield (%) = $\frac{(concentration of product at time t)}{initial concentration of reactant} \times 100.$

3.5 Liquid Sample Analysis

All liquid samples were analysed and quantified using Ultra High Performance Liquid Chromatography (UHPLC) equipped with Evaporative Light Scattering Detector (ELSD) and presence of reaction products were confirmed through High Resolution Mass Spectrometry (HRMS).

3.5.1 Ultra High Performance Liquid Chromatography with Evaporative Light Scattering Detector (UHPLC-ELSD)

The chromatographic analysis were performed using a ACQUITY UHPLC system (Waters, Milford, USA) consisting of a quaternary gradient pump (H-Class), a vacuum degasser, a sample manager with thermostat and Flow-Through Needle (FTN), a column compartment equipped with preheater and an evaporative light scattering detector (ELSD). Empower Pro Software, version3 were employed for controlling the system. The separations were performed using an ACQUITY BEH amide HILIC column (2.1 mm × 100 mm × 1.7 m, Waters, Mildford, MA, USA). The mobile phase consisted of gradient solvents A and B. Solvent A contained 80% acetonitrile: 20% water: 0.2% TEA and solvent B contained 30% acetonitrile: 70% water: 0.2% TEA. The injection volume used for standards and samples were 1 μ L and were performed with a flow rate of 0.17 mL/min for 18 min with gradient elution: 0 min (0–100% A), 0–10 min (40–100% A, 0–60% B), and 10–18 min (100% A).

3.5.2 High Resolution Mass Spectroscopy (HRMS)

High resolution mass spectroscopy studies were carried out for the identification of reaction products. Triple-TOF (Time of flight) high resolution mass spectrometer was used to analyze the samples through direct infusion. To assist the ionization and desolation, the liquid samples were diluted with a 1:1 mixture of acetonitrile and water. The full scan mass spectra were acquired in negative ionization mode with collision energy: -10 eV, mass scan range of m/z 30–500. The operating conditions maintained were: vacuum gauge pressure: 3×10^{-5} Torr, source temperature: 400 °C set point, tray temperature: 10 °C, injection volume: 60 µL, needle volume: 7 µL. The data were analysed with Peak View 2.1 Software (AB SCIEX Triple TOF 5600, Singapore), equipped with MasterViewTM (Version 1.0, AB SCIEX).

4 Results and Discussions

4.1 Spectral Analysis of Light Emitting Diode

The wavelength pattern is shown in the Fig. 1b. A UVA-LED strip containing 200 LEDs with light intensity of 35 mW/cm^2 was used as light source. The wavelength was found to be in the range of 380–400 nm which lies in the UVA region from the electromagnetic spectrum.

4.2 Characterization Studies

4.2.1 UV-Vis Absorption Spectroscopy

The UV–visible optical absorption spectra (300–700 nm) obtained at room temperature for undoped ZnO and Cu doped ZnO nanoparticles are presented in Figure S1a. The maximum absorption wavelength of undoped ZnO shifted to slightly lower wavelength when doped with Cu. This shift in lower end is referred to blue shift and the reason attributed to this is the increase of lattice distortion. The similar observation of wavelength shift to lower end was reported by Sindhu et al. [28] and Ashokkumar and Muthukumaran [29]. The

graph of $\alpha(E)^2$ v/s E was plotted and shown in the Figs. S1b & S2c for undoped and 5 wt% Cu doped ZnO, respectively. The extrapolation of the straight line to the axis of energy (E) gives the band gap energy value of the material. The energy band gap value obtained for undoped ZnO and Cu doped ZnO are 3.3 eV and 3.4 eV, respectively. This increase in the energy band gap is in correlation with the blue shift of absorption wavelength. Similar increase in energy band gap were reported by Ashokkumar and Muthukumaran [29] in their studies when the Cu concentration was increased from 0.01 to 0.5.

4.2.2 XRD Analysis

XRD analyses were carried out to identify the crystal structure, lattice parameters and crystal size of both undoped and Cu doped ZnO. The XRD spectra of undoped and Cu doped ZnO are depicted in Fig. S2. From the XRD spectra, it was observed that sharp and highly diffracted peaks implies particles exhibit good crystalline nature. "High Xpert score" software was employed to study the XRD patterns and the database available in the software showed same XRD pattern for both undoped and Cu doped ZnO with the reference code of (01-097-0207), indicating the Cu doping on ZnO particles have been successfully achieved.

The results obtained from the database showed particles exhibited hexagonal wurtzite phase. Also, the particles belonged to P63mc space group with JCPDS card (36-1451). Similar observation was reported by Sakai et al. [30]. The characteristics peak of undoped and Cu doped ZnO were observed at an angle 2 theta i.e. at 31.79°, 34.45°, 36.25°, 47.53°, 56.51°, 62.84°, 66.50°, 67.87°, 69.06° which

corresponds to miller indices (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), respectively. Another additional peak with very low intensity at 38.7° was observed in Cu doped ZnO, which corresponds to (1 1 1) plane exhibiting monoclinic structure of CuO. The diffraction peak of CuO were consistent with the values, as previously reported by Chen et al. [31] and Jiang et al. [32]. From the study Choi et al. [33] reported showed that Cu doped ZnO, prepared by conventional hydrothermal method had a similar plane of (1 1 1) and peak at 38.7° corresponding to CuO, when Cu loading were increased from 1.0 to 5.0 mol%.

The crystallite size of undoped ZnO and Cu doped ZnO were calculated by using the Eq. (2), and values were found to be 27.78 nm and 31.8 nm, respectively. From the XRD spectra, by careful observation of peak from 31.0° to 38.0° reveals that the slight shift in the 2 theta value and broadening of diffraction peak at 36° indicates that Cu has been incorporated into the ZnO lattice with no change in crystal lattice.

4.2.3 SEM and EDS Studies

The surface morphology of undoped ZnO and Cu doped ZnO were analysed through Scanning Electron Microscopy (SEM). From the Fig. 2a, b it can be seen that the undoped ZnO particles exhibited needle like structure. Since the particles were agglomerated, clear distinctive image of undoped ZnO nanoparticles could not be observed. In the Fig. 2c, d, it is evident that the particles were in hexagonal structure which corroborates with the results obtained from XRD analysis. Also, the elemental composition of undoped and Cu doped ZnO were studied and data are shown in the



Fig. 2 SEM images a, b undoped ZnO; c, d 5 wt% Cu doped ZnO EDS of e undoped ZnO f 5 wt% Cu doped ZnO

Fig. 2e and f, respectively The percentage composition measured in Energy dispersive spectrum (EDS) studies confirmed the presence of main constituents Zn, O in undoped ZnO and Zn, O, Cu in case of Cu doped ZnO, indicating that there were no presence of any impurities in the particles. Also, the amount of Cu added stoichimetrically during the preparation of Cu doped ZnO were comparable to the atomic weight % obtained from EDS analysis.

4.2.4 FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) spectrum was observed to investigate the chemical composition of the samples. The spectrum was obtained in the range from 400 to 4000 cm⁻¹ and shown in the Fig. S3a. The major peaks were observed in the range 400–600 cm⁻¹ wavenumber (shown in Fig. S3b) which is characteristic peak of metal oxide vibrations [34]. The peak at wavenumber 554 cm⁻¹ and 412 cm⁻¹ corresponds to Zn–O stretching of ZnO and the wavenumber at 600 cm⁻¹ corresponds to Cu ions incorporation [35]. The results are in correlation with the UV–Vis and XRD analysis proving that Cu doping on ZnO surface lattice has been successfully achieved.

4.3 Photocatalytic Studies

4.3.1 Synergistic Effect of Cu Doping and Addition of Glycerol on Photocatalytic Conversion of Xylose

The graph in the Fig. 3a shows degree of conversion of xylose by undoped ZnO and 5 wt% Cu doped ZnO nanoparticles. About 8% of xylose conversion was achieved within 7 h when 5 wt% Cu doped ZnO were used for the reaction while the undoped ZnO did not have any effect on the conversion of xylose. The reason could be due to the photocorrosion effect of undoped ZnO upon continuous exposure to UVA light [18]. From the results it is evident that doping has an effect on the photocatalytic conversion of xylose which could be due to the prevention of recombination of electron–hole pair and suppression of photocorrosion effect of ZnO particles [19] resulting in improving the photocatalytic activity of Cu doped ZnO.

Further, experiments were carried out using Cu doped ZnO nanoparticles with the addition of glycerol, as oxygen scavenger. The Fig. 3b shows the degree of conversion of xylose when both Cu doped ZnO nanoparticles and glycerol were used for the photocatalytic reaction. The results showed 21.63% conversion of xylose and 21.84% of glycerol along with the formation of valuable products such as 4% xylitol, 50% of DHA and 6.3% of erythritol. The considerable increase in the degree conversion of xylose could be attributed to the synergistic effect of glycerol and

Cu doped ZnO nanoparticles. The results obtained from our study were comparable with that obtained by Payormhorm et al. [36] where they achieved 6.45% of xylitol from photocatalytic conversion of glucose under UV irradiation ($\lambda = 365$ nm) by surfactant assisted fabricated TiO₂ as catalyst.

In our study, the reaction was carried out without any supply of external hydrogen source and using glycerol as sole hydrogen donor which further undergoes oxidation reaction. The results of our study is supported by the observations of [22], who proved that it is possible to produce hydrogen from glycerol aqueous solution using Cu doped ZnO as catalyst without the supply of external hydrogen gas. Also, Yi and Zhang [21] produced xylitol from hemicellulose in one-pot reaction conditions using Ru/C catalyst using isopropanol as hydrogen donor. The authors achieved more than 80% xylitol yield @140 °C, within 3 h. In the present study, in order to study the effect of addition of glycerol, reaction was carried out without the presence of xylose by Cu doped ZnO nanoparticles and the results are shown in the Fig. 3c. The results revealed that only DHA were formed as the reaction product when glycerol alone was used for reaction and no formation of xylitol and erythritol was observed. Díaz-Álvarez and Cadierno [23] reported that glycerol could be efficiently used as solvent and hydrogen donor in metal-catalysed transfer hydrogenation reactions. Their study showed that glycerol undergone oxidation reaction to produce DHA and release hydrogen molecule. Another study by Estahbanati et al. [37] proved that glycerol could be converted to hydrogen only when TiO₂ nanoparticles were loaded with Pt metal. These evidences prove that the hydrogen donor and doping are crucial parameters for the photocatalytic conversion of xylose into valuable compounds such as xylitol, erythritol and, also supports the results achieved in our study.

Figure 4 shows the possible schematic representation of the reaction and the mechanism of the photocatalytic conversion of xylose in the presence of glycerol and Cu doped ZnO nanoparticles are explained as follows:- (1) when the UV-LED (380–400 nm) is incident on surface of Cu doped ZnO creates electrons (e⁻) and holes (h⁺) which migrate to valence band and conduction band inside the ZnO nanoparticles (2) the generated electrons and holes are separated; electrons are trapped by Cu particles by preventing recombination of electron–hole pair (3) simultaneous oxidation of glycerol to DHA and reduction of xylose to xylitol and erythritol are formed.

4.3.2 Effect of Catalyst Dosage

In order to study the effect of dosage of catalyst, the catalyst load was varied and tested at three levels, i.e., 0.83 g/L,

Fig. 3 Photocatalytic conversion of xylose: **a** by undoped ZnO and 5 wt% Cu doped ZnO nanoparticle; **b** showing synergistic effect of Cu doped ZnO nanoparticles; **c** effect of addition of glycerol without the presence of xylose by Cu doped ZnO nanoparticles









Fig. 5 Effect of catalyst load on conversion and yield

1.66 g/L and 3.3 g/L, keeping other parameters such as initial xylose concentration (5 g/L), glycerol concentration (3.3 g/L) and duration of UVA-LED illumination (7 h), the constant.

From the Fig. 5 it can be observed that at 0.83 g/L of catalyst load degree of conversion of xylose and glycerol were 21.63% and 21.84%, respectively. As the catalyst load was increased to 1.66 g/L, the conversion also increased leading to increase in product yield. However, further increase to 3.3 g/L of catalyst load the degree of conversion showed decreasing trend, though the value was higher than that obtained at 0.83 g/L. The above trend observed in our study could be attributed to the availability of more surface active site when catalyst dosage is increased from 0.83 to 1.66 g/L, which also resulted in increase in formation of electrons and

holes which could be observed with the increase in degree of conversion of xylose. But on further increase in catalyst dosage to 3.3 g/L, the conversion of both xylose and glycerol decreased. The decrease in the photocatalytic activity may be related to increase in opacity of aqueous reaction solution making the penetration of UVA-LEDs light gradually difficult [22], thereby reducing the formation of electrons and holes for the reaction to carry out. Similar trend of decrease in xylose conversion and xylitol yield were reported by Liu et al. [38] when Ru nanoparticles loading was increased due to aggregation of Ru nanoparticles. At the optimum catalyst load condition (1.66 g/L), xylose and glycerol conversion were 33.72% and 33.61%, respectively, while product yield was 88.79% of DHA, 19.87% of xylitol and 13.29% of erythritol.

4.3.3 Effect of Reaction Temperature

The effect of temperature on conversion of xylose was studied by performing the reaction at 30 ± 2 °C and 50 ± 2 °C. The above temperature range was selected, as the recommended limit of operation for UVA-LED was < 60 °C (as per manufacturer). During the course of the reaction, rise in temperature was observed by nearly 5 °C. This is due to the heat generation due to continuous exposure of UVA-LED illumination for a long period (7 h) and mild stirring during this period. The other conditions of reaction were: initial xylose concentration of 5 g/L, 1.66 g/L of catalyst load, 3.3 g/L glycerol.

From the Fig. 6, it is observed that when the reaction temperature was increased to 50 ± 2 °C, the percentage yield of reaction products, namely, DHA, xylitol, erythritol decreased



Fig. 6 Effect of varying reaction temperature

its yield by 20.44%, 6.49%, 8.765% respectively than those formed at 30 ± 2 °C. Till date, there are no studies reported on obtaining xylitol, erythritol and DHA under mild temperature using Cu doped ZnO nanoparticles as catalyst. However, recent studies reported shows xylitol formation only at high temperature and using noble metal based nanoparticles as catalyst. Few such studies reported are by Mishra et al. [39] when Ru supported zeolite Y catalyst was used for hydrogenation of xylose to xylitol by varying temperature from 100 to 140 °C, the results showed that increase in temperature of the reaction decreased the xylitol selectivity due to formation of by-product such as arabitol though the xylose conversion increased. Another study by Liu et al. [40] reported that when reaction temperature was increased from 50 to 190 °C and at hydrogen pressure of 1 atm for 148 h of reaction time, achieved high selectivity in xylose to xylitol conversion at 50 °C using Ru nanoparticles combined with MOF (ZIF-67) catalyst. In our study, we have achieved the formation of xylitol, DHA and erythritol even at 30±2 °C which is nearly ambient temperature condition thereby minimising undesirable product formation.

4.3.4 HRMS Studies

The products obtained under optimum reaction conditions of 1.66 g/L of catalyst dose and 30 ± 2 °C reaction temperature were further characterised using HRMS technique to confirm the products. The total MS spectra obtained is shown in the Fig. S4. The presence of DHA, erythritol and xylitol were identified and confirmed based on their respective mass to charge (m/z) ratio of 89.0248, 121.0422 and 151.0602. Further the individual products were fragmented to match fragmented ions with the available database Pubchem and showed exact fragments which are detailed in Table 1.

5 Conclusion

The present work explored, the possibility of obtaining xylitol from photocatalytic conversion of xylose with Cu doped ZnO as photocatalyst under UVA-LED illumination. Under optimized conditions of photocatalytic reaction, 88.79% of DHA, 19.87% of xylitol and 13.29% of erythritol were obtained. Our study showed that the addition of glycerol (hydrogen donor) facilitates the conversion of xylose to xylitol successfully without the utilization of external hydrogen source for the hydrogenation reaction. The synergistic effect of glycerol and Cu doping on ZnO nanoparticles played a crucial role in the photocatalytic conversion of xylose. While catalyst increased the yield up to a level, increase in temperature of reaction from 30 °C to 50 ± 2 °C decreased yield of xylitol, erythritol and DHA. The study showed the potential application of photocatalytic conversion of biomass into valuable products without the addition of acid/alkali, use of noble metals, external hydrogen source, and high temperature or pressure. Further studies are needed to improve processing conditions so as to achieve higher yield.

Table 1MS/MS fragments ofvaluable compounds identifiedin the reaction product

Compound name	[M–H] [–]	Empirical formula	MS/MS fragment ion
DHA	89.03	C ₃ H ₆ O ₃	71.013, 59.013, 56.97, 41.02, 31.02, 29.03
Erythritol	121.04	$C_4H_{10}O_4$	103.04, 91.04, 89.03, 73.03, 61.03, 59.013, 43.0184
Xylitol	151.05	$C_5H_{12}O_5$	133.05, 119.034, 101.023, 89.023, 71.012, 59.012

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Compliance with Ethical Standards

Conflict of interest The authors declare that there is no conflict of interest.

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