

# Degradation, Mineralization Of Chloro Phenol Using Ceria Doped TiO<sub>2</sub> Under Photocatalytic Ozonation

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## ABSTRACT

An efficient photocatalytic activity of ceria doped TiO<sub>2</sub> (Ce/TiO<sub>2</sub>) for the photo-ozonation of tetrachlorophenol in aqueous solution was examined. Different loadings of catalyst materials Ce/TiO<sub>2</sub> (1%, 2.5% and 5%) were prepared and characterized by Powder X-ray diffraction (XRD), nitrogen adsorption-desorption (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM), inductively coupled plasma optical emission spectrometry (ICP-OES), and Ultraviolet-visible diffuse reflection spectrum (UV-DRS). Photocatalyzed ozonation with 2.5% Ce/TiO<sub>2</sub> yielded 100% degradation and mineralization of tetrachlorophenol in 1.5 h at neutral pH conditions. The extent of degradation of tetrachlorophenol and its mineralization were confirmed by GC-MS. For 100 mg/L of tetrachlorophenol, 0.05 g L<sup>-1</sup> of catalyst was found to be the optimum for effective mineralisation. The reused experiment confirmed that Ce/TiO<sub>2</sub> kept a good photocatalytic activity and stability, and it was a promising heterogeneous catalyst. The catalyst is fully recoverable and reusable multiple times with no loss of activity.

**Key words:** Tetrachlorophenol, Photo-catalyst, Advanced Oxidation; Ce/TiO<sub>2</sub>; Degradation.

## 1. INTRODUCTION

The control of organic contaminants in water is a significant extent in conservational protection (Ronald *et al.*, 2004; Rebecca *et al.*, 2005). In recent scenario, agricultural, chemical and medicinal contaminants in the aquatic environment have become one of the main apprehensions in the light of environmental protection (Rebecca *et al.*, 2005; Dana *et al.*, 2002). Their continuous eliminations, which may be direct or indirect, can source considerable increase of the unwanted pollutants in the aquatic environment. Among an unruly organic compound, chloro-phenols are one of the most toxic and is used extensively in chemical and pharmaceutical industries (Maddila *et al.*, 2016a; Ndabankulu *et al.*, 2016). An existence of chlorophenol in aqueous environments presents serious problems due to its toxicity, persistence in the environment, and bioaccumulation (Yaqi *et al.*, 2016). In humans, contact with chlorophenol can cause mouth sores, nausea, darkening of the urine, vomiting, and bloody diarrhea at varying focusses (Ademola and Etinosa 2011).

Consequently, chlorophenol elimination by environmentally friendly is a major consideration for current research. In recent time's substantial attention has been established on the use of photo-degradation with ozone as a means to oxidize toxic organic pesticides (Maddila *et al.*, 2015a, 2015b, 2016a).

Photo-catalysis is a vital in commencing with current inspiring demand for drinking water and in wastewater treatment technology (Oseghe *et al.*, 2015a). Titania as a photo-catalyst has been examined extensively for promising application in decontamination of the environment. It is also high band gap energy about 3.2 eV (Maddila *et al.*, 2016b; Oseghe *et al.*, 2015a). It is proved to be as a tremendous approach over than others owing to the use of oxygen as an oxidant, for photo-oxidation of the organic contaminants at its non-toxicity, low concentrations, at low temperatures, low cost and stability to attain an ample degradation and mineralization (Li *et al.*, 2011). To develop the reaction of titania with improving the separation of electron-hole pairs, there are various approaches to diminish electron-hole recombination rates and increase the photo-catalyst efficiency, comprising loaded titania with transition metal (Lathasree *et al.*, 2004). Moreover, pollutants adsorbed on the surface of the catalyst particles can directly react with the photo-chemically designed holes and electrons, promoting the processes of degradation and mineralization.

The photocatalytic decontamination of wastewaters is a distinctive demonstrative of Advanced Oxidation Processes (AOPs) (Mamaghani *et al.*, 2017). Recently, photocatalytic ozonation has established huge consideration owing to its great oxidation potential that initiates from the formation of OH radicals (Oseghe *et al.*, 2015b). In this method, the presence of the heterogeneous catalyst surfaces induces the decomposition of ozone, and consequently makes the OH radicals. CeO<sub>2</sub> is one of the most responsive lanthanide metal oxides with a 2.92 eV of band gap (Myilsamy *et al.*, 2015). It has a high photosensitive transparency in the visible region to preserve oxygen. Promisingly, ceria doped TiO<sub>2</sub> could significantly develop its visible photocatalytic activity. The ceria ions could enrich a considerable efficacy through preventing the recombination of photo-generated electrons and holes with acting as electron traps; expand the light absorption range and improve the redox potential of the

photogenerated radicals. Hence, ceria doped TiO<sub>2</sub> have been impressively studied for their high photocatalytic activities under ozonation to degradation and mineralization of chlorophenols.

## 2. MATERIALS AND METHOD

### 2.1 Photocatalytic Ozonolysis Experiment

For photoozone generation, The light source was a 500-W xenon lamp (CHFXQ500 W) with a UV filter that can cut off UV light with wavelengths shorter than 420 nm and a Fischer Ozone 500 generator was used. Ozone enriched oxygen stream was passed through a sintered glass (porosity 2) into the 50 cm<sup>3</sup> reactor at a flow rate of 10 mL per min. The reactor temperature was maintained at (19 ± 1) °C by circulating water through double walled jacket. For each run, 20 mL 10 % w/v of Tetradifon and fixed ozone concentration (0.05 M) and flow rate of 10 mL/min. A magnetic stirrer was used to ensure continuous mixing. Ozone concentration in oxygen stream was determined using KI method (Maddila *et al.*, 2013a; 2013b; 2013c). Before and after each of the experiment the flow rate and photoozone content were monitored in duplicate runs.

### 2.2. Catalyst preparation

Sol gel method adopted for the synthesis the material used. For a typical synthesis, 3 g of Pluronic F-127 was dissolved in absolute ethanol (60 mL) under continuous stirring for 3 h. To the resultant clear solution, 6 mL of TIP was added dropwise and stirring was continued for another 2 h. Then, 36 ml of deionised water with lanthanide precursor was added dropwise to the

solution. For the completion of addition, the solution changes colour from clear to white gel. The stirring of the gel suspension was continued for another 24 h and the resulting mixture was aged overnight in the dark at room temperature. After aging the gel separated from the solvent by decantation of the solvent. The resulting precipitate was filtered and washed thrice with deionized water and dried at 100-120 °C for overnight. The dried precipitate was calcined at 450 °C for 4 h, in the presence of air to obtain the 1.0%, 2.5% and 5.0% w/w of Ce/TiO<sub>2</sub> materials.

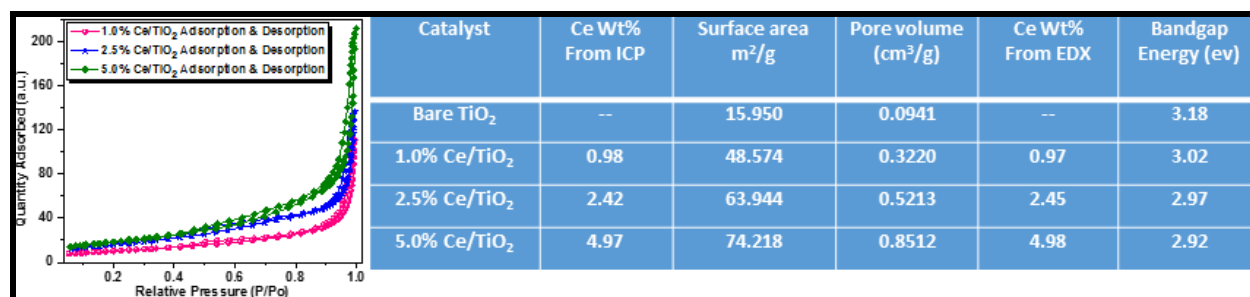
### 2.3. EQUIPMENT DETAILS

All the synthesized materials interpretation and analysis was accomplished approving the succeeding techniques like SEM, TEM, BET, PXRD, ICP, PL, FT-IR, GCMS, proton NMR spectrums (Maddila *et al.*, 2013a; 2013b; 2014c).

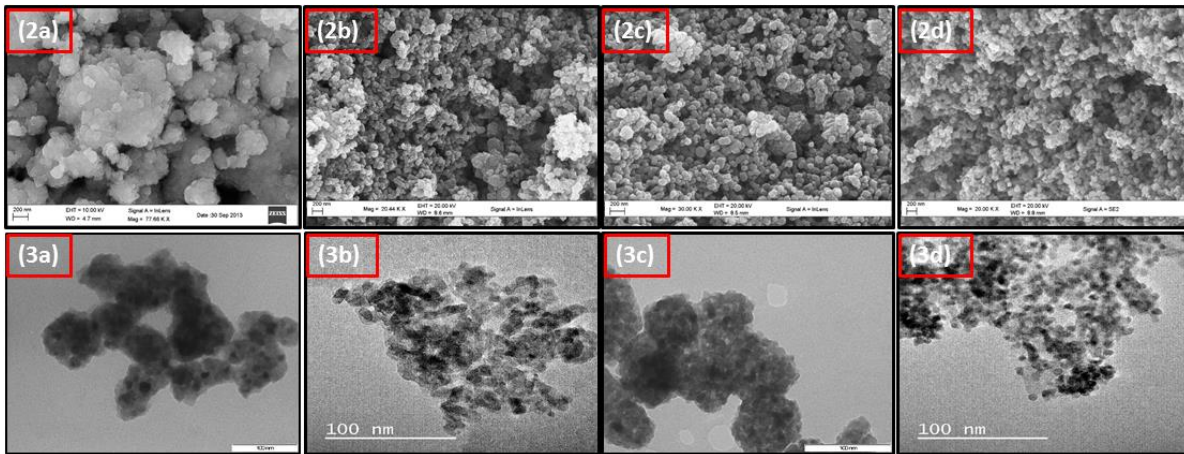
## 3. RESULTS AND DISCUSSION

### 3.1. N<sub>2</sub> sorption and elemental analysis

Figure 1 illustrations the N<sub>2</sub> sorption isotherms of the synthesized materials and BET surface areas, pore size of the catalysts are presented in Table 1. All the catalysts were showed by type IV isotherm through H1 hysteresis loop due to particles agglomeration in the materials and pore size homogeneity. The BET surface area for ceria amended catalysts is comparatively ranging from 48.5-74.3 m<sup>2</sup>g<sup>-1</sup> equated to 15.8 m<sup>2</sup>g<sup>-1</sup> for bare TiO<sub>2</sub>. As showed in table 1 there is an increase in pore volume with the increase in metal dopant and also it shows the actual metal loadings of material persevered with ICP analysis.



**Figure 1:** BET isotherms of catalysts & Table 1: BET surface area, bandgap & ICP for 1%, 2.5% & 5% Ce loaded on TiO<sub>2</sub> catalysts



**Figure 2a-d:** SEM images and **Figure 3a-d** TEM images of 1, 2.5 & 5% CeO<sub>2</sub>/TiO<sub>2</sub>

### 3.2. SEM and TEM

Figure 2a-d and 3a-d displays SEM and TEM micrographs of bare TiO<sub>2</sub> and ceria doped TiO<sub>2</sub> (1%, 2.5% & 5.0%) materials. It is observable that all the catalyst materials contain of unique irregular sphere-shaped and agglomeration particles with range (5-12 nm). Additionally the TEM dimensions were done to discover the microstructure of the ceria doped TiO<sub>2</sub> microspheres. It can be seen that the catalyst consists of huge contract of evident minor titania particles with (10-24 nm) size. EDX analysis was achieved for quantifiable analysis of ceria constituent in the synthesized material. The consequences offer that ceria ions are dispersed over TiO<sub>2</sub> surface.

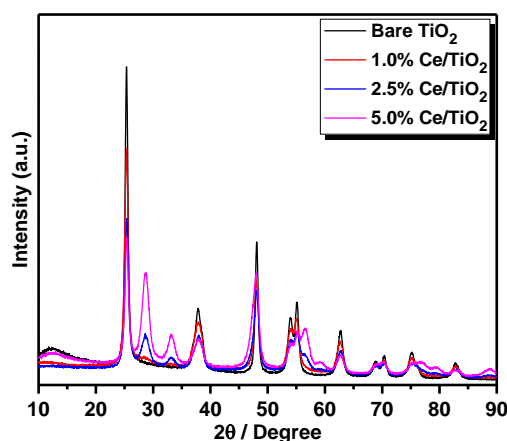
### 3.3. XRD analysis

Figure 4 displays a distinctive XRD patterns of bare TiO<sub>2</sub> and ceria doped TiO<sub>2</sub> catalyst samples. All the catalysts showed the diffraction sharp peaks at ( $2\theta = 25.5,$

37.5, 48.1, 54.1, 55.2, 62.7, 68.9, 70.1 and 75.1) for anatase phase of TiO<sub>2</sub> according to (JCPDS file no: 21-1272). Creation of CeO<sub>2</sub> (JCPDS file no: 34-0394) has been observed low intense peaks at ( $2\theta = 48.1, 55.4$  and  $69.4$ ) respectively due to it could be that the weight percentage of dopant is too small to be detected by the instrument. From the obtained diffraction pattern it was determined that the incorporation of ceria ions in the crystal structure of TiO<sub>2</sub> did not cause significant changes but rather only a slight shift in the diffraction peaks.

### 3.4. UV-DRS:

Figure 5 illustrates the UV-DRS spectra of bare TiO<sub>2</sub> and CeO<sub>2</sub> loaded titania catalyst materials. Bare TiO<sub>2</sub> showed a strong absorption at 384 nm resemble to band-gap energy of 3.2 eV calculated from the formula  $k = 1239.8/E_{bg}$ . The absorption intensity increases with the growing Ce content in the catalyst. Therefore these catalysts could be used for visible light photo-catalysis.



**Figure 4:** XRD spectra 1%, 2.5% & 5% CeO<sub>2</sub>/TiO<sub>2</sub> catalyst

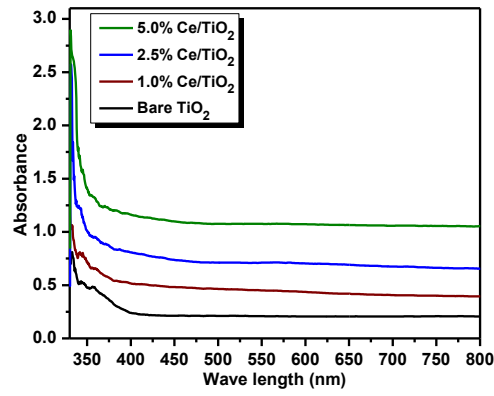


Figure 5: UV-DRS spectra bare & ceria loaded titania catalysts

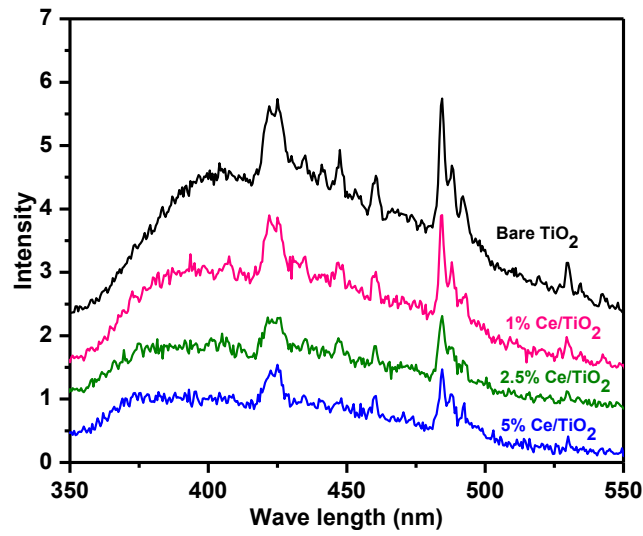


Figure 6: PL spectra bare & ceria loaded titania catalysts

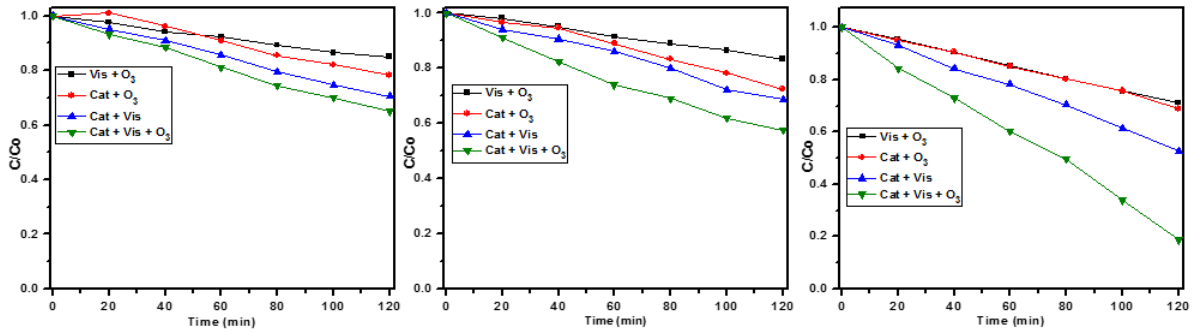


Figure 7: Effect of various pH at 3, 7 & 9

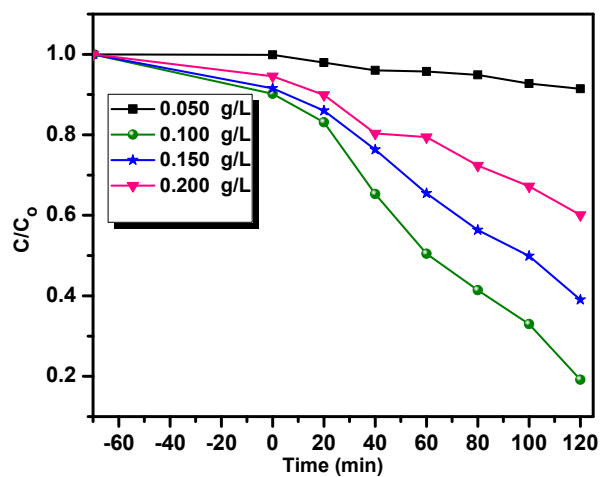


Figure 8: Influence of CeO<sub>2</sub>/TiO<sub>2</sub> catalyst amount at pH 11

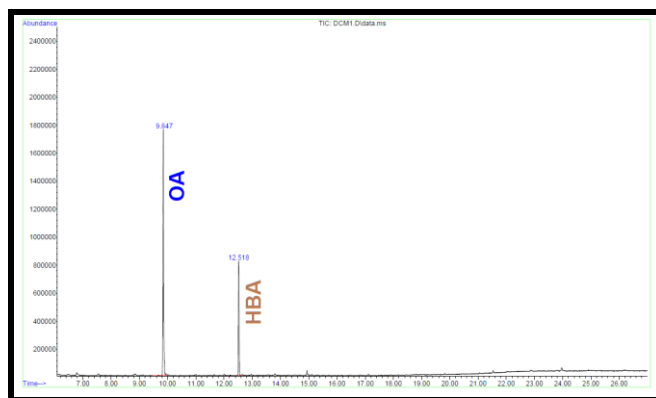


Figure 9: GC-MS spectra of product mixture

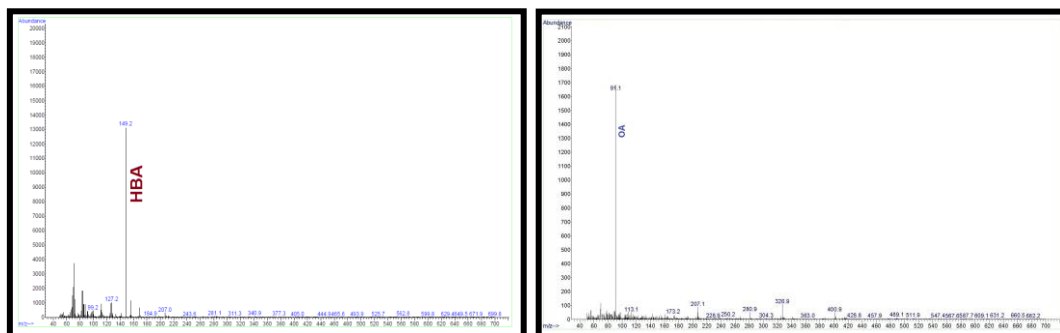
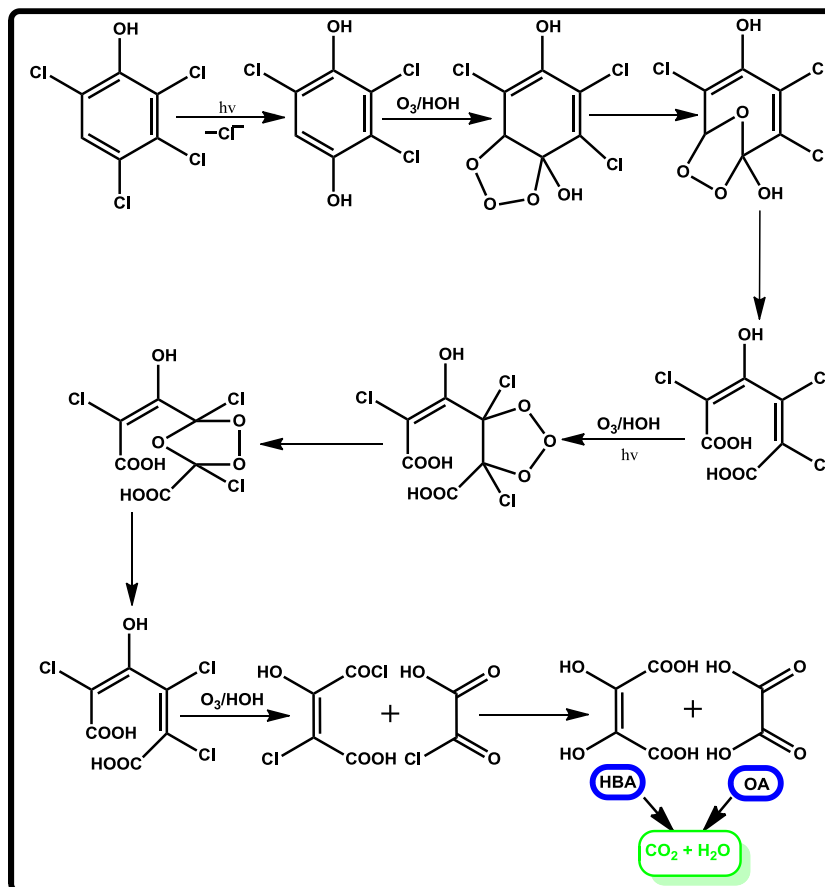


Figure 10: GC-MS spectra of products HBA & OA



**Scheme: Plausible reaction mechanism**

### 3.5. Photoluminescence Spectra

The PL radiation spectra of all the above catalysts was studied in range of 350–550 nm (Figure 6). The peak is the band-edge free exciton luminescence at 410 nm which the peak is the bound exciton luminescence at 470 nm. The recombination of excited electron-hole pair causes the PL emission spectra, thus lower PL intensity designates poorer recombination of the electron-hole pairs, which probably make from surface flaws in the TiO<sub>2</sub> crystals, such as lattice alterations and surface oxygen insufficiencies and an enhanced photocatalytic possessions. The intensity of ceria doped TiO<sub>2</sub> is significantly weaker than that of bare TiO<sub>2</sub>.

### 3.6. Effect of pH

A significant factor in the photocatalytic ozonation reactions fascinating on the Ce/TiO<sub>2</sub> particulate surfaces is the pH of the solution. It effects the surface charge assets of the photo-catalyst and consequently the adsorption activities of the contaminants hence influence of pH on the degradation of tetrachlorophenol in aqueous deferrals of Ce/TiO<sub>2</sub> was examined the pH range at (3, 7 & 9). Figure 7 was showed that the photonic efficacy increases with the increase in the reaction pH due to higher pH 9 assists the OH radical concentration, the influence of pH on the substrate reactivity is also equally vital for efficient conversion.

### 3.7. Effect of catalyst concentration

Figure 8 represents the influence of the photocatalyst concentration on the contaminant degradation. Various catalyst concentration amounts of 50 mg to 200 mg were observed for the tetrachlorophenol degradation. The best concentration of Ce/TiO<sub>2</sub> catalyst was noticed to be 100 mg. Increasing the amount of catalyst the superior the catalyst surface area. It could be described in relations of facilitate of surface active sites on the catalyst and also the permeation of visible light into the catalyst suspension. The greater the catalyst surface area with increasing the catalyst concentration. More than 100 mg catalyst showed decrease in visible light penetration due to screening effect of excess catalyst particle in the solution. Therefore, the suitable amount of Ce/TiO<sub>2</sub> in the level of 100 mg is preferred for tetrachlorophenol photodegradation.

### 3.8. Photo-catalyst studying and identification of products

All the photo reaction investigations were attended by catalyst with ozone revealing plus visible light region. The pollutant in reaction was mined and evaluated after each reaction intervals (20 mins). Two products were noticed by GC-MS (Figure 9). The GCMS peaks observed from 7.00-26.00 retention times denotes to two products formed owing to the further oxidation of the products of the reaction. The peaks at 9.847 and 12.518 retention time state to the compounds of Hydroxybutanoic acid (HBA) oxalic acid (OA). Moreover, the GCMS with their respective (M<sup>+</sup>) m/z values confirmed the degradation products. (Figure. 10). Furthermore, the degradation products were confirmed using with proton NMR and

infrared spectra. Additionally, the qualitative lime water test decided to the discharge of CO<sub>2</sub> and H<sub>2</sub>O of tetrachloro phenol.

### 3.10. Plausible mechanism

The possible reaction mechanism for the photo-catalyzed degradation of tetrachlorophenol on ceria doped TiO<sub>2</sub> via ozone is anticipated and based on the perceived investigational results are shown (Scheme). Highly oxidizing species like photo-induced holes and electrons in semiconductor particles were produced using with photo-catalyst via ozone and they show an important character in degradation of contaminants (Oseghe *et al.*, 2015a & 2015b). The catalytic efficiency influences to a copious possibility on the properties of metal/metal oxide on support catalyst surface, which mainly effect the active surface sites and photo-catalysed ozone disintegration in aqueous solutions. Other significant chemical possessions for the viable activity of catalyst have active surface sites and stability, which is liable for photo-catalyzed degradation reactions (Kasprzyk-Hordern *et al.*, 2003).

In electrophilic reactions, the photo-catalyzed ozonation can play on sites with robust electronic density. In specific, substituted organic compounds are vastly reactive with photo-induced electrons on carbons placed in the *o/p* positions owing to more electronic densities on carbons while organic substituted with electron withdrawing function (-Cl & OH) are dimly photolytically sensitive. The pollutant tetrachlorophenol comprises four electron-withdrawing functions (-Cl & OH), therefore photocatalyzed ozone reactions should result primarily on certain privileged sites. In order to elucidate this, sites with strong electronic density were noticed and the investigation revealed that it is likely that photocatalyzed ozone attack would take place at the hydroxyl group. Besides the electrophilic attack, ozone undergoes cycloaddition reaction with unsaturated bonds leads to the formation of compounds having the carbonyl group (-C=O) or the acid group (-COOH). With this in mind and in order to illustrate a possible reaction mechanism, further analysis was made with spectral analysis to identify the intermediate products. The spectral resulted in a number of compounds, which are shown in figure X. According to this postulate that the bonds C-OH and C-Cl are cleaved leading to the formation of products Hydroxybutenoic acid (HBA) and oxalic acid (OA). Further attacks of photo-ozone radicals leads to the conversion of HBA and OA to mineralization (CO<sub>2</sub> and H<sub>2</sub>O).

## 4. CONCLUSIONS

The conclusions of this study designate that ceria doped titania can efficiently catalyze the degradation and mineralization of the tetrachlorophenol in the presence of light with ozone. The outcomes also specify that rate of degradation might be effected not only by the various factors such as type of photo-catalyst, catalyst loading and pH ratio but also with the ideal contaminant. The size of catalyst particles and reaction parameters play a significant role in ozonolysis, so catalytic properties are strongly affected by the preparation method of the catalyst. The tetrachlorophenol photooxidation was quantitative with

100% degradation. Two products (HBA and OA) were identified using with GC-MS spectra. Photocatalysed ozonation is proved to be an effective method to remove chloro, and hydroxy functions from substituted organic pollutant.

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