Photocatalytic Ozonation for Treatment of Wastewater

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***Abstract*— Due increase in population worldwide the demand of fresh water increases. So researchers are focused on the wastewater treatment so maximum water can be reused or recycled. From last few years, with the development of new approaches, technologies or designs with the objective to solve new problems or to improve existing systems in this field have increased. The focus of the researcher is now to enhance the efficiency of conventional method and reduce the cost or limitations by merging them and make the methods more economical and environment friendly. One of these development under the advanced oxidation processes (AOP) with application of different technologies. Among them photocatalytic ozonation process forms more hydroxyl radicals.By using the catalyst the decomposition of ozone and hydroxyl radical formation is controlled in photocatalytic ozonation process.This process provide fast degradation and effective mineralization of pollutant present in wastewater.**

Keywords— Wastewater Treatments, Advanced Oxidation Process, Photocatalysis, Photocatalytic Ozonation

I.INTRODUCTION

Water and wastewater treatments are the major issue of today’s world. Due to increase in industrialization, increasing population, day by day the demand of fresh water is increases. So now a days researchers are focus on to find the way which is cost effective and environment friendly to reuse or recycle wastewater. Advanced oxidation processes (AOPs) are efficient in mineralizing any type of refractory compounds and so the mineralization of a wide range of recalcitrant compounds can be possible. AOPs are based on the generation of highly reactive free radicals by using chemical and/or other forms of energy, and under appropriate conditions the species to be removed are totally converted to carbon dioxide, water and inoffensive mineral salts [(Orge, Pereira, & Faria, 2015)].

Ozonation is an effective way of treating wastewater.There are mainly two ways via ozone can react with organic matter: (i) direct molecular ozone reactions and/or (ii)indirect pathway which leads to ozone decomposition and the formation of hydroxyl radicals (OH•). Ozonation of organic compounds generally form the aldehydes and carboxylic acids, which reacts very slowly with ozone. So that the mineralization of organics is the limitation of ozonation process. So to make the process satisfactorily fast, radical processes needs to be implemented. Reaction of radical with material is fast and non-selective [(Mahmoodi, 2011)].

Photocatalysis ranks among the AOPs that proved advantageous in remediation of contaminate waste water, although large-scale application remains somewhat expensive owing to the cost of artificial photons and slow oxidation kinetics. The basic process of photocatalysis consists in the irradiation of a semiconductor material by light with enough energy to excite the electrons from the valence band to the conduction band generating electron hole pairs, which migrate to the surface where they can react with adsorbed OH^- to produce $HO^\bullet$; or directly oxidize other adsorbed species [(Orge et al., 2015)].

In comparison with the simple ozonation process, photocatalytic ozonation allows for the effective formation of hydroxyl radicals.There are mainly two phenomena among all in photocatalytic ozonation which accelerates ozone decomposition and hydroxyl radical formation:
(i) Homogeneous photocatalytic ozonation using transition metal ions and (ii) Heterogeneous photocatalytic ozonation using solid catalysts [(Mahmoodi, 2011)].

The main aim of using this method to destroy the compounds which is poorly biodegradable or for improving the biological degradability of wastewater samples containing these compounds. Generally pharmaceutical compounds, surfactants, detergents , colouring matters, organic herbicides, pesticides , aromatics, aliphatic organohalogens, saturated aliphatic carboxylic acids, nitroaromatics, are the primary target compounds for photocatalytic ozonation [(Mehrjouei, Müller, & Möller, 2015)].

II. PHOTOCATALYTIC OZONATION

A. Photocatalysis: The word “photocatalysis” is originally from Greek word of two parts: the prefix “photo” (phos: light) and the word “catalysis” (katalyo: decompose). A process in which the source of light is used to activate photocatalyst, which accelerate the rate of a chemical reaction is known as photocatalysis. So the thermal catalyst is activated by heat whereas photocatalyst is that which activated by photons of appropriate energy. Semiconductors are useful as photocatalysts because of a favorable combination of electronic structure, light absorption properties, charge transport characteristics and excited-state lifetimes. The electron get started to excite and transfer from valance band to conduction band only when the energy equal to or higher than the band gap energy of semiconductor. This energy created an electron-hole pair is a crucial step in all semiconductor mediated photocatalytic processes. [(Kondarides, 2010)].

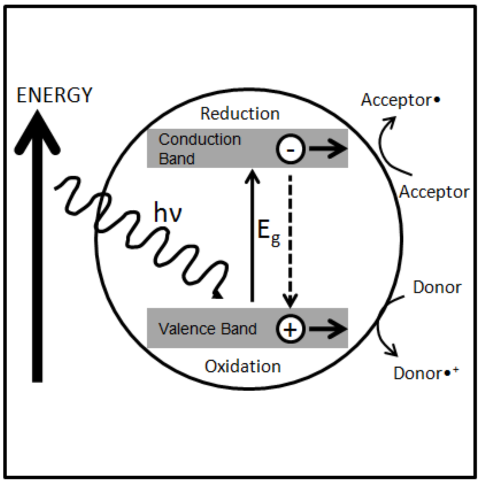

Figure : 1 Mechanism of Photocatalysis [(“photoactive Materials and Energy,”)]

Photocatalytic reactions takes place when charge separation are induced in large band gap semiconductor by excitation with ultra-band gap radiations. According to this, when the absorption of light by photocatalyst is greater than its band gap energy, it produces a positively charged hole in the valence band and an electron in the conduction band as shown in figure 1. The hole present in the valence band may react with water absorbed at the surface to form OH• .The electron available in conduction band can reduce absorbed oxygen to form peroxide radical anion that can further converted to form OH• through various pathways. The radicals like superoxide radical anion, hydro peroxide radical etc. are formed during the photocatalytic process. It is not clear under which experimental conditions, which reaction pathway is more important than the other. It is normallybelieved that the substrate adsorption in the surface of photocatalysts plays an important role in photocatalytic oxidation [(Agustina, Ang, & Vareek, 2005)].

B. Ozonation: The effluent from dye and textile industries are best treated by ozonation process. Being an extremely strong oxidant ozone (E° =2.07 V) reacts rapidly with most of organic compounds. There are mainly two different paths how ozone reacts with various organic compounds: (i) by a direct reaction of molecular ozone, (ii) through a radical type reaction involving the formation of hydroxyl radical by the ozone decomposition in water. The color removal by using ozonation is fast because the unsaturated bond of Chromophores are attacks by ozone molecule, but the mineralization is comparatively low. At low pH, the ozone is consider as main oxidizing agent and at high pH generally the formation of hydroxyl radical will take place. Complete mineralization of pollutant in to carbon dioxide and water is rarely possible in ozonation process but forms the intermediate products such as organic acids, aldehydes and ketones. [(Soares, Órfão, Portela, Vieira, & Pereira, 2006)]. Some of the limitations of ozonation like high production cost, relatively low solubility and stability in water and selectively reacts with organic compounds at acidic pH. In addition to that in many cases the complete mineralization of organic compounds like aromatics, saturated carboxylic acids does not take place.Due to mainly these disadvantages ozonation is not economically viable option to treat polluted water. So sometimes ozonation processes are modified by the addition of catalysts and/or irradiation to the oxidation medium to improve efficiency [(Mehrjouei et al., 2015)].

C. Photocatalytic Ozonation: A new advanced oxidation process called **photocatalytic ozonation,** is a combination of ozonation and photocatalysis process. This combination of these two AOP, and the its synergistic effects, is a promising technique for the removal of recalcitrant organic compounds in water [(Mehrjouei et al., 2015)]. Photocatalytic ozonation is an emerging technology that combines two AOPs with the main advantage of this integrate process being the formation of highest $HO^{\bullet}$ by using powerful oxidant character of ozone compared to oxygen. Thus, an additional and important way of $HO^{\bullet}$ formation is the O_3 capture of electrons in the conducting band of the catalyst to yield the ozonide ion radical ($O_3^{\bullet-}$) that eventually gives rise to $HO^{\bullet}$. This advantage, on the other hand, minimizes the undesirable recombination reaction of electrons and positive holes in the valence band, which results in the inhibition of the process rate [(Orge et al., 2015)]. The summary of compounds degraded by photocatalytic ozonation is shown in Table: 1.

III.MECHANISM OF PHOTOCATALYTIC OZONATION

First the basic mechanism of the reactions begin with exciting the surface of photocatalyst with UV-Vis radiation, which provide enough band gap energy to generate electron hole pairs as shown in reaction R1. At the same time, ozone molecules can adsorb on the surface of the photocatalyst via three different interactions: physical adsorption, formation of weak hydrogen bonds with surface hydroxyl groups, and molecular or dissociative adsorption into Lewis acid sites, each interaction resulting in the production of active oxygen radicals ($^{\cdot}O$) as shown in reaction R2.These active oxygen radicals react with water molecules to produce hydroxyl radicals as per reaction R10which play a key role in photocatalytic ozonation processes.

By providing the wavelengths shorter than 300 nm, ozone and hydrogen peroxide molecule would also absorb these wavelengths, producing active oxidising reagents as shown in R3 and R4. Hydrogen peroxide molecules are generated as an intermediate in ozone decomposition chain reactions R14–R16. Some researchers explained the possibility of hydrogen peroxide formation from the direct reaction of ozone with aromatic compounds, unsaturated carboxylic acids and methanol, respectively. The photo generated electrons on the photocatalyst surface R1 react with adsorbed oxygen and ozone molecules as electron acceptors R5 and R6, and these reactions are important to decreasing the recombination rate of electron–hole pairs [(Mehrjouei et al., 2015)] .

Table 1: Summary Of Compounds Degraded By Photocatalytic Ozonation

Type of Effluent	Catalyst	Source of Light	Results and Remarks	Reference
Reactive Red 198 and Reactive Red 120 dye solution	Copper Ferrite Nano particle	UV- C lamp, 9 W, Philips	Photocatalytic ozonation with Copper Ferrite nanoparticles has higher degradation efficiency than that of photo ozonation due to the catalytic effect of copper ferrite nanoparticles.	(Mahmoodi, 2011)
Oxalic Acid	TiO_2, Nb_2O_5, In_2O_3, WO_3, SnO_2, Fe_2O_3	300 W Xe lamp	The efficacy of the metal oxide semiconductors in the photocatalytic ozonation was in the order: $TiO_2>WO_3>In_2O_3 > BiVO_4> SnO_2>=Nb_2O_5>Fe_2O_3$.$WO_3$ showed the best performance for the photocatalytic ozonation system under visible light irradiation.	(Mano, Nishimoto, Kameshima, & Miyake, 2015)
Phenol aqueous solution	WO_3	300 W Xe lamp	It was expected that photocatalytic water treatment over visible-light-responsive photocatalysts combined with ozonation could effectively utilize solar light including available infrared light as a heat source to warm the treatment water, in addition to available UV-visible light as energy for photocatalysis.	(Mano, Nishimoto, Kameshima, & Miyake, 2011)
Tert-butyl alcohol (TBA)	TiO_2	7 UVA lamps were fixed in the reactor. The light intensity of UVA lamps was 1mW/cm^2	The oxidation of tert-butyl alcohol in water and wastewaterwas evaluated using TiO_2/O_3 systems in the dark (catalytic ozonation) and in the presence of UVA illumination (photocatalytic ozonation) by means of a falling film reactor. The results of TBA oxidation in water showed a removal of about 80% of the initial concentration of TBA from aqueous solutions after 10 min and al- most complete decomposition after 15 min using TiO_2/O_3/UVA systems. But very poor results were observed for the oxidation of this compound using a TiO_2/O_3 system in the dark.	(Mehrjouei, Müller, & Möller, 2014)
N,N-diethyl-meta-toluamide (DEET)	WO_3	1500 W Xe lamp	DEET degradation rate was highly increased during photocatalytic ozonation reaching more than 99% removal in less than 20 min compared to 60 min necessary for the other O_3 treatments. A synergistic effect between ozone and visible light irradiated WO_3 was produced leading to a higher efficiency in the combined process.	(Mena, Rey, Contreras, & Beltrán, 2014)
Oxalic and Oxamic acids	TiO_2	Heraeus TQ 150 medium-pressure mercury vapor lamp located axially and	The introduction of the selected catalyst in UV irradiation system increased the mineralizationrate 82timeswhencompared with neat photolysis. OXA is completely removed by using the photocatalytic ozonation compared to simple ozonation and photocatalysis.	(Orge et al., 2015)
4-Nitro Phenol	commercial TiO_2 Degussa Aeroxide P25	UVA radiation lamp	The synergistic effect has been observed in the combinationofPhotocatalysis and Ozonation which promotes the generation of free radicals, in particular hydroxyl radicals, which are the strongest oxidants in water	(Parrino, Camera-Roda, Loddo, Augugliaro, & Palmisano, 2015)
Benzenesulfonate	TiO_2	The photon flux of internal light source, 40 W, UVA range	It has been demonstrated that the combination of titanium dioxide based heterogeneous photocatalysis with ozonation for the oxidative degradation of benzenesulfonate results in a synergistic effect, achieving a significantly higher mineralization efficiency than the sum of those of the individual methods.	(Zsilák et al., 2014)

On the surface of the photocatalyst if the electrons and holes are recombine than this will negatively affect the oxidation and reduction reactions and this will results in reducing the performance of this process. The electron affinity of ozone (ca. 2.1 eV) is higher than that of oxygen (ca. 0.44 eV) which can promote photocatalytic reactions in the presence of ozone (photocatalytic ozonation) more positively than in the presence of oxygen (simple photocatalysis).

As shown in reaction R7 hydroxyl radicals are also formed due to the reaction between hydrogen peroxide molecules with photoexcited electrons on the photocatalyst surface. As per reaction R8 the photo generated hole directly attack the pollutant on the surface of the catalyst or it reacts with water molecule as shown in reaction R9 which oxidise the pollutant molecules. Other oxidative species such as oxygen atom radicals ($^{\cdot}O$) and superoxide and ozonide radical anions ($^{\cdot}O_2^-$ and $^{\cdot}O_3^-$) areassumed to be generated as reactive intermediates and could potentially oxidise the contaminants directly or reform to produce hydroxylradicals via different chain reactions as shown in R10–R20. Likewise, as shown in reaction R21 water pollutants such as phenols, amines and humic substances are supposed to act as initiators for ozone decomposition to ozonide radical anions ($^{\cdot}O_3^-$) and then hydroxyl radicals, which consequently quicken the degradation of these contaminants in water. Hydroxyl radicals produced in the above mentioned processes attackon target pollutant molecules and decompose them to less harmful substances R22. Three possible mechanisms are assumed for the decomposition of pollutants by hydroxyl radicals: electron transfer, radical addition and hydrogen abstraction. Initial reactions in the presence of photocatalyst, ozone and illumination [(Mehrjouei et al., 2015)]:

$\text{Photocatalyst} + h\nu \rightarrow \text{photocatalyst} + e^- + h^+$ (R1)
$O_3 + \text{photocatalyst (active surface sites)} \rightarrow {}^{\bullet}O + O_2$ (R2)
$O_3 + h\nu \rightarrow {}^{\bullet}O + O_2$ (R3)
$H_2O_2 + h\nu \rightarrow 2OH^{\bullet}$ (R4)

Possible reactions of photo generated electrons (e^-) on the surface of photocatalyst[(Mehrjouei et al., 2015)]:

$O_2(ads) + e^- \rightarrow {}^{\bullet}O_2^-$ (R5)
$O_3(ads) + e^- \rightarrow {}^{\bullet}O_3^-$ (R6)
$H_2O_2(ads) + e^- \rightarrow OH^{\cdot} + OH^-$ (R7)

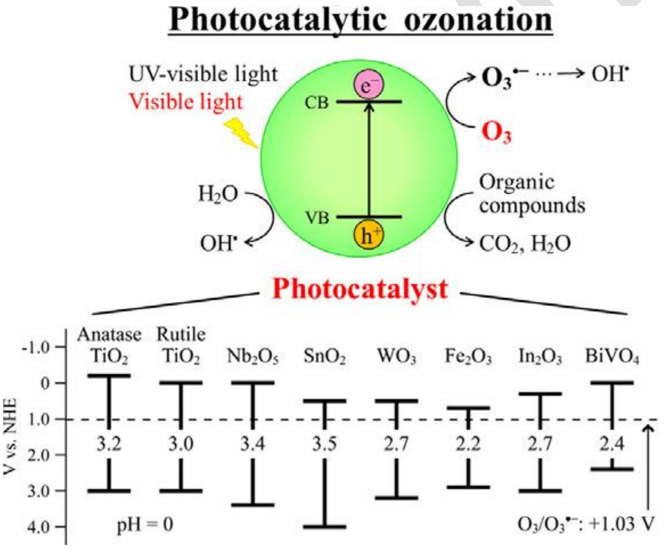

Figure 2: Mechanism of Photocatalytic Ozonation [(Mano et al., 2015)**]**

Possible reactions of photogenerated holes (h+) on the surface of photocatalyst [(Mehrjouei et al., 2015)]:

$\text{Pollutant}_{(ads)} + h^+ \rightarrow (\text{Pollutant})^+_{(ads)} \rightarrow CO_X, NO_X\ SO_X$, etc (R8)
$H_2O_{(ads)} + h+ \rightarrow OH^{\cdot} + H^+(pH<7)$ or $OH^-_{(ads)} + h^+ \rightarrow OH^{\cdot}$ (pH>7) (R9)

Possible further chain reactions in the oxidation medium [(Mehrjouei et al., 2015)]:

${}^{\bullet}O + H_2O \rightarrow 2OH^{\cdot}$ (R10)
${}^{\bullet}O_2^- + H^+ \leftrightarrow HO^{\cdot}_2$ (R11)
${}^{\cdot}O_3^- + H^+ \leftrightarrow HO^{\cdot}_3$ (R12)
$HO^{\cdot}_3 \rightarrow O_2^- + OH^{\cdot}$ (R13)
$O_3 + OH^- \rightarrow {}^{\bullet}O_2^- + HO^{\cdot}_2$ (R14)
$O_3 + OH^{\cdot} \leftrightarrow HO^{\cdot}_4 \rightarrow O_2 + HO^{\cdot}_2$ (R15)
$2HO^{\cdot}_2 \rightarrow H_2O_2 + O_2$ (R16)
$H_2O_2 + {}^{\cdot}O_2^- \rightarrow OH^{\cdot} + OH^- + O_2$ (R17)
$O_3 + HO^{\cdot}_2 \rightarrow 2O_2 + OH^{\cdot}$ (R18)
$O_3 + {}^{\cdot}O_2^- \rightarrow {}^{\cdot}O_3^- + O_2$ (R19)
$O_3 + H_2O_2 \rightarrow OH^{\cdot} + HO^{\cdot}_2 + O_2$ (R20)
$\text{Pollutant} + O_3 \rightarrow {}^{\cdot}[\text{pollutant}]^+ + {}^{\cdot}O^-_3$ (R21)
$\text{Pollutant}_{(ads)} + OH^{\cdot} \rightarrow {}^{\cdot}[\text{pollutant}]^+_{(ads)} + H_2O \rightarrow CO_X, NO_X, SO_X$ etc (R22)

IV. ECONOMIC ASPECTS

Though the photocatalytic ozonation is more effective compare to photocatalysis process the economic aspects has to be considered to commercialize the process. Comparing photocatalysis in the presence of oxygen which requires electricity for UV irradiation sources to photocatalytic ozonation which requires additional electrical energy for ozone generation,at first glance, photocatalytic ozonation systems appear to be more expensive than simple photocatalysis and may not be economically justifiable. The specific energy consumption for each oxidation system, where the energy consumed during the process is distributed to the decomposed materials is the viable option for cost assessment of this techniques [(Mehrjouei et al., 2015)].

Application of Photocatalyst to Photocatalytic Reactor: There are two different ways to use photocatalyst in processes. Some group of researchers are mixed photocatalyst with wastewater in the suspension form and whole suspension is subjected to photocatalytic process. Some other group used the photocatalyst particles immobilized on inert support materials. It seems that the mass transfer properties of the oxidation system is more effective in suspended photocatalyst particles, compared with those of immobilized particles, willresult in improved degradation efficiency. When system using the photocatalyst in suspension form the additional steps like filtration and recycling of photocatalyst from treated wastewater increases the total cost of process so it is still not commercialized and limited to laboratory experiments only. The immobilization of photocatalysts on a stable substrate solves this problem, as well as the issue of extinction due to scattering of the UV radiation by the photocatalyst particles. [(Mehrjouei et al., 2015)].

As far as the mineralization of refractory compounds form wastewater is concerned, the combination of ozone, proper selection of photocatalyst(s), optimum design and parameters will lead to higher degradation efficiencies compared to using ozonation and photocatalysis separately. In many cases the synergistic effects of this combination have been observed and are mainly due to the moregeneration of highly oxidative and non-selective reagents (such as hydroxyl radicals) in the oxidation medium of photocatalytic ozonation. The high mineralization rates of nearly all model pollutants in water by photocatalytic ozonation, and the simplicity of thisprocess, make it an excellent alternative to other oxidation treatment methods.Much like other successful technologies, in order to move this treatment method from the lab to commercial utilization, more attention should be focused on the immobilization of photocatalyst particles onto inert substrates, as slurry applications of photocatalytic ozonation are not economically justifiable, due to the additional high costs of photocatalyst filtration after treatment. Fortunately, photocatalytic ozonation can moderate the relatively poor mass transfer properties of immobilized photocatalysts in photocatalytic treatments.

V. CONCLUSIONS

Photocatalytic ozonation process, which is qualitatively and quantitatively different from renowned photocatalytic oxidation with oxygen and ozonation without photocatalyst.The main difficulty in any AOPs lies in the high cost of reagents or energy source such as ultra- violet light.For the photocatalytic ozonation methods the energy demand of the $O_3/TiO_2/UV$ could be considerably decreased by the use of solar-irradiation and in situ electrochemical O_3 generation. However, the use of solar radiation as an energy source can reduce costs.Photocatalytic ozonation is an excellent alternative to other oxidation treatment methods as it gives high mineralization rates of almost all model pollutant in wastewater.In addition to choosing a suitable photocatalyst, a proper irradiation source and an optimum ozone concentration for photocatalytic ozonation treatments, developing new operative designs for oxidation reactors, where these factors are combined and utilized together, is important. An effective reactor design could considerably stimulate the synergistic effects and benefits of photocatalytic ozonation systems [(Agustina et al., 2005); (Mehrjouei et al., 2015)].

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