

Review Paper

**FORMATION OF HYDROXYL RADICALS FOR WASTE WATER
TREATMENT BY PHOTO-CATALYTIC OXIDATION PROCESS**

Gupta, Amit Kumar and Sachin Gupta¹

Assistant Professor,
Chemical Engineering Department,
B.B.D.N.I.T.M., Lucknow.

¹ Botany Department,
B.N.D. College, Kanpur.

Abstract

Organic pollution is the term used when large quantities of organic compounds are found in waste water. It originates from domestic sewage, urban run-off; industrial effluents and agriculture wastewater. Water shortage and water quality are the main issues in the global water crisis. As the population increases, there is ever growing demand on water resources. Wastewater with organic pollutants contains large quantities of suspended solids which reduce the light available to photosynthetic organisms and, on settling out, alter the characteristics of the river bed, rendering it an unsuitable habitat for many invertebrates. Purification of water is essential for availability of good quality water. Advance oxidation process (Photo-catalytic oxidation process) is a method for degradation of organic compounds in waste water through a semiconductor catalyst i.e. TiO_2 with UV light. This paper discusses the organic and inorganic pollutants in waste water and their removal via photo-catalytic oxidation process. In this paper, the mechanisms of photo-catalytic oxidation process are discussed to radical formation i.e. OH^* . These radicals (i.e. OH^*) are capable to destroy the organic pollutants in waste water. This paper also discusses the several other conventional methods for purification of water.

Key words: Photo-catalytic oxidation process, Organic and inorganic pollutants, TiO_2 , UV light, Advance Oxidation Process, Hydroxyl radicals.

INTRODUCTION

The sources of pollution, including sewage and industrial discharge, affect water quality. Due to increase in population, expansion of urbanization and industrialization, the water pollution is increasing day by day. Due to increase in agricultural wastes, pharmaceutical wastages i.e. increase in pesticides, pharmaceuticals chemicals, which are not effectively removed by the conventional treatment steps in a water purification plant. Hence cost-effective treatment steps are being developed.

Among the various organic pollutants in wastewater, phenol and its derivatives are considered as most hazardous pollutants since it is harmful to plants, animals and human, even at low concentrations. The major sources of phenolic are steel mills, petroleum refineries, pharmaceuticals, petrochemical, coke oven plants, paints, coal gas, synthetic

resins, plywood industries and mine discharge. The wastewater with the highest concentration of phenol (>1000 mg/L) is typically generated from coke processing. Phenolic compounds are also generated from resin plants with a concentration range of 12–300 mg/L. Environmental Protection Agency (EPA) has set a limit of 0.1 mg/L of phenol in wastewater. The World Health Organization (WHO) has set a limit of phenol 0.001 mg/L for drinking water.

Conventional water treatment process like activated carbon adsorption, membrane filter, chemical precipitation, chemical flocculation, chlorination etc. produce extra waste during the purification system, which will further increase the cost and time. The some conventional methods are discussed below:

Water-chlorination is the process of adding chlorine (Cl_2) to water as a method of water purification. As a strong oxidizing agent, chlorine has oxidized the organic pollutants. When dissolved in water, chlorine converts to an equilibrium mixture of chlorine, hypochlorous acid (HOCl), and hydrochloric acid (HCl):



In acidic solution, the major species are Cl_2 and HOCl while in alkaline solution effectively only ClO^- is present.

The major drawback of chlorination is disinfection. Chlorine can react with naturally occurring organic compounds found in the water supply to produce compounds known as disinfection byproducts (DBPs). The most common DBPs are trihalomethanes (THMs) and haloacetic acids (HAAs).

Membrane filters are widely used for filtering both drinking water and sewage. For drinking water, membrane filters can remove particles larger than $0.2\ \mu\text{m}$. Membrane filters are an effective form of tertiary treatment when it is reused the water for industry, for domestic purposes, or before discharging the water into a river. They are widely used for making bottled water in industrial purpose.

Chemical precipitation is the most common method for removing dissolved metals from wastewater solution containing toxic metals. To convert the dissolved metals into solid particle form, a precipitation reagent is added to the mixture. A chemical reaction, triggered by the reagent, causes the dissolved metals to form solid particles. Filtration can then be used to remove the particles from the mixture. The process works is dependent upon the kind of metal present, the concentration of the metal, and the kind of reagent used. In hydroxide precipitation, a commonly used chemical precipitation process, calcium or sodium hydroxide is used as the reagent to create solid metal hydroxides.

In Chemical flocculation, fine solid particles dispersed in wastewater carry negative electric surface charges (in their normal stable state), which prevent them from forming larger groups and settling. Chemical coagulation destabilizes these particles by introducing positively charged coagulants that then reduce the negative particles' charge. Once the charge is reduced, the particles freely form larger groups. Next, an anionic flocculant is introduced to the mixture. Because the flocculant reacts against the positively charged mixture, it either neutralizes the particle groups or creates bridges between them to bind the particles into larger groups. After larger particle groups are formed, sedimentation can be used to remove the particles from the mixture.

Activated carbon is one of the most effective techniques for removing a wide range of contaminants from industrial and municipal waste waters, landfill and contaminated groundwater. As the world's most powerful adsorbent, it can cope with a wide range of contaminants. Different contaminants may be present in the same discharge and carbon

may be used to treat the total flow, or it may be better utilized to remove specific contaminants as part of a multistage approach.

Adsorption is a surface phenomenon with common mechanism for removal of organic and inorganic pollutants. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure then liquid-solid intermolecular forces of attraction occurs, some of the solute molecules from the solution is concentrated or deposited at the solid surface. The solute retained (on the solid surface) in adsorption processes is called adsorbate, whereas, the solid on which it is retained is called as an adsorbent. This process is called adsorption. Adsorption of phenolic compounds from aqueous solutions by activated carbon is liquid-phase applications of carbon adsorbents (13).

As a result, many studies and researches have been carried out to develop a sustainable and cost-efficient treatment process that can effectively remove or degrade these organic and inorganic chemicals in wastewater as photo-catalytic oxidation process.

In this context, advanced oxidation processes (AOPs) can play an important role due to their ability to produce highly oxidative hydroxyl radicals ($\bullet\text{OH}$), which is capable of destruction of organic pollutants (e.g., phenol, toluene, benzoic acid pharmaceuticals, etc.). In addition, use of renewable energy resources (Solar Energy), as in the case of solar photo-catalysis, would reduce the treatment costs and make AOPs more attractive to the water industry.

Nowadays, the use of UV and solar light for not only water disinfection but also for oxidation of undesirable chemical contaminants as well as germ cells, bacteria etc. which are damaged our eco system. Here, the oxidation is achieved by the production of highly oxidative $\bullet\text{OH}$ by combining light with a suitable catalyst (e.g., semiconductor catalyst as TiO_2). This article focuses on TiO_2 /UV solar light, which is heterogeneous photo-oxidation process.

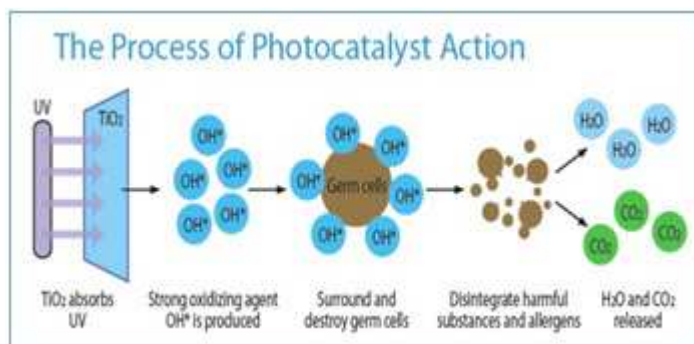


Fig.1 Photo-catalytic Oxidation Process for germs, bacteria etc.

Literature Review for Photo-catalytic Oxidation Process

A large literature is available on photo-catalytic oxidation of a variety of organic and inorganic compounds. Selective relevant literatures have been discussed.

De et al (3) have presented the study of oxidative degradation of phenol by H_2O_2 and UV radiation. They derived a kinetic model in order to represent the photo-oxidation reaction while Korman et al (11) have discussed the rate of photo-degradation of chloroform and several other organic molecules as a function of CHCl_3 , pH (O_2), light intensity and the presence of charged and neutral solutes. Organic pollutants like benzoic acid, salicylic acid, phenol, 2-chloro phenol, 3-chloro phenol, 4-chloro phenol, nitro benzene, methanol, ethanol, acetic acid and formic acid have discussed by Matthews R W (4) in areate aqueous suspensions of TiO_2 were illuminated with near U V light. Each solute was present over a range of generally 1-50 mg/L. Mitra and Pal (6) have discussed catalytic conversion of phenol, mainly to its coupling

products using cuprous chloride (Cu_2Cl_2) as a catalyst via free radical mechanism followed by stepwise addition polymerization. Photo catalytic oxidation of distillery waste has been investigated by Kulkarni (7) using solar radiations and TiO_2 as a photocatalyst. Kulkarni found that the presence of oxygen, which acts as an electron scavenger is essential for rapid photocatalytic mineralization. Due to destructive oxidation process, complete mineralization of effluent to CO_2 and H_2O is possible with 97% degradation of organic contaminants in 90 min. Ku and Jung (8) studied the reduction of hexavalent chromium in aqueous solution by UV/ TiO_2 reduction process under various solution pH values, TiO_2 dosages, light intensities, dissolved oxygen levels and other operative conditions. The Cr (VI) adsorbed on the surface of TiO_2 particles was observed to be photoreduced to Cr (III) almost completely. Ku and Hsieh (9) have discussed the degradation of 2-4 dichlorophenol in presence of TiO_2 suspensions by illumination with a low pressure UV light under various pH conditions, reaction time and TiO_2 loadings. Hung et al (5) have presented that the photo-catalysis of azo dye, Orange G by P 25 anatase TiO_2 . Mills and Haffmann (12) have discussed the result of a kinetic investigation of the photo-degradation of PCP in aqueous TiO_2 suspensions which was providing the mechanism of semiconductor photocatalysis.etc.

Heterogeneous photo-catalytic oxidation process

The presence of non-biodegradable and toxic organic compounds in wastewater is one of the major problems in wastewater treatment. Organic compounds like phenol and its derivatives are known for their toxicity. These compounds are hazardous to human health. Phenol and its derivatives are introduced to the water bodies by various means. Industrial manufacturers, normal households, and landfill are causes to increase these organic compounds into the water bodies and makes wastewater treatment more difficult. All these pollutants need to be removed from wastewater before it can be discharged to the environment. Exposure to high levels of phenol for several weeks results in paralysis and severe injury to the heart, kidneys, liver and lungs, followed by death in some cases.

Majority of the natural purification of aqueous systems such as aerated lagoons or ponds, rivers and streams, lakes etc. are caused by the action of sunlight. Organic molecules were breakdown by the action of sunlight to simpler molecules and finally to carbon dioxide and other mineral compounds.

The introduction of 'colloidal semiconductor' can be applied to natural purification process. Wastewater treatment using photo-catalysis involves the combination of heterogeneous photo-catalysis with solar technologies. Semiconductor photo-catalysis, especially titania-based photo-catalysis has been applied to various water treatment plants. Different studies have been carried out from fundamental to practical aspects to improve the process and the properties of the photo-catalyst in recent years. (7-12)

Many researchers reported in that the utilizations of irradiated semiconductors for the degradation of organic pollutants were well documented and have shown positive and encouraging results for various organic pollutants. Various studies have also been carried out from fundamental to practical aspects to improve the process and the properties of the photo-catalyst in recent years (1-6).

Mechanism of heterogeneous photo-catalysis with U.V. / TiO_2

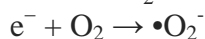
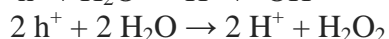
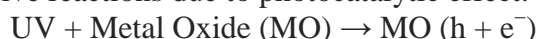
Photo-catalytic oxidation with TiO_2 powder is a heterogeneous process and forms the hydroxyl radicals with different phases (i.e. TiO_2 powder is a solid phase and waste water with phenol is a liquid phase). The main advantage of the process is that the catalyst can be separated from the treated water effluent.

The TiO_2 catalyst is not expensive. It is safe and can be reused. The catalyst can be immobilized on different types of substrates. The catalyst can be activated and excited by the solar light. Among different semiconductors, TiO_2 is the most used photo-catalyst since it is

affordable, Eco- friendly, non-toxic substance. The nano-sized catalyst and catalyst structure is provided a high specific surface area for degradation of phenol.

When a photon with energy equal to or greater than the materials band gap is absorbed by the semiconductor, an electron is excited from the valence band to the conduction band, generating a positive hole in the valence band. The excited electron and hole can recombine and release the energy gained from the excitation of the electron as heat. Recombination is undesirable and leads to an inefficient photocatalyst. The ultimate goal of the process is to have a reaction between the excited electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes to produce an oxidized product. Due to the generation of positive holes and electrons, oxidation-reduction reactions take place at the surface of semiconductors. In the oxidative reaction, the positive holes react with the moisture present on the surface and produce a hydroxyl radical.

Oxidative reactions due to photocatalytic effect:



Ultimately, the hydroxyl radicals are generated in both the reactions. These hydroxyl radicals are very oxidative in nature and non selective with redox potential of ($E_0 = +3.06 \text{ V}$)

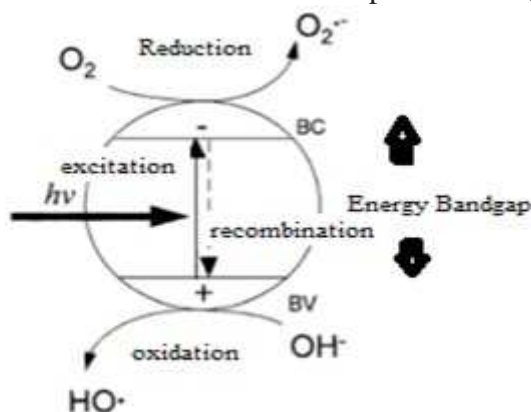
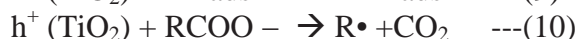


Fig. 2 Photo-catalytic Oxidation Process

The electronic structure of the TiO_2 semiconductor plays a key role in photo-catalysis. It consists of a valence band holes and a conduction band electrons. The energy difference between these two levels represents the band gap energy (E_g). When the TiO_2 semiconductor is excited by photons with an energy amount equal to or higher than its band gap energy, electrons receive energy from the photons and are thus transferred from the valence band to the conduction band as shown in figure. In the case of anatase TiO_2 , the band gap is 3.2 e V , therefore UV light ($\lambda \leq 387\text{nm}$) is required and the UV part of the solar light can be activated it (Fig.2).

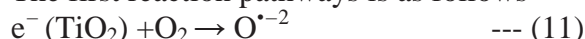
The holes can also be reacted directly with adsorbed substrate (e.g., carboxylic acids) and generates CO_2 as follows:



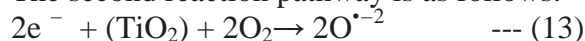
There are two reaction pathways for the electrons released by irradiation of photo-catalyst with dissolved molecular oxygen. Both of them are characterized by the production of superoxide

radical anion, $O^{\bullet-2}$. The other mechanism of the photo-catalytic oxidation process can be given below:

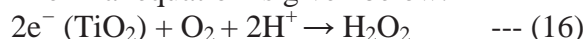
The first reaction pathways is as follows



The second reaction pathway is as follows:



The final equation is given below:



Therefore, one dissolved oxygen molecule can consume two electrons released by irradiation of the photo-catalyst. Oxygen acts as an electron scavenger and inhibits the electron hole recombination; on the other hand, hydroxyl radical can be produced due to the formation of hydrogen peroxide as shown in the following reactions (3)



Finally, the $\bullet OH$ radicals oxidize organic adsorbed pollutants onto the surface of the titanium dioxide particles in to water and carbon dioxide.



CONCLUSIONS

Advanced oxidation processes based on heterogeneous catalysis can be utilized to improve the quality of drinking water. Heterogeneous photo-catalysis can be applied in large scale water treatment plants. Photo-catalytic oxidation process can be used to treatment of organic impurities i.e. benzoic acid, salicylic acid, phenol, 2-chloro phenol, 3-chloro phenol, 4-chloro phenol, nitro benzene, methanol, ethanol, acetic acid and formic acid as well as inorganic impurities i.e. Cr (IV) etc.

Photo-catalysis has large capability for the water treatment. The photo-catalytic reaction was capable to destroy a spectrum of organic chemicals. It can be utilized for the decomposition of inorganic compounds as well as destruction of viruses and bacteria. The hydroxyl radicals are responsible to degradation of phenol and its derivatives. Hydroxyl radicals have quickly reacted with any organic contaminants in water, simultaneously breaking them down to CO_2 and H_2O .

The drawback of this method is that of being slow compared with other traditional methods as reverse osmosis, water chlorination etc. but it has the advantage not leaving toxic by product or sludge to be disposed. Due to electron hole recombination the rate of photo-catalytic oxidation process decreases, this is other drawback of the process Photo catalytic oxidation process can also be used for purification of sea water treatment. This technology might be useful for water pre-treatment of desalination process especially with reverse osmosis technique.

In heterogeneous photo-oxidation process, the renewable solar energy can be used in the activation of the catalyst which reduces the treatment costs and makes photo-catalytic oxidation process more attractive to the water treatment industry.

It was also studied that the nano-sized catalyst and catalyst structure has provided a high specific surface area for degradation of organic/inorganic contaminants in waste water.

Dedication: Dedicated to Ananya and Anushka (daughters of Amit Kumar Gupta, main author)

REFERENCES

1. Mills, G and Haffman , M.R. photocatalytic degradation of pentachloro phenol on TiO_2 particles: Identification of intermediates and mechanism of reaction. *Envir. Sci. and Tech.*, 27, 1993,1681
2. Gupta, Amit Kumar, Modeling and Simulation for “Photo-catalytic oxidation process of phenolic contaminants in waste water” *Journal of Teaching and Research in Chemistry*” 19(1), 2012, 59-64
3. De, A. K., Bhattacharjee, S. and Dutta, B.K., Kinetics of phenol photooxidation by hydrogen peroxide and ultraviolet radiation. *Indian Engg. Chemical Research*, 36,1997,3607
4. Matthews, R. W. , Purification of water with near U V illuminated suspension of titanium dioxide, *water research*, 24,1990,653
5. Hung, C. H., Ching, P. C., Yuan, C. and Chou, C. Y., Photocatalytic degradation of azo dye in TiO_2 suspended solution. *Water Science and Technology*, 43,2001,313
6. Mitra, P. P. and Pal, T. K., Treatment of effluent containing phenol by catalytic conversion. *Indian Chemical Engineer*, 41,1999,26.
7. Kulkarni, A. A., Solar assisted photocatalytic oxidation of distillery waste, *Indian Chemical Engineer*, 40,1998,59
8. KU, Y. and Jung I.L., Photocatalytic reduction of Cr (VI) in aqueous solution by UV irradiation with presence of Titanium dioxide. *Water Research*, 35,1999,135
9. KU, Y. and Hsieh C.B., Photocatalytic decomposition of 2,4-dichlorophenol in aqueous TiO_2 suspensions, *Water Research*,26,1992,1451
10. Bhattacharya, S. and Clements, C. P., Solar detoxification of waste water, *Indian Chemical Engineer*, 41,1998,150
11. Kormann, C, Bachnemann, D.W. and Haffmann, M.R., Photolysis of chloroform and other organic molecules in aqueous TiO_2 suspensions. *Environmental Science Technology*, 25, 1991, 494
12. Mills, A., Davies, R. H. and Worsley, D., Water purification by semiconductor photocatalysis, *Chemical Society Review*,21, 1993, 417
13. Srivastava V C et al, Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium kinetics and thermodynamics, *Elesvier*, 272, 2006, 89-104