

Waste water treatment by photo-catalytic oxidation process

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SUMMARY : 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. Due to increased industrial activities and urbanization, availability of good quality water is diminishing day by day. 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.* TiO₂ with UV light. This paper discusses the organic and inorganic pollutants in waste water and their removal via photo-catalytic oxidation process. The mechanisms of photo-catalytic oxidation process have been 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.

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Water is the one of the most important resources used by mankind. The sources of pollution, including sewage and industrial discharge, affect the 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 they are harmful to plants, animals and human, even at low concentrations. The major sources of phenolics 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:

This is the process of adding chlorine (Cl₂) 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 Cl₂ and HOCl while in alkaline solution effectively

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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:

There 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:

It 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.

Chemical flocculation:

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:

It 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 the 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 occur, some of the solute molecules from the solution are 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 (Srivastava *et al.*, 2006).

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.

Now-a-days, the use of UV and solar light for not only water disinfection but also for oxidation of undesirable chemical contaminants which damage 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.

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 the causes to increase these organic compounds into the water bodies and make 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 semi-conductor' 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. (Kulkarni, 1998; Ku and Jung, 1999; Ku and Hsieh, 1992; Bhattacharya and Clements, 1998; Kormann *et al.*, 1991; Mills *et al.*, 1993).

Many researchers reported that the utilizations of irradiated semi-conductors 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 (Mills and Haffman, 1993; Gupta, 2012; De *et al.*, 1997; Matthews, 1990; Hung *et al.*, 2001; Mitra and Pal, 1999).

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 overall process in the aqueous phase can be described with the following five steps:

- Transfer of the reactants from the bulk to the catalyst interface,
- Adsorption of the reactant on the surface of the catalyst,
- Reaction on the surface of the catalyst in the adsorbed state,
- Desorption of the products from the surface of the catalyst,
- Products removal from the catalyst interface region.

The photo-catalyst is a semi-conductor. It is activated by photons (step 3), where photons are consumed to form electron-hole pairs that initiate the oxidation reduction reactions. The process takes place at normal pressure and at ambient temperature. The oxygen demand for the electronic reactions can be directly obtained from atmosphere.

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 semi-conductors, 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.

The electronic structure of the TiO_2 semi-conductor 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 semi-conductor 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 Fig.1. 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. 1).

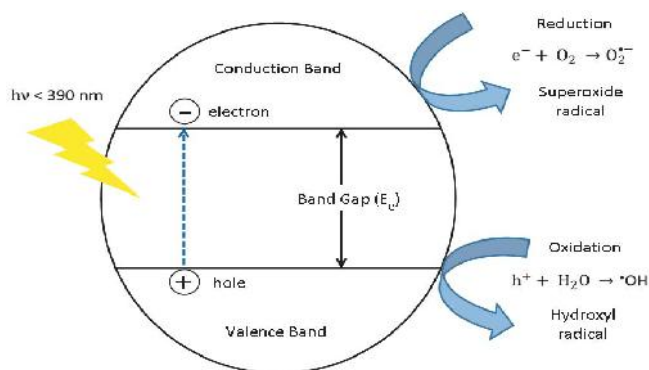
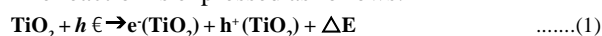


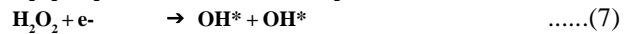
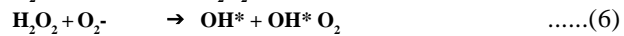
Fig. 1 : Photo-catalytic oxidation process

The reaction is expressed as follows:



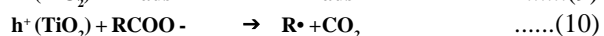
The photo-generated electrons and holes can recombine within a very short time, releasing energy in the form of heat. Therefore, oxygen is essential for capturing the electrons and for preventing hole-electron recombination. Electrons and holes migrate to the surface of the TiO_2 semiconductor without recombination. It can be reduced and oxidized the reactants which are absorbed by the semi-conductor. The basic mechanism of photo-catalytic oxidation process is oxidation reaction. Both surface adsorption as well as photo-catalytic reactions can be enhanced by nano-sized semi-conductors as more reactive surface area is available.

The step wise mechanism of radical formation is given below (Kulkarni, 1998):



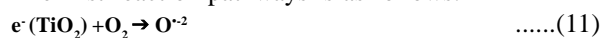
The positively charged hole reacts with the OH⁻ to produce hydroxyl radicals while the electrons react with the dissolved oxygen to produce superoxide anions (O₂⁻) that also form hydroxyl radicals. The presence of water and oxygen is essential along with photo-catalyst and light for rapid photo-catalytic degradation. The degradation efficiency of the process is substantially reduced due to the electron hole recombination, which corresponds to wastage of supplied photoelectric energy in the form of heat (arise in temperature is even more detrimental as it decreases the rates of photo-catalytic oxidation reactions).

The holes can also be reacted directly with adsorbed substrate (e.g., carboxylic acids) and generates CO₂ 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⁻². The other mechanism of the photo-catalytic oxidation process can be given below:

The first reaction pathways is as follows:



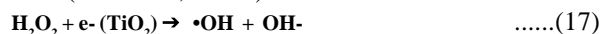
The second reaction pathway is as follows:



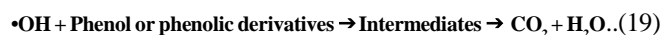
The final equation is given below:



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 (De *et al.*, 1997):



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



Conclusion:

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 for water treatment plants.

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 CO₂ and H₂O.

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 observed that the nano-sized catalyst and catalyst structure has provided a high specific surface area for degradation of phenol.

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