



## TREATMENT OF WASTEWATER BY PHOTOCATALYSIS USING TiO<sub>2</sub>

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### Abstract

Industrial wastewater is of global concern due to its severe effects on the environment. Compared with municipal wastewater, industrial wastewater generally contains high concentration of toxic or non-biodegradable pollutants. This report contains how to remove organic pollutant by photocatalysis. The report focuses on the removal of organic pollutant from wastewater, the sources from which wastewater comes from and detail of various contaminants in wastewater methods which is used for removal of organic as well as inorganic waste. Photocatalysis is the advanced oxidation method aiming at the entire conversion of harmful and poisonous dissolved contaminants in natural or drinking water into carbon dioxide, water and inorganics in presence of semiconducting materials such as TiO<sub>2</sub>, which acts as catalysts because of its non selective nature with regard to contaminants and use of renewable energy source. The advantages of photocatalysis process for removal of organic pollutant and photo catalyst TiO<sub>2</sub> is better than other catalyst. The destructive power of NTO photocatalysis is remarkable, comprising families of dyes, pesticides, herbicides, pharmaceuticals, cosmetics, phenolic compounds, toxins, and more.

**Index Terms:** photocatalysis, titanium dioxide, advance oxidation process, water treatment, degradation.

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### 1. INTRODUCTION

Due to a rise in human and stock population, industrial developments have raised the priority of safe drink and non-potable water whereas, environmental protection, waste management and pollution management are consistent with World Health Organization and United Nations International Children's Emergency Fund, impure drink and lack of sanitation square measure answerable for death of roughly 4500 - 5000 kids per day, and one billion individuals still lack access to safe water. The second most crucial issue is that the medical care of water for agricultural usage purpose. consistent with the Food and Agriculture Organization (FAO) of the United Nations, agricultural functions consume 70% of water used worldwide with enhanced over 95% of the accessible water huge current researches explore innovative techniques and concepts to treat waste stream of varied industrial sources. This review highlights the contaminated streams of agricultural fields, textile industries, and pharmaceutical industries to critically assess all potential practices of waste water treatment for getting ecofriendly discharge. This review additionally portrays regarding the relevance and up to date advancement of the photocatalytic

method for treating industrial waste (dyes, pesticides and pharmaceutical waste). In recent years, semiconductor photocatalytic method has shown an excellent potential being price effective, environment friendly and within the field of property treatment technology with zero waste discharge. Photocatalysis involves removal of water contaminants that are with chemicals stable and resistant to biodegradation. the strategy offers advantage over usual sewer water treatment techniques like activated charcoal adsorption, chemical oxidation, biological treatment and membrane separation. activated charcoal adsorption involves phase transfer of pollutants without decomposition. This incomplete removal method more will increase pollution load on surroundings. Chemical oxidation is additionally a cause for incomplete mineralization of organic substances with generation of undesirable harmful byproducts' complicated reaction mechanism. Biological treatment faces crisis for sludge removal, for terribly slow reaction rate and management of correct method conditions (microbial growth condition). The reversal of retentive elements, severe membrane.

Fouling and expensive method setup possess an excellent impact on membrane method. during this context, photocatalytic processes provide variety of benefits for the removal of pollutants from water, complete mineralization, use of affordable catalyst system and relatively untroubled arrangement. Advanced oxidation processes (AOPs), that have faith in the generation of extremely reactive and oxidizing hydroxyl group radicals ( $\cdot\text{OH}$ ), are thought-about as extremely competitive water treatment technologies. As a crucial technology of AOPs, photocatalytic oxidation (PCO) has attracted increasing attention in recent years due to its wonderful performance on pollutants removal, low price and photochemical stability  $\text{TiO}_2$  is the most widely used catalyst in heterogeneous photocatalysis, due to its photostability, nontoxicity, low cost, and stability in water below most environmental conditions. great amount of reactive oxygen species like hydroxyl group radicals ( $\cdot\text{OH}$ ) and superoxide radical anion ( $\cdot\text{O}_2$ ) are made on the surface of  $\text{TiO}_2$  below light-weight irradiation, and these reactive radicals are considered the most important accountable species for the degradation of organic pollutants in sewer water. Preis and coworkers studied the degradation of phenolic resin compounds in sewer water from shale below UV-light irradiation. The results disclosed that the sewer water quality characteristics have obvious influence on the photodegradation rate of the pollutants.

Homogeneous photo-Fenton technique is another economical AOP for the oxidation of water contaminants. However, the photo-Fenton method needs the employment of ferrous sulfate ( $\text{FeSO}_4$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). for instance, within the photo-Fenton oxidation of catechol,  $\text{H}_2\text{O}_2$  and  $\text{FeSO}_4$  were utilized in the experiment that according the best activity. In distinction, NTO photocatalysis might not need any extra reagents on the far side the NTO catalyst The PCO method can even be combined with made wetlands. The combined system was tested below natural irradiation, showing that organic pollutants, nutrients, and unhealthful bacteria will be effectively removed. more significantly,  $\text{TiO}_2$ -mediated solar photocatalytic oxidation is low price and environmentally friendly and therefore could also be a promising answer for sewer water treatment.

## 1.1 Pollutants contained in waste water: -

### 1.1.1 Chemical or Physical pollutants

Chemical pollutants embrace serious metals, as well as mercury, lead, and Cr organic particles like feces, hairs, food, vomit, paper fibers, plant material, humus, etc. soluble organic material like urea, fruit sugars, soluble proteins, drugs, pharmaceuticals, etc. inorganic particles like sand, grit, metal particles, ceramics, etc. Soluble inorganic material like ammonia, road-salt, sea-salt, cyanide, hydrogen sulfide, thiocyanates, thiosulfates etc Macro-solids like sanitary napkins, nappies or diapers, needles, children's toys, dead animals or plants, etc. gases like hydrogen sulfide, carbon dioxide, methane, etc. emulsions like paints, adhesives, mayonnaise, hair colorants blended oils, etc. pharmaceuticals

and hormones and alternative dangerous substances thermal pollution from power stations and industrial makers.

### 1.1.2 Biological Pollutants

Biological pollutants embrace bacteria (for example salmonella, shigella, campylobacter, vibrio cholera) viruses (for example hepatitis A, rotavirus, enteroviruses), Protozoa (for example entamoeba histolytic, giardia lamblia, cryptosporidium parvum) and Parasites like helminths and their eggs It may also contain non-pathogenic bacteria and animals like insects, arthropods, small fish.

### 1.3 Why only semiconductor?

Current and past analysis in photocatalytic materials has investigated many photocatalysts and their properties. Ideally, a photocatalyst should possess the subsequent properties: photoactivity, biological and chemical inertness, stability toward photo-corrosion, quality for visible or close to ultraviolet[ultraviolet illumination|UV|actinic radiation|actinic ray} light energy harnessing<sup>1,2</sup>

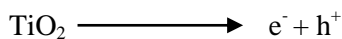
Photocatalyst, has wonderful pigmentary properties, high ultraviolet absorption and high stability which permit it to be employed in totally different applications like electro-ceramics, glass and within the photocatalytic degradation of it's been utilized in the form of a suspension, or a thin film in water treatment and has totally different crystalline forms, the most common forms being anatase and rutile while the third, brookite, is rare, unstable and therefore doesn't feature in discussion of catalyst materials. Anatase  $\text{TiO}_2$ , the most stable kind of  $\text{TiO}_2$  is regenerate to rutile by heating to temperatures higher than  $700\text{ }^\circ\text{C}$ . it's been utilized in several studies of photocatalytic degradation due to its chemical stability, prepared availableness, reliability and activity as a catalyst for oxidation processes. several semiconductors have enough band-gap energies for the effective catalysis of the many chemical reactions and this includes materials like  $\text{TiO}_2$ ,  $\text{WO}_3$  and  $\text{ZnO}$ . Though it's standard that metal oxides are sometimes less active catalysts than noble metals within the majority of applications, metal oxides are more appropriate since they're a lot of additionally, combining two or more metal oxide catalysts may improve or enhance catalytic activity.<sup>1,2</sup>

$\text{TiO}_2$  is that the most frequently used photocatalyst due to its photostability and low price, combined with its biological and chemical inertness and resistant to photo and chemical corrosion. On the other hand, binary metal sulfide semiconductors like  $\text{CdS}$  and  $\text{PbS}$  are considered insufficiently stable for catalysis and are harmful.  $\text{ZnO}$  is also unstable in illuminated aqueous solutions whereas  $\text{WO}_3$  has been investigated as a potential photocatalyst, but it's usually less active catalytically than  $\text{TiO}_2$ . However, these are often combined with different semiconductors as well as  $\text{TiO}_2$  to attain larger photocatalytic potency or stability. There are several semiconductor support materials that have been investigated. Usually, semiconductor supports are classified by their chemical nature and these is organic or inorganic

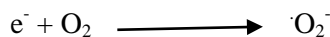
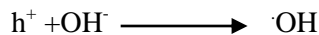
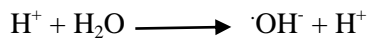
supports. They play a crucial role in restraint active catalyst, increase the surface area of catalytic material, decrease sintering and improve hydrophobicity, thermal, hydrolytic and chemical stability of the catalytic material.<sup>1,2</sup>

## 2. MECHANISM OF PHOTOCATALYSIS PROCESS

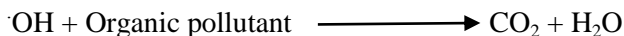
A semiconductor can be activated by photons with of energy,  $h\nu$  equal or greater than the band gap energy,  $E_{bg}$ . Of the semiconductor upon illumination, the semiconductor absorbs a photon onto its surface, causing excitation of an electron from the Valence Band to the Conduction Band (CB) thereby forming a positive hole,  $h^+$  in the Valence Band. This process is illustrated by the following reaction using titanium dioxide as the photocatalyst.<sup>3</sup>



After migrating to the surface of the semiconductor, the photogenerated holes oxidize and absorb water molecules or hydroxide ions according to the following reactions



The photo generated hydroxyl radical is very reactive and reacts rapidly and non-selectively in the oxidation of organic compounds. Its high oxidation potential (2.8V) enables it to oxidize most of the organic species into carbon dioxide and their mineral acids as shown below:



## 3. DESIGN OF PHOTOCATALYTIC REACTOR

In general, the photocatalytic performance for water purification greatly depends on the design of an economical photocatalytic reactor. Water contaminant removal by photocatalytic reactors could be a surface reaction process consisting of 3 vital steps

First the pollutants have to be compelled to transfer to the catalyst surface second adsorption/desorption phenomena occur; and third, the pollutants are decomposed by the photocatalyst. Thus, the main performance parameters of a photocatalytic reactor are the mass transfer rate, the kinetic reaction rate, and the reaction surface area. Normally, a photocatalytic reactor should contain 2 parts: the reactor structure and a light source. The reactor was designed on the

basis of fluidized bed concept, with 3 phase contact pattern and additionally maximizing the ultraviolet irradiation area. the development of water and air treatment systems supported heterogeneous photo catalysis is an area of major technical importance. the design of extremely economical.

Photo-catalytic systems are of significant interest and one in all the most desirable yet difficult goals within the research of environmentally friendly catalysts. the most obstacle within the development of extremely economical photocatalytic reactors is the establishment of effective reactor designs for intermediate and large-scale use, as demanded by industrial and commercial applications. to achieve a successful commercial implementation, many reactor design parameters should be optimized, like the photo reactor geometry, the type of photo-catalyst and therefore the utilization of radiated energy.

A fundamental issue concerning the successful implementation of photocatalytic reactors is that the transmission of irradiation in a very extremely scattering and absorbing medium composed of water and fine  $\text{TiO}_2$  particles. The successful scaling-up of photo-catalytic reactors involves increasing the quantity of photons absorbed per unit time and per unit volume. additionally to the reactor style strategies and therefore the catalyst choice, variety of important operating variables exist, affecting both the rate and the extent of chemical species transformation. These include semiconductor.

Concentration, reactive surface area, particle aggregate size, concentration of electron donors and acceptors, incident light intensity, pH, and temperature with the requirement to develop new photo-catalytic reactors, there's additionally the problem of establishing performance indicators to enable the comparison of photo-reactor performance on the basis of photochemical and thermodynamic principles. within the case of water treatment, it can be stated that current technologies regarding photo-catalyzed oxidative degradation processes can be considered as practical alternatives to existing waste water treatments. Photocatalysis has already found applications in small to medium sized units in the treatment of contaminated ground waters and in the production of ultrapure water for pharmaceutical and micro electronic industries.

## 4. $\text{TiO}_2$ ADVANCEMENTS METHODS

### 4.1. Activity Enhancement

$\text{TiO}_2$  may be excited only by ultraviolet radiation lights, that account for less than 5-hitter energy of the star spectrum. Thus, it's necessary to develop  $\text{TiO}_2$  primarily based materials which may utilize additional solar energy. to resolve this drawback, some noble metals and their derivatives like Ag, Pt, AgBr, and CdS, are tried to include with  $\text{TiO}_2$  forming hybrid photocatalysts, which might extend the photocatalytic activity of the photocatalysts into visible light vary.<sup>4</sup>

## 4.2. Doping

Modification of the band gap in NTO is, therefore, a well-studied analysis area. Modifications may be established either in bulk or on the surface of  $\text{TiO}_2$ . Surface modifications are usually achieved by anchoring colored inorganic semiconductors organic dyes on the  $\text{TiO}_2$  surface, where they act as sensitizers. However, most of these sensitizers are vulnerable to photo corrosion or degradation in aqueous solutions and don't seem to be appropriate for photocatalytic water-treatment applications. Instead, they're sensible candidates for solar cell devices. On the other hand, bulk modification is especially settled by doping metals or non-metals into bulk NTO. The changed catalysts seem to be photo-stable in aqueous solution and can be employed in photocatalytic water purification.<sup>4</sup>

## 4.3. Immobilization of $\text{TiO}_2$

Immobilization of  $\text{TiO}_2$  on numerous substrates is a crucial analysis area with its photocatalytic water treatment applications. the first aim of doing so is to avoid the post separation difficulties related to the powder type of the  $\text{TiO}_2$  catalyst. However, there are many alternative benefits including higher surface area, superior adsorption properties, and increased surface hydroxyl groups or reduced charge recombination are realizable in immobilized systems. Immobilization of  $\text{TiO}_2$  is done on powder/pellet substrates, soft/thin materials or on rigid/thick substrates. a number of the recent examples of powder/pellet substrates include activated carbon, magnesium-aluminum silicates. sedimentation of these  $\text{TiO}_2$  immobilized systems may be easier than the  $\text{TiO}_2$  catalyst alone systems, since they are heavier particles.  $\text{TiO}_2$  immobilized on soft/thin substrates, usually referred as  $\text{TiO}_2$  membrane or films, are applicable in ultra filtration and bacterial inactivation. Since they are immobilized with  $\text{TiO}_2$ , they will act as self cleaning surfaces. Recent samples of this category include  $\text{TiO}_2$  immobilized on alumina (1.5 micron thick), polyvinylidene difluoride, glass filter, cellulose fibers. Immobilization of  $\text{TiO}_2$  on numerous substrates is a crucial analysis area with its photocatalytic water treatment applications. the first aim of doing so is to avoid the post separation difficulties related to the powder type of the  $\text{TiO}_2$  catalyst. However, there are many alternative benefits including higher surface area, superior adsorption properties, and increased surface hydroxyl groups or reduced charge recombination are realizable in immobilized systems. Immobilization of  $\text{TiO}_2$  is done on powder/pellet substrates, soft/thin materials or on rigid/thick substrates. a number of the recent examples of powder/pellet substrates include activated carbon, magnesium-aluminum silicates. sedimentation of these  $\text{TiO}_2$  immobilized systems may be easier than the  $\text{TiO}_2$  catalyst alone systems, since they are heavier particles.  $\text{TiO}_2$  immobilized on soft/thin substrates, usually referred as  $\text{TiO}_2$  membrane or films, are applicable in ultra filtration and bacterial inactivation. Since they are immobilized with  $\text{TiO}_2$ , they will act as self cleaning surfaces. Recent samples of this category include  $\text{TiO}_2$

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## 4.4. Coupling with Other Treatment Technologies

Combining NTO photocatalysis with alternative oxidation techniques was found to be very effective in pollutant destruction. These technologies embody electrocatalysis, sonocatalysis/Fenton method, biodegradation, and land technology. the combination of NTO photocatalysis with any of those techniques can't only improve the full efficiency of the degradation however additionally has the advantage of treating large quantities of wastewater (in real systems), particularly with electrocatalysis, biodegradation, and land technology. Electrocoagulation of an effluent from pharmaceutical and cosmetic companies removed the majority of the suspended particles, followed by additional purification using NTO photocatalysis.<sup>4</sup>

## 5. CONCLUSION

$\text{TiO}_2$  have been suggested to be an efficient and profitable photocatalyst for mineralization of organic pollutant such as dyes, pesticide and EDCs in wastewater, in the presence of UV visible or solar light. But some researches have also aimed exposure novel low cost catalyst composition. The  $\text{TiO}_2$  assisted photocatalysis is an effective technique for water detoxification and disinfection.  $\text{TiO}_2$  photocatalyst under either UV light or solar irradiation has become more prominent owing to its low cost, safety, high photocatalytic activity, etc and as an advanced oxidation technology for the water treatment industry. The influence of catalyst concentration, initial pH, temperature and irradiation time on the degradation rate of Aniline were investigated in a vertical circulating photocatalytic reactor. The variation in pH has a pronounced effect on degradation rate, alkaline condition promote the rate considerably because of change of surface charge whereas acidic environment casts a negative effect on degradation.

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