

# WATER TREATMENT BY HETEROGENEOUS PHOTOCATALYSIS AN OVERVIEW<sup>1</sup>

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## **ABSTRACT**

*Photocatalysis process, as an environmental application is a relatively novel subject with tremendous potential in the near future. This paper describes the basics of heterogeneous photocatalysis, mainly on TiO<sub>2</sub> and the application of photocatalytic processes to water purification and treatment. The paper also reviews more than 50 references covering the wide scale of heterogeneous water phase applications. Finally, a short review of more interesting practical application of photocatalysis for the removal of natural organic matter from seawater is presented.*

## **1. INTRODUCTION**

Heterogeneous photocatalysis is a rapidly expanding technology for water and air treatment. It can be defined as the acceleration of photoreaction in the presence of a catalyst. The initial interest in the heterogeneous photocatalysis was started when Fujishima and Honda discovered in 1972 the photochemical splitting of water into hydrogen and oxygen with TiO<sub>2</sub> [18]. From this date extensive work has been carried out to produce hydrogen from water by this novel oxidation reduction reaction using a variety of semiconductors.

In recent years interest has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. This method has been suggested in environmental protection due to its ability to oxidise the organic and inorganic substrates [17].

In heterogeneous photocatalysis two or more phases are used in the photocatalytic reaction. A light source with semiconductor material is used to initiate the

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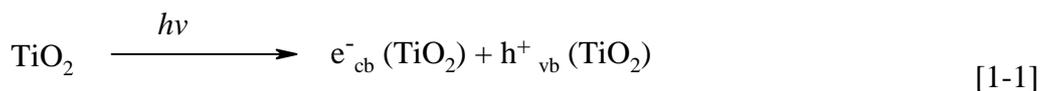
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photoreaction. The catalysts can carry out substrate oxidations and reductions simultaneously. UV light of long wavelengths can be used, possibly even sunlight.

Heterogeneous photocatalysis using semiconductors such as titanium dioxide can be more interesting than conventional methods for removing organic species in the environment. Because the process gradually breaks down the contaminant molecule, no residue of the original material remains and therefore no sludge requiring disposal to landfill is produced. The catalyst itself is unchanged during the process and no consumable chemicals are required. This results in considerable savings and a simpler operation of the equipment involved. Additionally, because the contaminant is attracted strongly to the surface of the catalyst, the process will continue to work at very low concentrations allowing sub part-per-million consents to be achieved. Taken together, these advantages mean that the process results in considerable savings in the water production cost and keeping the environment clean.

## 2. PRINCIPLES

Photocatalysis over a semiconductor oxide such as  $\text{TiO}_2$  is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor (ca. 3.2 eV for anatase), producing electron-hole ( $e^-/h^+$ ) pairs, as written in the equation (1-1):



where cb is conduction band and vb is the valence band

Consequently, following irradiation, the  $\text{TiO}_2$  particle can act as either an electron donor or acceptor for molecules in the surrounding medium.

The electron and hole can recombine, releasing the absorbed light energy as heat, with no chemical effect. Otherwise, the charges can move to "trap" sites at slightly lower energies. The charges can still recombine, or they participate in redox reactions with adsorbed species. A simplified mechanism for the photo-activation of a semiconductor catalyst is presented in Figure1. The valence band hole is strongly oxidizing, and the conduction band electron is strongly reducing. At the external surface, the excited

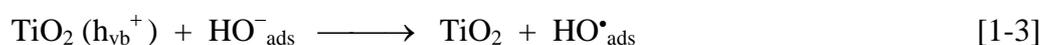
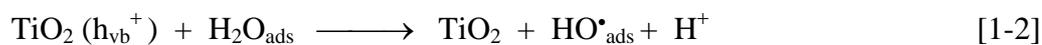
electron and the hole can take part in redox reactions with adsorbed species such as water, hydroxide ion ( $\text{OH}^-$ ), organic compounds, or oxygen. The charges can react directly with adsorbed pollutants, but reactions with water are far more likely since the water molecules are far more populous than contaminant molecules. Oxidation of water or  $\text{OH}^-$  by the hole produces the hydroxyl radical ( $\bullet\text{OH}$ ), an extremely powerful and indiscriminant oxidant. For a comparison, the oxidation potential of hydroxyl radical ( $\bullet\text{OH}$ ) is 2.8 V relative to the normal hydrogen electrode (NHE); cf. other substances used for water disinfection: ozone (2.07 V),  $\text{H}_2\text{O}_2$  (1.78 V),  $\text{HOCl}$  (1.49 V) and chlorine (1.36 V).

$\text{OH}$  radicals rapidly attack pollutants at the surface, and possibly in solution as well, and are usually the most important radicals formed in  $\text{TiO}_2$  photocatalysis. An important reaction of the conduction band electron is reduction of adsorbed  $\text{O}_2$  to  $\text{O}_2^{\bullet-}$ . This both prevents the electron from recombining with the hole and results in an accumulation of oxygen radical species that can also participate in attacking contaminants. [28, 35]

### 3. MECHANISM OF GENERATION OF OXIDATION SPECIES

Heterogeneous photocatalysis is a complex sequence of reactions. The oxidation pathway is not yet fully understood. However, Pirkanniemi suggested in 2002 that the heterogeneous photocatalysis reaction follows five steps. These are: “(i) diffusion of reactants to the surface, (ii) adsorption of reactants onto the surface, (iii) reaction on the surface, (iv) desorption of products from the surface, and (v) diffusion of products from the surface”. [44]

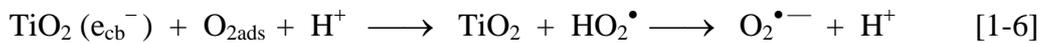
There are two routes through which  $\text{OH}$  radicals can be formed. The reaction of the valence-band “holes” ( $h_{\text{vb}}^+$ ) with either adsorbed  $\text{H}_2\text{O}$  or with the surface  $\text{OH}^-$  groups on the  $\text{TiO}_2$  particle. [1] equations (1-2 and 1-3).



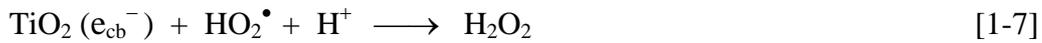
In general, donor (D) molecules such as H<sub>2</sub>O will adsorb and react with a hole in the valence-band and an acceptor (A) such as dioxygen will also be adsorbed and react with the electron in the conduction band ( $e_{cb}^-$ ), according to equations 1-4 and 1-5



It is generally accepted that oxygen plays an important role. Oxygen can trap conduction-band electrons to form superoxide ion ( $\text{O}_2^{\bullet -}$ ), equation (1-6). These superoxide ions can react with hydrogen ions (formed by splitting water), forming  $\text{HO}_2^{\bullet}$



H<sub>2</sub>O<sub>2</sub> could be formed from  $\text{HO}_2^{\bullet}$  via reactions (1-7)



Cleavage of H<sub>2</sub>O<sub>2</sub> by one of the reactions (1-8, 1-9, and 1-10) may yield an OH radical



Photoreduction, photooxidation and adsorption occur on or near the particle surface as shown from Figure 2. The illumination of semiconductor particles such as TiO<sub>2</sub> generates  $e_{cb}^-$  and  $h_{vb}^+$  as described previously. A competition reaction occurs between water, oxygen, organic molecules and trace metals which may be present in the system.[12]. Mercury (II) will be reduced to mercury(0), oxygen molecules will also be reduced and give active species ( $\text{O}_2^{\bullet -}$ ). Cr (VI) will also be reduced to Cr (III). Cd (II) can be adsorbed to TiO<sub>2</sub> and water will be oxidised by the hole in the valence band to give the very active free radical  $\bullet\text{OH}$  which can oxidize organic species.

#### 4. PHOTOCATALYTIC MATERIALS

A wide range of semiconductors may be used for photocatalysis, such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{MgO}$ ,  $\text{WO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CdS}$ . The ideal photocatalyst should possess the following properties (i) photoactivity, (ii) biological and chemical inertness, (iii) stability toward photocorrosion, (iv) suitability towards visible or near UV light, (v) low cost, and (vi) lack of toxicity [8].

$\text{TiO}_2$  is known to have excellent pigmentary properties, high ultraviolet absorption and high stability which allow it to be used in different applications, such as electroceramics, glass and in the photocatalytic degradation of chemicals in water and air. It has been used in the form of a suspension, or a thin film in water treatment [11, 23, 30].

Titanium dioxide has different crystalline forms. The most common forms are anatase and rutile. The third crystalline form is brookite, which is uncommon and unstable. Anatase is the most stable form by 8-12  $\text{KJ mol}^{-1}$  [14] and can be converted to rutile by heating to temperatures  $\sim 700^\circ\text{C}$ . [9]. The density of rutile is greater at 4.26  $\text{g/ml}$ , while anatase has a density of 3.9  $\text{g/ml}$ . In the photocatalysis applications, it is known that, anatase is more efficient than rutile, having an open structure compared with rutile.

Degussa P25, is commercially available, consists of two forms of  $\text{TiO}_2$  (closely approximating to 25% rutile, 75% anatase) [42] and has been used in many studies of photocatalytic degradation. Studies employing P25, have been widely reported because of its chemical stability, ready availability, reproducibility, and activity as a catalyst for oxidation processes [5, 6]. It has also been suggested as a standard for such studies [39]. Intensive studies are in progress to develop the existing materials or prepare new materials, which can be used under solar energy and hence shortening the time needed for the degradation. The development includes increasing the surface area, increase the active sites, and increase the absorption of photon energy and reducing the band gap energy.

## **5. PHOTOCHEMICAL REACTORS**

There are many types of reactors that can be used in the photocatalytic studies. The selection normally depends on the experimental conditions and the application. Reactors can be briefly classified into two types, reactors that use a catalyst as suspension form and reactors that used a thin film catalyst. Both kinds of reactors can be design as an immersion well or flat wall. Immersion well photoreactors are normally used at laboratory scale for evaluation purposes. It can be operated in batch or continuous mode. Oxidant flow and temperature can be easily monitored. The light source can be either single or multiple with or without reflectors. Catalyst in these reactors can be used as thin film or as suspension form, but suspension one is more preferable. The suspension form reactors are normally more efficient than thin film reactors and that are due to the large surface area in contact with the substrates. This allows more number of photons hit the catalyst and large adsorption capacity results.

Other kinds of reactors are flat wall and tubular photoreactors. These kinds of reactors are simple and easy to design. Air is an oxidant choice of this type. Solar energy can be used for both types. In the tubular reactors reflectors are always used to concentrate the light and enhance the photoreaction (Fig. 3).

## **6. APPLICATION OF PHOTOCATALYSIS**

Since 1972, when Fujishima and Honda discovered the photocatalytic splitting of water using  $\text{TiO}_2$  electrodes; research on the heterogeneous photocatalysis started growing rapidly [28]. The research work focused on energy storage, and in recent years applications have been directed towards environmental clean-up. Later, other applications of this technique have been implemented in many fields such as, drinking water treatment, industrial, and health applications.

### ***6.1 Removing trace metals***

Trace metal such as mercury (Hg), chromium (Cr), lead (Pb) and others metals are considered to be highly health hazardous. Thus, removing these toxic metals are essentially important for human health and water quality. The environmental applications of heterogeneous photocatalysis include removing heavy metals such as (Hg), chromium (Cr), lead (Pb), Cadmium (Cd), lead (Pb), Arsenic (As), nickel (Ni)

copper (Cu) [10, 43]. The photoreducing ability of photocatalysis has been used to recover expensive metals from industrial effluent, such as gold, platinum and silver [43].

## **6.2 Destruction of organics**

Photocatalysis has been used for the destruction of organic compounds such as alcohols, carboxylic acids, phenolic derivatives, or chlorinated aromatics, into harmless products e.g. carbon dioxide, water, and simple mineral acids [8, 12, 32, 34, 44]. Water contaminated by oil can be treated efficiently by photocatalytic reaction [24]. Herbicides and pesticides that may contaminate water such as 2,4,5 trichlorophenoxyacetic acid, 2,4,5 trichlorophenol, s-triazine herbicides and DDT can be also mineralised [43].

## **6.3 Removing inorganic compounds**

In addition to organic compounds, wide ranges of inorganic compounds are sensitive to photochemical transformation on the catalyst surfaces. Inorganic species such as bromate, or chlorate [33], azide, halide ions, nitric oxide, palladium and rhodium species, and sulfur species can be decomposed [32]. Metal salts such as AgNO<sub>3</sub>, HgCl and organometallic compound (e.g. CH<sub>3</sub>HgCl) can be removed from water [8], as well as cyanide, thiocyanate, ammonia, nitrates and nitrites [10].

## **6.4 Water disinfections**

Photocatalysis can also be used to destroy bacteria and viruses. *Streptococcus mutans*, *Streptococcus natans*, *Streptococcus cricetus*, *Escherichia coli*, *Saccharomyces cerevisiae*, *Lactobacillus acidophilus*, poliovirus 1 were destructed effectively using heterogeneous photocatalysis [35]. The increasing incidence of algal blooms in fresh water supplies and the consequent possibility of cyanobacterial microcystin contamination of potable water *Microcystin toxins* is also degraded on immobilized titanium dioxide catalyst [47]. Photodisinfection sensitized by TiO<sub>2</sub> had some effect on the degradation of *Chlorella vulgaris* (Green algae), which has a thick cell wall.

## 6.5 *Degradation of natural organic matter*

Humic substances (HS) are ubiquitous and defined as a category of naturally occurring biogenic heterogeneous organic substances that can be generally characterised as being yellow-brown and having high molecular weights [29]. These are also defined as the fraction of filtered water that adsorb on XAD-8 resin (non-ionic polymeric adsorbent) at pH 2.[41] They are the main constituents of the dissolved organic carbon (DOC) pool in surface waters (freshwaters and marine waters), and ground waters, commonly imparting a yellowish-brown color to the water system [46]. The concentration of humic substances varies from place to place; the values in seawater being normally from two to three mg l<sup>-1</sup>. Their size, molecular weight, elemental composition, structure, and the number and position of functional groups vary, depending on the origin and age of the material [20].

HS are known to affect the behavior of some pollutants significantly in natural environments, such as trace metal speciation and toxicity,[4, 48] solubilisation and adsorption of hydrophobic pollutants, [13, 49] and aqueous photochemistry [19].

HS act as substrates for bacterial growth, inhibit the bacterial degradation of impurities (some colour) in natural water, complex with heavy metals such as Fe, Pb, Mn making it harder to remove them, transport the metals in the environment, and also promote the corrosion of pipes [38]. HS act as a source of methyl groups and thus react with hypochlorite ion which is used as a biocide in water treatment plants, to produce disinfectant by-products e.g., trihalomethanes, haloacetic acids, other chlorinated compounds and nitriles, some of which are suspected to be carcinogenic [26, 31, 40, 45, 50]. More than 150 products have been identified when HS react with chlorine. Recently, 3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone [abbreviated as (MX)] was found in the chlorinated water containing HS [51].

Advanced oxidation has been applied to decreasing the organic content in water including humic acid [16, 21, 22, 27] It has the advantage of not leaving any toxic by-products or sludge. Degradation of the HA or other fraction of humic substances has not been studied in detail. The first work in this field was carried out by Bekbolet in 1996, who studied the effectiveness of photocatalytic treatment on the degradation of humic acid [7].

Bekbolet and Ozkosemen investigated the photocatalytic degradation using humic acid as a model. They found that after 1 h irradiation and in the presence of  $1.0 \text{ g l}^{-1}$   $\text{TiO}_2$  (P-25), 40% TOC and 75% of the color (400 nm) were removed [7]. The same authors studied the removal of colour caused by HA in the presence of common inorganic anions; (chloride, nitrate, sulphate and phosphate ions) at pH 6.8, and they found that there is some removal [6]. In other work where HA was used as an additional matrix for the degradation of some organic contaminants, it was shown that more than 80% of the commercial humic acid was removed by irradiation in the presence of  $\text{TiO}_2$  (P-25) [37]. Eiggins *et.al.*, found the suspension of  $\text{TiO}_2$  (P25) irradiated by a mercury lamp showed a very efficient reduction of the humic acid concentration (approx. 50% reduction in approx. 12 min) [16].

Heterogeneous photocatalysis was also coupled with other physical methods in order to increase the degradation rate of organic molecules including HA (sono-photocatalysis, ozonation photocatalysis) [15, 25].

## **6.6 Seawater treatment**

Recently, HS was also decomposed in highly saline water (artificial seawater) and natural seawater using different photocatalytic materials [2, 3]. The decomposition rate of HS in seawater was slow compared with pure water media. No toxic by products were detected during the decomposition.

Minero *et.al* (1997) studied the decomposition of some components in crude oil (dodecane and toluene) in the seawater media [36]. They found that no chlorinated compounds have been detected during the irradiation and complete decomposition was achieved after few hours of irradiation. Another study conducted on the decomposition of seawater-soluble crude-oil fractions found that it can be decomposed under illumination of nanoparticles of  $\text{TiO}_2$  using artificial light [52].

## **7. CONCLUSIONS**

Photocatalysis has large capability for the water treatment. It can be utilized for the decomposition of organic and inorganic compounds, and removal of trace metals as

well as destruction of viruses and bacteria. It can be used also to decompose natural organic matter (humic substances), which has many environmental and industrial impact. The drawback of this method is that of being slow compared with traditional methods but it has the advantage not leaving toxic by product or sludge to be disposed.

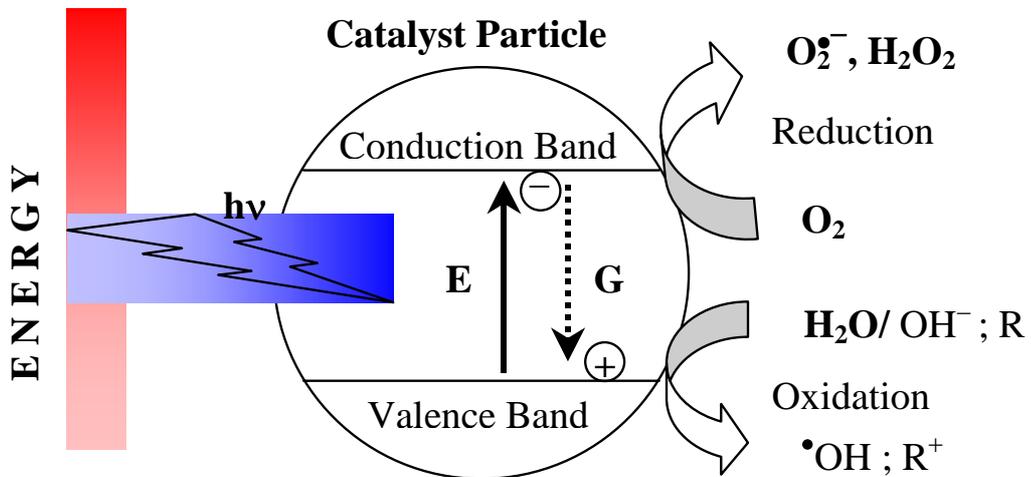
Little work has been made on the seawater treatment. Hence more work need to be accomplished to validate the method for the seawater treatment. This technology might be useful for water pre-treatment of desalination process especially with reverse osmosis technique.

## 8. REFERENCES

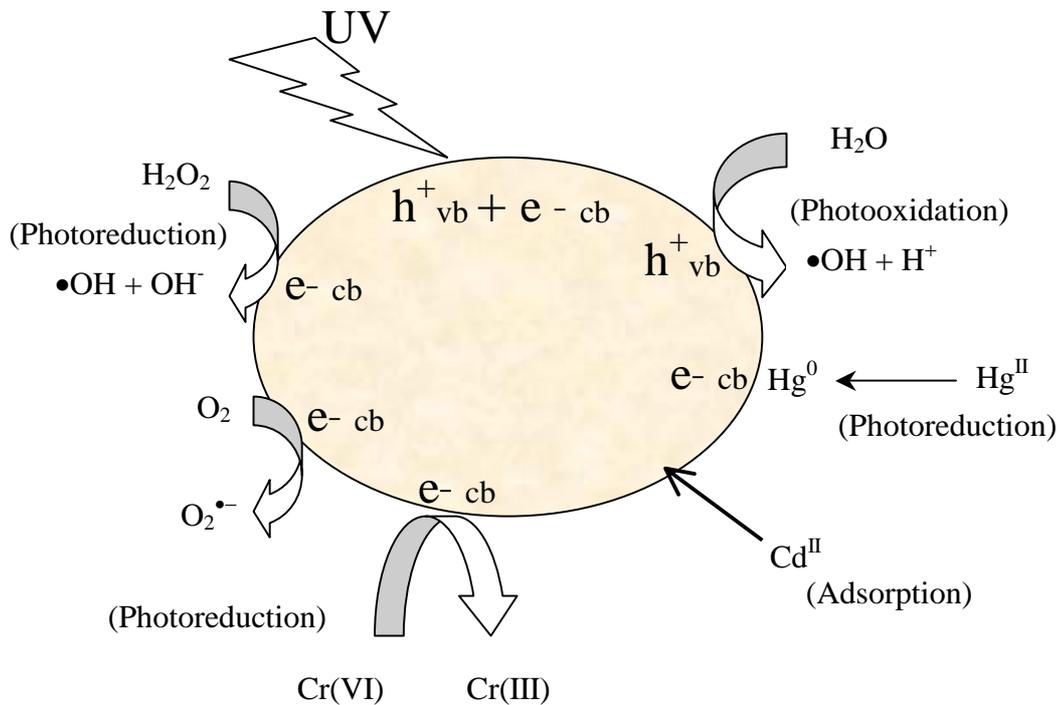
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**Figure 1. Simplified mechanism for the photo-activation of a semiconductor catalyst**



**Figure 2. Examples of some reactions that can occur on illumination of  $TiO_2$**



**Figure 3. Waste water treatment by solar energy using tubular (A) and flat sheet (B) reactors**