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A Review on Photo catalysis Processes for Environmental Applications

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Abstract: *In recent years, photo catalysis has become a progressively more capable technology in environmental wastewater treatment. This review focuses on the various applications of photo catalysis. The Pt/TiO_2 is coated on ceramic tiles and immobilized. Pt/TiO_2 catalyst was found effective for the solar photo catalytic removal of chemical and bacterial pollutants from water. The Pt/TiO_2/tile can be used in swimming pools, hospitals, water theme parks, and even industries for the decontamination of water. We have also studied that the combination of TiO_2-film photo catalysis reactor and ultra filtration can improve organic wastewater quality and increase the permeate flux of ultra filtration membrane, which may enhance the recycling and reuse of wastewater. Also, Semiconductor photocatalysishas been demonstrated to be one of the "green" and effective methods for water and air purification, water disinfection, hazardous waste remediation, antibacterial, and self-cleaning. The use of photo catalysis (PC) in the creation of low-power water treatment technologies is a promising direction in addressing environmental problems of the hydrosphere.*

1. INTRODUCTION

Semiconductor-mediated photo catalysis is fast becoming an efficient advanced oxidation process (AOP) for the removal of chemical and bacterial pollutants from water [1, 2]. The most widely studied catalyst in this respect is TiO2 in view of its favorable physicochemical properties, low cost, easy availability, high stability, and low toxicity. However, it is active only in the UV range which constitutes less than 5% of sunlight. Photo catalytic reactions take place when particles of the semiconductor absorb photon of energy equal to or greater than its band gap and the electrons get excited from the valence band to the conduction band. This results in the formation of an electron-hole pair which promotes oxidation/reduction of the adsorbed substrate. In aqueous solution, the reactive OH radicals can promote the oxidation and eventual mineralization of organic compounds. A number of studies have been reported on the modification of semiconductor oxides in order to extend the absorption of light to the visible range. These include dye sensitization, semiconductor coupling, impurity doping, use of coordination metal complexes, and metal deposition [1]. Composites such as TiO_2/carbon have also been reported [1]. Deposition of noble metals such as Pt, Pd, Au, and Ag, on TiO_2 enhances the catalytic oxidation of organic pollutants [9]. Pt/TiO_2 nano composites have been shown to have high photo catalytic activity for the decomposition of organic compounds. In this case, the enhancement is attributed to the increased light absorption and retarding of the photo generated electron-hole recombination [9].

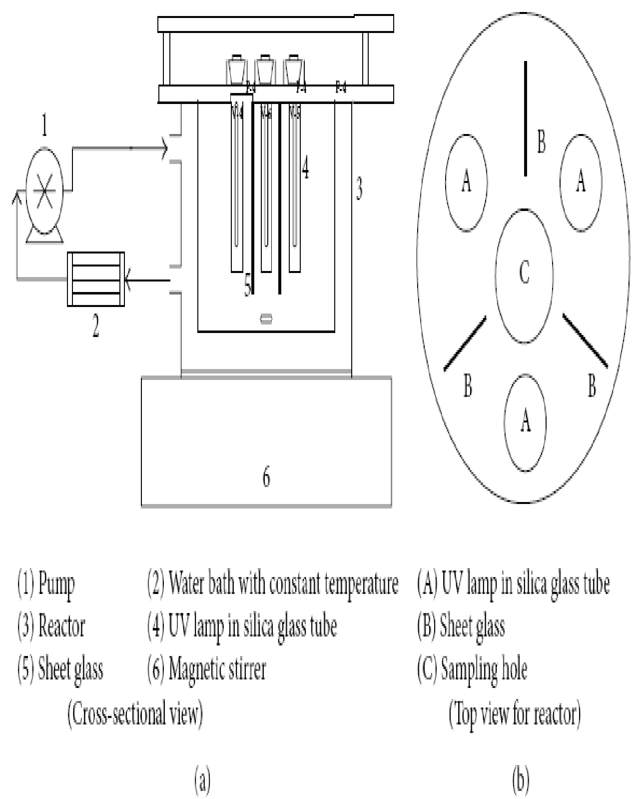

Figure 1: Equipment for TiO_2-film photo catalysis [3].

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However, since Pt is expensive, this type of catalysts will be unattractive from commercial application point of view unless they can be recycled. The problem can be overcome, at least partially by immobilizing the catalyst on suitable stable supports. TFT LCD manufacture is one of the booming high-tech industries in Taiwan in recent years. During the manufacturing process a large number of chemical solvents and water is needed to use, and a lot of wastewater will be produced. TFT-LCD manufacturing usually combines array, panel, and module processes. The wastewater of the TFT-LCD factory is divided into fluoride waste from rinsing, inorganic waste from etching, less toxic organic waste, and sewerage waste water. The wastewater mostly came from the array process. The developer, stripper, and rinse solvents were used in the array process, so less toxic matter was produced in the wastewater [4]. The less toxic organic waste and the sewerage wastewater could be treated together by biological or secondary treatment system, but the fluoride waste would be pretreated before being introduced to the biological treatment system. Water sources are insufficient in Taiwan, and it is difficult to obtain new ones because of environmental protests. Authorities have passed legislation compelling factory owners to increase the recovery rate of wastewater from the high-tech industry. To enhance the recovery rate of effluent from TFT-LCD factories, the suspended solids, colloid matter, and other trace elements need to be removed. Many methods have been studied and developed in Taiwan, of which reverse osmosis (RO) is one of the methods with the greatest potential due to its relatively higher removal rate, ease of set up, and minimal land requirements. However, before RO treatment, other membrane treatments, for example, microfiltration (MF) or ultra filtration (UF), are usually required. Otherwise, the RO membranes may be rapidly blocked by various fouling's from the influent water [3]. However, the UF or MF treatments have operational problems like concentration polarization and membrane fouling. Concentration polarization and membrane fouling decrease the permeate flux, the recovery rate, increase the operating cost, and shorten membrane life [4]. The former is induced by solute accumulation on the membrane. Two-liter reactor contains three UV lamps and three sheets of glass for TiO_2 coating, as shown in Figure 1. The selected wavelengths of UV light source in the reactor were 254 and 365 nm lamps, respectively. The water temperature in the reactor was constant controlled by a water bath with re-circulating cooling water. A magnetic stirrer at the bottom of the reactor was used to completely mix the feed water. Fresh water is getting scarcer. The number of people living in water-stressed or water-scarce countries is estimated to increase from half a billion now to three billion in 2025 [1]. Water reuse has been dubbed as the greatest challenge of the 21st century [2], and, as such, great emphasis is being put into the development of new technologies for the treatment of wastewater for reuse.

Since the discovery, in 1977, that titanium dioxide (TiO_2) could decompose cyanide in water [3], the field of photo catalysis has been receiving increasing interest. Photo catalysis is an advanced oxidation process (AOP) that uses a catalyst (often TiO_2), UV light, and an electron acceptor (O_2, O_3, H_2O_2) to completely decompose organic pollutants found in liquids or gases. The basis of the process is the use of low energy UV-A photons (for which the energy is greater or equal to the band gap energy of the catalyst) to excite the semiconductor catalyst into charge separation and generate electron-hole pairs. The electrons and holes, on separation, assist in the production of the very reactive hydroxyl radical in the aqueous phase which can destroy many toxic organic pollutants. This technology however works best at low pollutant concentrations (mgL^{-1} or $mmolL^{-1}$) and when the catalyst is finely dispersed within the medium. The overall process can be described by the following reaction equation:

$$\text{organic pollutants} + O_2 \xrightarrow{\text{semiconductor} + \text{UVA light}} CO_2 + H_2O + \text{mineral acid.} \quad \text{----------} (1)$$

Shower water is part of grey water and is produced by every household at a substantial amount (15–55 L day^{-1}) with a pollutant loading up to 100 mgL^{-1} [4]. Existing technologies for the treatment of grey water include membrane filtration, coagulation, ion exchange, and membrane bioreactors [5, 6]. However these techniques are either costly or merely transfer the pollutants from one medium to another. As a result, shower water is a good candidate for photo catalytic treatment. The treated water could be reused where potable water is not required. Such applications include toilet flushing, landscape irrigation, and car washing. Countless researches have been made on the photo catalytic treatment of single or a few organic components in water [8]. Real wastewaters on the other hand have a multitude of pollutants and take longer to treat (typically a few hours) [10]. The photo oxidation of surfactants, the main components of shower water, was extensively studied by Hidaka and coworkers [11].

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Table 1: Shower Water Characterization [4]

TOC (mgL^{-1})	24.62 ± 0.44
pH	7.37 ± 0.14
Main constituents (as per the products' ingredients list)	Anionic surfactants (sodium laureth sulphate, sodium cocoamphoacetate, sodium lauryl sulphate, ammonium laureth sulphate), cationic surfactants (cocamide MEA), nonionic surfactants (lauryl glucoside, cetyl alcohol), fragrance, antimicrobial agents.

Heterogeneous photo catalysis based on semiconductors has witnessed rapid progress in the last decades [1–3]. The semiconductor photo catalyst, of which the electrons in the valence band can be promoted to the conduction band when being excited by adequate photo energy, possesses photo generated electron-hole (e-h) pairs. The e-h pairs enable a series of reductive and oxidative reactions [4–6], and some of them further result in valuable reactions. This method has been initially put forward for the extraction of hydrogen energy from water via the conversion of photo energy in the 1970s, when the energy crises has emerged [7]. Later in the 1980s, it has been tested as an environmental purification alternative for water [8, 9] and gas [10] as well. This review focuses on the water purification by addressing the fundamentals that serves as a connection with the real-time application. Many reports have evidenced that numerous organic toxic compounds often present in water can be removed by the photo catalytic method. Chlorinated compounds, alkenes, alkanes, aromatics, dyes, and so forth, have been tested as the model pollutants [2, 3, 11, 12]. The rationale for TiO_2 photo catalytic method is predominantly based on the oxidation of pollutants by means of hydroxyl radicals (HO·) that feature the advanced oxidation technologies (AOTs) [13, 14].

The HO· production can be expressed as follows:

$$H_2O + h \xrightarrow{h\nu} {}^{\bullet}OH + H^+ \quad \text{------------ (2)}$$

The h (hole) is highly oxidative, and the oxidation of water by h leads to a formation of HO· radicals, which are extremely active and nonselective in attacking the substrates in aqueous solution. Meanwhile, the electron (e) needs to be scavenged by an electron acceptor. Accordingly, the photo generated e-h pairs are separated, leading to the transformation of pollutants. Otherwise, the photo generated e-h pairs will be self-combined with an undesired release of thermal energy. As desired, the photo generated e-h pairs should be separated as far as possible to improve the process performance of photo catalysis. The TiO_2 photo catalysis has attracted great attention as a promising water treatment technology due to quite a few intrinsic advantages. (i) Powerful ability to decompose the pollutants: the organic pollutants can be decomposed and even mineralized due to the dramatic powerful oxidation ability of HO·. Consequently, this technique can be utilized widely in the cases once the advanced treatment of water, particularly containing the recalcitrant organic compounds, is demanded. (ii) Ambient operating conditions: the process can be realized under ambient operating conditions, and thus is acknowledged as quite safe. (iii) Low cost: the sunlight can be employed as the energy source, and the oxidant is ambient O_2. Meanwhile, as the TiO_2 photo catalyst can be recycled, the cost can be further cut off to run the process. (iv) Environmentally friendliness: TiO_2 are chemically stable, nearly non-toxic, or relatively safe, even in the harsh conditions. Thus, the TiO_2 photo catalysis is thought as an environmentally-friendly approach, even if recent concerns arise on its environmental risks as it is released into the environment [15].

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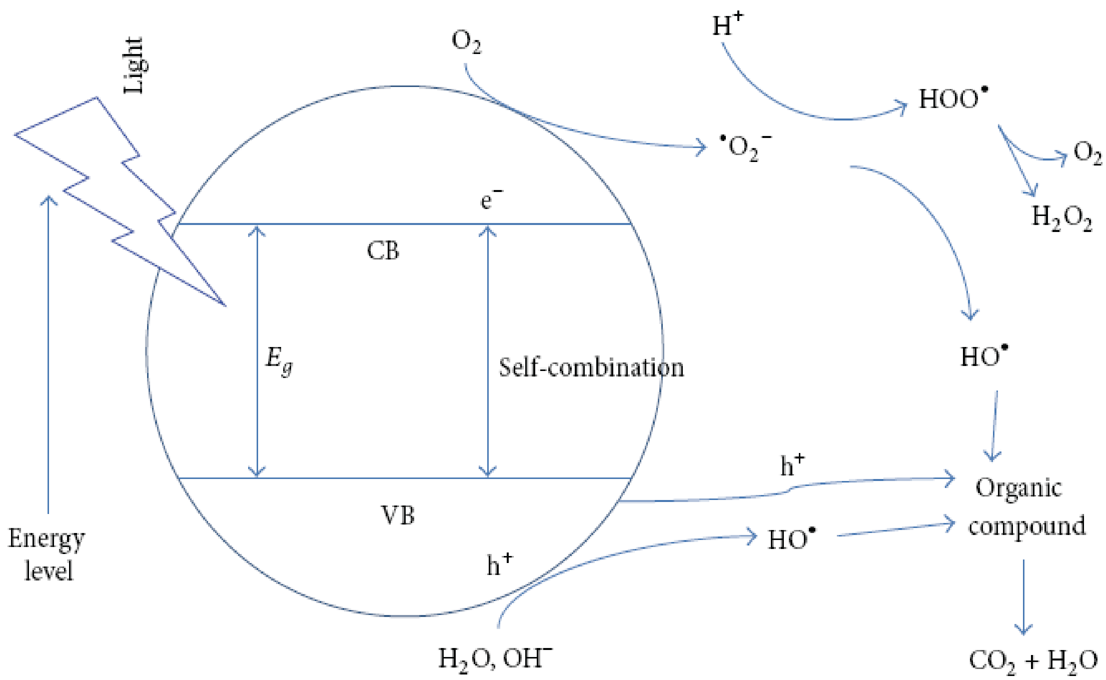

Figure 2: The scheme of TiO2 photo catalytic process [5]

2. LITERATURE REVIEW

S. P. Devipriya et al. [1] Semiconductor photo catalysis has become an increasingly promising technology in environmental wastewater treatment. The present work reports a simple technique for the preparation of platinum-deposited TiO_2 catalysts and its immobilization on ordinary ceramic tiles. The Pt/TiO2 is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDAX), and diffuse reflectance spectroscopy (DRS). Deposition of Pt on TiO_2 extends the optical absorption of the latter to the visible region which makes it attractive for solar energy application. Optimum loading of Pt onTiO_2 was found to be 0.5%. The Pt/TiO_2 is coated on ceramic tiles and immobilized. This catalyst was found effective for the solar photo catalytic removal of chemical and bacterial pollutants from water. Once the parameters are optimized, the Pt/TiO_2/tile can find application in swimming pools, hospitals, water theme parks, and even industries for the decontamination of water.

S.-H. You et. al. [3] states that combination of TiO2-film photo catalysis reactor and ultra filtration was used to treat the secondary effluent from the manufacturing of thin film transistor-liquid crystal display (TFT-LCD). TiO_2 particles, as a photo catalyst, were immobilized on silica glass to form TiO_2-film by the sol-gel and dip coating methods. TiO_2-film photo catalysis was done within three parameters, including number of coating times of TiO_2-film, wavelengths of UV light source, and operating time. During ultra filtration, the operating pressure and feed water temperature were controlled at 300 KN/m2 and 25degree Celsius, respectively. It was found that TiO_2-filmphotocatalysis followed by ultra filtration increased the removal of total organic carbon (TOC) to 47.13% and 49.94% for 5 KDa and 10KDa membranes, respectively. It was also found that the process increased the permeate flux rate (ca 23%) for 10KDamembraneafter 6 hours of operation, since some larger organic matter had been broken into small organic matter and some small organic matter had been mineralized into CO_2 following TiO_2-film photo catalysis. Therefore, combining TiO_2-film photo catalysis reactor and ultra filtration can improve organic wastewater quality and increase the permeate flux of ultra filtration membrane, which may enhance the recycling and reuse of wastewater.

Jiaguo Yu et al. [3] describes that Semiconductor photo catalysis has caused enormous attention in recent year and has been demonstrated to be one of the "green" and effective methods for water and air purification, water disinfection, hazardous waste remediation, antibacterial, and self-cleaning. However, owing to low photo catalytic efficiency, the environmental applications of various photo catalytic materials and technologies are still very limited. Thus, more improvement and investigations are highly required from the viewpoint of practical use.

Yash Boyjoo et al. [4] describes that Treatment of shower water deserves special consideration for reuse not only because of its low pollutant loading but also because it is produced in large quantities. In this study, a pilot scale study of photo catalytic degradation of impurities in real shower water was performed in a 31 L volume reactor using titanium dioxide as the photo catalyst. The reactor was operated in a continuous slurry recirculation mode. Several operational parameters were studied including the slurry initial pH, catalyst concentration, air flow rate, and slurry recirculation rate. Up to 57% of total organic carbon (TOC) elimination was obtained after 6 hours of treatment (for 3.0 slurry initial pH, 0.07 gL^{-1} catalyst concentration, 1.8 $Lmin^{-1}$ air flow rate, and 4.4 $Lmin^{-1}$ slurry recirculation rate). This study showed that photo catalysis could be successfully transposed from bench scale to pilot scale. Furthermore, the ease of operation and the potential to use solar energy make photo catalysis an attractive prospect with respect to treatment of grey water.

Chuan Wang et al. [5] state that recent years have witnessed a rapid accumulation of investigations on TiO2-based photo catalysis, which poses as a greatly promising advanced oxidation technology for water purification. As the ability of this advanced oxidation process is well demonstrated in lab and pilot scales to decompose numerous recalcitrant organic compounds and microorganism as well in water, further overpass of the hurdles that stand before the real application has become increasingly important. This review focuses on the fundamentals that govern the actual water purification process, including the fabrication of engineered TiO_2-based photo catalysts, process optimization, reactor design, and economic consideration. The state of the art of photo catalyst preparation, strategies for process optimization, and reactor design determines the enhanced separation of photo-excited electron-hole (e-h) pairs on the TiO_2 surface. For the process optimization, the kinetic analysis including the rate-determining steps is in need. For large-scale application of the TiO_2-based photo catalysis, economics is vital to balance the fundamentals and the applied factors. The fundamentals in this review are addressed from the perspective of a bridge to the real applications. This review would bring valuably alternative paradigm to the scientists and engineers for their associated research and development activities with an attempt to push the TiO2-basedphotocatalysis towards industrially feasible applications.

Catalina Daniela Stan et. al. [6] states that the effect of different heterogeneous and homogeneous photo catalytic systems on the oxidative degradation of chloride in aqueous solutions was investigated. In the case of heterogeneous reactions, the influence of five factors was studied: the type of catalyst, photo catalyst concentration, pH, pesticide concentration, and the presence of H_2O_2 and/or Fe3+. For homogeneous catalysis, other factors were studied: the oxidizing agent and the light source. Nearly complete degradation of mepiquat chloride was obtained after about 180 minutes in the presence of an acid medium (pH3) using a UV-A lamp and TiO_2P-25 catalyst (0.5 g/L),for an initial pesticide concentration of 10ppm. Degradation rates corresponding to homogeneous photo catalysis were lower compared to those corresponding to the use of TiO_2 as the photo catalyst.

R. V. Prihod'ko and N. M. Soboleva [7] describe that the efficiency of various homogeneous and heterogeneous systems photo catalytic processes destructive oxidation of organic compounds of different classes is considered. It is shown that photo catalytic methods can significantly increase the speed and depth (up to complete mineralization) of decomposition processes of toxicants. The use of photo catalysis (PC) in the creation of low-power water treatment technologies is a promising direction in addressing environmental problems of the hydrosphere.

3. CONCLUSION

In this paper we surveyed the current literature on photo catalysis. We studied photo catalytic treatment of water. Also, study the photo catalysis properties, applications and techniques used. In this paper the results of these studies and the literature data indicate a high efficiency of photo catalytic methods in the oxidative degradation of organic pollutants in aquatic environments.

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