RESEARCH ARTICLE OPEN ACCESS

# A Review on Applicability of Photocatalyst Titanium dioxide for Treatment of Greywater

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**ABSTRACT**
Greywater reuse has attracted great attention for sustainable management of water especially under water scarcity conditions. However, the effort has been limited by the presence of toxic organics in the effluent which in turn inhibits the public acceptance of recycling water. The existence of those organic pollutants, which cannot be eliminated by conventional primary and secondary treatment processes, can be problematic. Hence it is necessary to explore a sustainable, robust and affordable method for treatment of greywater. Photocatalytic oxidation is an emerging technology that could be suitable to remove refractory organic compounds found in greywater. Recently titanium dioxide ($TiO_2$) gained wide attention for photocatalytic oxidation of organic matter of wastewater. Because it is biologically and chemical inert, resistant to chemical corrosion and can work at ambient temperature and pressure, without addition of chemical species. The irradiation of titanium dioxide dispersions by ultraviolet (UV) (300-400 nm) light can lead to the formulation of highly reactive hydroxyl radicals which attack the pollutant molecule to degrade it into carbon dioxide, water and mineral acids.This technology has advantages, such as, the integration into small places, low maintenance and easy operation.
***Keywords*** **-** Greywater, Photocatalytic oxidation, Refractory organic compounds, Titanium dioxide ($TiO_2$).

## I. Introduction

Nowadays water is becoming rare source in the world. Globally water use increased six-fold during the twentieth century and by the year 2025 about 1.8 billion people will live under absolute water scarcity conditions and two thirds of the world's population will experience water stress. It is therefore essential to reduce surface and ground water use in all sectors of consumption to substitute fresh water with alternative water resources and to optimize water use efficiency through reuse options. These alternative resources include rainwater and greywater.[1]\

Greywater is commonly defined as wastewater generated from bathroom, hand basins, kitchen sinks and laundry machines. It account for approximately 50-80% of a household's total greywater with daily generation rates usually ranging from 30 to 120 L $capita^{-1}$ in low and middle income countries. The concentration of salts, solids, organic matter, nitrogen, phosphorus and pathogens in greywater vary widely and it is generally depend on country, location, personal habits, and cleaning products used in the home.[1,2]

The main target in greywater treatment is the reduction of easily degradable organic compound. The organic matter in treated water is the major precursor of disinfection by-products when chlorine is used for disinfection. Therefore removal of organic matter is usually desired before chlorination. The conventional primary and secondary treatment processes such as coarse filtration, chemical and biological processes are ineffective and costly for removal of organic pollutants from greywater. The advanced wastewater treatment systems such as microfiltration (MF) and ultrafiltration (UF) membrane systems also used for greywater treatment. In spite of the various advantages MF and UF systems offer, poor removal of organic pollutants are two major obstacles for treatment of greywater.[2]

Besides, greywater treatment technologies must be robust to handle variations in organic and pathogen concentration in greywater influent, and to consistently produce an effluent of an appropriate and safe quality to meet the required standards for reuse. Those characteristics are easily achieved by same advanced oxidation processes (AOPs), and more specifically by photcatalytic processes.[3]

Photocatalytic oxidation is an emerging technology that could be suitable to remove refractory organic compounds found in greywater. Recently titanium dioxide ($TiO_2$) gained wide attention for photocatalytic oxidation of organic matter of wastewater. Because it is biologically and chemical inert, resistant to chemical corrosion and can work at ambient temperature and pressure, without addition of chemical species. The irradiation of titanium dioxide dispersions by UV (300-400) light can lead to the formulation of highly reactive

hydroxyl radicals which attack the pollutant molecule to degrade it into carbon dioxide, water and mineral acids. This technology has advantages, such as, the integration into small places, low maintenance and easy operation.[3,4,5]

## II. Characteristics of Greywater

The organic matter content in greywater ranges between 13 and 8000 mg COD (Chemical Oxygen Demand) $L^{-1}$. The organic material originates from detergents, food, dirt and skin residues and is highly degradable under both aerobic and anaerobic conditions. The nitrogen content can range from 0.6 to 74 mg $L^{-1}$, which is low compared with household wastewater. The phosphorus level depends on whether phosphorus containing detergents are used, or prohibited by local or regional regulations. Phosphorus levels are within 4-14 mg P $L^{-1}$ in non-phosphorus detergent greywater and 6-23 mg P $L^{-1}$in areas where phosphorus containing detergents are still in use. Greywater can be contaminated with E.coli and enterococcus, while salmonella can be introduced into kitchen wastewater during food handling. Table 1 shows the typical greywater composition.[1]

**TABLE 1**
**Typical Greywater Composition** [1]

| Parameters | Concentration |
|---|---|
| pH | 6.3-8.35 |
| Temperature | - |
| Suspended solids (mg/L) | 76-1396 |
| Total dissolved solids (mg/L) | - |
| Biochemical oxygen demand (BOD) (mg/L) | 129-2287 |
| COD (mg/L) | 13-8000 |
| $NH_3$-N (mg/L) | 25-211 |
| Total Phosphorus (mg/L) | 2.4-27 |
| E-coli (MPN/100 mL) | $2\times10^5$ |

## III. Photocatalytic Redox Reactions

When titania particles absorbs ultraviolet energy, which is comparable to its band gap, photoexcitation of electron takes place and an electron-hole pair is produced. Reduced by the excited electron, oxygen forms super oxide anion ($\cdot O_2^-$). The hole reacts with water producing hydroxyl radicals ($\cdot OH$). The heterogeneous photocatalytic sequence reactions occur in water are described below [6]:

$$TiO_2(e^-cb)+O_{2ads}+H^+ \longrightarrow TiO_2+HO_2^{\cdot} \quad (1)$$

$$TiO_2+HO_2^{\cdot} \rightleftharpoons O_2^{\cdot} + H^+ \quad (2)$$

$$HO_2^{\cdot}+ TiO_2(e^-cb) + H^+ \longrightarrow H_2O \quad (3)$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + O_2^{\cdot-} \longrightarrow HO^{\cdot} + O_2 + HO^- \quad (5)$$

$$H_2O_2 + hv \longrightarrow 2\ HO^{\cdot} \quad (6)$$

$$H_2O_2 + TiO_2(e^-cb) \longrightarrow HO^{\cdot} + HO^- \quad (7)$$

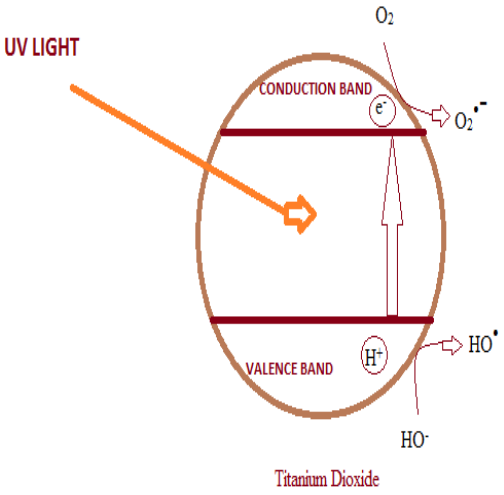


Fig.1 Simplified diagram of the heterogeneous photocatalytic reaction occurring on illuminated $TiO_2$ particle.

## IV. Various Litreature on Treatment of Greywater as well as other Wastewater by Photocatalyst Titanium dioxide

Haruna Banno et al. (2014), they found the effect of $TiO_2$ (Pt-loaded) crystallite diameter on the photocatalytic water splitting rate. They used $TiO_2$ powders with a wide range of crystallite diameters from about 16 to 45 nm with a blank region between about 23 and 41 nm were prepared by various annealing processes and methanol as an oxidizing sacrificial agent. It was found that the photocatalytic water splitting rate was sensitively affected by the crystallite diameter of the $TiO_2$ (Pt-loaded) powder. They found steep improvements in hydrogen production rates from around 15 and a little over 2 to about 30 $\mu mol.m^{-2}\ hr^{-1}$ in the two $TiO_2$ crystallite diameters ranging from 16 to 23 and from 41 to 45 nm respectively.[7]

Zhao Jin-hui et al. (2011), he conducted UV/ $TiO_2$ photocatalytic experiments on the filtered water of local waterworks. He used self-made glass supported nano-$TiO_2$ film and photocatalytic reactor for the experiment. He found that the supported $TiO_2$ thin film has a good removal effect on trace organic pollutants in drinking water, TOC removal efficiency can reached 45%-63% within 2h-3h which also increase the chemical safety of drinking water. He also studied influencing factors such as light intensity, dissolved oxygen (DO), reaction time and pH which affect the photocatalytic process. He

suggested that various factors should be reasonably controlled, and the light intensity should be controlled in 2-3 $mW/cm^2$, while reaction time is 2-3h.[8]

M. Sanchez et al.(2010), they conducted study of photocatalytic oxidation of grey water over titanium dioxide particles. In this study they conducted experiments on grey water coming from two different sources , a hotel and a household. They used different catalyst concentration for removal of dissolved organic carbon (DOC) and the result of experiments showed that the DOC removal was not proportional to the catalyst dosage while in hotel grey water DOC decreased when $TiO_2$ dosage increased. Hotel grey waters showed 65% of DOC removal in 150 minute of treatment at dosage of 2 g/l and the higher reduction for anionic surfactants concentration was close to 70% when the catalyst concentration was 0.5 g/L.[3]

G.Em.Romanos et al. (2011), they used prototype chemical vapor deposition reactor for the deposition of the $TiO_2$ layers on the nanofiltration (NF) membranes (γ-alumina). The pollutant degradation efficiency of the active $TiO_2$ modified membranes was investigsted in a continuous flow photocatalytic purification device and they examined that double side active $TiO_2$–modified membranes photodegraded almost double amount of a common pollutant like methyl orange, when operating in the common cross flow membrane mode under UV irradiation of both sides. The membranes exhibited high rate of purified water yield with no signs of fouling tendency. This novel device provided the the possibility to effectively illuminate with UV light each membrane surface ( internal and external ) separately and in this way it was possible to discriminate between the fractions of pollutant that were removed due to adsorption on the alumina substrate and the $TiO_2$ layer, due to photolysis and due to the $TiO_2$ photodegradation.[9]

Seiichi Deguchi et al. (2014), they found that the for enhancing photocatalytic water splitting rates with Pt/ $TiO_2$ powder, sufficient agitation of the biphasic medium is required to switch surficial reactions to volumetric reactions. They also studied water splitting rates under different heating conditions and examined that the hydrogen production was increase significantly with increase in temperature. They seen that the shallower solution increase the photocatalytic water splitting rates and they also concluded that Rayleigh convection approximately doubled photocatalytic water splitting rates. The rate enhancement achieved through Rayleigh convection is a result of its ability to disperse the ultrafine Pt/ $TiO_2$ particles throughout the whole medium leading to volumetric reactions. [10]

Xuning Li et al. (2014), they designed heterogeneous photo-Fenton catalyst by using Prussian blue/ titanium dioxide nanocomposites (PB/ $TiO_2$ NPs) to increase the $Fe^{+2}$ recovery in degrading organic contaminants in water. They synthesized PB/$TiO_2$ NPs with different loading of PB. The high photo-Fenton activity for decomposing selected organic pollutants by PB/$TiO_2$ NPs was investigated. By series of experiments they were concluded that weaker acidic conditions were favorable for the photo-Fenton process. They used Mossbauer spectroscopy study of excited electrons of $TiO_2$ by UV irradiation could accelerate the cycle of low spin $Fe^{+3}$ to $Fe^{+2}$ in PB and then led to the higher activity. The generation of $^{\cdot}OH$ radicals in the reaction system was identified using electron paramagnetic resonance spectroscopic techniques. The removal efficiency for rhodamine B (RhB) was still as high as 95 % noted. PB/ $TiO_2$ NPs were confirmed to have great potential applications on the degradation of various organic pollutants because of its stability and wide working pH range (2-11).[11]

Hisao Hidaka et al. (1989), they found that various kinds of anionic, cationic and nonionic surfactants have been photodegraded in a heterogeneous dispersion of $TiO_2$ semiconductor particles under UV illumination. These surfactants are ultimately converted to $CO_2$. They studied the relationship between the structure of surfactants and the photodegradation rate. $CO_2$ evolution from the photooxidation of anionic surfactants is faster than that observed from cationic surfactants in the initial stages of irradiation. The anionic surfactants were determined by the methylene blue active substance method. The nonionic surfactants photodegrade more slowly evolving $CO_2$ at about 20% mineralization yield. UV illuminated titanium dioxide affords strongly oxidizing catalytic sites, irrespective of the structure of surfactant.[12]

L.Zhang et al. (2009), they proposed a rotating-drum reactor coated with a $TiO_2$ photocatalyst, in which $TiO_2$ powders loaded with Pt are immobilized on the outer surface of a glass-drum. The reactor can receive solar light and oxygen from the atmosphere effectively. They were examined that phenol can be decomposed rapidly by this reactor under solar light. By experiments they concluded that the phenol with an initial concentration of 22 $mg/m^3$ was decomposed within 60 min and was completely mineralized through intermediate products with 100 minutes.[13]

Xianhuai Huang et al. (2007), they studied potential of $TiO_2$/UV photocatalytic oxidation to control fouling of membranes by natural organic matter (NOM). They investigated decomposition kinetics of NOM by using a commercial $TiO_2$ catalyst, and the effect of various experimental parameters including $TiO_2$ dosage and initial total organic carbon (TOC) concentration. They examined

that the reaction kinetics was increase with increasing $TiO_2$ dosage, but decrease with increasing initial TOC concentration. At a $TiO_2$ concentration of 0.5 g/L, fouling of both an MF and a UF membrane was completely eliminated after 20 min of treatment. The reduction in membrane fouling is attributed primarily to the changes in NOM molecular characteristics resulting from preferential removal of high molecular weight (MW), hydrophobic NOM molecules, which are the major NOM fraction responsible for membrane fouling.[14]

## V. Concluding Remarks

After study of various literature, the photocatalyst titanium dioxide ($TiO_2$) is effective for treatment of greywater as well as other wastewater. There are also a possibility of low cost treatment of greywater by photocatalytic reaction by $TiO_2$ in the presence of ultraviolet light. Treatment by using $TiO_2$ will become intermediate treatment process for reuse and recycling of greywater by advanced treatment processes. The titanium dioxide coating on inert film or media also reduces the loss of $TiO_2$ powder and deposition of $TiO_2$ particles at the bottom of photocatalytic reactor. $TiO_2$ coated film also increases the exposure of light to $TiO_2$ , so indirectly it also increase the degradation of organic matter present in wastewater.

## References

[1] Sahar Dalahmeh, Ph.D. Thesis, "*Bark and charcoal filters for greywater treatment-pollutant removal and recycling oppor tunities*", Swedish University of Agricultural Sciences Uppsala, 2013, pp.11, 17, 19

[2] Christina Berger, Master Thesis, "*Biochar and activated carbon filters for greywater treatment – comparison of organic matter and nutrients removal*", Swedish University of Agricultural Sciences, 2012, pp.5

[3] M. Sanchez, M.J. Rivero , I. Ortiz , "Photocatalytic oxidation of grey water over titanium dioxide suspensions" , *Desalination 262* (2010) 141–146,pp.1

[4] Mokhbi Yasmina, Korichi Mourad, Sidrouhou Hadj Mohammed, Chaouche Khaoula, "*Treatment heterogeneous photo catalysis; Factors influencing the photo catalytic degradation by TiO2*", *Energy Proce'dia 50* ( 2014 ) 559 – 566, pp. 560

[5] Wenny Irawatya, Felycia Edi Soetaredjoa, Aning Ayucitraa, "*Understanding the relationship between organic structure and mineralization rate of TiO2-mediated photo catalysis*", *Procedia Chemistry 9* ( 2014 ) 131 – 138, pp.131

[6] Marta I. Litter, "*Heterogeneous photo catalysis Transition metal ions in photo catalytic systems", Applied Catalysis B: Environmental 23* (1999) 89–114,pp.89-90

[7] Haruna Banno, Ben Kariya, Norifumi Isu, Muneaki Ogawa, Saeko Miwa, Keisuke Sawada, Junki Tsuge, Shoichiro Imaizumi, Hidenori Kato, Kyota Tokutake, Seiichi Deguchi, "*Effect of TiO2 Crystallite Diameter on Photocatalytic Water Splitting Rate*", *Green and Sustainable Chemistry*, 2014, *4*, 87-94

[8] Zhao Jin-hui, "*Research on UV/TiO2 Photocatalytic Oxidation of Organic Matter in Drinking Water and Its Influencing Factors", Procedia Environmental Sciences 12* (2012) 445 – 452

[9] G.Em. Romanos, C.P. Athanasekou, F.K. Katsaros, N.K. Kanellopoulos, "*Double-side active $TiO_2$-modified nanofiltration membranes in continuous flow photocatalytic reactors for effective water purification*", *Journal of Hazardous Materials 211– 212* (2012) 304– 316

[10] Seiichi Deguchi, Ben Kariya, Norifumi Isu, Shoji Shimasaki, Haruna Banno, Saeko Miwa, Keisuke Sawada, Junki Tsuge, Shoichiro Imaizumi, Hidenori Kato, Kyota Tokutake, "*Enhancement of Photocatalytic Water Splitting Rate via Rayleigh Convection*", *Green and Sustainable Chemistry*, 2014, *4*, 80-86

[11] Xuning Li, Junhu Wang, Alexandre I. Rykov, Virender K.Sharma, Huangzhao Wei, Changzi Jin, Xin Liu, Mingrun Li, Songhua Yu, Chenglin Sun, and Dionysios D. Dionysiou, "*Prussian blue/TiO2 nano composites as a heterogeneous photo-Fenton catalyst for degradation of organic pollutants in water*", *Catal. Sci. Technol.*, 2014, DOI: 10.1039/C4CY00947A.

[12] Hisao Hidaka, Shinya Yamada, Shinichi Suenaga, Jincai Zhao, "*Photo degradation of surfactants part vi. complete photo catalytic degradation of anionic, cationic and nonionic surfactants in aqueous semiconductor dispersions*", *journal of molecular catalysis, 59* (1990) 279-290

[13] Lianfeng Zhang, Tatsuo Kanki, Noriaki Sano and Atsushi Toyoda, "*photo catalytic degradation of organic compounds in aqueous solution by a TiO2-coated rotating-drum reactor using solar light*", *Solar energy vol. 70, no. 4*, pp. 331–337, 2001

[14] Xianhuai Huang, Marlen Leal, Qilin Li, "Degradation of natural organic matter by TiO2 photo catalytic oxidation and its effect on fouling of low-pressure membranes", *WATER RESEARCH 42* (2008 ) 1142 – 1150