

PHOTOCATALYTIC DEGRADATION OF ORGANIC COMPOUNDS IN WASTEWATERS

SCIENTIFIC REVIEW PAPER

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DOI: 10.5281/zenodo.2563022

RECEIVED
2018-11-15ACCEPTED
2018-12-29

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ABSTRACT: Due to the toxicity effects and endocrine disrupting properties of many organic compounds, their removal from water and wastewater has gained widespread global attention. This review summarizes photocatalytic degradation of different organic molecules present in wastewaters. This is an overview of photocatalytic degradation with the goal of presenting the technique as an attractive and viable process unit. This process has great potential for replacing other conventional methods for treatment of wastewaters and can be used at the advanced treatment stage. Photocatalytic degradation techniques should be more used in wastewater treatment because with this technique it is possible to decrease contaminants to certain acceptable discharge limits. However, the technique is still not being utilised on an industrial scale. This is mainly due to focus of researchers to study singular contaminants such as alcohols, carboxylic acid, phenol and its derivate, chlorinated aromatic compounds, colours, active pharmaceutical ingredients, and different type of surface active agents. TiO₂ can be used as a photocatalyst in water purification to degrade organic pollutants.

KEYWORDS: photocatalytic degradation, organic compounds, wastewater decontamination

INTRODUCTION

Water pollution is now an acute problem worldwide, and in developing countries in particular. Demand for high quality water (i.e., water that is free of toxic chemicals and pathogens) has increased due to population growth, more stringent health based regulations and economic development (Ali Ayati et al., 2014) [1]. The rapid development of manufacturing technology after the industrial revolution has improved the standards of living significantly but it is becoming a factor that is threatening human health and the environment (Seul-Yi Lee and Soo-Jin Park, 2013) [2].

The reuse of treated water is amongst the most suitable solutions to achieve a really sustainable use of water, especially in water-deprived countries. One of the most relevant issues in wastewater recycling is the presence of micro contaminants, also known as emerging contaminants (ECs). Wastewater from industries and municipal treatment plants can be recycled after the proper treatment. Amongst the different advanced oxidation processes, the use of photocatalysis based upon TiO₂ for water decontamination is receiving an increasing interest in recent years due to its high photostability, non-toxicity and cost effectiveness (Miranda-García et al., 2014) [3].

However, though it is a good catalyst, its wide band gap (3.2eV) limits the use of visible light as the light source. This has consequent implications for the use of titania materials as solar or room-light activat-

ed catalysts, because the majority of sunlight consists of visible light and only a 3–5% of UV light. Hence, increasing the efficiency of visible photocatalysis is important for the practical application of this technique (K. Maeda and K. Domen), [4]. Various attempts have been made to develop the visible light activity to TiO₂ such as doping with metal and non-metal ions (H.E. Chao et al., [5], (D. Chatterjee et al., 2005) [6], dye sensitization (G. Zhao et al. 1996) [7], and semiconductor coupling (D.L. Liao et al., 2008) [8], (B. Pant et al., 2014) [9] etc.

Among physical, chemical or biological waste treatment methods, chemical route stand, in particular, the photocatalytic procedures are considered the most interesting ones thanks to their wide applicability, low cost and environmental compatibility. Physical treatments mainly operate to concentrate the pollutants rather than remove them; on the other hand, biological processes are of great importance in many applications, but the operational conditions need to be strictly controlled to preserve the active bacterial colonials. Conventional chemical routes require the addition of dangerous or expensive chemical reagents (A. Galenda et al., 2014) [10].

ORGANIC COMPOUNDS

Wastewater becomes a serious hazard to ecological and human health due to increasing sewage discharge generated from industrial manufacture and agriculture irrigation like dyes, pesticides, plasticizers.

AROMATIC COMPOUNDS

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are mostly colourless, white, or pale yellow solids. They are a ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity. The mechanism of toxicity is considered to be interference with the function of cellular membranes as well as with enzyme systems which are associated with the membrane. It has been proved that PAHs can cause carcinogenic and mutagenic effects and are potent immune suppressants. PAHs are commonly detected in air, soil, and water (Hussein I. et al., 2016) [11]. Endocrine disrupting chemicals (EDCs) such as bisphenol A (BPA), estradiol, and estrone are typical emerging pollutants commonly found in water resources and effluents from wastewater treatment plants. Bisphenol A has been widely used in the plastic industry for the production of polycarbonate plastics and epoxy resin (Li-Fen Chiang and Ruey-an Doong, 2014, [12].

PESTICIDES AND HERBICIDES

Pesticides are biologically active compounds produced for use in agricultural production to prevent or limit the adverse effects of biological agents such as insects, grafts, plant pathogens, undesirable plant species (weeds) etc. However, pesticide application often monitors the risk of undesirable consequences for the environment. Pesticides can contaminate surface and groundwater, may adversely affect harmful crops, beneficial soil organisms, tiny siblings and birds, can be found as residues in food and can cause resistance to biological agents. It is therefore essential to understand the destiny of pesticides in the environment and to assess the potential exposure and risks to human health and the quality of the environment. Some persistent pollutants, including several pesticides, are carried in air and water over several hundred miles affecting the wildlife and general populace. These chemicals are non-biodegradable in nature and have been known to have carcinogenic, mutagenic or chronic toxic effects (Mukesh Goel et al., 2010) [13].

Chlorinated organic compounds are found to be resistant to biochemical degradation. Large quantities of higher chlorophenols (pentachlorophenol, tetrachlorophenol, etc.) are used in the wood preservation industry. Monochlorophenols and dichlorophenols serve as intermediates in the production of pesticides (S. Zuzana et al., 2008) [14]. They are also used as additives to inhibit microbial growth in a wide array of products such as adhesives, oils, textiles, and

pharmaceutical products (M. Contrerasa et al., 2003) [15].

Examples of herbicides include RS-2- (4-chloro-o-tolyloxy) propionic acid, (4-chloro-2-methylphenoxy) butyric acid and 3,6-dihydro-pyridine-2-carboxylic acid, whose photodegradation was studied with TiO₂ doped with nitrogen and iron as well as comparing their efficacy with the most commonly used TiO₂ Degussa P25 [16]. Among pesticides and herbicides, the following should be mentioned: DDT (dihloro-diphenyl-trichlorethane)-organohloric insecticide, s-triazine herbicide (2,4,5-trichlorophenoxyacetic acid). Quinmerac (7-chloro-3-methylquinoline-8-carboxylic acid) has been commercially used over the last ten years as a new class of highly selective herbicides. Clomazone (2- (2-chlorobenzyl) -4,4-dimethyl-1,2-oxazolidin-3-one) is a selective herbicide used to control weeds in soy, corn, tobacco, rice, sugar beet and other vegetables [17].

Increased use of pesticides and inadequate methods of wastewater disposal are of particular importance for freshwater (surface and groundwater), coastal and marine waters (Abdennouri, M. et al., 2011) [18]. Low level of pesticide residues in water generally does not produce acute toxic problems, but chronic effects are of great importance (Smith, C.N., et al., 1987)[19]. Pesticides contribute to the onset of cancer (Younes, M. and Galal-Gorchev, H. (2000) [20], Parkinson's disease, affect reproduction, foetal damage, delayed neurological event and possible immune disorders (Doull, J. (1989)) [21].

DYE

The toxicity level of a particular dye is very important due to its diverse effects on the environment and living organisms. Among all the techniques for dye removal, adsorption and photocatalysis are two important processes which have been gaining much attention in recent years. Some of the important ancient natural dyes used for textile dyeing were: Tyrian purple (6, 6'-dibromoindigo), kermes, indigo (5,7,3', 4'-tetrahydroxyflavone, C.I. Vat Blue 1) [22, 23, 24].

The first two colours were of animal origin, while the last colour was obtained from plants. According to the Colour Index classification, about 8,000 chemically different types of synthetic dyes are currently registered [25]. The increase in the production of synthetic colours is inextricably linked with the textile industry. Experts estimate that they produce about 7×10^5 ton colour per year for this type of industry only [26].

From the standpoint of the market, azo colours represent the largest and most significant class of organic colours. More than 50% of commercial dyes and pigments belong to azo compounds. The popularity of azo dye is most influenced by strong colour intensity; the molar extinction of the azo dye coefficient is about twice as high as the anthraquinone, the second largest colour group, which means that the double the amount of paint is needed to obtain the same colour intensity. Azo dye synthesis procedures are relatively simple. Also, there is a wide range of cheap petrochemical raw materials that can be used to synthesize a variety of azo dyes of specific characteristics. Most azo colours have good stability to light. Another advantage of azo colours is that they cover a whole spectrum of colours [27]. Azo dyes are most used in the textile industry for the dyeing of cotton, paper, silk, leather, wool, and dyeing of polyamide, acrylic, polyolefin, polyester, viscose and cellulose acetate fibers [28, 29]. In addition to the textile industry, azo dyes have been used in the past decades for other purposes: in the pharmaceutical and food industry, in the cosmetics industry and in the manufacturing industry, in photo making, photo/video filter dyeing, printer mugs and photocopiers, solar cells, etc. [30]. Heterocyclic azo dyes are important not only because of excellent textile dyeing properties but also for good application in other branches such as photodynamic therapy, lasers, reprographic technology, nonlinear optical systems. They are well known for their use on LCD screens and in inkjet printing [31]. The first monoation pyridone dyes were synthesized by Burkhard and associates of diazotized anilines and 3-cyano-6-hydroxy-4-methyl-2-pyridone in tartaric acid at 0-5 °C and at pH 4.5 [32]. The resulting dyes were used to stain synthetic materials, mostly in yellow [33, 34] or in green-yellow shades [35]. Subsequent modification of the amino component (e.g., 5-amino-4,6-dicyanindane) yielded red and orange shades [36]. Photomineralization of organic dyes to H₂O and CO₂ is a much researched area and of particular interest for the textile industry, which produces liquid dye waste in large quantities. Azo dyes continue to be heavily used, and disposing of them is difficult (Jussi Kasanen et al., 2011) [37].

PHOTOCATALYTIC DEGRADATION

Titanium dioxide (TiO₂) exhibits excellent photocatalytic activity and it has been extensively used in various applications, e.g., photovoltaics devices, pollutant decomposition and antibacterial materials (Warapong Krengrvirat et al., 2013) [38]. TiO₂ can be

used as a photocatalyst in water purification to degrade organic pollutants. Semiconductor mediated heterogeneous photocatalysis is considered as a promising alternative for the removal of organic pollutants and pathogens from wastewaters, as it can potentially work under solar irradiation without generating harmful by-products. Due to its high efficiency, low toxicity, excellent physical–chemical stability, and relative low costs, nanosized TiO₂ is the most widely used photocatalyst for environmental purifications (Lei Liu et al., 2013) [39]. Conventional water treatment technologies have limitations in complete decontamination of those emerging anthropogenic organic pollutants or disinfection of bacteria without harmful disinfection byproducts.

MECHANISM OF THE PHOTOCATALYTIC DEGRADATION WITH TiO₂

The photocatalytic mechanism starts when a photon with energy, $h\nu$ matches or exceeds the band gap energy, $E \geq E_g$, of the semiconductor. Conduction electrons, e_{cb}^- , are promoted from the valence band into the conduction band (CB), leaving a hole, h_{vb}^+ , behind. The lifetime of e^-h^+ pairs is only a few nanoseconds, but it is long enough to initiate redox reactions with semiconductor material in solutions or gaseous phases. The resulting e^-h^+ pairs within the semiconductor particle can be separated, diffused to the surface of the semiconductor and thus participate in the oxidation and reduction reactions of the organic and inorganic compounds or are subjected for the recombination process by decreasing the quantum yield of the reaction. The hole can either oxidize a compound directly or react with electron donors like water to form OH radicals, which in turn react with pollutants such as chlorophenols, dyes, and organic compounds resulting in the total mineralization of most of these compounds (A. Aguedach et al., 2005) [40]. The electrons in conduction band can react with oxygen, O₂ to yield super oxide anion, then in reaction with water can form hydrogen peroxide, O₂^{•-} and then give a hydroxyl radical, •OH (Figure 1). The resulting OH radicals are very strong oxidizing agents (standard redox potential +2.8 V). The most important species for photocatalytic processes of degradation of pollutants is hydroxyl radical. The hydroxyl radical is a non-selective oxidant with a high oxidation potential which leads to complete mineralization, to CO₂ and H₂O of the most of the organic molecules present in wastewater by oxidation reaction.

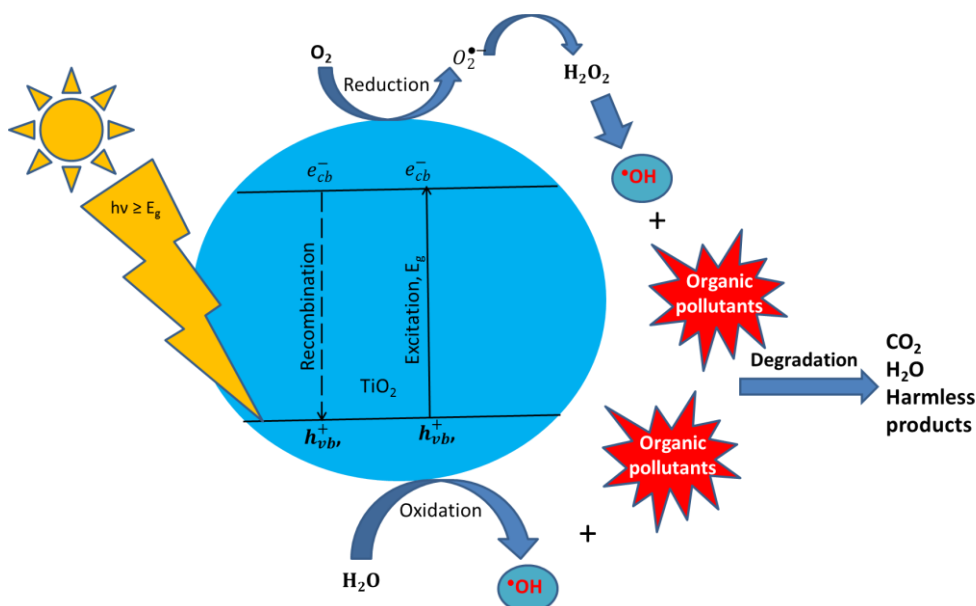


Figure 1. Mechanism of the photocatalytic degradation with TiO_2 .

TYPE OF WASTEWATERS

From industrial wastewaters where the most common organic molecules are found are:

1. synthetic colours/textile wastewaters
2. oil industry/refinery wastewaters
3. pesticides and herbicides/agricultural wastewaters
4. medicaments/pharmaceutical wastewaters.

TEXTILE WASTEWATERS

All textile colours are synthesized so that they are persistent during washing, chemical and microbiological activity and on the effects of light. Thanks to the properties of durability, textile colours are extremely persistent in the environment and prone to bioaccumulation.

Since textile azo is dyed by its xenobiotic nature and is hardly biodegradable, their removal from waste water attracts more and more attention of environmental protection researchers. For these reasons, azo dyes must be removed from the waste waters before discharge into natural watercourses. Removing paint does not always mean removing toxicity. Incomplete degradation and formation of degradation ingredients can increase toxicity.

REFINERY WASTEWATERS

Wastewater generated by petroleum industries is very complex, and includes several inorganic and organic components, such as Ca^{2+} , Mg^{2+} , S^{2-} , Cl^- , PO_4^{3-} , Fe^{2+} , Fe^{3+} , SO_4^{2-} , emulsified oil, sulphides, ammonia, cyanides and especially phenol and phe-

nolic derivatives that are the most important contaminants (A.M. Mansouri et al., 2014) [41].

Wastewater from petroleum refinery has the characteristics of high concentration of aliphatic and aromatic petroleum hydrocarbons, which could lead to heavy pollution on the surface of soil and rivers. Refineries generate polluted wastewater, containing COD (the amount of organic matter that can be chemically oxidised) levels of approximately 200–600 mg/l; 20–200 mg/l phenol; 1–100 mg/l benzene; 0.1–100 mg/l chrome and 0.2–10 mg/l lead; and other pollutants (F. Shahrezaei et al., 2012) [42].

Industrial wastewater containing dyes, such as indigo carmine, are discharged without previous treatment into the environment, causing a change in water colour, aquatic life disturbance and generation of toxic aromatic amines (F.A. Rodríguez et al., 2012) [43].

AGRICULTURAL WASTEWATERS

In intensive agricultural practice, repeated use of pesticides results in frequent occurrence of pesticides in European raw water resources. Pollution sources from agricultural activities are well known: unused treatment solutions, spray machine and pesticide container washing. Small volumes and high concentrations characterize these effluents. Numerous studies have demonstrated that the heterogeneous photocatalysis of pesticides is an effective process to degrade pesticides and to mineralize some of them (L. Lhomme et al., 2008) [44]. The study of Lhomme and co-workers has shown that by photocatalytic degradation are possible to remove 70% to 85% for an irradiation time ranging from 15 to 20 h. The re-

sults of this research also have shown that for the degradation of the target compounds and mineralization is very important nature of the additives in the commercial pesticide solutions. For example, in pure water the two pesticides were completely degraded by photocatalysis, whereas, in the case where additives were present, the degradation rate and the mineralization of the pesticide could be significantly decreased.

PHARMACEUTICAL WASTEWATERS

The presence of polluting substances such as medicines and personal hygiene products, dietary products, fragrance components, sun protection agents, are detected in many waste- and surface-waters [45, 46, 47]. These compounds, as well as their biologically active metabolites, continuously enter the aquatic environment through various pathways and primarily through untreated or inadequately treated wastewaters. The ever-increasing health and environmental problem in the world is medicine and personal hygiene, due to the fact that long-term exposure to low concentrations of these substances can have negative consequences for water and land ecosystems and/or human health. Uncontrolled discharge of drug-laden wastewater into natural streams can lead to the development of resistant bacteria, slowing oxidation of nitrite and methanogenesis, and potential increase in toxicity due to the synergistic effect of various drugs and their metabolites.

Active pharmaceutical ingredients are complex molecules with different functionalities, physical-chemical and biological properties. Mostly, they are polar compounds, molecular mass ranging from 200 to 500 or 1000 Da. They belong to the group of pollutants also referred to as micropollutants, since they are present in the aquatic environment in microgrammic ($\mu\text{g dm}^{-3}$) or nanogram concentrations (ng dm^{-3}).

Pharmaceuticals can be divided based on their purpose and biological activity on antibiotics, analgesics, antipyretics, antihistamines, antineoplastic agents, anti-inflammatory drugs. Classification of molecules of the active component of drugs based on the chemical structure is mainly used within a particular subgroup of drugs. Thus, antibiotic groups differ from subgroups: β -lactams, cephalosporins, penicillins or quinolones. Even small changes in the chemical structure can have a significant effect on their solubility and polarity, as well as on other traits relevant to their destiny in the environment. Active drug components generally have basic or acid functional groups, sometimes both within the same molecule. Under conditions that dominate the drug molecule's

environment, they can be neutral, cationic, anionic or in the form of zwitterion. All of this makes the behaviour of drugs in the environment extremely complex.

Over the last few years, it has been discovered that from the point of view of ecological risk assessment are not only active components of drugs, but also compounds that arise as a result of their structural changes in the environment. Once they get into the environment, active drug components are subject to various structural changes under the influence of biotic and abiotic processes. Also, structural changes occur during the treatment of wastewaters [48, 49, 50].

Studies in different countries have confirmed the presence of drugs in surface and municipal sewage waters in the concentration range of several ng dm^{-3} to several $\mu\text{g dm}^{-3}$. On the other hand, little is known about the appearance, destiny, and metabolite activity, which can also be detected in the environment [51].

It is known that some antibiotics (tetracyclines) tend to bind to particles or form complexes with ions present in the water [52, 53, 54]. Antibiotic sorption depends on the amount and nature of free and suspended particles in the aqueous phase and natural organic matter, of the present minerals and the distribution coefficient [52].

CONCLUSION

The classic methods of wastewater treatment include mechanical, chemical and biological treatment. Since chemical treatment implies the introduction of chemicals such as ferric chloride or aluminum sulphate and they remain in the environment for a long time and can decrease pH values as well they may have a harmful effect on the environment. Also, classical methods imply constant use of chemicals, while photocatalytic treatment can be carried out several times in mild conditions and the end products are environmentally acceptable. Since that, in photocatalytic processes for the photocatalyst activation is used UV/Vis light (sun light) as well as the oxygen found in air and these processes can operate at room temperature and pressure conditions they can be classified as more green processes than classic one. In recent decades, an increasing interest has been devoted to the development of photocatalytic processes both in homogeneous and heterogeneous phases. Especially in terms of heterogeneous systems, the use of photo-saturated semiconductors as a catalyst for organic processes has been of great interest due to its ease of use, recycling and low environmental impact. Photocatalytic

semiconductors are promising technologies that have a large number of applications in environmental protection systems such as water and air purification, water disinfection, and hazardous waste remediation. Photocatalytic degradation techniques should be more used in wastewater treatment because with this technique it is possible to decrease contaminants to certain acceptable discharge limits. Numerous studies have demonstrated that the heterogeneous photocatalysis of organic compounds is an effective process to degrade and to mineralize them.

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