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PHOTOCATALYSIS: PAST, PRESENT AND FUTURE TRENDS FOR REMEDIATION OF WASTEWATER.

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Abstract: The current paper examines the use of Photocatalysis in various wastewater treatment applications, beginning with a brief overview of how industrialization is causing various water threats and how wastewater treatment processes, particularly Advanced Oxidation Processes (AOP's), have improved in recent years. Then, we go over the current status of photocatalysis in wastewater clean up,as well as the numerous hurdles that are encountered along the way. The applications of photo catalytic technology in waste water treatment are highlighted ,as well as the most recent efforts to improve photocatalytic materials. A brief explaination of photocatalytic reactor design and system evaluation is also included. Finally, the tactics for boosting research outputs and the future prospects of photocatalysis are discussed.

Key words: photocatalysis, water pollution, redox process, Advanced oxidation process,wastewater,Nanotechnology,Doping,PMR's.

1.Introduction

In recent decades, the rise in industry has led to significant environmental degradation and serious threats to the sustainability of human society, particularly through the use of fossil water and natural resources[1-3]. Freshwater contamination is a global concern and leads individuals to find a way of repairing the polluted water environment effectively. Water contaminants are generally derivated mostly from industry sewer effluents (e.g. textile, paper, pharmaceutical, etc.) and home pollutants (e.g. medicines, pesticides, detergents, etc.)[4]. So far, many pollutants have been present, these pollutants are hazardous to organisms,classed as inorganic ions,organic compounds or pathogens[5–8]. One of the primary global issues for the 21st century is to provide reliable access to clean,safe water[8-14]. Demand for clean water continues to grow fast as people and the economy grow[15]. According to a recent[16] WHO projection, almost 50% of the world's population will live in water areas by 2025[17].
A series of procedures[18] has so far been invented to treat wastewater comprising chemical or physical coagulation[19],sedimentation[20],adsorption[21], membrane filtration[22], and biological way of degradation[23].
However there are still numerous limitations on this old technique, such as low efficiency, high energy consumption, and risk of secondary pollution[24-26] because of the complex composition and the varied physico-chemical characteristics of contamination [10]. As a result, the technology advocated for waste water remediation is widely coveted for high efficiency, low energy consumption and being environmentally benign.

Photocatalysis is one of the methods, the so-called Advanced Oxidation Processes (AOP). AOP break down the organic pollutants into harmless inorganic substances under moderate conditions. Photocatalysis is a process in which the catalyst changes the speed of a chemical reaction when exposed to light. This was discovered in 1972 by Fujishima and Honda, who wanted to split water by exposure to sunlight (photoelectrolysis) analogous to the photosynthesis process [27] [28] [29] [30]. AOPs are based on the production of highly oxidative radicals that enable the rapid breakdown and mineralization of a range of organic and inorganic pollutants from wastewater (Almomani et al., 2018). Among these AOPs, solar photocatalysis is drawing great attention in the treatment of emerging pollutants. In fact, the AOPs are chemical processes that can generate highly reactive hydroxyl radicals (.OH) in situ. The .OH in water has an extremely strong oxidizing property with a high oxidation potential of 2.80 V / SHE (OH / H_2O), so that it cannot oxidize the impurities selectively and finally convert them to CO_2, H_2O or small inorganic ions in a short time [31,32]. In most cases, the OH could be made in the presence of one or more primary oxidants and / or energy sources or catalysts. Therefore, the typical AOPs can be classified as Fenton reactions, electrochemical advanced oxidation processes and heterogeneous photocatalysis [31]. Among other things, photocatalysis is one of the most effective strategies for the AOPs that rely only on the light radiation from the photocatalysts to drive the oxidation reaction under ambient conditions, and no additional energy is needed and no toxic by-product will be produced during the entire reaction process; therefore it is a green chemical technique [33,34]. Semiconductors are the most employed heterogeneous photocatalysis for the AOPs. Photons with energy equal to or greater than the material's band gap are absorbed by a particulate catalyst. This leads to the formation of a conduction band electron (e^-_{cb})and valence band hole (h^+_{vb}) pair. Although both e^-_{cb} and h^+_{vb} can engage in a variety of redox events relevant to water treatment, the major oxidant is hydroxyl radicals (•OH), both surface-bound and in bulk phase[35]. Photocatalytic water treatment provides numerous advantages over homogeneous-phase AOPs. TiO_2, the industry's standard commercial semiconductor material, is cheap ($1/kg),[36] physically robust, and generally nontoxic. It is excited by low-energy ultraviolet radiation (UV-A), making it suitable for solar applications. It eliminates the requirement for constant supply of precursor chemicals as a heterogeneous catalytic process, which is a significant benefit for some applications, particularly those in distant or resource-limited places. Despite extensive study over the last few decades, photocatalysis' use in actual water treatment systems has been quite limited when compared to traditional AOPs. How should the research community see the photocatalytic water treatment technology horizon in light of these trends?

1.1 PRESENT STATUS OF PHOTOCATALYSIS IN WASTEWATER REMEDIATION:

In order to provide answers to this question, we looked at the current state of heterogeneous semiconductor photocatalytic water treatment, emphasising challenges to knowledge transfer, analysing the viability of practical applications, and identifying major research needs for overcoming obstacles. The modest number of systems currently employed in water treatment practise demonstrates the problems preventing economic success of photocatalytic AOPs. This contradicts a large body of research that describes the use of photocatalysis to remediate common surface and groundwater contaminants. These studies, which are usually done at a bench scale, tend to exaggerate the opportunities while underestimating the constraints that the technology demonstrates when used in the field. Overemphasis on material design and mechanistic analyses has led to some arrogance in the academic literature about the feasibility of photocatalysis, sustaining the divide between (burgeoning) academic research and (limited) industry use. As a result, scepticism has developed, prompting some to wonder whether photocatalysis will become a common water treatment technology in the next two decades. Low photo conversion efficiency is one of the most significant hurdles that has been discovered. (see diagram 1) There is a loss of efficiency associated with each phase of the photoconversion process. Even when evaluated using a probing substrate with monochromatic irradiation near the band gap, quantum yields (Φ) reported in the literature are consistently a few percent at most, while ranging significantly depending on the photocatalysts and experimental conditions (Table 1 insert in Figure 1). •OH generation is regarded the most severe drawback in photocatalytic water treatment when compared to other AOPs. Using UV/H_2O_2 AOPs as an example, photolytic decomposition of H_2O_2 in organic-free water at 254 nm has been reported to have a (Φ) of 50%, with a resultant •OH production yield approaching 100%,[37,38], making photocatalysis very difficult to compete in terms of energy efficiency. However, TiO_2 can absorb photons in the lower-energy UV-A range, allowing sunlight to be used, and it does not require the addition of H_2O2, which is a major cost in traditional AOPs.

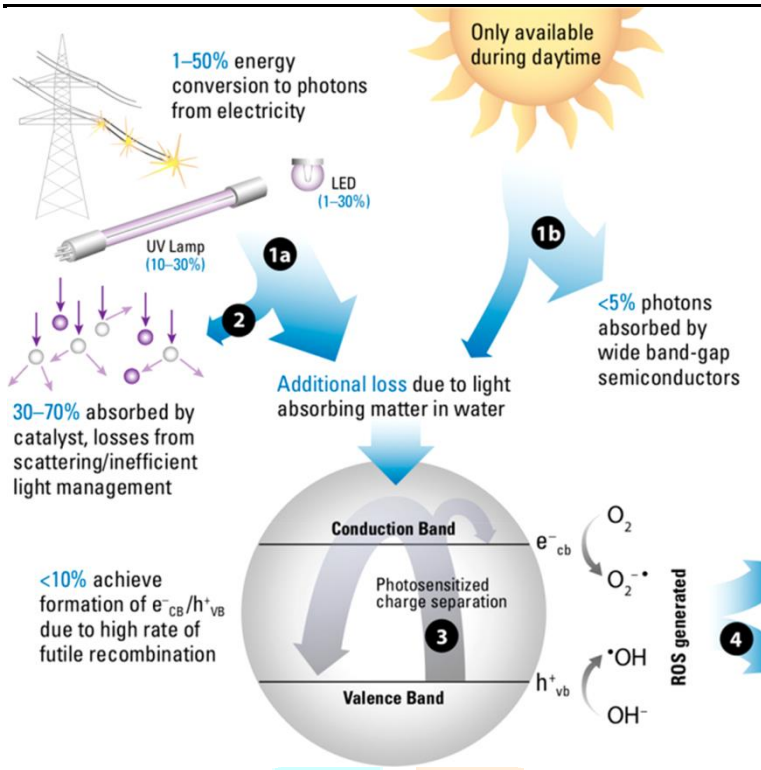

Table 1. Bench-scale Experimental Φ Reported for TiO_2

Probe	λ (nm)	I (mW)	Φ(%)	ref
Coumarin	365	1.25	0.36	10
Coumarin	470	30.5	0.27	10
Methanol	365		4	11
CCA	365	24	0.29	12
4-CP	360		1	13
4-CP	355–60	3.3	0.74	14
Iodide	313	35	2	15
Propanal	313	35	2–6	15
Formate	340–60		3.1	16

Figure:1-Detailing the low-energy conversion efficiencies in typical TiO_2 photocatalytic water treatment processes. Photons are generated either by electrical conversion or directly harnessing solar energy. (1a) Although low-pressure mercury lamps are typical, blue/UVA LEDs are being increasingly studied, with wall plug efficiencies nearing 30%.**[Khan, A.; Balakrishnan, K.; Katona, T. Ultraviolet light-emitting diodes based on group three nitrides. Nat. Photonics 2008.]**

(1b) Electrical conversion losses are obviated when harnessing solar energy; however, < 5% of solar photons are absorbed as the wide band gap (Eg = 3.0 − 3.2 eV; 390 − 410 nm) of TiO_2 is poorly matched to the solar spectrum.[**Loeb, S.; Hofmann, R.; Kim, J. H. Beyond the pipeline: Assessing the efficiency limits of advanced technologies for solar water disinfection. Environ. Sci. Technol. Lett. 2016]** (2) Photons entering the reactor can be lost through intrinsic scattering by the particulate and inefficient light management leading to catalytic absorption of 30 − 70% of the photons emitted into a typical slurry reactor.**[Grcic, Li Puma, G. Six-flux absorption-scattering models for photocatalysis under wide-spectrum irradiation sources in annular and flat reactors using catalysts with different optical properties. Appl. Catal., B 2017]** (3) Photons absorbed by the catalyst can then produce e^-_{cb} and h^+_{vb} ,which further perform redox reactions at the catalyst surface to generate ROS. Regardless of the source of light, a majority (>90%) of photogenerated e^-_{cb} / h^+_{vb} pairs recombine rapidly (within subμs), **[Serpone, N. Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. J. Photochem. Photobiol., A 1997]** leading to quantum yields (Φ) of less than 10% for most materials. The inset table shows a list of experimentally reported bench-scale material Φ for •OH production from various TiO_2 photocatalysts.**[Zhang, J.; Nosaka, Y. Quantitative detection of OH radicals for investigating the reaction mechanism of various visible-light TiO2 photocatalysts in aqueous suspension. J. Phys. Chem. C 2013].** (4) The availability of generated ROS for pollutant destruction is greatly decreased through scavenging. As an illustration, a representative estimate of natural water containing 3 mg-C/L (k(•OH) = 108 L/mol-C·s) and 50 mg/L of bicarbonate alkalinity as $CaCO_3$ (k(•OH-HCO_3^-) = 8.5 × 107 /M· s) suggests that <5% of •OH would be available compared to distilled water (i.e., in the absence of scavengers) at the same pH.

1.2 Efforts to Advance Photocatalytic Materials:

The lack of widespread industry usage hasn't slowed the continual stream of research towards the development of new photocatalytic materials. A growing percentage of research has aimed to develop superior catalyst materials, driven on by developments in materials science and nanotechnology.Modifications to anatase TiO_2 were the starting point for early efforts. Flame pyrolysis production of the well-known P25 TiO_2 powder, for example, is not only cost-effective at industrial scale, but also produces a minority rutile phase fraction, which improves photocatalytic activity[39]. Indeed,

photocatalytic materials science research continues to focus on two fundamental constraints of TiO_2 as avenues for enhancing catalyst performance: restricted absorption and the high recombination rate of photogenerated primary species e^-_{cb} and h^+_{vb}. Many major improvements to TiO_2 have been made. The incorporation of transition metals (e.g., Fe, Cr, and V)[40,41] and later the introduction of nonmetal dopants (e.g., N, C, F, and S)[42] to create oxygen vacancies or low lying interband states at the localised energy levels of the dopant were the first steps in extending photoactivity to lower energy wavelengths. Surface hydrogenation was used to create numerous disorder-induced midgap states, upshifting the valence band-edge, and resulting in black/blue-colored TiO_2 crystals with absorbance around the infrared region in a new leap-ahead use of this method. [43] Though effective at improving absorption of visible light, too many midgap states can lead to excessive recombination and an overly narrowed band structure, reducing the redox potential of the e^-_{cb} /h^+_{vb} pair and impacting the type of ROS produced[44]. The formation of heterojunctions with smaller band gap semiconductors[45] or sensitization with organic chromophores[46] can also widen the absorption toward visible light. Similarly, visible light-absorbing noble metal nanoparticles can inject electrons into the photocatalyst conduction band[47] .Junctions with metals have also been extensively employed to reduce recombination, acting as electron withdrawing centers through the formation of a rectifying Schottky barrier[48] However, high loadings of cocatalysts can limit the surface area, complicate the synthesis procedure, and result in a physically fragile composite material. This same composite architecture can be achieved by replacing metals with semi metallic carbonaceous materials such as graphene,[49] but the intrinsic instability of these materials in an oxidative environment remains an unresolved challenge. Nanoscale control over structural hierarchy and porosity present additional opportunities to improve the efficiency of TiO_2 by promoting charge migration and increasing surface area[50,51].

1.3 PHOTOCATALYTIC REACTOR DESIGN AND SYSTEM EVALUATION

Academic research that focuses on materials development rather than reactor or systems engineering may be missing possibilities to increase the performance of photocatalytic water treatment systems by utilising creative reactor design. Figure 2(a) shows a photocatalytic reactor for water or wastewater treatment that comprises of TiO_2 coated glass beads with a UV light in the centre [52]. However, in recent years, photocatalytic reactors have been modified in a variety of ways to expand the irradiated surface area and improve efficiency. Despite multiple studies in this area,[53] in practise, the sparse configurations have mostly been limited to reactor systems with light emitted into a slurry of well-mixed TiO_2 particles to enhance photon absorption and redox species mass transfer[54].These systems may be competitive with other AOPs, but they are still unoptimized, with drawbacks such as low energy efficiency, delayed reaction kinetics, and, in certain circumstances, catalyst fouling or photoaggregation[55]. Due to its advantages over gas discharge lamps, such as less fragile casings, lack of toxic components, small size, and rapid warm up time, recent rapid improvements in light emitting diode (LED) technology are poised to inspire a new generation of creative reactor designs[56,57]. Not only comparing different photocatalytic systems, but also between photocatalysis and its competitor AOP technologies, is comparison difficult. The most widely used figure of merit is electrical energy per unit order (EE/O), which is defined as the amount of electric energy (or, alternately, solar radiation area) required to degrade a target contaminant by one order of magnitude in a unit volume of polluted water [58]. EE/O is a versatile design aid that is simple to calculate in a treatment scenario with low concentrations of target pollutants compared to background scavengers. By determining and reporting EE/O for typical pollutants, translation from bench to pilot to full-scale applications can be easily reviewed. While values ranging from 0.5 to 10 kWh/m3 are deemed competitive for drinking water applications,[59] common slurry TiO_2/UV systems typically record values of 10 kWh/m3 or greater, whilst rival AOPs such as UV/H_2O_2 and H_2O_2/O_3 can report values of less than 1 kWh/m3. [60] Although it is advised to report EE/O or other metrics such as electron efficiency[61], the limits of comparing technologies using a single number should be acknowledged. Other aspects, such as the embedded energy requirements (or costs) of applying consumable chemicals, should be considered as well.

2. STRATEGIES FOR IMPROVING RESEARCH OUTCOMES

Opportunities to improve photocatalytic water treatment performance may emerge when current developments in materials research and reactor engineering are combined. The following are some tips for researchers who want to enhance photocatalytic water treatment methods without falling into the problems that have slowed progress over the last three decades:

(1) Increase the number of performance requirements for photocatalytic water treatment systems.

(2) Evaluate photocatalyst performance under well-defined conditions:

Testing should be done under standardised conditions, using well-characterized probe compounds and solution conditions (e.g., pH, ionic composition, concentration of ROS scavengers) that are similar to those encountered in actual treatment systems as candidate photocatalysts progress toward practical application.
(3) Think outside the box and look for breakthrough photocatalysts while keeping in mind the challenges of adapting materials from other disciplines: While reusing new materials from adjacent sectors can be an useful method for developing innovative water treatment photocatalysts, a blind pursuit can lead to the promotion of materials not suitable for practical AOP application.
(4)Develop and test materials for specific uses:
The qualities of the pollutant being treated, as well as the relative amounts of other interfering components, determine the efficacy of a photocatalyst. As a result, academics may be able to design photocatalysts for applications that are either impracticable or uninteresting to industry[62]. To overcome this obstacle, researchers must either overcome the major challenges that traditional applications like drinking water and municipal wastewater treatment face[63], or develop niche areas where photocatalytic water treatment may compete with existing AOPs.

2.1 Future challenges and prospects

One of the fundamental characteristics that makes heterogeneous photocatalysis such a promising water treatment process is its ability to operate at room temperature and pressure while using atmospheric oxygen as an oxidant. Additionally, this technique can be used to remove a wide range of hazardous contaminants, including organic contaminants like pesticides, herbicides, and detergents, as well as industrial toxins like dyes and harmful metal ions. However, many features of this mechanism remain unknown after over 30 years of significant research and exhaustive investigations of hundreds of photocatalytic semiconductors. To begin, decide whether the photocatalytic process should be employed as a pre-treatment or as a stand-alone water purification procedure. If utilised as a stand-alone technique, the needed reaction time would still be substantially longer due to poor kinetics of the reaction, even with recent advances. The elimination of operational parameter limitations is the second most critical difficulty. Because the chemical composition and pH of industrial effluent vary by area, efforts should be made to develop photocatalytic materials that can be used under a variety of operating circumstances, including temperature, pH, and contaminant concentrations. Another problem is the catalyst immobilisation approach, which must be improved in order to maximise the photocatalyst's irradiated surface area. To minimise the difficulties of catalyst recovery and agglomeration, which are common in slurry-based photoreactors, catalyst immobilisation is required. Furthermore, by eliminating the separation and washing unit, catalyst immobilisation can minimise the reactor's scale.
In the coming years, further study should be concentrated on visible-light driven photocatalysis, as well as the design of photocatalytic reactors, to address the above challenges. Visible light-driven water treatment technologies have a lot of promise to replace traditional water and wastewater treatment methods by providing a more sustainable and environmentally friendly option. There are several approaches to improve the visible-light activity of semiconductors, as detailed in section 1.2. Doping and photosensitization are thought to be two of the most promising techniques for the future. Furthermore, doping semiconductors with noble metals such as gold or silver has been shown[64] to be an effective technique to boost visible-light activity. Preventing electron–hole recombination in photocatalytic nanomaterials is a critical issue that still needs to be addressed. Despite the fact that semiconductorgraphene heterojunctions have made significant contributions to solving this problem, there is still a need to improve these heterojunctions in order to achieve more effective charge separation. It's also worth noting that while combining heterogeneous photocatalysis with other AOPs may not result in much visible light activity, it has a lot of potential for improving the process's time efficiency. Aside from visible light activity, effective design of photocatalytic reactor systems is necessary, which can provide a cost-effective, long-term, and flexible alternative to traditional water and wastewater treatment procedures.
Future design developments in photocatalytic reactor design may discover continuous or fixed-bed reactors to be more useful, as well as time and cost-effective. So far, there have been two most efficient strategies to improve the performance of continuous processes: one is to combine heterogeneous photocatalysis with membrane processes PMRs), and the other is to increase the amount of time the solution is in contact with the immobilised photocatalyst. If the existing restrictions are solved, heterogeneous photocatalysis might be used as a long-term process for treating water and wastewater in

the next decades, and could provide a low-cost, environmentally friendly alternative to meet the world's growing water demands.

3.Conclusion

Photocatalysis has been shown to have substantial potential for degrading organic chemicals, bacteria, and microbes, as well as lowering harmful metal ions in water and wastewater. This technique's ecologically benign characteristics makes it a good contender for various applications. In addition, over the last three decades, several photocatalytic compounds have been tested on a variety of possible pollutants, with some of them proving helpful in visible light as well. However, this technology has primarily been investigated in laboratory and has yet to be widely applied in industry. Future research should not only focus on materials, but also on the design of photocatalytic reactors, according to the authors. This approach can address almost one-third of the remaining problems by optimising the photocatalytic reactor design.

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