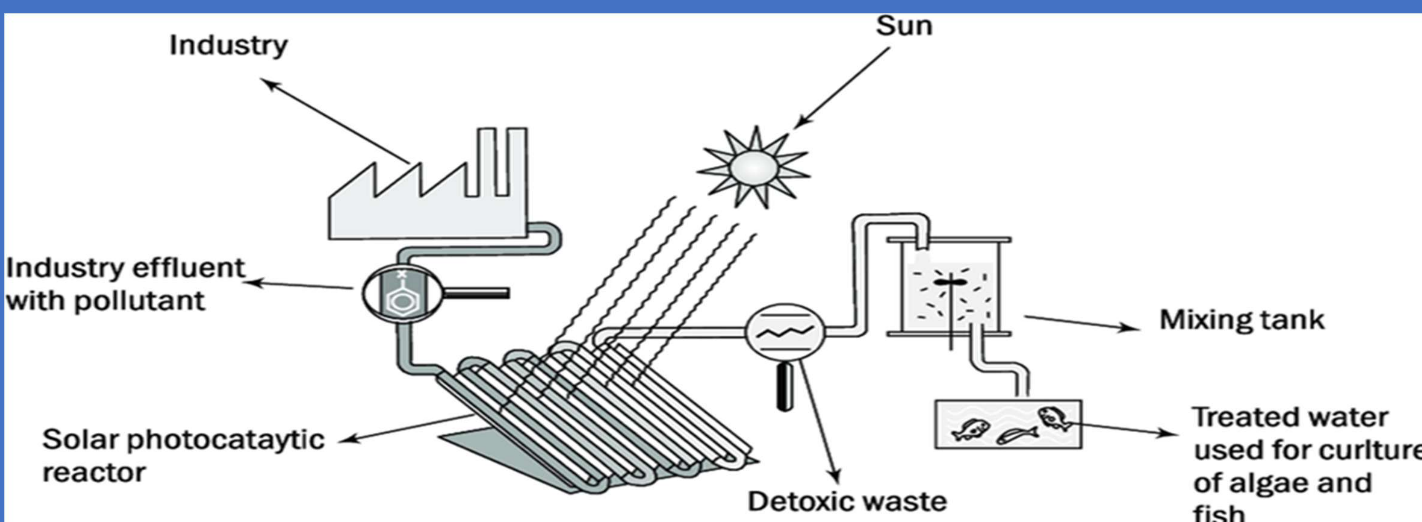
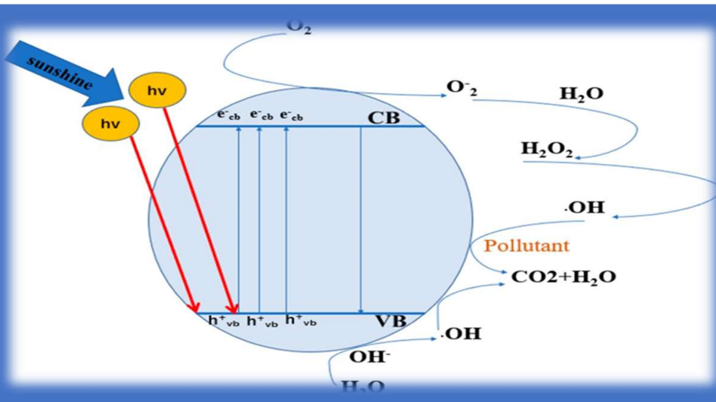
THE ROLE OF PHOTOCATALYTIC MATERIALS IN WASTE WATER TREATMENT





Author Details

Praneel Bhattacharya

Department of Chemical Engineering,

Heritage Institute of Technology Kolkata

3rd Year, 6th Semester

College Roll No.: 2055008

Autonomy Roll No.: 12620006032

Under the guidance of: Professor (Dr.) Diptendu Datta

Acknowledgements:

In this report, I would like to extend my sincerest thanks and deep sense of gratitude to my mentor, Professor (Dr.) Diptendu Datta for his guidance and support throughout this work and providing valuable inputs concerning the content and format, which are indispensable to the completion of this report. His vast knowledge and expertise in the field of chemical engineering have been a constant source of inspiration for me.

I am grateful to Professor (Dr.) Abhyuday Mallick for his invaluable guidance on advanced oxidation processes and their applications in waste water treatment. His expertise in the field and insights have greatly enhanced the quality of my work and deepened my understanding of this complex subject. I would like to express my sincere thanks to him for his generous support and encouragement throughout my research.

I would also like to express my gratitude to Professor (Dr.) Ritayan Chatterjee, who introduced me to this field of Material Science and Photocatalysis, and helped me work on the synthesis and characterization of photocatalytic materials. His guidance and support have been invaluable in shaping my understanding of the subject.

Moreover, I would like to extend my heartfelt thanks to my father, Dr. Prabhatish Bhattacharya, for providing me with materials on the protocols and types of technologies of waste water treatment. His expertise as an Environment Safeguard Analyst has helped me to broaden my knowledge and understanding of the field of waste water treatment.

In conclusion, I would like to thank everyone who has played a role in the creation of this report and made it possible. Their guidance and support have been invaluable, and I am truly grateful for their contributions.

Table of Contents

Page Number

Abstract:

The use of photocatalytic materials in waste water treatment has gained significant attention in recent years as a promising solution for the removal of contaminants from wastewater. Photocatalytic materials, such as TiO_2 and ZnO, have been shown to effectively degrade organic pollutants in wastewater through a combination of oxidation and reduction reactions in the presence of light. The process involves using a photocatalyst in a reactor equipped with an agitator, light source, and filters to remove contaminants and purify the water. Several studies have demonstrated the efficacy of photocatalytic materials in the treatment of wastewater, including the removal of dyes and organic pollutants from textile wastewater and dye-containing wastewater. The use of photocatalytic materials in wastewater treatment not only has environmental benefits but also has the potential to reduce energy consumption compared to traditional treatment methods.

Keywords: Photocatalysis, TiO_2, Waste water treatment, Advanced Oxidation Process, Unit Operations

1.Introduction:

Waste water treatment is a vital process in ensuring the safe disposal of water used in various industrial and domestic activities. Secondary treatment is the critical process that removes the organic putrescible organic matters and brings down the BOD of the effluent to meet the discharge standards. Various conventional secondary treatment technologies have been considered in the sewage treatment process after the primary treatment consisting of screening and grit removal, for e.g., Waste Stabilization Ponds; Aerated Lagoons; Up Flow Anaerobic Sludge Blanket (UASBR) + FAL; Conventional Activated Sludge Process; and Cyclic Activated Sludge Process/Sequential Batch Reactor (SBR).

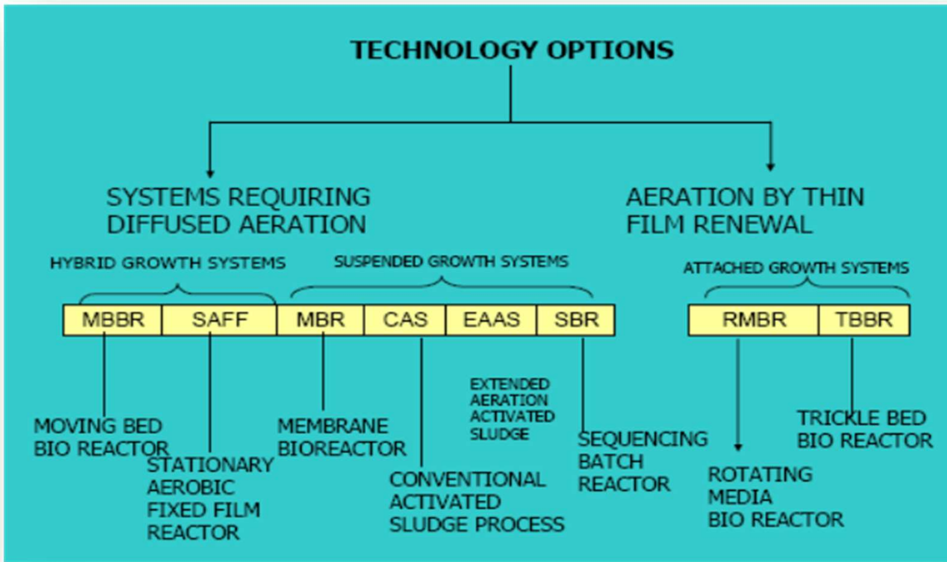


Figure 1: Different Technology Options for Sewage Treatment Process

The genesis of selecting a suitable treatment process is primarily correlated with degree of treatment aimed to be achieved.

Table 1: Treated Wastewater Characteristics for STP Design

S. No	Parameter	Proposed Discharge Standards for STP (Latest as per NGT order, Application no. 1069/2018, dated 30th April, 2019) to be as follows	MOEF&CC STP Discharge Standards, 2017	CPCB discharge standards, 2015#	IFC Guideline value for sewage discharge	WHO Guideline Value for safe use in agriculture
1	pH	5.5 – 9.0	6 – 9	6.5-9.0	6 - 9	6 – 9
3	Biochemical Oxygen Demand (BOD) (mg/l)	≤10	<30 <20 (metro cities)	<10	30	-
4	Chemical Oxygen Demand (COD) (mg/l)	≤50	-	50	125	-
5	Total Suspended Solids (TSS) (mg/l)	≤20	<100 and <50 (Metro cities)	<20	50	-
6	Total Nitrogen (mg/l)	≤ 10	-	<10	10	-

7	Ammoniacal Nitrogen (mg/l)	<5	-	<5	-	-
8	Residual Chlorine, mg/L	≤ 1	-	-	-	-
9	Total Phosphate as P (mg/l) (for discharge into pond, lake)	≤ 1.0	-	-	2	-
10	Fecal Coliform MPN/100 ml	Desireable-100 Permissible-230	<1000	<100	-	<1000
11	Oil and grease, mg/l		-	-	10	-
13	Nematodes, number of eggs per litre	-	-	-	-	1

MOEF&CC= Ministry of Environment, Forest and Climate Change; CPCB = Central Pollution Control Board; IFC = International Finance Corporation, the World Bank Group
 # in April 2019, the National Green Tribunal (NGT) in one of its orders directed MOEFCC to reconsider the standards issued in 2015 for STPs.

1.1 Advanced Oxidation Processes (AOPs) in Waste-Water Treatment

A major advantage of AOPs is related to the degradation of organic compounds to simpler stable compounds such as water, carbon dioxide, and salts with little or no sludge production, which need not any further treatment. Advanced oxidation processes use Fenton's reagent, hydrogen peroxide, ozone, photocatalysts to produce highly reactive hydroxyl radicals. These reagents may be used in the presence of UV light, catalyst, ultrasound to enhance the oxidation process. [a]
AOPs may be classified broadly into four groups: photocatalytic processes, the Fenton reaction-based processes, ozone-based, and other less explored advanced oxidation processes which may include processes such as activated persulfate, ionizing radiation or electron beam technology. Typical AOPs are shown below:

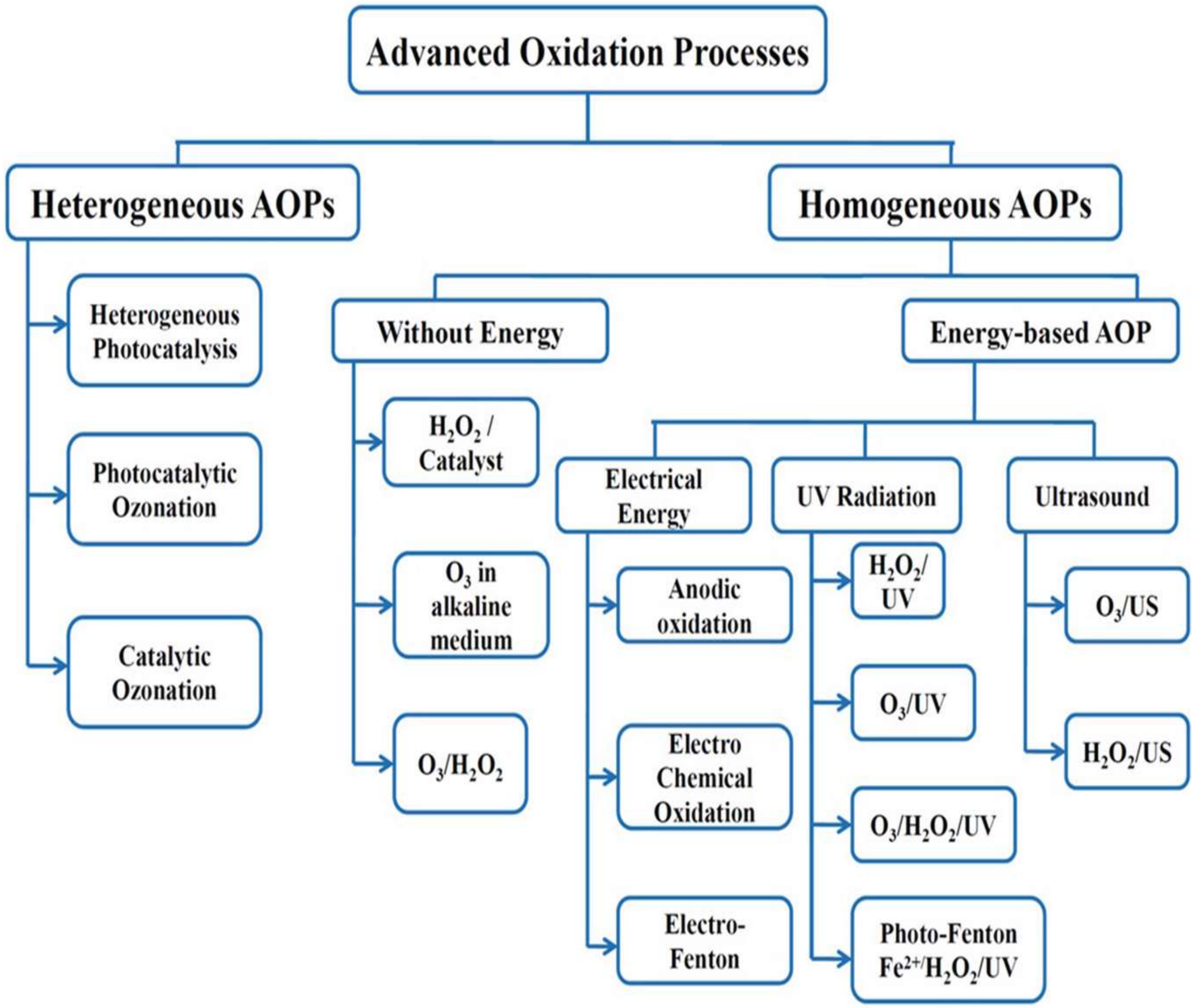


Figure 2: Classification of Advanced oxidation processes (Tijanietet al. 2014)

1.2 Photocatalysis and Photocatalytic Materials

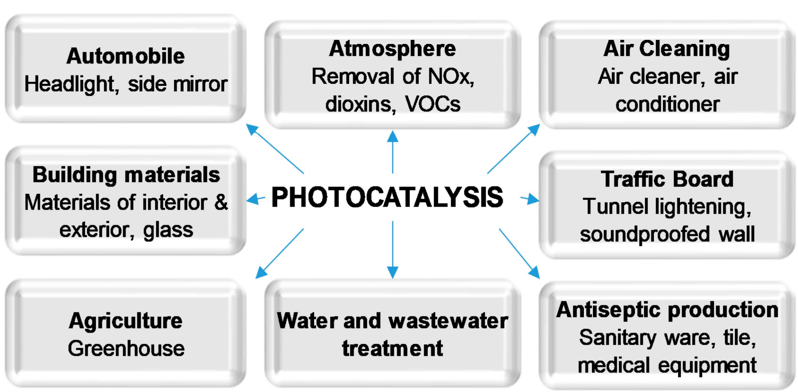
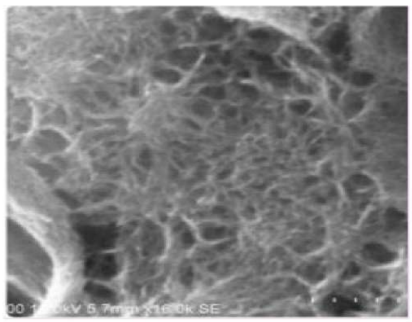


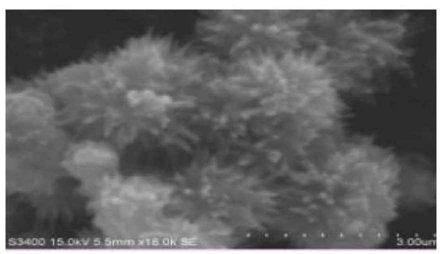
Figure 3: Various Applications of Photocatalysis

Photocatalysis is a process in which a substance called a photocatalyst, when exposed to light, catalyzes a chemical reaction. Photocatalytic materials are substances that can act as photocatalysts. These materials can use light energy to break down pollutants in water, such as organic compounds and bacteria. Photocatalytic materials have a wide range of applications, including air purification, self-cleaning surfaces, and waste water treatment.

1.3 Types of Photocatalytic Materials



(a)



(b)

Figure 4: SEM image of TiO_2 and ZnO catalysts (https://doi.org/10.1016/j.sajce.2020.11.004)

There are many different types of photocatalytic materials available, each with their own unique properties and mechanisms of action. Some of the most commonly used photocatalytic materials include:

1. Titanium dioxide (TiO_2): One of the most widely used photocatalytic materials, TiO_2 is known for its high photocatalytic activity and stability. It is commonly used in air purification and waste water treatment.

1. Zinc oxide (ZnO) and Iron oxide (Fe_2O_3): These widely used photocatalytic materials, known for their high stability under visible light.

2. Silver (Ag): Silver is known for its high photocatalytic activity and high stability, and additionally, it can be used in the form of nanoparticles.

2. Mechanisms of Action of Photocatalytic Materials

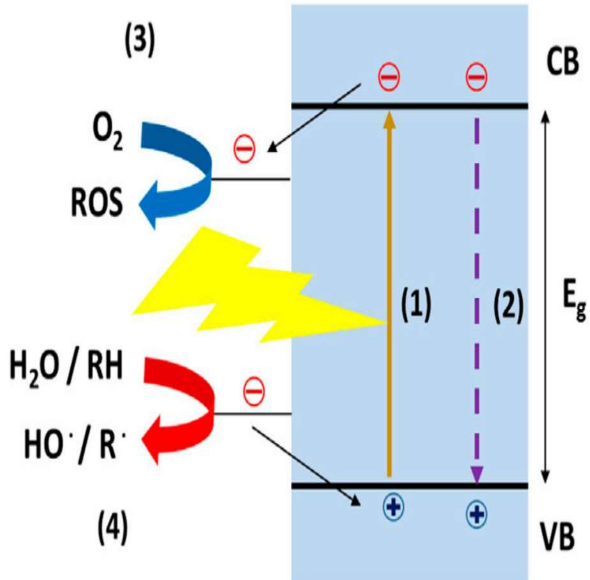


Figure 5: General mechanism of photocatalysis (https://doi.org/10.3389/fceng.20)

Photocatalytic materials are materials that can catalyze chemical reactions when exposed to light. In the context of waste water treatment, photocatalytic materials are used to break down pollutants and contaminants in water using light as a source of energy.

One of the most common mechanisms of photocatalysis is the oxidation of pollutants and contaminants through the generation of hydroxyl radicals (OH•). This process can be represented by the following equation:

$TiO_2 + h\nu \rightarrow TiO_2(h+e-)$,

where TiO_2 is the photocatalyst, hν is the light energy, and $TiO_2(h+e-)$ represents the photocatalyst in its excited state, with a hole (h+) and an electron (e-).

When the photocatalyst is in its excited state, the hole (h+) can react with water to generate hydroxyl radicals (OH•):

$h^+ + H_2O \rightarrow OH\bullet + H^+$

These hydroxyl radicals are extremely reactive and can then go on to oxidize pollutants and contaminants in the water.

Another mechanism of photocatalysis is the reduction of pollutants and contaminants. This process occurs when the electron (e^-) generated during the photocatalytic process is used to reduce pollutants and contaminants. This can be represented by the following equation:

e^- + Pollutant → Reduced Pollutant

3. Treating Waste-water using Photocatalytic Materials

In waste water, there are a variety of pollutants that can be present, including organic compounds, inorganic compounds, and microorganisms.

Organic compounds are a common class of pollutants found in waste water. These include compounds like phenols, which are found in industrial wastewater, and dyes, which are found in textile wastewater. Photocatalytic oxidation is one of the most common methods used to degrade organic compounds in waste water. The hydroxyl radicals (OH•) generated during photocatalysis can oxidize organic compounds like phenols, as shown in the following equation[b]:

Phenol + OH• → Phenoxide + H_2O

Similarly, dyes can be oxidized by the hydroxyl radicals:

Dye + OH• → Oxidized Dye + H_2O

Inorganic compounds, such as heavy metals and dissolved gases, can also be present in waste water. Photocatalytic reduction is a method that can be used to remove these pollutants. The electrons (e-) generated during photocatalysis can be used to reduce pollutants like heavy metals, as shown in the following equation:

Metal ion + e^- → Metal

In addition, photocatalysis can also be used to remove dissolved gases like carbon dioxide, as shown in the following equation:

$CO_2 + e^- \rightarrow CO$

Microorganisms such as bacteria and viruses can also be present in waste water and can cause health hazards. Photocatalysis can be used to inactivate these microorganisms by generating reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2) and hydroxyl radicals (OH•) which can damage their cell walls and inactivate them.

Table 2: ROS generation reactions and standard redox reduction potential (E°) respect to the reversible hydrogen electrode (RHE). (Nosaka and Nosaka (2017))

ROS	**Reaction**	**E^O (V vs. RHE)**
O_2^-/	$O_2 + e^- \longrightarrow O_2^-$	-0.046
HO_2	$O_2 + e^- + H^+ \longrightarrow HO_2$	Not reported

E° vs. RHE = + 0.059×pH, the normal electrode.

H_2O_2	$O_2 + 2e^- + 2H^+ \longrightarrow H_2O_2$ $HO_2 + e^- + H^+ \longrightarrow H_2O_2$	+0.695 +1.44	
HO	$H_2O_2 + e^- \longrightarrow HO + HO^-$ $HO_2 + H^+ \longrightarrow HO + H^+$	+1.14 +2.38	

(E° vs. NHE) where NHE is hydrogen

The end products of photocatalytic reactions in waste water treatment are typically removed through a combination of physical and chemical methods:

- Physical methods include filtration and sedimentation. Filtration can be used to remove solid particles and microorganisms that have been inactivated by photocatalysis. Sedimentation can be used to separate heavier particles from the water.
- Chemical methods include adsorption and oxidation. In adsorption, pollutants are removed from water by binding to the surface of an adsorbent material, such as activated carbon. Oxidation can be used to further degrade the end products of photocatalysis, such as phenoxides and oxidized dyes, into more benign compounds.
- In addition, advanced oxidation process (AOP) like UV/H_2O_2 can be used to degrade the end products of photocatalysis into more benign compounds like CO_2 and H_2O. This process uses UV radiation and hydrogen peroxide (H_2O_2) to generate highly reactive hydroxyl radicals (OH•) that can oxidize a wide range of pollutants.
- Another method is using biological methods like bacteria that can degrade the end products formed by photocatalysis into non-harmful compounds.

4. Industrial Implementation:

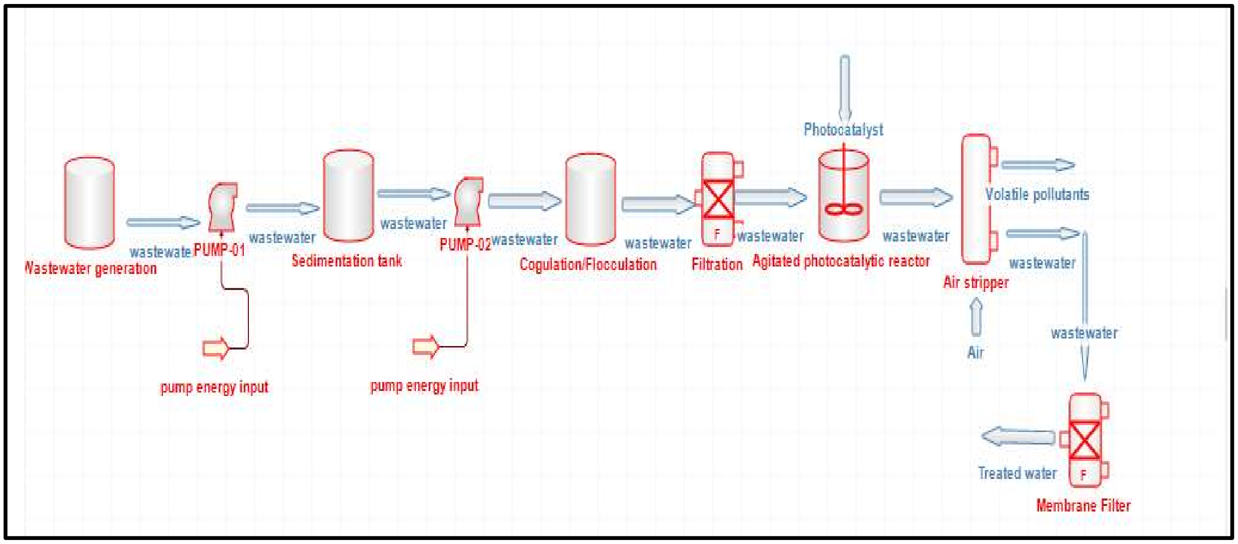


Figure 6: Process Flow Diagram of the concept of a photocatalysis-based wastewater treatment system, created in DWSIM

The industrial implementation of photocatalytic materials for waste water treatment involves several unit operations and equipment. The process can be divided into four main stages:

1. Pre-treatment of waste water: The waste water is passed through a series of physical and chemical processes to remove large particles and dissolved impurities. This includes processes such as coagulation, flocculation, sedimentation and filtration.

2. Photocatalytic reactor design: The reactor design is crucial for the efficient operation of the photocatalytic process. A common reactor design for the treatment of waste water using photocatalytic materials is a fluidized bed reactor. This design allows for a large surface area for the photocatalytic material to come into contact with the waste water, thereby increasing the rate of reaction. Other reactor designs include fixed bed reactors and slurry reactors.

3. Selection of photocatalytic material: The choice of photocatalytic material is important as it affects the efficiency and rate of the photocatalytic reaction. TiO_2 is a commonly used photocatalytic material due to its high stability and low cost. Other materials include ZnO, WO_3 and Ag_3PO_4.

4. Control of process parameters: The process parameters that need to be controlled include the pH of the waste water, the concentration of the photocatalytic material, the intensity of the light source and the flow rate of the waste water. The pH should be maintained between 6-8 for optimal performance of the photocatalytic process. The concentration of photocatalytic material should be maintained at a level sufficient to achieve a desirable rate of reaction, but not so high as to cause a significant increase in the cost of the process.

5. Agitation and mixing: Agitation and mixing are necessary to ensure that the photocatalytic material is well-dispersed and that the waste water is well-mixed. This ensures that all the impurities in the waste water are exposed to the photocatalytic material, thereby increasing the rate of reaction.

6. Post-treatment of waste water: After the photocatalytic treatment, the waste water is passed through a series of physical and chemical processes to remove any remaining impurities. This includes processes such as oxidation, adsorption and membrane filtration.

7. Monitoring and control of the process: The process should be constantly monitored and controlled to ensure that the desired level of treatment is achieved. This includes monitoring the pH, the concentration of photocatalytic material, the intensity of the light source and the flow rate of the waste water.

4.1 Equipment and Industrial Processes

Some of the common equipment and processes used include:

1. Photocatalytic Reactors: The most crucial piece of equipment used in the industrial implementation of photocatalytic treatment of wastewater is the photocatalytic reactor. These reactors are designed to provide an optimal environment for the photocatalytic reaction to take place, by providing adequate light intensity, mixing, and mass transfer. Common types of photocatalytic reactors include slurry reactors, fixed-bed reactors, and fluidized-bed reactors.

2. Agitators: Agitators play a vital role in maintaining the suspended solid-liquid mixture and ensuring proper mass transfer in photocatalytic reactors. Common types of agitators include pitched-blade impellers and marine propellers.

3. UV Light Sources: UV light is the driving force behind photocatalytic reactions, and therefore, UV light sources are an essential component of photocatalytic systems. These light sources can be in the form of low-pressure mercury vapor lamps, medium-pressure mercury vapor lamps, and LEDs. They are used to provide the required light intensity for the photocatalytic reaction to take place.

4. Air Stripping Columns: Air stripping columns are used to remove volatile pollutants from the wastewater. They work by passing the wastewater through a packed bed of a suitable absorbent material, such as activated carbon, while simultaneously providing an upward flow of air. This causes the volatile pollutants to be stripped out of the water and into the air stream.

5. Clarifiers: Clarifiers are used to separate the photocatalyst particles from the treated wastewater. They work by allowing the treated water to flow through a series of inclined plates or tubes, where the heavier particles settle to the bottom, while the

clarified water flows out of the top. Common types of clarifiers include inclined plate settlers and tube settlers.

6. Pumps: Pumps are used to transfer the wastewater from one piece of equipment to another, and to provide the necessary pressure for the various processes. They can be in the form of centrifugal pumps, positive displacement pumps, or diaphragm pumps.

7. Automation and Control Systems: Automation and control systems are used to monitor and control the various process parameters, such as pH, temperature, and flow rate. They can also be used to control the operation of the various pieces of equipment, such as the agitator and the UV light source.

4.2 Process control parameters and control equipment:

The key process control parameters and control equipment that need to be considered when using photocatalyst (for e.g., Titanium dioxide (TiO_2)) for waste water treatment are as follows[c,d]:

1. Light intensity: TiO_2 has high photocatalytic activity under UV light. It is important to control the light intensity to ensure that it is sufficient to drive the photocatalytic reaction. Light intensity controllers, such as light meters, UV lamps, and light timers, can be used to control the light intensity.

2. pH: The optimal pH range for TiO_2 is between 5 and 9. pH controllers, such as pH meters, pH probes, and pH adjusters, can be used to control the pH of the water.

3. Temperature: The photocatalytic activity of TiO_2 is not significantly affected by temperature, but it is important to control the temperature to ensure that it is within a range that is comfortable for the microorganisms present in the water. Temperature controllers, such as thermocouples, thermistors, and temperature controllers, can be used to control the temperature of the water.

4. Photocatalyst dosage: The optimal dosage of TiO_2 can vary depending on the specific application and the type and concentration of pollutants present in the water. Dosage controllers, such as pumps, flow meters, and weigh feeders, can be used to control the dosage of the photocatalyst.

5. Retention time: The optimal retention time can vary depending on the specific application and the type and concentration of pollutants present in the water, but typically it can be between 30 minutes to 2 hours. Retention time controllers, such as timers, flow meters, and level sensors, can be used to control the retention time of the water in the treatment process.

6. Recycling of photocatalyst: TiO_2 is a relatively stable photocatalyst, but it can become fouled over time, which can lead to a reduction in photocatalytic activity and treatment efficiency. Recycling controllers, such as sedimentation tanks, centrifuges, and filters, can be used to control the recycling of photocatalyst.

7. Data logging and monitoring equipment: Data logging and monitoring equipment, such as data loggers, sensors, and analysers, can be used to monitor and log data about the process parameters, such as light intensity, pH, temperature, dosage, retention time, agitation, and recycling of photocatalyst.
8. Safety equipment: Safety equipment, such as gloves, goggles, respirators, and emergency shut-off valves, can be used to ensure the safety of the operators and the equipment during the treatment process.

5. Economic Advantages and Challenges

Photocatalytic treatment has several advantages over existing treatment technologies, including:

- High efficiency in removing a wide range of pollutants, including dissolved organics, bacteria, viruses, and heavy metals.
- Low energy consumption and operating costs.
- No generation of secondary pollutants.
- Low land requirements and easy to integrate with other treatment methods.

5.1 Major Engineering Problems

There are several major engineering problems that can arise when using photocatalytic materials for waste water treatment. Some of the most significant include:

1. Low photocatalytic activity: Photocatalytic materials with low photocatalytic activity may not be effective in breaking down pollutants and contaminants in the water. This can lead to a lack of treatment efficiency and a higher outlet BOD.[e]
2. Light intensity: Photocatalytic materials require light to function, so the intensity and quality of light used can have a significant impact on the efficiency of the treatment process. Poor lighting conditions can reduce the photocatalytic activity of the material and decrease treatment efficiency.
3. Stability: Photocatalytic materials can be degraded over time, which can lead to a decrease in photocatalytic activity and treatment efficiency.
4. Cost: Photocatalytic materials can be relatively expensive to produce, especially at an industrial scale, which can make the treatment process cost-prohibitive.
5. Scalability: Scaling up the process of waste water treatment with photocatalytic materials can be difficult and requires careful consideration of the unit operations and equipment used.

6. Maintenance and cleaning: Photocatalytic materials can become fouled over time, which can lead to a reduction in photocatalytic activity and treatment efficiency. This requires frequent cleaning and maintenance of the equipment.
7. Recycling of photocatalyst: Photocatalytic materials can be expensive to produce, so recycling the photocatalyst is an important consideration in order to minimize costs and make the process more sustainable.
8. Safety: Handling and disposal of photocatalyst and the pollutants can be difficult and dangerous, appropriate safety precautions must be taken to avoid harmful exposure to pollutants and photocatalyst.
9. Environmental Impact: The photocatalytic waste water treatment process can have an impact on the environment, for example, the generation of by-products, the release of pollutants and the use of energy.

These problems can be mitigated by choosing the appropriate photocatalytic material, optimizing the process conditions, using appropriate equipment and by properly maintaining the equipment. Additionally, ongoing research and development efforts are aimed at addressing these issues and improving the efficiency and effectiveness of photocatalytic waste water treatment.

6. Conclusion:

Overall, photocatalytic materials have the potential to revolutionize waste water treatment by providing a cost-effective and efficient alternative to conventional methods. They can be used in a variety of industrial processes and unit operations. However, more research is needed to fully understand the mechanisms of photocatalytic materials and to develop more effective and efficient methods for their use in waste water treatment. The challenges need to be addressed by chemical engineers through proper design, optimization, and control of the process and equipment.

7. References:

a. Ameta R, Solanki MS, Benjamin S, Ameta SC. Photocatalysis. InAdvanced oxidation processes for waste water treatment 2018 Jan 1 (pp. 135-175). Academic Press.

b. Ahmed S, Rasul MG, Martens WN, Brown R, Hashib MA. Heterogeneous photocatalytic degradation of phenols in wastewater: a review on current status and developments. Desalination. 2010 Oct 15;261(1-2):3-18.

c. Leong S, Razmjou A, Wang K, Hapgood K, Zhang X, Wang H. TiO2 based photocatalytic membranes: A review. Journal of Membrane Science. 2014 Dec 15; 472:167-84.

d. Carbajo, J., Bahamonde, A., & Faraldos, M. (2017). *Photocatalyst performance in wastewater treatment applications: Towards the role of TiO_2 properties. Molecular Catalysis, 434, 167–174.*

e. Wang L, Ali J, Zhang C, Mailhot G, Pan G. Simultaneously enhanced photocatalytic and antibacterial activities of TiO2/Ag composite nanofibers for wastewater purification. Journal of Environmental Chemical Engineering. 2020 Feb 1;8(1):102104.