International Journal of Engineering and Science Invention (IJESI)
ISSN (Online): 2319-6734, ISSN (Print): 2319-6726
www.ijesi.org ||Volume 13 Issue 9 September 2024 || PP 82-98

A Review: Photocatalysis Used for Degradation of Textile Dye from Industrial Wastewater

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Abstract:
Rapid industrialization and globalization lead to water pollution. Annually, thousands of tons of dye effluents from various textile industries are discharged into the water stream. Therefore, cost-effective and environmentally friendly techniques are needed to remove dye effluent from industrial water. In this regard, a photocatalytic process of dye degradation is needed to cure for water pollution from dyes. Recently, photocatalysts like TiO_2, ZnO, SnO_2, g-C_3N_4, MoS_2, ZnS, CeO_2, ZrO_2, etc. are arising as advanced materials to degrade dye effluents from wastewater. Researchers have developed the concept of nanocomposite, doping, core shell, etc. to improve the photocatalytic performance of metal oxide and sulfide. This review focuses on the classification of dyes, the impact of dyes on aquatic life as well as human beings, and their removal methods from industrial wastewater. Furthermore, type of photocatalyst and factor affecting photocatalytic degradation of dye are discussed in detail.
Keywords: *Dye, pollutants, degradation, photocatalyst, semiconductor*

Date of Submission: 09-09-2024 Date of Acceptance: 25-09-2024

I. Introduction:

Population growth and economic development lead to contamination of water resources. Numerous health issues are arising due to the exposure of tons of wastewater from industries into water resources like rivers and seas **[1].** Mostly industries release pollutant like aromatic hydrocarbons, dyes, and antibiotics such as 4 nitrophenol, methyl blue dye, malachite green dye, etc. **[2].** Textile industries play a major role in polluting water by releasing dyes and other waste into the water stream **[3].** Some dyes, like methylene blue, crystal violet, etc., are non-degradable in nature, and some are soluble in water, like reactive and acid dyes. These types of dyes have carcinogenic behavior and cause various types of disease in humans, water animals, and crops when released with water as effluents. In addition to the toxic behavior of dyes, these also reduce light penetration through water, resulting in a decrease in oxygen levels for the biodegradation of microorganisms **[4].** Thousands of tons of dyes and antibiotics are released into water resources yearly. According to the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD), direct and basic dyes showed the highest level of toxicity **[5].** Therefore, the removal of dyes from wastewater is critically important for the environment. Over the last few years, different methods of dye removal from wastewater have been used, such as biological, reverse osmosis, chemical precipitation, coagulation, membrane filtration, adsorption on activated carbon, solvent extraction, ozonation, ion exchange, adsorption, and electrochemical destruction **[6].** However, these types of techniques convert non-biodegradable waste into sludge, which further requires another advanced process for purification. Therefore, a process named ‘advanced oxidation process' is required for the treatment of wastewater in which a photocatalyst is used for the removal of dye completely or partially from water. Photocatalytic processes are efficient enough to degrade pollutants like organic, inorganic, and microbial agents into biodegradable compounds or convert them into water and carbon dioxide **[7].** Commonly used photocatalysts are TiO_2, ZnO, SnO_2, SnO_2, MoS_2, and g-C_3N_4 because of their large surface area, ease of production, nontoxicity, and high stability in aqueous solutions **[8].** Moreover, the improved light absorption capability, electronic structure, excited lifetime, and favorable shape and size of metal oxide and sulfide for photocatalytic processes make them a good catalyst for dye effluent removal from wastewater **[9].**

This review mainly focuses on nanotechnology used in waste water treatment, various types of dyes, photocatalysts, hazard of wastewater containing dyes on aquatic and human life, and impact of various parameters such as light intensity, loading amount, pH, etc. on photocatalytic degradation of dye effluents.

II. Classification of dye:

Dyes, which are substances specifically designed for coloring purposes which are utilized to add color to a wide range of materials, including paper, plastic, textiles, and several other objects, as shown in figure (1). These substances are organic compounds that possess colour and can dissolve in water. A dye is employed to impart colour to items with which it is included. Dyes are extensively employed in several industries, including textiles, printing, and cosmetics, to provide colour to items and materials, etc. **[10].** Dyes can be classified based on their chemical structure, colour properties, and application methods. Dyes can be categorized into several groups, which include**: [11-13]**

2.1. Categorization of dyes according to their source:
2.1.1. Organic dyes
2.1.2. Artificial dyes
2.2. Dyes can be classified based on their chemical structure.
2.2.1. Azo dyes
2.2.2. Anthraquinone dyes
2.2.3. Triphenylmethane dyes
2.2.4. Phthalocyanine dyes
2.2.5. Quinoline dyes
2.2.6. Nitroso dyes
2.2.7. Indigoid dyes
2.2.8. Natural dyes
2.3. Categorization of dyes according to the technique of application:
2.3.1. Direct dyes
2.3.2. Reactive dyes
2.3.3. Acid dyes
2.3.4. Basic dyes
2.3.5. Disperse dyes
2.3.6. Vat dyes
2.3.7. Pigments
2.4. Classification of dyes based on solubility:
2.4.1. Dyes that dissolve in water
2.4.2. Dyes that dissolve in oil
2.4.3. Dyes that dissolve in solvents
2.5. Categorization of dyes according to their application:
2.5.1. Dyes used for coloring textiles
2.5.2. Dyes used for coloring food
2.5.3. Dyes used for coloring ink
2.5.4. Dyes used for coloring leather
2.5.5. Dyes used for coloring hair
2.5.6. Dyes are used for medical purposes.
2.6. Various categories of dyes based on structure and application are discussed here: **[11-14]**

2.6.1. Synthetic dyes: These dyes, which are artificially created chemical compounds, are utilized to provide color to various objects, including paper, plastic, food and textiles, foods. Due to their greater uniformity ,lower cost, , and wider range of colors, synthetic dyes are often preferred over natural dyes**.**

2.6.2. Catalytic or basic dyes: Acrylic fibers are predominantly dyed with water-soluble basic dyes. Basic dyes are employed in conjunction with a mordant to color cotton, linen, nylon, polyester, acrylic, and modacrylic materials.

2.6.3. Acid dyes: These are water-soluble dyes that can be used to color protein fibers such as wool, nylon and silk. Because of acidic environment usually with acetic or citric acid, these are referred as acidic dyes. The acidic groups of acid dyes enable them to create a strong bond with the amino groups in protein fibers, resulting in the production of vibrant and intense hues. They have exceptional performance when used with wool and silk fabrics.

2.6.4. Direct dyes: These dyes have the ability to color cellulose fibers directly, without the requirement of mordants. These dyes are applicable for dyeing viscose, cotton, silk, nylon, wool and other fabrics. Although these dyes have a somewhat fast lightfastness, they exhibit low brightness and poor washing fastness.

2.6.5. Mordant or chromium dyes: Chrome dyes have an acidic tendency. Sodium or potassium bichromate is added to the dyebath or applied after the dyeing process to interact with them. This is done to acquire the chrome's binding activity. They are predominantly utilized on wool that has undergone treatment with chromium dyes to enhance colourfastness.

2.6.6. Reactive dyes generate chemical compounds through their reaction with fiber molecules. These dyes are applied either from neutral solutions that are then alkalized in a separate procedure or from alkaline solutions.

2.6.7. Disperse dyes: These dyes are insoluble in water. The finely pulverized pigments are available in two variants: a viscous paste and a soluble powder when mixed with water. These particles impart color to the fibers by dissolving within them.

2.6.8. Sulfur dyes: can be rendered soluble by utilizing caustic soda and sodium sulfide. In order to ensure the color penetrates the fiber, dyeing is carried out at an elevated temperature with a significant amount of salt. After dyeing, the cloth undergoes oxidation, which can be achieved through exposure to air or the application of chemicals, in order to obtain the desired colors. Thoroughly washing eliminates surplus chemicals and dyes. The primary application of these dyes is on cotton and linen due to their rapid responsiveness to light, washing, and perspiration.

2.6.9. Nitro dyes: Generally, nitro dyes consist of polynitro derivatives of phenols in which at least one nitro group is located orthogonally or paragonally to the hydroxyl group. In terms of industry, their significance is limited due to the sluggish rate at which the colors change. Examples of compounds in this class include picric acid (2,4,6-trinitrophenol), and naphthol yellow S (2,4-dinitro-1-naphthol-7-sulphonic acid).

2.6.10. Pigment Dyes: Pigment dyes, although not technically classified as dyes, are commonly used to color fabrics made of cotton, wool, and synthetic fibers due to their excellent resistance to fading in light.

2.6.11. Fluorescent dyes: The fluorescent dye emits visible light when it is exposed to energy sources. They are commonly employed to generate vibrant, luminous hues for highlighters, paints, inks, and other items that require high visibility.

2.6.12. Solvent dyes: These dyes have the ability to be dissolved in various organic solvents such as acetone, toluene, and benzene. They are commonly employed to impart pigmentation to plastics, waxes, petroleum-derived products, and other substances that include hydrocarbons.

2.6.13. Vat dyes: Vat dyes are unable to directly color textiles since they do not dissolve in water. Nevertheless, they can be chemically transformed into a soluble form by an alkaline solution, allowing them to attach to textile strands.

III. The toxicity of dyes:

Particles called textile dyes are used to provide clothes and fabrics with long-lasting color. Commercial dyes can be categorized using a variety of criteria, including color, composition, and application techniques. The Society of Dyes and Colorists established the Color Index (CI), used to categorize dyes [**15].** It lists dyes by giving them a 5-digit CI number based on their chemical structure, if known, after giving them a generic name based on their use and color **[16].** Another way to categorize dyes would be by solubility. Direct, basic, acidic, metal complex, reactive, and mordant dyes are examples of soluble dyes. Conversely, azoic, sulfur, dispersion, and vat dyes are included in the category of insoluble dyes **[17].** Dyes are categorized as azoic, anthraquinonic, hetero-polyaromatic, nitro, aryl methane, indigo, and so on according to the functional group that makes them up**.** Two categories are found in dyes: chromophores and auxochromes. The set of atoms known as chromophores is what gives dye its color. An electron-withdrawing or-donating substitute called aurochrome is necessary for the intensification chromophores' color. The most significant chromophores are azo (-N=N-), carbonyl (-C=O), methine (-CH=), and nitro (-NO_2) while most significant auxochromes are amine (-NH3), carboxyl (-COOH), sulfonate (-SO3H), and hydroxyl (-OH) [**18].** Any dye's color intensity is determined by its auxochrome group count. Because dye molecules absorb light at a specific wavelength in the visible portion of the solar spectrum, they take on color **[19].** The discharge of wastewater containing dyes into water bodies has a worst effect on the life of aquatic organism. Hazardous effect of textile dyes industries on health and environment are shown in figure (3) .Several studies have demonstrated that dyes discharged as effluents can break down into carcinogenic and mutagenic by-products. Furthermore, these dyes have a long half-life in the environment if improperly handled. The dyes affect the environment by absorbing and reflecting sunlight into waterbodies, which further diminishes

the photosynthetic activity of marine plants. The presence of minuscule amounts of dyes in water, despite their remarkable presence, degrades the transparency and quality of water bodies, including rivers**,** lakes, and other bodies of water, ultimately causing damage to the aquatic ecosystem. Long-term human exposure to colored wastewaters has been linked to a variety of immunological suppression, cardiovascular, respiratory, central nervous system, and neurobehavioral symptoms, including leukemia, lung edema, vomiting, allergy, salivation, and cyanosis, as shown in figure (2) **[20-21].** The degradation of the environment is undoubtedly one of the biggest issues facing both developed and developing countries today. Ineffective regulation, improper use of natural resources, and lack of concern for the environment have a negative impact on the environment. In recent years, many scientific studies have been used as an important tool for improving new treatment techniques and even in the implementation of protocols and environmental measures that are environmentally responsible.

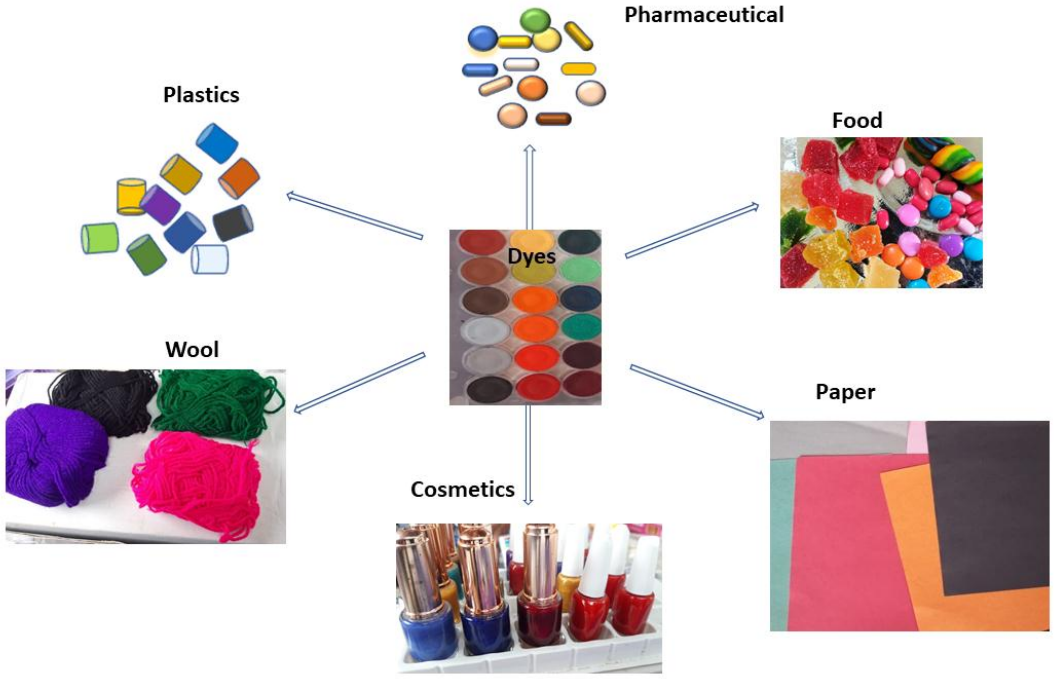

Figure 1: Usage of dyes in different sector

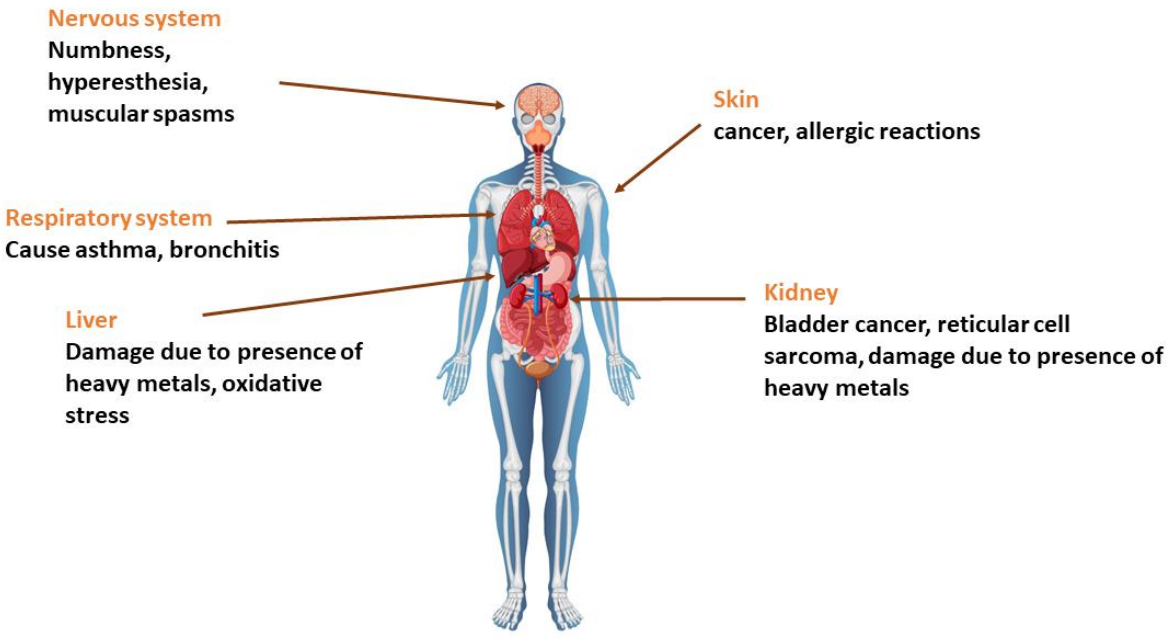

Figure.2. Impact of wastewater containing dyes on human health (Human body picture adopted from www.freepik.com)

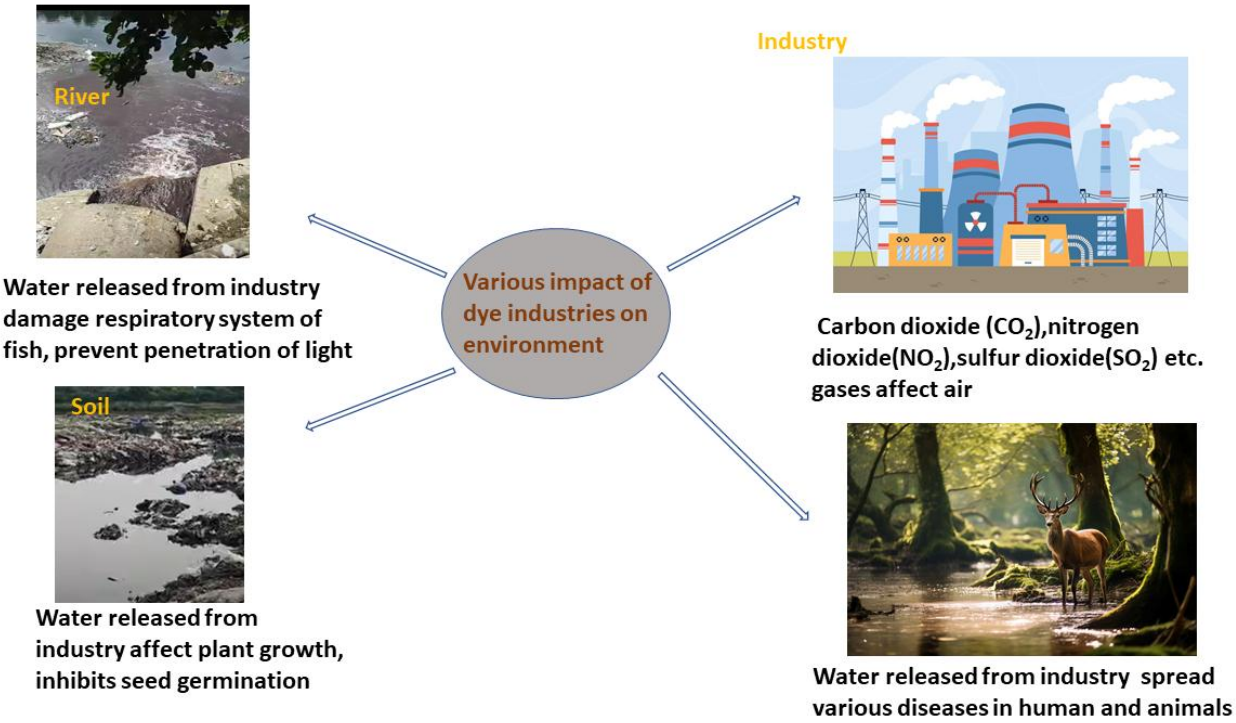

Figure 3: Hazardous effect of textile dyes industries on health and environment **(**Industry and dear picture adopted from www.freepik.com)

IV. Treatment of Waste Water:

One of the most vital resources in the world for humans as well as for animals and plants, is water. The quick advancement of science and technology has led to numerous sectors, including chemical, petrochemical, pharmaceutical, mining, semiconductors, and microelectronics, being established. Every one of these industries requires a large volume of water for their functioning, and the water that comes out of them is tainted with harmful organic contaminants. Furthermore, the need for clean water for domestic use and drinking is growing along with the world's population. The hydrosphere is becoming more and more contaminated with inorganic and organic matter due to the high population density and degree of industrialization. Furthermore, a great deal of pesticides and herbicides are used in agriculture to meet the world's expanding demand for food supplies, which exacerbates the lack of clean water. More significantly, environmental regulations are tightening daily to maintain a human-friendly environment. In order to address the issue of water pollution and comply with strict environmental rules, scientists and researchers have been working to develop new water purification processes or enhance those that already exist. On the other hand, people are becoming more conscious of the global problem of water contamination and are beginning to understand that water is no longer an endless resource. The perfect water treatment method is one that completely mineralizes all organic pollutants without creating any harmful by-products.

In general, contaminated water can be cleaned using biological, mechanical, thermal, chemical, or physical treatments, or a combination of these. The type and amount of contaminants in the water, determine which water treatment method is best. Water treatment studies have two main goals: Water treatment studies have two main goals: reducing the amount of pollutants in the discharge stream to meet environmental regulations, and enhancing water quality.so that it can be used in the pharmaceutical, semiconductor, and microelectronic sectors. Furthermore, selecting the specific technique is heavily influenced by how cost-effective the water treatment method is. Currently, a number of wastewater treatment techniques are being used, with differing degrees of success. Every procedure has certain drawbacks. Rather than totally eliminating the pollutants, air stripping procedures, which are frequently employed to remove volatile organic pollutants from aqueous media, only move the pollutants from the water phase to the air phase. The removal of organic contaminants from wastewater is traditionally achieved by the use of granular activated carbon (GAC) adsorption. Adsorption requires the regeneration or incineration of the used carbon, which turns the contaminants that have been adsorbed into harmless by-products **[22].** Two destructive oxidation and water disinfection processes used in the water treatment

process are ozonation and chlorination. Trihalomethanes, for example, are potentially hazardous disinfection by-products that might arise from a chlorination-based water disinfection method. Since ozonation prevents the development of disinfection by-products linked to chlorinated organic compounds, it is seen to be a superior method of treating water than chlorination **[23–24].** Although burning organic trash was common, it is not the best method for treating water since burning many organic dangerous compounds can release other harmful substances into the atmosphere. Many of the drawbacks of the conventional wastewater treatment process have been thought to be addressed by a relatively recent class of technologies known as advanced oxidation processes (AOPs), which sprang from research studies.

4.1. Water treatment using conventional methods:

The first textile industry effluent treatment facilities relied on independent thermal processes, with wastewater usually evaporated in a brine concentrator and then treated with an evaporation pond or a brine crystallizer. While the created materials are either disposed of in a landfill or recovered as valuable by-products of salt production, Reuse is made possible by collecting the condensed distillate water. Reverse osmosis, nanofiltration, and other membrane-based filtration technologies have been incorporated recently to reduce the volume of water entering the brine concentrator, which lowers the energy usage. Another name for this multi-stage or collective water treatment is Zero Liquid Discharge (ZLD**) [25].** The steps of the traditional water treatment process are depicted in figure (4).

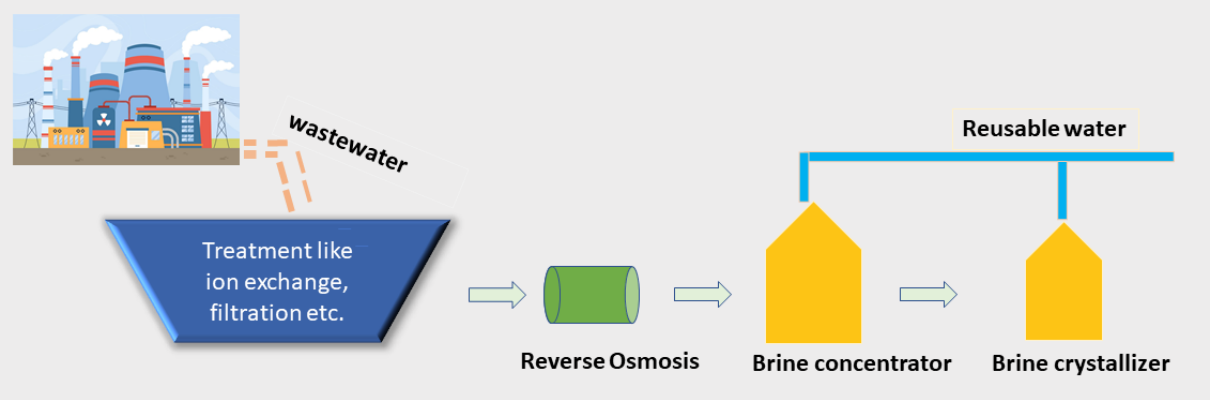

Figure 4: Schematic illustration of conventional water treatment method

4.2. Nanotechnology used in photocatalysis:

A relatively new and developing branch of technology, nanotechnology works at the nanoscale, or less than 100 nm. Since Richard Feynman's 1959 lecture, "There's Plenty at the Bottom," it has been a subject of study since the turn of the century. We have achieved ground breaking discoveries in every field of study thanks to nanotechnology. Materials exhibit distinct properties at the bulk scale and unique properties at the nanoscale, where their surface to volume ratio increases with size **[27].** When used as a catalyst, this surface to volume ratio feature increases efficiency over bulk materials. In the energy industry, we can improve the efficiency of producing hydrogen by employing nanomaterials as a catalyst in the water splitting process **[28].** Nanotechnology for clean water is revolutionizing the commercial landscape in both rich and developing nations when it comes to pollution, particularly water pollution. The amazing qualities of nanomaterials include their photocatalytic nature, high surface area, high aspect ratio, high reliability, electrostatic properties, ability to compress without compromising surface area, pore volume, magnetic capabilities, short intra-particle diffusion distance, and hydrophobic and hydrophilic properties, among others **[29].** The interaction between nanoparticles and pollutants is regulated by their high surface to volume ratio. We can tackle the current issue with traditional water filtration methods thanks to nanotechnology. Water microbes are only a few thousand nanometers in size, but standard purifiers only use bacteria. Nanotechnology-based purifiers can combat viruses without the need of chemicals, electricity, or high-temperature crushing. The emergence of organic–inorganic nanostructured composites is a new development in the use of nanoparticles in photocatalysis. A variety of materials for catalytic technologies are produced by the interactions of organic and inorganic molecules **[30].**

4.3. Process of photocatalysis:

The term "catalysis" refers to a hybrid term made from the word's "photo" and "catalysis." By lowering the activation energy of a reaction, a material can accelerate it through a process known as catalysis without changing or being consumed in the process**.** In photocatalysis, a material called a photocatalyst is activated by light (photons) to alter the rate of a chemical reaction without getting consumed **[31].** Chlorophyll, a common

natural photocatalyst, powers the photocatalysis process of photosynthesis in plants **[32].** When a semiconductor (artificial photocatalyst) is exposed to light with an energy greater than the semiconductor band gap (hv > Eg), an electron (e-) from the valence band (VB) is excited into the conduction band (CB), leaving behind a hole (h+) in the VB. As a result, the generated e-/h+ couples have the ability to move to the semiconductor's surface and take part in redox processes (fig. (5)) [**33].** The three parts of a semiconductor photocatalyst are the reduction co-catalyst, oxidation co-catalyst, and photo-harvester. Co-catalysis with semiconductors facilitates charge transfer and inhibits charge recombination. The structure just has a photo-harvester and a reduction co-catalyst since the majority of the semiconductor photo-harvester also acts as an oxidation site, eliminating the requirement for an oxidation co-catalyst **[34].**

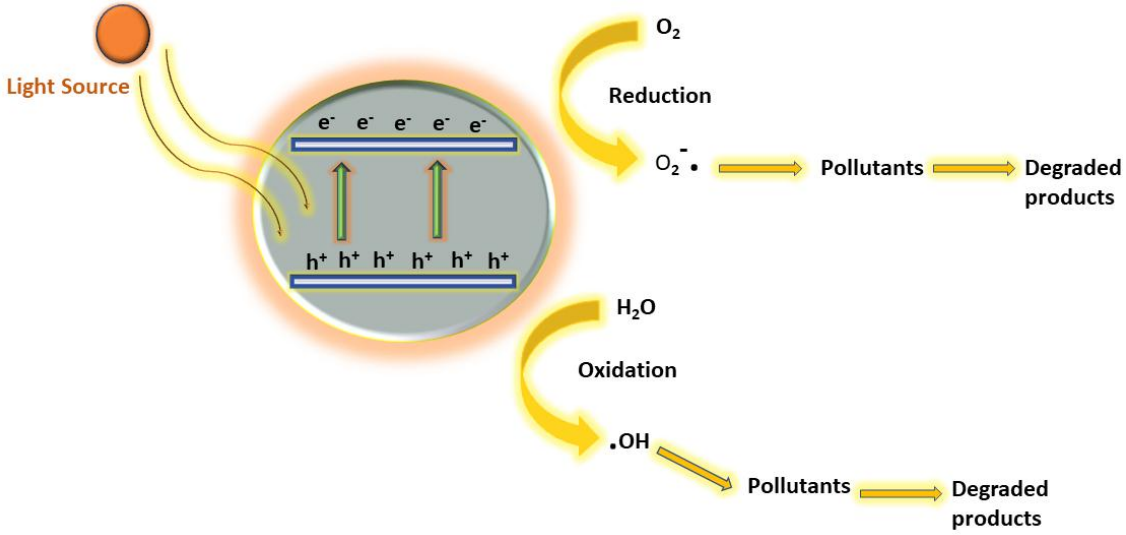

Figure. 5: Schematic illustration of redox reaction involved in photocatalytic process of degradation of organic contaminant**.**

4.4. Photocatalysis in the Treatment of Wastewater:

Recent advancements in chemical water treatment methods have resulted in an enhancement of the oxidative breakdown process for dissolved or distributed via photochemical or catalytic techniques in aqueous media. These are known as Advanced Oxidation Processes, or AOPs, and as of late, they have been viewed as a viable substitute for traditional water treatment methods. AOPs primarily depend on the production of oxygen-containing intermediates with a brief half-life, such as superoxide ($\bullet O^{2-}$) and hydroxyl radical (OH•**) [35].** The hydroxyl radical is an easily produced, highly reactive, and nonselective reagent. In order to oxidize things, these procedures combine conventional oxidants (H2O2 and/or O3) with extra stimuli like ultraviolet (UV) light to produce extremely reactive species (hydroxyl radicals). Saturated organic compounds and insecticides, which are exceedingly challenging to handle with other methods, can be oxidized by AOPs.

Among the AOPs, photocatalytic oxidation has drawn a lot of interest recently as a substitute for treating water contaminated by hazardous organic pollutants because of its many special qualities and ability to be sensitized by semiconductor photocatalysts like TiO2/UV. Using low intensity UV-A light and reusable catalysts, photocatalysis is different from other AOPs because it doesn't require the addition of any additional strong oxidants. Furthermore, as the UV-A wavelength region makes up around 3% of the solar spectrum that reaches Earth, photocatalysis can potentially benefit from sunshine **[36].** The following is a summary of the benefits of photocatalysis over other traditional techniques: **[37-38]**

i. Nearly all organic contaminants in wastewater, including those that are resistant to hydroxyl radicals like carbon tetrachloride, can be mineralized.

ii. Because the degradation products (carbon dioxide, water, and mineral acids) are safe for the environment, this process is referred to as "green technology."

iii. No additional oxidant is needed because atmospheric oxygen serves as an oxidant.

iv. The photocatalysts are inexpensive, safe, stable, inert chemically and biologically, insoluble in most situations, and reusable.

v. Photocatalyst activation is achieved by low energy UV light, although solar light can also be employed.

vi. For intermediate and large capacities, it is economically equivalent to the activated carbon adsorption method.

The basis of a photocatalytic reaction is the exposure of semiconductor particles, such as titanium dioxide (TiO_2), to UV light with energy greater than the semiconductor's band gap, which is defined as the space between the

semiconductor's valence and conduction bands. When sufficient light is applied to a semiconductor, holes and electrons will form inside the semiconductor. These holes and electrons have the ability to oxidize or reduce the organic and inorganic molecules that have been adsorbed **[39].**

Due to its intriguing benefits for purifying water, semiconductor photocatalysis has drawn a lot of attention in the past 20 years. This is because it was first used by Fujishima and Honda (1972) to divide water into hydrogen and oxygen using a UV-irradiated TiO_2 electrode **[40].**

A semiconductor photocatalyst and an appropriate light source are the two primary components of a conventional photocatalytic process that decide whether the reaction can be carried out effectively or not.

4.5. Types of photocatalysis

The process of photocatalysis involves a subsequent creation of electron-hole pairs under photon stimulation. Photocatalysis is an approach to chemical solar energy conversion that can be used to eliminate organic contaminants that are hazardous and refractory from our environment. It is also a viable means of producing clean hydrogen energy through water splitting. The discovery of the "Honda-Fujishima effect" on photo-electrochemical water splitting by titania (TiO_2) electrodes is credited with popularizing photocatalytic activity **[40].** Since then, photocatalysis process have been used in various applications such as air cleaning, self-cleaning surfaces, water cleavage, and the treatment of home and industrial wastewater **[41-42].** TiO_2 is used to create self-sterilizing tiles for hospital operating room walls. Industrial water that has been contaminated by microorganisms and photosynthesis is treated using sand-supported TiO_2. Anticancer activity, super-hydrophilic materials for automotive mirrors, and the creation of sound-proofed walls are on the verge of commercialization that are based on photocatalysis. [**43-44**].

In order to remove pollutants from air and water streams, photocatalysis has been the subject of extensive research during the last few years. Low operating costs, ambient conditions, and total annihilation of chemicals and their intermediate compounds make the photocatalytic process an advanced technique for the removal of industrial effluents from wastewater.

4.5.1. Homogeneous photocatalysis:

The reactants and the photocatalysts are in the same physical state during homogeneous photocatalysis**.** The two homogeneous photocatalysts that are most frequently utilized are Fenton systems ($Fe+/H_2O_2$) and ozone. The OH° is the reactive species and is essential to the dye degradation process.

The following reaction sequence is how hydroxyl radicals are produced in the Fenton reaction**: [45-46]**

$Fe^{2+} + H_2O_2 \rightarrow OH° + Fe^{3+} + OH-$

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + 2OH° + H+$

$Fe^{2+} + OH° \rightarrow Fe^{3+} + OH-$

In photo-Fenton type processes, additional sources of OH radicals should be considered: through photolysis of H_2O_2, and through reduction of Fe3+ ions under UV light:

$H_2O_2 + h\nu \rightarrow OH° + OH°$

$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH° + H+$

Numerous operational parameters, such as pH, UV light intensity, and the initial concentration of hydrogen peroxide, influence the efficacy of Fenton type operations. This method's main benefit is its ability to use sunlight. Therefore, costly UV lights or any other electrical energy are not needed for this method to work**.** It is discovered that this technique works better than the other photocatalysis techniques. The primary disadvantage of the procedure is that low pH levels are necessary for the breakdown of contaminants **[47].**

4.5.2. Heterogeneous photocatalysis:

Both the reactants and the catalysts are in distinct physical states during heterogeneous catalysis. A wide range of reactions, including dehydrogenation, partial or complete oxidations, deuterium-alkane isotopic exchange, hydrogen transfer, water detoxification, metal deposition and removal of gaseous pollutants, etc., are included in the field of heterogeneous photocatalysis **[48].** Titanium dioxide (TiO_2), metal organic frameworks (MOFs), cadmium sulfide, cadmium selenide, etc. are some examples of heterogeneous photocatalysts.

4.5.3. Semiconductors photocatalysis:

Photocatalytic reactions on semiconductors have found many uses in the last few years, including antibacterial, self-cleaning, and air-cleaning materials. The reactions, which start with electrons and holes generated by photons with energy larger than semiconductor band gaps being adsorbed, are generally acknowledged as promising techniques. The holes' potent capacity to expel electrons from both organic and inorganic contaminants causes the polluted materials found in effluents to completely degrade. Since there is an energy gap, or band gap, between the top of the full valence band and the bottom of the unfilled conduction band, a semiconductor is by definition nonconductive in its undoped ground state. Because of this, electron transit between these bands can only happen when there is a noticeable energy shift. Because of their favorable electronic

structure, light absorption capabilities, charge transport attributes, and excited-state lifetimes, semiconductors are very effective as photocatalysts **[49].**

4.5.3.1. Titanium dioxide (TiO_2) as photocatalyst:

Tuneable physicochemical properties of semiconductor metal oxide make them a promising material for photocatalytic processes. Among other metal oxide semiconductors, TiO_2 has gained much attention due to its low cost, strong chemical stability, non-toxic behavior, high electron affinity, and environmental friendliness **[50].** Crystallite size, surface area, morphology, particle size, energy band gap, etc. are various parameters that decide the photocatalytic performance of a TiO_2 photocatalyst. Among these parameters, the wide band gap (3.2 eV) of TiO_2 lies in the UV region, which is only 3% of the solar spectrum and therefore limits the catalytic performance of TiO_2 **[51].** Doping of metal or non-metal, co-doping, and composite formation with other catalysts are some methods to enhance the light absorbance capability and hence the photocatalytic performance of TiO_2. Ravindra Haribhau Waghchaure et al. reported recently that only 0.8 gm/L of 5% Fe-doped TiO_2, synthesized via the coprecipitation method showed 96.45% of eosin yellow dye degradation [52]. Anna Grzegorska et al. successfully synthesized the TiO2/Ti3C2 composite via the solvothermal method and showed 96% of acetaminophen degradation within 60 minutes [**53].**

4.5.3.2. Zinc oxide (ZnO) as photocatalyst:

ZnO is an n-type semiconductor that is an alternative to TiO2 due to its high absorption capacity in the solar spectrum and nearly the same band gap as that of the TiO2 photocatalyst **[54].** In the photocatalytic process, electron hole pairs are generated due to light incident on the photocatalyst surface. These generated electron hole pairs recombine and hinder the efficiency of photocatalysts to degrade dye effluents from wastewater. Doping, co-doping with metals or non-metals, and heterostructure formation significantly reduce the electron-hole pair recombination rate in ZnO. Yihua Sun et al. synthesized Z-scheme Ti-Ga co-doped ZnO/g-C_3N_4 to degrade 95% of methylene blue dye within 105 minutes under visible light illumination [55]. Hamdah S. Alanazi et al. recently reported Gd/N co-doped ZnO prepared using the coprecipitation method. Removal efficiency of methylene blue reached up to 87% under UV light and 93% under direct sunlight [**56].**

4.5.3.3. g-C_3N_4 as photocatalyst:

g-C_3N_4 is a semiconductor compound that absorbs light in a visible region. The unique properties of high chemical stability, tuneable band gap, ease to produce, and eco-friendliness make g-C_3N_4 an excellent material for photocatalytic processes **[57].** However, low surface area, fast recombination rate of electron hole pair, and inadequate light absorption hinder the photocatalytic performance of g-C3N4 [58**].** Heterojunction formation and element doping significantly improve g-C3N4's photocatalytic performance. N.A. Chopan et al. showed in their recent study that synthesized polypyrrole-decorated ZnO/g-C_3N_4 S-scheme photocatalyst removes 99% of rhodamine b dye within 60 minutes [59]. Various metals were doped in g-C_3N_4 and have been studied for degradation of methyl orange dye under visible light. Copper doped g-C_3N_4 showed the highest degradation efficiency of 62% in comparison to iron- and nickel doped g-C_3N_4**[60].**

4.5.3.4. Molybdenum Disulfide (MoS_2) as photocatalyst:

MoS_2 with a 2D nanostructure exhibits strong photocatalytic activity towards dyes and other industrial waste. The two-dimensional MoS_2 layered structure, where the bulk is formed by the individual layers piled on top of one another by weak van der Waals forces. Each layer is made up of two planes of S atoms and one plane of Mo atoms **[61].** The modest indirect bandgap (1.3 eV) of bulk MoS_2 makes it unsuitable for charge carrier separation and insufficient to trigger photocatalytic processes. However, 2D nanostructures like nanosheets change the band gap of MoS_2 from indirect (1.2 eV) to direct (1.9 eV), which enhances the photocatalytic activity of MoS_2 photocatalyst **[62].** Therefore, low-dimensional MoS_2 is thought to be a potential photocatalyst that responds to visible light. Based on symmetry and number of layers, MoS_2 has four types of crystal structure named 1T, 1H, 2H, and 3R. **[63].** The most prevalent phase in the MoS_2 crystal structure is 2H, or semiconductor, which shows encouraging photocatalytic activity. Investigating MoS_2 photocatalytic activity using 1T/2H crystal structures is the main focus of current research. By using a different phase engineering procedure, the 2H (semiconductor) phase can become the 1T (metallic) phase. Using a scalable hydrothermal process, Dongdong Li1 et al. synthesized 1T/2H MoS_2 phase. This demonstrates that the addition of 1T/2H-MoS_2 raises the photocatalytic degradation rate toward methylene blue dye from 19% to 98% in comparison to 2H MoS_2 **[64]**. Recently, reported that in 1T/2HMoS_2 ,1T phase intermixed with 2H phase and investigated for photocatalytic degradation of methylene blue dye, showed 90% removal efficiency, as reported by D. Mouloua et.al. **[65].**

V. Influential elements:

However, there are a few issues with semiconductor materials, such as aggregate formation, which subsequently causes a surface area decrease and a large band gap inhibiting efficient flow of electrons. As a result, creating novel photocatalysts is crucial. When designing a visible light-responsive photocatalytic system, three key factors must be taken into account. Initially, the band structure of the photocatalysts is determined by their electrical structure as well as their optical characteristics. Visible light should be absorbed by the semiconductor material. Additionally, the band gap needs to be sufficiently small for photons of visible light to stimulate it. The semiconductor's crystallinity is another important characteristic**.** The last key surface character is a property that is crucial to surface chemical reactions, such as photogenerated holes and electrons, which cause oxidation and reduction, respectively. Furthermore, additional elements, including the morphological architecture, selection of material, and surface attributes, need to be considered. The selection of appropriate semiconductor material is particularly significant since it establishes the level of the visible light response and, as a result, the total effectiveness.

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5.1. Energy band gap:

The photocatalysts' band structure has a significant impact on the efficiency of dye degradation. The semiconductor photocatalyst's ability to accept photons at a certain wavelength depends on the energy of the band gap. Conversely, band gap energy specifies the range of wavelengths to be obtained and the photonic efficiency throughout the processes leading to photocatalytic degradation. Moreover, the CB and VB's band edge placements are another important aspect that affects the efficiency of photocatalysis. The locations of the band edges define the thermodynamic constraints for the light-induced reactions and can specify the resulting material's redox capability, holes and electrons. If the VB's location is more favorable than the redox potential pair, oxidation takes place, and a reduction process is sparked by further negative **CB [66].** Figure. 2. depicates semiconductors' band gap and band edge locations. The band gap shouldn't be too big (>3.0 eV) to enhance dye degradation because it will be activated by the neither be too tiny (<1.3 eV) to reduce the high likelihood of an electron-hole pair in visible light. Bandgaps between 1.3 and 3.0 eV have generally been reported to be appropriate for photocatalytic reactions **[67].** Cobalt doping in TiO_2 significantly reduced the band gap and improved the photocatalytic degradation of 2,4-dichlorophenol.Removal efficiency of 2,4-dichlorophenol recached up to 98.5% in the presence of cobalt doped TiO_2 [**68].**Carbon doping in ZnO reduces the band gap from 3.1 to 2.8 eV, which plays a major role in the removal of methylene blue dye from wastewater **[69].**

5.2. Engineering of band gaps:

To allow for the absorption of semiconductor photocatalyst, the material must have a tiny band gap. Large band gap energy materials can be doped to improve their responsiveness to light. Dopants like metal ions or non-metal elements creates a level that is formed in the space between VB and CB to allow electronic states transition. The electronic change in band Compared to band-to-band semiconductor material, these states need less energy. Photons of visible light can therefore stimulate electrons and cause redox reactions. Adsorbed dye molecules, on the other hand, act as antennae to absorb light energy inside the system of degradation. The adsorbed dye's excited states provide electrons for injection, photochemical reactions can be induced by introducing molecules into the semiconductor material's CB **[70].**

5.3. Material stability and charge mobility:

Other crucial concerns that must be addressed include enhancing charge mobility and charge carrier lifetime examined in photocatalysts for semiconductors. Since electron-hole pairs produced by photolysis are recombinant, therefore extending their mobility and the period of separation is important. These elements can be investigated in a number of ways to produce heterojunctions by utilizing new morphologies to combine several semiconductors, including the introduction of defects into the substance, as well as porous architecture. Additionally, there are some effective methods for improving surface reactions and charge mobility in the semiconductor material's structure, for instance, combining conductive substances like graphene or dye compounds to enhance the transparency. In order to promote charge transfer at the dye-dye contact, photocatalysts, unique coatings, or surface treatments can be used. The main requirements for photocatalysts are stability in aqueous solutions and resistance to corrosion. Yongmei Xiaet al. reported that efficient charge separation in $BiOI/Cu_2O$ composites significantly improved the photocatalytic performance towards methylene blue dye degradation [**71].** A. Jenifer et al. synthesized zn doped V_2O_5 nanoparticles by the sol-gel method. Charge carrier lifetime significantly increased due to Zn doping, which further helped in degrading MB, MV, and MG dyes [**72].**

5.4. Loading of catalysts:

The pace of reaction and overall dye degradation are significantly impacted by the mass of a photocatalyst. As the loading of the photocatalyst increases, more electron-hole pairs are created, leading to an

increased degree and speed of deterioration. But according to reports **[73], the** quantity of catalyst won't have a direct impact on the rate of deterioration. Once a specific threshold is reached, a rise in rate ceases and may even go down as a result of the quantity of active radicals that are generated using a catalyst's photoexcitation being reduced . Generally speaking, the more catalyst there is, the more sites that are active. Nevertheless, following the ideal concentration, catalyst particles begin to clump together, reducing the catalyst's surface area and lowering the quantity of accessible, active sites. Turbidity rises with increasing photocatalyst loading **[73].** Moreover, suspension increases prevent radiation from flowing through solution, hence lowering light penetration into the reaction mixture and increasing light scattering, which also lowers the quantity of active surface sites, which further lowers the rate of dye deterioration from wastewater **[74].** According to Abdullah A. Al-Kahtani , as the amount of catalyst increased, the degree of degradation first increased up to a certain level and then decreased. Removal efficiency of rhodamine dye from wastewater first increased due to an increase in catalyst dosage up to 0.25 gm and then decreased **[75].** The reduction of photocatalytic performance was linked to lower penetration and more light scattering due to a high density of photocatalysts per unit volume [**76].**

5.5. Adsorption of dye:

Dye adsorption on a photocatalyst's surface is reliant on the binding affinity and electrostatic interactions between the dye molecule and the photocatalyst surface. Reasonable dye molecule adsorption on a photocatalyst's surface is beneficial for degradation efficiency, depending on how well adsorption and photocatalysis work together. The process of dye molecules adhering to the photocatalyst surface is crucial for effective deterioration through photocatalysis. Positive Dye molecules are able to adsorb more easily on the surface of the component of the photocatalyst that is negatively charged **[77].** Mean opposite charged surface leads to more adsorption and hence more removal of dye from wastewater. Highly effective adsorption-based photocatalysts can both degrade and adsorb dye at the same time. Positively charged methylene blue dye strongly adsorbed on the surface of the TiO2 photocatalyst, as reported by Fadhel Azeez et al. **[78**].

5.6. The loading of dyes:

Electrostatic interactions and binding affinity between the catalyst and dye molecule decide the amount of pollutant adsorbs on the surface of a photocatalyst**.** The rate of photocatalytic degradation of dye is affected by dye coverage on the catalyst surface. As the concentration of dye increases, more active sites covered by dye ions result in a decrease in the production of OH radicals on the surface of the photocatalyst and also decrease the penetration of light entering the solution **[79].** These effects lead to a decrease in dye degradation efficiency. Recently, it has been reported that as the initial acid blue 74 dye concentration increased from 20 ppm to 60 ppm, more dye molecules covered the surface of the catalyst, preventing interaction with photons and hence reducing the rate constant from 0.046 to 0.016 min^{-1} **[80].**

5.7. The intensity of the light:

Photons of light provide the energy necessary for photocatalysis. The degree of lightness has a vital part in dye degradation. In the VB, electron-hole pairs are produced when they receive photons with energy equivalent to or higher than the band gap. The impact of light intensity on wastewater containing reactive yellow azo dye has been investigated. A recent review showed that low light intensity increases the rate of dye degradation, and after an optimal intensity of light, further increase doesn't affect the rate of degradation [**81]**. According to the findings, the removal efficiency increases as the intensity increases, up to 70 mW/cm for CR dye and up to 90 J/cm for BP4B **[82].**

5.8. Temperature:

An experimental study examining the relationship between temperature and the pace at which organic colors degrade has been researched. Numerous studies have been reported on how temperature affects the activity of photocatalysis. Raising the temperature initially favors the rate of degradation, but an optimal temperature of around 80^0C often causes more recombination of electron-hole pairs and the adsorbed reactant species' desorption, hence lowering photocatalytic degradation efficiency [**83].** The Arrhenius equation, for which this finding is consistent, according to reference, the apparent first-order rate constant Kapp rises linearly with exp(-1/T) **[84].**

5.9. Solution pH:

In waste water containing dye, pH influences various parameters, including surface charge, particle size, valence band position, conduction band position, and radical generation on the surface of the photocatalyst **[85].** The rate at which dyes photodegrade is significantly influenced by pH. The solution pH significantly alters the surface charge of photocatalyst particles. Consequently, the amount of dye's adsorption on the surface of the photocatalyst changes, which alters the rate of reaction. A single pH value does not work for all dyes because each color molecule correlates differently with changes in the surrounding pH. Additionally, industrial wastewater effluent usually contains dye mixtures from several wet processes that vary in pH. As a result, one dye molecule cannot accurately depict the characteristics of wastewater. The electrostatic interaction between dye molecules

and the photocatalyst surface is determined by the pH of wastewater containing dye. A low pH value results in low efficiency of dye degradation, whereas a pH range of 5–10 results in increased activity of the photocatalyst, and a pH of above 10 results in further decreases in efficiency **[86].** It indicates high dye degradation efficiency in alkaline media, although some azo dyes are more efficient in acidic media. Holes and hydroxide ions (OH-) can combine to form hydroxyl radicals on the catalyst's surface. These radicals are believed to be the primary catalyst for the process of photooxidation. F. Han reported the effect of pH on the photocatalytic degradation of acid orange 7 dye. The results showed that the reaction rate is much higher in an acidic condition than a basic one. The removal efficiency of dye was 96%, 87%, and 40% under initial pH of 3.0, 5.0, and 9.0, respectively **[87].** According to Vasiljevic ZZ et al., a higher pH value favors the rate of dye degradation. Removal efficiency increased up to 97% at pH value 11, which is higher than that of value at pH 3 **[88].**

Table: Some examples of photocatalytic degradation of dyes

Photocatalyst	**Source of light**	**Dye used**	**Catalyst/dye amount**	**Degradation Efficiency (%)**	**Time taken in degradation(minutes)**	**References**
C doped ZNO	15 W Sylvania UV-A lamp	Fluorescein dye, Rhodamine dye	100mg,10ppm	99,100	240,120	**89**
rGO/NiO nanocomposites	450 W, Mercury lamp	malachite green	0.005gm,10ppm	96.15	120	**90**
Cu-doped $BaTiO_3$	Discharge lamp (Philips,Colour CDM-R/830)	Methylene blue, Rose Bengal	25mg for MB &40 mg for RB,100ml,10mg/L	98.2,99.4	120,45	**91**
rGO@ZnO	direct sunlight	Methylene blue	20mg,15 ppm	99	120	**92**
$FeMn_2O_4$ nanocomposite	A UV-light)	Congo red, methylene blue	5mg,5.10^{-5} M, 10^{-4} M	83.2,100	40	**93**
NiO/Ag/TiO2 hetereostructure	400 W halogen lamp	Methylene blue	1gm/L,5mg/L	93	60	**94**
magnetized TiO_2-supported SiO_2 nanoparticles	LED lamp	Methylene blue	15%,10ppm	96	75	**95**
CeO_2/GCN nanocomposite	two 200 W xenon lamp	Rose Bengal, Crystal violet	0.01mg,10mg/L	79,76	90	**96**
ZnO/g-C_3N_4 composite	Under visible light	Methylene blue	20mg,5ppm	91.5	120	**97**
Nitrogen-doped titania and molybdenum sulfide nanocomposite	Under visible light	Methylene blue	0.025gm,50ppm	99	150	**98**
MoS_2/g-C_3N_4 heterojunction	Under visible light	Methylene blue	20mg,20ppm	98	105	**99**
1T@2H-MoS_2	Under natural sunlight	Methylene blue	25mg,10ppm	100	5	**100**
Tb:SnO_2	4 UV tubes (18 W each)	Rhodamine b	40mg,	90	70	**101**
SnO_2	fluorescent light source	Sudan black B	15mg,20mg/L	90	100	**102**
(WO3/ZnO) nanocomposite	Under solar illumination	Methylene blue, Rhodamine b	20mg,3ppm	94,85.7	105	**103**

VI. Conclusion:

We discussed that dye degradation from industrial wastewater is needed to prevent their impact on human health and the aquatic environment. Photocatalytic process is an advanced technique among all other techniques of removal of dye effluents from industrial waste water. The photocatalytic process removes dye effluents completely or partially from wastewater, and the catalyst further remains in a state of reuse. However, the capability of a photocatalyst to degrade dye effluents depends on various parameters like loading amount value, light intensity, etc., which are briefly discussed here. In spite of advanced technique, photocatalytic processes also needed some work to enhance their efficiency in the future. Maximizing use of sunlight, understanding the in-depth mechanism of photocatalysts, formation of intermediates, and design of photocatalysts are major issues that future prospective need to be resolved in the future.

Declaration of Competing Interests: The author's declare that they have no known competing financial interests.
Acknowledgements: The authors are thankful to the vice chancellor (Prof Anand Srivastava), NSUT for providing the essential resources required for the research.

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