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# PHOTOCATALYTIC METHODS USED FOR DEGRADATION OF DIRECT YELLOW 12 DYE: A COMPREHENSIVE REVIEW

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## Abstract

*This review article examines various photolytic techniques and parameters for direct yellow 12 dye degradation. It has been thoroughly reviewed how a photocatalyst's structure and physio-chemical characteristics, particularly its absorption capacity and surface area correlate to its photocatalytic activities in the photo-degradation of dyes that contain azo group. The most widely used dye classes for adding color to cotton fabrics are direct dyes. Because of their degraded products, which include aromatic amines, which are thought to be extremely carcinogenic, reactive azo dyes pose a particular environmental and health risk. Because of its stability in both acidic and alkaline solutions, direct yellow 12 dye, also referred to as chrysophenine G, is used in a variety of industrial processes. Direct dye 12 is extremely toxic to both human and animals, and it can result in irreversible eye damage. Previously, effluents containing azo dyes were treated using chemical coagulation or adsorption onto activated carbon. However, conventional techniques primarily transfer pollutants from wastewater to solid waste. Thus, in order to degrade such dangerous dyes, cutting-edge, environmentally friendly techniques must be used. The photodegradation of direct yellow 12 dye by photocatalytic process is regarded as a promising methodology for industrial discharges treatment methods due to its low cost, non-toxic nature, and minimum pollution. Several operational parameters governing the photodegradation of harmful dyes are critical for determining the oxidation rates and efficiency of the photocatalytic system. Our findings revealed that a few fundamental factors influence photodegradation: substrate concentration, photocatalyst amount, pH of the solution, reaction medium temperature, light intensity and duration of irradiation, photocatalyst surface area, oxygen dissolution in the reaction medium, substrate and photocatalyst nature, doping of metal and non-metal ions, and substrate and photocatalyst structure. These outcomes will be useful in identifying the most practical and affordable solutions to degrade direct yellow 12 dye through photocatalytic based degradation processes.*

## INTRODUCTION

Dyes and pigments rank among the most hazardous contaminants that are discharged directly into the environment. Due to their mutagenic, teratogenic, and carcinogenic properties, which even at low concentrations can result in numerous health disorders in humans, including malfunctions of liver, kidney, central nervous system, reproductive system, and brain (Ozdes *et al.*, 2010). Anionic dyes are the most prominent group of dyes which are soluble and are known to cause major health and environmental issues. They are categorized as cationic which are basic in nature, anionic which are direct, reactive and acidic, and nonionic which are in dispersed phase. Due to these factors, dye removal from water and wastewater is a very crucial.

**Dyes pollution and toxicity**

Significant environmental contamination is caused by the persistent presence of harmful organic dyes in industrial effluents from the textile, garment and paper industries (Chiu *et al.*, 2019). Ten to twelve percent of many dyes, including Victoria blue, Caramine Rhodamine B, Indigo Red, Black-T, Rose Bengal, Red 120, Methylene Blue, and Thymol blue, are used per annum in the textile industry; however, during different industrial processes like synthesis and cleaning a major amount of twenty percent is lost and enter into the canal systems according to several studies (Deng *et al.*, 2013, Xu *et al.*, 2010). Due to the damaging effects on marine life and impending carcinogenic effects on humans, dyes discharged from industrial effluents into water body systems must be eliminated (Khan *et al.*, 2024; Kumar *et al.*, 2017). These industrial coloured effluents contained extremely toxic and harmful organic molecules which are difficult to degrade (Chen *et al.*, 2010).

Dyes are even visible in water at low concentrations and pollute aquatic environments (Daneshvar *et al.*, 2003). The major threat is the release of effluents from textile factories into the surrounding environment. It is time-consuming to decolorize them due to their high color and organic content. As a result, dye removal from wastewater is an extremely important task (Wahab *et al.*, 2019). Due to extremely harmful impact of these dyes on human, plants and animals, the discharged of these detrimental substances from industrial wastewater into water bodies must be eliminated (Khan *et al.*, 2024).

The textile industry signifies a global environmental pollution problem because of unplanned release or disposal of contaminated effluents into canals, which has a momentous influence on the quality of clean water assets. This harmful impact of these dyes cause a substantial environmental test for the textile companies. There is a need of time to increase the awareness about the harmful effects of these organic molecules and efforts must be made to remove or degrade these substances from wastewaters (Rafiq *et al.* 2021)

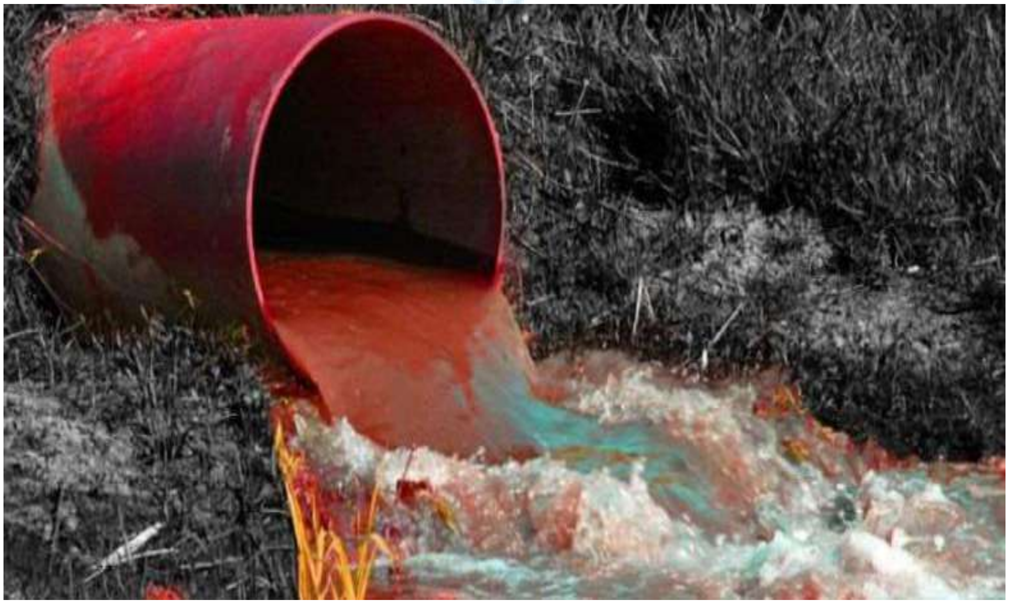

**Figure 1: Water pollution caused by textile dyes**

It is reported that a lot number of contaminants which were released by dying industries were untreatable. There are some organizations which are established to protect the workers working in dye industries from the harmful effects of these dyes effluents. The tested samples from the wastewaters of dyeing factories showed that a lot number of samples had LD$^{50}$ (lethal dose) more than 95%. The highest rates of poisonousness were found in basic and direct dyes, followed by diazo (Deng *et al.*, 2013).

## Classification of dyes

Dyes typically have numerous structural varieties, making complete classification based on a single parameter difficult and useless in terms of practical understanding (Figure 2). Though, dyes are normally classified into many groups and different classes based on their source, structure, and the type of fabric which they are most well-matched, as illustrated in the figure 2.

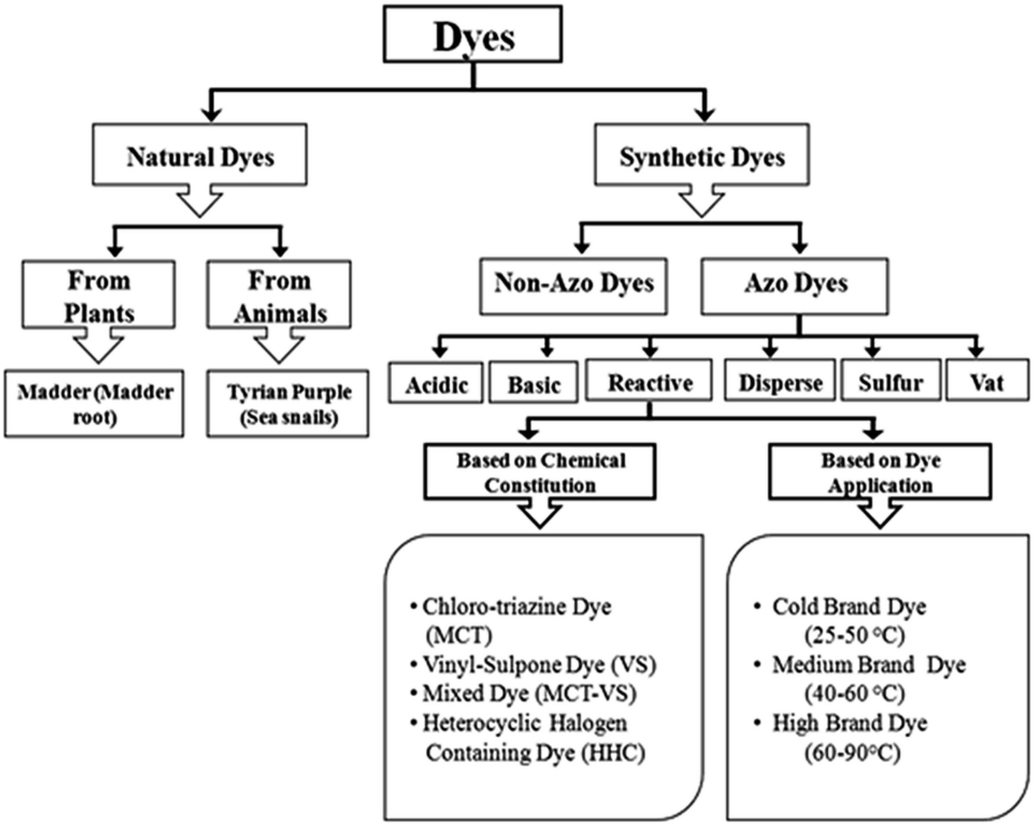

**Figure 2: Classification of different dyes**

In the textile industries most commonly used dyes are azo group containing dyes. These azo pigments share a mutual structure with group –N=N-, which is linked to two carbon atoms on both sides by sp2 hybridization. The azo groups are naturally related to complex aromatic systems, and the resultant stability of these aromatic structures is unsafe to the environment system (Sohrabi *et al.*, 2010; Havuz *et al.*, 2010). Furthermore, they possess amphoteric properties because they contain additional sulfoxyl, carboxyl, hydroxyl, or amino functional groups. The chemical activity of these structure is largely depending on the pH of the system, the dyes will be anionic in which acidic group is deprotonated, while the cationic form the amino group will be protonated, or non-ionic (Zaharia and Suteu, 2012).

Acidic dyes are the most common among them, while basic dyes are cationic in environment, direct dyes are called functional dyes, on the other hand disperse dyes are non-ionic. There are large classes of dyes which are being classified on the basis of their structure. The functionality of these dyes are also mainly depends on their structure (Robinson *et al.*, 2001).

Acidic dyes are mostly applied on the fabric that contain nitrogenous group, or they comprise the acidic structure, this is the reason these dyes are called acidic while the basic dyes are those which produce cations in solution form and they commonly applied to the acrylic fabric. On the other hand, the other kind of dyes which are direct dyes have large applications in textile industries. They consist of ionic salts and electrolytes and the association of these dyes with fabric is mostly associated with electrostatic forces (Christie, 2001). Disperse dyes exhibit low water solubility. These dyes have the ability to interact with polyester chains and produce dispersed particles. The strength of association between fabric and disperse dyes can be different depending on the variety of fabric on which these dyes are applying. The reactive dyes are largely employed on cellulosic fibers. They have capability to form covalent bonds with protein fibers and nylon. Cellulosic fibers are dyed with sulfur to produce dull colors. They bear enough fastness in most of the cases, but also fade quickly when exposed to chlorine. The dyes which are not faded even when they come in contact with chlorine are vat dyes. (Golob & Ojstrsek, 2005). The class and its characteristics are described in Table 1.

**Table 1: Classes and properties of different dyes**

| **Dyes** | **Properties** |
|---|---|
| Direct dyes | Soluble in water |
| Basic dyes | Brighter dyes, soluble in water |
| Acidic dyes | Soluble in water |
| Sulphur dyes | containing sulfur or |
| Reactive dyes | Soluble in water, anionic compounds and major dye class |
| Vat dyes | chemically complex, water-insoluble |
| Dispersive dyes | Insoluble in water |

### Direct Yellow 12 Dye

The direct yellow 12 dye belongs to anionic class of dyes (Figure 2). This direct yellow 12 dyes have vast application in different industries due to its chemical structure which provide him excellent stability in basic as well as acidic solutions. Thus direct yellow 12 dye are being used by textile industries for the processing of jute, leather, silk and wool. It is also being used for the dyeing of cotton and textile products as well as ink manufacturing and paper producing industries. These dyes also have biological applications in veterinary medicines and dermatology (Khaled *et al.*, 2009).

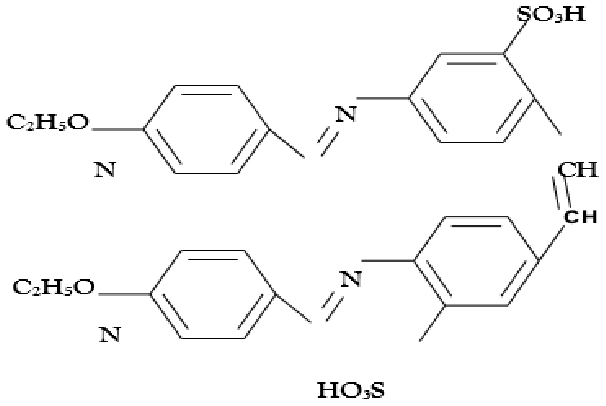

Figure 3

Direct Yellow 12 dye has been described as an extremely toxic dye for the environment, humans and animals, with the potential to cause permanent eye injuries (Ozmihci and Kargi 2006). It has high tinctorial strength and a reddish yellow hue (Sanghavi & Ranga, 2019) (Table 2).

**Table 2: Main characteristics of Direct Yellow 12 Dye**

| Colour Index No. | Synonym | Formula | M.W ($g/mol^{-1}$) | λ max in nm |
|---|---|---|---|---|
| 24895 | Chrysophenine yellow | C30H26N4O8S2 Na | 680.70 | 65 |

## Dyes treatment methodologies

In recent years, treating or degrading the harmful dyes and pollutants has become very difficult and a tedious process (Naseem *et al.*, 2018). Several strategies have been employed to deal with this specific issue, such as membrane filtration (Wang *et al.*, 2018), ozonation (Aziz *et al.*, 2018), removal by ion exchange method (Wahab *et al.*, 2019), bioadsorption (Chen *et al.*, 2010), adsorption (Naseem *et al.*, 2018), catalytic reduction (Anaraki & Ejhieh, 2015), photocatalytic degradation (Borandegi *et al.*, 2015), biological or aerobic treatment (Ejhieh and Samani, 2013), and the absorption process is typically preferred due to its cost effectiveness and efficiency (Shirzadi and Ejhieh, 2017).

However, disadvantages such as less efficient in absorption, inadequate pollution removal, and reduced mechanical firmness of adsorbents impede effective pollution removal (Martinez *et al.*, 2019; Salimi *et al.*, 2018). Photodegradation of pollutants has become highly prevalent in recent years (Nasrollahzadeh *et al.*, 2018). Photocatalytic degradation is required for the successful removal of harmful organic contaminants from wastewater, which is critical to ecological and environmental safety. Photocatalysis, an advanced oxidation process, has recently gained popularity for water remediation (Ozmihci and Kargi, 2006).

The phenomenon of photocatalytic water splitting by employing ultraviolent light source on a TiO2 electrode was also a milestone (Ghahfarokhi *et al.*, 2015). This discovery caused the usage of heterogeneous catalysis technique to cope with the prevailing degradation issue. Researchers have focused heavily on the photocatalytic properties of inorganic semiconductors (Guillard *et al.*, 2003). A lot of researcher focused their research to study the photocatalytic phenomenon for the treatment of harmful dyes presents in industrial wastewaters and evaluated the efficiency of these processes. In order to modify the performance and working of titanium photocatalyst a comprehensive research was done by Akbal in 2005. This study was planned to enhance the photocatalytic degradation efficacy of titanium oxide. The finding of this study depict that the structure, size and nature of photocatalyst is very significant for the degradation of harmful pollutants and dyes from wastewaters. (Akbal, 2005).

A number of studies explored a variety of photocatalytic methods being used for treating the dyeing industrial waste samples, containing dyes pigments and other harmful pollutants (Ikram *et al*., 2021). The current study investigates from literature the most suitable options for the degradation of azo dyes and their products in wastewaters. The article focuses on the fundamental essential variables affecting dye photocatalytic decolorization through different photocatalysts. Different parameter effecting the performance of these processes were assessed and investigated thoroughly to study the treating efficacy of these photocatalytic phenomenon.

Adsorption is now the preferred and most effective dye removal technique because it is used to remove a wide range of dyeing materials, including the treatment through biological method and by using activated carbon. However, each of these techniques has some drawbacks, for example the adsorption by activated carbon convert the harmful dyes from liquid to solid phase. The other drawback is that the biological processes are very difficult to control and sometimes these processes cannot degrade the dyes completely, resulting in increased total treatment costs due to the need for additional treatment (Reza *et al*., 2017). Conventional chemical, biological and physical processes for treating textile dye-containing wastewater have also some disadvantages like generation of harmful byproducts and non-economical.

**Photocatalytic degradation**

Photocatalytic degradation is a very effective process in which different dyes and many other harmful contaminants present in industrial wastewaters and canals are being treated by the help of different type of photocatalysts containing semiconductor materials. In this process sunlight is being absorbed by the catalyst and this light source helps in degrading the toxic dyes as well as other harmful effluents from wastewater to make them clean. This degradation is far more efficient and economical as compared to the other already available classical methods (Zhang *et al*., 2018, Li *et al*., 2018). This photocatalysts can degrade a large number of dyes in very short period of time and irradiation. During these photocatalytic treating processes, no harmful by products of dyes are formed, thus make it very affordable and efficient method (Najeeb *et al*., 2021).

The main phenomenon of photo degradation of dyes contaminants involves the generation of reactive hydroxyl species, these hydroxyl radicals help in oxidizing the harmful organic molecules and convert these harmful substances into harmless molecules like CO2 and H2O and some other non-toxin inorganic structures. This manuscript reviews the degradation of harmful dyes by implying photocatalytic methods using solar and some other high intensity light sources like UV irradiation. The degradation of dyes is influenced by both reaction temperature and light intensity. The other important parameters which influence the performance of catalytic process are surface area, particle size, and usage of co-catalyst. Synthetic dyes are commonly used in food technology (Slampova *et al.* 2001), the textile and leather industries (Sakthivel *et al.* 2003), photoelectrochemical cells (Haferlach *et al.* 2008) and medicine (Wrobel *et al.* 2001).

Modern oxidation technology is gaining popularity for the treatment of harmful dyes. For the degradation of harmful pollutants and dyes present in waste from different fabric and chemical industries, photocatalysis is the most feasible option which help in treating a large range of environmental contaminants and dye stuffs. This process is very economical as well as eco-friendly for the degradation purposes. There is need to extensively study the photocatalysis process and parameters which effect the performance of this photocatalytic system to enhance the efficiency of degradation of all the dyes and other effluents being released into our environmental system and contaminate it. In order to improve the photocatalytic degradation process it is required to focus on the photocatalysis process by using different type of photocatalysts. These photocatalysts can be synthesized from a large range of elements which possess photolytic properties like transition metals, metalloids and noble metals.

During this process different kinds of doping materials can also be studies to further improve the degradation efficacy at large scale dye treatment which will benefit us to improve the quality of our environmental system (Koe *et al.*, 2020).

Several operational parameters effect the entire photodegradation process which involve the adsorption of dye molecule on the surface of specific photocatalyst and decomposition of these dyes into harmless molecules (Ikram *et al.*, 2020). These different parameters effect the performance of the photocatalytic process. Extensive study has been done on the optimization of different parameters which are pH of the system, concentration of substrate, photocatalysts and dyes, irradiation time, doping materials, temperature and effect of pro-catalysts (Raza *et al.*, 2020), For example in some photocatalytic process the photodegradation efficiency decreases as the initial dye concentration increases (Lee *et al.*, 2017). Semiconductor based photocatalysts used in the photocatalysis are also very useful for the remediation of harmful dyes (Seyedi *et al.*, 2018).

Currently, there are a lot of treatment methods are being employed for the elimination of toxic dyes from wastewaters including the chemical treatment methodologies. In these chemical processes different oxidizing molecules are used which hinder the efficacy of dyes removal from aqueous samples. As compared to this process photocatalysis degradation of dyes with the help of heterogeneous semiconductors as a photocatalysts are very efficient, eco- friendly and cost effective method (Zhang *et al.* 2023).

## Photocatalytic degradation of direct yellow 12 dye

Synthetic dyes are among the most common pollutants found in wastewater today. The main reason behind the toxicity of these dyes lies in the fact that all the industries release their wastewaters into canal system without any biological or chemical treatment. These untreated toxic and harmful substances enter aquatic system and disturb the aquatic life by hindering the sunlight entering into the water which is essential for the natural marine life (Sima and Hasal 2013). Among different dyes methylene blue, methyl orange and rhodamine B are widely studied. Aromatic amines can be produced as a result of dye contamination which are extremely harmful to the human and their environment system (Hickman *et al.* 2018).

These harmful dyes as well as their detrimental byproducts must be degraded and treated before their release into the wastewater system. Scientists and researchers have been struggling in finding the best solution to degrade or remove toxic dyes for the betterment of humanity and environment. The degradation of these dyes by implying photocatalytic processes is very effective and energy efficient. In these processes different kind of photocatalysts are used which help in the catalyzing the dye molecule and break it into simple structures by attacking the most fragile bonding site (Ye *et al.*, 2018). After this process these harmful chemicals go through a series of reaction which convert harmful organic structures into environment friendly small (Saravanan *et al.* 2017). The degradation potential can be foreseen by the structure and physical properties of dye molecule (Isari *et al.* 2018). A lot of research is being done on the photodegradtion of dyes by using visible light and some UV source (Jorfi *et al.*, 2018).

## Degradation of Direct yellow 12 dye by UV Assisted Ozone Process

Investigated the process of photodegradation of yellow 12 dye by using O3 and UV and study the progress by implying the strong analytical technique, HPLC-MS/MS. In this study different factors are studies which can alter the photocatalytic activity of the system. The most prominent factor is pH which significantly affects the degradation potential of the system. The other factors which were investigated during this study were the concentration of dye, time of reaction and reaction temperature which can affects the process of degradation of yellow 12 dye. It was noticed that the removal of colour substances is most effective in alkaline medium as compared to acidic system. During this study ozone and UV were used collectively and observed the upsurge in dye removal. It is also observed that by using these two light sources together the reaction time of degradation reduced significantly. These findings suggested that using UV can reduce the reaction time and dose of ozone. The COD was also decreased considerably by this process (El Nemr *et al.* (2018).

### Photodegradation of yellow 12 dye using UV with semiconductor

Bahrami & Nezamzadeh-Ejhieh conducted a detailed research in (2015) to study the biodegradation of yellow 12 dye by using a UV source with a series of semiconductors. It was observed that the usage of UV enhances the efficacy of degradation process by reducing the reaction time noticeably. HPLC-MS/MS was used in this study to observe the progress of these reactions by measuring the percentage of degradation of yellow 12 dye. The chemical oxygen demand decreased by more than 83% compared to the untreated direct yellow 12 dye concentration. The efficacy of this reaction was also measured at different pH to see the maximum photodegradation rate. The table 3 depicts the rate of colour removal caused by the presence of yellow 12 dye at different rates by applying different pH.

**Table 3: Degradation rate at different pH**

| Photocatalyst | pH | Initial Catalytic Value (g/L) | K (min$^{-1}$) |
|---|---|---|---|
| UV \ TiO2 | 2.1 | 2.0 | 0.0176 |
| | 3.3 | 2.0 | 0.0281 |
| | 3.7 | 2.0 | 0.0254 |
| | 6.2 | 2.0 | 0.0096 |
| | 7.1 | 2.0 | 0.0092 |
| | 9.2 | 2.0 | 0.0129 |
| | 11.3 | 2.0 | 0.0169 |
| | 3.5 | 1.0 | 0.0158 |
| | 3.4 | 3.0 | 0.019 |
| | 3.5 | 4.0 | 0.0320 |
| | 3.5 | 5.0 | 0.0399 |
| | 3.4 | 6.0 | 0.0341 |
| UV\H2O2\TiO2 | 3.5 | 5.0 | 0.0629 |
| | 3.3 | 5.0 | 0.0079 |
| | 3.3 | 5.0 | 0.0041 |
| | 3.5 | 5.0 | 0.0040 |

### Degradation through photocatalytic process of direct yellow 12 dye in the presence zinc oxide

used zinc oxide as a photocatalyst to study the degradation potential against the yellow 12 dye. In this study zinc oxide under the UC source was applied to degrade the yellow 12 dye and observed the efficacy of the system. During this research different factors like pH, reaction temperature, concentration of dye and amount of catalyst were also studied to optimize the best conditions under which maximum degradation was observed. It is observed that the maximum degradation was achieved in alkaline medium (Rao *et al.* (2009).

### Titanium dioxide photocatalyst for the degradation of direct yellow 12 dye

In another important study comprehensively examined the photodegradation of yellow 12 dye present in water sample by using titanium dioxide as a photocatalyst. Solid state dispersion method was used in this study to reduce the harmful yellow 12 dye. The result of these study shows the efficacy of titanium dioxide as a dye degradation. 90% removal of harmful yellow 12 dye was noticed during this study which depicts the importance of this photocatalyst (Nikazar *et al.* (2007).

### Photodegradation of yellow 12 dye using UV, UV+H2O2 and UV+H2O2 +Fe$^{2+}$

Evaluated the photodegradation of three commercial dyes including direct yellow 12 dye, direct red 28, and reactive black by using different type of catalyst under the UV source. The colour reduction and absorbance of yellow 12 dye in contaminated wastewater was observed in this experiment. After 60 minutes of irradiation, reactive black showed 99% removal while and direct yellow 12 dye expressed 98% removal which shows the high efficiency of this photodegradation process (Bali *et al.* (2004).

Direct red 28 had a maximum color removal efficiency of 39% after 50 minutes of irradiation, but increased to 68% after 110 minutes. Comparable mineralization efficacy was 45, 65 and 15%, respectively. While the addition of iron based catalyst to the system significantly improved the color removal, the efficiencies being 95, 90 and 84% for the reactive black dye, yellow 12 dye and react 28 dye only after 5 min of irradiation. The resultant efficiencies of these systems were 98% for 45 min irradiation, 100% for 59 min irradiation and 94% for 88 min irradiation, respectively. However, the bordering advantage was less significant as H2O2 and Fe(II) concentrations improved.

Inspected the photocatalytic reduction of another dye, hodamine B dye by using ferum- titanium oxide photocatalyst which was reinforced on reduced graphene oxide. The degradation efficiency of this system was assessed by the presence of sulphate, nitrate, chloride and phosphate anions. It is studied that the removal efficiency of this system was decreased by the presence of these anions ranging from 90% to 40%. The presence of nitrate decreased the efficiency by 89%, phosphate caused 68% decrease in performance, chloride reduced the efficiency by 80% while chloride caused 40% decrease. This variation in efficiency caused by the extent of light absorption by each anions which effects the efficiency of photolytic degradation. The textile wastewater was tested for its total organic corban which was reduced by 70%, COD reduction was recorded at 60% while average oxidation state and carbon oxidation state shows enhancement in biodegradation. This study showed that the efficiency of this system to remove the harmful dyes from wastewater and also enhancing the quality of waste water by decreasing the toxic contaminates from industrial wastewater (Isari *et al.* (2018).

Conducted a series of experiments on the degradation of some toxic dyes which were present in contaminated industrial effluents. They observed that in real waste water samples collected from the industrial discharge, the efficacy of titanium dioxide was not as much impressive as they were tested in the laboratory water samples. The catalyst and the UV light source were used collectively and studied the degradation of dyes. It was observed that the colour was decreased over the time, BOD and TOC reduction were also seen after more than 24 hours under continuous UV irradiation. The study was very useful to see the potential of one of the best photocatalyst, titanium dioxide under UV light show the reduction of harmful substances in real industrial effluents (Touati *et al.* (2016).

Jorfi (2018) employed the modern analytical tool to investigate the performance of biodegradation process for the removal of toxic dyes from aqueous samples. The study showed the presence of many harmful organic molecules in water samples taken from industrial waste including quinolone, dimethylquinoline, fluoroacetamide, palmitic acid, methylisoquinoline and linoleic acid. These contaminated samples were treated while using photocatalysts containing TiO2 being doped with different elements like lanthanum manganese, molybdenum, and activated carbon for different time duration of irradiation at different pH. With different type of catalysts, the efficiency of dye removal was different ranging from 70% to 95% removal. This study also revealed that the oxidation of contaminants and their intermediates are very important for the complete conversation of harmful pollutants into harmless materials. The colour of wastewater was also improved by utilizing this system (Khan *et al.* 2016).

### Photocatalysts

Photocatalysts are the most important materials which are being used for the degradation of harmful dyes from different kind of wastewaters. There are different kind of photocatalysts which shows different efficiencies depending upon many factors which effect the performance of these photocatalysts. These photocatalysts use the solar energy to degrade harmful and toxic pollutants and making the while process of photodegradation very economical and environment friendly (Khalid *et al.*, 2017). There are many studies reported in literature which shows that photocatalysts can also performed efficiently in degrading long-lasting organic contaminants through light absorption in the water (Pang *et al.* 2016; Hak *et al.* 2018). In the photocatalysis processes the most commonly employed photocatalysts are ZnO and TiO2 which possesses high potential to degrade the dyes from water samples (Han *et al.* 2018).

These photocatalysts, however, have some disadvantages, mainly the wide band in energy gaps, reduced absorption at low light and high recombination rates of photo-induced electrons and holes, which bound their practical application in these methods (Huang *et al.* 2017). A high energy gap value necessitates some extra energy absorption to achieve the charge carrier separation (Michael *et al.* 2019). Furthermore, there is also an option that the holes and electrons present in the photocatalytic system could combine together and become unable to play its important role in the degradation of dyes. This phenomenon can significantly reduce the overall efficacy of the photocatalytic system (Jo *et al.* 2018).

The photocatalysts modification has been the subject of interest of many researchers in an attempt to overcome these challenges. If a doping agent is introduced into a bulk photocatalyst, the electron transfer kinetics are influenced due to the presence of high dipole moments. This enables a larger number of electrons to be transferred from the VB of the photocatalyst to its CB, thus bringing the energy gap value closer (Chiu *et al.* 2019). As witnessed by the low energy gap value, visible light or sunshine can be absorbed more efficiently. As mentioned by Zhang and Jaroniec (2018). Consequently, the nature of the matrix material, as well as the microstructure, size, and form of the composite also affect the performance of the composition (Li *et al.* 2018).

Characterized the photocatalytic capabilities of Fe2TiO5 nanoparticles to degrade toxic dyes in wastewaters. A band gap of approximately 2.16 eV for the mesoporous Fe2TiO5 nanoparticles and good light absorption in the visible region were observed. To assess the photocatalytic performance, we observed how methylene blue faded when exposed to natural sunlight. In this study, attempts were made to identify the conditions for the degradation of methylene blue by changing the concentration of the catalyst, initial concentration of dye and the pH of dye solution. Fe2TiO5 corroded quickly in very high pH condition which possibly results from the higher concentration of OH radicals (Vasiljevic *et al.*, 2020).

The adsorption of the organic contaminants was also different when comparing the different allotropes of the photocatalyst type even though they are photo catalytically active (Lopez *et al.*, 2013). Due to the interaction between metal oxide and support, it is possible to form very small nanoparticles at the active areas of the support. In the study by Unlu *et al.* (2018), this might result in increased the surface area for photocatalyst which act as supportive materials to behave as electron reservoirs. Thus, greater number of pollutants can be decomposed and the rate of recombination of the photo-generate electrons and holes decreases. Graphene, carbon nanotubes, a wide range of biomass, and clay are well-known examples of oxygen-rich support materials.

Classification of photocatalysts depends on the physical and chemical properties of the elements that are used to produce them This includes whether they are noble metals, transition metals or nonmetals or metalloids. There are several noble metals, including gold, palladium, ruthenium, and rhodium. The transition metals include copper, zinc, and titanium, while the non-metals and metalloids are nitrogen, clay, graphene, and CDs. The following sub-section provides an elaborated discussion on these materials.

### Rhodium

Rhodium complex is the photosensitizer that is employed most frequently. These photosensitizers are the material that may remain chemically unreactive while transferring photons from the visible light to alternative substance to augment its natural activity. Rh has certain merits including the photocatalyst life and long excited state energy, chemical stability, and electron transporting ability. This may enhance its photodegradation of pollutants because of its high visible light absorption which enhances radical generation as stated by Ozawa *et al.* (2014). However, the Rh photosensitizer unit can deliver electrons to another photocatalyst unit at a fast rate, which enhances the photocatalysis reaction and prevents the charge carriers from regenerating (Kumar *et al.* 2018).

### Silver

Among various nanoparticles, the distinctive characteristic of silver (Ag) was attributed to its superior antibacterial properties (Mahmoudi *et al.* 2015). Not only it may be incorporated in optical and electronic devices, but it has also antibacterial consumer products and medicinal application due to its characteristic and low material cost than other noble metal such as gold and platinum (Murphy *et al.* 2015). Silver in various forms including as a co-catalyst, membrane nanofiller and also as an effective adsorbent has been a topic of interest in water treatment applications (Das *et al.*, 2013; Mahmoudi *et al.*, 2015). Currently, Germs such as Staphylococcus aureus and Escherichia coli (E.coli) are found significantly in water and wastewater and therefore its efficiency as a disinfectant is a plus for water treatment technologies (2018).

### Platinum

Pt catalysts are characterized by some unique features that allow them to be widely used in various industries such as electronics, biomedical, and catalyst (Atabaev *et al.*, 2016). Another issue that arises with commercialization is the high cost of Pt as highlighted by Mahy *et al.* (2019). In the group of all the noble metals, platinum is the best suitable co-catalyst for reducing contaminants employing photogenerated electrons because it can promptly capture the electrons in the conduction band of the semiconductor, thus enhancing the photocatalytic efficiency and minimizing the charge carrier recombination (Xie *et al.* 2014). While Oh *et al.* (2014) and Jaramillo-Paez *et al.* (2018) revealed that Pt enhances the photocatalytic efficiency of semiconductor photocatalysts through boosting their light absorption and transferring it to them.

### Titanium

Out of all the diverse categories of heterogeneous photocatalysts, one can use titanium dioxide (TiO2). In addition to being able to consistently absorb light and facilitate charge transfer, it is non-toxic and inexpensive and does not present any toxicity problems. Bagheri *et al.* (2015) investigated the crystal structures of the three most common polymorphs, namely anatase, rutile, and brookite of TiO2.

### Copper

The heterogeneous photocatalyst based on copper (Cu) has seen extensive application because of its plentiful supply, high selectivity, ease of use in creating semiconductor layers, inexpensive cost, and satisfactory photocatalytic activity (Saraswat *et al.* 2018). As a result of its smaller Eg (2.17 eV), copper oxide is a widely utilized the p-type semiconductor for photoelectrodes in pollution removal (Isherwood 2017).

Along with the metals already mentioned, researchers also created and studied hybrid photocatalysts that contained ions of other metals. Hybrid photocatalysts like $Cu^{2+}$ /TiO2, $Fe^{2+}$/TiO2, $Ru^{3+}$ /TiO2, $Ir^{n+}$ /TiO2, $Ru^{3+}$ /TiO2 and $Rh^{3+}$ /TiO2), $Pd^{2+}$ /TiO2 were created by Kitano *et al.* (2016) by combining TiO2 with a variety of metal ions. The resulting materials include rutile, anatase, and mixtures of these crystalline structures.

### Zinc oxide

Zinc oxide (ZnO) is a crystalline powder that has a white to yellowish-white color. It has a wurtzite crystal structure which is completely soluble in water (Dimapilis *et al.* 2018). The most commonly employed as a bulk heterogeneous photocatalyst is ZnO, because of its impressive physio-chemical characteristics and its capacity to enhance antibacterial activity (Al-Fori *et al.* 2014).

### Ferum oxide

Iron oxide has primarily four crystallographic forms which are α- Fe2O3 also known as hematite, γ-Fe2O3, β- Fe2O3 and ε- Fe2O3. While α- Fe2O3 is the most thermodynamically favorable phase of $Fe_2O_3$ and has found numerous practical applications as a catalyst, a sorbent, in solar cell and biomedical applications (Machala *et al.* 2011). One of the most prominent features of α- $Fe_2O_3$ is its stability in chemical and thermal processes. It is quite available and hardly affects the environment. Also, it is characterized by a remarkably high light absorption capacity, which can make it desirable for conversion of solar energy, as showed by Abdul Rashid *et al* 2016. Moreover, the properties of nanosized α- $Fe_2O_3$ are uniquely magnetic in nature. Roldán *et al* in their study published in 2013 observed that α- $Fe_2O_3$ bears better magnetic performance than ferum. The ferromagnetic behaviour is particularly advantageous in the photocatalytic treatment process as it allows for easy isolation of the photocatalyst from the solution after the process (Micheal *et al.* 2019).

**Titanium dioxide photocatalyst**

There is no doubt that $TiO_2$ or titania is one of the most widely recognized and documented materials due to the stability of its chemical structure, biocompatibility, and unique physical and optical and electrical characteristics. There are four different mineral forms of it: anatase, rutile, brookite as well as titanium dioxide or $TiO_2$. Anatase form of titanium dioxide has crystalline structure that is categorized in tetragonal system of crystallography. It is mainly used as a photocatalyst when irradiated with ultraviolet or UV light according to the figure referred by Zhang *et al* in 2018. Rutile $TiO_2$ possesses a tetragonal form of crystal structure. This specific form of titania is primarily used in paints, as a white pigment. The structure of brookite form of $TiO_2$ bears orthorhombic crystalline structure. The catalyst $TiO_2$ is a mineral that crystallizes in the monoclinic symmetry and is relatively new member of the titania family. Importantly, it must be noted that $TiO_2$ is a multifunctional material with numerous applications. Some applications include in paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells, as a food colorant, and in toothpastes (Puma *et al.*, 2008).

If photons strike $TiO_2$, the electrons on its surface are activated and then transferred to the conduction band. On the other hand, positive holes formed in the valance band at the same instance. Electrons and the positive holes have a decision to either release energy in the form of heat or interact with other molecules. In an interesting way, some species have the capacity to form highly reactive and strong oxidizing free radicals such as hydroxyl radicals. These radicals then move forward and oxidize the organics that are present on the given surface Figure. Also, these holes have the capacity to reduce the substrate through electron transfer through the holes in the structure. In other words, the formation of radical types in the $TiO_2$+UV system can be defined by the following diagram illustrated in Figure 4.

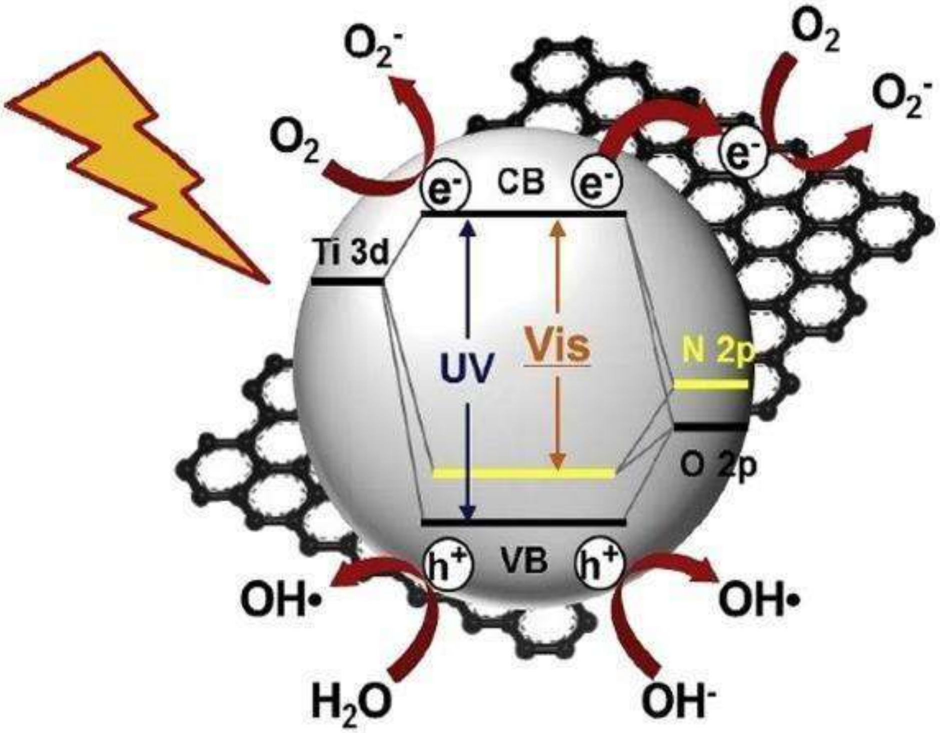

**Figure 4: Schematic diagram of photodegradation mechanism**

The potential use of this material as a photocatalyst in a large-scale water treatment facility is attributed to various factors (Aramendia *et al*., 2005):

A photocatalytic reaction occurs at ambient temperature.

Photocatalytic reactions have the advantage of not producing intermediate products like photolysis reactions do. This means that organic pollutants can be fully converted into non- toxic substances such as CO2, HCl, and water.

This affordable photocatalyst can be easily applied to a wide range of surfaces, including glass, fibers, stainless steel, inorganic materials, sand, and activated carbons (ACs), enabling repeated use without interruption.

Photogenerated holes have a highly oxidizing effect, while photogenerated electrons undergo sufficient reduction to generate superoxide's from dioxygen's (Figure 6).

$TiO_2$ + hv $\longrightarrow$ $^{e}CB$ + $h_{VB}$

• +

+

•

hVB + OH $\longrightarrow$ OH + H hVB + OH

OH

$^{e}CB$ + $h_{VB}$ $\longrightarrow$ Heat

$^{e}CB$ + $O_2$ $\longrightarrow$ $O_2$

Dye + OH• $\longrightarrow$ Degradation Products

Dye + Dye +

$\longrightarrow$

$^{e}CB$ $h_{VB}$ $\longrightarrow$

Reduction Products Oxidation Products

+ Figure 5: Photodegradation mechanism

**Photocatalysis**

Photocatalysis can be defined as a process that is activated by light and further accelerated by the presence of a photocatalyst. These reactions occur when a photon is absorbed with sufficient energy. When light is absorbed it promotes the electron from the valence band to the conduction band in the semiconductor catalyst. This leads to a charge separation in which there is an empty space called a hole in the valence band. For a photocatalyzed reaction to occur, it is essential that the electron and the hole do not recombine.

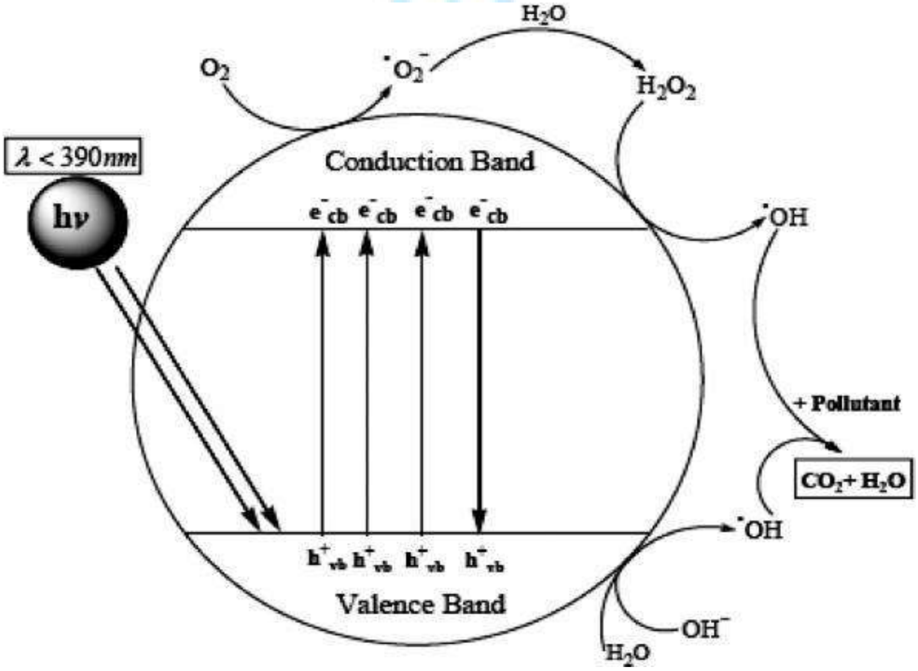

Figure 6: General Mechanism of Photocatalysis

The overall goal of the process is to enable the activated electrons to interact with an oxidant so as to form a reduced product. Also, it seeks to cause a reaction between the generated holes and a reductant to form an oxidized product. In a study done by Gaya *et al.* in 2008, the electrons generated by light can donate it to the dye or get transferred to electron acceptors (Figure 7).

**Operating parameters in photocatalytic processes**

The photocatalytic degradation of dyes is affected by some factors that have to be taken into account. Some of these factors are the pH level, the size and concentration of photocatalyst particles, initial dye concentration, temperature of reaction, dopant content, the presence of electron acceptors and intensity of light. The following operating parameters will be explained one by one since they are all affected by the photocatalytic methods that occur in the photodegradation of dyes in effluents of wastewaters.

**Effect of pH on photocatalytic degradation of dyes**

In photocatalytic dye decolorization, the pH has a great impact with regard to the reaction rates of the dye at different manners. The dye adsorption on the surface of a semiconductor depends with the pH of the solution since the catalyst surface charge is governed by the pH (Borker and Salker, 2006). Earlier researches have also been made in the past to analyze the effect of pH level on the photocatalytic degradation of harmful dyes (Huang *et al.*, 2008). While investigating the effects of pH on the photocatalytic degradation of dyes there is two major aspects to look at. It is clear that industrial pollutants do not have only a neutral effect. In addition, the pH of the reaction mixture affects the surface charge characteristics of the photocatalyst as pointed by Chakrabarti and Dutta in their 2004 study.

The task of comprehending the effects of most important factor which is pH on the effectiveness of the photodegradation procedure is an intricate one since there are three possible reaction pathways involved in dye demineralization. Such mechanisms include the interaction with hydroxyl radicals, positive holes direct oxidation, and direct reduction by electrons from the (CB) conducting band. The extent of contribution for every mechanism varies with pH as well as the nature of substrate (Reza *et al.*, 2017). In a research by Zhu *et al* in 2012, the authors analyzed the effect of pH on the photocatalytic surface charge characteristics. They further observed that it could be attributed to the point of zero charge phenomenon. A study carried out by Alaton *et al* in 2002 revealed that for TiO2 particles, the pH pzc is 6.8. At an acidic environment or when the pH is below 6.8, the surface of the photocatalyst gains a positive charge. On the other hand, the surface of the electrode becomes negatively charged at the alkaline or basic pH values.

The pH can also have a substantial effect on how fast the photocatalytic dye decolorization occurs as well as its overall rate. For instance, positive holes act as important oxidation agents at lower pH levels. Under higher or neutral pH conditions, the oxidation process is driven by hydroxyl radicals (OH). Lachheb *et al.* conducted a study in 2002 where they investigated the influence of pH on Methyl Red, Crocein Orange G, Congo Red, Alizarin S and disappearance kinetics. According to their findings, the pH did not affect disappearances rates significantly. At the very high pH values adsorption of MB is more favorable onto negatively charged surfaces. However, due to presence sulfonate group which carries negative charge, the adsorption of OG decreases with increasing alkalinity. Several other dyes having different functional groups exhibited behavior similar to that observed with respect to MB.In their research, Baran *et al.*, found that Bromocresol purple dye degrades better under acidic rather than alkaline conditions (Baran et. al., 2008).

$TiOH + H^{+} = TiOH_2^{+}$ 2

$TiOH + OH = TiO + H_2O$ 3

**Effect of dye concentration on photocatalytic degradation of dyes**

Photocatalysis depends on the absorption of dyes by the photocatalyst's surface. What is important for the process of photocatalysis is not how much dye there is in the whole solution but rather the amount that gets adsorbed onto the surface of the photocatalyst through photodegradation. The initial concentration of dye with respect to its adsorption plays a significant role in every photochemical reaction. This percentage decreases as long as we keep constant quantities of reactants and increase them (Reza *et al.*, 2017). More organic substances will be adsorbed onto the surface area if more amounts are taken up; hence fewer photons will reach this region thereby reducing decolorization percentages since OH ions generation also reduces because many OH radicals are consumed during oxidation processes (Azad and Gajanan, 2017). It has been shown from earlier works that when dye concentrations rise so does degradation rate constant drop (Mahvi *et al*., 2009).

The speed at which something deteriorates under light exposure can be influenced by its starting point concentration level. Photodegradation was studied by Illinous *et al*., in 2013 where they looked into what happens when different amounts of initial concentrations were used for reactive yellow 12 dye during photodegradation process. As per Akerdi *et al*.'s findings last year there appeared to have been less efficiency observed during decomposition with higher amounts of dyestuff being applied than those lower down the scale were employed.

Another example includes manipulating initial quantity which caused researchers see change in path-length traveled by entering photon into solution inversely proportional where lesser volume had more paths crossed through it compared against larger ones as illustrated in Kansal *et al*.'s study back in 2008 (Table 4).

**Table 4: Effect of initial concentration of dye on photocatalytic degradation**

| Initial dye-12 conc. (mg/l) | Constant Parameters | kd ($min^{-1}$) UV + O3 | kd ($min^{-1}$) O3 |
|---|---|---|---|
| 100 | UV source: 254 nm pH: 12<br>Ozone : 400 mg/h | 0.0269 | 0.0260 |
| 200 | UV source: 254 nm pH: 12<br>Ozone : 400 mg/h | 0.0183 | 0.0143 |
| 300 | UV source: 254 nm pH: 11<br>Ozone : 400 mg/h | 0.0121 | 0.0105 |
| 400 | UV source: 254 nm pH: 10<br>Ozone : 350 mg/h | 0.0112 | 0.0100 |
| 500 | UV source: 254 nm pH: 9<br>Ozone : 350 mg/h | 0.0079 | 0.0078 |

**Effect of photocatalyst concentration on photocatalytic degradation of dyes**

The concentration of photocatalyst is additionally a factor in the degradation of dye. The degradation of dye through photodegradation can be improved by increasing the amount of photocatalyst. A greater quantity of active sites is available on the entire surface of the photocatalyst when there is a higher catalyst concentration. This leads to an increased production of OH radicals which results in discoloration of the dye solution. At a certain point, when catalyst concentration exceeds some limit value or go above certain level then solutions become cloudy; this cloudiness cuts off necessary UV radiation for continuation of reaction and thus decolorization falls down (Coleman *et al*., 2007).

In another study during 2007 by Riga *et al*., it was noticed that with higher TiO2 loading or when other catalysts were used there tends to be an increase in concentration adsorbed dyes on surface area per unit mass (Figure 5). MO dye photodegradation at different concentrations is shown in figure 5. The percent photodegradation noticeably increased as more photocatalysts were introduced into system however this was only observed through experimental findings which showed direct relationship between concentration levels and %degradation rates achieved (Kumar and Pandey, 2017). Several researchers have studied about how different factors affect dyes degradation rate within wastewater treatment plants such as Abdellah *et al*., 2018 who reported on what impacts does catalyst loading have towards improving these processes? In their research work Konstantinou and Albanis investigated TiO2-assisted photocatalytic degradation process for azo dyes under aquatic condition back in year 2004 where they found out that initial rates are directly proportional to quantities used indicating presence heterogeneous regime only works well with large amounts but also has its limitations since beyond specific point no further significant changes may occur until some additional measures taken into account so as still remain effective enough even if efficiency decreases drastically beyond expected thresholds levels achieved before this had been reached otherwise none whatsoever would suffice according expectations made before starting any experiments at all.

It has been shown by various experiments that the number of active sites on the surface of photocatalyst increases with an increase in catalyst concentration. This consequently leads to more OH and superoxide radicals which come into contact with dye molecules causing it degrade or break down into simpler compounds until very few bonds are left intact between atoms within its structure thereby reducing stability hence making easy for microbial attack on such substrates thus enabling faster biodegradation rates to occur eventually resulting complete mineralization process taking place rapidly than usual expected time frames required under normal circumstances where only partial degradation occurs due limited availability catalysts surfaces areas available for photon absorption (Huang *et al.*, 2008; Sun *et al.*, 2008).

## Influence of dopants on photocatalytic degradation of dyes

The photodegradation of harmful organic dyes is one of the most potential applications of heterogeneous photocatalysis. Dopants have been extensively studied about their impact on

the photocatalytic activity of photocatalysts (Kumar and Pandey, 2017). Doping can improve the efficacy of the photocatalyst in many ways such as contraction its band gap, creating oxygen vacancies which act as unique surface adsorption sites for organic molecules, forming impurity energy levels and trapping electrons at these levels (Barakat *et al.*, 2013). Generally speaking, catalysts having low energy levels between the conduction and valence bands are efficient visible light responsive photo catalysts because they generate more number of electron-hole pairs. Indeed, under visible light irradiation some features like oxygen-deficient sites; narrowness in band gaps; presence of impurity energy levels etcetera has shown to greatly enhance Yousefi *et al.*'s (2013) found that photocatalysts with oxygen deficiency sites did exhibit significant increase in their ability to adsorb visible light. Photocatalytic activity refers to how effectively a given substance drives chemical reactions using energy derived from absorbed photons but it depends on whether or not photo-induced charges recombine before reacting with other species within Barakat *et al.*, 2013 showed that dopant atoms could trap photo induced Zhang *et al.*, 2023 work revealed that when electrons were allowed to move freely without any recombination, then this leads enhanced by preventing holes from combining back again with them thus making them available for creation these new compounds.

The catalyst can include dopant ions via interstitial or substitutional methods. In the crystal lattice of the catalyst, dopants can modify electronic properties in the visible light region (Pouretedal *et al.*, 2009). The absorption edge of the material shifts towards the red due to d electron transfer as illustrated by figure (Chang and Cho 2016) but after an optimal level of doping contents, decrease in photocatalytic activity happens through; (i) lessening the space charge region or (ii) reducing surface area of the catalyst as well as the penetration depth of radiation into photocatalyst beyond space charge layer. Besides this, sometimes doping contents may act as electron-hole recombination centers when average distance among trap sites is reduced by aggregating the dopant contents (Xu *et al.*, 2002), thus reducing photodegradation. When subjected to UV light source, Bouras *et al.*'s study showed that under same conditions Basic Blue 41 dye was better degraded with pristine TiO2 than Fe-doped TiO2.

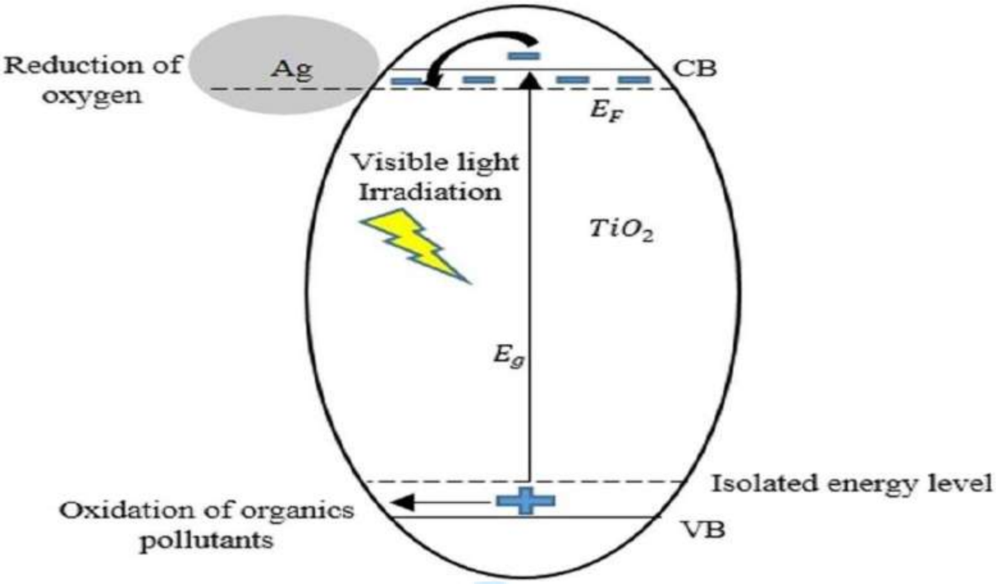

**Figure 7: Photocatalytic mechanism of Ag-doped TiO2 photocatalysts**

The amount of dye that was decolorized decreased significantly when the concentration of Fe increased from 0 to 30 at%. The same trend was observed for Co-TiO2 and Cr-TiO2 at different reduction levels. This means that transition metals (TM) in TiO2 photocatalysts obstructs the photo catalytic degradation process of some dyes (Bouras *et al.*, 2007). Semiconductors energy levels, surface states, optical, structural and electromagnetic properties can be changed considerably by altering doping levels. The presence of dopants within a semiconductor determines material behavior more so than any other factor. Dopants in semiconductor nanocrystals decide what kind of optical and electronic behavior they will exhibit specifically (Wang *et al.*, 2013). Moreover, photons absorbed by them transfer their energy quickly to their surroundings which prevents undesirable reactions on the surface of nanocrystals through rapid localization. Chauhan *et al.* (2014) found out that introducing ZnS to photocatalysts together with other transition metals like Ni, Cu, and Mn enhances their reactivity.

### Effect of the intensity of light and irradiation time on photocatalytic degradation

Both the intensity of light and the time of irradiation affect the fading of dye (Gaya and Abdullah, 2008). When photocatalysts captivate light energy which is equal to or greater than band gap energy, it results into transferring electrons from valence band to conduction band leaving holes in valence band (Sohrabnezhad *et al.*, 2009).

Radiation can be also increased by intensifying the rate of photodegradation. The probability for exciting a photocatalyst is increased with higher intensity incident light (Saleh *et al.*, 2011). However, recombination of electron-hole pair remains one big problem in photocatalysis. At low light intensity there is difficultness with separation electron-hole pairs due to increase recombination which leads to less production free radical thus reducing degradation organic molecules. This can be solved by using more intense lights (Pirhashemi *et al.*, 2018).

Therefore; wavelength and intensity of UV source in a photo-catalytic reactor affects degradation of dye in aqueous solution of photo catalysts. In terms reproducibility an artificial UV source provides good reproducibility as compared to solar light enabling higher efficiency in degrading textile dyes. On other hand solar light being non-hazardous and abundant has been considered cost effective alternative light sources because it usually employed along with different parabolic collectors or straightly used solar irradiation (Mariselvam *et al.*, 2016).

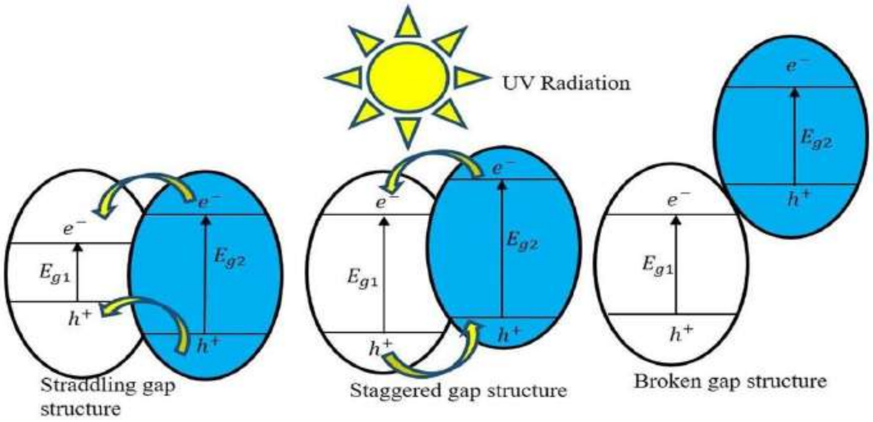

**Figure 8: Three types of semiconductor heterojunction structure**

### Effect of reaction temperature on photocatalytic degradation of harmful dyes

The gradual increase in temperature raises the rate of photodegradation of organic compounds. This occurs because at higher temperatures, the solution begins to bubble thereby generating free radicals. Furthermore, a rise in heat also aids electron-hole recombination by enhancing degradation reactions. Additionally, increasing temperatures heighten oxidation rates between organic molecules at interfaces (Karimi *et al*., 2014).

In their research on Acid Red 18 dye, Mozia *et al*., 2009 discovered that the constant for rate of reaction during photochemical decomposition increases with increasing temperatures. In another study conducted by Soares *et al*., 2007 they also found out that there was an ideal operational range between 40–50oC where most efficient results were obtained. However at lower temperatures desorption from surface becomes slower than degradation so this step limits the reaction while adsorption of dye onto photocatalyst becomes limiting when we raise temperature but not too much above room temperature since according Zhou and Ray (2003) optimal ranges are usually around 293K – 353 K .

At low temperatures it is energetically more favorable for reactants to adsorb which leads to release of heat spontaneously. Over 80 C charge carrier recombination takes place leading to decrease in efficiency again the best temperature region falls within the interval from twenty degrees Celsius up till eighty degrees celsius for successful decolorization process Kumar *et al*., (2015).

### Effect of various photocatalysts on photocatalytic degradation of dyes

The various photocatalysts' chemical reactions differ due to the lattice mismatch and BET surface area difference. Equally, how effluent is absorbed, and the duration as well as rate at which electron-hole pairs recombine are altered by the presence of impurities on the surface of a photocatalyst. It can have a significant role in some photodegradation reactions to have a large surface area. There have been great strides made towards increasing the specific surface areas of photocatalysts for full utilization of their properties (Birnal *et al*., 2020).

Decolorization kinetics of gentian violet were studied by Saquib and Muneer through examination of three different photocatalysts; PC500, P25, UV100. Among other photocatalysts P25 degrades dye fastly and causes mineralization also quickly. For a photo-catalytic reaction to occur it should have larger numbers of electrons and holes available for appropriate reactants This is because it takes longer time for recombination between electron- hole pair in P25 hence more efficient reactions are allowed (Saquib *et al*., 2003).

The titanium dioxide is one eminent photo-catalyst that exists in four different mineral forms. Anatase TiO2 has proven itself as an excellent photo-catalyst relative to other types of TiO2 because its bandgap energy is higher than that of rutile form which means wider range absorption ability by anatase type compared with rutile type under similar conditions such as wavelength or intensity etcetera where this could lead into more number excited states being accessible potentially along with greater possibility being there for initiating conjugate reactions involving electrons since conduction band level might become shifted upwards correspondingly so as to match up with them better according law conservation charge. Besides that, it was found out during investigations that there is formation highly stable surface peroxide groups due to photo-oxidation reaction taking place within anatase $TiO_2$ However it has been shown through research work that mixed phase composite containing both rutile and anatase exhibits higher activity than pure anatase (Reza *et al.*, 2017).

### Effect of inorganic salts

It is common to find mineral ions in the dye contents of waste water. Some cations such as copper, phosphate and iron have been found to decrease the efficiency of photo-degradation at particular concentrations. This is because they can compete for active sites on the $TiO_2$ surface with dyes which may deactivate photocatalyst leading to reduction in targeted dyes degradation (Chong *et al.*, 2010).

Calcium, magnesium and zinc were among the metals that have received much attention due their impacts on organic compound's photodegradation. Research has shown that these elements do not exhibit any inhibitory effects when they are present in higher oxidation states. The formation of chloride radical anions can also block catalyst surface active sites while previous studies had already reported about chloride ion and phosphate ion inhibiting photocatalytic degradation (Liao *et al.*, 2001).

### Effects of Oxidizing agents on photocatalytic degradation of dyes

Certain agents can affect the degradation of dyes through photocatalysis. For instance, Saquiba *et al.* found that certain chemicals such as hydrogen peroxide, ammonium persulphate and potassium bromate were observed to participate in the breakdown processes of Fast Green FCF (1) and Patent Blue VF (2). The experiment employed Hombikat UV 100 and Degussa P25 as the photocatalysts. They noticed that some compounds promote the decomposition of

dye 1 when exposed under UV 100 rays while all electron acceptors greatly enhance the degradation rate of dye 2 in the presence of P25.

In another study carried out by Huang *et al.*, they also investigated how incorporating $H_2O_2$ affects methyl orange decolorization. The higher the concentration of hydrogen peroxide, the faster the rate at which color is lost. The range in concentration used was from 0.4-2 mM/l $H_2O_2$. What they found was that among all other concentrations tested with their system, adding 1.2mM/l $H_2O_2$ gave them maximum results against the photocatalytic degradatio of methyl orange solution, this reaction got better with addition H2O2. According to Zhiyong *et al.*'s work [158], one-hour sunlight exposure led to complete disappearance of MO after it had been mixed with deugussa P25(0.5g/L) and $H_2O_2$ (1mm).

### Conclusion

In this review article the previously available literature on the different photocatalytic methods being used for the photo-degradation of direct yellow 12 dye and some others harmful dyes has been reviewed comprehensively. The negative impact of these harmful dyes on the environment and human health which are being released into the canal system in the form of industrial waste has also been studied. Literature date shows that the yellow direct 12 dye is extremely toxic to human as well as animal health. Therefore, there has always been top priority for the researchers to find the easy, economic, quick and environment friendly methods to degrade or remove these toxic dyes from the wastewaters. From the literature survey we find that a large number of classical as well as advanced degradation methods are being used for the degradation purpose. Among these methods photocatalytic degradation is extensively used because these methods are efficient and environment friendly. Different studies have been done on photocatalytic degradation by employing different types of photocatalysts and light sources. Each type of catalyst has its own unique degradation potential against the different type of dyes. This review has also investigated the impact of different parameters like pH, reaction temperature, initial concentration of dyes and substrate, type of photocatalyst, pro-catalyst, and doping of another element. Each parameter affects the performance of photocatalytic activity of the degradation process. This review study will help the scientist and environmental researchers to choose the most affordable method foe the degradation or of direct yellow 12 dye from the dying contaminated wastewaters.

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