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Photocatalytic Removal of Dyes from Aqueous Solution: Review

SWATI GOYAL, DIVYA PATIDAR

Department of Chemistry, Dr. A. P. J. Abdul Kalam University, Indore (M. P.) -452016
Corresponding Author Email: swatipc2011@gmail.com

Abstract— Several researchers have carried out several analysis activities to explore the foremost appropriate and economical technique for the removal of dyes from industrial effluent. Numerous techniques particularly coagulation, precipitation, filtration, reverse osmosis, ion exchange, adsorption, and photocatalytic degradation are accustomed to taking away organic and inorganic compounds from the aquatic environment. Among all the reportable strategies, the photocatalytic degradation study has been found a most promising technique for the removal of these types of contaminants. Photocatalysis may be a method that utilizes the energy input from incident radiation and therefore the catalytic properties of the surface of a material to carry out and/or accelerate certain chemical reactions. Photocatalysis is understood to be ready to produce thermodynamically uphill reactions, that otherwise high-temperature intense energy inputs in terms of high temperature (or pressure). Recent studies are devoted to the utilization of photocatalysis within the removal of dyes from wastewaters, significantly, attributable to the ability of this technique to fully mineralize the target pollutants. This review paper would be supportive to search out the most capable technique for removing dye contaminants from industrial effluent considering deserves and demerits of every technique.
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Index Terms— Degradation, Organic dyes, Photocatalytic, Removal techniques, Wastewater.

I. INTRODUCTION

The effluents, gaseous or liquid produced by a number of our industries are harmful to man's health and general well-being. Once undesirable substances are present in liquid effluents; it can be disastrous as their presence cause a severe threat to the immediate recipients. Wastewaters from various industries, factories, laboratories, etc. are severe problems to the environment. The discharged wastes containing dyes are harmful to microorganisms, aquatic life, and human beings [1]. These injurious effects of chemicals on the earth's ecosystems are cause for serious concern. Many of those chemicals like azo dyes, herbicides, and pesticides have been found in rivers and lakes, and are considered account for 1–20 percent of global dye production lost during the coloring process and released into textile effluents. The release of these colored wastewaters into the environment could be a significant source of non-aesthetic pollution and eutrophication, as well as a source of harmful byproducts from oxidation, hydrolysis, and other chemical reactions occurring in the affluent phase. It's worth noting that dyes have negative consequences and limit lightweight penetration in contaminated waters [2].

Numerous studies are conducted to assess the harmful impacts of colorants on the scheme. It had been found that colorants might cause issues in water in many ways:

- Dyes will have acute and/or chronic effects on exposed organisms with this depending on the dye concentration and on the exposure time.
- Dyes are inherently highly visible; minor unharnessed effluent may cause abnormal coloration of surface waters that captures the attention of each public and also the authorities.
- The ability of dyes to absorb/reflect sunlight entering the water has forceful effects on the growth of bacteria and upsets their biological activity.
- Dyes have many different and sophisticated molecular structures and so, troublesome to treat and interfere with municipal waste treatment operations.
- Dyes in sewer water bear chemical and biological changes, consume dissolved oxygen from the stream, and destroy aquatic life.
- Dyes tend to sequester metal ions producing micro toxicity to fish and different organisms.

The release of these colored wastewaters within the scheme may be a dramatic source of esthetic pollution, eutrophication, and perturbations within the aquatic life. As international environmental standards have become additional demanding technological systems for the removal of organic pollutants, such as dyes are recently developed. Among them, physical ways, like adsorption [3], biological ways (biodegradation) [4, 5], and chemical ways (chlorination, ozonation) [6] are the most often used the standard processes for treatment of these effluents prove to be insufficient to purify the necessary quantity of wastewaters when the various operations of textile coloring and washing. Some ways such as combined coagulation, electrochemical oxidation, and active sludge have recently been investigated and proved to be adequate [7]. Other ways like flocculation, reverse osmosis, and adsorption on activated carbon have also been tested [8–10]. The drawbacks of those ways in the main creation of an additional concentrated pollutant-containing phase, the processes by bacterial beds are less custom-made because of the fluctuations of the wastewater composition [11, 12]. The oxidative breakdown of organic molecules dissolved or dispersed in liquid media has improved as a result of recent advances in chemical wastewater treatment. The so-called "advanced oxidation processes" are among the novel oxidation methods (AOP)

heterogeneous photocatalysis has appeared as an emerging damaging technology resulting in the total mineralization of most organic pollutants [13–14].

To date, photocatalysis has been considered as one of the most appealing choices for sewer water treatment because of its great potential and high potency by exploiting sunlight to remove organic pollutants and harmful bacteria with the help of a solid photocatalyst. Photocatalytic degradation has gained popularity in recent years as a cleaner and greener method of removing hazardous organic and inorganic pollutants from water and effluent. Semiconductor photocatalysis seems to be a promising technology that contains a range of applications in an environmental system like air purification, water disinfection, water purification, and dangerous waste remedy. TiO2 catalyzed photochemical degradation of organic pollutants generally, and a dye, particularly in an affluent, maybe a favored and promising technique [15].

II. AN OVERVIEW OF PHOTOCATALYTIC TECHNIQUE

Photocatalytic degradation is considered a favored, promising, cleaner and greener technology for the removal of harmful organic and inorganic pollutants from water and effluents. It holds several advantages over conventional oxidation processes, such as (i) complete mineralization of pollutants, (ii) usage of near-UV or solar radiation, (iii) no other chemicals added, and (iv)operation at room temperature [16–19]. In photocatalytic degradation, a nontoxic semiconductor catalyst is utilized. When the semiconductor is illuminated with radiation of an appropriate wavelength it becomes a powerful oxidant that converts most of the organic materials into CO2 and H2O. Photolysis is a chemical process by which molecules are dissociated through the absorption of light. Photons, with their energy being inversely proportional to their wavelength, can affect the chemical bonds of a chemical compound by the cleavage of one or more covalent bonds in a molecular entity [20]. The general photolysis reaction can be given as

$$H_2O + hv \longrightarrow H^+ + OH^- \qquad (1)$$

III. PHOTOCATALYSTS

The nature of the photocatalyst determines the rate and potency of the method. The most commonly studied photocatalysts are TiO2, ZnO, ZnS, and Cds. In addition; In2O3, SrTiO3, SnO2, and WO3 are used as photocatalysts however all showed lower levels of photo-activity [21], and SiO2 and MgO are found to be inactive. Photoactivity, biological and chemical inertness, durability against photo corrosion, appropriateness for visible or near ultraviolet light, cheap cost, and absence of toxicity are all desirable features in photocatalysts [22]. Because most metal oxides and sulphides will photo-corrode irreversibly on the surface [23], these types of semiconductors aren't appropriate for semi-permanent treatment processes. Some metal sulfides can also be photocatalytic; however, they need some weaknesses in terms of corrosion. Iron oxide is also cheap, it can even be corroded. Zinc oxide is maybe the nearest challenger to titanium oxide however its weaknesses are instability in some solutions and a tendency for its hydroxide to cover its surface inflicting lower photocatalytic activities [24].

However, TiO2 is an inert compound and might be reused several times. TiO2 (titania) is that the most generally used as a result of its relatively nontoxic, cheap, and stable. As a result of naturally occurring pigment is sometimes complex with alternative minerals and metals, when pure grades are required, it's synthetically manufactured rather than mine. The most commonly used synthetic TiO2 is Degussa's P25, manufactured from flame synthesis mistreatment TiCl4. The ultimate product, with a median primary particle size of 21nm, is comprised of two crystalline structures of TiO2, anatase (70 %) and rutile (30 %). The flexibility of the technique to completely degrade organics into water and carbon dioxide, without generating any harmful by-products, has popularized its role as a waste material purifier. The technique has additionally been utilized for the photo mineralization of a large range of dyes like thiazine, direct and acid dyes, azo dyes, and reactive black [25]. The photocatalytic degradation of various kinds of organic molecules on nontoxic TiO2 has been analyzed in terms of Langmuir–Hinshelwood mechanics [26]. However, despite its promise, the event of a practical treatment system based on heterogeneous photocatalysis has not however been achieved due to several operational parameters, that should be considered. It's ordinarily known that certain styles of photosensitive semiconductors generate active gas upon ultraviolet exposure. The active oxygen oxidizes and decomposes organic substances. titanium dioxide, which may be a metal compound semiconductor, is that the most most well-liked material, since it's with chemicals and biologically inactive, cheap, photostable, and photoactive, though it will have an oversized bandgap [27] (ca. 3.2 eV) and solely absorbs within the ultraviolet radiation (i.e., <388 nm). There are 3 differing types of titanium dioxide, anatase, rutile, and brookite. Most of the studies are performed on the anatase and rutile types. The adsorptive affinity of anatase for the decomposition of organic compounds is larger than that of rutile. Because of irradiation of anatase titanium dioxide particles by ultraviolet radiation|ultraviolet illumination|UV|actinic radiation|actinic ray} light (λ<300 nm), it's an oversized bandgap around 3.2 eV; rutile contains a a3.0 eV bandgap beneath wavelengths less than 410 nm (Fig. 1).

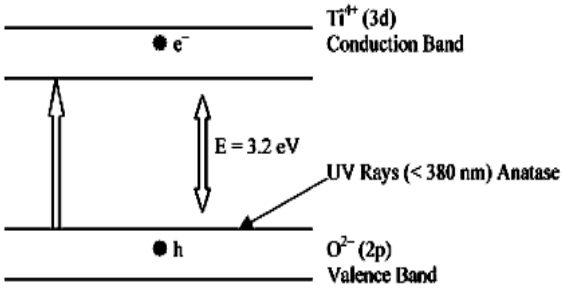

Figure 1: Energy band gap between anatase and rutile

Crystal Structure	Band Gap (eV)	Absorption Edge (nm)
Anatase	3.2	388
Rutile	3.0	410

TiO_2 + UV Rays ⟶ $h^+ + e^-$ (2)

$H_2O + h^+$ ⟶ H+ + $OH^{\bullet}$(Radical) (3)

$O_2 + e^- + h^+$ ⟶ $HO_2^{\bullet}$(Radical) (4)

This provides for anatase comparably large numbers of electrons and holes produced in the conduction and valence bands respectively. Electrons have a high potential for reduction reactions on the catalyst surfaces. This mechanism in some respects is close to photosynthesis by plants. It can also be called artificial photosynthesis, although unlike photosynthesis titanium dioxide absorbs only UV light. When photons with energy equal to or more than the bandgap energy are irradiated onto TiO2 particles, an electron is promoted from the valence band (VB) to the conduction band (CB). The outcome of this process is a region of positive charge, termed a hole (h+), in the VB and a free electron (e−) in the CB:

$TiO_2 + h\nu$ TiO_2 (e^- CB + h^+ VB) (5)

The charge carrier species can recombine with the absorbed energy dissipated as heat, or they can migrate to the particle surface, where the holes can react with surface-bound hydroxyl groups (OH^-) and adsorbed water molecules to form hydroxyl radicals ($OH^{\cdot}$):

OH + h ·OH (6)

H_2O + h ⟶ OH + H (7)

In the absence of an electron acceptor, electron-hole recombination dominates. The presence of oxygen prevents recombination by trapping electrons through the formation of superoxide ions, maintaining electrical neutrality within the TiO_2 particle. The final product of the reduction is usually hydroxyl radicals (·OH) and hydroperoxyl radical HO_2:

$2O_2^{\cdot-} + H$ ⟶ $2OH + O^{\cdot 2}$ (8)

$2O_2^{\cdot-} + H$ ⟶ $HO_2^{\cdot}$ (9)

Hydroxyl radicals are known to be powerful, indiscriminate oxidizing agents and they can react with organic compounds in the photocatalytic process and bacterial species adsorbed onto, or very close to the semiconductor surface, resulting in degradation.

IV. Literature Review

Dye degradation in industrial wastewaters has thus gained increased attention, and a few repair approaches have been proposed. For the removal of dye pollutants, traditional physical approaches (adsorption on activated charcoal, ultrafiltration, reverse osmosis, coagulation with chemical agents, natural process on synthetic adsorbent resins, etc.) are utilised [28, 29]. These approaches only succeed in transporting organic chemicals from one phase to another, resulting in secondary contamination. This may necessitate further solid waste treatment and adsorbent regeneration, raising the method's cost. Dyes have been removed from wastewaters via microbiological or enzymatic decomposition [30], biodegradation [31], ozonation [32], and sophisticated oxidation processes such as Fenton and photo-Fenton catalytic reactions [33], as well as H2O2/UV processes. Recent researches [34, 35] have focused on the use of photocatalysis in the removal of dyes from wastewaters, owing to this method's ability to totally mineralize the target pollutants [36]. Among AOPs, heterogeneous photocatalysis has proved to be of real interest as an efficient tool for degrading both aquatic and atmospheric organic contaminants [37]. Heterogeneous photocatalysis involves the acceleration of a photoreaction in presence of a semiconductor photocatalyst. Photocatalytic oxidation (PCO) is a popular technique of heterogeneous catalysis for partial or whole mineralization of gas phase or liquid phase pollutants to benign compounds [38]. Despite the fact that photocatalytic degradation begins with partial degradation, the phrase usually refers to complete photocatalytic oxidation or photo mineralization, primarily to CO2, H2O, NO3-, PO43-, and halide ions [39]. Regarding that, the use of TiO2 in the total destruction of numerous halogenated hydrocarbons, such as trichloroethane, methylene chloride, and chloroform, was described. and carbon tetrachloride. It had been found that a simple Langmuirian rate equation represented the destruction of those materials [40]. It had been investigated the development of a variety of waste treatment cells employing a TiO2 photocatalyst including immobilized film and suspended particle reactors [41-42].

One of the primary reported cases of the utilization of semiconductor photocatalysis within the destruction of organic compounds was reported. They reported the successful degradation of biphenyl and chlorobiphenyls within the presence of TiO2. Since then the destruction of many materials using TiO2 has been investigated [43]. One researcher reported that several aromatic hydrocarbons might be oxidatively cleaved when reversibly adsorbed onto the surface of an irradiated suspension of TiO2 [44]. A review of the past work aims to provide a concept for the systematic study of the use of low-cost adsorbents for the removal of dyes from aqueous solutions and from industrial effluents. Among various ways of treating industries' effluents containing dyes, one can utilize the resources of cheap techniques. The summary of the published data with some of the latest important results with up-to-date literature on the adsorption properties of some alternative adsorbents used for the removal of the dyes. Photocatalytic and adsorption studies on the removal of dye Congo red from wastewater investigated The photocatalytic results of the study indicate that anatase titanium dioxide, as a catalyst is very efficient and effective to enhance the photocatalytic activity[45]. Recent developments in dye removal from wastewater utilising a

photocatalytic technique based on the synergetic effect of adsorption have been examined [46].

The goal of this review of previous work is to provide inspiration for systemic research of the use of low-cost adsorbents for the removal of dyes from aqueous solution and industrial effluents. Among the different methods for treating dye-containing industrial effluents, one can make use of low-cost procedures. The summary of published data, including some of the most recent and important results, as well as current literature on the adsorption properties of several alternative adsorbents employed for dye removal. Researchers investigated photocatalytic and adsorption experiments on the removal of the dye Congo red from wastewater. The study's photocatalytic results show that anatase titanium dioxide is a very efficient and effective catalyst for increasing photocatalytic activity. To get a high breakdown rate of Congo red, several catalyst concentrations and additives like H2O2 were utilised. Thr analysts [47] reported on the removal of colour from different dye wastewater using ferric oxide as an adsorbent. Batch experiments revealed that Fe2O3 powder is used for removing colour from textile dye effluent. Within 45 minutes, adsorption equilibrium is achieved. In comparison to Langmuir and Tempkin isotherms, it followed the Freundlich isotherm model. Pseudo-second-order kinetics influenced the adsorption order of disperse blue 73 (Anthraquinone dye).A team of researchers investigated the removal of dyes from wastewater using bottom ash [48] and they represent The bottom ash generated in an MSWI was used as a low-cost adsorbent for the removal of alizarin yellow, fast green, and methyl violet from wastewater. The exothermic adsorption of alizarin yellow and fast green has been discovered, whereas the endothermic adsorption of methyl violet has been discovered. Both the Freundlich and Langmuir models can be used to fit the data and estimate the model parameters, according to the data. In Research paper [49] published a work titled Degradation of Congo Red Solution by Zinc Oxide/Silver Composite Preheated at Different Temperatures. Sunlight damaged Congo red dye with a high photo degradation efficiency. The reaction was carried out without focusing the sun's rays, and the catalyst functioned appropriately. The photo oxidation of methanol in the photodeposition process transforms the Ag ion to the Ag_2O system, resulting in excellent doping on the ZnO surface. The utilization of chromium waste sludge for the adsorption of color from dye effluent streams was investigated [50].

Unlike other fields of science, this is a field where research is conducted all around the world. Research in specific fields of science is limited to specific locations of the globe, but dye degradation has been investigated in nearly all countries and regions, including practically all underdeveloped countries.

Recently, advanced oxidation processes (AOP) are focused on dye removal from wastewater is advantageous since it is environmentally friendly, cost-effective, and capable of degrading a wide range of colours and organic contaminants found in water.

III. CONCLUSION

This paper aims to review and summarise the role of important operating parameters on the photocatalytic degradation in wastewater together with recent achievements. The Photocatalysis process is the most widely used and effective method. This technique offers much potential in the treatment of dye-containing effluents. It has been concluded that removal of dyes with the photocatalytic technique using low cost. The obtained results demonstrated a good catalytic efficiency of nanocrystalline semiconductors. Further investigation needs to be performed in order to properly elucidate the kinetic mechanism and to study the intermediate organic compounds of the degradation process.

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