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Review

Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution

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ABSTRACT

Synthetic dyes are a major part of our life as they are found in the various products ranging from clothes to leather accessories to furniture. An unfortunate side effect of their widespread use is the fact that up to 12% of these dyes are wasted during the dyeing process, and that approximately 20% of this wastage enters the environment (mostly in water supply). Not surprisingly, various approaches have been developed to remove and degrade these carcinogenic dyes from the natural environment. Advanced oxidation processes (AOPs) are the most widely used approach that is employed for dye degradation studies. Over the past few years, there has been an enormous amount of work that has been done with AOPs and as a result various kinds of AOPs have been developed. The aim of this review is to address the fundamentals of one kind of AOP, namely, photocatalytic, and how it is used for dye degradations in aqueous suspensions using TiO_2 as a catalyst. Since AOPs rely on the generation and subsequent reaction of highly reactive oxygen radicals with dyes, there are many factors that can affect the efficiency of this process. Hence, this review will attempt to summarize and highlight the effect of a variety of conditions on TiO_2-photocatalysed decoloration of dyes, such as amount of catalyst, reaction pH, light intensity, concentration of organic dye, and the presence of additives such as ions. This review also summarizes the degradation pathways that azo dyes undergo, with some of the intermediates that are generated during their degradation. Finally, a survey is presented of the various classes of dyes and their relative ease of degradation by AOPs.

1. Introduction

Water bodies comprising both polluted wastewaters and groundwater from seas, rivers and lakes are of special concern to people working in water purification and the environment in general. In this regard water quality control standards and regulations against hazardous pollutants have become stricter in many countries. With increasing revolution in science and technology, there was a bigger demand on opting for newer chemicals which could be used in various industrial processes. Organic dyes came up as one of the many new chemicals which could be used in many industrial activities. Due to the extensive use of these dyes in industries, they have become an integral part of industrial effluent. In fact, of the 450,000 ton of organic dyes annually produced worldwide, more than 11% is lost in effluents during manufacture and application processes [1]. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental problem [2]. Various methods have been suggested to handle the dye removal from water; these include the biodegradation, coagulation, adsorption, advanced oxidation process (AOP) and the membrane process [3–8]. All these processes have some advantages or disadvantages over the other method. A balanced approach is therefore needed to look into the worthiness on choosing an appropriate method which can be used to degrade the dye in question. Among these techniques, the advanced oxidation processes [9] appears to be a promising field of study, which have been reported to be effective for the near ambient degradation of soluble organic contaminants from waters and soils, because they can provide an almost total degradation [10–20]. The various AOPs include the following:

(1) photolysis (UV or VUV),
(2) hydrogen peroxide (this includes the H_2O_2 + UV, Fenton: $H_2O_2 + Fe^{2+}/Fe^{3+}$, Fenton-like reagents: $H_2O_2 + Fe^{2+}$-solid/Fe^{3+}-solid and photo-Fenton: $H_2O_2 + Fe^{2+}/Fe^{3+}$ + UV),
(3) ozone (this includes ozonation, photo-ozonation, ozonation + catalysis and $O_3 + H_2O_2$ and $O_3 + Fe^{2+}/Fe^{3+}$) and
(4) photocatalysis (this includes heterogeneous catalysis and photocatalysis and TiO_2 + CdS + combinations).

The aim of this review is to address the fundamentals of heterogeneous photocatalytic dye degradation in solution using TiO_2 as a

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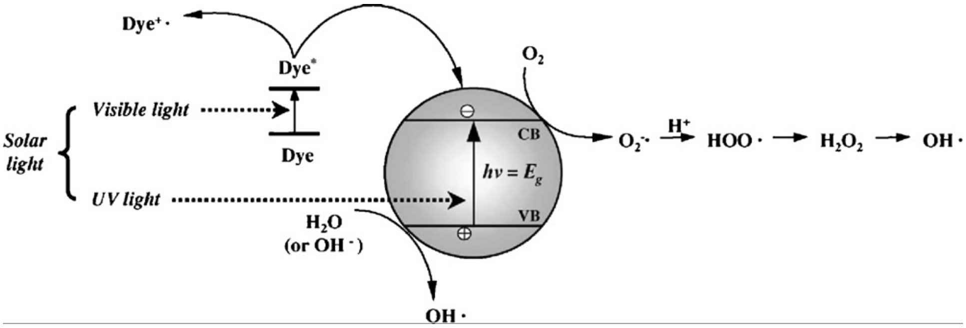


Fig. 1. Schematic diagram showing the generation of oxidative species in a photocatalytic study.

catalyst. The review can be beneficial for researchers who wish to pursue their research interest in this area.

2. Experimental techniques used for studying dye degradation

Different experimental techniques have been proposed for both qualitative and quantitative analysis of various dyes concerning their degradation. These methods usually involve analysis by instrumental methods such as UV–vis spectrophotometry [21,22], GC/MS [23], HPLC [24], ion chromatography [25], capillary electrophoresis [26], radiometry [27] etc. In this regard prior procedures of extraction of the aqueous sample with an organic solvent or filtration are adopted when a heterogeneous catalyst or solid reactant is employed. Since most of the dyes would ultimately breakdown into smaller molecules, an important aspect of this study is also to evaluate the total organic carbon of the system under investigation [28–30]. The most typical laboratory-scale experimental set up includes a vigorously stirred batch photochemical cell, cylindrical flasks or vessels and glass dishes [31–34]. On the other hand, upflow type, membrane based and coated surfaces have also been reported as photo-catalytic reactors for dye studies [35–38].

3. Principles of photocatalysis and mechanistic pathways

Photocatalytic degradation is a part of AOP which has proven to be a promising technology for degrading organic compounds [33,37,39–48]. The technique is more effective as compared to other AOPs because semiconductors are inexpensive and can easily mineralize various organic compounds [49].

The photocatalytic discoloration of a dye is believed to take place according to the following mechanism. When a catalyst is exposed to UV radiation, electrons are promoted from the valence band to the conduction band. As a result of this, an electron–hole pair is produced [33]

$$\text{Catalyst} + h\upsilon \rightarrow \ e^-{}_{cb} + h^+{}_{vb} \tag{1}$$

where, $e^-{}_{cb}$ and $h^+{}_{vb}$ are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases $h^+{}_{vb}$ can react easily with surface bound H_2O to produce $^{\bullet}OH$ radicals, whereas, $e^-{}_{cb}$ can react with O_2 to produce superoxide radical anion of oxygen [38]

$$H_2O + h^+{}_{vb} \rightarrow \ ^{\bullet}OH + H^+ \tag{2}$$

$$O_2 + e^-{}_{cb} \rightarrow \ O_2{}^{-\bullet} \tag{3}$$

This reaction prevents the combination of the electron and the hole which are produced in the first step. The $^{\bullet}OH$ and $O_2{}^{-\bullet}$ produced in the above manner can then react with the dye to form other species and is thus responsible for the discoloration of the dye.

$$O_2{}^{-\bullet} + H_2O \rightarrow H_2O_2 \tag{4}$$

$$H_2O_2 \rightarrow \ 2^{\bullet}OH \tag{5}$$

$$^{\bullet}OH + \text{dye} \rightarrow \text{dye}_{ox} \qquad (k = \ 10^9 - 10^{10}\,M^{-1}\,s^{-1}) \tag{6}$$

$$\text{Dye} + e^-{}_{cb} \rightarrow \ \text{dye}_{red} \tag{7}$$

A schematic presentation of the mechanisms of generation of oxidative species in a photocatalytic study is shown in Fig. 1.

Direct and Indirect photocatalytic pathways are the two suggested mechanisms for a given photocatalytic reaction. These are discussed below.

3.1. Direct photocatalytic pathway

Two different approaches have been suggested for this type of mechanism:

(i) Heterogeneous photocatalysis—the Langmuir–Hinshelwood process

The Langmuir–Hinshelwood process is applied to heterogeneous photocatalysis and can be explained on the basis of production of electrons and holes by the photoexcitation of the catalyst. The hole is then trapped by the adsorbed dye molecule on the catalyst surface to form a reactive radical state which can decay as a result of recombination with an electron. The catalyst is regenerated as a result. Langmuir–Hinshelwood (L–H) expression in its simpler form is given by [50]:

$$1/r = 1/k_r + 1/(k_r k_a C) \tag{8}$$

where r is the reaction rate for the oxidation of reactant (mg/l min), k_r is the specific reaction rate constant for the oxidation of the reactant (mg/l min), k_a is the equilibrium constant of the reactant (l/mg) and C is the dye concentration.

When the chemical concentration C_o is a millimolar solution (C_o is small) the equation can be simplified to an apparent first-order equation:

$$\ln(C_o/C) = kKt = k_{app}t \quad \text{or} \quad C = C_o \exp(-k_{app}t) \tag{9}$$

A plot of $\ln C_o/C$ versus time represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k_{app}. Generally first-order kinetics is appropriate for the entire concentration range up to few ppm and several studies were reasonably well fitted by this kinetic model. The L–H model was established to describe the dependence of the observed reaction rate on the initial solute concentrations. Numerous examples of dye degradation adhering to such a process are reported in the literature [51,52]. Fig. 2

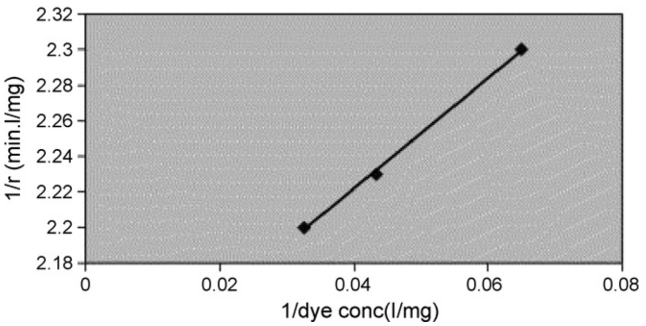


Fig. 2. Langmuir–Hinshelwood plot in the case of Coomassie Blue degradation.

Table 1
Effect of V_2O_5/TiO_2 on % decoloration of dye solution in the presence of UV light [33].

Dye	V_2O_5/TiO_2				
	10	20	25	30	40
Toluidine Blue	15	40	47	41	27
Safranin Orange	8	11	21	12	–
Crystal Violet	6.5	12	–	17	15

shows one such example of L–H model applied to dye degradation.

(ii) The Eley–Rideal process

In this process, the free carriers are initially photofragmented followed by subsequent trapping of the holes by surface defects. The surface active centers (S) can then react with the dye (chemisorption) to form an adduct species such $(S\text{–}dye)^+$ which can further decompose to produce products or can recombine with electrons. The reaction scheme is outlined below [52]:

$$\text{Catalyst} + h\upsilon \rightarrow e^- + h^+ \quad \text{(photogeneration of free carriers)} \tag{10}$$

$$S + h^+ \rightarrow S^+ \quad \text{(hole trapping by surface defects)} \tag{11}$$

$$S^+ + e^- \rightarrow S \quad \text{(physical decay of active centers)} \tag{12}$$

$$S^+ + \text{dye}^+ \rightarrow (S\text{–}CP)^+ \quad \text{(chemisorption)} \tag{13}$$

$$(S\text{–}\text{dye})^+ \rightarrow S + \text{products} \tag{14}$$

3.2. *Indirect photocatalytic mechanism*

In this process, electron–hole pairs are photogenerated on the surface of the catalyst. The hole is then trapped by the water molecules leading to the formation of $HO^\bullet$ radicals and H^+ and the electrons allow the formation of H_2O_2 which further decomposes in more OH^- radicals by means of its reaction with the oxygen supplied in the medium. Finally, the radicals formed during this mechanism are responsible for the oxidation of the organic molecule producing intermediates and end products [31].

The stepwise mechanism is illustrated below:

$$h\upsilon \rightarrow e^- + h^+ \tag{15}$$

$$h^+ + H_2O(\text{ads}) \rightarrow HO^\bullet(\text{ads}) + H^+(\text{ads}) \tag{16}$$

$$O_2 + 2e^- \rightarrow O_2{}^{-\bullet}(\text{ads}) \tag{17}$$

$$O_2{}^{-\bullet}(\text{ads}) + H^+ \leftrightarrow HO^\bullet{}_2(\text{ads}) \tag{18}$$

$$HO^\bullet{}_2(\text{ads}) \rightarrow H_2O_2(\text{ads}) + O_2 \tag{19}$$

$$H_2O_2(\text{ads}) \rightarrow 2HO^\bullet(\text{ads}) \tag{20}$$

$$HO^\bullet + \text{dye} \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \tag{21}$$

4. Effect of operational parameters

4.1. *Effect of pH*

The pH has a great effect on the photodegradation efficiency of dyes. The variation of solution pH changes the surface charge of TiO_2 particles and shifts the potentials of catalytic reactions. As a result, the adsorption of dye on the surface changes thereby causing a change in the reaction rate. Under acidic or alkaline condition the surface of titania can be protonated or deprotonated respectively according to the following reactions:

$$TiOH + H^+ \rightarrow TiOH_2{}^+ \tag{22}$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \tag{23}$$

Thus titania surface will remain positively charged in acidic medium and negatively charged in alkaline medium. Titanium dioxide is reported to have higher oxidizing activity at lower pH but excess H^+ at very low pH can decrease reaction rate. For example, Acid Yellow 17(an anionic dye) has shown to be more degraded at pH 3 [53], whereas, Orange II and Amido Black 10B showed maximum degradation at pH 9 [54]. Similar results have been reported for TiO_2 mediated photolytic reactions for the removal of chlorophenols [55].

4.2. *Effect of the dose of semiconductor*

Dye degradation is also influenced by the amount of the photocatalyst. The dye degradation increases with increasing catalyst concentration, which is characteristic of heterogeneous photocatalysis. The increase in catalyst amount actually increases the number of active sites on the photocatalyst surface thus causing an increase in the number of $^\bullet OH$ radicals which can take part in actual discoloration of dye solution. Beyond a certain limit of catalyst amount, the solution becomes turbid and thus blocks UV radiation for the reaction to proceed and therefore percentage degradation starts decreasing [56,57]. A representative example showing the effect of catalyst amount on % decoloration is presented in Table 1.

Table 2
Apparent rate constants and percentage decoloration of dye solution [33].

[Dye] (μM)	Toluidine Blue		Safranin Orange		CrystalViolet	
	k_{app} (min^{-1})	% Decoloration	k_{app} (min^{-1})	% Decoloration	k_{app} (min^{-1})	% Decoloration
80	0.0065	15	0.0063	8.0	–	–
70	0.0070	22	–	–	–	–
60	0.0076	30	–	–	–	–
50	0.0412	57	–	–	–	–
40	–	–	0.0124	13.5	0.0039	6.5
30	–		0.0190	15.5	0.0067	8
20	–		0.0240	16.5	0.0106	19

4.3. *Effect of the initial concentration of dye*

The initial concentration of dye in a given photocatalytic reaction is also another factor which needs to be taken into account. It is generally found that percentage degradation decreases with increasing amount of dye concentration, while keeping a fixed amount of catalyst [57]. This can be rationalized on the basis that as dye concentration increases, more organic substances are adsorbed on the surface of TiO_2, whereas less number of photons are available to reach the catalyst surface and therefore less $^{\bullet}OH$ are formed, thus causing an inhibition in degradation percentage. Table 2 exemplifies the effect of dye concentration on its % decoloration.

4.4. *Effect of additives*

The photocatalytic degradation of dyes is also effected by the presence of additives in solution matrix [53,54,58–60]. These additives are generally present as ions which are initially added to the dye solution as ionic compounds in order to improve the industrial process. However on release of wastewater, the ions become an integral part of the effluent. Many common ions present in dye wastewater are Fe^{+2}, Zn^{+2}, Ag^{+}, Na^{+}, Cl^{-}, PO_4^{3-}, SO_4^{2-}, BrO_3^{-}, CO_3^{2-}, HCO_3^{-} and persulphate ions. Each of these added ions causes a certain decrease in percentage degradation of the dye solution. The change in dye degradation in the presence of some selective ions is explained below on the basis of their chemical reactions in solution. For example, Fe^{+2} ions most likely undergoes the following chemical reaction in solution with $HO^{\bullet}$ radicals already produced in solution:

$$HO^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \qquad (24)$$

The above reaction has an appreciably high rate constant value of $3.5 \times 10^{8}\ M^{-1}\ s^{-1}$ [61]. Thus in the presence of Fe^{2+}, $HO^{\bullet}$ radicals are easily converted into OH^{-}, thereby decreasing their concentration and thus less degradation of dye solution is observed.

Likewise, the presence of CO_3^{2-} and HCO_3^{-} ions are usually added to the dye bath to adjust the pH of the dye solution. In the presence of these ions, dye degradation also decreases. This can be explained on the basis that the presence of these ions scavenge the $HO^{\bullet}$ radicals according to the following reactions thus causing a decrease in percentage degradation.

$$CO_3^{2-} + HO^{\bullet} \rightarrow CO_3^{\bullet -} + OH^{-} \qquad k = 3.9 \times 10^{8} \qquad (25)$$

$$HCO_3^{-} + HO^{\bullet} \rightarrow CO_3^{\bullet -} + H_2O \qquad k = 8.5 \times 10^{6} \qquad (26)$$

Similarly, a decrease in degradation value in the presence of Cl^{-} is due to its hole and hydroxyl radical scavenging effect, which occurs as follows [33]:

$$Cl^{-} + h_{VB}^{+} \rightarrow Cl^{\bullet} \qquad (27)$$

$$Cl^{-} + Cl^{\bullet} \rightarrow Cl^{\bullet -} \qquad (28)$$

$$HO^{\bullet} + Cl^{-} \rightarrow HOCl^{\bullet -} \qquad (29)$$

$$HOCl^{\bullet -} + H^{+} \rightarrow Cl^{\bullet} + H_2O \qquad (30)$$

The presence of sulphate ions in solution also causes a decrease in percentage degradation because these ions can react with $HO^{\bullet}$ radicals in solution and result in their depletion as follows [62]:

$$SO_4^{2-} + HO^{\bullet} \rightarrow SO_4^{\bullet -} + OH^{-} \qquad (31)$$

Addition of a strong oxidizing agent such as persulphate ions ($S_2O_8^{2-}$) also decreases the degradation percentage because of the reason that it can produce sulphate ions in solution:

$$S_2O_8^{2-} + e^{-}_{cb} \rightarrow SO_4^{\bullet -} + SO_4^{2-} \qquad (32)$$

Table 3
Change in percent decoloration of dye solution in the presence of various ions [33].

Ions	% Decoloration of dyes		
	Toluidine Blue	Safranin Orange	Crystal Violet
–	40	21	17
Fe^{2+}	6	3.5	8.5
Zn^{2+}	11	–	7.5
Ag^{+}	23	7.5	10
CO_3^{2-}	23	7	10
HCO_3^{-}	23	12.5	10
Cl^{-}	11	9	15
BrO_3^{-}	29	–	9.5
$S_2O_8^{2-}$	12	11	12
SO_4^{2-}	38	9	12.5
PO_4^{3-}	33	17	9

The sulphate ions can then react with $HO^{\bullet}$ radicals as shown above. The sulphate radicals can further react with water molecules to produce more sulphate ions as follows:

$$SO_4^{\bullet -} + H_2O \rightarrow HO^{\bullet} + SO_4^{2-} + H^{+} \qquad (33)$$

Since $SO_4^{\bullet -}$ is less reactive than $HO^{\bullet}$ radicals, therefore SO_4^{2-} concentration increases in solution which leads to less dye degradation.

The addition of bromate ion (BrO_3^{-}) can also decrease percentage degradation. This can be explained on the basis that this species is an efficient electron scavenger and can react in the solution as follows [33]:

$$BrO_3^{-} + 6e^{-}_{cb} + 6H^{+} \rightarrow Br^{-} + 3H_2O \qquad (34)$$

The bromide ions produced in the reaction can react with $HO^{\bullet}$ radicals in solution (rate constant value = $1.1 \times 10^{9}\ M^{-1}\ s^{-1}$) thus decreasing their concentration which result in less degradation.

$$Br^{-} + HO^{\bullet} \rightarrow {}^{\bullet}Br + OH^{-} \qquad (35)$$

Table 3 shows the effect of ions on % decoloration on some dyes. Likewise the addition of ethanol can inhibit the photodegradation of a dye solution. This is because of the reason that ethanol can quench hydroxyl radicals which are the main source of dye degradation chemistry [53].

Photocatalytic degradation is also influenced by the presence of oxygen or air [62–67]. The degradation becomes less in the absence of oxygen and this has been attributed to the recombination of photogenerated hole–electron pairs. Oxygen adsorbed on the surface of a semiconductor prevents the recombination process by trapping electrons according to the reaction:

$$O_2 + e^{-} \rightarrow O_2^{\bullet -} \qquad (36)$$

It is known that the reaction rate is a function of the fraction of adsorption sites occupied by dissolved oxygen which thus makes it a limiting factor towards the photoxidative process [68].

4.5. *Effect of temperature*

Experimental studies on the dependence of the reaction rate of degradation of organic compounds on temperature have also been carried. Many researchers have reported the effect of photocatalytic activity on temperature [69–72]. In general, an increase in temperature increases the recombination of charge carriers and also the desorption process of adsorbed reactant species, thereby resulting a decrease of photocatalytic activity. This is in accordance with the Arrhenius equation, for which the apparent first order rate constant K_{app} should increase linearly with $\exp(-1/T)$.

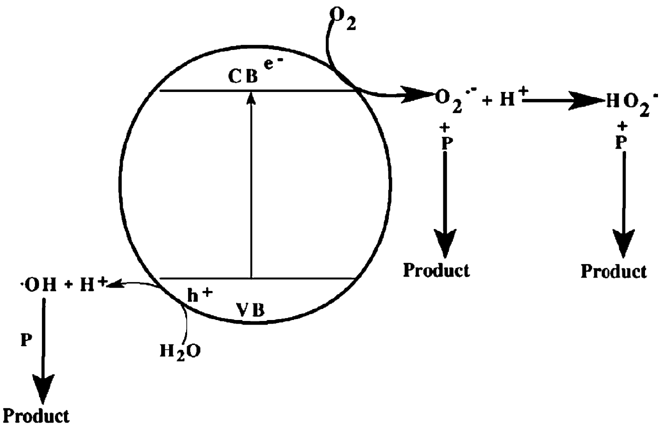


Fig. 3. Degradation of pollutants (P) using TiO_2 in the presence of UV light.

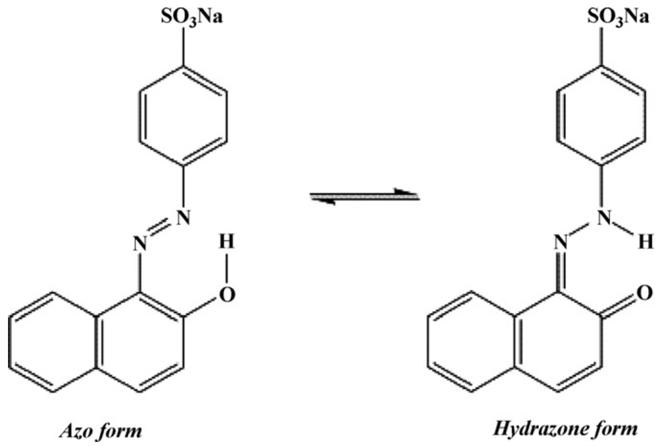


Fig. 4. Tautomeric forms of Acid Orange 7 in aqueous solution.

5. Degradation studies of dyes

5.1. General considerations

With the advancement of experimental techniques, various semiconductors have been tested for their efficiencies towards dye degradation. Some of these include TiO_2, V_2O_5, ZnO, WO_3, CdS, ZrO_2 and their impregnated forms [33,63,64–67]. Titanium dioxide mediated photocatalytic oxidation has been applied more extensively for dye studies [41,61–63]. This is mainly because of its low cost, stable nature and its optical absorption in the UV region. The use of TiO_2 has also guaranteed good results in detoxification of water samples loaded with molecules like anilines, alcohols, and organochlorides [68–72]. A quick comparison between TiO_2 and other semiconductors such as ZrO_2 reveals that the photocatalytic efficiencies are quite different. Although the bandgap energies for both TiO_2 and ZrO_2 are the same (3.1 eV) the higher activity of TiO_2 could be assigned to a higher efficiency in the separation of the photogenerated charges (less e^-/h^+ recombination rate) due to the structure of the material. On the other hand, ZrO_2 presents a low absorbance in the UV range which is due to intrabandgap surface states, thereby causing its low activity. A schematic diagram showing the degradation of pollutants (P) using TiO_2/UV radiation is illustrated in Fig. 3.

5.2. Photocatalyic degradation scheme for an azo dye

Azo-dyes are characterized by nitrogen to nitrogen double bonds (—N=N—) that are usually attached to two radicals of which at least one but usually both are aromatic groups (benzene or naphthalene rings). The color of azo-dyes is determined by the azo bonds and their associated chromophores and auxochromes. Azo bonds are the most active bonds in azo-dye molecules and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band. The cleavage of —N=N— bonds leads to the decoloration of dyes.

The photocatalytic degradation of aqueous solutions of an azo dye, namely Acid Orange 7 AO7) has been examined with the use of a solar light-irradiated TiO_2 catalyst [73]. This dye mainly exists in two tautomeric forms, i.e., the azo form and the hydrazone form as shown in Fig. 4. However the hydrazone is predominant in aqueous solution. It was found that the photocatalytic degradation of this leads to decoloration of the solution and, eventually, to complete mineralization of the dye solution. AO7 adsorbs on the photocatalyst surface via the oxygen of its hydrazone form and the two oxygen atoms of the sulfonate group. Interaction with solar light results initially in cleavage of the dye molecule in the vicinity of the azo bond followed by the formation of molecules containing naphthalene- and benzene-type rings. This step takes place to a significant extent via the photosensitized mechanism and results in decoloration of the solution but is not accompanied by significant decrease of the chemical oxygen demand. The primary reaction intermediates were found to undergo a series of successive oxidation steps which lead to the formation of aromatic acids and then to aliphatic acids of progressively lower molecular weight. This results in the decrease of pH and an increase of the conductivity of the solution. Eventually, complete mineralization of carbon and of nitrogen and sulfur heteroatoms is achieved, into CO_2 and $SO_4{}^{2-}$, $NH_4{}^+$ and $NO_3{}^-$ ions, respectively.

Likewise the use of TiO_2 in degrading various azo dyes such as Acid Red 18, Methyl Orange, and others of the same class have been investigated and the results are reported in the literature [28,49,74–78]. These included both the monoazo and diazo dyes. Their degradation rates can be compared with the disappearance of dye color and total organic carbon elimination rates. On this basis, it can be demonstrated that diazo dyes are less degradable than monoazo dyes. Major intermediates identified in these studies were aromatic amine, phenolic compounds and several organic acids. The results also indicated that in the photocatalytic degradation of azo dye, adsorption of dye to TiO_2 is one of the important factors which determine the degradation rate. Photocatalytic degradation of azo dye was proposed to proceed predominantly through oxidation by positive hole (or •OH) and reduction by conduction band electron and to some extent by electron injection from dye to conduction band. A general degradation pathway of an azo dye is shown in Fig. 5.

5.3. Effect of substituents

The photocatalytic degradation of many other dyes with different structures and containing different substituent groups has also been investigated using TiO_2 as photocatalyst in aqueous solution [79–100]. For example, the photocatalytic degradation of triazine-containing azo dyes, Procion Red MX-5B and Reactive Brilliant Red K-2G, in aqueous TiO_2 dispersions is reported in the literature [101]. The results showed that decoloration and desulfuration occurred at almost the same rate in the first step of photo-oxidation. The substituents attached to the naphthalene group of a dye molecule were hydroxylated more easily than those linked to the triazine group. Most of intermediates were aromatic and aliphatic carboxylic acids, which were further oxidized slowly to CO_2. The mineralization rates of the selected dyes were much slower than the decoloration rates. Cyanuric acid was the final organic products for both azo dyes, showing stable structure for photocatalysis.

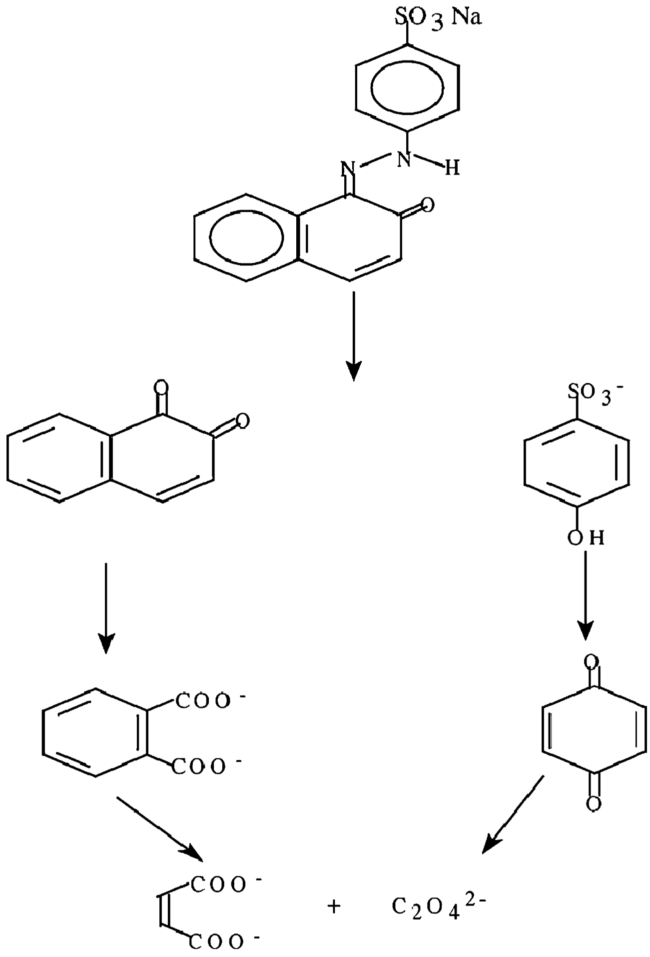


Fig. 5. Degradation pathway of an azo dye.

5.4. Effect of TiO_2 form on dye degradation

Since various forms of TiO_2 forms are available such as P-25 Degussa TiO_2, Tiona PC 100, TiO_2 Tiona PC 500 and nano-sized TiO_2, it is interesting to note that in such cases where the former form was used, the degradation rates were appreciably lower. This is generally attributed to the fact that the dye molecules bound strongly to the catalyst surface and blocks the active sites leading to saturation and lower degradation rate. On the other hand, the use of nano sized TiO_2 catalyst increases the surface area of the catalyst which can lead to more degradation of dye molecules at the end.

A representative example of the photocatalytic degradation of Indigoid dye AB74 using various forms of TiO_2 is reported in the literature [82]. The results indicated that TiO_2 P25, TiO_2 Tiona PC 100, TiO_2 Tiona PC 500, with a predominant anatase crystalline phase, were effective catalysts for the degradation of AB74, whereas rutile TiO_2 R900 and TiO_2 TC4 do not efficiently induce the oxidation of the dye. Consequently, the catalytic ability of titanium dioxide is dramatically dependent on its crystalline form. However, the reasons for the quantitative differences between the photocatalytic activities of rutile and anatase are not really transparent. From the thermodynamical point of view, photooxidation should occur with the same efficiency for both anatase and rutile. But despite the greater free-carrier mobility in anatase, the surface recombination of photoexcited electron and positive holes is higher in rutile. Moreover, a range of photoactivities was observed for each polymorph. This suggests that variables such as crystal and particulate sizes, manufacturing route (temperature, heating time, etc.) give rise to subtle changes in activity. Samples of mixed morphology (TiO_2 P25) were found to be generally the most photoactive. It was postulated that electrons produced in anatase microcrystallites quickly diffuse to become localized in rutile regions. The breakdown-products varied with the nature of the photocatalyst. Increasing quantities were obtained as follows: TiO_2 Tiona PC 500 < TiO_2 Tiona PC 100 < TiO_2 P25 < TiO_2 R900. This phenomenon may be related to a variation in the reaction mechanism and also ascribed to the difference in the total surface exposed. One can observe that for by-products with higher adsorption constants, photocatalysts with a large surface area would probably readsorb more organic intermediates as soon as they appear in solution.

5.5. Comparison of cationic and anionic dye

Several cationic and anionic dyes have been subjected to photocatalytic degradation in the presence of UV light and TiO_2 [102]. It was found that TiO_2 adsorbed almost only cationic dyes, except for the anionic Quinizarine (adsorption efficiency of 21.8%) and the cationic color index (C.I.) Basic Orange 2 which displayed no adsorption. This fact was explained in relation to the surface structure of TiO_2. On the surface of unmodified crystal TiO_2, mainly oxygen atoms with a high electron density (negative centers) are present. Thus, the TiO_2 particles have a negative charge and, therefore, more readily adsorb cationic molecules. The highest values of photocatalytic degradation rate constant are observed for cationic dyes. These results confirm the hypothesis that the adsorption of dye has a significant effect on its susceptibility to photocatalytic degradation. However, there was no correlation between adsorption efficiency and the values of the photodegradation rate constant. There was a linear correlation between absorbance of illuminated solution of dyes and reverse values of the dyes photodegradation rate constant. Only cationic dyes could be adsorbed on the surface of the photocatalyst. Simultaneously, their photocatalytic degradation is faster than that of anionic dyes.

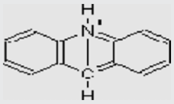
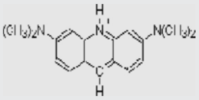
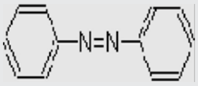
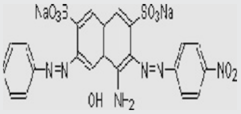
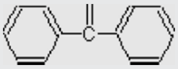
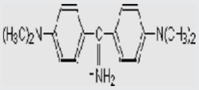
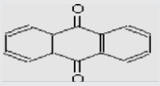
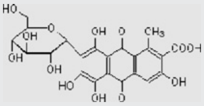
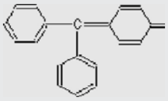
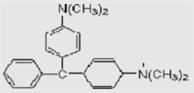
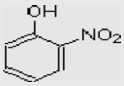
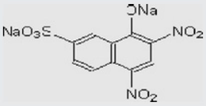
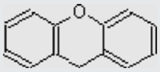
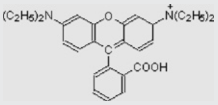
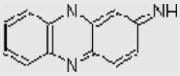
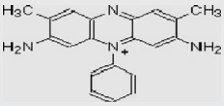
5.6. Correlation of dye degradation with its type

Dyes are mainly classified on their structure, source, color and method of application in color index, which has been continuously edited since 1924. Depending on the chromophores, different groups of dyes are considered. The diverse classes of dyes include the acridine dyes, azo dyes, arylmethane dyes, anthroqinone dyes, nitro dyes, xanthene dyes and the quinine–amine dyes, etc. Table 4 summarizes the structures of various classes of dyes along with an example of each class. Although literature survey has revealed many examples of degradation studies, however, there is no example of any correlation which might exist between % degradation and structure or class of dyes. Our own studies on different classes of dyes have helped us establish a relative rank order of ease of dye degradation as follows: Auramine O > Safranin O > Malachite Green > Amido Black > Rhodamine B > Carmine [103]. The above dyes belong to different classes of dye as classified in Table 5 along with other parameters of such studies. Although, this rank order was established using the UV/H_2O_2 photolytic AOP, we believe the same rank order will be observed for other AOPs as hydroxyl radicals (which are responsible for dye degradation) are generated in all the AOPs. In general, our findings have revealed that diarylmethane class dyes are most effectively degraded, whereas anthraquinone class dyes are least degraded. At this stage it might not be possible to elaborate more on this aspect as more detailed studies are needed in this direction.

5.7. Effect of doping and mixed semiconductors

Generally speaking, any semiconductor doped with a secondary dopant would increase its activity. Several metals have been used

Table 4
Structures of various dye classes.

Class	Structure	Representative dye	Structure
Acridine		Acridine O	
Azo		Amido B	
Diarylmethane		Auramine O	
Anthraquinone		Carmine	
Triarylmethane		Malachite green	
Nitro		Naphthol Y	
Xanthene		Rhodamine B	
Quinone-imine		Safranin O	

for doping; these include Pt, Li^+, Zn^{2+}, Cd^{2+}, Ag^+, Co^{3+}, Cr^{3+}, Fe^{3+}, Al^{3+}, etc. [61,62,104,105]. The presence of transition metals increases the photocatalytic activity either by scavenging electrons that reduce the recombination of charges and therefore favors the $HO^\bullet$ formation, or by modifying the surface properties of the material regarding the active sites, presence of defects etc., which could increase the adsorption and favor the interfacial reactions. In mixed semiconductor photocatalysts the synthesis procedure has a marked effect on the catalytic activity of the hybrid photocatalyst as reported in the case of TiO_2–SiO_2 [106,107], TiO_2–V_2O_5 [33], etc. This might perhaps be because the recombination is increased by crystallite defects. The following primary processes leading to interparticle electron transfer (IPET) has been widely used to describe the promotion effect in mixed systems [108].

Table 5
Comparative % degradation of various classes of dyes (ref. [103]).

Dye	$k \times 10^{-2}$ (min^{-1})	% Degradation	Dye class
Auramine O	5.5	81	Diarylmethane
Safranin O	4.8	77	Quinone-imine
Malachite green	4.5	76	Triarylmethane
Amido Black	3.8	68	Azo
Rhodamine B	2.2	50	Xanthene
Carmine	2.1	49	Anthraquinone
Auramine O	5.5	81	Diarylmethane
Safranin O	4.8	77	Quinone-imine
Malachite green	4.5	76	Triarylmethane
Amido Black	3.8	68	Azo
Rhodamine B	2.2	50	Xanthene
Carmine	2.1	49	Anthraquinone

$$CdS + h\nu \rightarrow CdS(h^+ + e^-) \quad (37)$$

$$TiO_2 + h\nu \rightarrow TiO_2(h^+ + e^-) \quad (38)$$

$$CdS(h^+ + e^-) + TiO_2 \rightarrow CdS(h^+)TiO_2(e^-) \quad (39)$$

$$CdS(h^+ + e^-) + TiO_2(h^+ + e^-) \rightarrow CdS(h^+ + h^+) + TiO_2(e^- + e^-) \quad (40)$$

The excess electrons on the TiO_2 can be scavenged by chemisorbed diatomic molecular oxygen [109].

6. Conclusion

Based on the literature findings, the following conclusive remarks can be highlighted.

- That TiO_2 can be used as an effective catalyst for the degradation/decoloration of various dyes in solution.
- The findings also indicate that degradation/decoloration rate can be influenced by operational parameters such as the amount of a photocatalyst, pH and concentration of organic dyestuff besides the presence of electron acceptors and other additives.
- The TiO_2 sample when loaded with metal ions enhances its photocatalytic activity.
- Cationic dye undergoes faster degradation than the anionic dyes.

- Although this review is non-exhaustive in the scope of photocatalytic degradation of dye degradation, it, however, addresses the fundamental principles and application in this area.

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