

## A review on Advanced Oxidation Processes for the treatment of Textile effluent

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### ABSTRACT

Dyes are those synthetic and natural compounds which applied in form of aqueous based solutions with many additives to strong attachment of dye molecule with a fabric for persistence the colour on it while pigments are usually insoluble. There are various methods of dye all over the world for dye fabrications. Dyes fabrication processes require thousands liters of water for coloring materials which need very small amount of it and remaining water discharged as a dye waste water and become hazardous to ecology. As an effluent from textile and printing industries having remaining dyes and several additives it become one of the central sources with severe pollution complications worldwide and hard to treat by conventional Chemical/Biological processes. This complex nature of dye wastewater can be converted into less harmless/useful by products along with conventional biological treatment, chemical treatment or set of chemical treatments like Advanced Oxidation processes are used. This paper reviews various Advanced Oxidation processes (AOPs) like Hydrogen peroxide, ozonation, ultra violet radiations, alone or in combinations for the treatment of textile effluent and their efficiency regarding detoxification and color removal. The current review describes the efficiency of various advanced oxidation processes in which hydroxyl radical was generated for color removal dye bath.

**Key words:** textile waste water, AOPs, Dyes, detoxification.

### HIGHLIGHTS

- The applications of AOPs for the treatment of organic dyes compounds in water are reviewed.
- AOPs displayed debauched kinetics and excessive degrees of mineralization of organic dyes compounds.
- The Kinetics were discussed in relation with concentration of dyes in waste.
- Mechanism of dye mineralization is presented.

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## 1. INTRODUCTION

*Advanced oxidation processes* (AOPs), in an extensive vision, which involve a set of chemical oxidant generates hydroxyl radical ( $\cdot\text{OH}$ ) to significantly enhanced the oxidation procedures premeditated to eradicate organic/dye/sometimes inorganic) materials in water and waste water<sup>1</sup>. The AOPs are preferred over other treatment technologies because they are fast, efficient and completely oxidize the wastewater into  $\text{CO}_2$  and  $\text{H}_2\text{O}^{2,3}$ . The AOPs are broadly divided into two categories such as i) non-photochemical advanced oxidation methods and ii) light assisted AOPs known as advanced oxidation photochemical methods.

The discharge management methods, that breed OH radicals include the application of  $\text{H}_2\text{O}_2$  and ozone alone or in combination, such as hydrogen peroxide and ozone ( $\text{H}_2\text{O}_2/\text{O}_3$ ) and hydrogen peroxide and ferrous ions ( $\text{H}_2\text{O}_2/\text{Fe}^{+2}$ ) known as Fenton process to managed sewage without using light energy are referred a as non-photochemical methods.

### 1.1. Advanced Oxidation Methods

Several methods are available for generating OH radicals.

These include non- photochemical and photochemical methods:

- Ozonation at elevated pH (> 8.5)
- Ozone + hydrogen peroxide ( $\text{O}_3/\text{H}_2\text{O}_2$ )
- Ozone + catalyst ( $\text{O}_3/\text{CAT}$ )
- Fenton system ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ )
- $\text{O}_3/\text{UV}$
- $\text{H}_2\text{O}_2/\text{UV}$
- $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$
- Photo-Fenton/Fenton-like systems
- Photocatalytic oxidation ( $\text{UV}/\text{TiO}_2$ )

### 1.1.1. Application of Hydrogen Peroxide ( $H_2O_2$ )

Hydrogen peroxide decomposes into water and oxygen therefore is considered as a friendly oxidant. It has been used, alone or in conjunction with a catalyst and/or UV light, to degrade many harmful organic compounds and dyes in wastewaters<sup>4-9</sup>. However, the rate of de-colorization by  $H_2O_2$  is extremely slow for many dyes and numerous research workers have shown the inefficiency of  $H_2O_2$  alone for the removal of color<sup>10-13</sup>. The addition of  $H_2O_2$  in water though generates hydroxyl radicals but excess of hydrogen peroxide adversely affects the oxidation kinetics due to scavenging effect wherein  $H_2O_2$  consumes highly reactive hydroxyl free radicals<sup>14,15</sup>.

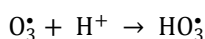
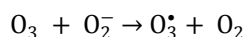
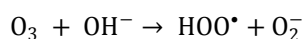
The effectiveness of the advanced oxidation process (UV/ $H_2O_2$ ) in decolorizing real textile wastewater polluted with commercial reactive dyes – Reactive Yellow 84 and Reactive Red 141 –. The dyeing wastewater was decolorized in 5 hours. After its acidification to pH 3.0 the decolorization process was more efficient. Full decolorization was then achieved in 2 hours and the decrease in COD exceeded 70%. The reaction rate constants obtained were as follows: at pH 11.4,  $0.0065 \text{ min}^{-1}$ ; at pH 7.0,  $0.0044 \text{ min}^{-1}$ , and at pH 3.0,  $0.019 \text{ min}^{-1}$ , showed the significance of pH in UV/ $H_2O_2$  oxidation process<sup>16</sup>.

### 1.1.2. Ozonation Process.

Ozone has been used for water treatment because of its higher oxidation potential (2.07 V) compared to chlorine (1.36 V) and  $H_2O_2$  (1.78 V)<sup>17</sup> since from the time of discovery by Schönbein in 1840. But this method of treatment is cost consuming due to the production of ozone gas. However, with the advancement of technology, the cost of ozone production dropped by 50% in the last decade and, therefore, a great number of new industrial applications have appeared in recent years<sup>18</sup>.

Ozonation process has been regarded as one of the most effective means of decolorizing textile effluents and has been shown by numerous research workers to achieve high color removal and improved biodegradability<sup>19-25</sup>. Ozone can quickly break down unsaturated bonds and aromatic structures, such as  $-C=C-$  or  $-N=N-$ , which form the chromophoric part of synthetic dyes due to higher oxidation potential<sup>26</sup>. Ozone treatment neither forms sludge<sup>27</sup> nor produces toxic byproducts<sup>28</sup>. It also lowers COD of the effluent rendering it suitable to discharge into aqueous systems<sup>29</sup>. Another advantage of ozone application is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge.

Ozone reacts with organic compounds in two different ways: by direct oxidation as molecular ozone or by indirect reaction through the formation of secondary oxidants like hydroxyl radicals<sup>30,31</sup>. In aqueous solutions, ozonation process may involve following reactions.



The reaction between hydroxides ions and ozone leads to the formation of super oxides anion radicals  $O_2^-$  and hydroperoxyl radicals  $HOO^\bullet$ <sup>32</sup>. In acidic pH, the ozone is available in molecular form<sup>33</sup>. It has been reported that ozone decolorizes all dyes, except nonsoluble disperse and vat dyes which react slowly and take longer time<sup>34-36</sup>.

A number of studies have been carried out to optimize process conditions which are mainly pH, dye concentration, temperature and applied ozone dose<sup>25,37-40</sup>. Reaction pH is considered an important operating parameter, which influences the performance of ozonation process significantly<sup>41</sup>. At high pH, ozone reacts almost indiscriminately with all organic and inorganic compounds present in the reacting medium. Ozonation at elevated pH is a promising technique for rapid de-colorization of concentrated exhausted textile wastewater<sup>42</sup>. Ozonation process for treating textile wastewater is also depended on dye concentration. It would take longer treatment time and higher ozone consumption as the initial concentration of dyes is increased<sup>39,43</sup>. Ozonation process is also affected by temperature, and color removal rates are reported to be decreased with increasing temperatures<sup>44</sup>. As the applied ozone dose is increased, its treatment efficiency is increased because an increased ozone dosage enhanced the mass transfer due to elevated ozone content in liquid<sup>45</sup>.

Ozone applied to decolorize effluent of dyes of different classes and found it very effective to decolorize effluent but considerably less efficient for TOC removal<sup>46</sup>. Three textile dyes, reactive black 5 (RB5), direct red 28 (DR28) and basic green 4 (BG4) were selected and concluded that i) ozone removed color after two minutes of ozone contact time, ii) the complete decomposition of dyes occurred after 25 min of ozonation, iii) final products of the dyes after ozonation were harmless maleic and oxalic acids, and iv) pretreatment of dye residual water with simple ozonation had been shown to lower the toxicity since all intermediates formed during ozonation were completely decomposed and ozonation did not generate any toxic chemicals for microorganisms<sup>47</sup>. Decolorization behavior of two types of dye were

studied (Direct Pink 3B and Reactive Violet SH) at wide concentration range (100-1000 ppm) and reported 98% color removal in short period of time. However, the treatment time increased with increasing dye concentration<sup>1,48</sup>.

### 1.1.3. Ozone/ H<sub>2</sub>O<sub>2</sub> (Peroxone) System

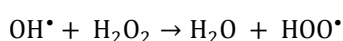
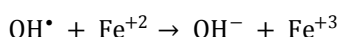
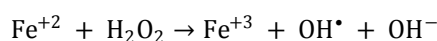
The use of ozone in blend with H<sub>2</sub>O<sub>2</sub> proved to be real system to treat textile wastewater<sup>49,50</sup> that accelerated the disintegration of ozone and enriches production of the hydroxyl radicals. At acidic pH, H<sub>2</sub>O<sub>2</sub> reacts very slowly with O<sub>3</sub> whereas at pH values above 5, a rapid decomposition of O<sub>3</sub> by H<sub>2</sub>O<sub>2</sub> has been observed<sup>51</sup>. At higher pH, even very small concentration of H<sub>2</sub>O<sub>2</sub> will be dissociated into HO<sub>2</sub><sup>-</sup> ions that can initiate the ozone decomposition more effectively than OH<sup>-</sup> ion<sup>51,52</sup>. A complete de-colorization of C.I. Reactive Blue 220 and C.I. Reactive Yellow 15 using H<sub>2</sub>O<sub>2</sub> / O<sub>3</sub> process in 90 min; however, they found C.I. Reactive Blue 220 the most difficult to decolorize and C.I. Reactive Yellow 15 the easiest<sup>49</sup>. The decomposition of H<sub>2</sub>O<sub>2</sub> into OH free radicals however takes place slowly in general, but decomposition rate can be enhanced either by assisting with UV light or increasing temperature<sup>32,53</sup>. UV radiation plus hydrogen peroxide (UV/H<sub>2</sub>O<sub>2</sub>), Fenton's reagent (H<sub>2</sub>O<sub>2</sub>/Fe<sup>+2</sup>), photo-Fenton (UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+2</sup>), and ozone processes in different combinations (O<sub>3</sub>/UV; O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) was considered as an effective system for the oxidation of effluents from pulp and paper industries by the generation of hydroxyl radicals which is commonly accelerated by combining oxidizing agents<sup>54</sup>.

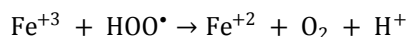
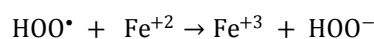
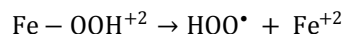
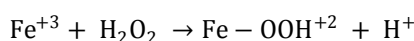
**Table. 1:** Comparison of rate constant of ozone and OH radical for the degradation of various ORGANIC COMPOUNDS<sup>55,56,57</sup>

Species	Rate Constant of O <sub>3</sub> (mol <sup>-1</sup> s <sup>-1</sup> )	Rate Constant of OH (mol <sup>-1</sup> s <sup>-1</sup> )
Alcohols	10 <sup>-2</sup> -1	10 <sup>8</sup> -10 <sup>9</sup>
Aromatics	1-10 <sup>2</sup>	10 <sup>8</sup> -10 <sup>10</sup>
Benzene	2	7.8 x 10 <sup>9</sup>
n-Butanol	0.6	4.6 x 10 <sup>9</sup>
t-Butanol	0.03	0.4 x 10 <sup>9</sup>
Bicarbonate Ion		8.5 x 10 <sup>-6</sup>
Carbonate Ion		3.9 x 10 <sup>8</sup>
Chloride Ion		4.3 x 10 <sup>9</sup>
Chlorinated Alkenes	10 <sup>3</sup> -10 <sup>4</sup>	10 <sup>9</sup> -10 <sup>14</sup>
Chlorobenzene	0.75	4 x 10 <sup>9</sup>
Dihydrogen Phosphate Ion		<10 <sup>6</sup>
Hydrogen Sulphate Ion		3.5 x 10 <sup>5</sup>
Ketones	1	10 <sup>9</sup> -10 <sup>10</sup>
N - Containing Organics	10-10 <sup>2</sup>	10 <sup>8</sup> -10 <sup>10</sup>
Nitrate Ion		1.4 x 10 <sup>8</sup>
Phenols	10 <sup>3</sup>	10 <sup>9</sup> -10 <sup>10</sup>
Sulphate Ion		1 x 10 <sup>10</sup>
Tetrachloroethylene	<0.1	1.7 x 10 <sup>9</sup>
Trichloroethylene	17	4 x 10 <sup>9</sup>
Toluene	14	7.8 x 10 <sup>9</sup>

### 1.1.4. Fenton System (H<sub>2</sub>O<sub>2</sub>/Fe<sup>+2</sup>)

The Fenton system involves the combined application of hydrogen peroxide and iron catalyst and a voluminous literature on its application to treat industrial wastewater is available<sup>58-62</sup>. The Fenton system as compared to other AOPs is advantageous as it offers a cost effective source of hydroxyl radicals, and is easy to operate and maintain<sup>64-66</sup>. The Fenton process involves following reactions:





The overall efficacy of the system is directly affected by operating parameters like pH and  $\text{Fe}^{2+}$  contents. At pH lower than 3.5,  $\text{H}_2\text{O}_2$  and ferrous ions are more stable and results into better color removal efficiency<sup>67</sup>. However, at pH values higher than 4.0, ferrous ions easily form ferric ions which have a tendency to produce ferric hydroxo complexes.  $\text{H}_2\text{O}_2$  is unstable and easily decomposes itself in the basic environment ( $\text{pH} > 10$ )<sup>68, 69</sup>. The efficiency of the system increases with increasing  $\text{Fe}^{2+}$  contents because it accelerates the production of hydroxyl radicals<sup>70-72</sup>. An increase in  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio, increases the efficiency at certain level but further increase stops the reaction as excess  $\text{H}_2\text{O}_2$  causes the scavenging of  $\text{HO}^\bullet$  radicals<sup>73</sup>.

The removal of reactive Black 5 (RB5) from synthetic wastewater using Fenton's oxidation (FO) process was performed in a systematic approach searching optimum values of  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  concentrations, pH and temperature. Optimum pH and temperature for  $100 \text{ mgL}^{-1}$  of RB5 were observed as 3.0 and  $40^\circ\text{C}$ , respectively, using  $100 \text{ mgL}^{-1}$  of  $\text{FeSO}_4$  and  $400 \text{ mgL}^{-1}$  of  $\text{H}_2\text{O}_2$  resulted in 71% chemical oxygen demand (COD) and 99% color removal. For  $200 \text{ mgL}^{-1}$  of RB5, 84% COD removal was obtained using  $225 \text{ mgL}^{-1}$  of  $\text{FeSO}_4$  and  $1000 \text{ mgL}^{-1}$  of  $\text{H}_2\text{O}_2$  yielding 0.05 molar ratios at pH 3.0 and  $40^\circ\text{C}$ . Color removal was also more than 99%. The optimum conditions determined in accordance with the literature data. The  $\text{H}_2\text{O}_2$  requirement seems to be related to initial COD of the sample.  $\text{FeSO}_4/\text{H}_2\text{O}_2$  ratios found were not changed for both concentrations. The temperature affected the COD removal significantly at high degrees. Toxicity was completely removed for each concentration of RB5 at optimum removal conditions<sup>74</sup> while 97% color removal observed after 10 min reaction by Fenton system for RB5<sup>75</sup>. De-colorization of reactive black CNN studied by chemical oxidation and reduction, using  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$  and Ferrioxalate as oxidizing agents and  $\text{Na}_2\text{SO}_3$  as reducing agent individually as well as in combination, on batch scale using UV-visible spectroscopy where  $\text{H}_2\text{O}_2$  and ferrioxalate could remove only 50.71 and 44.21% dye, respectively while 97.64% of color removal of dye by  $\text{KMnO}_4$ <sup>76</sup>. Chemical oxygen demand (COD) and total organic carbon (TOC) contents of treated wastewater decreased appreciably from 83.6 to 63.7 mg/L and 86.8 to 72.8 mg/L, respectively. FTIR study revealed the degradation of reactive black CNN after treatment into non-toxic products. The effect of porous phosphate heterostructures as catalyst sorbent of  $\text{Fe}^{2+}$  synthesized by different procedures were planned. The examined PPH- $\text{Fe}/\text{H}_2\text{O}_2$  as oxidant in a heterogeneous process under mild conditions at pH 5 was found to be very efficient for discoloration of a simulated wastewater containing  $50 \text{ mg L}^{-1}$  of a commercial azo dye (Reactive Black 5) reaching 95% of decolorization. Under the described conditions total visual decolorization was achieved after 360 min<sup>77</sup>.

The effect of Fenton and Fenton-like reactions were studied on the removal of many hazardous organic and Methyl Orange pollutants. The efficiency of the reactions were stimulated by the mixtures of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and catalysts (metal iron;  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) to generate hydroxyl free radical ( $\text{OH}^\bullet$ ) at a pH range of 2.5 - 3.0. Maximum removal was achieved at pH 3.0 within 10 min, with % decoloration of 84 and 99 %<sup>78</sup>. The decoloration of C.I. Reactive Blue 4 (RB4) and C.I. Reactive Red 2 (RR2) by Fenton reaction was studied where 99.8% and TOC degradation of 39.8, 42.5% were achieved within 60 minutes of reaction<sup>79</sup>.

The de-coloration behavior of Reactive Black 5 (RB5) by Fenton's Reagent (FR) system was studied. The reaction was dose depended of peroxide and  $\text{Fe}^{2+}$  which were 7 mM and 1 mM, respectively and decolorized dye in the first minute<sup>80</sup>. The dye was also found to enhance the decomposition of the peroxide. This suggests the possibility of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  "redox-recycled" as experienced in a Hamilton-like system favoring the use of FR process for the degradation of the dye. Oxidation of RB5 was observed by using Fenton reaction where COD decrease 84% with color removal of 99%<sup>74</sup>.

The high COD of dye waste water was controlled by fenton and electro-fenton reaction<sup>81</sup> from the range of 30,000 to 50,000 mg/L. 86% less at pH 3.0. These results suggest that, the Fenton process proved to be more efficient for removal of COD from the real dye intermediate wastewater. Kinetics decolorization of RY84 followed pseudo second-order reaction. The reaction characteristic of oxidative reaction for decolorization efficiency process was evaluated as thermodynamically spontaneous under natural conditions. The value of activation energy is determined and is equal to 16.78 kJ/mol, this low value may show that the oxidative reaction proceeds with low energy barrier<sup>82</sup>. The Fenton reaction was effective azo dye (Reactive Yellow 84) at pH 3.0.

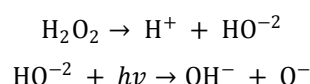
The decolorization kinetics of Malachite green (MG), Rhodamine B (RB), Methylene blue (MB) and Crystal violet (CV) in water by using a Fenton-like reagent at different parameters like the initial dye concentration,  $\text{Fe}^{3+}$ , concentration of  $\text{H}_2\text{O}_2$ , pH of the solution, reaction temperature, and added electrolytes. The highest decoloration was obtained in the range between pH 3.0 and 4.0. The  $\text{H}_2\text{O}_2$  dose  $0.01\text{--}0.04 \text{ mol dm}^{-3}$  was effective for complete removal of dyes<sup>83</sup>.

### 1.1.5. Photo-Fenton system ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ )

UV light assisted Fenton process, known as Photo Fenton process, is also considered to be one of the most effective methods for decomposing water-soluble organic pollutants<sup>84</sup>. The UV light of wavelength ranging between 100-400 nm is commonly generated by using UV lamp, and a mercury lamp is the most common UV light source<sup>85</sup>.

Many organic contaminants absorb UV energy of wavelength in the range of 200-300 nm. UV light provides energy to break covalent bonds, since the energy of UV light is of the same order as that of covalent bonds. When a chemical bond is cleaved by UV light, the remaining fragmented by-products themselves are further degraded or become excited and more susceptible to chemical oxidants leading to their complete mineralization in  $\text{CO}_2$  and  $\text{H}_2\text{O}$ <sup>86,87</sup>.

UV irradiation of  $\text{H}_2\text{O}_2$  accelerates the production of highly reactive species, mainly hydroxyl radicals ( $\text{OH}^\cdot$ )<sup>84</sup>. An alternate pathway is through the generation of  $\text{HO}_2^\cdot$  ions, which also absorb the UV radiation of 254 nm wavelength and produce hydroxyl radicals as:



These hydroxyl radicals can oxidize organic compounds producing organic radicals ( $\text{R}^\cdot$ ), which have potential to initiate a radical chain oxidation<sup>88,89</sup>.

Factors that influence the efficiency of Photo Fenton process include initial color intensity,  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  concentration, pH, temperature, alkalinity<sup>90,91,92</sup>. The coagulation also plays an important role in the pollution removal<sup>67,93</sup>. The effective degradation of various reactive dyes by the application of ferri oxalate – photo-Fenton and titanium dioxide-mediated heterogeneous photo catalytic treatment processes was studied<sup>94</sup>. Decolorization by the ferri oxalate – photo-Fenton oxidation process was found to proceed three times faster than the photo catalytic process; the results of these experiments showed that low concentration dye house effluent has faster decolorization rate. The photo degradation of three commercially available dyestuffs were studied (C.I. RB5, C.I. DY12, and C.I. DR28) by using UV alone and combinations, including UV/ $\text{H}_2\text{O}_2$  and UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ . The addition of  $\text{Fe}^{2+}$  to the system greatly enhanced the color removal<sup>70</sup>. The de-colorization of the azo dye Reactive Black 5 in aqueous solution, using  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  and initial pH was reported<sup>95</sup>. The effects of operating parameters, such as pH,  $\text{H}_2\text{O}_2$  dosage,  $\text{Fe}^{2+}$  dosage and the initial dye concentration, were investigated. The results declared that the de-coloration effectiveness of Reactive Black 5 in Fenton oxidation was considerably faster than that of the Fenton-like oxidation in the initial stages and the de-colorization competence was alike for both systems after 45 min. The removal of two azo dyes, Acid Orange 7 and Reactive Black 5 as an indicator of synthetic dyes by Fenton-like reaction was studied<sup>96</sup>. In this process,  $\text{OH}^\cdot$  radicals were generated by using  $\text{Fe}$  and UV light. Various parameters such as pH, amount of iron powder, initial dye concentration, UV light and contact time were studied in terms of their effect on the reaction progress. It was observed that high removal of dyes for UV system obtained at pH=11.0, while in the  $\text{Fe}$  and  $\text{Fe}/\text{UV}$  system, high removal occurred at pH=3.0. Color removal was directly linked with mass of iron and contact time which was achieved in 120 min.

The mineralization of azo dyes Acid Violet 7 (AV7) and Reactive Black 5 (RB5) was investigated in aqueous solutions using electro-Fenton (EF) and Photo electro-Fenton (PEF) methods<sup>97</sup>. The PEF system comprises a glassy carbon mesh electrode (cathode) with a concentric outer steel mesh as anode. The optimized parameters were: 0.01 mM of  $\text{Fe}^{2+}$  ions, and 250 mA of applied current at pH 3.0 at 35°C. The degradation leads to mineralization into carbon dioxide. The decolorization of C.I. Reactive Black 5 was investigated by the combination of hydrogen peroxide and UV radiation<sup>98</sup>.

The observed kinetic reaction coefficient was determined and correlated as a function of hydrogen peroxide concentration and UV intensity. The validity of the rate expression was tested experimentally in a parameterization study. The decolorization rate follows pseudo-first order kinetics with respect to dye concentration. The rate increases linearly with UV intensity and nonlinearly with increasing hydrogen peroxide concentration, going from a linear relationship at low  $\text{H}_2\text{O}_2$  concentrations to a maximum as hydrogen peroxide concentration continues to increase. Photo-Fenton process used for the removal efficiency of Basic Yellow 2 (a dye) from aqueous medium in which a visible light source was used to provide the radiation needed in the photo-Fenton method (i.e.  $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ ). The results showed that the Photo-Fenton method completely oxidizes and degrades Basic Yellow 2 into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ <sup>99</sup>.

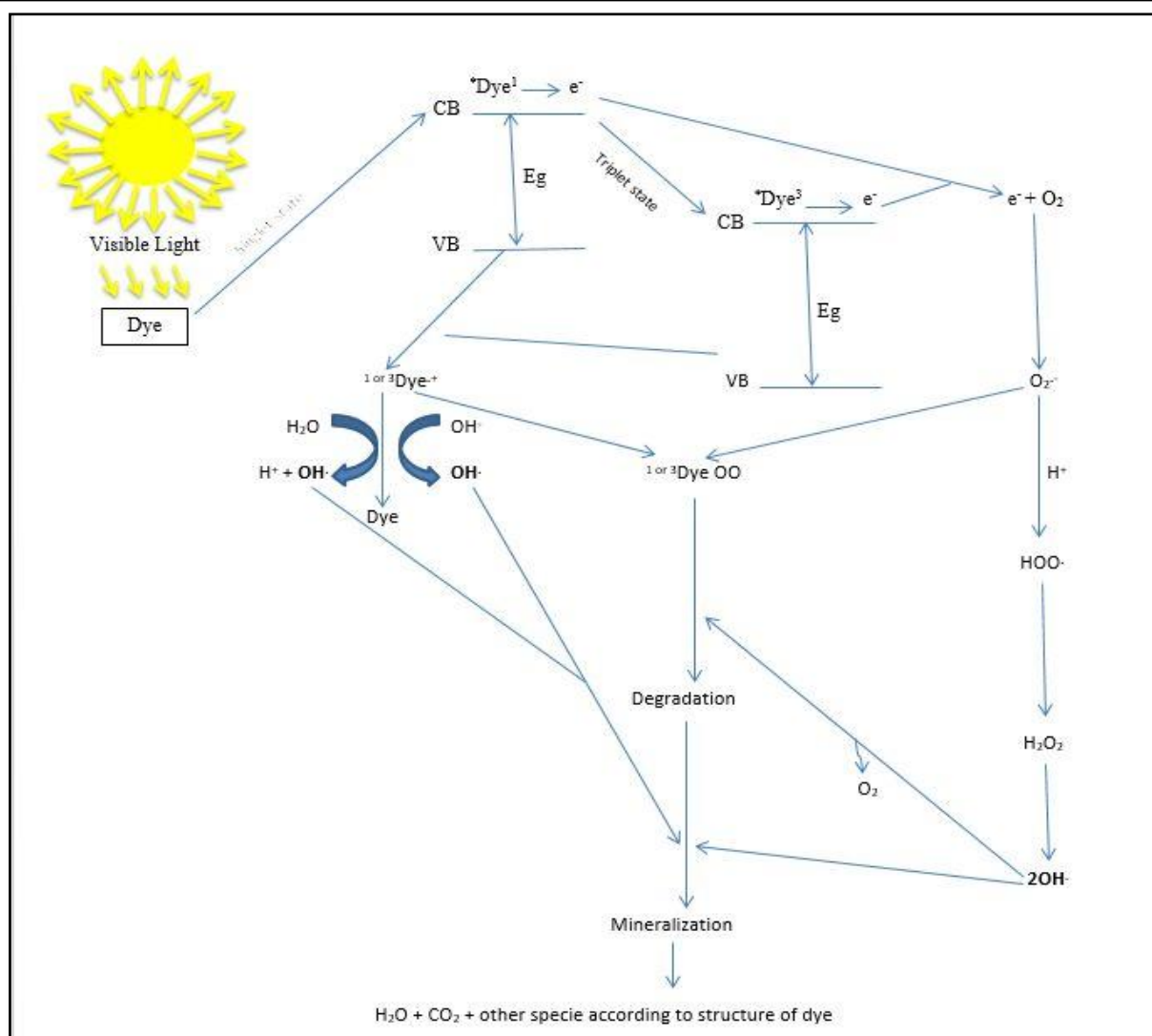


Fig. 1: A probable scheme of mineralization of Dye with OH radical

#### 1.1.6. Catalytic/Photo Catalytic Oxidation

In current era, lot of research has been conducted for the development in the area of heterogeneous photo catalytic water purification process due to its effectiveness in degrading and mineralizing the recalcitrant organic compounds as well as the possibility of utilizing the solar UV and visible spectrum. The photocatalytic degradation of Reactive Black 5 (RB5) dye was investigated with TiO<sub>2</sub>-coated magnetic nanomaterial using UV-photocatalytic path. TEM and SEM technology was used for characterization of nanoparticles which confirmed the core-shell structure of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> nanocomposite and spherical morphology with sizes ranging from 140 to 160 nm respectively. The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> showed 91% de-colorization within 60 min<sup>100</sup>. A batch reactor was used for photocatalytic degradation of reactive black-5 (RB-5) dye using supported TiO<sub>2</sub> photo-catalyst based adsorbent as a semiconductor photo-catalyst. The synthesized photo-catalyst composition was developed using TiO<sub>2</sub> as photoactive component and zeolite (ZSM-5) as the adsorbents which gave the highest efficiency with 98% degradation of 50 mgL<sup>-1</sup> RB-5 solution in 90 min. The reduction in the chemical oxygen demand (COD, 88%) proves the mineralization of the RB-5 dye along with the colour removal. The supported TiO<sub>2</sub> was found to be stable for repeated use<sup>101</sup>. The (TiO<sub>2</sub>) suspensions as photocatalyst were applied for photocatalytic degradation of commercial azo dye (Remazol Red 133). The extent of photocatalytic degradation was found to increase with increasing TiO<sub>2</sub> concentration. The effect of various operational parameters, such as pH of dye solution and catalyst concentration on the photocatalytic degradation process, was examined. The mineralization of dye was also evaluated by measuring the chemical oxygen demand of the dye solutions. 97.9% decolorization was obtained for RR dye solutions, in 120-min with 87.6% degradation at catalyst loading of 3 gL<sup>-1</sup>. Furthermore, complete decoloration was obtained in acidic condition when textile dye effluent was used<sup>102</sup>. The photocatalytic degradation of an azo dye Amaranth (AM) was investigated in TiO<sub>2</sub>/UV in aqueous suspensions which showed the highest de-colorization rate in combination of (UV + TiO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub>)<sup>103</sup>. The decolorization efficiencies were 17%, 26%, 38% and 64% in the runs UV, UV + H<sub>2</sub>O<sub>2</sub>, UV + TiO<sub>2</sub> and (UV + TiO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub>) after approximately 100 min illumination periods, respectively. The reaction was pseudo first order and rate of reaction was temperature dependent with decrease in COD of the dye. In addition, an enhancement in

the photo-degradation rate was observed by the addition of hydrogen peroxide as an electron acceptor. Heterogeneous photo catalysis described for producing oxidative agent (hydroxyl radical) for controlling dye waste hazardous as an environmentally harmonious decontamination process<sup>104</sup>. Such safe and low energy consumable photo catalytic system is required for purification of polluted water. Bromophenol blue, crystal violet and reactive red dyes were successfully photo reduced using ZnS nanoparticles after 3.0 h of irradiation. Since the photocatalytic activity depends on the generation of electron hole pairs and the existence of different phases. Photocatalytic degradation of rhodamine B dye by ZnO nanoparticles was studied<sup>105</sup>. The rhodamine B dye considerably degraded by ~95% within 70 min in the presence of as-synthesized ZnO NPs. An excellent rate constant ( $k=0.0343 \text{ min}^{-1}$ ) was obtained for the degradation of rhodamine B dye. Current verdicts recommended that diverse parameters, like type of photo-catalyst and composition, light intensity, initial substrate concentration, amount of catalyst, pH of the reaction medium, ionic components in water, solvent types, oxidizing agent's/electron acceptors, mode of catalyst application, and calcination temperatures can play an important role on the photocatalytic degradation of dye waste water/phenolic compounds. Extensive research has focused on the enhancement of photocatalysis by modification of TiO<sub>2</sub> employing metal, non-metal and ion doping. Recent developments in TiO<sub>2</sub> photocatalysis for the degradation of various phenols and substituted phenols were investigated.

**Table. 2:** Photocatalytic Relative Oxidation Power of various Oxidizing Species<sup>55,106-108</sup>

Oxidizing Species	Electrochemical Oxidation Potential (EOP) V	Relative Oxidation Power
Bromine	1.09	
Chlorine	1.36	1.00
Chlorine Dioxide	1.27/1.50	0.93
Fluorine	3.03/3.06	2.25
Hydrogen Peroxide	1.78	1.31
Hydroperoxyl Radical	1.70	
Hydroxyl Radical	2.80	2.05
Hypobromous Acid	1.59	
Hypochlorous Acid	1.49	1.10
Hypochloric Acid	1.45	
Iodine	0.54	
Oxygen (Atomic)	2.42	1.78
Oxygen (Molecular)	1.23	0.90
Ozone	2.07/2.08	1.52
Permanganate	1.67	1.24
Positively Charged Hole on TiO <sub>2</sub>		2.35

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