

# Chapter 9

## Chemical and Biological Treatment of Dyes

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### ABSTRACT

*Life of living or non-living being depends on water; in short, water is life. But these days, with the growing industrialization, it is spoiling a lot. Wastewater contains contaminants like acids, bases, toxic organic and inorganic dissolved solids, and colors. Out of them, the most undesirable are colors caused mainly by dyes. Color and other compounds present in water are always not desirable for domestic or industrial needs. The wastes of dyes are predominant amongst all the complex industrial wastewater. This water is dark in color and highly toxic, blocking the sunlight and affecting the ecosystem. Among all the dyes, azo dyes contribute to commercial dyes used widely in textile, plastic, leather, and paper industries as additives. The removal and degradation of azo dyes in aquatic environment is important because they are highly toxic to aquatic organisms. For every industry, clean technology has become an important concern. In this chapter, the authors discuss about existing processes as well as promising new technologies for textile wastewater decolorisation.*

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## **INTRODUCTION**

The consumption of water and chemicals in textile industries is tremendous for the wet processing of textiles. The reagents used varies from inorganic or organic compounds to polymers (Mishra & Tripathy, 1993; Juang *et al.* 1996). The low concentration of dye effluent presence in water is visible and not desirable (Nigam *et al.* 2000). Almost there are more than 100,000 dyes are available commercially and over tons of dye-stuff are produced annually (Meyer, 1981). Dye has complex structure and due to that they are resistant for degradation to light and also to many chemicals (Poots & Mckay, 1976a). The dyes according to structural varieties are classified as acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes. Municipal sewerage systems are not effective in decolouration of textile dye effluent (Willmott *et al.* 1998). There are other varieties of dyes like cationic, nonionic or anionic type. Anionic dyes are the acid, direct as well as reactive dyes. The most problematic are those dyes which are bright in colour, water-soluble, reactive and acid dyes because they are unaffected by the conventional treatment systems. The general aerobic municipal treatment systems are not effective in removal of these dyes (Moran *et al.* 1997). The nonionic dyes are disperse dyes as they do not ionise in an aqueous medium. There is great concern because most of the dyes used in textile industry are highly carcinogenic such as benzidine and other aromatic compounds (Baughman & Perenich, 1988). Azo and nitro-compounds are reduced in sediments (Weber & Wolfe, 1987) and similarly (Chung *et al.* 1978) illustrated their reduction in the intestinal environment, resulting in the formation of toxic amines. Because of fused aromatic ring structure the anthroquinone-based dyes are most resistant to degradation. The ability of some disperse dyes for bioaccumulation has also been demonstrated (Baughman & Perenich, 1988).

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### **By Fentons's Reagent**

#### **Fenton Process**

Henry John Horstman Fenton discovered Fenton's reagent which is a solution of hydrogen peroxide and ferrous ions reported in 1894 that this solution in acid medium had high oxidizing power (Fenton, 1894). The use of Fenton's reagent in oxidation processes to destroy toxic organic compounds has been reported (Neyens & Baeyens, 2003). This classic reactive system discovered by Fenton in the last century, now today is underlined by a significant number of investigations

devoted to its applications in wastewater treatments. The discovery found out that this reagent has ability to destroy toxic compounds in waste waters such as phenols and herbicides. Production of  $\bullet\text{OH}$  radicals by Fenton reagent occurs by means of addition of  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{2+}$  salts (Haber & Weiss, 1934).



This is a very simple way of producing  $\bullet\text{OH}$  radicals. Neither special reactants nor apparatus is required for this type of reactions. This reactant is an attractive oxidative system for waste water treatment due to the fact that iron is very abundant and non toxic element and hydrogen peroxide is easy to handle and environmentally safe. The oxidation using Fenton's reagent has proven a promising and attractive treatment method for the effective decolorization and degradation of dyes (Wang *et al.* 2005). The Fenton system uses ferrous ions to react with hydrogen peroxide, producing hydroxyl radicals with powerful oxidizing abilities to degrade certain toxic contaminants (Titus *et al.* 2004). Ferrous ions react with hydroxyl radicals to form ferric ions or react with organics:



Hydroxyl radicals can also react with hydrogen peroxide to produce other radicals, and may also combine with each other to produce hydrogen peroxide, as shown below (Titus *et al.* 2004)



During the reaction, radicals and ferrous ions are produced. The other reactions taking place during the oxidation are as follows (Titus *et al.* 2004):



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The degradation of Amido black 10B in aqueous solution by Fenton oxidation process was investigated (Sun *et al.* 2007). They assessed the different parameters like initial pH, the initial hydrogen peroxide concentration, the initial ferrous concentration, the initial Amido black 10B concentration and also the temperature. It was observed that 99.25% degradation efficiency was achieved under optimal conditions. The UV–visible changes were also studied during Fenton treatment process. The azo linkage (–N=N–) group was easy to destruct than the aromatic rings of Amido black 10B by Fenton oxidation. The experimental result of Fenton oxidation was found to be an effective process for the degradation of azo dye Amido black 10B keeping the concentration of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  low. The decolorization of commonly used disperse and reactive dyestuffs was also studied by combination of chemical coagulation and Fenton oxidation (Kim *et al.* 2004). Also they compared the performances between  $\text{Fe}^{3+}$  coagulation and Fenton oxidation of dye solutions and they measured the COD and removal of dye, zeta potential distribution and concentration of suspended solid. On combining with  $\text{Fe}^{3+}$  coagulation Fenton oxidation was found to be highly effective in removal of COD and dye. At optimum condition about 90% of COD and 99% of dye removals were obtained. When compared to reactive dyes, the disperse dyes have lower solubility, higher suspended solids concentrations and lower SCOD/TCOD ratios. It was observed that the COD and the removal of dye per unit  $\text{Fe}^{3+}$  coagulant was higher for disperse dye as compared to reactive dye solutions. Therefore, the decolorization of disperse dye solutions are more easily decolorized by chemical coagulation than reactive dye solutions. It was concluded that the solution of reactive dye have high applicability than disperse dye solutions. The removal of Reactive Black 5 was investigated by Fenton's oxidation process from synthetic wastewater (Meric *et al.* 2004). It was found out that 75 milligram per litre of RB5 caused 25% toxicity on 24-h born daphnids whereas 100  $\text{mg L}^{-1}$  of RB5 displayed 100% toxicity on *Daphnia magna*. At optimum condition 99% color removal was observed. At 200  $\text{mg L}^{-1}$  of RB5, 84% COD removal was obtained using 225  $\text{mg L}^{-1}$  of  $\text{FeSO}_4$  and 1000  $\text{mg L}^{-1}$  of  $\text{H}_2\text{O}_2$ . Removal of COD significantly affects temperature at high degrees. The toxicity was completely removed at optimum removal conditions.

An effective degradation of various mono- and bifunctional aminochlorotriazine reactive dyes by the heterogenous photocatalytic treatment process using ferrioxalate-photo-Fenton and titanium dioxide was carried out (Arslana *et al.* 2004). These advanced oxidation processes was irradiated by a solar simulating installation in a

novel batch photoreactor. It was found that the process of decolorization was three times faster by the ferrioxalate-photo-Fenton oxidation process. After the treatment process partial mineralization and complete decolourization in time period of 1 hour were observed for ferrioxalate-Fenton/UV-A and  $\text{TiO}_2$ /UV-A processes, respectively with 17–23% total organic carbon (TOC) and 73–86% UV280 nm removals. The emphasis was laid on the effect of dye house effluent strength on decolourization kinetics. It was observed that the more dilute the dye house effluent the faster was the rate of decolourization. The treatability of synthetic azo dye production wastewaters via Photo-Fenton-like process from Acid Blue 193 and Reactive Black 39 production and real Reactive Black 39 production effluent was investigated (Alaton *et al.* 2009). They employed response surface methodology for the assessment of critical process parameters on treatment performance in terms of color, COD and total organic carbon (TOC) removal efficiencies. Under optimum conditions, 98% color, 78% COD and 59% TOC removals were obtained that fitted the model predictions well. This same model also explained the treatment of synthetic Reactive Black 39 production wastewater satisfactorily. (Iurascua *et al.* 2009) synthesized a novel photo-Fenton catalyst by the use of synthetic layered clay laponite (laponite RD). They had synthesized two series of Fe-laponite catalysts with or without thermal treatment of the mixture Fe polycations-laponite in the intercalation procedure. In each series, they calcined the intercalated solids at four different temperatures, 250, 350, 450 and 550 °C. Fenton conversion of phenol was done using this catalyst that analyzes the influence of five operating factors: the wavelength of the light source, the amount of the catalyst, the initial phenol concentration, initial concentration of hydrogen peroxide and the initial pH of the solution keeping the temperature constant in all experiments. It was observed that only after 5 min. of reaction time the conversion of phenol was possible. The catalyst prepared and calcined at 350 °C showed the best catalytic performance. For the process, a kinetic model was proposed which tests the validity and also estimate the rate constants. (Kalal *et al.* 2016) dealt with the degradation of non-biodegradable Evans blue azo dye using heterogeneous photo-Fenton process by the use of copper pyrovanadate ( $\text{Cu}_2\text{V}_2\text{O}_7$ ) and chromium tetravanadate ( $\text{Cr}_2\text{V}_4\text{O}_{13}$ ) as catalysts prepared by wet chemical method. The catalyst was characterized by different techniques. They also studied the effect of various parameters such as initial pH, dye concentration, catalyst amount,  $\text{H}_2\text{O}_2$  amount and light intensity on the reaction rate. The degradation efficiency was found to be 77.78 for copper pyrovanadate ( $\text{Cu}_2\text{V}_2\text{O}_7$ ) and 79% for chromium tetravanadate ( $\text{Cr}_2\text{V}_4\text{O}_{13}$ ). The observations of this study revealed that the rate of photo-Fenton-like degradation of dye followed pseudo-first-order kinetics. A model for azure-B degradation by photo-Fenton reagent using ultrasound in homogeneous aqueous medium was described (Vaishnav *et al.* 2014). They

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observed that the rate of decomposition of azure-B increased in the presence of ultrasound which is a cheaper method for wastewater treatment. They also studied the effect of different variables on the reaction rate. The rate of sono-photochemical degradation was monitored spectrophotometrically. They observed that the dye was completely oxidized and degraded into CO<sub>2</sub> and H<sub>2</sub>O. A study was also done on the photochemical degradation of phenol-red using photo-Fenton reaction. The reaction rate was monitored spectrophotometrically. They had also observed the effect of various organic additives e.g. resorcinol, hydroquinone and catechol on the rate of photodegradation (Jain et al. 2009).

### **By Ozonation**

There are two pathways of mechanism of reaction of ozone, first one is the direct action of molecular ozone, and the second one is the indirect action in which there is deterioration of ozone to radicals and this decay is supported by alkaline pH in which the response is started by hydroxyl ions. (OH<sup>•</sup>) (Hoigne, 1988; Dore, 1990). For decolorization of dyes present in wastewaters, ozone is very effective because of its ability to target conjugated double bonds which are often associated with color (Carriare *et al.* 1993). An investigation was done on degradation of azoic dyes present in chlorinated wastewater (Sarasa *et al.* 1998). Firstly they carried out the characterization of the spillage water by GC/MS and GC/FID and secondly, ozone and Ca(OH)<sub>2</sub> was combined to determine its efficiency on waste water. It was found that the aniline derivatives and azo compounds were present in the wastewater majorly. Some organochloride compounds were also identified as a result of chlorination treatment which is being the most important with respect to the legislative control, namely: chloroanilines, chloronitrobenzenes and chlorophenols. The results showed that the concentration of the compounds present in wastewater is reduced to good extent after ozonation. The nitrobenzene derivatives and organic acid compounds were mainly formed as by-products after the treatment. The addition of Ca(OH)<sub>2</sub> along with ozone leads to almost total elimination of the remaining compounds after complete treatment process. However, after chemical coagulation aniline and chloroanilines are formed due to the strong basic medium at which the sample in this process is set. COD is reduced 25% after ozonation, while it decreased 50% after the final treatment. In ozonation treatment TOC remained constant, but a 42% reduction was observed after chemical coagulation. During ozonation reaction, color faded gradually and after the treatment the reduction in color was 62%. Thus, the complete process of ozonation and chemical coagulation with Ca(OH)<sub>2</sub> is, in general, very effective to treat this kind of wastewaters. For the reduction of recalcitrant present in water, the combination of chemical and biological water treatment processes is a promising

technique. The key to the efficiency of such a system is a better understanding of the mechanisms involved during the degradation processes. Ozonation process is very important in many fields for water and wastewater treatment. Ozonation process is highly efficient to enhance biodegradability, destroy phenols, high color removal, and reduce the chemical oxygen demand (COD) for textile mill effluents. In ozonation there is some information about the reaction intermediates and products formed during ozonation. (Koch et al. 2002) studied the degradation of hydrolyzed Reactive Yellow 84 (an azo dye), which is widely used in textile finishing processes. The ozonation of the dye solution was performed in a laboratory scale cylindrical batch reactor. The degradation of dye was determined by measuring the optical density of light in the visible range ( $\lambda_{\text{max}} = 400 \text{ nm}$ ). The result revealed that the ozone concentration was reduced to 18.5 and 9.1 mg/L after 60 and 90 min, respectively. After ozonation, the COD value was decreased to 50% of the initial value and the TOC/TOC<sub>0</sub> ratio was about 30%. The BOD to COD ratio was increased from 0.01 to 0.8. After the oxidation and breakdown of the azo group, nitrate group was obtained. The amount of sulfate was also increased due to release of the sulfonic acid groups of aromatic rings. The major oxidation products were formic acid and oxalic acid determined by high performance ion chromatography (HPIC). The concentrations of these major products were monitored after the regular time intervals during ozonation. The ozonation of wastewater containing azo dye in a semi-batch reactor was studied (Wu *et al.* 2001). Results demonstrated that the rate of ozonation was increased with the increase in the initial dye concentration with the applied ozone dosage and temperature. This model empowers the assumption of mass exchange coefficient of ozone from the accompanying parameters: applied ozone dose, temperature, initial dye concentration, and concentration of dissolved ozone in the organic-free water. It has found its application for large size reactors also. The kinetic studies also revealed to be pseudo-first-order. The estimation of apparent rate constant was also increased with the applied ozone dose and temperature. However, the apparent rate constant diminished logarithmically with increasing initial dye concentration. Additionally, ozonation diminished chemical oxygen demand and improved the biodegradability of the wastewater. (Ciardellia & Ranieri *et al.* 2001) reported two oxidation processes, i.e., ozonation and electroflocculation, on a pilot scale to test their effectiveness in expelling contaminating substances from wastewaters of textile industries. Both pilot plants utilized to reproduce a full-scale treatment in order to obtain indications about the plausibility of a transfer on industrial scale. Extremely high color removal (95– 99%) was accomplished by ozone treatment and treated waters were reused in dyeing again with light colors also. This proof in spite of the fact that the COD of treated waters was still in a range (75– 120 mg/L, a reduction up to 60%) that was normally viewed as unreasonably high to reuse purposes,

particularly especially for dyeing with light colors. Treating plants working at the previously mentioned conditions should ensure low operating costs. A biological pre-treatment and a sand filtration are significant. The transfer on industrial scale of the treatment is as of now in progress under already financed European project. Electrochemical treatment appeared to be extremely effective in evacuating color (80– 100%) and chemical oxygen demand (70– 90%). Additionally, a reasonable depletion of chloride and sulfate particles were identified. Expulsion of flocculated material (post-treatment) must be perfect so as to build up a right costs-to-benefits ratio and hence, propose a usage of the method on an industrial scale.

Central composite design experiment is utilized to study the impact of ozone treatment for acid dye effluents and to optimize the variables such as salt concentration, pH and time, which impact the efficiency of color and COD removal of dye effluents (Muthukumar *et al.* 2004). Acid Red 88 dye is used in this study and sodium sulphate, the salt additive is varied between 5 and 15 g/L, pH is varied between 3 and 11 and the treatment duration is varied between 30 and 360 s. It is observed from the outcome that the treatment time plays a key role in dye effluent's decolouration and COD removal. As the treatment time increases decolouration efficiency also increases. The efficiency of ozone, in terms of decolouration is low at neutral pH when compared with that at acidic and alkaline pH. The effluent decolourizes faster at lower salt concentration while an increase in the salt concentration interferes with the decolouration efficiency. At lower salt concentration maximum amount of COD removal was obtained with 64% in time duration of 195 s at alkaline pH. The ozonation of raw textile wastewater was carried out in a pilot-scale plant and the efficiency of this treatment was assessed based on the parameters of color removal and soluble organic matter measured as chemical oxygen demand (COD), at values of two pH (9.1 and 3.0) was investigated (Somensi *et al.* 2010). Identification of intermediate and final degradation products of ozone pre-treatment, as well as the evaluation of the final ecotoxicity (Lumistox test) of pre-treated wastewater, was also carried out. After 4 h of ozone treatment with wastewater recirculation (flow rate of  $0.45 \text{ m}^3 \text{ h}^{-1}$ ), the average efficiencies for color removal were 67.5% (pH 9.1) and 40.6% (pH 3.0), while COD reduction was 25.5% (pH 9.1) and 18.7% (pH 3.0) for an ozone production capacity of  $20 \text{ g h}^{-1}$ . Furthermore, ozonation enhanced the biodegradability of textile wastewater (BOD<sub>5</sub>/COD ratios) by a factor of up to 6.8 fold. A GC-MS analysis of pre-treated textile wastewater showed that some products were present at the finish of the pre-treatment time. Despite this fact, the bacterial luminescence inhibition test (Lumistox test) showed a noteworthy toxicity reduction on comparing the raw and treated textile wastewater. In conclusion, pre-ozonation of textile wastewater is a critical step for improving wastewater biodegradability, as well as reducing acute ecotoxicity, which should be removed completely through sequential biological



treatment. (Tehrani *et al.* 2010) investigated the decolorization and degradation of an anthraquinone dye (C.I. Reactive Blue 19) by ozonation using cylindrical batch reactor. Ion chromatography (IC), UV–Vis, chemical oxygen demand (COD) and total organic carbon (TOC) analyses were determined. The effect of operational parameters such as ozone dosage, pH, dye concentration and the electrolytes on decolorization was observed. It was shown that for decolorization, the ozonation was proved to be effective method for reactive dye. During the ozonation process, there is a rapid decrease of pH which gave the evidence for production of acidic by-products like sulfate, nitrate, formate, and acetate. The COD and TOC values were decreased which showed the partial degradation and mineralization of the dye. Due to the application of ozonation has been increasing in current years, it should be studied much and more. But the ozonation treatment has main drawback related to by-products, which can have poisonous and carcinogenic properties, and therefore should be studied much and more. (Souza *et al.* 2010) reported the combined treatment of ozonation and subsequent biological degradation with a biofilm, to reduce the color and chemical oxygen demand (COD). This experimental study contained two parts. The first part was the ozonation process, the results obtained in this showed that the ozonation of Remazol Black B dye at pH values of 3–11 was effective, partially oxidizing and completely decolorizing the waste matter, even at relatively high concentrations of the dye (500 mg/L). Color removal efficiencies were greater than 96% obtained in all cases. The kinetics of degradation with ozone is of pseudo-first-order reaction with respect to the dye concentration. It was verified that the ozonation process as a pre-treatment increases the dye degradation efficiency. For the biological treatment, there is a reduction in dye concentration with increase in ozonation time for hydrolyzed dye synthetic effluent. The toxicological results of the tests with *Daphnia Magna* demonstrated that the increase in toxicity after ozonation and a decrease after submitting the ozonized synthetic wastewater to biological treatment with a biofilm. The mineralization of an azo-dye, the Congo red, in aqueous solutions by ozonation process was investigated (Khadhraoui *et al.* 2009). Phytotoxicity and the inhibitory outcomes on the microbial activity of the raw and the ozonated solutions were also lead to achieve the goal of water reuse and environment protection. Primary parameters like decolorization of the aqueous solutions, chemical oxygen demand (COD), disappearance of the parent compound and total organic carbon (TOC) removal have been monitored in this observation. To control the mineralization of the Congo red, pH of the ozonated solution and heteroatoms released from the mother molecule such  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were analysed. It was concluded that ozone through itself was strongly sufficient to decolorize these aqueous solutions in the early stage of the oxidation process. Nonetheless, efficient mineralization had not been achieved. Significant drops in COD (54%) were registered. The extent of

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TOC removal turned into almost 32%. Sulfur heteroatom was totally oxidized to  $\text{SO}_4^{2-}$  ions while the central  $-\text{N}=\text{N}-$  azo ring was partially converted to  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Results of the kinetic studies demonstrated that ozonation of the selected molecule was a pseudo-first-order reaction with respect to dye concentration. The obtained results also showed that ozone process decreased the phytotoxicity of the raw solution and enhanced the biodegradability of the treated azo-dyes-wastewater. The treatment of organic dyes in wastewater with ozone showed that it is one of the effective technologies for the discoloration and the detoxification of dyes. To take into consideration of stringent environmental rules imposed through regional, national, and international (e.g., European Union) authorities for better environment, the technologies used for treatment of dye-contaminated effluents should be innovative and environment friendly are needed in color industries. The production of dye effluents from industries were subjected to various treatment pathways to follow an initial qualitative characterization (Vanhulle *et al.* 2008). The parameters such as toxicity, residual color, on human cells, and genotoxicity was undertaken for comparing the effectiveness of ozonation and a treatment using white rot fungi (WRF) and their enzymes. Further a combined ozonation/WRF process was also undertaken for study. The effluent exhibited significant toxicity that was achieved a 10% reduction through ozonation, whereas the fungal treatment decreased up to 35%. A combined treatment (ozone/WRF) induced an abatement of the toxicity by more than 70%. In addition, the initial genotoxicity of the effluent was still present after the ozone remedy, while it was completely removed through the fungal treatment.

(Wang *et al.* 2003) investigated the effect of ozonation ( $20.5 \text{ mg l}^{-1}$ ) on the degradation methods of an azo dye, Remazol Black 5 (RB5; CI). Conventional parameters such as pH, chemical oxygen demand (COD), conductivity, total organic carbon (TOC), colour removal, biodegradability (BOD<sub>5/28</sub>), and toxic potential of the dye and its degradation products were monitored during the process. The results showed that for the removal of color from a corresponding dye solution, ozonation is a highly effective way. However, high COD and TOC residues clearly indicated that a considerable organic load still left. The COD, TOC reductions were about 40% and 25% for 6 h ozonation of  $2 \text{ g l}^{-1}$  RB5 aqueous solution. The formation of acidic by-products and small fragments and ions during the ozonation process indicates the rapid decrease of pH and the sharp increase of conductivity which were identified by high performance ion chromatography. The BOD<sub>28</sub> data revealed that first by-products after partial ozonation (10–150 min) of RB5 were more biodegradable than the parent compound and ozonation can enhance the biodegradability of azo dyes. During the first 150 min of total 360 min of oxidation, The formation of first by-products with high toxic potential took place as it could be confirmed by two acute toxicity-screening tests, the bioluminescence test (*Vibrio fischerii*) and the neutral red

cytotoxicity assay (rat hepatoma cells). A long-term ozonation significantly enhances the microbial biodegradability and it could also be seen in form of decrement in toxic intermediates during ozonation time as indicated in BOD<sub>28</sub> biological degradation test results. There is two important process related to textile yarns and fabrics are dyeing and finishing which are necessary for quality as well as for environmental concerns. Disperse dyestuffs in the commercial textile dyes are of more useful in form of environment interest because of their widespread use because of their low removal rate during aerobic waste treatment and their potential for formation of toxic aromatic amines as well as advanced chemical oxidation. Thus, (Arslan, 2001) studied the ozonation, ferrous iron coagulation and ferrous iron-catalyzed ozonation were employed in the range of pH of 3–13 and doses of Fe(II)-ion in the range of 0.09–18 mM for the treatment of a simulated disperse dye-bath (average initial apparent color as absorbance at 566nm=815.4 m<sup>-1</sup>; COD<sub>0</sub>=3784 mg l<sup>-1</sup>; TOC<sub>0</sub>=670 mg l<sup>-1</sup>; BOD<sub>5,0</sub>=58 mg l<sup>-1</sup>) that more closely resembled an actual dye house effluent than an aqueous disperse dye solution. At pH 11 coagulation with 5000 mg l<sup>-1</sup> FeSO<sub>4</sub>·7H<sub>2</sub>O (18 mM Fe<sup>2+</sup>) decolorizes 97% color and 54% of COD, whereas oxidation by ozonation alone at dose of 2300 mg l<sup>-1</sup> was only effective at pH 3, resulting in 77% decolorization and 11% removal of COD takes place. Fe (II)-ion-catalyzed ozonation (3.6 mM Fe<sup>2+</sup> at pH 3; Fe<sup>2+</sup>:O<sub>3</sub> molar ratio 1:14) eliminated 95% color and 48% COD and appeared to be the most attractive option among the available methods of chemical treatment for its applicability at the natural acidic pH of the disperse dye-bath effluent and at relatively low Fe<sup>2+</sup> ion doses as compared to ferrous sulfate coagulation. In the reaction conditions of 14 g l<sup>-1</sup> O<sub>3</sub> at pH 3 there is reduction in TOC was not observed for ozonation and catalytic ozonation. An average six-fold enhancement in the biodegradability parameter of the synthetic dye wastewater expressed in terms of the BOD<sub>5</sub>/COD ratio could be achieved by the investigated chemical treatment methods. (Ince & Tezcanli, 2001) studied the degradation of a reactive dye by combined sonolysis (520 kHz) and ozonation using C.I. Reactive Black 5 as a model dye. It was observed that the action of ultrasound followed by ozone induced a synergistic effect on both the decolorization of the dye and the overall degradation process. Inefficiency of ultrasonic irradiation by itself causes significant degradation under the conditions employed, the synergy was attributed mainly to mechanical effects of ultrasound to enhance the mass transfer of ozone in solution. During thermolysis of water and ozone in collapsing cavities radical chain reactions take place. This reaction may contribute chemically to the synergy by providing additional decomposition pathways for ozone, and an excess of electron-deficient chemicals in solution. Effluents from dyeing processes of woolen textile finishing industries are highly polluted with recalcitrant compounds compared to effluents from rinsing and finishing processes. (Baban *et al.* 2003)

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investigated the oxidation of woolen textile dyeing effluent consisting of wastewater generated from spent dye baths and first and second rinses (remaining composite wastewater). Ozone oxidation ( $\text{CO}_3=18.5$  mg/l; input rate) was applied for various time intervals on remaining composite wastewater, before and after the biological treatment. The efficiency of treatment was monitored by decolorization rates and COD removal rates. Additionally, toxicity tests (bioluminescence test) were carried out to determine the effect of oxidation process. The obtained results indicate that 40 min ozonation of biologically treated wastewater yielded nearly colorless effluent with a decolorization efficiency about 98–99% with a related ozone absorption rate of 58.0 mg/l. the overall toxicity reduced about 92% by biological treatment followed by 10 min ozone oxidation. The result of ozonation was found to have slightly effect on COD removal.

## **By Photochemical Method**

The efficiency of heterogeneous photocatalytic processes for degradation of many persistent chemicals has been extensively documented, especially with the use of titanium dioxide (Hoffmann *et al.* 1995; Linsebigler *et al.* 1995). Recently, several papers on photochemical degradation of isolated dyes have been published (Vinodgopal & Kamat, 1994; Vinodgopal *et al.* 1996). Advanced oxidation processes (AOPs) have proved very effective in treatment of the various hazardous organic pollutants present in water. In the UV/ $\text{H}_2\text{O}_2$  process the photochemical decolorization of three dyes, Methyl Orange (MO), Acid Orange 8 (AO8) and Acid Blue 74 (AB74) by using a continuous photochemical reactor with a 15 W low pressure mercury lamp was studied (Aleboye *et al.* 2003). Decolorization completes in very short time and follows apparent first order kinetics with respect of dye concentration. In visible maximum absorption wavelength region the rate of disappearance of a given dye was monitored spectrophotometrically. It was found that by increasing the initial amount of  $\text{H}_2\text{O}_2$  up to a “critical” value at which it shows maximum the rate of decolorization rises and beyond which it is inhibited. The pathway of simple reactions describe adequately the process has been studied. Based on this reaction schema, A mathematical relationship is established between the apparent rate constant of the dye removal and applied  $\text{H}_2\text{O}_2$  dosage which presented by the ratio of its initial mass concentration to that dye. The rate constant values for the three dye solutions are obtained by model in good agreement with the experimental data and the model parameters have been determined. (Muruganandham & Swaminathan, 2004) studied the photooxidation of a chlorotriazine reactive azo dye Reactive Orange 4 in the presence of  $\text{H}_2\text{O}_2$  using UV-A light. The effects of pH of reaction, UV light power, and applied  $\text{H}_2\text{O}_2$  amount have been studied. These parameters strongly influence

the decolourisation and degradation. Removal rate decreases by increasing the initial dye concentration. The kinetics of degradation and decolourisation follow pseudo-first order. The efficiency of solar-  $\text{H}_2\text{O}_2$  process is comparable with UV-  $\text{H}_2\text{O}_2$  and solar-  $\text{H}_2\text{O}_2$  process is also able to oxidize the dye. The influence of dye assisting chemicals such as NaOH, NaCl and  $\text{Na}_2\text{CO}_3$  on photodecolourisation has been investigated. Addition of these chemicals inhibits the removal rate. Dye is used in order to colour the products in many industries such as paper, food, cosmetics, and textiles industries. The presence of these dyes in water even at very low concentration is highly visible and undesirable. Colour is the first recognizable contaminant. Colour from wastewater can be removed by photocatalytic technique and adsorption methods. In the present paper these two methods were used for removal of Congo red and both the techniques were found to be very useful and cost effective for a better removal of dye. The results were compared. The operating variables such as adsorbent dose, adsorbate concentration, pH etc were optimized (Jain & Sikarwar, 2006). (Alaton & Balcioglu, 2001) studied that aqueous solutions of hydrolyzed Reactive Black 5 (RB5) dye is a well-known surrogate for non-biodegradable azo dyes and it is photochemically and photocatalytically treated by employing the  $\text{TiO}_2$ /UV-A and  $\text{H}_2\text{O}_2$ /UV-C advanced oxidation systems. The observed effects of oxidant dose, reaction pH and initial dyestuff concentration were used to explain the OH-induced color disappearance kinetics empirically. Accordingly, the waste dyestuff solutions could be effectively mineralized ( $k_{\text{TOC,max}}=0.01 \text{ min}^{-1}$ ;  $\text{H}_2\text{O}_2$ /UV-C system) and completely decolorized ( $k_{\text{d,max}}=0.155 \text{ min}^{-1}$ ;  $\text{H}_2\text{O}_2$ /UV-C system) with an average overall TOC removal of 78% after 120 min advanced oxidation take place at specified optimized reaction conditions. The bleaching effect of the  $\text{TiO}_2$ /UV-A process could be successfully fitted to the empirical Langmuir-Hinshelwood (L-H) kinetic model ( $k_{\text{L-H}}=4.47 \text{ mg l}^{-1} \text{ min}^{-1}$ ;  $K_{\text{L-H}}=2.01 \text{ l mg}^{-1}$ ). (Gupta *et al.* 2012) investigated the photo-catalytic degradation of an azo dye Amaranth (AM) –in  $\text{TiO}_2$ /UV aqueous suspensions. The obtained results from the experiments during addition of  $\text{H}_2\text{O}_2$ /  $\text{TiO}_2$  show that the highest decolorization rate is provided by the combination of (UV +  $\text{TiO}_2$  +  $\text{H}_2\text{O}_2$ ). The decolorization efficiencies for UV, UV+  $\text{H}_2\text{O}_2$ , UV +  $\text{TiO}_2$  and (UV +  $\text{TiO}_2$  +  $\text{H}_2\text{O}_2$ ) were 17%, 26%, 38% and 64% in the runs after approximately 100 min illumination periods, respectively. The dye degradation rate follows pseudo-first order kinetics with respect to the substrate concentration under the experimental conditions used. Different experimental conditions, such as pH, temperature and presence of electron acceptor were investigated. The effect of temperature was investigated at the range of 293–313 K and it was observed that decolorization rate increased by increasing the temperature. Dye absorbance and chemical oxygen demand of the photodegraded dye solution substantially decreased. Effect of pH was also investigated and if lower the pH than higher will be the

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degradation of dye. It was observed that by the Addition of hydrogen peroxide as an electron acceptor enhances the photodegradation rate. The adsorption trends of Amaranth dye at various initial concentrations followed the Langmuir isotherm trend. The role of this work at global level is discussed for advanced oxidation processes in water treatment. (Rosa *et al.* 2015) studied that ten different dyeing were made using reuse water obtained from effluent after treatment by homogeneous photocatalysis. The concentration of sodium chloride (NaCl), the absorbance (Abs) and the amount of total organic carbon (TOC) were monitored before and after the UV/H<sub>2</sub>O<sub>2</sub> treatments. The removal of TOC was above 88% and all rates of decolorization were above 92% in all treatments. The total deviation ( $\Delta E^*$ ) between the colors did not exceed compared for the same dyeings made with deionized water was 1.05. Currently the monthly production of 20 dyeing of 100 kg each, 160 m<sup>3</sup> of water is consumed and an equal volume of effluent is generated. The same dyeing made by the process proposed in this study, with an addition of 10 m<sup>3</sup> of water after 20 dyeing, would consume just 60 m<sup>3</sup> of water. (Jain *et al.* 2005) reported photocatalytic and adsorptive treatment of a hazardous xanthene dye, Rhodamine B, in wastewater. The photocatalytic degradation was carried out in the presence of the catalyst TiO<sub>2</sub> and the effects of pH, amount of TiO<sub>2</sub>, temperature, concentration of the dye, and electron acceptor H<sub>2</sub>O<sub>2</sub> on the degradation process were observed. It was found that removal of Rhodamine B from aqueous solutions by photocatalytic degradation by TiO<sub>2</sub> is an effective, economical and faster mode. The attempts were also made for utilization of activated carbon and rice husk as potential adsorbents to remove Rhodamine B from wastewater. The adsorption studies were carried out at 40, 50 and 60°C, and the effects of pH, temperature, amount of adsorbents and concentration of adsorbate etc., on the adsorption were measured. Langmuir and Freundlich adsorption isotherm models were also confirmed by adsorption data. The adsorption isotherm constants thus obtained were employed to calculate thermodynamic parameters like change in enthalpy, entropy and Gibb's free energy. To observe the quality of wastewater COD measurements were also carried out after and before treatments. A significant decrease in the COD values was observed, which clearly indicates that both photocatalytic and adsorption methods offer good potential to remove Rhodamine B from industrial effluents. (Chang *et al.* 2004) carried out treatment of the lignin-containing wastewater by photochemical UV/TiO<sub>2</sub> oxidation process for parameters dissolved organic carbon (DOC), color and reducing A<sub>254</sub>(wavelength 254 nm). The data obtained in this study confirms that the UV/TiO<sub>2</sub> process is effective in oxidizing the lignin thus reducing DOC and the color of the wastewater treated. The better removal of DOC and color obtained from combined UV/TiO<sub>2</sub> treatment rather than the UV treatment alone. If the pH is maintained at 3.0 by the addition of 1 g l<sup>-1</sup> TiO<sub>2</sub> than color removal based on

American Dye Manufacture Index (ADMI) measurement is greater than 99%. The oxidation reduction potential (ORP) value is reached to result in an 88% removal of both DOC and color when  $10 \text{ g l}^{-1}$   $\text{TiO}_2$  is applied. A model was developed to simulate the decoloring process based on the variation of ORP during the photochemical reaction. The proposed model can also use for prediction of color removal efficiency of the UV/ $\text{TiO}_2$  process. (Gad-Allah *et al.* 2009) prepared a photocatalyst  $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$  (TSF) that was used for the treatment of synthetic dyes wastewater. To determine the optimum operating conditions different operating conditions such as catalyst load, pH and dye concentration were investigated. The optimum operating conditions were found to be dose of  $\text{TiO}_2$  photocatalyst 2500 ppm and pH 3. More catalyst dose led to increase the opacity inside photoreactor as well as reduction in rate of reaction due to aggregation of photocatalyst. The rate of reaction increases for acidic medium favored adsorption of studied dyes on photocatalyst. Under optimum conditions, complete decolorization and degradation of the organic dyes could be achieved within less than 45 min. Rate of reaction depends on three parameters- dye concentration, photocatalyst load, and transmittance inside photoreactor in kinetic studies. When TSF photocatalyst was used several times efficiency was nearly the same. The reuse of the photocatalyst decreases the final cost of the treatment process. (Rahmani *et al.* 2012) studied ultrasonic irradiation (US), ultraviolet radiation (UV), UV/ $\text{H}_2\text{O}_2$  and US/ $\text{H}_2\text{O}_2$  processes for degradation of Basic Violet 16 (BV16) in a laboratory-scale batch photoreactor equipped with a low-pressure mercury vapor lamp and a sonoreactor. The results indicated that in the UV/ $\text{H}_2\text{O}_2$  and US/ $\text{H}_2\text{O}_2$  systems a very high concentration of  $\text{H}_2\text{O}_2$  would inhibit the reaction rate so sufficient concentration of  $\text{H}_2\text{O}_2$  was enough. The optimum  $\text{H}_2\text{O}_2$  concentration was achieved in the range of 17 mmol/L at dye concentration of 30 mg/L. A degradation of BV16 was obtained 99% with UV/ $\text{H}_2\text{O}_2$  within 8 minutes while decolorization efficiency by using UV (23%), US (<6%) and US/ $\text{H}_2\text{O}_2$  (<15%) processes were negligible for this kind of dye. Pseudo-first order kinetics with respect to dyestuffs concentrations was found to fit all the experimental data. In this work (Goel *et al.* 2010) studied the performance of integrated photocatalytic and biological treatment was studied for the degradation of 4-chlorophenol (MCP) present in wastewaters. For pre-treatment of biological degradation photocatalysis was used. Pollutant removal efficiency was expressed using MCP removal and total organic carbon (TOC) removal. By use of  $\text{TiO}_2$  as the photocatalyst both photocatalytic as well as biological treatments were carried out in batch reactors. Effect of  $\text{TiO}_2$  concentration on the photocatalytic degradation of MCP was studied along with the effect of the duration of photochemical oxidation and glucose concentrations (0 g/L, 1 g/L and 2 g/L) on the biodegradation of MCP. At higher concentrations (400 mg/L) integrated biological and photochemical degradation was found to be more

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effective for treating MCP. 96 h required for complete mineralization of initial MCP concentration of 400 mg/L when treated with the process combination, whereas for biodegradation the treatment went on up to 264 h when it was done alone. (Pandey *et al.* 2015) carried out the photocatalytic degradation of methylene blue using naïve titanium dioxide, nano-sized titanium dioxide and H<sub>2</sub>O<sub>2</sub> under visible light. The catalysts, naïve and nano-sized titanium dioxide were prepared by the sol–gel method. Characterization of synthesized catalysts has been done by SEM, XRD and UV–Vis. spectroscopy. By measuring absorbance of dye at regular time intervals the rate of degradation of dye was monitored spectrophotometrically. The effect of various parameters such as concentration of dye, pH, dose of catalyst, added amount of H<sub>2</sub>O<sub>2</sub> and light intensity on the rate of reaction has been studied. Various parameters like conductance, chemical oxygen demand (COD), TDS, pH, salinity and dissolved oxygen (DO) for the reaction mixture have also been determined. The rate of reaction drastically reduced in the presence of .OH radical and participation was confirmed by using 2-propanol (scavenger). The heterogeneous photo-Fenton process is a green chemical pathway for removal of dye. In photo-Fenton processes does not requirement of removal of ferrous/ferric ions in the form of sludge. By wet chemical method (Kalal *et al.* 2014) prepared copper pyrovanadate or Volborthite (Cu<sub>3</sub>V<sub>2</sub>(OH)<sub>2</sub>O<sub>7</sub>•2H<sub>2</sub>O) composite as photocatalyst. The photocatalyst was characterized by numerous spectroscopic techniques. Experiments demonstrated that catalyst could effectively catalyze degradation of neutral red and azure-B in presence of H<sub>2</sub>O<sub>2</sub> in visible light. When Cu<sub>3</sub>V<sub>2</sub>(OH)<sub>2</sub>O<sub>7</sub>•2H<sub>2</sub>O used alone as photocatalyst than photo-Fenton-like catalytic activity of Cu<sub>3</sub>V<sub>2</sub>(OH)<sub>2</sub>O<sub>7</sub>•2H<sub>2</sub>O was much higher than CuO and V<sub>2</sub>O<sub>5</sub>. The effect of variation of different parameters like pH, concentration of dye, amount of photocatalyst, amount of H<sub>2</sub>O<sub>2</sub> and light intensity was also investigated. The kinetics of degradation for neutral red and azure-B was well fitted under pseudo-first-order reaction with a rate constant of 2.081×10<sup>-4</sup> sec<sup>-1</sup> and 3.876×10<sup>-4</sup> sec<sup>-1</sup>, respectively. The high catalytic activity of Cu<sub>3</sub>V<sub>2</sub>(OH)<sub>2</sub>O<sub>7</sub>•2H<sub>2</sub>O shell not only increases the surface hydroxyl groups, but also enhances the interfacial electron transfer.

## **BIOLOGICAL TREATMENT**

### **By White Rot Fungi**

(Swamy and Ramsay, 1999) investigated that decolorization of dyes Amaranth, Remazol Black B, Remazol Orange, Remazol Brilliant Blue, Reactive Blue, and Tropaeolin O by five species of white rot fungi in agar plates, Bjerkandera sp., Phanerochaete chrysosporium, BOS55, and Trametes versicolor displayed the



greatest extent of decoloration. Three cultures of fungal mats which did not decolorize any dye in static aqueous culture. The biomass grew as mycelial pellets when agitated at 200 rpm. *Bjerkandera* sp. BOS55 pellets decolorized only Amaranth, Remazol Black B, and Remazol Orange. *T. versicolor* and *P. chrysosporium* pellets were capable to decolorize most dyes. Decoloration by *T. versicolor* being several times more rapid than *P. chrysosporium*. Batch cultures of *Bjerkandera* sp. BOS55 and *P. chrysosporium* could not decolorize the repeated dye additions but *T. versicolor* was able to rapidly decolorize repeated additions of the different dyes and dye mixtures without any visual sorption of any dye to the pellets. The choice of buffer had a profound effect of addition of dye on pH stability and consequently decoloration. For excellent pH control and high decoloration ability 2,2'-dimethylsuccinic acid is used. (Faraco *et al.* 2009) evaluated for models of colored industrial wastewaters the effect of *Phanerochaete chrysosporium* and *Pleurotus ostreatus* whole cells and their ligninolytic enzymes. Models of acid, direct and reactive dye wastewaters from textile industry have been defined on the basis of discharged amounts, economic relevance and representativeness of chemical structures of the contained dyes. *Phanerochaete chrysosporium* provided an effective decolourization of direct dye wastewater model, reaching about 45% decolourization in only 1 day of treatment, and about 90% decolourization within 7 days, whilst *P. ostreatus* was able to decolorize and detoxify acid dye wastewater model providing 40% decolourization in only 1 day, and 60% in 7 days. For wastewater models decolourization the laccase production (up to 130,000 U/l) is induced by the growth conditions of *P. ostreatus*. By known composition of laccase isoenzyme a extra-cellular enzyme mixtures were produced. Laccases is the main agents for wastewater decolourization by *P. ostreatus*. The mixtures of laccase detoxified and decolorized the acid dye wastewater model. The immobilized mixture of laccase was used for investigation and the immobilized enzymes were also effective in batch decolourization, however the additions of dye for a total exposure of about 1 month. (Revankar & Lele, 2007) investigated that an indigenous strain of white rot fungus isolated from bark of dead tree is used for decolorization of recalcitrant dyes and WR-1 identified as *Ganoderma* sp. A combination of one factor at a time and orthogonal array method is used for optimization of fermentation. Maximum decolorization (96%) of 100 ppm amaranth was achieved in 8 h with medium containing 2% starch and 0.125% yeast extract. Rate of dye decolorization for the indigenous isolate *Ganoderma* sp. WR-1 was very high compared to the most widely used strains of *T. versicolor* and *P. chrysosporium*. By using chemically different dyes the broad-spectrum decolorization efficiency of the isolate was assessed. For decolorization of industrial effluent the isolate was further evaluated. Complete decolorization by *Ganoderma* sp. was achieved in 12 days. (Selvama *et al.* 2003) investigated that a white rot fungus *Thelephora* sp. was

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used for decolourization of azo dyes such as orange G (50  $\mu\text{M}$ ), congo red (50  $\mu\text{M}$ ), and amido black 10B (25  $\mu\text{M}$ ). Decolourization using the fungus was 33.3%, 97.1% and 98.8% for orange G, congo red and amido black 10B, respectively. An enzymatic dye decolourization study showed that a maximum of 19% orange G was removed by laccase at 15 U/ml whereas lignin peroxidase (LiP) and manganese dependent peroxidase (MnP) at the same concentration decolourized 13.5% and 10.8%, orange G, respectively. A maximum decolourization of 12.0% and 15.0% for congo red and amido black 10B, respectively, was recorded by laccase. In batch and continuous modes the dye industry effluent was treated by the fungus. A maximum decolourization of 61% was observed in batch mode on third day and a maximum decolourization of 50% was achieved on seven day in the continuous mode. The obtained results suggest that the batch mode of treatment using *Thelephora* sp. may be more effective than the continuous mode for decolorization of dye industry effluents. (Kim *et al.* 2004) studied that a membrane bioreactor (MBR) using white-rot fungi was used for the decolorization of dye solutions. *Trametes versicolor* KCTC 16781 and membrane filtration were combined for decolorization of dye solutions and applicability of this process was investigated by using reactive dye solutions. A study is carried out for the feasibility of MBR using fungal biodegradation with nanofiltration and reverse osmosis (RO) membranes to improve separation efficiencies and permeate flux. The effects of dye types on fungal biodegradation and membrane filtration (permeate flux and rejection) were also investigated. The fungal MBR combined with RO was found effective for decolorization and organic removal of dye from wastewater. Decolourization activity of *P. chrysosporium* for three synthetic dyes viz., congo red, malachite green and crystal violet was carried out (Pant *et al.* 2008) and impact of additional carbon and nitrogen supply on decolourization capacity of fungus. Urea is used as nitrogen source and glucose as carbon source for addition which significantly enhances decolourizing capacity (up to 87%) of fungus. In all the cases, both colour and COD were reduced more in non-sterilized treatments as compared to sterilized ones. By additional of carbon and nitrogen significant reductions in COD content of dye solutions (79- 84%) were recorded by fungus. (Nilsson *et al.* 2006) described a batch and continuous reactors inoculated with white-rot fungi operated in order to study decolorization of textile dyes. For first part of the study of synthetic wastewater containing either Reactive Blue 4 (a blue anthraquinone dye) or Reactive Red 2 (a red azo dye) was used while in the later part Tanzania was used for real wastewater from a textile industry. When glucose was added as a carbon source then *Trametes versicolor* decolorize both Reactive Blue 4 and Reactive Red 2. Reactive Blue 4 was also decolorized by growth of fungus on birch wood discs in a continuous biological rotating contactor reactor. The absorbance decreases by 70% during treatment at wavelength of 595 nm at

which the dye absorbs maximum. The initial concentration of dye in the medium was 200 mg/l and the hydraulic retention time in the reactor was 3 days as well as no amount of glucose was added in this experiment. Aromatic structures of the dyes were altered when exposed to UV range which indicates changes of the absorbance in this region. *Pleurotus flabellatus* growing on luffa sponge packed was used for real textile wastewater decolorization in a continuous reactor. Hydraulic retention time of the reactor for operating was 25 h. The absorbance decreases from 0.3 in the inlet to approximately 0.1 in the effluent at wavelength of 584 nm at which the wastewater absorbed the most. (Kiran *et al.* 2013) studied a two stage sequential Photo-Fenton's oxidation followed by two white rot fungi *P. ostreatus* IBL-02 (PO) and *P. chrysosporium* IBL-03 (PC) for aerobic biological treatment to check decolorization and enhancement in mineralization of azo dye Reactive Blue 222 (RB222). Decolorization percentage of selected dye for Photo-Fenton's oxidation was ~90% in first stage but when it is subjected to aerobic treatment using two white rot fungi *P. ostreatus* IBL-02 (PO) and *P. chrysosporium* IBL-03 (PC) than it further increases to 96.88% and 95.23% respectively. Mineralization efficiency was accessed by measuring the water quality assurance parameters like COD, TOC, TSS and Phenolics estimation. For two stage sequential processes reduction was observed for COD, TOC, TSS and Phenolics were found to be 95.34%, 90.11%, 90.84% and 92.22%, respectively. By UV-visible and FTIR spectral techniques degradation products were characterized and their toxicity was also measured. Both fungal strains were able to oxidize and mineralize the selected azo dye was confirmed by the evidence of results into non-toxic metabolites. (Yang *et al.* 2009) obtained two microbial cultures exhibiting high decolorization efficiencies of reactive dyes. Dye mineralization rates were obtained about 50–75% and efficiencies of color removal were obtained 70–80%. Additionally the microbial community on the biofilm was monitored during whole running process. The obtained results indicates that fungi as a dominant population in the decolorization system with the ratio of fungi to bacteria from 6.8:1 to 51.8:1 under all the tested influent conditions. Under sterile conditions a variety of white-rot fungi can oxidize textile dyes as well as similar degrees of treatment can be achieved under non-sterile conditions for their use in treating wastewater containing textile dyes studied (Libra *et al.* 2003). C.I. Reactive Black 5 (RB5) is a wastewater containing diazo textile dye which is treated by using the fungus *Trametes versicolor* in non-sterile culture, four strategies were investigated for this. In suspended culture the decolorization activity increases from a given amount of *T. versicolor* inoculums, three strategies with suspended culture were designed and amount of *T. versicolor* inoculums is based on its pH reduction in medium, production of extracellular enzymes, and its ability to produce enzymes independent of growth (nitrogen limitation in medium). The results showed that

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reduction of the medium pH to 3 did not suppress bacterial growth, while enzyme production by *T. versicolor* ceased. The decoupling of the process of fungal growth from wastewater treatment by use of the extracellular enzymes alone would allow however, under non-sterile conditions the enzyme activity of an enzyme suspension decreased rapidly. Under non-sterile conditions cultivation of fungi is done on organic solids to produce inocula for a decolorization process. Under non-sterile conditions a high degree of decolorization of RB5 was achieved with *T. versicolor* grown on grains as sole substrate. The rate of decolorization was dependent on the amount of fungal inoculum used.

### **By Anaerobic Bioremediation Methods**

The degradation of an azo dye mixture by an aerobic bacterial consortium in a rotating biological reactor was studied (Abraham *et al.* 2003). On gramophone records laterite pebbles of particle size 850  $\mu\text{m}$  to 1.44 mm were fixed using an epoxy resin on which the developed consortium was immobilized. Rate of degradation, biomass determination, BOD, enzymes involved, and fish bioassay etc. were studied. For high concentrations of dye (100  $\mu\text{g}/\text{mL}$ ) RBC has a high efficiency for dye degradation and high flow rate (36 L/h) at alkaline pH and salinity conditions normally encountered in the textile effluents. Bioassays (LD-50) using *Thilapia* fish in treated effluent showed that the percentage mortality was zero over a period of 96 h, whereas the mortality was 100% in untreated dye water within 26 h. Effluent obtained from RBC can be discharge safely into the environment was confirmed by fish bioassay. (Mohan *et al.* 2012) evaluated the functional behavior of anoxic-aerobic-anoxic microenvironment on azo dye (C.I. Acid black 10B) degradation in a periodic discontinuous batch mode operation for 26 cycles. Until 13th cycle dye removal efficiency and azo-reductase activity ( $30.50 \pm 1 \text{ U}$ ) increased with each feeding event and further stabilizes. Gradually increment and stabilization of ( $2.0 \pm 0.2 \mu\text{g}/\text{ml}$ ) dehydrogenase activity also indicates the stable proton shuttling between metabolic intermediates which provides higher number of reducing equivalents for dye degradation. For dye removal there is consumption of reducing equivalents during stabilized phase showed drop in redox catalytic currents for voltammetric profiles. The observed dye removal and biocatalyst behavior is correlated with change in polarization resistance, Tafel slopes and other bioprocess parameters. Microbial community analysis documented the involvement of specific organism pertaining to aerobic and facultative functions with heterotrophic and autotrophic metabolism. A biological method for decolorizing wastewater from fiber reactive dyeing of cotton by sequential anoxic/aerobic treatment steps using a single biomass was investigated and evaluated for color removal and chemical oxygen demand

(COD) (Smith *et al.* 2007). For a sequential anoxic/aerobic treatment process a viable biomass was developed that effectively removes both color and chemical oxygen demand from wastewater. For treating dyeing wastewater this method is the retrofitted to existing aerobic wastewater treatment systems that are typically used. The upflow of anaerobic sludge blanket (UASB) reactor for its usefulness in reduction in chemical oxygen demand (COD) and decolorization of real textile wastewater (RTW) under different operational conditions were evaluated (Somasiri *et al.* 2008). The efficiency obtained by UASB reactor in reducing COD was 90% as well as colour removal because of biodegradation was achieved 92%. During the treatment of textile wastewater the activities of the anaerobic granules were not affected. In textile wastewater treatment Cocci-shaped bacteria were the dominant group over Methanotrix like bacteria. In textile wastewater treatment volatile fatty acids (VFA) content, alkalinity, and pH present in effluents indicated that the anaerobic process was not inhibited. It is concluded that for the treatment of textile wastewater UASB reactor system can be effective for removal of colour and in the reduction of COD. Inhibitory effect of azo dyes on anaerobic methanogenic wastewater treatment (AMWT) has been studied (Dai *et al.* 2016) which mainly focus on biological toxicity in the batch test with simulated sole co-substrate. Mechanism of azo dyes and detailed information on inhibitory effect during the long-term operation with real complex co-substrate is limited. Moreover, under the complex scenario redox mediator (RM) could remediate the inhibition is still unclear in previous studies. In this study, a lab-scale high-rate anaerobic methanogenic bioreactor was operated for 127 days with the real textile wastewater and alternative concentrations of azo dyes (0-600 mg/L) were used as well as 50  $\mu$ M anthraquinone-2-sulfonate (AQS) was also added as RM at the last period of operation. An overall (decolorizing and methanogenic) performance of AMWT with concentration of 600 mg/L of azo dyes could cause significant inhibition on AMWT. Acetoclastic methanogens was more susceptible to high concentration azo dyes for specific methanogenic activity than hydrogenotrophic methanogens. In the anaerobic granular sludge (AGS) spatial distribution of extracellular polymeric substance showed the high biological toxicity of azo dyes which was mainly caused to enrichment effect in tightly bound-EPS (TB-EPS). The channels of AGS were clogged by azo dyes, which was evidenced by the hard release of aromatic amines in EPSs as well as decreased porosity of AGS and scanning electron microscope images. Meanwhile, the settling ability, particle size and strength of AGS all deteriorated after azo dyes concentration exceeded 450 mg/L. Overall performance of the bioreactor was remediate by dosing of AQS even if the recovery of acetoclastic methanogens was slow. It suggested that additional attention should be paid to prevent sludge from washout if RM was practically used to remediate the anaerobic reactor inhibited by azo dyes. (Pandey *et al.* 2007)

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studied that azo compounds constitute the largest and the most diverse group of synthetic dyes and are widely used in a number of industries such as textile, food, cosmetics and paper printing. Azo dyes compound are having xenobiotic nature due to this generally recalcitrant to biodegradation. However under certain environmental conditions microorganisms enzyme systems were developed for the decolorization and mineralization of azo dyes being highly versatile. In the bacterial metabolism of azo dyes initially reductive cleavage of azo bond take place leading to the formation of aromatic amines in the reaction. Decolorization of azo dyes by several mixed and pure bacterial cultures for anaerobic/anoxic, under these conditions this reaction is non-specific with respect to organisms as well as dyes. For non-specific reductive cleavage various mechanisms was proposed which include enzymatic as well as low molecular weight redox mediators. Azo dyes as growth substrates used by only few aerobic bacterial strains have been isolated. These types of organisms generally have a narrow substrate range. Chemical structure and the conditions play a role for degradation of aromatic amines. It is now known that sulfonated aromatic amines are resistant while simple aromatic amines are not, on the other hand mineralization of sulfonated aromatic amines require specialized aerobic microbial consortia and aromatic amines can be mineralized under methanogenic conditions.

### **By Enzymes and Bacteria**

The implementation of increasingly stringent standards for the discharge of wastes into the environment has necessitated the need for the development of alternative waste treatment processes (Karam & Nicell, 1999). Enzymatic treatment systems were developed for solid, liquid and hazardous wastes. For waste treatment applications a large number of enzymes have been reported from a variety of different plants and microorganisms. Enzymes can remove specific recalcitrant pollutants by action of precipitation or transformation to other products. Enzymes can also change the characteristics of a waste material to render it more amenable to treatment or converting waste material into value added products. In future reaction by-products, the disposal of reaction products and reduction of the cost of enzymatic treatment will be researched. (Ali *et al.* 2009) investigated effluent of a local textile mill that physicochemical and bacteriological status showed considerably high values of temperature, pH, EC, BOD, COD, TSS, TDS, heavy metals ions and color above the prescribed fresh water limits. However, almost all pollution indicators from source to sink indicate signs of natural remediation. Ten bacteria strains isolated from effluent showed comparatively higher resistance (MRL) ( $\text{mg l}^{-1}$ ) (average) for 10 heavy metals than against four structurally different dyes tested on solid media of mineral salt. Overall bacterial resistance was quite high against  $\text{Cr}^{3+}$  (1203),  $\text{Fe}^{3+}$

(2820),  $Mn^{2+}$  (804),  $Zn^{2+}$ (1122), and  $Pb^{2+}$  (435), whereas, it varied amid 300–500 in four dyes. Experiments carried out in liquid broth on solid media for bacterial degradation/decolorization of dyes was confirmed. (Won *et al.* 2004) studied that the removal of Reactive Orange 16 (RO16) by the use of protonated waste biomass of *Corynebacterium glutamicum* discharged from an industrial lysine fermentation plant. The biomass show maximum sorption capacities as high as  $186.6 \pm 7.1$  and  $154.8 \pm 2.8$  mg  $g^{-1}$  at pH 1 and 2, respectively, which can compare with activated carbons and ion-exchange resins type of commercial sorbents. If the solution pH decreases then dye uptake increases and under neutral conditions it was negligible. RO16 cannot be bound to a negatively charged carboxyl and/or phosphonate sites of the biomass because the RO16 molecule has two negatively charged sulfonate groups. Dye binding sites can be positively charged amine-occurring protein molecules. A high concentration of salts do not affect the uptake of RO16, and the biomass can be repeatedly reused up to eight times per sorption/desorption cycle. Toxic chemical waste water generated from textile industry is considered as one of the largest way in India. Dyes released by the textile industries are responsible for environmental safety. Recently, dye decolourization through biological means has gained momentum as these are cheap methods and can be applied to wide range of dyes. (Saranraj, 2013) focused on the bacterial biodegradation of toxic textile dyes. Various biological methods for the biodegradation of textile dyes by microorganisms are given in this study. He indicated that biological decolourization by bacteria has a great potential to be developed further as a decentralized wastewater treatment technology for small textile or dyeing units. However, further research work is required to study the toxicity of the metabolites formed by dye degradation and the possible fate of the utilized biomass in order to ensure the development of an eco-friendly technology. (Khouni *et al.* 2012) investigated the biological decolourisation of a widely used textile reactive dye in Tunisia, the Blue Bezaktiv S-GLD 150 dye, using a sequencing batch reactor (SBR). SBR was inoculated with an acclimated novel microbial consortia 'Bx'. Under aerobic conditions decolourisation efficiency was studied for different volumetric dye at loading rates (3–20 g dye/ $m^3$ ·d) at room temperature and at pH 7. When volumetric dye loading rates were under 15 g dye/ $m^3$ ·d than experimental results indicated that under aerobic conditions Bx displayed highest purification capabilities giving COD removal percentages of about 95–98% and maximum decolourisation rates in the range of 88–97%. Rates of decolourisation and COD removal were decreased to 70% and 90% respectively when volumetric dye loading rates were increased to 20 g dye/ $m^3$ ·d. Obtained results indicate that the efficiency of dye removal through a sequencing batch reactor influenced by the volumetric dye loading rate. The removal of coloured textile effluents in the aquatic environment is undesirable as these reduce light penetration, therefore affecting life

of aquatic species and limits utilization of the water media. These toxic effluents can be treated by microbial bioremediation, it is an alternative treatment option available other than the commonly employed physicochemical and biological methods. (Leena & Selva, 2008) worked on the decolourization of an actual textile effluent that contained the diazo dye compound Reactive Black-B. In their study they observed the potentials of certain selected bacteria on effluent soil-adapted and non-adapted bacteria. Among all Five effluent-adapted and four non-adapted bacterial isolates were tested. The results confirm that non-adapted species were not better option for decolourizing the effluent than the effluent-adapted strains. Wastewater effluents from the textile and other dye-stuff industries contain significant amounts of synthetic dyes that require treatment to prevent groundwater contamination. In research aimed at biotechnology for treatment of azo dyes. (Khalid *et al.* 2008) studied 288 strains of azo-dye degrading bacteria to identify efficient strains and determine incubation times required for decolorization. Initial enrichment cultures were carried out using a mixture of four structurally different dyes (Acid Red 88, Direct Red 81, Reactive Black 5, and Disperse Orange 3) as the sole source of C and N to isolate the bacteria from activated sludge, soil, and natural asphalt. To decolorize the dyes individually or in mixtures six bacterial strains were selected for further study based on their prolific growth and ability to rapidly decolorize. 4 h are required for complete decolorization of 100 mg l<sup>-1</sup> of AR-88 and DR-81 dyes under static conditions by the most efficient strain AS96 (*Shewanella putrefaciens*) and it is the shortest treatment time. 6 and 8 h are required respectively for complete decolorization of RB-5 and DO-3. For azo-dye degradation these bacterial strains are the most efficient bacteria and may have practical application for biological treatment of dye-polluted wastewater streams. The use of microorganisms to clean up contaminated environment is the cheapest alternative method to the conventional treatment methods. But a major challenge arises that is the choice of easily grown, viable and effective natural occurring microorganism to do the cleaning. The application of photosynthetic bacteria in bioremediation were presented and reviewed (Idi *et al.* 2015) due to their minimum nutrients requirement and the possibility of generating valuable products simultaneously cleaning the contaminated environment. The specific photosynthetic bacteria are capable to degrade pollutants such as heavy metals, pesticides, dyes, crude oil and odour. The possible value added products to be generated as well as the mechanism of degradation are also discussed. The use of these bacteria in bioremediation have environmental as well as economic benefits because utilization of CO<sub>2</sub> and the generation of value added products while cleaning up polluted environment are the major advantages of using bacteria. Ligninolytic extracellular enzymes, including lignin peroxidase, have high redox potential and prospective industrial applications. (Falade *et al.* 2017) studied some articulated applications of these enzymes including ethanol production, textile effluent treatment



and dye decolorization, coal depolymerization, treatment of hyperpigmentation, and skin-lightening through melanin oxidation.

(Mahmood *et al.* 2016) critically reviewed biological treatment of dye polluted wastewater and the role of bacterial reductive and oxidative enzymes/processes. The complete mineralization of azo dyes normally includes two-step process: first anaerobic treatment for decolorization, and second an oxidative process that results in degradation of the toxic intermediates that are formed during the first step. They did a molecular study revealing first reductive process which can be brought by two classes of enzymes involving flavin-dependent and flavin-free azoreductases under anaerobic or low oxygen conditions. The second step that is carried out by oxidative enzymes that primarily involves broad specificity peroxidases, laccases and tyrosinases. Laccases are ecofriendly biocatalyst having capacity to transform complex xenobiotics making them useful in enzymatic bioremediation. (Mate & Alcade, 2017) reviewed the most significant recent advances on the use of laccases and their future perspectives in biotechnology. (Meerbergen *et al.* 2018) aimed to study, isolate and characterize bacterial strains that are capable of decolorizing or degrading azo dyes commonly applied in textile production. They followed a prescreening of 125 isolates and out of that five strains were retained for further evaluation of decolorization rate. Out of those five strains, one strain belonging to the genus *Acinetobacter* and another belonging to *Klebsiella* out performed the other tested strains. It was found that both strains exhibited strong decolorization ability (>80%) within a wide temperature range (20 °C–40 °C).

## **CONCLUSION**

The dye waste not only cause environmental pollution but also medical and aesthetic problems associated with human health and society. Although the biological treatment is a promising technology for degradation of dyes, the method relies on success of finding out a suitable organism and designing of condition for the process. Also the biological method of degradation alone cannot tackle the problem successfully. Hence, along with biological processes some other pre and post treatment methods are required. Pre-treatment of dyeing effluent by advanced oxidation processes (AOP) catalyzed by a source of ultraviolet (UV) light and a powerful oxidant is a promising alternative for the effective removal of color and refractory organics from the effluent. Some metal oxides like  $\text{TiO}_2$  in combination with a agents like UV rays are used for this process. Zinc oxide appeared to be a suitable alternative to  $\text{TiO}_2$  for water treatment. An understanding of the use of bacteria and fungi for dye degradation will further enhance the efficiencies of these processes towards its successful application.

## REFERENCES

- Alaton, I. A., & Balcioglu, I. A. (2001). Photochemical and heterogeneous photocatalytic degradation of waste vinylsulphone dyes: A case study with hydrolyzed reactive black 5. *Journal of Photochemistry and Photobiology A Chemistry*, *141*(2-3), 247–254. doi:10.1016/S1010-6030(01)00440-3
- Alaton, I. A., Tureli, G., & Hanci, T. O. (2009). Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation processes: Optimization by response surface methodology. *Journal of Photochemistry and Photobiology A Chemistry*, *202*(2-3), 142–153. doi:10.1016/j.jphotochem.2008.11.019
- Aleboye, A., Aleboye, H., & Moussa, Y. (2003). “Critical” effect of hydrogen peroxide in photochemical oxidative decolorization of dyes: Acid orange 8, acid blue 74 and methyl orange. *Dyes and Pigments*, *57*(1), 67–75. doi:10.1016/S0143-7208(03)00010-X
- Ali, N., Hameed, A., & Ahmed, S. (2009). Physicochemical characterization and bioremediation perspective of textile effluent, dyes and metals by indigenous bacteria. *Journal of Hazardous Materials*, *164*(1), 322–328. doi:10.1016/j.jhazmat.2008.08.006 PMID:18818017
- Arslan, I. (2001). Treatability of a simulated disperse dye-bath by ferrous iron coagulation, ozonation, and ferrous iron-catalyzed ozonation. *Journal of Hazardous Materials*, *85*(3), 229–241. doi:10.1016/S0304-3894(01)00232-1 PMID:11489526
- Arslana, I., Balcioglu, A., & Bahnemann, D. W. (2000). Advanced chemical oxidation of reactive dyes in simulated dyehouse effluents by ferrioxalate-Fenton/UV-A and TiO<sub>2</sub>/UV-A processes. *Dyes and Pigments*, *47*(3), 207–218. doi:10.1016/S0143-7208(00)00082-6
- Babana, A., Yediler, A., Lienert, D., Kemerdere, N., & Kettrup, A. (2003). Ozonation of high strength segregated effluents from a woollen textile dyeing and finishing plant. *Dyes and Pigments*, *58*(2), 93–98. doi:10.1016/S0143-7208(03)00047-0
- Baughman, G. L., & Perenich, T. A. (1988). Fate of dyes in aquatic systems: I Solubility and partitioning of some hydrophobic dyes and related compounds. *Environmental Toxicology and Chemistry*, *7*(3), 183–199. doi:10.1002/etc.5620070302
- Carri re, J., Jones, J.P., & Broadbeut, A.D. (1993). Effect of a dyeing aid on the oxidation reaction of color from an insoluble and a soluble dye in a simulated effluent. *Proceedings of the 11th Ozone World Congress*, *1*, S10-98-S10-107.

- Chang, C.-N., Ma, Y.-S., Fang, G.-C., Chao, A. C., Tsai, M.-C., & Sung, H.-F. (2004). Decolorizing of lignin wastewater using the photochemical UV/TiO<sub>2</sub> process. *Chemosphere*, *56*(10), 1011–1017. doi:10.1016/j.chemosphere.2004.04.021 PMID:15268968
- Chung, K. T., Fulk, G. E., & Egan, M. (1978). Reduction of azo dyes by intestinal anaerobes. *Applied and Environmental Microbiology*, *35*, 558–562. PMID:25047
- Ciardellia, G., & Ranieri, N. (2001). The treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation. *Water Research*, *35*(2), 567–572. doi:10.1016/S0043-1354(00)00286-4 PMID:11229013
- Dai, R., Chen, X., Luo, Y., Ma, P., Ni, S., Xiang, X., & Li, G. (2016). Inhibitory effect and mechanism of azo dyes on anaerobic methanogenic wastewater treatment: Can redox mediator remediate the inhibition? *Water Research*, *104*, 408–417. doi:10.1016/j.watres.2016.08.046 PMID:27579869
- Dore, Â.M. (1990). Les criteries de choix d'un oxydant. *Journal Franc°ais d'Hydrologie*, *21*, 9-30.
- Falade, A. O., Nwodo, U. U., Iweriebor, B. C., Green, E., Mabinya, L. V., & Okoh, A. I. (2017). Lignin peroxidase functionalities and prospective applications. *MicrobiologyOpen*, *6*(1), e00394. doi:10.1002/mbo3.394 PMID:27605423
- Faraco, V., Pezzella, C., Miele, A., Giardina, P., & Sannia, G. (2009). Bio-remediation of colored industrial wastewaters by the white-rot fungi *Phanerochaete chrysosporium* and *Pleurotus ostreatus* and their enzymes. *Biodegradation*, *20*(2), 209–220. doi:10.1007/10532-008-9214-2 PMID:18758969
- Fenton, H. J. H. (1894). Oxidation of tartaric acid in the presence of iron. *Journal of the Chemical Society*, *65*(0), 899–910. doi:10.1039/CT8946500899
- Gad-Allah, T. A., Kato, S., Satokawa, S., & Kojima, T. (2009). Treatment of synthetic dyes wastewater utilizing a magnetically separable photocatalyst (TiO<sub>2</sub>/SiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>): Parametric and kinetic studies. *Desalination*, *244*(1-3), 1–11. doi:10.1016/j.desal.2008.04.031
- Goel, M., Chovelon, J.-M., Ferronato, C., Bayard, R., & Sreekrishnan, T. R. (2010). The remediation of wastewater containing 4-chlorophenol using integrated photocatalytic and biological treatment. *Journal of Photochemistry and Photobiology. B, Biology*, *98*(1), 1–6. doi:10.1016/j.jphotobiol.2009.09.006 PMID:19914843

### **Chemical and Biological Treatment of Dyes**

- Gupta, V. K., Jain, R., Mittal, A., Saleh, T. A., Nayak, A., Agarwal, S., & Sikarwar, S. (2012). Photo-catalytic degradation of toxic dye amaranth on TiO<sub>2</sub>/UV in aqueous suspensions. *Materials Science and Engineering C*, 32(1), 12–17. doi:10.1016/j.msec.2011.08.018 PMID:23177765
- Haber, F., & Weiss, J. (1934). The catalytic decomposition of hydrogen peroxide by iron salts. *Proceedings of Royal Society Series A*, 147(861), 332–351. doi:10.1098/rspa.1934.0221
- Hoffmann, M. R., Martin, S. T., Choi, W., & Bahnemann, D. W. (1995). Environmental applications of semiconductor photocatalysis. *Chemical Reviews*, 95(1), 69–96. doi:10.1021/cr00033a004
- Hoigne, Â. J. (1988). *The Chemistry of Ozone in Water. Process Technologies for Water Treatment* (S. Stucki, Ed.). Plenum Publishing Corporation.
- Idi, A., Nor, M. H. M., Wahab, M. F. A., & Ibrahim, Z. (2015). Photosynthetic bacteria: An eco-friendly and cheap tool for bioremediation. *Reviews in Environmental Science and Biotechnology*, 14(2), 271–285. doi:10.1007/11157-014-9355-1
- Ince, N. H., & Tezcanlí, G. (2001). Reactive dyestuff degradation by combined sonolysis and ozonation. *Dyes and Pigments*, 49(3), 145–153. doi:10.1016/S0143-7208(01)00019-5
- Iurascua, B., Siminiceanua, I., Vione, D., Vicentec, M. A., & Gild, A. (2009). Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite. *Water Research*, 43(5), 1313–1322. doi:10.1016/j.watres.2008.12.032 PMID:19138784
- Jain, A., Lodha, S., Punjabi, P. B., Sharma, V. K., & Ameta, S. C. (2009). A study of catalytic behaviour of aromatic additives on the photo-Fenton degradation of phenol red. *Journal of Chemical Sciences*, 121(6), 1027–1034. doi:10.1007/12039-009-0115-7
- Jain, R., Mathur, M., Sikarwar, S., & Mittal, A. (2007). Removal of the hazardous dye rhodamine B through photocatalytic and adsorption treatments. *Journal of Environmental Management*, 85(4), 956–964. doi:10.1016/j.jenvman.2006.11.002 PMID:17239520
- Jain, R., & Sikarwar, S. (2006). Photocatalytic and adsorption studies on the removal of dye congo red from wastewater. *International Journal of Environment and Pollution*, 27(1/2/3), 158–178. doi:10.1504/IJEP.2006.010460

- Juang, R. S., Tseng, R. L., Wu, F. C., & Lin, S. J. (1996). Use of chitin and chitosan in lobster shell wastes for colour removal from aqueous, solutions. *Journal of Environmental Science and Health. Part A, Environmental Science and Engineering & Toxic and Hazardous Substance Control*, 31(2), 325–338. doi:10.1080/10934529609376360
- Kalal, S., Chauhan, N. P. S., Ameta, N., Ameta, R., Kumar, S., & Punjabi, P. B. (2014). Role of copper pyrovanadate as heterogeneous photo-fenton like catalyst for the degradation of neutral red and azure-B: An eco-friendly approach. *Korean Journal of Chemical Engineering*, 31(12), 2183–2191. doi:10.1007/11814-014-0142-z
- Kalal, S., Pandey, A., Ameta, R., & Punjabi, P. B. (2016). Heterogeneous photo-Fenton-like catalysts Cu<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Cr<sub>2</sub>V<sub>4</sub>O<sub>13</sub> for an efficient removal of azo dye in water. *Cogent Chemistry*, 2(1), 1–12. doi:10.1080/23312009.2016.1143344
- Karam, J., & Nicell, J. A. (1999). Potential applications of enzymes in waste treatment. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, 69(2), 141–153. doi:10.1002/(SICI)1097-4660(199706)69:2<141::AID-JCTB694>3.0.CO;2-U
- Khadhraoui, M., Trabelsi, H., Ksibi, M., Bouguerra, S., & Elleuch, B. (2009). Discoloration and detoxification of a Congo red dye solution by means of ozone treatment for a possible water reuse. *Journal of Hazardous Materials*, 161(2-3), 974–981. doi:10.1016/j.jhazmat.2008.04.060 PMID:18515006
- Khalid, A., Arshad, M., & Crowley, D. E. (2008). Accelerated decolorization of structurally different azo dyes by newly isolated bacterial strains. *Applied Microbiology and Biotechnology*, 78(2), 361–369. doi:10.1007/00253-007-1302-4 PMID:18084755
- Khouni, I., Marrot, B., & Amara, R. B. (2012). Treatment of reconstituted textile wastewater containing a reactive dye in an aerobic sequencing batch reactor using a novel bacterial consortium. *Separation and Purification Technology*, 87, 110–119. doi:10.1016/j.seppur.2011.11.030
- Kim, H. T., Park, C., Yang, J., & Kim, S. (2004). Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. *Journal of Hazardous Materials*, 112(1-2), 95–103. doi:10.1016/j.jhazmat.2004.04.008 PMID:15225935
- Kim, T.-H., Lee, Y., Yang, J., Lee, B., Park, C., & Kim, S. (2004). Decolorization of dye solutions by a membrane bioreactor (MBR) using white-rot fungi. *Desalination*, 168, 287–293. doi:10.1016/j.desal.2004.07.011

## **Chemical and Biological Treatment of Dyes**

- Kiran, S., Ali, S., & Asgher, V. (2013). Degradation and mineralization of azo dye reactive blue 222 by sequential photo-fenton's oxidation followed by aerobic biological treatment using white rot fungi. *Bulletin of Environmental Contamination and Toxicology*, *90*(2), 208–215. doi:10.1007/00128-012-0888-0 PMID:23272326
- Koch, M., Yediler, A., Lienert, D., Insel, G., & Kettrup, A. (2002). Ozonation of hydrolyzed azo dye reactive yellow 84 (CI). *Chemosphere*, *46*(1), 109–113. doi:10.1016/S0045-6535(01)00102-3 PMID:11806521
- Leena, R., & Selva, R. D. (2008). Bio-decolourization of textile effluent containing reactive black-B by effluent-adapted and non-adapted bacteria. *African Journal of Biotechnology*, *7*, 3309–3313.
- Libra, J.A., Borchert, M., & Banit, S. (2003). *Competition strategies for the decolorization of a textile-reactive dye with the white-rot fungi Trametes versicolor under non-sterile conditions*. Academic Press.
- Linsebigler, A. L., Lu, G., & Yates, J. T. (1995). Photocatalysis on TiO<sub>2</sub> surfaces: Principles, mechanisms and selected results. *Chemical Reviews*, *95*(3), 735–758. doi:10.1021/cr00035a013
- Mahmood, S., Khalid, A., Arshad, M., Mahmood, T., & Crowley, D. E. (2016). Detoxification of azo dyes by bacterial oxidoreductase enzymes. *Critical Reviews in Biotechnology*, *36*, 639–651. PMID:25665634
- Mate, D. M., & Alcalde, M. (2017). Laccase: A multi-purpose biocatalyst at the forefront of biotechnology. *Microbial Biotechnology*, *10*(6), 1457–1467. doi:10.1111/1751-7915.12422 PMID:27696775
- Meerbergen, K. K., Willems, A., Dewil, R., Impe, J. V., Appels, L., & Lievens, B. (2018). Isolation and screening of bacterial isolates from wastewater treatment plants to decolorize azo dyes. *Journal of Bioscience and Bioengineering*, *125*(4), 448–456. doi:10.1016/j.jbiosc.2017.11.008 PMID:29273268
- Meriç, S., Kaptan, D., & Ölmez, T. (2004). Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. *Chemosphere*, *54*(3), 435–441. doi:10.1016/j.chemosphere.2003.08.010 PMID:14575758
- Meyer, U. (1981) Biodegradation of synthetic organic colorants. Microbial degradation of xenobiotic and recalcitrant compounds. In *FEMS Symposium 12*. Academic Press.
- Mishra, G., & Tripathy, M. (1993). A critical review of the treatments for decolourization of textile effluent. *Colourage*, *40*, 35–38.

- Mohan, S. V., Babu, P. S., Naresh, K., Velvizhi, G., & Madamwarb, D. (2012). Acid azo dye remediation in anoxic–aerobic–anoxic microenvironment under periodic discontinuous batch operation: Bio-electro kinetics and microbial inventory. *Bioresource Technology*, *119*, 362–372. doi:10.1016/j.biortech.2012.05.125 PMID:22750504
- Moran, C., Hall, M. E., & Howell, R. C. (1997). Effects of sewage treatment on textile effluent. *Journal of the Society of Dyers and Colorists*, *113*(10), 272–274. doi:10.1111/j.1478-4408.1997.tb01847.x
- Muruganandham, M., & Swaminathan, M. (2004). Photochemical oxidation of reactive azo dye with UV–H<sub>2</sub>O<sub>2</sub> process. *Dyes and Pigments*, *62*(3), 269–275. doi:10.1016/j.dyepig.2003.12.006
- Muthukumar, M., Sargunamani, D., Selvakumar, N., & Rao, J. V. (2004). Optimisation of ozone treatment for colour and COD removal of acid dye effluent using central composite design experiment. *Dyes and Pigments*, *63*(2), 127–134. doi:10.1016/j.dyepig.2004.02.003
- Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials B*, *98*(1-3), 33–50. doi:10.1016/S0304-3894(02)00282-0 PMID:12628776
- Nigam, P., Armour, G., Banat, I. M., Singh, D., & Marchant, R. (2000). Physical removal of textile dyes and solid state fermentation of dye adsorbed agricultural residues. *Bioresource Technology*, *72*(3), 219–226. doi:10.1016/S0960-8524(99)00123-6
- Nilsson, I., Möller, A., Mattiasson, B., Rubindamayugi, M. S. T., & Welander, U. (2006). Decolorization of synthetic and real textile wastewater by the use of white-rot fungi. *Enzyme and Microbial Technology*, *38*(1-2), 94–100. doi:10.1016/j.enzmictec.2005.04.020
- Pandey, A., Kalal, S., Ameta, C., Ameta, R., Kumar, S., & Punjabi, P. B. (2015). Synthesis, characterization and application of naïve and nano-sized titanium dioxide as a photocatalyst for degradation of methylene blue. *Journal of Saudi Chemical Society*, *19*(5), 528–536. doi:10.1016/j.jscs.2015.05.013
- Pandey, A., Singh, P., & Iyengar, L. (2007). Bacterial decolorization and degradation of azo dyes. *International Biodeterioration & Biodegradation*, *59*(2), 73–84. doi:10.1016/j.ibiod.2006.08.006

### **Chemical and Biological Treatment of Dyes**

- Pant, D., Singh, A., Satyawali, Y., & Gupta, R. K. (2008). Effect of carbon and nitrogen source amendment on synthetic dyes decolourizing efficiency of white-rot fungus, *Phanerochaete chrysosporium*. *Journal of Environmental Biology*, *29*, 79–84. PMID:18831336
- Poots, V. J. P., & McKay, J. J. (1976a). The removal of acid dye from effluent using natural adsorbents ± I Peat. *Water Resources*, *10*, 1061–1066.
- Rahmani, Z., Kermani, M., Gholami, M., Jafari, A. J., & Mahmoodi, N. M. (2012). Effectiveness of photochemical and sonochemical processes in degradation of basic violet 16 (BV16) dye from aqueous solutions. *Iranian Journal of Environmental Health Sciences & Engineering*, *9*(1), 14. doi:10.1186/1735-2746-9-14 PMID:23369268
- Revankar, M. S., & Lele, S. S. (2007). Synthetic dye decolorization by white rot fungus, *Ganoderma* sp. WR-1. *Bioresource Technology*, *98*(4), 775–780. doi:10.1016/j.biortech.2006.03.020 PMID:16730976
- Rosa, J. M., Fileti, A. M. F., Tambourgi, E. B., & Santana, J. C. C. (2015). Dyeing of cotton with reactive dyestuffs: The continuous reuse of textile wastewater effluent treated by ultraviolet/hydrogen peroxide homogeneous photocatalysis. *Journal of Cleaner Production*, *90*, 60–65. doi:10.1016/j.jclepro.2014.11.043
- Saranraj, P. (2013). Bacterial biodegradation and decolourization of toxic textile azo dyes. *African Journal of Microbiological Research*, *7*, 3885–3890.
- Sarasa, J., Roche, M. P., Ormad, M. P., Gimeno, E., Puig, A., & Ovelheiro, J. L. (1998). Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation. *Water Resources*, *32*, 2721–2727.
- Selvama, K., Swaminathan, K., & Chae, K.-S. (2003). Decolourization of azo dyes and a dye industry effluent by a white rot fungus *Thelephora* sp. *Bioresource Technology*, *88*(2), 115–119. doi:10.1016/S0960-8524(02)00280-8 PMID:12576004
- Smith, B., O'Neal, G., Boyter, H., & Piszczek, J. (2007). Decolorizing textile dye wastewater by anoxic/aerobic treatment. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *82*(1), 16–24. doi:10.1002/jctb.1629
- Somasiri, W., Li, X.-F., Ruan, W.-Q., & Jian, C. (2008). Evaluation of the efficacy of upflow anaerobic sludge blanket reactor in removal of colour and reduction of COD in real textile wastewater. *Bioresource Technology*, *99*(9), 3692–3699. doi:10.1016/j.biortech.2007.07.024 PMID:17719776



- Somensi, C. A., Simionatto, E. L., Bertoli, S. L., Wisniewski, A. Jr, & Radetski, C. M. (2010). Use of ozone in a pilot-scale plant for textile wastewater pre-treatment: Physico-chemical efficiency, degradation by-products identification and environmental toxicity of treated wastewater. *Journal of Hazardous Materials*, *175*(1-3), 235–240. doi:10.1016/j.jhazmat.2009.09.154 PMID:19879043
- Souza, S. M., Bonilla, K. A. S., & Souza, A. A. U. (2010). Removal of COD and color from hydrolyzed textile azo dye by combined ozonation and biological treatment. *Journal of Hazardous Materials*, *179*(1-3), 35–42. doi:10.1016/j.jhazmat.2010.02.053 PMID:20227826
- Sun, J. H., Peng, S., Liang, S. G., Li, W., & Qiao, P. (2007). Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process. *Dyes and Pigments*, *74*(3), 647–652. doi:10.1016/j.dyepig.2006.04.006
- Swamy, J., & Ramsay, J. A. (1999). The evaluation of white rot fungi in the decoloration of textile dyes. *Enzyme and Microbial Technology*, *24*(3-4), 130–137. doi:10.1016/S0141-0229(98)00105-7
- T.E., R.C., T.S., J.J., T.P., & P.P. (2003). Bioremediation of textile azo dyes by an aerobic bacterial consortium using a rotating biological contactor. *Biotechnology Progress*, 1372–1376. PMID:12892505
- Tehrani-Baghaa, A. R., Mahmoodi, N. M., & Menger, F. M. (2010). Degradation of a persistent organic dye from colored textile wastewater by ozonation. *Desalination*, *260*(1-3), 34–38. doi:10.1016/j.desal.2010.05.004
- Titus, M. P., Molina, V. G., Banos, M. A., Gimenez, J., & Esplugas, S. (2004). Degradation of chlorophenols by means of advanced oxidation processes: A general review. *Applied Catalysis B: Environmental*, *47*(4), 219–256. doi:10.1016/j.apcatb.2003.09.010
- Vaishnav, P., Kumar, A., Ameta, R., Punjabi, P. B., & Ameta, S. C. (2014). Photo oxidative degradation of azure-B by sono-photo-Fenton and photo-Fenton reagents. *Arabian Journal of Chemistry*, *6*(6), 981–985. doi:10.1016/j.arabjc.2010.12.019
- Vanhulle, S., Trovaslet, M., Enaud, E., Lucas, M., Taghavi, S., Lelie, D. V. D., ... Corbisier, A. M. (2008). Decolorization, Cytotoxicity, and Genotoxicity Reduction During a Combined Ozonation/Fungal Treatment of Dye-Contaminated Wastewater. *Environmental Science & Technology*, *42*(2), 584–589. doi:10.1021/es071300k PMID:18284166

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- Vinodgopal, K., & Kamat, P. V. (1994). Photochemistry of textile azo dyes. Spectral characterization of excited state, reduced and oxidized forms of acid orange 7. *Journal of Photochemistry and Photobiology A Chemistry*, 83(2), 141–146. doi:10.1016/1010-6030(94)03810-4
- Vinodgopal, K., Wynkoop, D. E., & Kamat, P. V. (1996). Environmental photochemistry on semiconductor surfaces: Photosensitized degradation of a textile azo dye, acid orange 7, on TiO<sub>2</sub> particles using visible light. *Environmental Science & Technology*, 30(5), 1660–1666. doi:10.1021/es950655d
- Wang, A., Qu, J., Ru, J., Liu, H., & Ge, J. (2005). Mineralization of an azo dye acid red 14 by electro-Fenton's reagent using an activated carbon fibre cathode. *Dyes and Pigments*, 65(3), 227–233. doi:10.1016/j.dyepig.2004.07.019
- Wang, C., Yediler, A., Lienert, D., Wang, Z., & Kettrup, A. (2003). Ozonation of an azo dye C.I. Remazol Black 5 and toxicological assessment of its oxidation products. *Chemosphere*, 52(7), 1225–1232. doi:10.1016/S0045-6535(03)00331-X PMID:12821003
- Weber, E., & Wolfe, N. L. (1987). Kinetics studies of reduction of aromatic azo compounds in anaerobic sediment/water systems. *Environmental Toxicology and Chemistry*, 6(12), 911–920. doi:10.1002/etc.5620061202
- Willmott, N., Guthrie, J., & Nelson, G. (1998). The biotechnology approach to colour removal from textile effluent. *Journal of the Society of Dyers and Colorists*, 114(2), 38–41. doi:10.1111/j.1478-4408.1998.tb01943.x
- Won, S. W., Choi, S. B., Chung, B. W., Park, D., Park, J. M., & Yun, Y.-S. (2004). Biosorptive decolorization of reactive orange 16 using the waste biomass of *Corynebacterium glutamicum*. *Industrial & Engineering Chemistry Research*, 43(24), 7865–7869. doi:10.1021/ie049559o
- Wu, J., & Wang, T. (2001). Ozonation of aqueous azo dye in a semi-batch reactor. *Water Research*, 35(4), 1093–1099. doi:10.1016/S0043-1354(00)00330-4 PMID:11235876
- Yang, Q., Li, C., Li, H., Li, Y., & Yu, N. (2009). Degradation of synthetic reactive azo dyes and treatment of textile wastewater by a fungi consortium reactor. *Biochemical Engineering Journal*, 43(3), 225–230. doi:10.1016/j.bej.2008.10.002

## **KEY TERMS AND DEFINITIONS**

**Advanced Oxidation Process (AOPs):** Advanced oxidation processes (AOPs) in a broad sense, are a set of chemical treatment procedures designed to remove organic or sometimes inorganic materials in water and wastewater by oxidation through reactions with hydroxyl radicals (OH).

**Fenton Process:** Fenton process is attractive alternative to conventional oxidation processes in effluent treatment of recalcitrant compounds. The oxidation of organic substrates by iron (II) and hydrogen peroxide is called the “Fenton chemistry” and it was first described by H.J.H. Fenton.

**Photo-Catalysis Process:** Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate.