

Chemical Oxidation for Degradation of Textile Dyes using Hydrogen Peroxide

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ABSTRACT

Textile dye effluents are intensively colored due to the presence of residual dyes. Residual dyes presence in water courses is toxic and aesthetically displeasing. Removal of color from C.I. Acid Red 52, C.I. Acid Green 1, C.I. Basic Red 2, C.I. Reactive Red 11 and C.I. Basic Blue 9 is investigated by advanced oxidation process by using Hydrogen peroxide oxidant. Studies with H_2O_2 resulted in excellent color removal. Hydrogen peroxide exhibited maximum color removal of 99%, 47.5% and 91% was obtained for C.I. Acid Red 52, C.I. Basic Red 2 and C.I. Basic Blue 9 respectively at favorable pH 12. In case of C.I. Acid green 1 yielded maximum color removal was 91% at favorable pH 3 and for C.I. Reactive Red 11 was 50% maximum color removal at favorable pH 10.5. The probable oxidative degradation pathways of the dyes are also proposed.

Key words: color removal, Dyes, Hydrogen peroxide, Oxidative degradation pathways.

1. INTRODUCTION

Synthetic dyes are used extensively in textile, paper, leather and printing industries and are generally classified into application classes like Acid, Basic, Direct, Reactive, Disperse, Vat, etc., and chemical classes like azo, Azine, thiazine, anthraquinone, nitro, nitroso, phthalocyanine, polymethine, carbonium, etc. Many of these dyes are manufactured through different stages involving nitration, reduction, halogenation, amination, sulfonation, diazotization and oxidation using benzene, toluene, xylene, naphthalene, anthracene, as raw materials [Abrahart, 1977]. The effluents from these industries vary widely in composition and contain inorganic and organic compounds and have high level of color and COD. Textile colored effluents contains significant amounts of residual dyes, many of them are reported to be toxic and carcinogenic [Anliker, 1979]. Discharge of these dye effluents can cause formation of toxic aromatic amines under anaerobic conditions in receiving media and contaminate the soil and groundwater, requiring proper treatment before discharging into the environment.

Generally employed methods for color removal such as adsorption, coagulation–flocculation, oxidation and electrochemical methods are quite expensive and have operational problems [Lin and Peng, 1996; Ramakrishna and Viraraghavan, 1997]. Many of synthetic dyestuffs are resistant to biological degradation due to the presence of aromatic compounds and thus color removal by bio processing is difficult and incomplete [Carliell et al. 1996]. Primary and secondary treatment methods are ineffectual for removal of color due to the complex structure and stability of dyes and produce large amount of sludge the disposal of which need further treatment [Ghoreishi and Haghghi, 2003]. Advanced oxidation processes (AOPs) employing oxidising agents namely $NaOCl$, H_2O_2 , Fenton reagent (FR) and O_3 , UV, either alone or in combinations, photocatalysis, are credible alternatives for the oxidation of many refractory organic compounds encountered in industrial effluents because Chlorine, Ozone and $HO\bullet$ are powerful oxidants with oxidation potentials of 1.49, 2.07 and 2.85 electron volts respectively [Kommineni et al. 2008]. Durr et

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al. [2012] reported color removal from textile wastewaters by H_2O_2 alone was less effective: 21% and 45% respectively. In this study, decolorisation of C.I. Acid Red 52, C.I. Acid Green 1, C.I. Basic Blue 9, C.I. Basic Red 2 and C.I. Reactive Red 11 is investigated by AOP using oxidizing agent H_2O_2 . Efficiency of color removal is investigated in terms of percent color removal by changing oxidant dose, contact time and solution pH.

2. EXPERIMENTAL METHODOLOGY

2.1 Chemicals and Dyes

All chemicals used in the experimental work were of Analytical Reagent grade. Chemicals like Ferric chloride ($FeCl_3$), Aluminum sulfate $Al_2(SO_4)_3$, Aluminum chloride ($AlCl_3$), Hydrogen peroxide (H_2O_2 , 30% V/V, Merck), Ferrous sulfate ($FeSO_4$, Merck) were used. Adjustment of solution pH, 0.1N sulphuric acid and 0.1N sodium hydroxide was used. C.I. Acid Red 52, C.I. Acid Green 1, C.I. Basic Blue 9, C.I. Basic Red 2 and C.I. Reactive Red 11 (Atul industries, Ahmadabad, Gujarat, India), textile dyes are employed as test dyes in the present study.

2.2. Color Measurement

To evaluate color removal, residual color concentration after the experiment was measured by measuring % T/OD at optimum wavelength and reading for the dye color concentration from the calibration graph.

2.3. Hydrogen peroxide oxidation process

To a 300 mL of test dye stock solution taken in a 1000 mL glass beaker, varying doses of oxidant H_2O_2 was added and the contents were mixed, first at high speed 100rpm for two minutes and then speed was reduced to 30 rpm and mixed for 20 minutes and equilibrated for two hours (Sureyya Meric 2005) and analysed for residual color concentration. Experimentations were conducted in 3 stages. In the first stage, varying doses of H_2O_2 were added, oxidation tests were conducted as detailed above and residual color concentration was measured to find the minimum chemical dose producing maximum color removal which was designated as favorable dose. In the second stage, 40-80% of favorable dose was added to the test dye stock solution adjusted to pH of 3.0, 4.0, 5.0, 6.0, 8.0, 9.0, 10.5 and 12.0; reaction carried out and the pH value producing maximum color removal was found and designated as favorable pH. In third stage, experiments were conducted at favorable pH employing varying doses just in the range of favorable dose to determine optimum dose i.e. the smallest dose that produces maximum color removal.

3. RESULTS AND DISCUSSION

All experimental results are presented in graphical form and are followed by a discussion of the results.

3.1. Color removal by Hydrogen peroxide

Test dyes were subjected to chemical oxidation with varying doses of H_2O_2 and the experimental results in terms of removal of color (%) are given in Figure 1.

Color removal data presented in Figure 1 shows that, CI Acid Red 52 exhibited maximum color removal and whereas color removal from CI Acid Green 1, C.I. Basic Red 2, C.I. Basic Blue 9 and C.I. Reactive Red 11 dyes was relatively less with C.I. Reactive Red 11 being the least. When H_2O_2 was added in the range of 5g/L to 60g/L 70% color removal was accomplished at 5g/L, 74% at 20g/L dose and removal remain constant even as the dose was increased to 60g/L for C.I. Acid Red 52. Alike pattern of color removal was observed in the case of other dyes also; however, the maximum color removal obtained was very less: 30% C.I. Basic Red 2 and C.I. Basic Blue 9, 22% for CI Acid Green 1 and 17% for C.I. Reactive Red 11. While

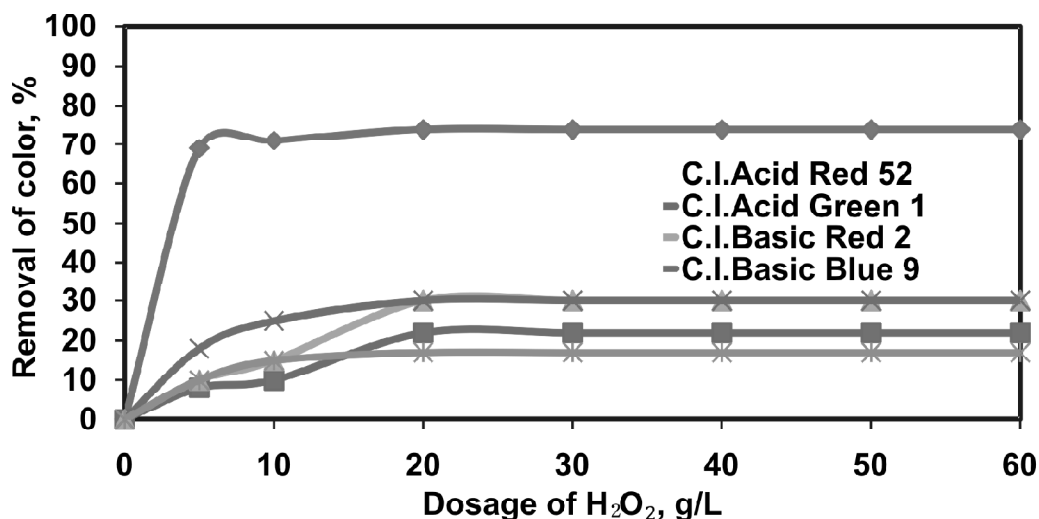


Figure 1: Removal of color from dyes at varying doses of hydrogen peroxide

color removal increased gradually with progressive increase of dose for C.I. Basic Blue 9 and C.I. Reactive Red 11, there was a sudden increase in color removal as H₂O₂ oxidant dose was increased from 10g/L to 20g/L and then remain constant thereafter even up to dose of 60g/L.

Further, experiments were conducted to find the effect of pH of the dye solution by adjusting the pH of the dye solution to 3.0, 4.0, 5.0, 6.0, 8.0, 9.0, 10.5 and 12 and adding oxidant at favorable dose as determined from above and the results of color removal are depicted in Figure 2.

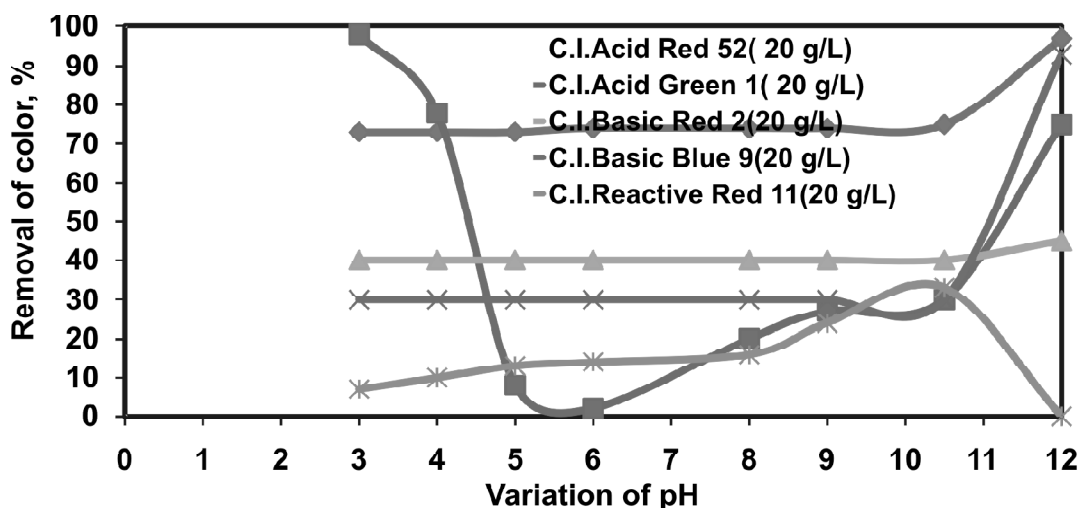


Figure 2: Effect of pH of the solution for color removal from dyes at favorable dose

Color removal data presented in Figure 2 follows two patterns-one which more or less constant color removal at acidic, neutral and moderate alkaline pH conditions and increases significantly as pH is increased from 10.5 to 12.0 (C.I. Acid Red 52, C.I. Basic Red 2 and C.I. Basic Blue 9) while in the case of C.I. Reactive Red 11 color removal was very less 7% at pH 3.0 and increased to 33% at pH 10.5 and decreased drastically to no removal at pH 12.0. In another pattern exhibited by C.I. Acid Green 1, color removal was very high (98%) at pH 3.0, reduced drastically to very less (2%) color removal at pH 6.0 and increased gradually and then abruptly to 75% at high pH value of 12.0.

Experiments were conducted at favorable pH values to find whether at favorable pH conditions the dose of oxidizing agent decreases or percentage of color removal increases or both and the results are shown in Figure 3.

Color removal studies at different dye solution pH values presented above and also suggested favorable pH i.e. pH at which maximum removal occurs. Favorable pH was deduced as pH 3.0 for C.I. Acid Green 1, pH 12.0 for C.I. Acid Red 52, C.I. Basic Red 2 and C.I. Basic Blue 9 and 10.5 for C.I. Reactive Red 11.

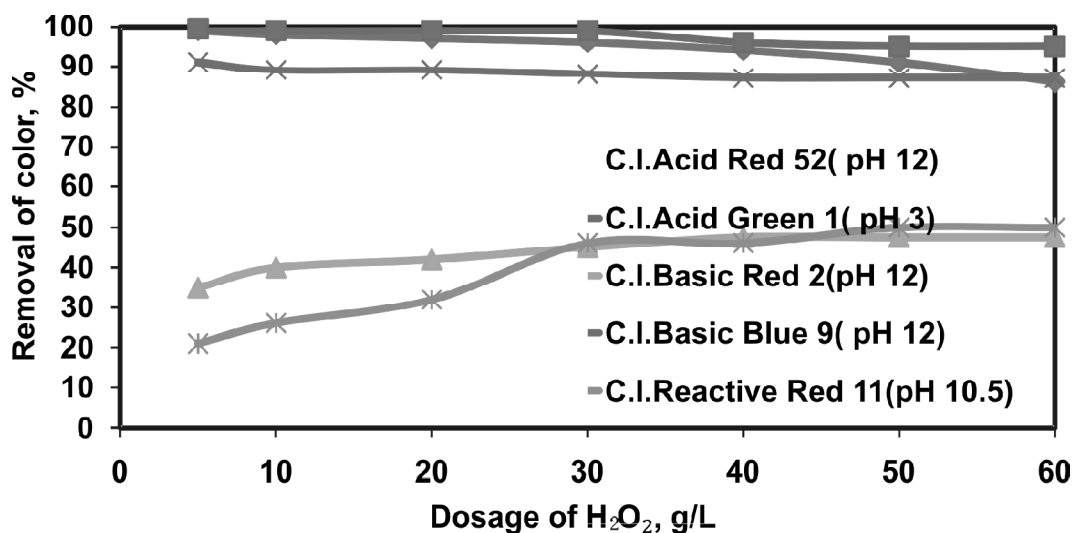


Figure 3: Removal of color from dyes with varying doses of H₂O₂ at favorable pH

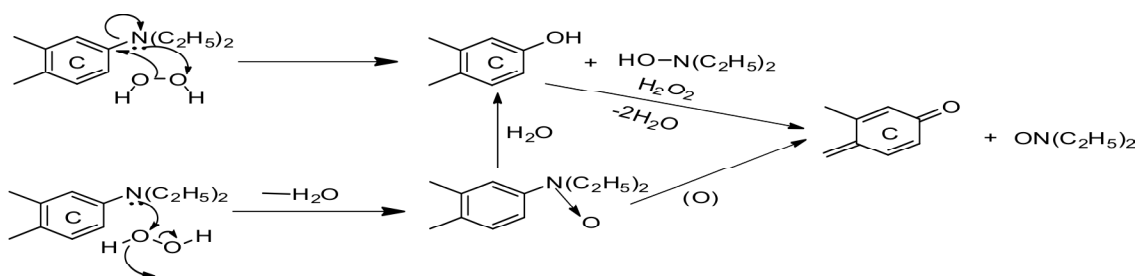
The following observations may be made from the color removal data presented in Figure 1 and Figure 3. For C.I. Acid Red 52, color removal which was 74% at 60 g/L at a system pH 6, at a favorable pH of 12 not only increased to 99%, but also resulted in a drastic reduction in dose to 5 g/L. C.I. Acid Green 1, color removal which was 22% at 60 g/L at a system pH of 6.0, increased drastically to 99.5% at favorable pH condition of 3.0 even at a less dose of 5 g/L. In case of C.I. Basic Blue 9, at favorable pH conditions, color removal was 30% at a pH of 6.0 and at a dosage of 60 g/L, increased remarkably to 91% at a dose of 5 g/L. So also in the case with C.I. Basic Red 2 color removal which was 30% at 60 g/L at a pH of 6 increased slightly to 47.5%, but at a dose of 40 g/L. For C.I. Reactive Red 11 color removal was 17% at 60 g/L at system pH of 6.0 increased significantly to 50% at favorable pH conditions of 10.5 with a dose of 40 g/L. It is thus evident that color removal from the dyes at favorable pH conditions not only decreases the dose of oxidant but also increases color removal significantly.

Not much information is available on the use of H₂O₂ alone as oxidant for color removal from textile dye wastes. Olcay et al. (1996) investigated color removal from textile wastewaters and found that H₂O₂ alone is ineffective at both acidic and alkaline pH conditions. Durr et al. (2012) observed that the effectiveness of color removal by H₂O₂ alone was negligible and reported a maximum color removal of 21% for Blue and Black textile dye effluent.

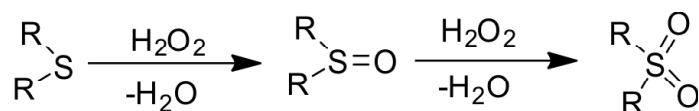
3.2. Oxidation degradation chemistry of dyes

C.I. Acid Red 52

The Acid Red 52 is a polycyclic aromatic compound substituted with extended chromophoric C_{ar}-N, C_{ar}-SO₃ and C_{ar}-O-C_{ar} functional groups. The chemical reactions involved during this oxidative decolorisation process may be represented in the following schemes. Aromatic amines are known to be directly oxidized to hydroquinones and quinones by atmospheric oxidation [Robert Thornton Morrison, 2001]. In the same way, the tertiary amino group present in the dye is transformed to the corresponding hydroxyl compound and quinone either directly or through the corresponding N-oxides as depicted in Scheme 1.

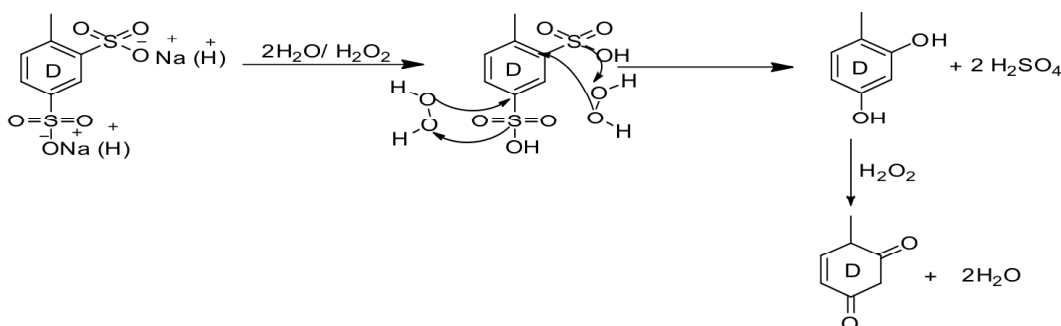
Scheme 1: Hydrogen peroxide oxidation of $C_{ar}-N(C_2H_5)_2$ in C.I. Acid Red 52

Organic sulfides are oxidized by H_2O_2 progressively to sulfoxides and sulfones depending on its concentration as portrayed in Scheme 2.



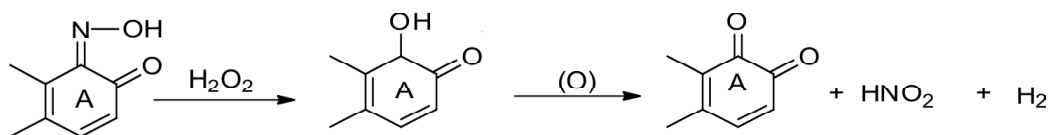
Scheme 2: Oxidation of C-S-C functional group in C.I. Acid Red 52

Likewise oxidation of sulfonic acid $-(C-SO_2-OH^-)$ or its sodium salt $(C-SO_2-O^-Na^+)$ present in the dye molecule may transfigure to sulfuric acid and corresponding hydroxyl and carbonyl compounds as described in Scheme 3.

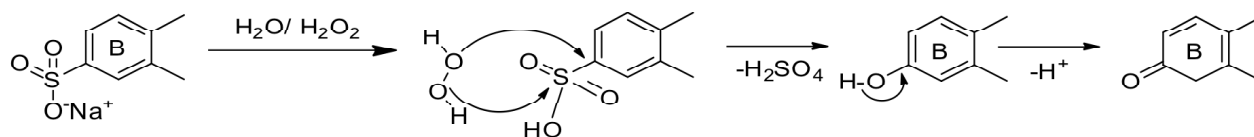
Scheme 3: H_2O_2 oxidation of $C_{ar}-SO_3OH$ group in C.I. Acid Red 52

C.I. Acid Green 1

The dye Acid Green 1 is an iron complex of 3 naphthyl -6-sulfonate to -1- amino oxime units. The presence of transition metal Fe, chromophoric groups SO_3Na , $C=N-O-Fe$ and $C=O$ impart color to this compound. The 1-amino naphthalene itself is vulnerable even for aerial oxidation. The presence of other functional groups (SO_3Na or $C=O$) and $(C=N-O-Fe)$ in this dye make it much more easily degradable by chemical oxidant H_2O_2 . The process of its oxidative destruction during decolorisation in water by these oxidants is presented in the following schemes. Ring A of the dye contain $C=N$ group to undergo oxidative hydrolysis and form corresponding phenolic compound and finally quinones as described in scheme 4.

Scheme 4: Hydrogen peroxide oxidation of $C_{ar}-N$ in C.I. Acid Green 1

The sulfonic acid $-(C-SO_2-OH^-)$ or its sodium salt $(C-SO_2-O^-Na^+)$ present in the dye compounds suffer oxidative hydrolysis to corresponding hydroxyl and carbonyl compounds as shown in scheme 5.



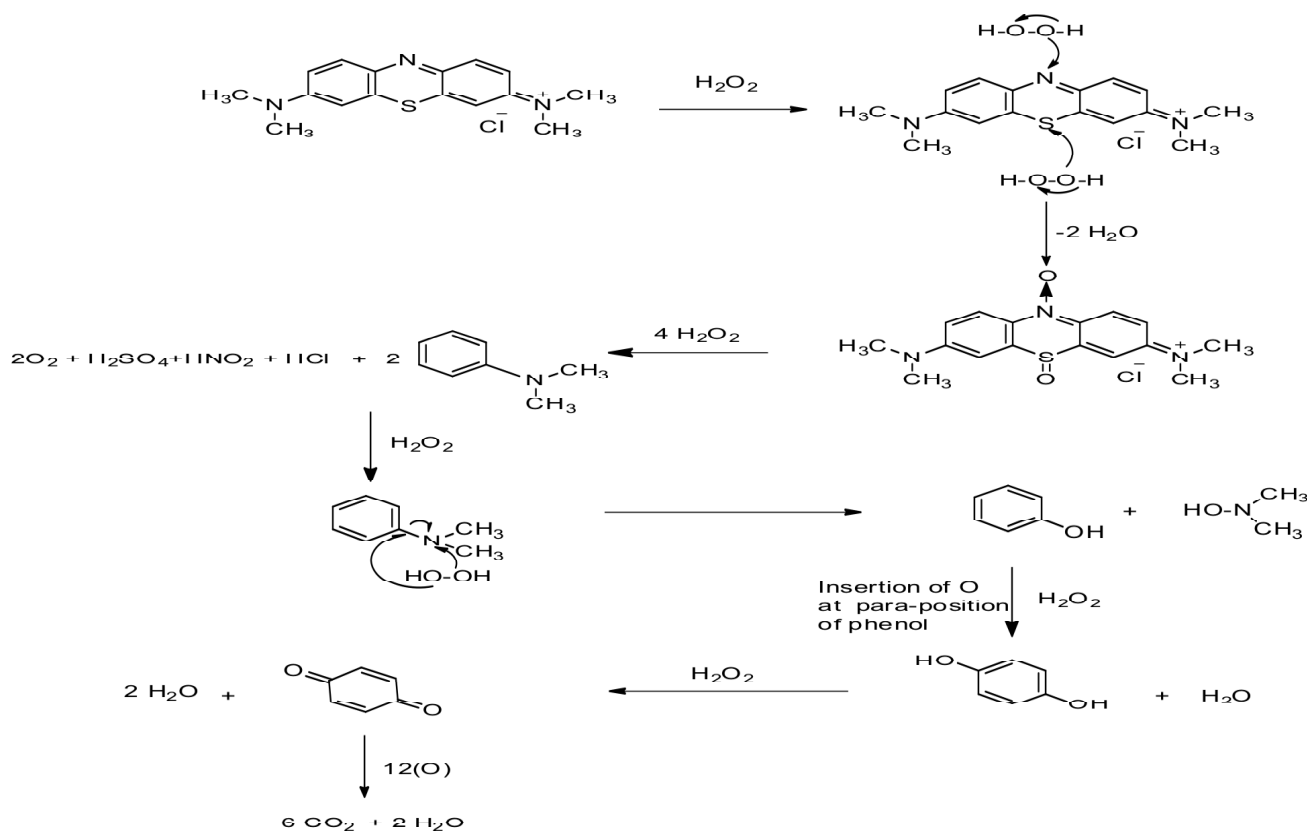
Scheme 5: H_2O_2 oxidation of $C_{ar} - SO_3OH$ group in C.I. Acid Green 1

C.I. Basic Red 2

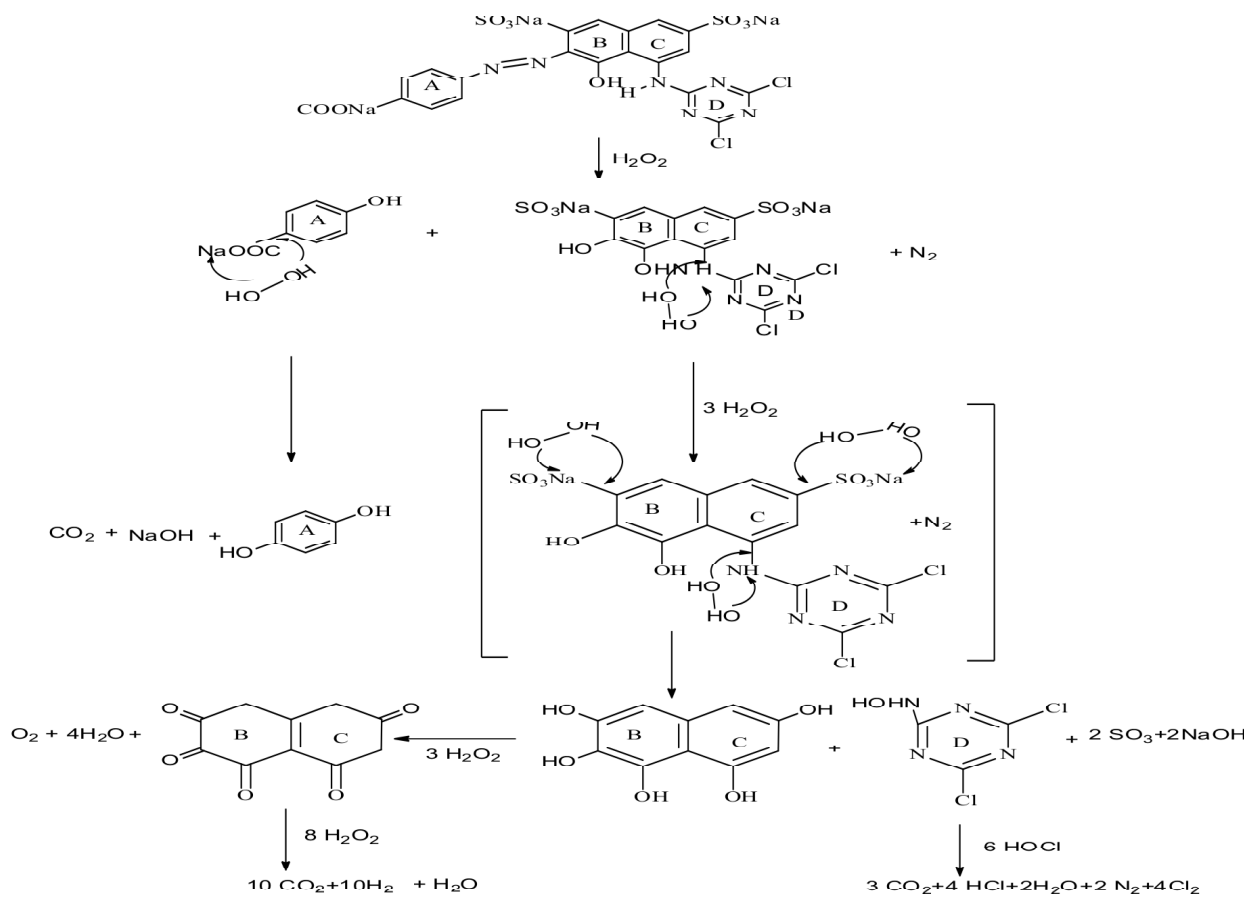
The dye is a three highly functionalized phenyl-azine system. Presence of methyl and amino substituents in the two phenyl rings renders the molecule vulnerable for oxidative degradation in water when subjected to advanced oxidation process (Fatima et al 2007). The central pyrazine ring in the dye is more susceptible for oxidative cleavage because of the low bond energy of $C=N$ (147 Kcal/mol) when compared to that of highly resonance stabilised benzene ring. Similarly the three exocyclic $C-N$ bonds with only 73 Kcal/mol can break up easily under these conditions. As a result of oxidative cleavage, the dye breaks down under advanced oxidation process to two units of 5-methyl-4-hydroxy 1, 2-benzo quinone and a phenol.

C.I. Basic Blue 9

In the case of Methylene Blue, H_2O_2 brings out its oxidative degradation by oxidizing organic nitrogen and sulphur present in it into corresponding oxides with cleavage of thiazine ring present in it. Subsequently it may further get oxidised to *N*-dimethyl benzene phenol, hydroquinone and 1,4-benzoquinone and finally to CO_2 and H_2O as shown in scheme 6 (Omura 1994; Manohar and Shrivastava, 2014).



Scheme 6: oxidative degradation pathway of C.I. Basic Blue 9 by using H_2O_2



Scheme 7: H_2O_2 oxidative degradation pathway of C.I. Reactive Red 11

C.I. Reactive red 11

Reactive Red 11 is a functionalized azo dye compound containing a phenyl, naphthyl and triazine rings. This molecule being an unsaturated system substituted with a carbonyl, sulfonic, chloro and hydroxyl groups is easily oxidisable by oxidizing reagents used in the AOP. H_2O_2 is a potential oxidant as it releases hydroxyl free radicals and nascent oxygen in acidic and alkaline solutions (Lee 2007). It degrades organic residues in water with 47% atom efficacy with formation of water as a byproduct (Ryogi Noyori et al. 2003) and therefore regained importance as green oxidant. The probable degradation path of the dye is outlined as shown in Scheme 7.

4. CONCLUSION

Decolorisation and degradation of C.I. Acid Red 52, C.I. Acid Green 1, C.I. Basic Blue 9, C.I. Basic Red 2 and C.I. Reactive Red 11, textile dyes are investigated by AOP resulted in good color removal. Hydrogen peroxide exhibited maximum color removal of 99%, 47.5% and 91% was obtained for C.I. Acid Red 52, C.I. Basic Red 2 and C.I. Basic Blue 9 respectively at favorable pH 12. In case of C.I. Acid green 1 at favorable pH 3 maximum color removal was 91% and C.I. Reactive Red 11 was 50% maximum removal of color at favorable pH 10.5. Color removal from the dye molecule is subjected to oxidation with H_2O_2 might be oxidative degradation of the chromophoric groups in the dye molecule to colorless hydroxyl, carbonyl, ozonide, carboxylic acids residues and finally to CO_2 and H_2O depending on the nature, concentration and contact time of the oxidant used and also on the pH of the medium. The probable oxidative degradation pathways of dyes are proposed. Therefore Hydrogen peroxide chemical oxidant is being effective treatment for removal of color from textile dyes.

REFERENCES

- [1] E.N. Abrahart, "Dyes and their Intermediates" *Edward Arnold Ltd.*, London, 1977.
- [2] R. Anliker, "Ecotoxicology of dyestuffs-A joint effort by industry" *Ecotoxicology and Environment Safety*, 3, 59-74, 1979.
- [3] R.D. Bach, M.D. Su and H.B. Schlegel, "Oxidation of amines and sulphides with hydrogen peroxide and alkyl hydrogen peroxide- The nature of the oxygen transfer step", *Journal of American chemical Society*, 116, 5379-91, 1994.
- [4] C.M. Carliell, S.J. Barclay and C.A. Buckley, "Treatment of exhausted reactive dye bath effluent using anaerobic digestion: Laboratory and full-scale trials", *Water S.A.*, 22, 225-233, 1996.
- [5] Durr Shahwar E, Abdullah Yasar, and Sumara Yousaf, 2012. Solar assisted photo Fenton for cost effective degradation of textile effluents in comparison to AOPs. *Global Nest J.* 14(4): 477-486.
- [6] H. Fatima Abdulla, M.A. Rauf and S. Salman Ashraf, "Photocatalytic oxidation of safranin-O with H₂O₂", *Dyes and Pigments* 72, 349-352, 2007.
- [7] S. Ghoreishi and R. Haghghi, "Chemical catalytic reaction and biological oxidation for treatment of non biodegradable textile effluent" *Journal of Chemical Engineering*, 95, 163-169, 2003.
- [8] S. Kommineni, J. Zoekler, A. Stocking, S. Liang, A. Flores and M. Kavanaugh, "Advanced oxidation processes", *International water research institute*, 111-208, 2008.
- [9] J.D. Lee, "Concise inorganic chemistry", fifth ed., black well science Ltd, Oxford UK, 2007.
- [10] S.H. Lin and F.C. Peng, "Continuous treatment of textile wastewater by combined coagulation, electro-chemical oxidation and activated sludge" *Water Research*, 30, 587-593, 1996.
- [11] R. Manohar Patil and V.S. Shrivastava, Pelagia research library, *der chemical sinica*, 5(2):8-17, 2014.
- [12] T. Olcay, K. Isik, E. Gülen and O. Derin, "Color removal from textile wastewaters", *Water Science and Technology*, 34:9-11, 1996.
- [13] T. Omura, "Design of chlorine -fast reactive dyes-part 4- degradation of amino containing azo dyes by sodium hydrochloride", *Dyes and Pigments*, 26, 33-38, 1994.
- [14] K.V. Ramakrishna and T. Viraraghavan, "Dye removal using low cost adsorbents", *Water Science and Technology*, 36, 189-196, 1997.
- [15] Robert Thornton Morrison and Robert Neilson Boyd, *Organic Sixth Edition*, Prentice Hall of India, 2007.
- [16] Ryoji Noyori, Masao Aoki and Kazuhiko Sato, "Green oxidation with aqueous hydrogen peroxide", *Chemical Communications*, 1977-1986, 2003.
- [17] Sureyya Meric, Giusy Lofrano and Vincenzo Belgiorno, "Treatment of reactive dyes and textile finishing wastewater using Fentons oxidation for reuse", *International journal of Environmental Pollution*, 23(3), 248-258, 2005.