Removal of Color from C.I. Basic Blue 9 by Hydrogen Peroxide and Fenton Oxidation Processes

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Abstract - Color and COD removal from aqueous solution of C.I. Basic Blue 9 dye was investigated by chemical coagulation employing Al2(SO4)3, AlCl3, FeSO4, FeCl3, and advanced oxidation process with H2O2 and Fenton reagent (FR). Coagulation experiments yielded no color removal whereas studies with AOP resulted in excellent color removal. Experiments were conducted by varying doses of oxidant, pH of the solutions. Oxidation with H2O2 produced a color removal of 95% and COD removal of 65% at favorable pH 12. With FR oxidation total color removal and COD removal of 87% at pH 3 occurred.

Key words: C.I. Basic Blue 9, H2O2, Fenton Reagent, color and COD removal.

I. INTRODUCTION

Textiles colored effluents contain significant amounts of residual dyestuffs, many of which are reported to be toxic and carcinogenic [1]. Discharge of these effluents can cause formation of toxic aromatic amines under anaerobic conditions in the receiving media and contaminate the soil and groundwater, necessitating proper treatment before discharge into the environment.

General methods employed for color removal such as adsorption, coagulation–flocculation, oxidation and electrochemical are quite expensive and have operational problems [2, 3]. Most of the synthetic dyestuffs are resistant to biological degradation due to the presence of aromatics, and hence color removal by bio processing is difficult and incomplete [4]. Primary and secondary treatment methods are ineffective for color removal due to the complex structure and stability of dyes and produce large amount of sludge the disposal of which need further treatment[5,6]. Advanced oxidation processes (AOPs) employing oxidising agents namely NaOCl, H2O2, Fenton reagent (FR) and O3, 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• are powerful oxidants with oxidation potentials of 1.49, 2.07 and 2.85 electron volts respectively[7].

Durr Shahwar et al. [8] and Olkay et al.[9] reported color removal from textile wastewaters by H2O2 alone was less effective only 21% and 45% respectively. Sundararaman et al. [10] reported 90% and 80% of color and

COD removal from Reactive Yellow dye with Fenton oxidation. Saeedeh et al.[11] observed 95.5% decolorisation and 58.5% COD removal of Methyl Violet with Fenton process.

In the present study, decolorisation of a thiazine dye C.I. Basic Blue 9 was investigated by coagulation process employing FeCl3, Al2(SO4)3, AlCl3, FeSO4. Further color removal was also investigated by AOP using oxidizing agents like H2O2 and FR. Color removal efficiency was investigated in terms of percent color removal at different doses, contact time and solution pH. At favorable conditions of color removal, COD removal data was also obtained.

II. MATERIALS AND METHODS

2.1. Chemicals

Chemicals $FeCl_3$, $Al_2(SO_4)_3$, $AlCl_3$, H_2O_2 (30% V/V, Merck), $FeSO_4$ (Merck, GR) are used in the experimental work were of Analytical Reagent grade in the present study. FR of required ratio was prepared by mixing $FeSO_4$ and H_2O_2 solutions in the required proportions. For pH adjustment, 0.1N H_2SO_4 and 0.1N NaOH were used.

2.2. C.I. Basic Blue 9 dye

C.I. Basic Blue 9 (Atul industries, Ahmadabad, Gujarat, India), a textile dye was employed as test dye in the present study.

2.3. Dye stock solution

A test dye solution of $100mgL^{-1}$ was prepared by adding appropriate amount of accurately weighed dye by dissolving directly in distilled water as and when required.

2.4. Color and COD Measurement

Color concentrations of the dye were determined colorimetrically using a VIS Spectrophotometer (Spectrophotometer 106, Systronics India Limited, Hyderabad, India) by measuring %T/OD at optimum wavelength and reading for the dye color concentration from the calibration curve. To evaluate color removal, residual color concentration after the experiment was measured. Similarly, residual COD was measured by standard methods as per APHA.

2.5. Coagulation experiments

Standard jar test procedures using a six place jar test apparatus (Biological Enterprises, Delhi, India) were used for coagulation experiments. To a 300 mL sample of the dye stock solution taken in a beaker, coagulant dose in the range of $1gL^{-1}$ to $16gL^{-1}$ was added and mixed for a typical rapid mixing time of 2 minutes at 120 rpm followed by slow mixing at 30rpm for 20 minutes. The contents were then sedimented for 2 hours and the supernatant aliquot was withdrawn and analyzed for color concentration.

2.6. Advanced Oxidation Process Methods

AOP methods employing oxidants like H_2O_2 and FR for color removal by oxidation processes was investigated.

2.7. Test procedure with H2O2 and Fenton Reagent

To an aliquot of test dye solution of 100mgL-1, varying doses of oxidants like H_2O_2 and FR were added and oxidation reaction was carried out and analyzed for residual color concentration. Experiments were conducted in three stages. In the first stage, H_2O_2 doses from $5gL^{-1}$ to $60gL^{-1}$ were added, residual color concentration was measured and least chemical dose producing maximum color removal was designated as favorable dose. In the case of FR, varying ratios of $Fe:H_2O_2$ like 1:05 to 1:50 , 3:05 to 3:50; 5:05 to 5:50; 10:05 to 10:50 were added, analysed for residual color concentration and favorable dose was found. In the second stage 50-80% of favorable dose was added to the test dye stock solution maintained at a pH of 3, 4, 5, 6, 8, 9,10.5 and 12; reaction carried out and the pH value producing maximum color removal was designated as favorable pH. In third stage, experimentation was conducted at favorable pH; employing varying doses just in the range of favorable dose and optimum dose i.e. the least dose that produced maximum color removal was determined.

III. RESULTS AND DISCUSSION

3.1. Color removal by chemical coagulation

Chemical coagulation employing coagulants like $Al_2(SO_4)_3$, $AlCl_3$, $FeSO_4$ and $FeCl_3$ at dose varying from 1gL-1 to 16 gL-1 has not resulted in any color removal.

3.2. Color removal by Hydrogen Peroxide

It is a dibasic acid and acts as strong oxidant since it could release highly reactive nascent oxygen in acidic and alkaline solutions [12]. Hydrogen peroxide oxidizes aqueous organic residues effectively with atom efficiency of 47% with the formation of H_2O as a byproduct [13] and is increasingly being used as a green oxidant in wastewater treatment. Hydrogen peroxide was added in doses from $5gL^{-1}$ to $60gL^{-1}$ and the results of color removal are presented in Figure 1.

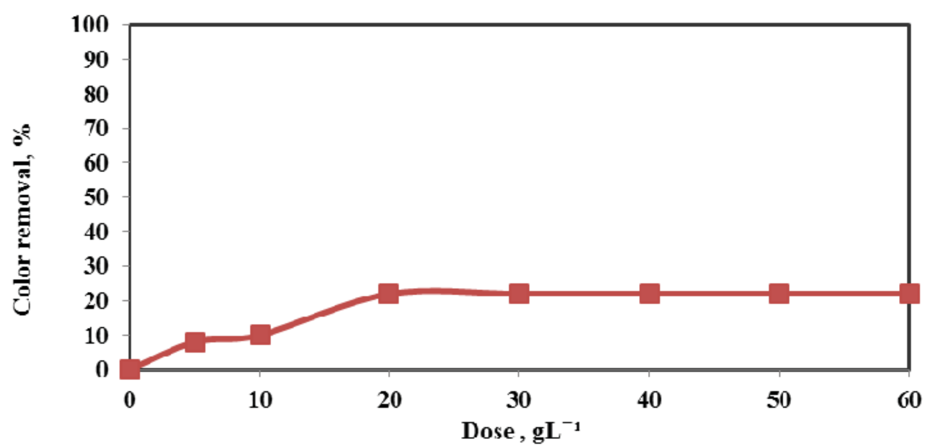

Figure 1: Color removal at varying doses of H_2O_2

The results presented in Figure 1 showed that color removal was very low; 22% at a dose of 30 gL^{-1} and further increase in steps to 60 gL^{-1} has not increased any color removal. A dose of $30gL^{-1}$ was selected as the test dose and experiments were conducted to find the effect of pH of the dye solution in the range of 3.0 to 12.0 on color removal and the results are presented in Figure 2.

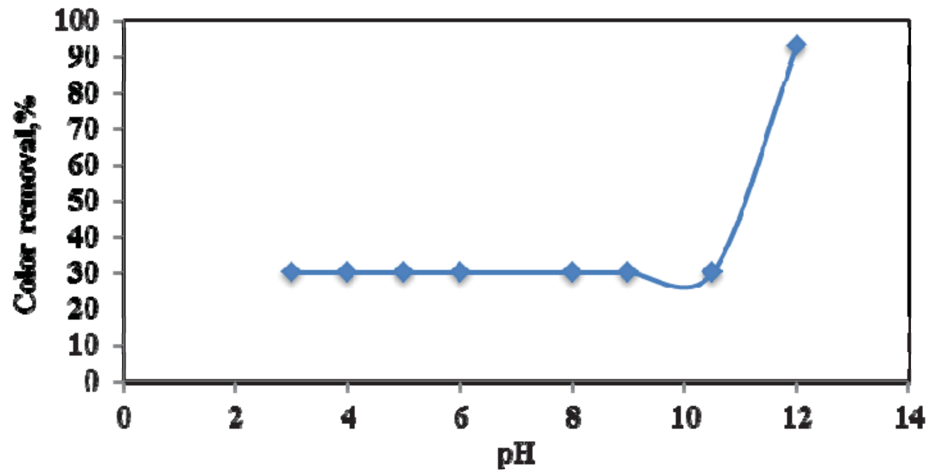

Figure 2: Effect of pH on color removal at favorable dose

It may be observed from the Figure 2 that color removal (30%) remained constant from pH of 3 to 10.5. Color removal increased rapidly to 93% between pH 10.5 and 12. A pH of 12 was selected as favorable pH for color and COD removal by employing varying doses from $5gL^{-1}$ to $60\ gL^{-1}$ and the results are depicted in Figure 3.

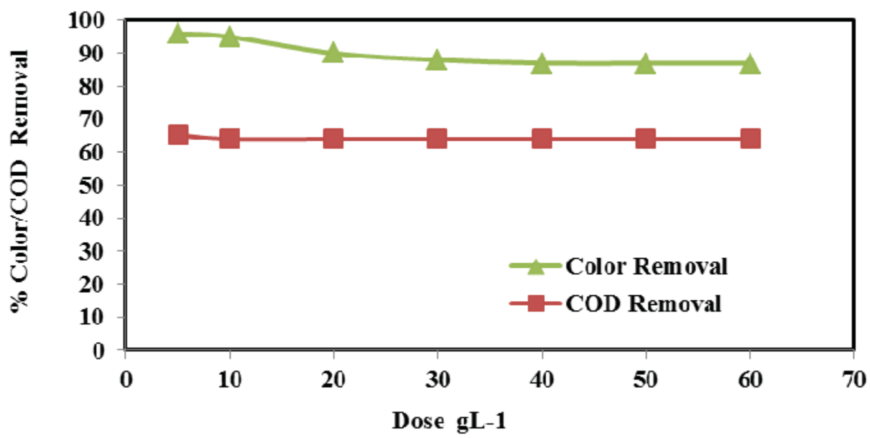

Figure 3: Color and COD removal at varying doses of H_2O_2 at favorable pH

The color removal data from the Figure 3 shows that the favorable pH not only results in a reduction of the dosage of H_2O_2 ($10\ gL^{-1}$) but also color removal was increased to 95%. Maximum COD removal was 65 % at a dose of $10gL^{-1}$. Little information on color removal from textile dye wastes by H_2O_2 is available. Olkay et al.[9] investigated color removal from textile wastewaters and reported that H_2O_2 alone has been found ineffective at both acidic and alkaline pH conditions. Durr Shahwar et al.[8] observed that the efficiency of color removal by H_2O_2 alone was negligible and reported a maximum color and COD removal of 21% and 32% for Blue and 21% and 44% for Black textile dye effluent respectively.

Oxidation of Methylene Blue with H2O2

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 [14].

3.3. Color removal by Fenton Reagent

Treatment with FR is a strong oxidative process where Fe^{2+} catalyses decomposition of H_2O_2 releasing $^{\cdot}OH$ free radicals which subsequently oxidise the dye molecule to the colorless species. Results of dye color removal from aqueous solution of C.I. Basic Blue 9 investigated by applying varying doses of Fenton Reagent of 1:05 to 1:50 , 3:05 to 3:50; 5:05 to 5:50; 10:05 to 10:50 are presented in Figure 4.

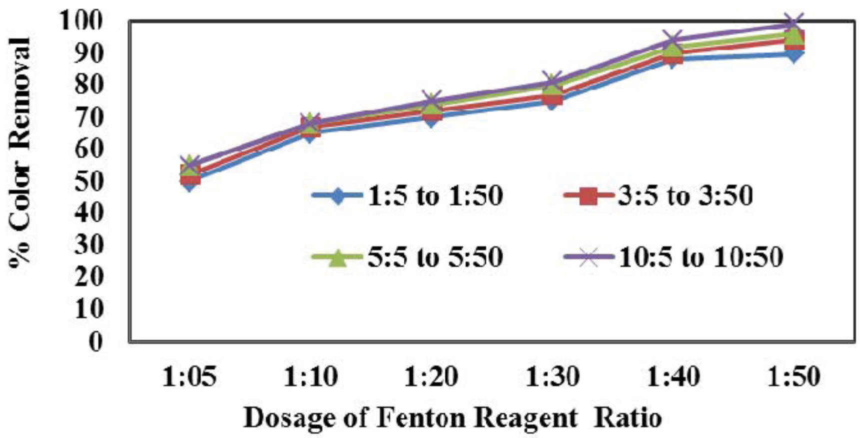

Figure 4: Dye color removal at different ratios of Fe and H_2O_2

It may be observed from Figure 4 that different Fe: H_2O_2 ratios follows similar trend of color removal, so least dose of 1:05 to 1:50 was selected, further investigating the effect of varying H_2O_2 maintaining Fe constant. A Fe: H_2O_2 ratio of 1:5 to 1:50 was used and color removal results are presented in Figure 5.

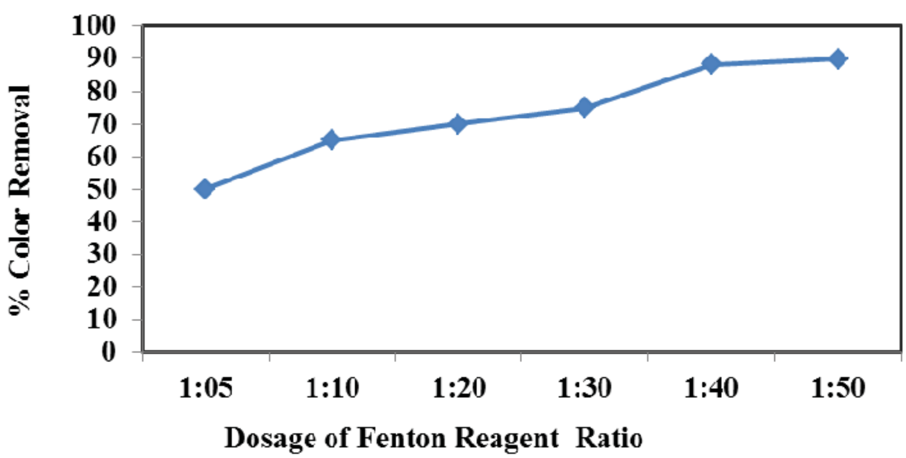

Figure 5: Color removal at varying doses of Fenton reagent

The data presented in Figure 5 illustrate that as the proportion of H_2O_2 was increased from 5 to 50, color removal increased gradually to 75% at 1:30 and increased slowly to 90% at a ratio of 1:50. A 1:40 ratio of Fe: H_2O_2 was selected as favorable dose and experiments were conducted to find the effect of dye solution pH on color removal at different pH values of 3, 4, 5, 6, 8, 9, 10.5 and 12 and the results are depicted in Figure 6.

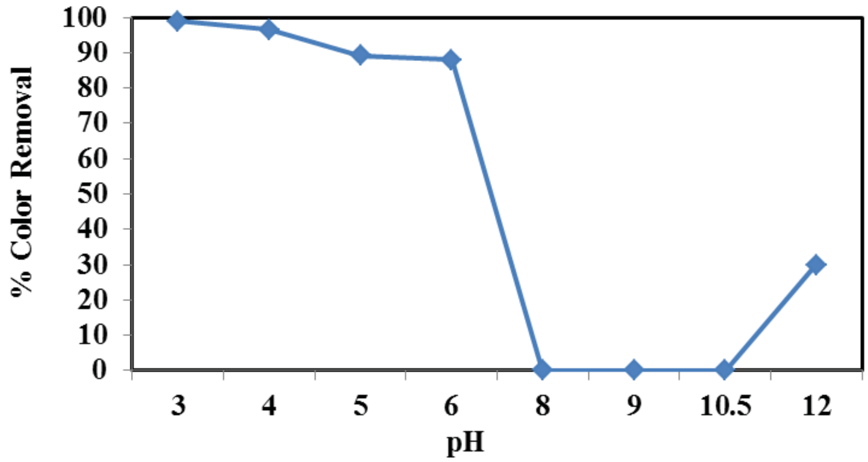

Figure 6: Effect of pH on color removal at favorable Fe: H_2O_2 ratio

It may be observed from Figure 6 that maximum dye color removal of 99% was observed at pH 3. As the pH value was increased through 4 to 6, there was a decrease in color removal to 88% at pH 6 there is a sudden dramatic decrease to 0% as the pH was increased to 10.5. But increase in color removal was 30% at pH 12. It thus follows that color removal by FR was high in acidic medium and remarkably low in basic medium; therefore a pH value of 3.0 was chosen as favorable pH. Experiments were conducted at this favorable pH employing different ratios of Fe: H_2O_2 and color and COD removal data are portrayed in Figure 7.

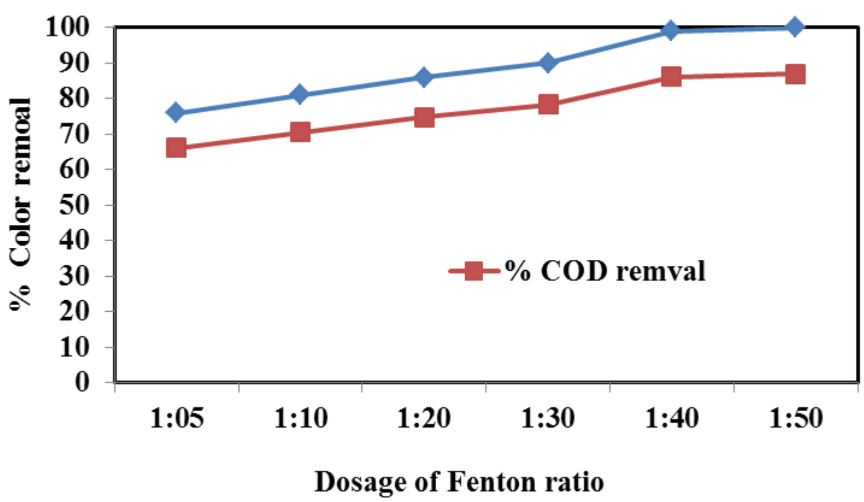

Figure 7: Color and COD removal at different ratios of Fe: H_2O_2

At a favorable pH of 3, color removal increased from 76% to 90% as the proportion of H_2O_2 was increased from 5 to 30 and reached 100% at 50. Similarly COD removal was low (66%) at 2:5 and gradually increased to 87% at 1:50.

Investigations by Perkowski and Kos[15] on treatment of textile dye wastewater by H_2O_2 and Fe ions showed that after coagulation with $FeSO_4$ the color reduction was 75% and with the addition of excess H_2O_2 the wastewater was completely decolorised and COD reduction increased from 65 to 88%. Swaminathan et al. [16] investigated decolorisation and degradation of H acid, Red M5B and Blue MR dyes using ferrous hydrogen peroxide system and reported that after coagulation with $FeCl_3$ and with addition of H_2O_2, color removal increased from 50-100%. At optimum conditions, COD removal of H acid, Red M5B and Blue MR are 100%, 78% and 82% respectively. Color removal efficiency of Acid Red 18 rapidly increased to 95.4% within first 60 minutes and slight increase in color removal was observed up to 240 minutes [17]. Investigations on decolorisation of Reactive Black 5 by using FR oxidation was effective and more than 95% color removal and 58.9% COD removal was obtained at pH 3 [18].

Oxidative degradation of Basic Blue 9 by Fenton Reagent

C.I. Basic Blue when subjected to AOP by FR, initially gets oxidised to aryl, aryloxy and aryl peroxy free radicals which may couple with or disproportionate to give stable molecules or they may react with Fe ions . These organic intermediates formed in the initial stages react further with $HO^{\cdot}$ and $O_2^{\cdot}$- leading to mineralisation to CO_2, H_2O and inorganic acids.

IV. CONCLUSION

Decolorisation and degradation of C.I. Basic Blue 9 was investigated by chemical coagulation and advanced oxidation process (AOP). Coagulation experiments yielded no color removal whereas studies with AOP resulted in good color removal. Treatment with H_2O_2 exhibited a good color removal of 95% and COD removal of 65% at a pH of 12 with a dose of $10gL^{-1}$. With Fenton Reagent, 100% color removal and a COD removal of 87% at a pH of 3 with Fe: H_2O_2 ratio of 1:50 was observed. Among the oxidants investigated, Fenton Reagent was found best both in terms color and COD removal.

REFERENCES

[1] Anliker R. "Ecotoxicology of dyestuffs-A joint effort by industry". *Ecotoxicology Environment and safety*, 1979, 3, 59–74.

[2] Lin S.H. and Peng F.C. "Continuous treatment of textile wastewater by combined coagulation, electro-chemical oxidation and activated sludge". *Water Resesrch,* 1996, 30, 587–593.

[3] Ramakrishna K.V. and Viraraghavan T. "Dye removal using low cost adsorbents". Water Science and Technology, 1997,36 (2–3), 189–196.

[4] Carliell C.M., Barclay S.J. and Buckley C.A. "Treatment of exhausted reactive dye bath effluent using anaerobic digestion:Laboratory and full-scale trials". *Water S.A.* 1996, 22, 225–233.

[5] Karthikeyan J. "A study on colour removal from textiles dye wastes by chemical treatment". Ph.D. Dissertation, IIT Kanpur, India, 1990.

[6] Ghoreishi S. and Haghighi R. "Chemical catalytic reaction and biological oxidation for treatment of non biodegradable textile effluent". *Journal of Chemical Engineering*, 2003, 95, 163-169.

[7] Kommineni S. Zoeckler J., Stocking A, Liang S, Flores A. and Kavanaugh M. "Advanced oxidation Processes". *International water research institute*, 2008, 111-208.

[8] Durr Shahwar E., Abdullah Yasar and Sumara Yousaf. "Solar assisted photo fenton for cost effective degradation of textile effluents

in comparison to AOPs". *Global Nest Journal,* 2012, 14(4), 477-486.

[9] Olcay T, Isik K, Gülen E and Derin O. "Color removal from textile wastewaters". Water Science and Technology, 1996, 34, 9-11.

[10] Sundararaman T. R., Ramamurthi V and Partha N. "Decolorisation and COD removal of Reactive Yellow 16 by fenton oxidation and comparision of dye removal with photo fenton and sono fenton process". *Modern Applied Science Journal,* 2009, 3(8), 15-22.

[11] Saeedeh Hashemian, Msoumah tabatabaee and margan gafari, "Fenton oxidation of meth]yl violet in Aqueous solution". Journal of chemistry, 2013,1-6.

[12] Lee J.D. "Concise inorganic chemistry", 5th ed.; black well science Ltd, Oxford UK, 2007.

[13] Ryoji Noyori, Masao Aoki, Kazuhiko Sato. "Green oxidation with aqueous hydrogen peroxide". *Chemical Communications,* 2003, 1977-1986.

[14] Omura T. "Design of chlorine –fast reactive dyes-part 4; degradation of amino containing azo dyes by sodium hydrochloride". Dyes and Pigments, 1994, 26, 33-38.

[15] Perkowski J and Kos L. "Treatment of textile dyeing wastewater by hydrogen peroxide and ferrous ions". Fibres Text East Eur. 2002, 78-81.

[16] Swaminathan K, Sadhya S, Carmalin Sophia A, Pachhade K and Subramanyam Y. V. "Decolorisation and degradation of H acid and other dyes using ferrous hydrogen peroxide system". Chemosphere, 2003, 50, 619-625.

[17] Barbusinski K. "The modified fenton process for decolorisation of dye waste water". Polish Journal of Environmental Studies, 2005, 14(3),281-285.

[18] Pegah bahmani, Afshin Maleki, Esmail Ghahramani and Ahmad Rashidi,. "Decolorisation of the dye Reactive Black 5 using fenton oxidation". African Journal of Biotechnology, 2013, 12 (26), 4115-4122.