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The Fenton Chemistry and Its Combination with Coagulation for Treatment of Dye Solutions

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Abstract: Aqueous solutions of Acid Blue 74, Acid Orange 10, and Acid Violet 19 were subjected to Fenton/Fenton-like oxidation and its combination with lime coagulation. The analysis indicated no dependence of chemical oxidation efficacy on dye concentration in the range of $0.1-1\ g\,L^{-1}$. Complete or nearly complete (higher than 95%) color removal of all treated samples was observed. Dye:H_2O_2 weight ratio of 1:2 proved optimal for treatment of all dye solutions by means of Fenton/Fenton-like oxidation. Moderate doses of hydrogen peroxide led to the improvement of biodegradability of dye solutions. No formation of any toxic intermediates during the oxidation of Acid Orange 10 and Acid Violet 19 was detected. Only a slight toxicity increase was observed after Acid Blue 74 degradation by Fenton chemistry. H_2O_2/Fe^{3+} system with pH adjusted to 3 proved the most effective oxidation process. The combination of Fenton chemistry and subsequent lime coagulation was the most feasible treatment method of removing COD and UV_{254} and UV_{max} absorbance of dye solutions. Combined oxidation and coagulation was more effective for Acid Blue 74 and Acid Orange 10 elimination than for Acid Violet 19.

Keywords: Acid dyes, chemical oxidation, Fenton modifications, lime coagulation

INTRODUCTION

One million tons and more than ten thousand kinds of synthetic dyes and pigments are produced annually worldwide and used extensively in many

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fields of current technology, e.g., in various branches of the textile and leather tanning industry, in paper production, in food technology, in agricultural research, in light-harvesting arrays, in photo-electrochemical cells, and in hair coloring (1, 2).

It has been estimated that about 15% of the dyes produced in the world are released into the environment during their synthesis and processing, causing serious environmental pollution (3). Wastewater originating from textile industry commonly contains a high concentration of organic substances, different types of dyes, surface active materials, oil and grease, sulphide compounds, solvents, heavy metals, inorganic salts and fibers, in amounts depending on the processing system and are characterized by very high COD and TOC values as well as strong color (1). Thus, the discharge of textile wastewater in natural environments is adverse not only for aesthetic reasons but also because many dyes and their intermediate products are biorecalcitrant, toxic to aquatic life, and mutagenic to humans (4, 5).

The treatment techniques commonly applied in textile wastewater, such as coagulation, flocculation, membrane separation or elimination by activated carbon adsorption, only transfer the pollutant from one phase to another, and biological treatment is not a complete solution to the problem due to the biological resistance of some dyes (6).

A wide range of methods has been developed for the removal of dyes from water and wastewater to decrease their impact on the environment. The technologies include adsorption on organic or inorganic matrices, decolorization by photocatalysis and/or by oxidation processes, and microbiological decomposition. However, there is still no universally feasible technology available for treatment of dye wastes, probably because of the complex and very varied chemical structures of these compounds.

Ozonation was found to be an effective way to remove color and reduce toxicity of different dye solutions and textile wastewater, although alone it could not remove all COD from wastewater samples (7–9). The application of heterogeneous catalytic ozonation to textile wastewater proved effective not only in decolorization, but also in TOC removal (5, 10). Also, different combinations of treatment methods, e.g., vacuum UV photolysis and subsequent biodegradation (11), UV-TiO_2 process and ozonation (12), pre-ozonation and subsequent coagulation (13), pre-ozonation coupled with UV/H_2O_2 process (14), chemical oxidation by O_3/H_2O_2 and UV-irradiation (15), and a combination of ozonation and biological treatment (16), resulted in a nearly complete decolorization and detoxification of textile wastewater, both artificial and industrial.

The Fenton chemistry has also been demonstrated as an effective decolorization tool. The classic Fenton reagent was mostly applied, and resulted in fast color (17), moderate COD (7), but slow TOC (18) removal and detoxification (4) of textile wastewater and synthesized dye solutions. Various modifications of the Fenton oxidation were also investigated in order to treat dye contamination: H_2O_2/coal fly ash system (19), H_2O_2 and heterogeneous catalysts with transition metals (3), chelator-mediated Fenton treatment (20), and Cu(II)/organic acids/hydrogen peroxide system (21). During the photo-Fenton oxidation of the dye solution, efficient color removal but no biodegradation improvement was observed (1, 6, 22). The advantages of the combination of the Fenton reagent and biological treatment in color and COD removal were shown for wastewater from textile industry (23).

Therefore, the Fenton oxidation seems a feasible process to completely decolorize and partially mineralize the textile industry dye containing wastewater. Moreover, it is easy in operation and cheap compared to other oxidation processes. However, because of the non-specific reactivity of hydroxyl radicals and the tendency of some substances to scavenge them, the treatment process is strongly dependent on several parameters and needs to be tested before it is applied to degrade different types of dyes.

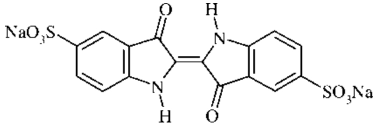
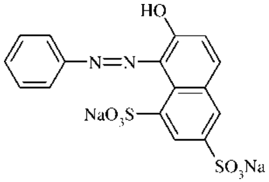
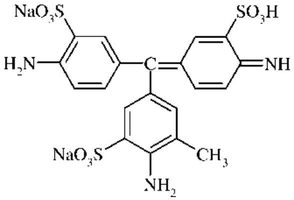
In the present work, aqueous solutions of acidic dyes—Acid Blue 74, Acid Orange 10, and Acid Violet 19—were treated by means of Fenton chemistry and its combination with subsequent coagulation. The Fe^{2+}/H_2O_2 system has a dual function of hydroxyl radicals' pre-oxidation as well as ferrous/ferric coagulation. Thus, coagulation with polymer hydroxocomplexes of Fe^{3+}, which are formed during the Fenton reaction and mostly with the increase of pH, was applied. A coupled ferric/lime post-coagulation was also studied. The influence of catalyst, pH, hydrogen peroxide, and dye concentrations on the efficacy of the treatment processes was analyzed. The effectiveness of the dye solution treatment was ascertained by COD, UV absorbance, and color removal. Dye solutions' toxicity and biodegradability were estimated using the *Daphnia Magna* acute toxicity test and BOD measurement, respectively.

METHODS

Materials and Chemicals

Acid Blue 74, Acid Orange 10, and Acid Violet 19, obtained from Sigma-Aldrich Co., were of analytical grade and were used without further purification. Molecular structures and the main properties of synthetic dyes studied in a non-hydrolyzed form are presented in Table 1. The dye solutions were prepared by dissolving a respective acid dye in twice-distilled water. The initial concentrations of dye solutions used are 0.2, 0.5 and $1\,g\,L^{-1}$. H_2O_2 (PERDROGEN®, 30% w/w), $FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3 \cdot xH_2O$, and Na_2SO_3 were of reagent grade obtained from Sigma-Aldrich Co. pH of reaction solutions was adjusted using H_2SO_4 and NaOH aqueous solutions or pure reagents.

Table 1. Chemical structures and general properties of synthetic dyes studied

I.C. name, I.C. number	Class	Chemical structure	λ_{max}, nm	Molecular weight, g mol^{-1}
Acid Blue 74 73015	Indigoid		287 and 610	466.4
Acid Orange 10 16230	Azo		330 and 478	452.4
Acid Violet 19 42685	Triarylmethane		290 and 545	585.6

Experimental Procedure

Batch experiments, for the Fenton and Fenton-like oxidation, were performed in a cylindrical glass reactor. 0.2 L samples of dye solutions were treated without any agitation for a period of 24 hours. The catalyst ($FeSO_4 \cdot 7H_2O$ or Fe^{3+} solution prepared by dissolving $Fe_2(SO_4)_3 \cdot xH_2O$ in twice-distilled water) was added first and the reaction was subsequently initiated by adding H_2O_2 all at once. The weight ratio of H_2O_2:Fe^{2+} was kept invariable at 6:1, which is the optimal ratio between hydrogen peroxide and ferrous ions (24). The same weight ratio was used for Fenton-like experiments with Fe^{3+} catalyst. For the Fenton oxidation experiments, the pH of the dye solution sample was adjusted to 3. Fenton-like experiments with Fe^{2+} ions were carried out without pH regulation and with Fe^{3+} both with and without pH regulation. After the end of the reaction time, the pH of samples was adjusted to 11 by adding 40% aqueous solution of NaOH and/or 8% aqueous solution of lime (prepared by dissolving CaO in twice-distilled water). The lime, consumption of which ranged between 200–400 mg L^{-1}, was utilized in order to maintain basic pH and to carry out post-coagulation. The samples were kept for a period of 1–2 hours to allow the settling of solids. Precipitated iron ions and slaked lime were separated from treated dye solutions by a paper (blue ribbon, pores' size 2 μm) filter. Na_2SO_3 aqueous solution (20%) was used to quench the oxidation by residual hydrogen peroxide, if any occurred, before the spectrophotometric analysis.

The experiments of dye oxidation with non-catalyzed hydrogen peroxide were conducted in the same reactor and treatment conditions as the corresponding Fenton treatment trials.

In coagulation experiments, $Fe_2(SO_4)_3 \cdot xH_2O$ and CaO used as a coagulant were added to the dye aqueous solution samples with a volume of 0.6 L. The pH of dye solution samples for Fe^{3+} coagulation was kept at 9; no pH adjustment was done during CaO coagulation. The jar test was conducted with a 30-second rapid mixing at 400 rpm, followed by 20 minutes slow mixing at 40 rpm. Then, the mixed samples were allowed to rest without any agitation for 60 minutes. Afterwards, the samples were filtrated through a paper (blue ribbon, pores' size 2 μm) filter.

All experiments were duplicated and the data on the untreated (initial) dye solutions samples was verified by the analysis of at least four replicates. The experiments were carried out at 20 ± 1°C.

Analytical Methods

The chemical oxygen demand (COD) was determined by the closed reflux titrimetric method (25). Additionally, the 7-day biochemical oxygen demand (BOD) for the treated and untreated dye solutions samples was determined (25).

The samples of dye solutions were analyzed in a UV–VIS scanning spectrum 200–700 nm, using Heλion-β UV/VIS (Cambridge, United Kingdom). The absorbance of the dye solution samples at 254 nm representing the aromatic carbon content and at maximum wavelength representing the general organic content in the UV spectrum (Table 1) was measured.

The color of the dye solutions in the initial and treated samples was obtained by measuring the absorbance at maximum wavelength in visible spectrum 610, 478, and 545 nm for Acid Blue 74, Acid Orange 10, and Acid Violet 19, respectively, and by computing the concentration from the calibration curve.

Acute toxicity of the initial and treated dye aqueous solution samples to *Daphnia magna* (*Cladosera, Crustecea*) was studied and a 24-hours toxicity test was carried out (26). The medium effective concentration values (EC_{50}) and their 95% confidence limits were determined for the samples.

The iron concentration in the solution was quantified by means of the phenanthroline method (25). The initial and residual hydrogen peroxide concentrations were determined by the spectrophotometric method (Heλion-β UV/VIS) (27).

RESULTS AND DISCUSSION

The Fenton Treatment

The Fenton treatment was applied to Acid Blue 74 (indigoid dye), Acid Orange 10 (azo dye), and Acid Violet 19 (triarylmethane dye) aqueous solutions. Complete decolorization of Dye solutions took place during the oxidation process. Only for dye:H_2O_2 weight ratio of 1:0.5 color removal was incomplete at 96, 95, and 99% for Acid Blue 74, Acid Orange 10, and Acid Violet 19, respectively. The color removal was easier than COD elimination, indicating that the chromophoric groups were destroyed during the degradation of dyes, and were partly mineralized to CO_2 and H_2O. Accordingly, in order to demonstrate the highest available COD removal of studied dye solutions, the duration of oxidation trials was 24 hours.

The results of the dye 0.5 g L^{-1} solution degradation by means of the Fenton treatment are presented in Figs. 1 and 2. All dyes investigated showed similar COD removal dependence on the hydrogen peroxide dosage. Dye:H_2O_2 weight ratio of 1:2 proved optimal and resulted in 37, 27, and 40 percent of COD residual for Acid Blue 74, Acid Orange 10, and Acid Violet 19, respectively. The same effect of the hydrogen peroxide dose in the Fenton oxidation was observed for the aromatic carbon (UV_{254}) and general organic content (UV_{max}) removal in dye solutions (Fig. 2). Thus, the residual absorbance at UV_{254} and UV_{max} was 6–19 and 4–9%, respectively, at Dye:H_2O_2 weight ratio of 1:2. Similar optimal conditions were established by Dutta et al. (28). for thiazine dye oxidation by Fenton reagent.

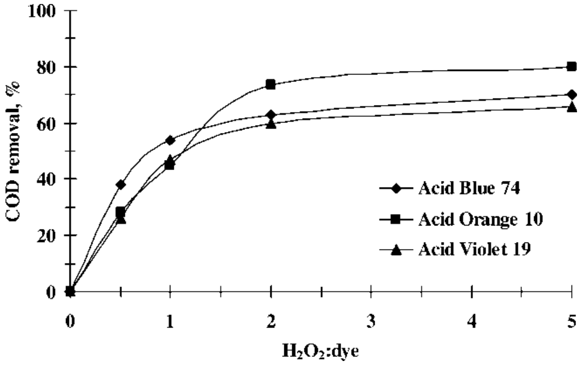


Figure 1. COD removal versus H_2O_2:dye weight ratio for the Fenton treatment of 0.5 g L^{-1} dye solutions.

Further increase of the hydrogen peroxide amount did not markedly increase the dye degradation. The hydrogen peroxide is known as a scavenger of the hydroxyl radicals (29). At a higher hydrogen peroxide concentration, there is a competition between the substrate and H_2O_2 to react with hydroxyl radicals. Therefore, H_2O_2 in high concentrations acts as a scavenger of the hydroxyl radicals and produces hyperoxyl radicals, which have a much lower oxidation capacity than hydroxyl radicals.

The Fenton treatment was found to be the most effective in azo dye degradation. The removal of indigoid and triarylmethane dyes was slightly lower both by COD and UV absorbance values.

This study also examined different concentrations of dye solutions. Thus, 0.2, 0.5, and 1 g L^{-1} dye solutions samples were treated by means of the

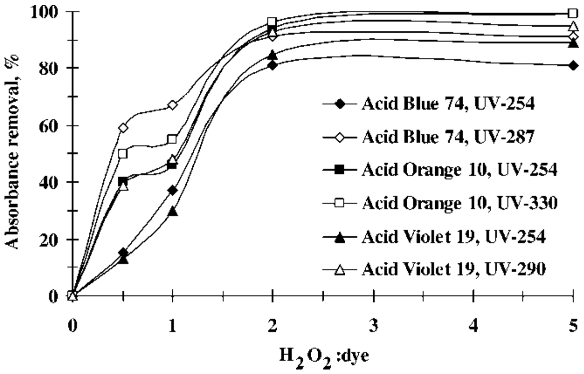


Figure 2. UV_{254} and UV_{max} absorbance removal versus H_2O_2:dye weight ratio for the Fenton treatment of 0.5 g L^{-1} dye solutions.

Fenton treatment. The results indicated the same removal of UV absorbance and COD in all cases. Hence, the optimal efficacy of the Fenton treatment in the range of the dye the content from 0.1–1 g L^{-1} could be maintained in a stable manner by means of the same process conditions.

The Fenton treatment was applied as a system with a dual function of hydroxyl radicals' pre-oxidation as well as ferric coagulation. The coagulation with polymer hydroxocomplexes of Fe^{3+}, which are formed with the increase of pH, was applied after the oxidation step. Moreover, it is known that hydrogen peroxide is unstable and easily decomposes at pH values higher than 10 (30). Hence, after the adjustment of pH to 11 the amount of any residual H_2O_2 in treated solutions was reasonably reduced.

In order to verify the Fenton oxidation efficacy, blank experiments in coagulation with Fe^{3+} and oxidation by hydrogen peroxide alone were conducted. Coagulation with $Fe_2(SO_4)_3 \cdot xH_2O$ resulted in no color removal of Acid Orange 10 samples and very moderate decolorization of Acid Blue 74 and Acid Violet 19 solutions even at high Fe^{3+} dosages (Fe^{3+}:dye weight ratio more than 0.6). In trials with hydrogen peroxide, complete color and moderate UV absorbance removal in Acid Blue 74 and Acid Violet 19 aqueous solutions was observed. In the case of Acid Orange 10, hydrogen peroxide oxidation was absolutely ineffective. A similar result of azo dye resistance to hydrogen peroxide was observed by Solozhenko et al. (31).

The BOD experiments indicated that the application of H_2O_2/Fe^{2+} oxidation improved the biodegradability of all studied dye solutions (Fig. 3). Thus, the Fenton pre-oxidation of Acid Blue 74 and Acid Violet 19 even at dye:H_2O_2 weight ratio of 1:0.5 resulted in a twofold increase of the BOD/COD ratio in comparison with the initial samples. In the case of Acid Orange 10, low hydrogen peroxide doses were ineffective in enhancing subsequent biodegradation. However, a further increase of the oxidant dosage in the pre-treatment step to dye:H_2O_2 weight ratio of 1:1 raised the value of BOD/COD ratio from 0.18 to 0.46. A possible explanation to this is the breakdown of the azo bonds during azo dye decolorization, which leads to the formation of aromatic amines that are only partially degraded by low doses of hydrogen peroxide. The formed intermediates are not biodegradable and are more toxic than the dye molecules themselves (4).

Also, an acute toxicity of the initial and treated dye aqueous solutions to *Daphnia magna* was studied by 24-hours test. The original dye solutions and pre-treated with moderate hydrogen peroxide doses Acid Orange 10 and Acid Violet 19 samples proved to be non-toxic. In the case of Acid Blue 74, a moderate dosage of hydrogen peroxide led to the formation of toxic compounds, which retarded the BOD/COD ratio increase (Fig. 3) and resulted in a slight toxicity of the pre-treated dye solution. Thus, the Fenton treatment could be effectively applied as a biodegradability improvement tool for azo and triarylmethane dye solutions. In the case of indigoid dyes, the hydrogen peroxide dosage should be carefully controlled due to the probable residual toxicity of Fenton-treated samples.

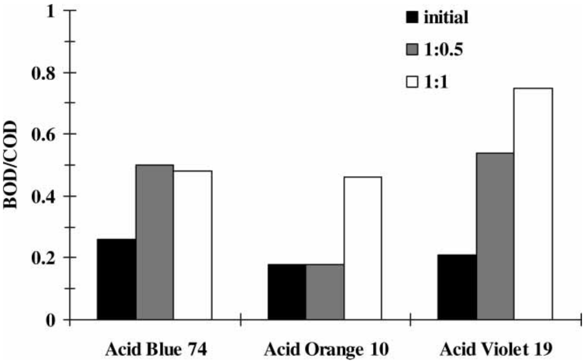


Figure 3. BOD/COD ratio for initial and Fenton pre-treated (dye:H_2O_2 weight ratio of 1:0.5 and 1:1) 0.5 g L^{-1} dye solutions.

Fenton-like Treatment

In the experiments of Acid Blue 74, Acid Orange 10, and Acid Violet 19 degradation by means of modified Fenton treatment, three different systems were used. Hydrogen peroxide was catalyzed by Fe^{2+} ions without dye solutions' pH regulation and by Fe^{3+} ions with and without pH regulation. In the application of all studied Fenton-like systems complete or nearly complete color removal was observed.

Hydrogen peroxide oxidation with Fe^{2+} addition without pH adjustment resulted in the same COD and UV absorbance removal as the Fenton treatment trials. The reason for this is a rapid drop of solutions' pH from the initial level (3.6, 5.7, and 4.4 for Acid Blue 74, Acid Orange 10, and Acid Violet 19, respectively) to 3 within seconds and subsequent decrease to 2.7–2.9 during the next 1–2 minutes, as in the case of the classic Fenton reaction. Consequently, the difference of the pH process between H_2O_2/Fe^{2+} systems with and without the pH adjustment was negligible. The fast drop in pH at the beginning of oxidation is probably due to the formation of some acidic intermediates. A similar rapid decrease of solution pH during the Fenton-like oxidation of basic thiazine dye was observed by Dutta et al. (28).

In the case of hydrogen peroxide catalyzed by Fe^{3+} ions without pH adjustment, no rapid pH decrease was observed. However, after 24 hours of oxidation, pH values of dye solutions decreased to 2.8, 2.9, and 3.4 for Acid Blue 74, Acid Orange 10 and Acid Violet 19, respectively. Thus, the mechanism of H_2O_2/Fe^{3+} oxidation principally differs from the classic Fenton reaction pathway, but intermediates in both cases are acidic compounds.

The results of Fenton-like oxidation of Acid Blue 74, Acid Orange10, and Acid Violet 19 are shown in Fig. 4. As mentioned before, the use of H_2O_2/Fe^{2+} without a pH regulation system yield removal efficacy similar to the

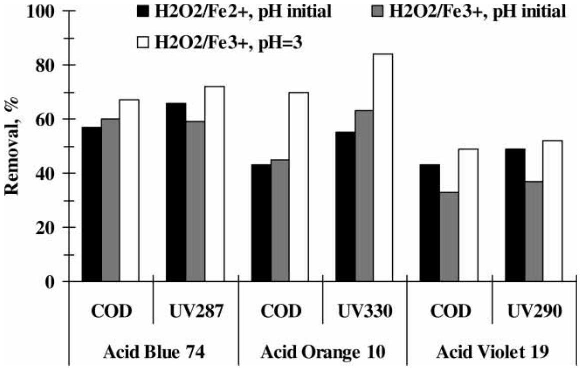


Figure 4. COD and UV absorbance removal at dye:H_2O_2 weight ratio of 1:1 by means of Fenton-like treatment from 0.5 g L^{-1} dye solutions.

classic Fenton oxidation. Therefore, it was ascertained that moderate doses of hydrogen peroxide catalyzed by Fe^{3+} at initial dye solutions' pH values have a degradation effectiveness of Acid Blue 74 and Acid Orange 10 comparable with the Fenton treatment. In the case of Acid Violet 19, the removal of COD and UV absorbance was lower than for the H_2O_2/Fe^{2+} system. However, the increase of oxidant dose in the H_2O_2/Fe^{3+} system to dye:H_2O_2 weight ratio of 1:5 resulted in higher degradation of each dye than for the Fenton treatment. Thus, 80, 84, and 74% of COD was removed in Acid Blue 74, Acid Orange 10, and Acid Violet 19 solution, respectively. Moreover, more than 89 and 94% elimination of UV_{254} and UV_{max} was achieved for all studied dye solutions.

The adjustment of pH to 3 in H_2O_2/Fe^{3+} system improved the oxidation efficacy of all investigated dyes. Furthermore, as presented in Fig. 4, in the case of moderate (cost-effective) doses of hydrogen peroxide, the use of the Fe^{3+} catalyst and the regulation of reaction solution pH to 3 turned out to be the most feasible of the investigated methods in COD, aromatic carbon, and general organic content removal from indigoid, azo, and triarylmethane dye solutions.

Similar to the Fenton treatment, modified Fenton oxidation was found to be more effective in Acid Orange 10 degradation. The removal of Acid Blue 74 and Acid Violet 19 was somewhat lower according to COD and UV absorbance values.

Combined Fenton Chemistry and Lime Coagulation

The efficiency of the Fenton pre-oxidation and subsequent ferric/lime coagulation combination in Acid Blue 74, Acid Orange 10, and Acid Violet 19 degradation was also studied. In all trials with the application of combined

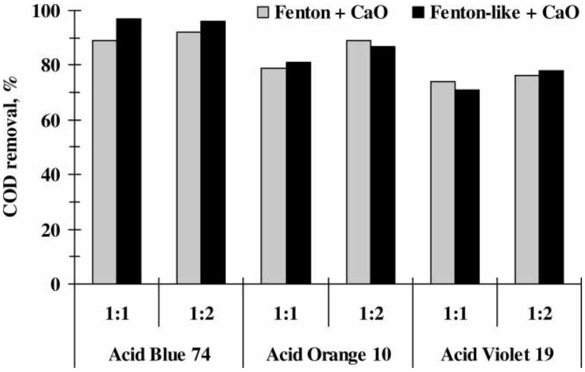


Figure 5. COD removal versus dye:H_2O_2 weight ratio for combined Fenton/Fenton-like (H_2O_2/Fe^{3+}, pH initial) treatment and lime coagulation of 0.5 g L^{-1} dye solutions.

Fenton chemistry and lime coagulation, the CaO dosage was kept between 200–400 mg L^{-1}, although less than 200 mg of CaO per liter was enough to remove the solutions' color completely. Preliminary blank experiments in coagulation with lime milk indicated no decolorization of Acid Orange 10 and Acid Violet 19 solutions. In the case of indigoid dye, 75% of the color was removed by 400 mg of CaO per liter of the dye solution coagulation (CaO:dye weight ratio of 0.4).

The post-coagulation with lime milk resulted in similar degradation efficacy both for the Fenton and Fenton-like pre-treated dye solutions at the same hydrogen peroxide dosage (Fig. 5). Moreover, a combined treatment proved the most feasible COD and UV absorbance removal method: UV absorbance of Acid Blue 74, Acid Orange 10, and Acid Violet 19 was almost entirely removed even in trials with low hydrogen peroxide doses. dye:H_2O_2 weight ratio of 1:1 proved sufficient to achieve the maximum possible treatment efficacy of Acid Blue 74 and Acid Violet 19 solutions and resulted in more than 30, 50, and 35% of additional COD, UV_{254}, and UV_{max} absorbance removal, respectively, in comparison with the Fenton oxidation solely. As for Acid Orange 10, the most effective pre-oxidation dye:H_2O_2 weight ratio was 1:2, and additional COD, UV_{254}, and UV_{max} absorbance removal comprised 32, 65 and 48%, respectively.

The combined Fenton chemistry and subsequent lime coagulation proved more effective for indigoid and azo dye contamination removal. In the case of triarylmethane dye, the removal efficacy was slightly lower.

CONCLUSION

The Fenton and modified Fenton treatment with and without lime post-coagulation was applied to Acid Blue 74, Acid Orange 10, and Acid Violet 19 aqueous solution. The results indicated that the efficacy of chemical oxidation and subsequent coagulation is not dependent on dye concentration in solution in the range of 0.1–1 g L^{-1}. Moreover, all investigated treatment processes resulted in complete or nearly complete (higher than 95%) color removal.

In most cases, the optimal dye:H_2O_2 weight ratio for dye solutions treatment by means of Fenton/Fenton-like oxidation was 1:2. The highest COD and UV absorbance removal was achieved in the case of the azo dye. Moderate doses of hydrogen peroxide improved the biodegradability of Acid Blue 74, Acid Orange 10, and Acid Violet 19 solutions. No formation of toxic intermediates during the oxidation of Acid Orange 10 and Acid Violet 19 was detected. Only insignificant toxicity increase was observed after Acid Blue 74 degradation by Fenton chemistry. The H_2O_2/Fe^{3+} system turned out to be more effective than the classic Fenton treatment. Furthermore, the adjustment of pH to 3 resulted in the subsequent removal efficacy improvement for all dyes studied.

The combination of Fenton chemistry and subsequent lime coagulation proved the most feasible treatment process in the removal of COD and UV_{254} and UV_{max} absorbance of Acid Blue 74, Acid Orange 10 and Acid Violet 19 solutions. Thus, UV absorbance of dye solutions was almost entirely removed even in trials with low hydrogen peroxide doses. In the case of COD, combined oxidation and coagulation was more effective for Acid Blue 74 and Acid Orange 10 degradation and resulted in 96 and 93% removal, respectively. In the case of Acid Violet 19, COD removal efficacy was somewhat lower (80%).

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