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Performance comparison of Fenton process, ferric coagulation and H_2O_2/pyridine/Cu(II) system for decolorization of Remazol Turquoise Blue G-133

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Abstract

This paper evaluates the Fenton process (involving oxidation and coagulation), ferric coagulation and H_2O_2/pyridine/Cu(II) system for the removal of color from a synthetic textile wastewater containing polyvinyl alcohol and a reactive dyestuff, Remazol Turquoise Blue G-133. Experiments were conducted to investigate the effects of operating variables such as pH, coagulant dose, polyelectrolyte type, H_2O_2 and Fe(II) concentrations, optimum pyridine and Cu(II) dosages on decolorization efficiency. Optimal operating conditions were experimentally determined. A decolorization efficiency of 96% was possible to achieve with Fenton's reagent at an optimum [Fe(II)]:[H_2O_2] molar ratio of 1.21:1. However, 27% of initial Fe(II) was still in the effluent which required further treatment. Optimum pH and coagulant dose were found to be 7 and 100–125 $\mathrm{mg\,l^{-1}}$, respectively, and the corresponding efficiency was ~100%. Cationic polyelectrolyte was found to be the most suitable type and 2 $\mathrm{mg\,l^{-1}}$ of it enhanced the decolorization by 10% and 75% for filtered and nonfiltered samples, respectively. The maximum efficiency achieved by H_2O_2/pyridine/Cu(II) system was about 92% with a high initial reaction rate different from the H_2O_2/pyridine system which also led to 92% removal. However, the required H_2O_2 dosage was very high in this system with a low Cu(II).

Keywords: Decolorization; Ferric coagulation; Fenton process; H_2O_2/pyridine/Cu(II) system; Remazol Turquoise Blue G-133

1. Introduction

Synthetic dyes and pigments released into the environment mainly in the form of wastewater effluents by textile, leather and printing industries cause severe ecological problems. These compounds have a great variety of colors and chemical structures and are recalcitrant to microbial attack. Most of the dyes are non-toxic, except for azo-dyes which comprise a large percentage of synthetic dyes and are degraded into potentially carcinogenic amines [1,2]. Moreover, their color causes an aesthetic problem in the receiving waters.

Biological degradation of different dyestuffs has been extensively studied by both aerobic and anerobic cultures [3–8]. However, the degradation of such compounds by either mixed cultures or isolated enzymes is usually very slow. Chemical treatment systems, on the other hand, are generally more effective with respect to biological processes in decolorization of textile dyestuffs although their application is limited with their high costs. Nevertheless, it seems, in some cases, obligatory to apply these processes alone or in connection with a biological process to overcome the inadequate performance of biological treatment systems. A very recent study carried out by Golob et al. [9], for instance, showed that the conventional coagulation–flocculation method was very effective in decolorization and also in biodegradability enhancement of textile dyebaths' effluents. Another recent investigation performed by Kim et al. [10] reported that ferric

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chloride coagulation of disperse dyes can give decolorization efficiencies ranging between 97.7% and 99.6% depending on the type of dyestuff. However, they also reported lower efficiencies for reactive dyes due to their higher solubility values with respect to disperse dyes. Another widely used chemical treatment method for decolorization of dyebaths' effluents is the Fenton process which is mainly based on oxidative degradation by $OH^{\bullet}$ radicals and slightly on coagulation of dyestuffs. This process can also be adopted readily in a wastewater treatment system without the need for reconstructing existing coagulation unit. It is possible, in most cases, to achieve high decolorization efficiencies (90–99%) with this process with low iron concentrations in relatively short reaction times [2,11–13]. However, it has also been reported that some dyes are either not or only partially decomposed with Fenton's reagent [2,14]; and more importantly, the rate of degradation in this process is pH dependent [15].

There is a considerable interest in the development of transition metal–ligand complexes that can perform hydrogen peroxide decomposition with the resulting production of reactive oxygen species such as hydroxyl radicals. Among such systems, less attention has been paid to color removal through reactions based on Cu(II) [16] although copper-based radicals-generating systems have been used for the degradation of lignin [17] or polycyclic aromatic hydrocarbons [18]. The oxidation of Quinaldine Blue through activation of H_2O_2 by Cu(II)–different ligand complexes has been studied [19]. Decolorization of azo, heterocyclic, triphenylmethane and polymeric dyes by using Cu/pyridine/H_2O_2 process was first investigated by Nerud et al. [2] and significant decolorization efficiencies were achieved for a number of structurally different dyestuffs. One important finding of that study was that this process was not affected by pH between 3 and 9. The authors have also focused on the effectiveness of different metal–ligand complexes on decolorization of synthetic dyes [20–22]. Literature survey has not pointed out any other study on the use of Cu/pyridine/H_2O_2 process.

It is aimed, in this study, to optimize the important components of coagulation (pH, coagulant dose and polyelectrolyte type) and Fenton oxidation conditions (Fe(II):H_2O_2 molar ratio and dose) of Remazol Turquoise Blue G-133 dye solution and to compare the performances and discuss the advantages and drawbacks of these two processes with the preoptimized H_2O_2/Cu(II), H_2O_2/pyridine and H_2O_2/pyridine/Cu(II) systems using decolorization efficiency as the comparison parameter.

2. Materials and methods

2.1. Chemicals

The commercially available dyestuff, Remazol Turquoise Blue G-133, the properties of which is given in Table 1, was obtained from Dystar Hoechst Corporation. $CuSO_4 \cdot 5H_2O$, $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, H_2O_2 (35% w/w) and pyridine were supplied from Merck and were of analytical grade. NaOH and H_2SO_4 (98%) were used to adjust the pH of the reaction mixture to the desired value. Anionic (A-130, anionic polyacrylamide), cationic (C-577, polyquaternary amine) and nonionic (N-100, acrylpolymer) polyelectrolytes were supplied from CYANAMID (Netherlands). Polyvinyl alcohol (PVA) was purchased from Sigma. Distilled water was used for the preparation of reaction mixture and metal stock solution.

Table 1
Characterization of Remazol Turquoise Blue G-133

Parameter	Remazol Turquoise Blue G-133
Class	Copper phthalocyanine
Color index name	Reactive Blue 21
Reactive group	Sulphatoethylsulphone
pH	5.12
COD[a]	31
TOC[a]	12.3
λ_{max} (nm, visible–UV)[b]	624
Molecular weight (g/mol)	576.10
BOD_5	Not detectable
Purity (%)	50

[a] Values for 50 mg l^{-1} dyestuff concentration.

[b] Monitored in 1 cm quartz cells at their natural pH.

2.2. Experimental apparatus and analytical methods

All experiments were conducted with 250 ml working volume using a standard jar test apparatus, VELP SCIENTIFICA FC6S. The pH was measured by using a WTW inoLab Level 2 model pH meter. A Pharmacia LKB Novaspec II model spectrophotometer was used for absorbance measurements. The supernatants in each beaker were filtered through 0.45 μm Millipore membrane filter before measuring absorbance unless otherwise indicated. The decolorization was expressed as a decrease in dyestuff concentration (absorbance–concentration calibration curve of Remazol Turquoise Blue G-133 was predetermined) at the absorbance maximum (λ_{max}). Fe(II) and Fe(III) concentrations were measured by NOVA 60 model MERCK spectrophotometer.

2.3. Synthetic textile wastewater

The most common refractory COD and color components of textile wastewater are polyvinyl alcohol (PVA) and dyestuffs. In this study, PVA and Remazol Turquoise Blue G-133 were used to simulate COD and color, respectively. Based on our analysis, 100 mg l^{-1} PVA is equivalent to 182 mgCOD l^{-1} and 50 mg l^{-1} Remazol Turquoise Blue G-133 is equivalent to 31 mgCOD l^{-1}. The synthetic textile wastewater was prepared by mixing a solution of 50 mg l^{-1} Remazol Turquoise Blue G-133 with a solution of 100 mg l^{-1} PVA. The COD in the final solution was, therefore, 213 mg l^{-1}. However, the focus in this study was on decolorization rather than COD removal.

2.4. Coagulation and flocculation experiments

As the other processes studied, the chemical coagulation experiments were conducted with the Jar test method. The operating variables were dosage of the coagulant and pH, and the effect of existence of cationic, anionic and nonionic polymers. Ferric chloride was used as the coagulant. The coagulation experiments proceeded with rapid mixing of water samples at 200 rpm for 3 min, slow mixing at 45 rpm for 30 min and then standstill for 30 min. Anionic, cationic and nonionic polyelectrolytes at a dose of 2 mg l^{-1} were added as the coagulant aid 3 min after the beginning of slow mixing step. After 30 min settling, the supernatant was withdrawn for color analyses. Fe(III) concentration was also measured in the supernatant at the end of the reaction.

2.5. Fenton process

The operating variables for Fenton process were H_2O_2 and Fe(II) dosages and the different combinations of H_2O_2/Fe(II). Concentration–time profile was studied to find out the reaction order and rate constant. Residual Fe(II)/Fe(III) was also analysed. All experiments were carried out at pH 3. The reaction time was kept constant at 45 min. H_2O_2 (35% w/w) and $FeSO_4 \cdot 7H_2O$, as the Fe(II) source, were added into the solution following the adjustment of pH to 3 and the solution was mixed rapidly for 45 min and settled for 15 min. The supernatant samples were filtered and analysed for color.

2.6. H_2O_2/pyridine/Cu(II) process

Prior to the experiments carried out with H_2O_2/pyridine/Cu(II) process, some runs were conducted with H_2O_2 alone, H_2O_2/pyridine and H_2O_2/Cu(II) processes for comparative reasons. The H_2O_2, pyridine and Cu(II) concentrations were kept constant at 125 mM, 0.5% and 0.1 mM, respectively. For H_2O_2/Cu(II) process, however, Cu(II) concentration was 0.5 mM which was found to be the minimum concentration after which no significant removal was achieved. The reaction time was kept constant at 60 min and samples of reaction mixture were taken at predetermined time intervals (every 10 min) and analysed for decolorization. Samples taken for spectrophotometric measurements were poured back into the reaction mixture after analysis in order not to decrease the total volume.

3. Results and discussion

3.1. Coagulation/flocculation process

Experiments were performed to find the optimum pH value and concentration of coagulant, $FeCl_3 \cdot 6H_2O$, that result in maximum dye removal. Effect of polyelectrolyte addition was also investigated. Destabilization of Remazol Turquoise Blue G-133 dye solution was examined at pH 4–9 at ferric chloride doses of 0–150 mg l^{-1} and at a constant polyelectrolyte dose of 2 mg l^{-1}. Effect of pH is illustrated in Fig. 1. For this set of experiments, coagulant dose was kept constant at 25 mg l^{-1} and no polyelectrolyte was added into the solution. As can be seen from the figure, between pH 4 and 5, the difference in dye removal efficiency was relatively insignificant. However, it started to increase at pH > 5 and reached a maximum value of 76.2% at pH 7. The decolorization efficiency decreased slightly at pH 8 and considerably at pH 9. This was most probably because at pH values above 7, the dye particles were more negatively charged and decolorization efficiency decreased. This may be due to the increasing concentration of $Fe(OH)_4^-$ that occurs at these pH values [10,23]. Ferric species in the pH range between 4 and 8 are almost completely insoluble. The hydrolysis of ferric chloride generates ferric hydroxide particles. These particles agglomerate forming macroscopic flocs and are apparently readily adsorbed onto colloids [10,24].

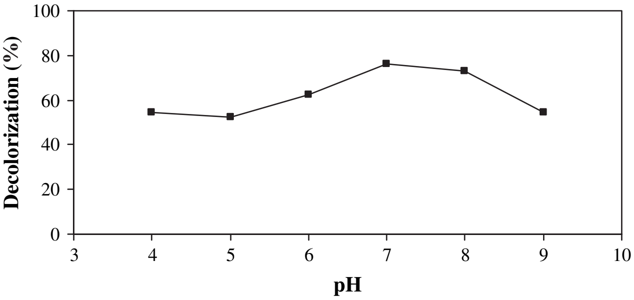

Fig. 1. Effect of pH on decolorization efficiency (coagulant dose = 25 mg l^{-1}, no polyelectrolyte).

The optimal concentration of ferric chloride coagulant for Remazol Turquoise Blue G-133 decolorization was determined by varying the coagulant dose at the optimal pH (pH 7). Decolorization efficiency as a function of coagulant dose is illustrated in Fig. 2. The efficiency increased with increasing coagulant dose until 100 mg l^{-1}, did not change between 100 and 125 mg l^{-1} and decreased at a dose of 150 mg l^{-1}. The maximum efficiency (100%) was achieved at a ferric chloride dose of 100 mg l^{-1}. However, decolorization was still significant (97%) at a coagulant dose of 75 mg l^{-1}. The efficiency obtained at a dose of 150 mg l^{-1} (93.6%) was lower than that obtained at 75 mg l^{-1}. This trend was also observed by Kim et al. [10] who studied the removal of disperse and reactive dyes by chemical coagulation.

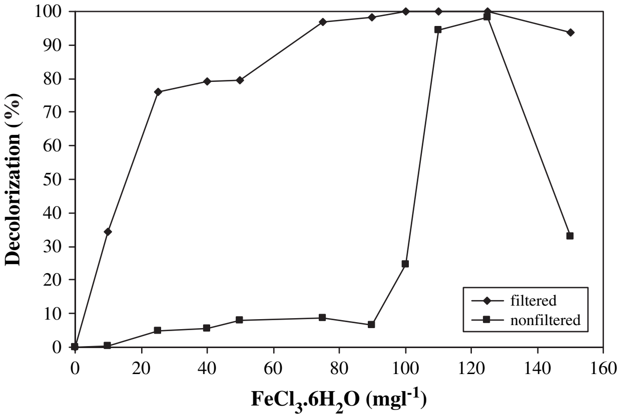

Fig. 2. Effect of coagulant dose on decolorization efficiency (pH = 7, no polyelectrolyte).

According to their study, adequate addition of chemical coagulant yielded zeta potential values close to zero and a charge reversal was observed with increasing coagulant concentration. The decrease in efficiency at 150 mg l^{-1} coagulant dose in this study was probably due to this charge reversal of dye particles from negative to positive.

The decolorization efficiency by chemical coagulation depends upon not only the solubility of the dyes, but also the final floc formation and its settling quality. The effect of coagulant dose on settling quality of the flocs is also clear from Fig. 2. Although sludge volume index of the produced flocs was not measured, the difference in measured decolorization values between filtered and nonfiltered samples showed that at low concentrations of coagulant, settling quality of the flocs was so poor that there was a great difference in filtered and nonfiltered samples. However, as the coagulant concentration was increased, settling properties were also improved. At a coagulant dose of 125 mg l^{-1}, there was no difference in decolorization between filtered and nonfiltered samples (both were 100%). At lower concentrations of coagulant, the number of flocs was more, however, the size was smaller; and at higher concentrations of coagulant, the number of flocs was less, however, the size was larger which promotes settling.

The residual Fe(III) in supernatant was also measured. The residual Fe(III) concentration decreased with increasing coagulant dose being incorporated into flocs. Fe(III) removal increased from 83.2% to 99.3% and then to 99.8% when the initial ferric chloride dosage was increased from 50 to 90 mg l^{-1} and then to 125 mg l^{-1} (Fig. 3). Further increase in ferric chloride dose to 150 mg l^{-1} led to an increase in residual Fe(III) concentration from 0.06 to 0.35 mg l^{-1}. This change in residual coagulant dose was parallel to the change in decolorization with coagulant dosage and the relationship was explained with the function $E(\%) = 101.3 - 12.36 \times \mathrm{Fe(III)}_{\mathrm{residual}}$ with an r^2 of 0.98.

The effect of polyelectrolyte addition on decolorization efficiency at different initial coagulant dosages was also investigated. For this purpose, 2 mg l^{-1} cationic, anionic and nonionic polyelectrolytes were added separately into the reaction mixture, 3 min after the beginning of slow mixing step. Absorbance measurements were conducted on both filtered and nonfiltered samples. When no coagulant was used, about 20% decolorization was achieved with all polyelectrolytes for filtered samples. The most effective polyelectrolyte was, however, cationic one. At a coagulant dose of 50 mg l^{-1}, for instance, the efficiency increased from 79.4% to 89.3% with cationic polyelectrolyte. Anionic and then nonionic polyelectrolytes followed cationic one. At coagulant doses ≥ 75 mg l^{-1}, effect of polyelectrolytes was not clear. The small decrease in decolorization at 150 mg l^{-1} ferric chloride dose was, however, not observed when polyelectrolytes were used (Fig. 4). The difference in decolorization for nonfiltered samples, however, was quite significant (Fig. 5). The critical coagulant dose which should be considered was 90 mg l^{-1}. At this concentration, the efficiency of coagulant was only around 6.52% and increased to 19.4%, 49.4% and 94.4% when nonionic, anionic and cationic polyelectrolytes were used, respectively. The efficiency further increased to 98.2% with cationic polyelectrolyte when the coagulant dose was increased to 100 mg l^{-1} and no filtration was necessary.

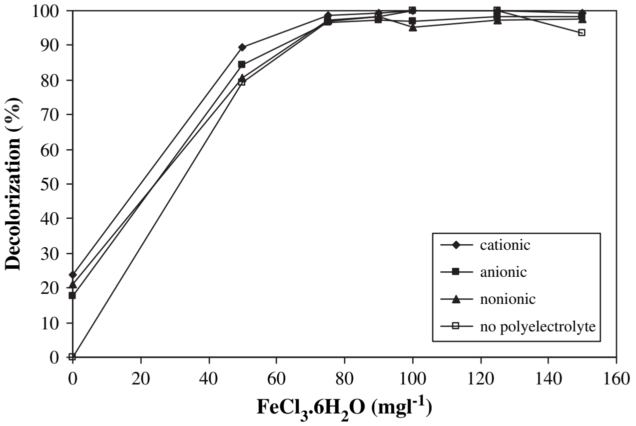

Fig. 4. Effect of polyelectrolyte addition on decolorization efficiency for filtered samples.

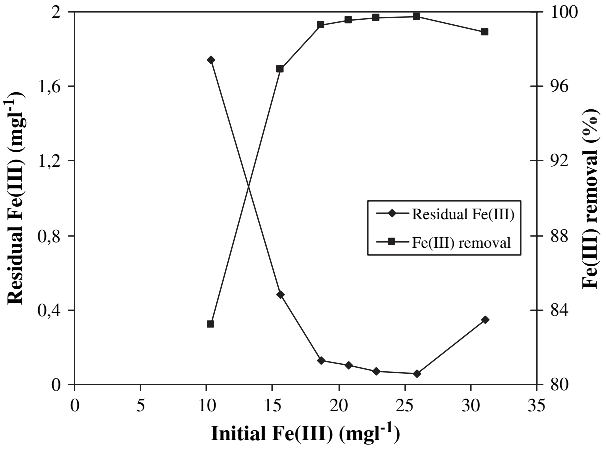

Fig. 3. Variation of residual Fe(III) concentration in the effluent as a function of initial Fe(III) dosage.

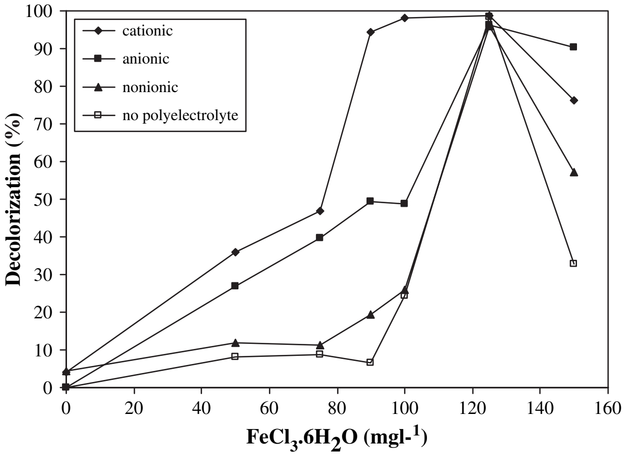

Fig. 5. Effect of polyelectrolyte addition on decolorization efficiency for nonfiltered samples.

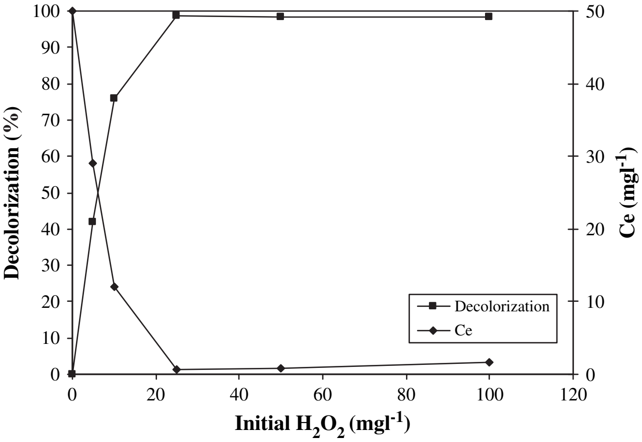

Fig. 6. Effect of initial oxidant concentration on decolorization efficiency ([Fe(II)] = 50 mg l^{-1}, pH = 3).

3.2. Fenton process

The pH has been observed to be a highly important factor for effective Fenton treatment [25,26]. The Fenton oxidation is not applicable to alkaline solutions. When pH > 8, Fe(II) ion begins to form floc and precipitates. H_2O_2 is also unstable and may decompose to give oxygen and water, and finally loses its oxidation ability. Most studies show that pH between 2 and 3 is most effective in the degradation reactions [11,12,27,28]. Therefore, the initial pH of the reaction mixture, in this study, was adjusted to 3 prior to the addition of Fenton reagents for all experiments. The experiments were carried out at a constant reaction time of 45 min and the reaction mixture was then left to standstill for 15 min to allow the ferric hydroxide flocs to settle out.

The effects of H_2O_2 and Fe(II) concentrations were investigated and the molar ratios of Fe(II) and H_2O_2 were optimized. Some additional experiments at the optimum molar ratio but at different concentrations of both reagents were also carried out to see the degree of efficiency at lower concentrations. The first step was to investigate the effect of H_2O_2 concentration on decolorization. For this purpose, H_2O_2 concentration was changed between 0 and 100 mg l^{-1} and Fe(II) was kept constant at 50 mg l^{-1}. Fig. 6 illustrates decolorization efficiency as a function of initial H_2O_2 concentration. The efficiency increased with increasing H_2O_2 concentration up to 96.2% at an initial concentration of 25 mg l^{-1} oxidant and did not change at higher concentrations. Therefore, in the second step, initial H_2O_2 concentration was kept constant at 25 mg l^{-1} and initial Fe(II) concentration was changed between 0 and 150 mg l^{-1}. The efficiency increased from 63.4% for an initial Fe(II) concentration of 5 mg l^{-1} to 96.2% at an initial Fe(II) concentration of 50 mg l^{-1} and did not change at higher concentrations (Fig. 7). These optimum concentrations of H_2O_2 and Fe(II) correspond to a [Fe(II)]:[H_2O_2] molar ratio of 1.21:1. No $OH^{\bullet}$ radical scavenging effect was observed within the concentration range studied. This was most probably due to the relatively low concentrations of H_2O_2 applied. Concentration–time profile of Remazol Turquoise Blue G-133 at this [Fe(II)]:[H_2O_2] molar ratio is illustrated in Fig. 8. As can be seen from the figure, the majority (68%) of the color was removed at a rather short oxidation time of 5 min. Shorter and also longer time periods for similar initial trends were also reported by some other authors such as 1 min [13], 10 min [29] and 15 min [30]. The degradation reaction did not stop, however, and went on with a lower reaction rate. In the study carried out by Verma et al. [20], they reported that the concentration of $OH^{\bullet}$ in the reaction mixture was the highest during the first few minutes of incubation. They also reported the proceeding of decolorization even after no $OH^{\bullet}$ radicals were being generated, indicating the existence of mechanisms other than the direct attack of $OH^{\bullet}$ radicals. The probable explanation was that the hydroxyl radicals initiate a series of further reactions [19,31]. It is thought in this study that this explains the high rates of decolorization at the end of 5 min and the slow down of the reaction rate thereafter. Kinetic analysis of Fig. 8 showed that degradation of Remazol Turquoise Blue G-133 followed a second order reaction rate with respect to dyestuff with a reaction rate constant, k, of 0.0102 l mg^{-1} min^{-1} and an r^2 of 0.99. It should also be noted that large amounts of small flocs were observed during the reaction which was most probably due to the reaction of produced ferric ions with hydroxide ions to generate ferric hydroxide which also contributes to removal process through coagulation [28].

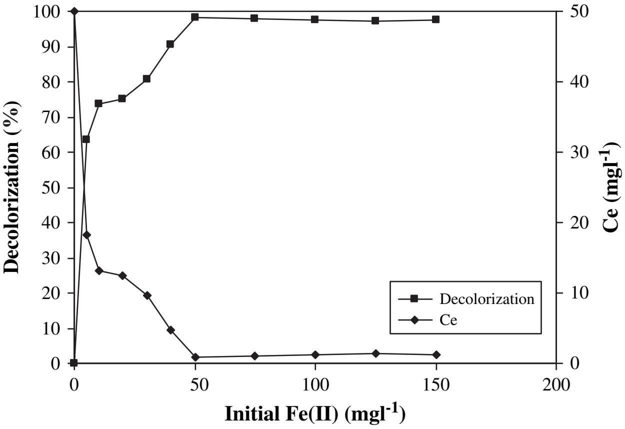

Fig. 7. Effect of initial Fe(II) concentration on decolorization efficiency ([H_2O_2] = 25 mg l^{-1}, pH = 3).

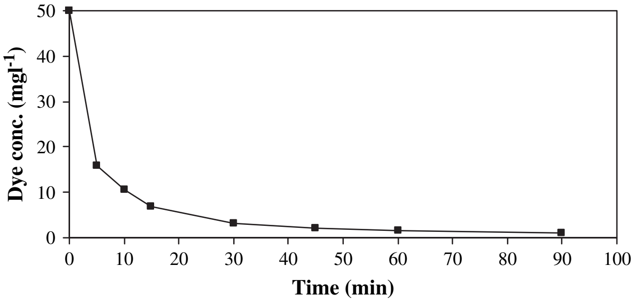

Fig. 8. Concentration–time profile of Remazol Turquoise Blue G-133 degradation at optimum [Fe(II)]/[H_2O_2] molar ratio.

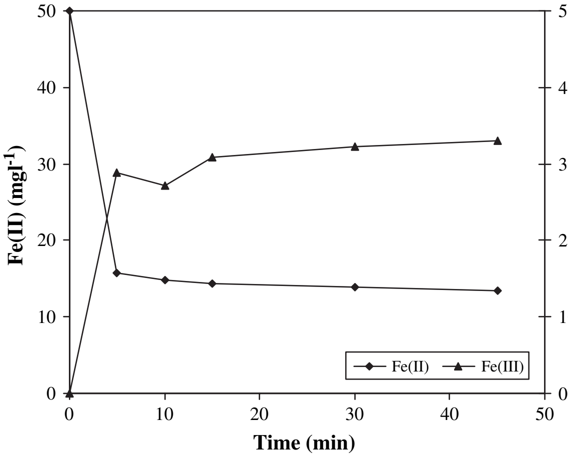

Fig. 9. Variation of Fe(II) and Fe(III) concentrations with time during the reaction at the optimum [Fe(II)]/[H_2O_2] molar ratio.

The Fe(II)/Fe(III) concentration–time profile was also monitored during the reaction and is illustrated in Fig. 9. As can be seen from the figure, a rapid decrease in Fe(II) concentration from 50 to 13.6 mg l^{-1} and a simultaneous increase in Fe(III) concentration from 0 to 28.9 mg l^{-1} was observed within the first 5 min of reaction which corresponds to the first sampling point.

Fig. 10 illustrates the results of a series of experiments carried out with different concentrations of H_2O_2/Fe(II), however, at the optimum molar ratio. A high initial reaction rate followed by slow down of it was the general trend as encountered in a typical Fenton reaction. The efficiency increased from 55.8% at a concentration couple of 5 mg l^{-1}/10 mg l^{-1} up to 98.6% at a concentration couple of 25 mg l^{-1}/50 mg l^{-1} and did not change for higher concentrations.

3.3. H_2O_2/pyridine/Cu(II) process

This part of the experimental study actually consists of different combinations of oxidant/ligand/catalyst system such as oxidant alone, oxidant/ligand, oxidant/catalyst and oxidant/ligand/catalyst systems. For this study, hydrogen peroxide was selected as the oxidant, pyridine as the ligand and copper as the catalyst. A number of set of experiments were conducted to optimize the concentrations of each component and the decolorization efficiency values for optimized concentrations as a function of time are given in Fig. 11. As can be seen from the figure, H_2O_2 alone was not effective in decolorization of Remazol Turquoise Blue G-133. The efficiency obtained was only 3.6%. The addition of 0.5 mM catalyst (Cu(II)) significantly increased the efficiency. The maximum decolorization achieved after 60 min of reaction period was, however, only around 56.2%. When compared to H_2O_2/pyridine process by which an efficiency of 90% was possible, H_2O_2/Cu(II) process was less effective. The reason may be the formation of insoluble hydroxide by Cu(II) which decomposes H_2O_2 on the surface of the solid particles in the absence of a strong-binding ligand. Nevertheless, a considerable efficiency (56.2%) was possible to obtain, since the pH of the reaction mixture was not high enough (pH 7) for the formation of a serious amount of hydroxide. In a study carried out by Verma et al. [20], the authors pointed out to the existence of precipitation when Cu(II)/H_2O_2 (without ligand) was used in alkaline conditions ($pH > 7$). This result is also supported by Robbins and Drago [19] who studied the activation of hydrogen peroxide by copper(II) complexes at pH 9.1 and found that only a small amount of Quinaldine Blue could be oxidized in the absence of a ligand and gave the above mentioned reason for lower efficiencies. Another explanation to higher efficiencies obtained in ligand-containing reaction systems was put forward by Verma et al. [20], who found out that the reactivity of free radicals present in the reactions without ligand was lower than that of complex-associated radicals. According to Shah et al. [22], hydroxyl radicals probably exist as a radical–metal–ligand complex in this situation. When the efficiency achieved by H_2O_2/pyridine/Cu(II) was investigated (0.1 mM Cu(II)), it can be seen that almost no difference exists between the

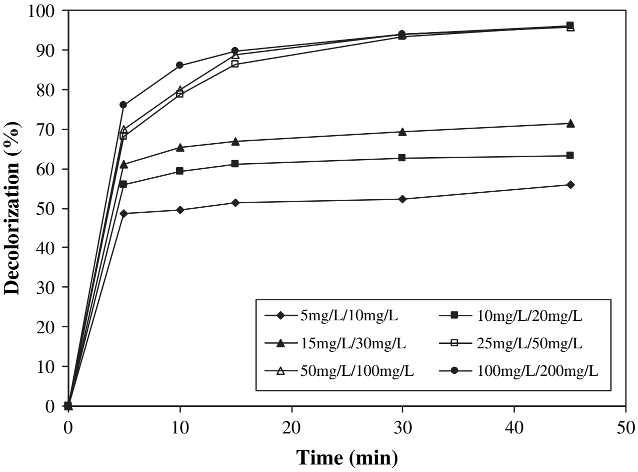

Fig. 10. Variation of decolorization efficiency as a function of reaction time at the optimum [Fe(II)]/[H_2O_2] molar ratio but at different concentrations.

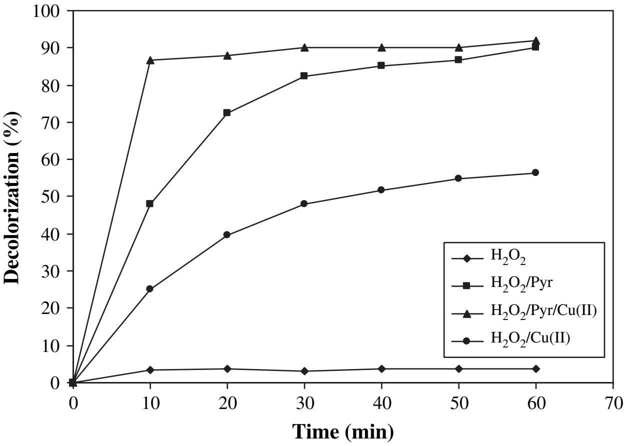

Fig. 11. Decolorization–time profile of H_2O_2, H_2O_2/pyridine, H_2O_2/Cu(II) and H_2O_2/pyridine/Cu(II) processes at optimum conditions ($[H_2O_2] = 4250$ mg l^{-1}, [pyridine] = 0.5%, pH = 7 for all processes, [Cu(II)] = 0.5 and 0.1 mM for H_2O_2/Cu(II) and H_2O_2/pyridine/Cu(II) processes, respectively).

performances of H_2O_2/pyridine and H_2O_2/pyridine/Cu(II) processes, H_2O_2/pyridine/Cu(II) being 2% more efficient. However, the initial rate of degradation for H_2O_2/pyridine/Cu(II) process was quite higher than that of H_2O_2/pyridine process. While the efficiency achieved after 10 min with H_2O_2/pyridine process was around 48%, it increased up to 86.8% for H_2O_2/pyridine/Cu(II) process, providing higher treatment efficiencies at shorter reaction periods due to the existence of catalyst.

4. Conclusions

In this study, our aim was to optimize coagulation conditions (pH, coagulant dose and polyelectrolyte type) and Fenton oxidation conditions (Fe(II):H_2O_2 molar ratio and dose) of Remazol Turquoise Blue G-133 dye solution and to compare the performances and discuss the advantages and drawbacks of these two processes with the preoptimized H_2O_2/Cu(II), H_2O_2/pyridine and H_2O_2/pyridine/Cu(II) systems using decolorization efficiency as the comparison parameter.

It was possible to achieve 100% decolorization efficiency using ferric coagulation at an initial $FeCl_3 \cdot 6H_2O$ concentration of 100 mg l^{-1} at the optimum pH which was found to be 7. To achieve similar efficiencies on nonfiltered samples, a dose of 125 mg l^{-1} was necessary. The 99.5% of initial Fe(III) was incorporated into precipitate with a 0.1 mg l^{-1} residual concentration in the effluent. The cationic polyelectrolyte was the most suitable type which enhanced the decolorization by ~10% for filtered samples. However, on nonfiltered samples, its effect was much more significant and it increased the efficiency from 24.5% up to 98.2% indicating an almost 75% increment in efficiency at the optimum initial $FeCl_3 \cdot 6H_2O$ concentration.

Optimum [Fe(II)]:[H_2O_2] molar ratio, H_2O_2 and Fe(II) concentrations in Fenton process were found to be 1.21:1, 25 and 50 mg l^{-1}, respectively. The efficiency increased with increasing H_2O_2 and Fe(II) concentrations and reached up to 96% at the optimum ratio. Keeping the optimum ratio same, lower concentrations led to lower efficiencies and higher concentrations did not increase the efficiency. However, 13.5 mg l^{-1} of 50 mg l^{-1} initial Fe(II) was still in the effluent which corresponds to 27% of initial dose and requires further precipitation. In addition, this process requires pH adjustment and generates a large number of small flocs which take time to settle out.

H_2O_2 alone was not effective in decolorization. The highest achievable efficiency with H_2O_2/Cu(II) process was only around 55%. This value was increased up to 92% with the addition of pyridine to the system. H_2O_2/pyridine system gave the same ultimate efficiency but the initial reaction rate of H_2O_2/pyridine/Cu(II) process was much more higher like that in Fenton's reagent. Although a satisfactory result was achieved with this process, the hydrogen peroxide consumption was very high (4250 mg l^{-1}), especially when compared to that used in Fenton's reagent (25 mg l^{-1}). The optimum Cu(II) and pyridine concentrations were 0.1 mM and 0.5%, respectively. However, applicability at a wide pH range is the advantage of this process.

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