Decolorization of Remazol-Turquoise Blue G-133 and other dyes by Cu(II)/pyridine/H$_2$O$_2$ system

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Abstract

The H$_2$O$_2$/pyridine/Cu(II) process was found to be very effective in the decolorization of synthetic dyes. The efficiencies achieved with Cu(II) as the catalyst were over 90% after 10 min of reaction for all dyes except for Rifacion Yellow HE-4R and Levafix Yellow Brown E-3RL which were more resistant to oxidation and have decolorization efficiencies of 74% and 68.8%, respectively, after 60 min of reaction in the presence of 125 mM H$_2$O$_2$, 0.5% pyridine and 0.1 mM Cu(II). The rate of decolorization was not affected by pH in the range of 3—9. At pHs 2 and 11, however, a decrease in the initial rate of reaction was monitored, at pH 11, the initial rate being much more slower than that observed at pH 2. The effectiveness of the metals was in the rank of Cu(II) > Co(II) > Zn(II) > Fe(II) = Mn(II). When compared with H$_2$O$_2$/pyridine system, the H$_2$O$_2$/pyridine/Cu(II) process was more advantageous due to the shorter reaction time required to reach a certain decolorization efficiency although the decolorization efficiencies of both processes were almost same at extended reaction periods. The decolorization efficiency increased with increasing pyridine and H$_2$O$_2$ concentration until a certain value after which the increase in concentrations of both had negligible effect. Further increases in Cu(II) concentration, however, led to decreases in decolorization. The decolorization of Remazol-Turquoise Blue G-133 with H$_2$O$_2$/pyridine system was found to follow zero order reaction rate for low concentrations and first order for high concentrations with high r^2 values.
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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 colours 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. Conventional treatments of textile effluents such as coagulation, flocculation [9], sorption [10], electrochemical and oxidative degradation [11,12] are limited by their high costs. Furthermore, since most of these processes achieve the removal by separation, they merely transfer the pollutants from one phase to another, leaving a problem of disposal of transferred material.

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. Various methods have been employed for the generation of hydroxyl radicals such as O$_3$/UV, H$_2$O$_2$/UV, TiO$_2$ photo-catalysis, photo-assisted Fe(III)/H$_2$O$_2$ reaction [13—15]. These can quickly and

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non-selectively oxidize a broad range of organic pollutants [13]. However, it has been reported that some dyes are either not or only partially decomposed with, for instance, Fenton's reagent [16,2] and more importantly, the rate of degradation, in most of these processes, is pH dependent [17]. Less attention has been paid to similar reactions based on Cu(II) [12] although copper-based radicals-generating systems have been used for the degradation of lignin [18] or polycyclic aromatic hydrocarbons [19]. The oxidation of Quinaldine Blue through activation of H_2O_2 by Cu(II)–different ligand complexes has also been studied [20]. Decolorization of azo, heterocyclic, triphenylmethane and polymeric dyes by using Cu/pyridine/H_2O_2 process was, first, investigated by Nerud et al. [2]. Literature survey has not pointed out any other study on the use of Cu/pyridine/H_2O_2 process. They have also focused on the effectiveness of different metal–ligand complexes on decolorization of synthetic dyes [21–23]. In this study, a more detailed investigation of H_2O_2/pyridine, H_2O_2/Cu(II) and H_2O_2/pyridine/Cu(II) processes was carried out for decolorization of Remazol-Turquoise Blue G-133, considering the effect of different components in the system such as initial Cu(II), pyridine, H_2O_2 and dyestuff concentrations, pH, mixing speed, reaction time and the existence of different metal ions (Cu(II), Zn(II), Fe(II), Mn(II), and Co(II)). After the determination of optimum concentrations of Cu(II), pyridine and hydrogen peroxide, the effectiveness of the process was also studied on some other dyestuffs for above-mentioned metal ions and the results were evaluated on a comparative basis. The kinetics of decolorization has also been investigated.

2. Materials and methods

2.1. Chemicals

The commercially available dyestuffs, Remazol-Turquoise Blue G-133 (λ_{max}: 624 nm), Rifacion Yellow HE-4R (λ_{max}: 411 nm), Remazol Black B-133 (λ_{max}: 598 nm), Remazol Brilliant Blue RN New (λ_{max}: 587 nm), Levafix Yellow Brown E-3RL (λ_{max}: 401 nm), Levafix Brilliant Blue E-B (λ_{max}: 597 nm) and Sumufix Orange 3R (λ_{max}: 491 nm) were obtained from Dystar Hoechst Corporation. $FeSO_4 \cdot 7H_2O$, $CoCl_2$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $MnSO_4 \cdot H_2O$, H_2O_2 (35% w/w), pyridine, NaOH and HCl (37%) were supplied from Merck and were analytical grade. Polyvinyl alcohol (PVA) was from Sigma. Distilled water was used for the preparation of reaction mixture and metal stock solution.

2.2. Experimental procedure and physical measurements

All experiments were conducted at 200 ml working volume using a standard jar test apparatus (VELP SCIENTIFICA FC6S). Initial dyestuff and PVA concentration were kept constant at 50 mg l^{-1} and 100 mg l^{-1}, respectively, for all runs unless otherwise indicated. PVA was added to the synthetic reaction mixture since it is one of the main components of refractory organic compounds in textile wastewaters. NaOH and HCl were used to adjust the pH in the range of 2–12 prior to

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.

the addition of hydrogen peroxide, pyridine and $CuSO_4 \cdot 5H_2O$. The pH was measured by using a WTW inoLab Level 2 model pH meter. In optimization experiments, the concentrations of respective components (e.g. H_2O_2, pyridine, and Cu), pH, and mixing speed were varied. The reaction time was kept constant at 60 min and samples of reaction mixture were taken at predetermined time intervals (every 10 min) and analyzed for decolorization. The decolorization was expressed as a decrease in dyestuff concentration (absorbance–concentration calibration curve of each dye was predetermined) at the absorbance maximum (λ_{max}). A Pharmacia LKB Novaspec II model spectrophotometer was used for absorbance measurements. Furthermore, $FeSO_4 \cdot 7H_2O$, $CoCl_2$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $MnSO_4 \cdot H_2O$ were used to compare the performance of different metal ions. Samples taken for spectrophotometric measurements were poured back into the reaction mixture after analysis in order not to decrease the total volume. Optimization experiments were carried out for Remazol-Turquoise Blue G-133 properties of which are presented in Table 1 and then the runs were repeated at optimum conditions for other dyes in the presence of different metal ions at equimolar concentrations of Cu(II). It should also be noted that the molar concentrations of the metal ions given throughout the article are actually the molar concentrations of the compounds used to add the metal ion of concern into the solution.

3. Results and discussion

3.1. H_2O_2/pyridine process

3.1.1. Effect of initial pH, mixing speed and reaction time

The first set of experiments was carried out to determine the effect of mixing speed and reaction time on decolorization of Remazol-Turquoise Blue G-133. For this set, hydrogen peroxide, pyridine and dyestuff concentrations were kept constant at 100 mM, 0.5% and 50 mg l^{-1}, respectively. The pH was 7. It was observed that the mixing speed had no effect on efficiency between 30 and 200 rpm (30, 45, 60, 90, 120, and 200 rpm, *data not shown*). The second set was conducted to determine the effect of pH. For this purpose, pH was varied between 2 and 12

(pH 2, 3, 5, 7, 9, 11, and 12). The difference in efficiency between pH 3 and 11 after 60 min of reaction was negligible ($E_{pH:3} = 87\%$, $E_{pH:11} = 88.1\%$). However, a decrease in pH from 3 to 2 led to a drastic decrease in efficiency from 87% to 20.2%. The decrease in decolorization when the pH was increased over 11 (pH 12) was relatively lower, the efficiency being 75.6% at the end of reaction (180 min, *data not shown*). As can be understood, contrary to the most advanced oxidation processes like Fenton reaction, the H_2O_2/pyridine process has the advantage to proceed at a wide range of pH being unaffected from the changes. All runs mentioned above continued 180 min and it was observed that the main part of the degradation took place within the first 30–45 min. After 60 min, the increase in decolorization efficiency was less than 2%. The rest of the experiments were, therefore, conducted at neutral pH (pH 7), an average mixing speed of 60 rpm and a reaction time of 60 min.

3.1.2. Effect of initial pyridine concentration

This set of experiments was carried out in the absence of Cu(II) just to determine the efficiency of H_2O_2/pyridine process to decolorize Remazol-Turquoise Blue G-133. For this purpose, the initial concentration of pyridine was varied between 0% and 2% and H_2O_2 molar concentration was kept constant at 100 mM (Fig. 1). As can be seen from the figure, in the absence of pyridine (Py:0%), decolorization with H_2O_2 alone was very low (only 3%). The addition of pyridine, however, markedly accelerated the decolorization and its contribution to decolorization was obvious even at very low concentrations. Efficiency increased with increasing pyridine concentration to as high as 88% at a pyridine concentration of 0.5%. It is also clear from the figure that the reaction rate increases much faster until a certain concentration of pyridine (0.5%) and then slows down at higher concentrations indicating the existence of an optimum pyridine dosage. However, this does not necessarily mean that all ligands will be more
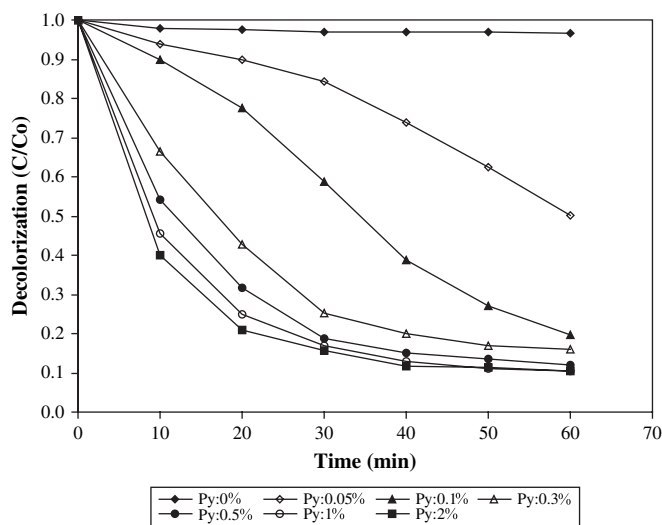
or less effective even if no metal exists in solution. Picolinic acid, for instance, was found to be not effective in catalyzing the oxidation by H_2O_2 although it was very efficient in the existence of Cu(II) together with H_2O_2 [20].

3.1.3. Effect of initial H_2O_2 concentration

In the second set of experiments, pyridine concentration was kept constant at 0.5% and H_2O_2 concentration was varied between 0 and 200 mM. Increasing H_2O_2 concentration from 10 to 125 mM led to an increase in decolorization from 39% to a highest value of 90% (Fig. 2). At H_2O_2 dosages over 125 mM, the resulting efficiency did not change although the initial reaction rate went on increasing slightly. A parallel decrease in effluent pH with increasing decolorization efficiency was also recorded till 125 mM H_2O_2. The relationship between effluent pH and decolorization was linear with a r^2 value of 0.998 and a function of $E(\%) = -87.026$ $pH_e + 624.12$.

3.1.4. Effect of different combinations of H_2O_2/pyridine ratio

Following the determination of optimum H_2O_2 (125 mM) and pyridine (0.5%) combination for a given concentration of dyestuff (50 mg l^{-1}), experiments at the same H_2O_2/pyridine ratio but different concentrations were carried out to see if it was possible to achieve the same efficiency at lower concentrations of both. However, the results showed that an H_2O_2/pyridine ratio of 125 mM/0.5% was the minimum value achieving the highest efficiency available. Ratios lower than this led to decreases in efficiency and values higher than this ratio did not change decolorization (Fig. 3).

3.1.5. Effect of initial dyestuff concentration

The aim of this set of experiments was to determine the capacity of the system in case it is exposed to higher
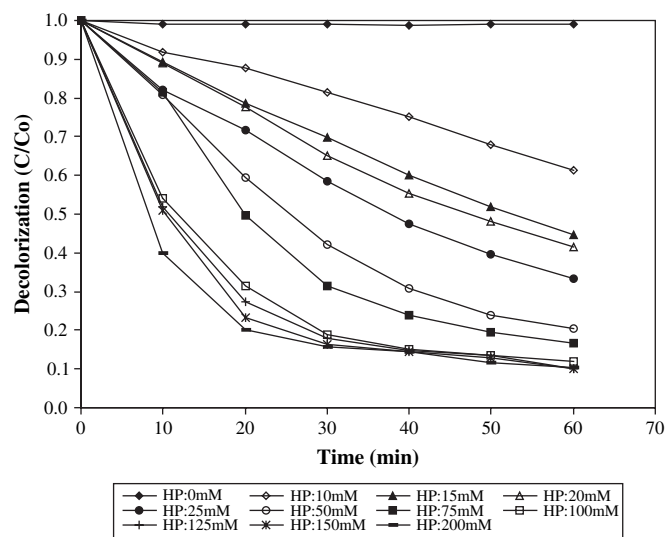

Fig. 1. Effect of initial pyridine concentration on decolorization of Remazol-Turquoise Blue G-133 with H_2O_2/pyridine process (100 mM H_2O_2, pH = 7).

Fig. 2. Effect of initial H_2O_2 concentration on decolorization of Remazol-Turquoise Blue G-133 with H_2O_2/pyridine process (0.5% pyridine, pH = 7, HP = H_2O_2).
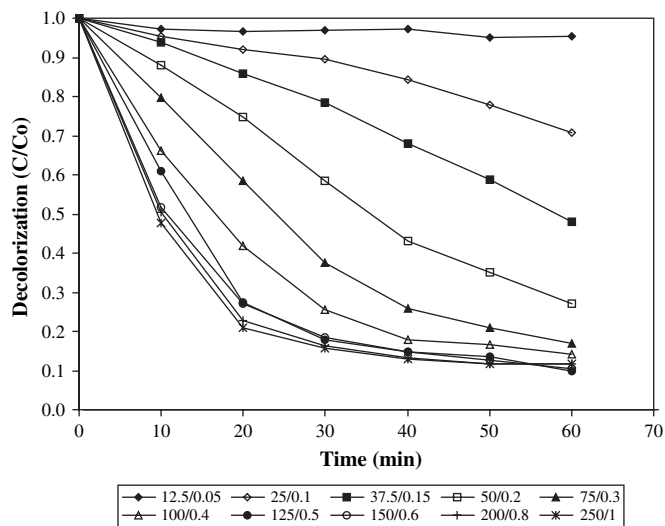
Fig. 3. Effect of different combinations of H_2O_2 and pyridine concentration on decolorization of Remazol-Turquoise Blue G-133 with H_2O_2/pyridine process (pH = 7).

concentrations of dyestuff. At the predetermined optimum pH, H_2O_2 and pyridine concentrations, reaction time and mixing speed (pH 7, 125 mM, 0.5%, 60 min, and 60 rpm, respectively), the concentration of Remazol-Turquoise Blue G-133 was varied between 25 mg l^{-1} and 500 mg l^{-1}. The H_2O_2/pyridine system decolorization efficiency slightly decreased with increasing dyestuff concentration. It is interesting to note that the decrease in decolorization efficiency was only 22% (from 89% to 67%) when the dye concentration was increased 20-fold from 25 mg l^{-1} to 500 mg l^{-1} (Fig. 4). Corresponding effluent dye concentrations were 2.7 mg l^{-1} and 164.9 mg l^{-1}, respectively, indicating that the system is incapable to lower the concentration under a certain value even if a low concentration of dye was fed to the system. And at higher concentrations of dyestuff, it was possible to remove much more dyestuff in quantity indicating the feasibility of using the system as a pretreatment step for decolorization of highly colored effluents.
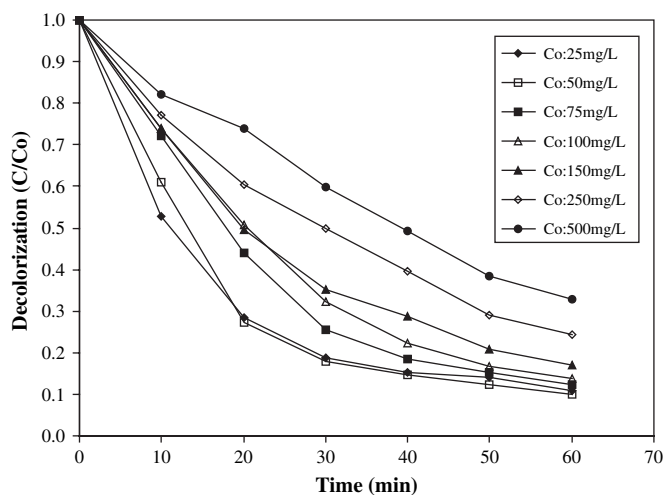
3.2. H_2O_2/Cu(II) process

3.2.1. Effect of initial Cu(II) concentration

For the purpose to find out the contribution of pyridine to H_2O_2/Cu(II) process to decolorize Remazol-Turquoise Blue G-133, a set of experiments was also conducted with H_2O_2/Cu(II) to obtain reference data for comparative reasons. H_2O_2 concentration was kept constant at 125 mM and Cu(II) was varied between 0 and 3 mM for this set of experiments. The efficiency increased with increasing Cu(II) concentration till 0.5 mM and did not change at higher concentrations (Fig. 5), indicating an optimum H_2O_2/Cu(II) molar ratio of 125 mM/0.5 mM = 250. However, the maximum decolorization achieved after 60 min of reaction period was only around 55%. 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 (55%) 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. [21], the authors pointed out 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 (1997) [20] 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. [21], who found out that the reactivity of free

Fig. 4. Effect of initial dyestuff concentration on decolorization of Remazol-Turquoise Blue G-133 with H_2O_2/pyridine process (125 mM H_2O_2, 0.5% pyridine, pH = 7).
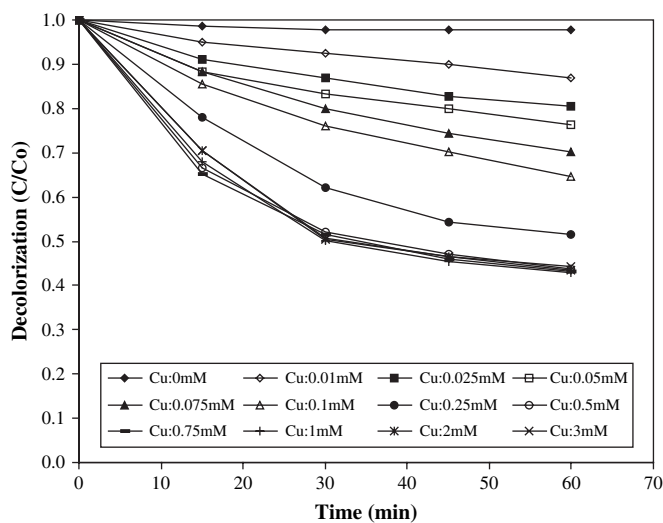

Fig. 5. Effect of initial Cu(II) concentration on decolorization of Remazol-Turquoise Blue G-133 with H_2O_2/Cu(II) process (125 mM H_2O_2, pH = 7).

radicals present in the reactions without ligand was lower than that of complex-associated radicals. According to Shah et al. [23], hydroxyl radicals probably exist as a radical—metal—ligand complex in this situation.

3.3. H_2O_2/pyridine/Cu(II) process

3.3.1. Effect of initial pH

In order to determine the optimum operating pH for the H_2O_2/pyridine/Cu process, a set of experiments was conducted at a pH range of 2—11 (pH 2, 3, 5, 7, 9, and 11), H_2O_2 concentration of 125 mM, 0.5% pyridine and 0.5 mM Cu(II). No difference was observed in both ultimate decolorization efficiency after 60 min and in the rate of reaction during the reaction period for a pH range between 3 and 9 (data not shown). At pHs 2 and 11, however, a decrease in the rate of reaction was monitored, at pH 11, the reaction being much more slower than that observed at pH 2. The resulting efficiency after 60 min, however, did not change. Therefore, the rest of the experiments carried out with H_2O_2/pyridine/Cu(II) process were conducted at neutral pH (pH 7). No precipitation was observed at any pH for the above-mentioned concentration of $CuSO_4 \cdot 5H_2O$ (0.5 mM).

3.3.2. Effect of initial Cu(II) concentration

This set of experiments was carried out at constant H_2O_2 and pyridine concentrations of 125 mM and 0.5%, respectively. Cu(II) concentration was varied between 0 and 3 mM. As shown in Fig. 6a, the metal/ligand ratio influences the decolorization of Remazol-Turquoise Blue G-133. The solution containing 0.5% pyridine, 0.1 mM Cu(II) and 125 mM H_2O_2 was found to be the most effective. Both increase and decrease in the metal/ligand ratio resulted in a drop in the decolorization rate. The efficiency increased with increasing Cu(II) concentration until 0.1 mM and then started to decrease at higher concentrations, most probably due to the side reactions of reactive oxygen species with excess H_2O_2. The highest efficiency achieved at 0.1 mM Cu(II) after 60 min was 92% which is much higher than that obtained with H_2O_2/Cu(II) process (55%) and slightly higher than that achieved with H_2O_2/pyridine (90%). Although the contribution of Cu(II) on overall decolorization efficiency seems to be negligible when compared to H_2O_2/pyridine process, its effect on reaction rate was considerable. While the efficiency obtained with H_2O_2/pyridine process after 10 min of reaction was only 39%, it increased up to 86.8% with the addition of 0.1 mM Cu(II) (Fig. 6b), decreasing the required reaction time almost six-fold to obtain an overall efficiency of $\cong 90\%$. Another point worth to note is that, the efficiency obtained after 10 min of reaction was actually reached much before. Since this was clear to see even with the eye, a second experiment was performed and a sample was taken every 2.5 min. The results showed that the efficiency after 2.5 min (85.2%) was almost same with that obtained after 10 min (86.8%). After this time, the efficiency increased very slowly and reached around 92% after 60 min. In the study carried out by Verma et al. [21], they reported that the concentration of OH$^{•}$ in the reaction mixture was the highest during the
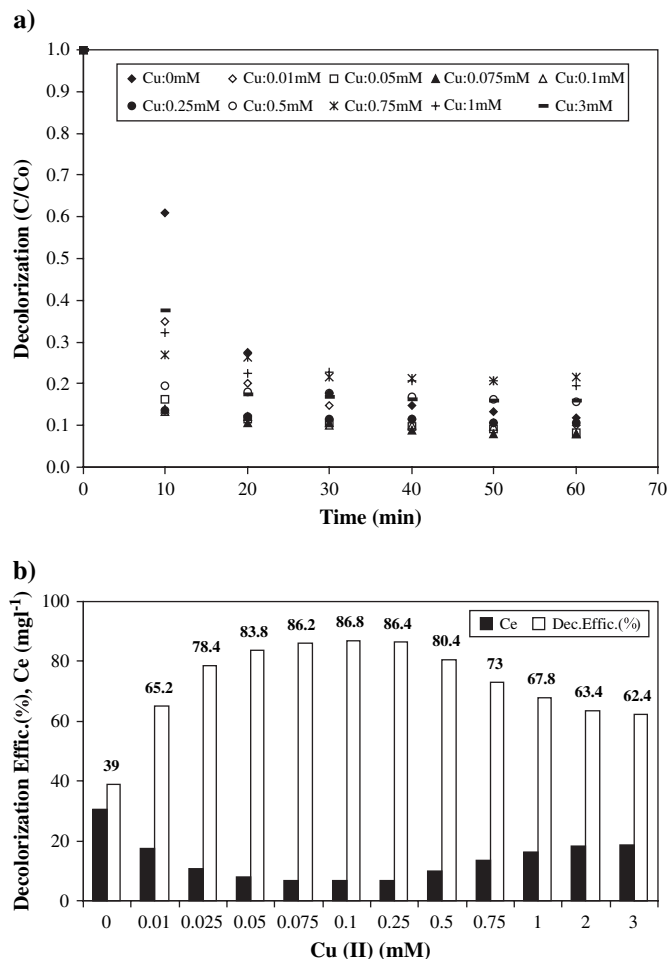

Fig. 6. Effect of initial Cu(II) concentration on decolorization of Remazol-Turquoise Blue G-133 with H_2O_2/Cu(II)/pyridine process: (a) reaction time: 60 min; (b) reaction time: 10 min (125 mM H_2O_2, 0.5% pyridine, pH = 7).

first few minutes of incubation. They also reported the proceeding of decolorization even after no OH$^{•}$ radicals were being generated, indicating the existence of mechanisms other than the direct attack of OH$^{•}$ radicals. The probable explanation was that the hydroxyl radicals initiate a series of further reactions [20,24]. It is thought in this study that this explains the high rates of decolorization at the end of 2.5 min and the slow down of the reaction rate thereafter. The involvement of hydroxyl radicals in the decolorization of dyes in similar reactions has previously been reported [10,2,22]. However, existence of different oxidant species other than hydroxyl radical have also been reported for Cu(II)/pyridine/H_2O_2 system [18,25,20]. Another point worth to note is that the optimum Cu(II) concentration decreased from 0.5 mM in Cu(II)/H_2O_2 process to 0.1 mM in Cu(II)/H_2O_2/pyridine process indicating a five-fold decrease in Cu(II) requirement although the efficiency was increased from 55% to 92%.

3.3.3. Effect of different metal ions on decolorization of Remazol-Turquoise Blue G-133

In order to compare the performance of different metal ions, additional experiments were performed. The metals of

concern were Fe(II), Cu(II), Zn(II), Co(II) and Mn(II). They were all added in equimolar concentration of optimum Cu(II) which was previously found to be 0.1 mM in Section 3.3.2 for Cu(II)/H_2O_2/pyridine process for comparative reasons. Hydrogen peroxide and pyridine concentrations were kept constant at 125 mM and 0.5%, respectively. The results showed that the difference in overall efficiency after 60 min for different metals were negligible (<5%), Cu(II) being the most efficient (92%) and Mn(II) = Fe(II) being the least efficient (88%) (Fig. 7a). However, initial rate of reactions significantly differed from each other (Fig. 7b). The efficiencies obtained after 10 min for wm (without metal), Mn(II), Fe(II), Zn(II), Co(II) and Cu(II) were 39%, 39.2%, 40%, 54.7%, 74.6% and 86.8%, respectively. In other words, the effectiveness was in the order of Cu(II) > Co(II) > Zn(II) > Fe(II) = Mn(II) after 10 min of reaction. It should also be noted that very small precipitates occurred in the reaction vessel when Fe(II) was used as the catalyst.
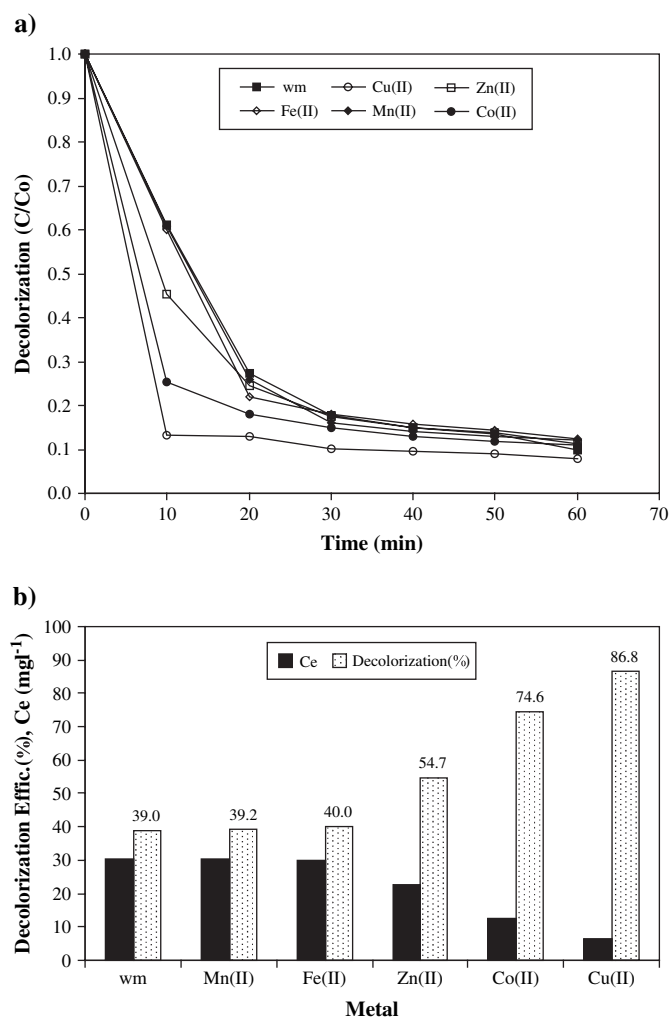
3.3.4. Comparison of all processes used to decolorize Remazol-Turquoise Blue G-133

An overall comparison of all processes used to decolorize Remazol-Turquoise Blue G-133 is illustrated in Fig. 8. As can be seen from the figure, H_2O_2 alone was quite ineffective in decolorization (4%). Addition of Cu(II) ions significantly increased the efficiency up to 55%. It is clear from the figure, however, that the efficiency curve reaches a plateau after 60 min and does not increase any further with this process. H_2O_2/pyridine process was found to be more effective than H_2O_2/Cu(II). With this process, it was possible to increase the efficiency up to 90%. Although the efficiencies obtained with H_2O_2/Cu(II)/pyridine and H_2O_2/Co(II)/pyridine systems after 60 min of reaction (92%) were almost same with that obtained by H_2O_2/pyridine process (90%), the difference in initial reaction rates were considerable. While the efficiency obtained with H_2O_2/pyridine process after 10 min was around 48%, it increased to 75% with H_2O_2/Co(II)/pyridine and 87% with H_2O_2/Cu(II)/pyridine process, providing high efficiencies at short reaction periods.

3.3.5. Performance of different metal ions in decolorization of other dyestuffs

Although the H_2O_2/pyridine system was capable of degrading Remazol-Turquoise Blue G-133 resulting in an efficiency of 90% after 60 min, it was incapable to increase the decolorization over 12% for a number of structurally different dyestuffs such as Rifacion Yellow HE-4R, Remazol Brilliant Blue RN New, Levafix Yellow Brown E-3RL, Remazol Black B-133, Sumufix Orange 3R and Levafix Brilliant Blue E-B (*data not shown*). Therefore, following the experiments carried out for oxidation of Remazol-Turquoise Blue G-133 by metal(II)/pyridine/H_2O_2 system, additional runs were performed on above-mentioned dyes using Fe(II), Cu(II), Zn(II), Co(II) and Mn(II) as the metal(II) ions to see the effect of metal ion addition on decolorization of the dyes of concern (Fig. 9). The H_2O_2, pyridine, metal concentrations and the
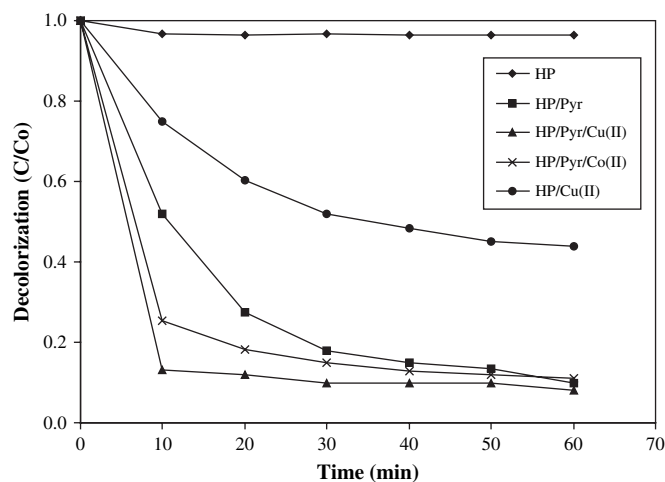
Fig. 7. Effect of different metal ions on decolorization of Remazol-Turquoise Blue G-133 with H_2O_2/metal/pyridine process: (a) reaction time: 60 min; (b) reaction time: 10 min (125 mM H_2O_2, 0.5% pyridine, 0.1 mM metal(II), pH = 7).

Fig. 8. Comparison of H_2O_2, H_2O_2/pyridine, H_2O_2/Cu(II), H_2O_2/pyridine/Cu(II) and H_2O_2/pyridine/Co(II) processes for decolorization of Remazol-Turquoise Blue G-133 (125 mM H_2O_2, 0.5% pyridine, 0.1 mM metal(II), pH = 7).
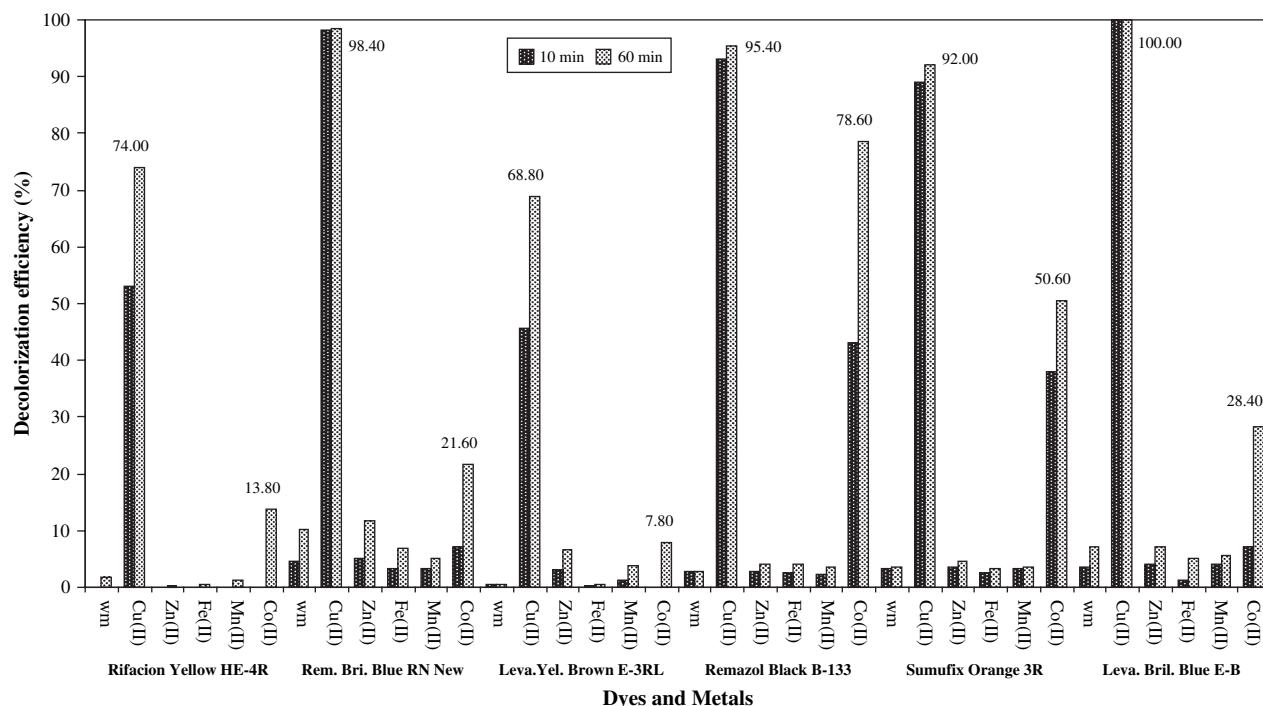
Fig. 9. Performance of different metal(II) ions on decolorization of various dyestuffs with H_2O_2/pyridine/metal(II) process (125 mM H_2O_2, 0.5% pyridine, 0.1 mM metal(II), pH = 7).

pH were kept constant at 125 mM, 0.5%, 0.1 mM and 7, respectively, which were previously found to be the optimum values in Cu(II)/pyridine/H_2O_2 system for decolorization of Remazol-Turquoise Blue G-133. Although the samples were taken every 10 min for a period of 60 min, only the values of samples taken at 10 min and 60 min are presented in Fig. 9 due to space limitations since the efficiency did not change much in between these two points.

As can be seen from Fig. 8, the first point to note is that the decolorization achieved with Cu(II) was significantly higher than those obtained with other metals for all dyes. The efficiencies achieved with Cu(II) were over 90% after 60 min of reaction for all dyes except for Rifacion Yellow HE-4R and Levafix Yellow Brown E-3RL which were more resistant to oxidation and have decolorization efficiencies of 74% and 68.8%, respectively. Co(II) followed Cu(II) in effectiveness and the efficiencies obtained increased from 7.8% for Levafix Yellow Brown E-3RL up to 78.6% for Remazol Black B-133. The efficiencies obtained with other metals were, in general, not higher than 10%. The second point worth noting is the small difference in efficiencies between the 10 min and 60 min samples and the possible reason is explained in Section 3.3.2.

4. Conclusions

The H_2O_2/pyridine/Cu(II) process was found to be very effective in the decolorization of synthetic dyes. The decolorization was very fast and was usually complete within a few minutes after the mixing of the reaction components. The efficiencies achieved with Cu(II) as the catalyst were over 90%

after 10 min of reaction for all dyes except for Rifacion Yellow HE-4R and Levafix Yellow Brown E-3RL which were more resistant to oxidation and have decolorization efficiencies of 74% and 68.8%, respectively, even after 60 min of reaction. When compared with H_2O_2/pyridine system, the H_2O_2/pyridine/Cu(II) process was more advantageous due to the shorter reaction times required to reach a certain decolorization efficiency although the decolorization efficiencies of both processes were almost same at extended reaction periods (after 60 min). Remazol-Turquoise Blue G-133 was also partially (55%) decolorized with Cu(II)/H_2O_2 but the addition of pyridine markedly accelerated the decolorization (92%). The decolorization efficiency increased with increasing pyridine and H_2O_2 concentration until a certain value after which the increase in concentrations of both had negligible effect on H_2O_2/pyridine process. Further increases in Cu(II) concentration in H_2O_2/pyridine/Cu(II) process, however, led to decreases in decolorization. No decolorization was observed when only pyridine or hydrogen peroxide was used.

Since the increase in dyestuff concentration did not significantly decrease the decolorization efficiency, H_2O_2/pyridine process (without any metal catalyst) may seem to be a feasible alternative for decolorization of highly colored effluents. However, since this situation was only valid for Remazol-Turquoise Blue G-133, it can be concluded that the addition of Cu(II) ions is obligatory for the treatment of wastewaters containing a mixture of structurally different dyes together.

The rate of decolorization in H_2O_2/pyridine/Cu(II) process was not affected by pH changes in the range of 3–9. At pHs 2 and 11, however, a decrease in the initial rate of reaction was monitored, at pH 11, the initial rate being much more slower

than that observed at pH 2. As can be understood, contrary to the most advanced oxidation processes like Fenton reaction, this process has the advantage to proceed at a wide range of pH being unaffected from the changes.

The effectiveness of the metals in H_2O_2/pyridine/metal process was in the rank of $Cu(II) > Co(II) > Zn(II) > Fe(II) = Mn(II)$.

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