

Full Length Research Paper

Decolorization and mineralization of brilliant golden yellow (BGY) by Fenton and photo-Fenton processes

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The decolorization and mineralization of an azo dye, brilliant golden yellow (BGY, λ_{\max} 416 nm, $\epsilon = 7.81 \times 10^3 \text{ Lmol}^{-1} \text{ cm}^{-1}$) by Fenton and photo-Fenton processes were investigated. The rate of decolorization is strongly dependent on the pH, initial concentrations of the dye, Fe(II) and H_2O_2 . The effect of these parameters has been studied and the optimum operational conditions of these two methods were found. The optimum conditions were obtained at pH=3 for both processes. The photo-Fenton method proved to be the most efficient and occurs at a much higher oxidation rate than Fenton process. The results showed that about 99% of the dye decolorized within 20 and 5 min for Fenton and photo-Fenton processes, respectively. Characterization of the products after mineralization is discussed.

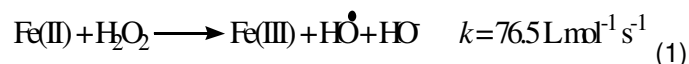
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INTRODUCTION

Synthetic azo dyes are the major industrial pollutants and water contaminants (Brown et al., 1981; Vaidya and Datye, 1982). Textile wastewater introduces intensive color and toxicity to aquatic systems (Muruganandham and Swaminathan, 2004) which is mostly non-biodegradable and resistant to demolition by physico-chemical treatment methods (Daneshvar et al., 2005). Therefore, it is necessary to find an effective method of wastewater treatment, both in terms of limited watercourses management and the need for nature of preservation. In this direction, Advanced Oxidation Processes (AOPs) have attracted wide interests in wastewater treatment since the 1990s. In principle, AOPs are based on the generation of hydroxyl radicals ($\text{HO}^\bullet + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}$, $E = 2.8 \text{ V vs NHE}$), which are highly reactive and nonselective oxidants being capable to oxidize organic compounds, in particular, unsaturated organic compounds and azo dyes (Andreozzi et al., 1999). Among them, Fenton's and photo-Fenton's type

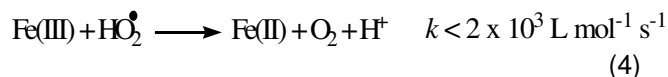
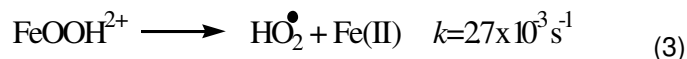
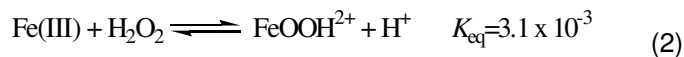
reactions are very promising since they achieve high reaction yields with a low treatment cost (Bauer and Fallman, 1997). These AOPs have been successfully applied to treat reactive dyes (Neamtu et al., 2003; Swaminathan et al., 2003; Torrades et al., 2004) and textile effluents (Perez et al., 2002; Rodriguez et al., 2002; Solmaz et al., 2006).

Fenton's and photo-Fenton's reactions are AOPs where oxidant species are generated from hydrogen peroxide and Fe(II)/Fe(III) as a catalytic couple. In Fenton's reaction (Haber and Weiss, 1934), ferrous salts react with H_2O_2 to generate the HO^\bullet radicals as follows (reaction (1)):

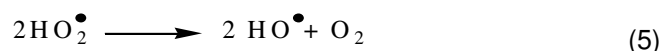


Then, Fe(III) ion can be reduced by reaction with excess H_2O_2 to form again Fe(II) ions and more HO^\bullet radicals. This second process called Fenton's-like (Pignatello, 1992), is slower than Fenton's reaction and allows Fe(II) regeneration giving place to a catalytic mechanism (Reactions (2) – (4)):

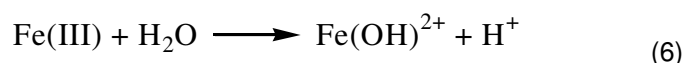
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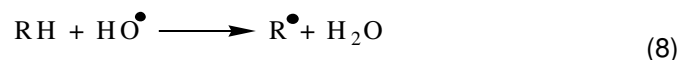
The perhydroxy radicals (HO_2^\bullet) are very unstable and converted into hydroxyl free radicals (HO^\bullet) as shown in Reaction (5):



The rate of contaminant degradation can be considerably increased via photochemical reaction in the photo-Fenton's process (Pignatello, 1992; Pignatello et al., 2006). In this case, the regeneration of Fe(II), with production of new hydroxyl radicals, follows a photo reduction process (Reactions (6) and (7)):



Thus, the hydroxyl free radicals are generated from both the Fenton or photo-Fenton processes, and this is a strong oxidizing agent that oxidizes the organic compounds through generation of new organic free radicals as shown in Reaction (8):



Then the free radicals (R^\bullet) scavenge oxygen molecules from the environment to form perhydroxy radicals (RO_2^\bullet) (Li et al., 1997) which are very reactive and in the presence of Fe(II), they are converted into stable products e.g., H_2O , CO_2 or HNO_3 etc as shown in Reactions ((9) and (10)):



It has been reported by Kang et al. (2000) that Fenton process could be adopted rapidly in a textile wastewater treatment system, without the end for reconstructing the existing coagulation unit. The use of Fe(II)/ H_2O_2 system as an oxidant for wastewater treatment is attractive since iron is highly abundant and non-toxic, and a 30% H_2O_2 aqueous solution is easy to handle and environmentally not harmful. Malik and Saha (2003) reported that the removal rate is strongly dependent on the initial concentration of the dye, Fe(II) and H_2O_2 .

Muruganandham and Swaminathan (2004) have carried out studies where similar results were obtained; they suggested a pH of 3 is the optimum for Fenton and photo-Fenton processes.

In the present study, Fenton and photo-Fenton processes have been used to find out the optimal conditions of experimental parameters for the mineralization of brilliant golden yellow (BGY) which is extensively used in textile, dyeing and in ball-point industries worldwide.

MATERIALS AND METHODS

Chemicals

Chemical structure of brilliant golden yellow (BGY) is shown in Table 1, Mohr's salt, hydrogen peroxide, hydrochloric acid, sodium hydroxide, sulfuric acid, nitric acid and potassium nitrate were purchased from BDH; all the chemicals were AnalaR grade except BGY which was laboratory reagent grade and used without further purification. Double distilled and deionized water was used throughout the experiment.

Experimental procedures

Fenton process's: The experiments were carried out batch wise. Dye solution of 40 mg L^{-1} was adjusted to $\text{pH} = 3.0 \pm 0.1$ with NaOH or HCl as required. A known amount of H_2O_2 and Mohr's salt ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) were added to 500 ml of the solution. A magnetic stirrer was used for stirring in order to achieve homogeneous mixture.

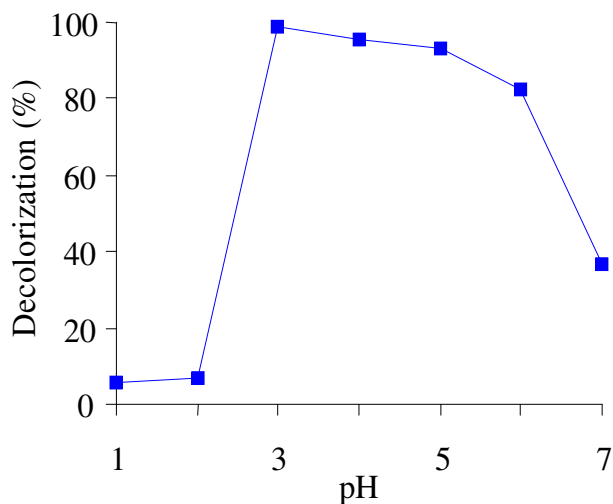
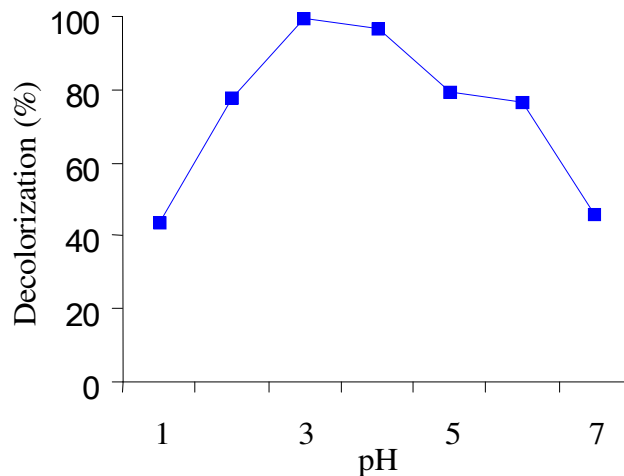
Photo-Fenton's process: All experiments were carried out in a batch photoreactor. The radiation source was a low-pressure mercury lamp, UV light source (254 nm) (PASCO Scientific) was used for photolysis. The intensity of the light source was measured using spectroradiometer (model IL 1700) with a light source (model XPS 200, Solar light Co.). The lamp was positioned apart from cylindrical Pyrex vessel in such a way that the distance between the light source and the surface of the solution was 10 cm. The vessel was surrounded by circulating water jacket to control the temperature. In each experiment, a known amount of H_2O_2 and Mohr's salt was added to the requisite volume of dye solution and desired pH of the solution was adjusted with NaOH or HCl as required. A magnetic stirrer was used in order to achieve a homogeneous mixture.

Analytical methods

The pH of the solution was measured by using a pH meter (digital, Orion, Japan). Sample solutions were withdrawn at certain time intervals for spectrophotometric analysis. The decolorization of BGY was measured with UV-visible spectrophotometer (Shimadzu 160 A, Japan) at 416 nm. Chemical structure and absorption maxima are shown in Table 1. Calibration plot based on Beer-Lambert's law was established by relating the absorbance to the concentration. The absorbance at 416 nm due to the color of the dye solution is used to monitor the decolorization of the dye. Mineralization was investigated by monitoring the evolving of CO_2 gas (turned transparent lime water to milky white). Moreover, a peak was observed at 224 nm after assuming decolorization when water was reference but this peak disappeared when nitrate solution was reference. All the experiments were performed at 29°C .

Table 1. Chemical structure and absorption maxima of BGY.

Name	Chemical structure	λ_{max} (nm)
Brilliant golden yellow (BGY)		416 224

**Figure 1.** Effect of pH on decolorization of BGY in Fenton process (Color online). (BGY)=20 mgL⁻¹, H₂O₂= 400 mgL⁻¹, Fe(II) = 0.05 mmol.**Figure 2.** Effect of pH on decolorization of BGY in photo-Fenton process (Color online). BGY = 20 mgL⁻¹, H₂O₂ = 400 mgL⁻¹, Fe(II) = 0.05 mmol, *I*₀ = 30.3 W m⁻²

RESULTS AND DISCUSSION

Effect of pH

Solution pH affects the oxidation of organic substances both directly and indirectly. The Fenton and photo-Fenton reactions are strongly pH dependent. The pH values influence the generation of hydroxyl free radicals and thus enhances oxidation efficiency. The effects of pH on Fenton and photo-Fenton processes are shown in Figures 1 and 2, respectively. A maximum decolorization of 99% at 20 min was observed in Fe(II)/H₂O₂ process at pH = 3.0 and decolorization of 99% within 5 min was observed in UV/Fe(II)/H₂O₂ system at the same pH value. As can be seen from Figures 1 and 2, the color removal efficiency increases from 5.6 to 99.0% in Fenton process after 20 min and from 43.6 to 99.2% in photo-Fenton process after 5 min as a function of solution pH from 1 to 3. On the other hand, increasing pH value from 3 to 7 decreases the color removal from 99.0 to 36.45% and 99.2 to 45.8% for Fenton and photo-Fenton processes, respectively. These results are in good agreement with

those reported in previous studies (Titus et al., 2004).

At a pH above 4, the decolorization decreases because iron starts to precipitate as hydroxide (Base and Mesmer, 1986). Additionally, the oxidation potential of hydroxyl radical was known to decrease with increasing pH and at a pH below 2, hydrogen peroxide can stay stable, probably solvating a proton to form a hydroxonium ion (H₃O₂⁺). The hydroxonium ion makes H₂O₂ electrophilic to enhance its stability and presumably to reduce significantly the reactivity with Fe(II) ion (Ghaly et al., 2001; Zhao et al., 2004). Therefore, the amount of hydroxyl radicals would decrease and as a result the removal efficiency decreases. Deng et al. (2000) also found higher degradation rate for dye wastewater by Fenton's and photo-Fenton's processes in a pH range 3.0 - 4.0.

Effect of the initial H₂O₂ concentration

The effect of H₂O₂ concentration on decolorization of BGY by Fenton and photo-Fenton processes are shown in Figures 3 and 4, respectively. The results indicate that

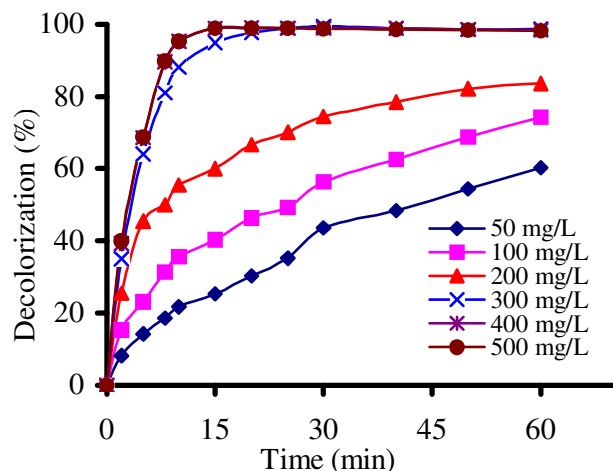


Figure 3. Effect of the initial concentration of H_2O_2 in Fenton process (Color online). $[\text{BGY}] = 20 \text{ mg L}^{-1}$, $[\text{Fe(II)}] = 0.05 \text{ mmol}$, $\text{pH} = 3$.

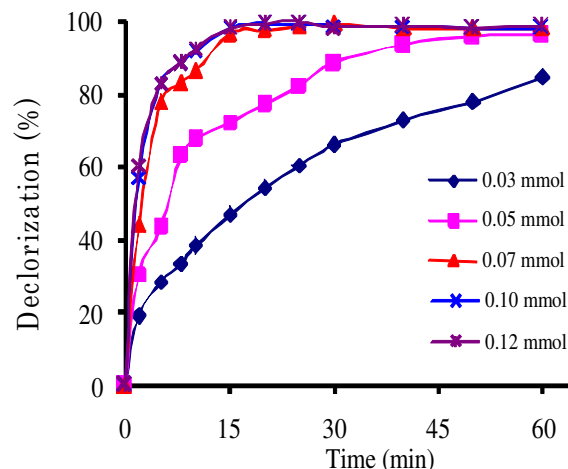


Figure 5. Effect of the initial concentration of Fe(II) in Fenton process (Color online). $[\text{BGY}] = 20 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg L}^{-1}$, $\text{pH} = 3$.

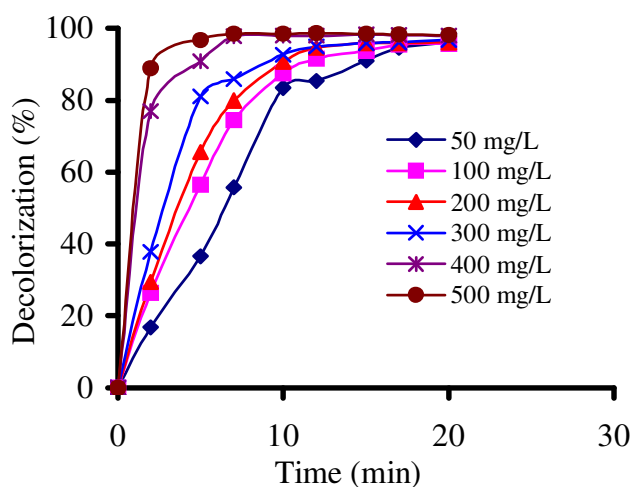
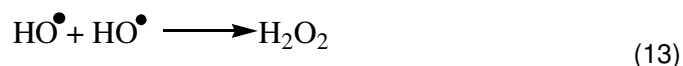
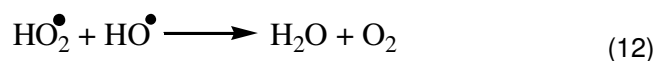
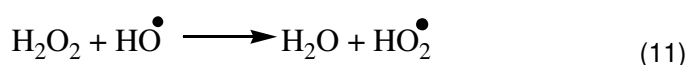


Figure 4. Effect of the initial concentration of H_2O_2 in photo-Fenton process (Color online). $[\text{BGY}] = 20 \text{ mg L}^{-1}$, $[\text{Fe(II)}] = 0.05 \text{ mmol}$, $\text{pH} = 3$, $I_0 = 30.3 \text{ W m}^{-2}$.

the decolorization of BGY was increased by increasing the concentration of H_2O_2 . This is because excess H_2O_2 produce more hydroxyl free radicals resulting in increase in percentage of decolorization. With increasing H_2O_2 concentration from 50 mg L^{-1} to 500 mg L^{-1} , the decolorization percentage increases but above these ranges improvement was not obvious. This may be due to recombination of hydroxyl radicals and also reactions occur between hydroxyl radicals and H_2O_2 , contributing to the HO^\bullet scavenging capacity (reactions (11)-(13)) (Ghaly et al., 2001).



Therefore, it can be concluded that H_2O_2 should be added at an optimum concentration to achieve the highest decolorization rate; hence 400 and 300 mg L^{-1} of H_2O_2 concentrations appear to be an optimum dosage for 40 mg L^{-1} of BGY in Fenton and photo-Fenton processes, respectively.

Effect of Fe(II) concentration

Iron in its ferrous (Fe(II)) or ferric forms Fe(III) acts as photo-catalyst and requires a working pH below 4.0 (Xu et al., 2003). Concentration of Fe(II) ion is one of the main parameters to influence the Fenton's and photo-Fenton's processes. Figures 5 and 6 show the effect of Fe(II) ion concentration on the decolorization of BGY.

As can be seen from Figures 5 and 6, decolorization rate of BGY significantly increased with the increasing of concentration of Fe(II) ion and reaches a maximum at 0.1 mmol and then decreases upon further addition of Fe(II) ion in both the processes. In Fenton's process, generation of hydroxyl free radicals from H_2O_2 depends on the concentration of Fe(II) ion but in photo-Fenton's process, that depends on both the concentration of Fe(II) and intensity of light. Addition of Fe(II) ion above 0.1 mmol in the present study, did not affect the decolorization rate. The decolorization of BGY began to decrease when the concentration of Fe(II) ion was higher than 0.1 mmol.

It is known that Fe(II) had catalytic decomposition effect

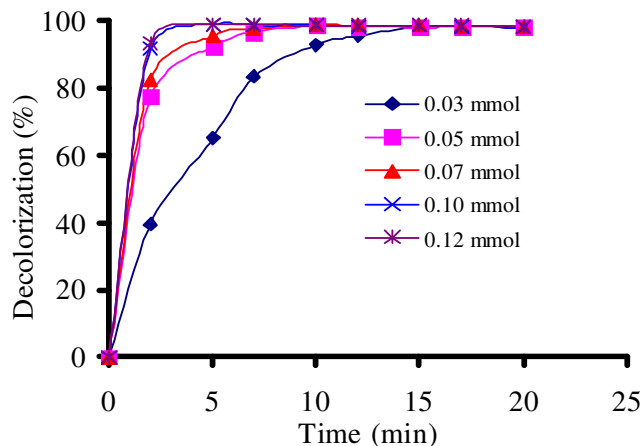


Figure 6. Effect of the initial concentration of H_2O_2 in photo-Fenton process (Color online). $[\text{BGY}] = 20 \text{ mg L}^{-1}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg L}^{-1}$, $\text{pH} = 3$, $I_0 = 30.3 \text{ W m}^{-2}$.

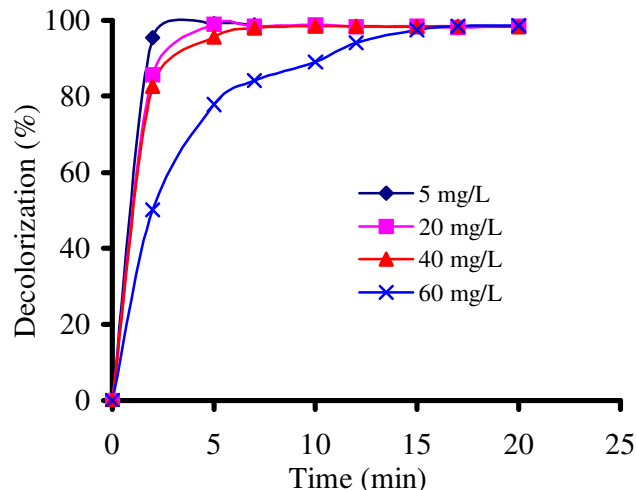


Figure 8. Effect of the initial concentration of BGY in photo-Fenton process (Color online). $[\text{Fe(II)}] = 0.05 \text{ mmol}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg L}^{-1}$, $\text{pH} = 3$, $I_0 = 30.3 \text{ W m}^{-2}$.

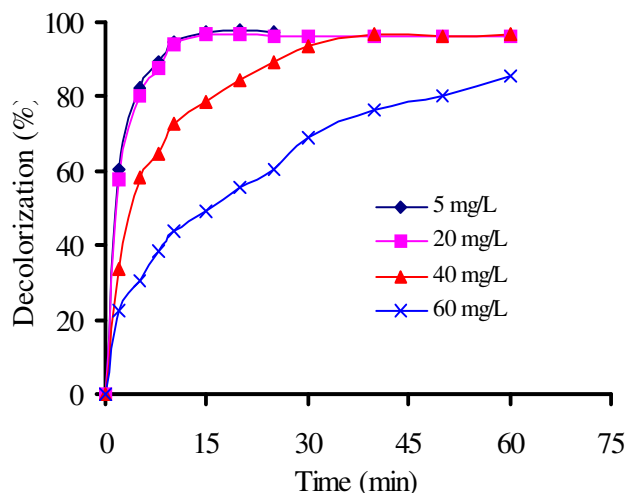
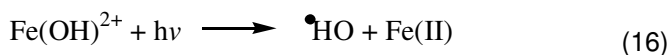


Figure 7. Effect of the initial concentration of BGY in Fenton process (Color online). $[\text{Fe(II)}] = 0.05 \text{ mmol}$, $[\text{H}_2\text{O}_2] = 400 \text{ mg L}^{-1}$, $\text{pH} = 3$.

on H_2O_2 . When Fe(II) concentration is increased, the catalytic effect also accordingly increases and when its concentration is higher, a significant amount of Fe(III) is produced. Then Fe(III) undergoes a reaction with hydroxyl ions to form Fe(OH)^{2+} which has strong absorption tendency and as a result the strength of UV light would decrease (reactions (14)-(16)) (Zhao et al., 2004; Titus et al., 2004).



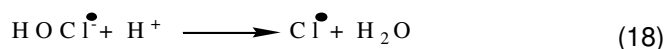
Effect of initial BGY concentration

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of the dye. Therefore, the effect of dye concentration on the decolorization efficiency was investigated at various BGY concentrations. The results are shown in Figures 7 and 8. It was observed that the decolorization decreased with increased in initial concentration of the dye in both the Fenton and photo-Fenton processes. It can be considered that when the initial concentration of the dye is increased, the hydroxyl radical concentrations remain constant for all dye molecules and the removal rate decreases. Once the concentration of the dye increased, it also caused more dye molecules to adsorb light photons and ultimately the efficiency of photodegradation decreases significantly. (Daneshvar et al., 2005).

Effect of salt concentration

Sodium chloride is usually found in wastewater from textile and dyeing industries. Consequent, a study was carried out to investigate the effects of sodium chloride on degradation of BGY. In the absence of salt, the dye decolorization was 99% in less than 20 and 5 min for Fenton and photo-Fenton processes, respectively. The addition of NaCl (200 mg L^{-1}) to the dye solution caused only a 2% decrease in decolorization. The small decrease in the decolorization is due to the scavenging effect of chloride ion as shown in Reactions (17) and (18) (Muruganandham and Swaminathan, 2004). Further addition of the salt did not reduce the decolorization rate considerably. It is known that the percentage of

chloro-/chloro-oxo species of iron (FeCl_2^+ , FeOCl_2^- , FeCl^{2+} , FeCl_3 etc) in dye solution is much higher compared to hydroxy-species ($\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_3$ etc) at high chloride concentration and at low pH (e.g., pH = 3) (Base and Mesmer, 1986) which might show increasing trend of decolorization of the dye, on the other hand, chloride ion acts as a scavenger of hydroxyl radicals. Therefore, eventually no effect of the chloride ion on the decolorization was observed upon addition of excess amount of sodium chloride in dye solution.



The decolorization/degradation results indicate that the dye seems to be completely mineralized after degradation. The aqueous solution after complete mineralization is expected to contain Na^+ , NO_3^- and SO_4^{2-} (Li et al., 1997). The carbon dioxide gas, one of the products of mineralization has been detected. Moreover, after mineralization, the aqueous solution showed a peak at about 224 nm as distilled water as reference but no peak was observed at the same wave length (224 nm) when very dilute solution of nitrate salts (e.g., KNO_3) was used as reference.

Conclusions

The results show that Fenton and photo-Fenton are powerful methods for degradation of BGY, but in comparison, photo-Fenton process is more efficient. The results indicated that the degree of decolorization of BGY was strongly affected by the initial concentrations of the dye, $\text{Fe}(\text{III})$, H_2O_2 and value of pH. The optimum conditions for mineralization of BGY in Fenton and photo-Fenton processes were observed at pH = 3.0, with an initial concentration of 0.1 mmol $\text{Fe}(\text{II})$ and initial H_2O_2 concentration of 400 mg L^{-1} for Fenton process and 300 mg L^{-1} for photo-Fenton process with a dye concentration 40 mg L^{-1} .

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