DECOLOURIZATION OF AZO DYE ORANGE G BY FENTON AND PHOTO-FENTON PROCESSES IN AQUEOUS SOLUTION

CHENINI HALIMA, DJEBBAR KAMEL[*], BAGHRICHE OUALID, SEHILI TAHAR and BOUCHOUL ABDELKADER[a]

Laboratoire des Sciences et Technologie de l'Environnement,
Université Mentouri Constantine, ALGÉRIE
[a]Laboratoire de chimie moléculaire, du contrôle de l'environnement et de mesures physico-chimiques,
Université Mentouri Constantine, ALGÉRIE.
E-mail: bouchoul@caramail.com Tel/Fax: (213) (31)818497,

ABSTRACT

The degradation of an azo dye orange G (OG) in aqueous solution by Fenton oxidation process has been investigated. The effects of different reaction parameters such as initial pH, the initial hydrogen peroxide concentration ($[H_2O_2]_o$), the initial ferrous concentration ($[Fe^{2+}]_o$) on dye decolourization are demonstrated in detail. The optimum pH for both; Fenton and photo-Fenton reactions in this study are about pH 3.0. The decolourization rate of OG distinctly increases with the increasing amount of Fe^{2+}. The optimal levels of H_2O_2 required for the process are also examined. High levels of H_2O_2 appear to reduce dye decolourization. The experimental results showed that the photo-Fenton process was an effective process for the degradation of OG.

Key words: AOPs, Azo dye, Orange G, Decolourization, Photo-Fenton, Fenton.

INTRODUCTION

Azo dyes, aromatic moieties linked together by azo (-N=N-) chromophores, represent the largest class of dyes used in textile-processing and other industries. The release of these compounds into the environment is undesirable, not only because of their colour, but also because many azo dyes and their breakdown products are toxic and/or mutagenic to life. It has been estimated that colorant release to the environment without proper treatment represents 15 % of total world production or 150 tons per day[1]. These commercial dyes are also resistant to light degradation, the action of atmospheric gases,

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[*] Author for correspondence; E-mail : kedjebbar@yahoo.fr ; Tel/Fax: (213) (31)818867

acids and bases. The same properties make these dye stuffs difficult to degrade or decolorize.

Various physical, chemical and biological pre-treatment, main treatment and post treatment techniques can be employed to remove colour from dye containing wastewaters[2–8]. Physicochemical techniques include membrane filtration, coagulation / flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic mineralization, electrolysis, biological techniques include bacterial and fungal biosorption and biodegradation in aerobic, anaerobic, anoxic or combined anaerobic/aerobic treatment processes. advanced oxidation (chlorination, bleaching, ozonation, Fenton oxidation and photocatalytic oxidation). Several factors determine the technical and economic feasibility of each single dye removal technique:

(i)   Dye type

(ii)   Wastewater composition

(iii)   Dose and costs of required chemicals

(iv)   Operation costs (energy and material)

(v)   Environmental fate and handling costs of generated waste products

Chemical oxidation is an attractive technique for the purification of water contaminated with organic compounds, especially with those which are not susceptible to undergo biological degradation. Advanced oxidation processes (AOPs) are mostly based on the generation of highly reactive radical species (especially the hydroxyl radical $HO^{\bullet}$) that can react with a wide range of compounds and also with compounds and that are otherwise difficult to degrade, e.g. dye molecules. There are several methods for generating hydroxyl radicals: Fenton (H_2O_2/Fe^{2+}) and photo- Fenton ($H_2O_2/Fe^{2+}/UV$). A drawback for application of Fenton or photo- Fenton oxidation for the treatment of the usually highly alkaline- textile-processing wastewaters is that this process requires low pH[2–5]. At higher pH, large volumes of waste sludge are generated by the precipitation of ferric iron salts and the process loses effectiveness as H_2O_2 is catalytically decomposed to oxygen[9]. Fenton or photo-Fenton oxidation will furthermore be negatively affected by the presence of radical scavengers and strong chelating agents in the wastewater. Malik and Saha[10] reported that the removal rate is strongly dependent on the initial concentration of the dye, Fe^{2+} and H_2O_2. Muruganandham and Swaminathan[11] have carried out studies where similar results were obtained. They suggested a pH of 3 is the optimum pH for Fenton and photo-Fenton processes.
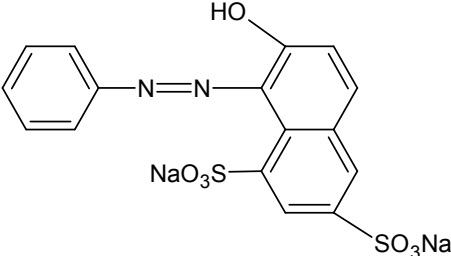
The aim of the present work is to analyze the feasibility of decolourization of OG by Fenton and photo-Fenton processes. The effects of pH, dosages of hydrogen peroxide and ferrous ions, which affect the efficiency of Fenton and photo-Fenton reactions in reactive OG oxidation were also investigated

EXPERIMENTAL

Material

The azo dye, OG was used without further purification. Molecular structure of OG in non-hydrolysed form is illustrated in Table 1. Iron (II) sulphate hexahydrate was provided by Labosi puriss (> 99 %). Aqueous solution containing 33 wt % of hydrogen peroxide (purity 99.9 %) was obtained from prolabo. pH of the reaction solutions was adjusted using HCl and NaOH solutions. Bidistilled water was used throughout this study.

Table 1. Chemical structure and absorption maxima of OG

Name	Chemical structure	λ_{max} (nm)
Orange G		476 nm

Experimental procedures

All experiments have been carried out in a cylindrical reactor in quartz (100 cm of length and 2 cm of internal diameter) surrounded symmetrically by three externals low-pressure mercury lamps (germicides) emitting mainly at 254 nm. Ventilator located at the bottom of the enacting part assure the cooling of the system. The entire system is placed in a cylindrical enclosure. A predetermined quantity of $FeSO_4$ and H_2O_2 was dripped into the reactor. Samples were taken from the reactor periodically using a pipette, and were immediately analyzed.

Analytical methods

The UV-vis spectra of dye were recorded from 200 to 800 nm using a UV-vis spectrophotometer (Unicam Heliosα) with a spectrometric quartz cell (1 cm path length).

The maximum absorbance wavelength (λ_{max}) of OG is 476 nm. Therefore, the concentration of the dye in the reaction mixture at different reaction times were determined by measuring the absorption intensity at λ_{max} = 476 nm and a calibration curve. The photodegradation efficiency of OG was defined as follows:

$$\text{Photodegradation efficiency (\%)} = (1- C_t / C_o) \times 100\ \%$$

Where the C_o is the initial concentration of OG, and C_t is the concentration of OG at reaction time t (min).

RESULTS AND DISCUSSION

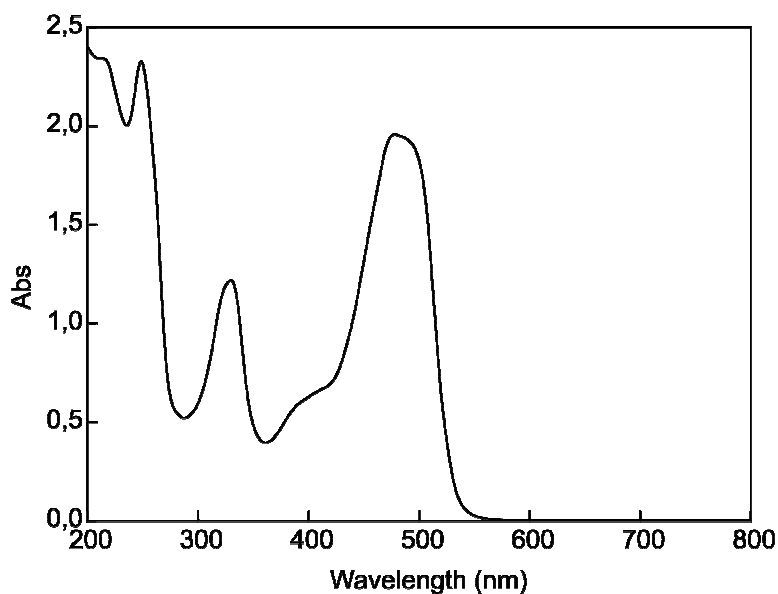Absorption spectra of the dye solutions with the concentration of 50 mg/L is shown in Fig. 1.

Fig. 1: UV absorption spectra of OG

The maximum absorption wavelength (λ_{max}) for orange G was located at 476 nm. This peak accounts for the orange colour of solutions and can be attributed to the n—π^* transition of the non-bonding nitrogen electrons to the antibonding π^* group orbital of the double bond system and it is used to monitor the decolourisation of dye. In the UV region, there is a second group of bonds, with an increasing absorbency towards lower wavelengths (nm), characteristic of aromatic rings.

Effect of pH

Fenton oxidation is highly pH dependent process. Under proper pH range, H_2O_2 will be decomposed by Fe^{2+} to generate hydroxyl radical. Fig. 2 illustrates the variation of concentration of OG (depradation efficiency) for photo-Fenton oxidation as a function of time at different pH. The experiments were carried out in pH range 1.3 - 9.5.
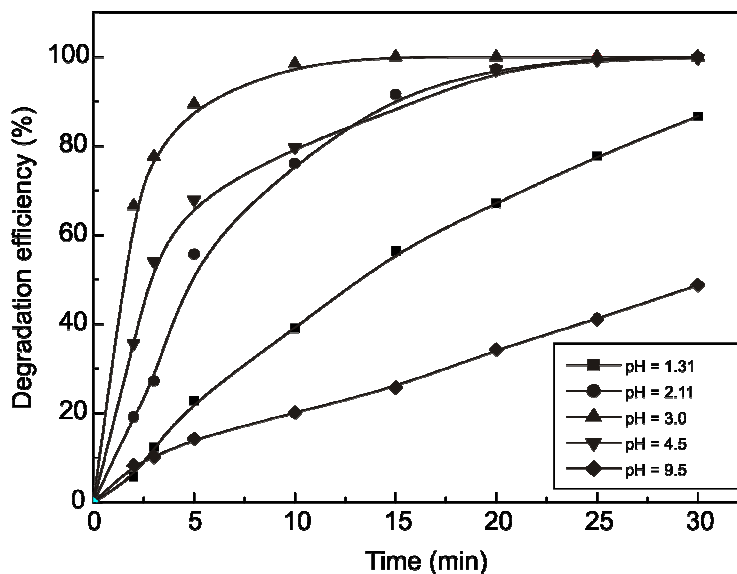

Fig. 2: Effect of pH on the degradation of OG during photo-Fenton oxidation treatment. Reaction conditions: $[dye]_o = 50$ mg/L, $[H_2O_2]_o = 10^{-2}$ M, $[Fe^{2+}]_o = 5 \times 10^{-5}$ M

The results indicated that the degradation of OG was significantly influenced by the pH of the solution and the optimal solution pH was observed at about 3. At pH 1.3, the dye decolourisation rate dramatically decreased revealing that the scavenging effect of the $^\bullet$OH by H^+ is severe at low pH. At a pH higher than 3, it also showed low dye decolourization efficiency. It may be explained by the hydrolysis of Fe^{3+} in the solution to reduce $^\bullet$OH producing rate.

Effect of initial H_2O_2 concentration

To render the Fenton and photo-Fenton processes competitive with other processes, it is essential that their applications represent a low cost operation, which basically implies a better control of H_2O_2 dosage.
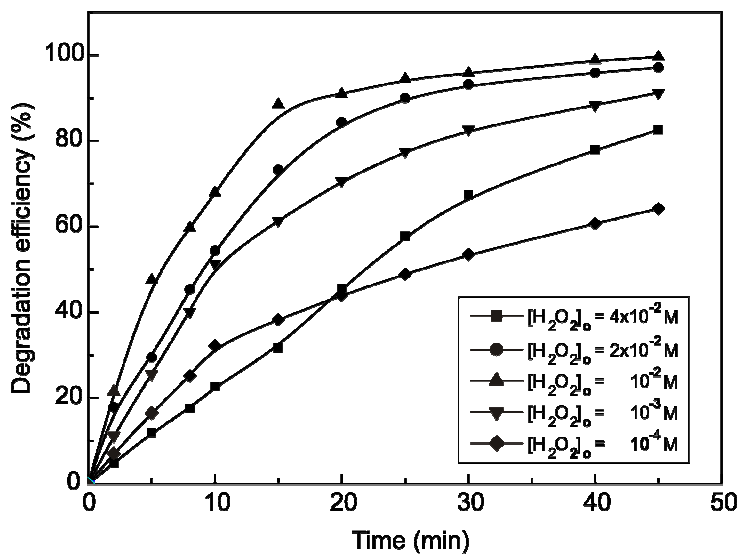
Fig. 3: Effect of initial H_2O_2 concentration on the degradation of OG during Fenton oxidation treatment. Reaction conditions: $[Dye]_o$ = 50 mg/L, $[Fe^{2+}]_o$ = 5.0 x 10^{-5} M, pH = 3.0
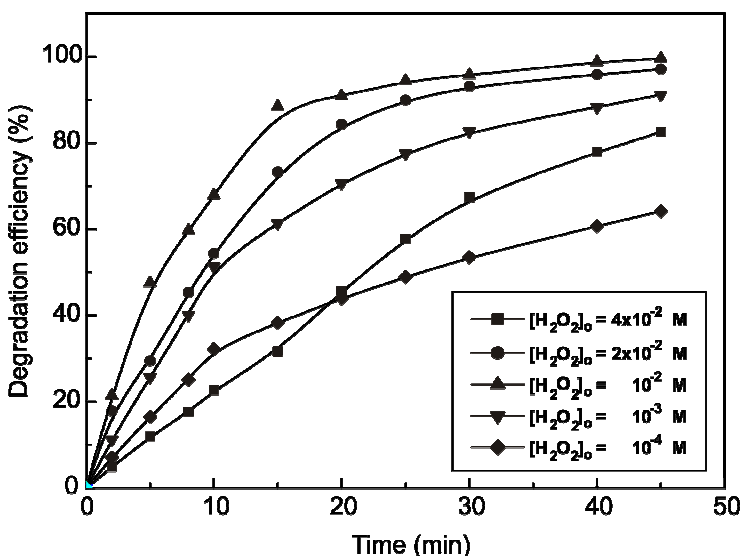

Fig. 4. Effect of initial H_2O_2 concentration on the degradation of OG during photo-Fenton oxidation treatment. Reaction conditions: $[Dye]_o$ = 50 mg/L, $[Fe^{2+}]_o$ = 5.0 x 10^{-5}, pH =3.0

Fig. 3 and 4 show the concentration of OG as a function of reaction time when different concentration of H_2O_2 was used. As it can be seen, the effect of increasing $[H_2O_2]_o$ from 10^{-4} M to 10^{-2} M was first positive for the degradation of OG. This is due to the oxidation power of Fenton process, which was improved with increasing $^{\bullet}OH$ radical amount in solution obtained from the decomposition of increasing hydrogen peroxide. However, with continuous increasing of the $[H_2O_2]_o$ to 2×10^{-2} M and 4×10^{-2} M, the degradation rate of OG has been reduced. This may be explained by the fact that the very reactive $^{\bullet}OH$ radical could be consumed by H_2O_2 and results in the generation of less reactive $^{\bullet}OOH$ radical (Eq. 1)[12,13]:

$$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}OOH + H_2O \qquad \ldots(1)$$
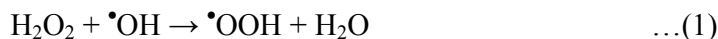
Generally, the degradation rate of organic compounds increases as the H_2O_2 concentration increases until a critical H_2O_2 concentration is achieved. However, when a concentration higher than the critical concentration is used, the degradation rate of organic compounds will decrease as a result of the so-called scavenging effect[14, 15].

It can be postulated that H_2O_2 should be added at an optimum concentration to achieve the best degradation; hence, 10^{-2} M of H_2O_2 concentration appears to be an optimum dosage for 50 mg/L of OG in Fenton and photo-Fenton processes.

Effect of the initial Fe^{2+} concentration

Amount of ferrous ion is one of the main parameter to influence the Fenton and photo-Fenton processes. To elucidate the role of initial concentration of Fe^{2+} ($[Fe^{2+}]_o$) on the degradation of OG, a series of experiments were conducted with different $[Fe^{2+}]_o$ ranging from 10^{-5} M to 10^{-4} M. The results for Fenton and photo-Fenton processes are shown in Fig. 5 and 6.

From the experimental results, it can be seen that decolourisation rate of OG distinctly increased with the increasing amount of Fe^{2+}. In the Fenton process, addition of Fe^{2+} from 10^{-5} to 10^4 M increases colour removal from 14.10 % to 96.72 % at 10 min whereas in photo-Fenton process, the increase is from 82.92 % to 99.93 % for the same time. This is because more $^{\bullet}OH$ radicals are produced with the increase of $[Fe^{2+}]_o$ according to Eq. (2).
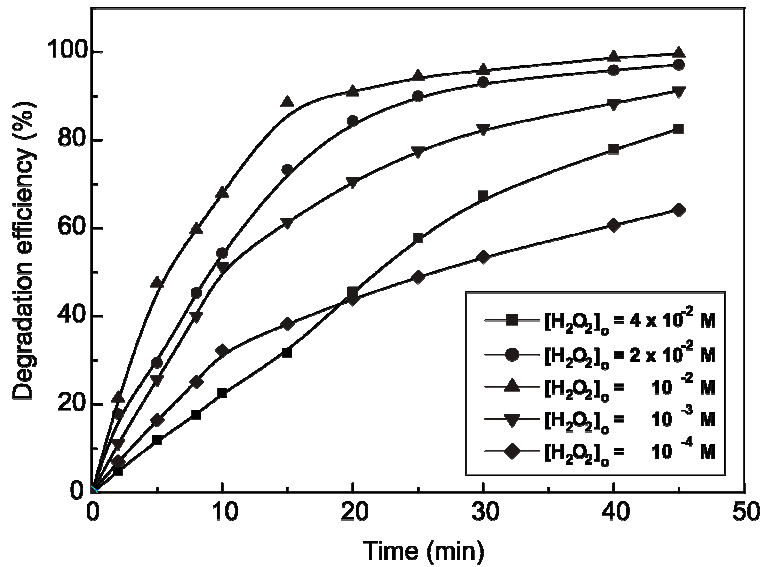
$$Fe^{2+} + H_2O_2 + H^+ \rightarrow \quad Fe^{3+} + {}^{\bullet}OH + H_2O_2 \qquad \ldots(2)$$

Fig. 5: Effect of initial Fe²⁺ concentration on the degradation of OG during Fenton oxidation treatment. Reaction conditions: [[Dye]ₒ = 50 mg/L, [H₂O₂]ₒ = 10⁻² M, pH = 3.0
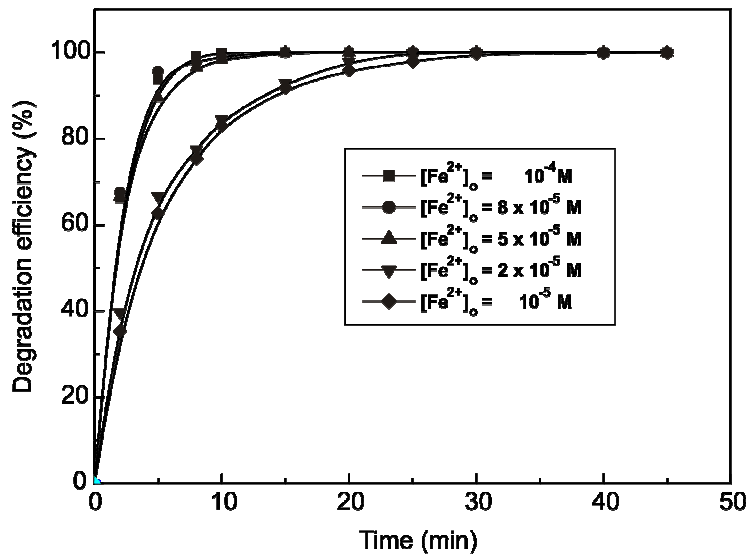

Fig. 6: Effect of initial Fe²⁺ concentration on the degradation of OG during photo-Fenton oxidation treatment. Reaction conditions: [[Dye]ₒ = 50 mg/L, [H₂O₂]ₒ = 10⁻² M, pH = 3.0

The results show that there is almost no difference in the degradation efficiency between 5×10^{-5} M and 10^{-4} M of Fe^{2+} for the dye decolourisation during 10 min. reaction time for photo-Fenton process. Moreover, many studies have revealed that the use of a much higher concentration of Fe^{2+} could lead to the self scavenging of $^\bullet OH$ radical by Fe^{2+} (Eq. 3)[16] and induce the decrease in degradation rate of pollutants.

$$^\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad \qquad \ldots(3)$$

Comparison of photodecolourization between Fenton and photo-Fenton process

Fig. 7 and 8 show the decolourization efficiencies of OG with the variation of H_2O_2 and Fe^{2+}, respectively for a reaction time of 10 min.
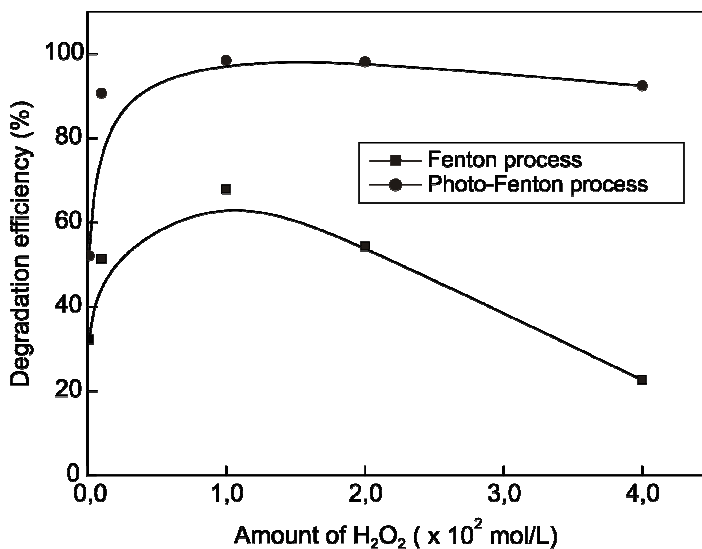

Fig. 7: Comparison between Fenton and photo-Fenton process (λ_{irr} = 254 nm) after 10 min. Reaction conditions: [Dye]$_o$ = 50 mg/L, [Fe^{2+}]$_o$ = 5.0 x 10^{-5} M, [H$_2$O$_2$]$_o$ = variable, pH = 3.0

The results indicated that the extent of decolourization increases until the optimum value of 10^{-2} M for H_2O_2, either for Fenton or photo-Fenton process. For a bigger value of H_2O_2, it is clear from Fig. 7 that the decolourization efficiencies of OG decreases. This is due to the fact that at higher H_2O_2 concentration, scavenging of OH radicals will occur (Eq. 1); thus, decreasing the decolourization. As shown in Fig. 8, the photodegradation efficiency of OG distinctly increased with increasing amounts of Fe^{2+}. Hence, in both the processes, the value of the concentration of Fe^{2+} (10^{-4} M) can be used as optimum dosage.
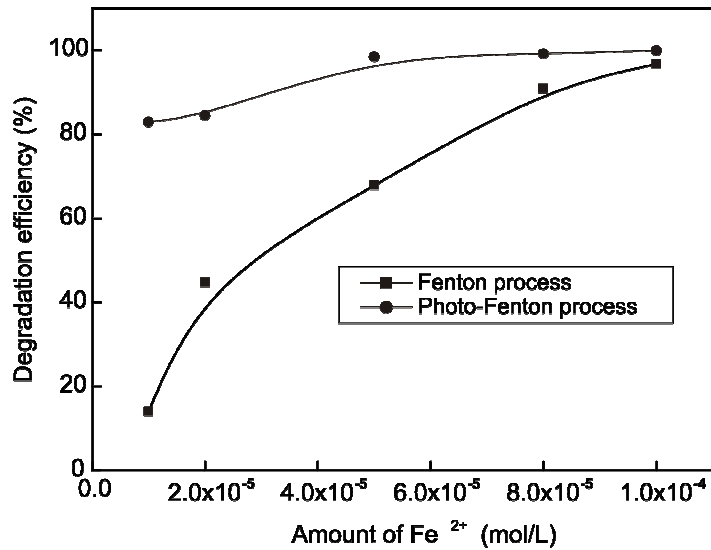
Fig. 8: Comparison between Fenton and photo-Fenton process (λ_{irr} = 254 nm) after 10 min. Reaction conditions: $[Dye]_o$ = 50 mg/L, $[H_2O_2]_o$ = 10^{-2} M, $[Fe^{2+}]_o$ = variable, pH = 3.0

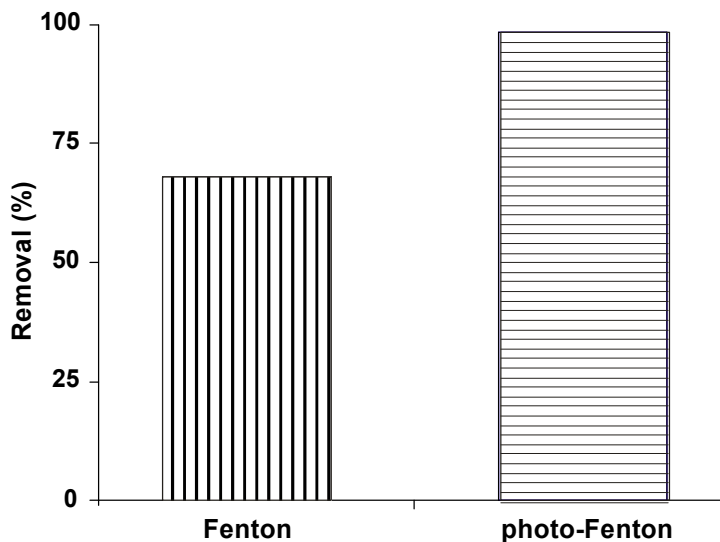**Fig. 9: Removal percentage of decolourisation for Fenton and photo-Fenton processes. $[Dye]_o$ = 50 mg/L, $[H_2O_2]_o$ = 10^{-2} M, $[Fe^{2+}]_o$ = 5×10^{-4} M, pH =3,**

The experimental results in Fig. 9 showed that photo-Fenton process presents a percent removal higher than Fenton process. The efficiency of the photo-Fenton process is due to the increase in hydroxyl radical production in the process. It is possible to include that the UV lamp is very useful in Fenton process to aid the dye decolourisation [11, 17].

CONCLUSIONS

The results showed that Fenton and photo-Fenton processes provide good performance in the decolourization treatment of OG, but photo-Fenton process is more efficient. It has been found that pH, initial concentration of H_2O_2 and Fe^{2+} are the main factors that influence the degradation of OG. The optimum conditions for the decolourization were observed at pH = 3.0; with an initial Fe^{2+} concentration of 10^{-4} M and an initial H_2O_2 concentration of 10^{-2} M with a dye concentration of 50 mg/L. Although H_2O_2 is essential to generate $^{\bullet}OH$, very high levels of H_2O_2 could reduce decolourisation because of scavenging effect.

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