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Article

Comparing Photo-Fenton Degradation of Malachite Green Using Fe^{II} and Fe^{III} Salts Under UVA Light Irradiation

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Photo-Fenton degradation of pollutants involves the reaction of Fe^{II} salts with hydrogen peroxide under ultraviolet A irradiation, which significantly enhances the process. The reaction with Fe^{III} salts is slower and therefore less studied. In this work, we compared the efficiencies of Fe^{III} and Fe^{II} salts in the photo-Fenton degradation of malachite green (MG), a known carcinogen. We optimized the concentration of reagents and the pH to achieve the highest MG degradation with the lowest amounts of reagents. Complete MG degradation was achieved under 2 h for the Fe^{III} system and 1 h for Fe^{II}, reaching a high degree of mineralization, even in the presence of chloride and sulfate anions. The results show that although slower, the reaction with Fe^{III} salts allows significant photodegradation of MG under mild reaction conditions.

Keywords: photo-Fenton, malachite green, ferrous, ferric, degradation

Introduction

Industrial wastewater is an important source of toxic and non-biodegradable contaminants that can potentially reach natural water sources. The environmental effects of such hazardous pollutants are a major concern worldwide, especially considering the water scarcity problems that are foreseen for future decades.[1] Therefore, the development and application of effective wastewater treatments has been an important research topic over the last few decades.[2] Among the many treatments available, advanced oxidation processes (AOPs) have gained much interest in the last several years due to their great potential for the detoxification of a wide range of organic pollutants.[1-4] AOPs are based on the generation of highly reactive species such as hydroxyl radicals ($OH^\bullet$), which allow the efficient oxidation of organic matter.[1-4] An efficient way of generating these radicals is the Fenton reaction,[5-8] originally described in 1894.[9] In the Fenton reaction, Fe^{II} ions are oxidized to Fe^{III} ions by hydrogen peroxide with the generation of $OH^\bullet$ radicals (equation 1).[7,10] These radicals oxidize pollutants in the presence of oxygen leading to breakdown products (equation 2).

$$Fe^{II} + H_2O_2 \rightarrow Fe^{III} + OH^- + OH^\bullet \quad k = 63\text{-}76\ L\ mol^{-1}\ s^{-1} \tag{1}$$

$$Pollutant + OH^\bullet / O_2 \rightarrow Oxidation\ products \tag{2}$$

Although very efficient, the fact that the reaction is fast generates homogeneity problems in large-scale treatment plants due to mixing problems. The reaction with Fe^{III} ions is much slower compared to Fe^{II} (equations 3 and 4).[7,10] The generation of Fe^{II} ions as a product of these reactions leads to the Fenton reaction (equation 1) and pollutant degradation (equation 2).

$$Fe^{III} + H_2O_2 \rightarrow Fe^{II} + H^+ + HO_2^\bullet \quad k = 0.001\text{-}0.01\ L\ mol^{-1}\ s^{-1} \tag{3}$$

$$Fe^{III} + HO_2^\bullet \rightarrow Fe^{II} + H^+ + O_2 \tag{4}$$

Enhanced degradation of organic pollutants is achieved when the Fenton reaction is used in combination with ultraviolet A (UVA) irradiation,[5,8,11-13] due to the photolysis of photoactive Fe^{III} species, which generates a second hydroxyl radical (equation 5) in a cyclic manner.

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{II} + OH^\bullet\ \lambda < 450\ nm \tag{5}$$

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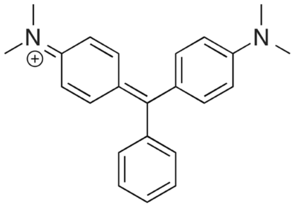
There are many studies for the degradation of organic pollutants using Fe^{II},[5-8] and fewer studies using Fe^{III} compounds.[14-17] Therefore, we studied the photodegradation efficiency for a model compound focusing on the comparison of Fe^{III} and Fe^{II} salts under UVA irradiation. We chose the organic pollutant malachite green (MG) (Scheme 1) because it is widely used in the industry as a dye and fungicide, in spite of being related to carcinogenesis risks.[18-22] The degradation of MG has been studied by a wide range of other AOPs including H_2O_2/UV,[23] H_2O_2/microwave,[24] TiO_2/UV,[25] Fenton,[15,26-28] sono-Fenton,[29] bio-Fenton,[30] and electro-Fenton.[31,32] Even though some reports have dealt with the visible light-assisted degradation of MG (sometimes called photo-Fenton), the mechanism is different than the reaction shown on equations 1-5. In the former, the dye is excited instead of the $Fe(OH)^{2+}$ complex inducing an electron-transfer reaction.[7,10,33-35] In the present work, the main parameters for the photo-Fenton degradation of MG were studied and optimized for Fe^{III} and Fe^{II} salts, and the processes were compared. The effects of UVA irradiation and added anions were also investigated.



Scheme 1. Structure for malachite green (MG).

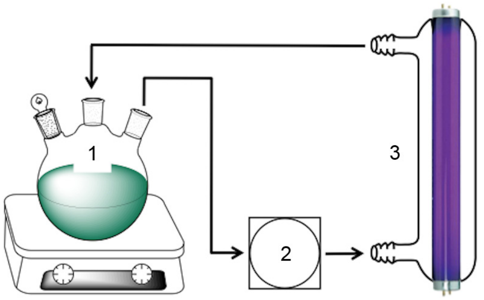
Experimental

Materials

Malachite green oxalate (C.I. 42000), ferric chloride hexahydrate, hydrogen peroxide (30% m/m), sulfuric acid, anhydrous sodium sulfate and ferrous sulfate heptahydrate were purchased from Merck. Sodium hydroxide and sodium chloride were obtained from Riedel-de Haën. All reagents were of analytical grade and were used as received. Fe^{III} and Fe^{II} stock solutions (10 g L^{-1} of iron) were prepared in 1 mol L^{-1} sulfuric acid, stored at 4 ºC in the dark and replaced with fresh solutions frequently. Deionized water was used for experimental runs and dilutions.

Photo-reactor

A cylindrical pyrex glass photo-reactor of in-house design (57 cm long, 51 mm external diameter and 30 mm internal diameter) with recirculation (Scheme 2) was used for the photodegradation experiments. A Phillips TLD 18W/08 black light was employed as the light source. The lamp spectrum is centered at 365 nm, with a wavelength distribution between 300 and 410 nm, according to the manufacturer. The photon flux that enters the reactor at this wavelength was estimated to be 4×10^{-5} Einstein m^{-2} s^{-1}, determined by ferrioxalate actinometry.[36] A peristaltic pump (model EW-07543-30, Masterflex L/S, Cole-Parmer) was used for the recirculation of the solution. The flow system was assembled with glass tubing. The reactor volume was 545 mL. Samples for analysis were taken from the mixer. After an experiment was conducted, the system was cleaned with 2 mol L^{-1} sulfuric acid, rinsed with water and methanol, and air-dried before starting a new experimental run.



Scheme 2. Representation of the photo-degradation system used in this study. (1) Mixer, (2) peristaltic pump, and (3) photo-reactor with UVA light source. The arrows indicate the direction of the flow.

Photodegradation procedure

In each experiment, 1 L of aqueous 10 mg L^{-1} MG solution was prepared and the solution was placed in a pyrex container under continuous stirring. The required amount of Fe^{III} or Fe^{II} were added from a stock solution and the required amount of hydrogen peroxide was immediately added from the concentrated 30% reagent. The pH was adjusted to the desired value adding drops of 2 mol L^{-1} sulfuric acid or sodium hydroxide, if necessary. The solution was homogenized and immediately pumped into the photo-reactor (flow rate of 23 mL min^{-1}). The time at which the solution enters the reactor was considered to be time zero. Subsequently, the absorbance of the mixture was measured at regular time intervals. Volume changes due to the mixing were minimal due to the use of concentrated stock solutions. All the experiments were carried out at 22 ± 2 °C and were conducted at least twice under identical conditions with a variation of less than 2% for consecutive measurements.

Analytical methods

The samples were analyzed immediately to avoid further reaction. A Cecil UV-Vis spectrophotometer was used to measure the absorbance of the dye at 618 nm. The pH of the solution was measured at the start of the run using a pHmeter (Orion Research Digital Ionalyzer, model 501) with a glass electrode. The chemical oxygen demand (COD) was determined by the dichromate titrimetric method as described elsewhere.[37] Before the COD was measured, the samples were pretreated with NaOH and heated at 40 °C to remove any residual H_2O_2 as described.[13] The stock hydrogen peroxide solution was standardized regularly by permanganimetric titration.

The degradation efficiency for each sample was calculated according to equation 6, where A_0 corresponds to the initial absorbance at time zero and A_t to the final absorbance at time t (min).

$$\text{MG degradation} = \left(1 - \frac{A_t}{A_0}\right) \times 100 \qquad (6)$$

Results and Discussion

Optimization of the degradation of MG using Fe^{III}/H_2O_2/UVA

Initial experiments were performed with a 10 mg L^{-1} MG solution to determine the optimal measurement conditions for the degradation of MG in the photo-reactor. This concentration was chosen in order to achieve a high degree of degradation in a manageable time for the experimental runs. Control experiments showed that the loss of MG due to absorption on the glass of the photo-reactor was less than 2% after 1 h of recirculation in the absence of UVA light. Additionally, the irradiation of MG with UVA light in the absence of both Fe^{III} and H_2O_2 did not produce any significant decrease in the concentration of MG, which agrees with the fact that the quantum yield for the direct decomposition of MG at 365 nm is very low ($\Phi = 1.1 \times 10^{-5}$).[38] The initial parameters used for the photodegradation of a 10 mg L^{-1} MG solution were 2 mg L^{-1} Fe^{III}, 30 mg L^{-1} H_2O_2 and pH 2.7. Under these conditions, 100 min after the start of the experiment, more than 90% degradation was achieved (Figure 1). Subsequently, the degradation efficiency of a 10 mg L^{-1} MG solution after 100 min was measured as a function of the initial concentration of Fe^{III}, H_2O_2 and the pH to optimize the reaction conditions.

Effect of initial hydrogen peroxide concentration for the Fe^{III}/H_2O_2/UVA system

Experimental runs were conducted at different initial concentrations of H_2O_2 in the range 0-500 mg L^{-1} for fixed initial concentrations of Fe^{III} of 10 mg L^{-1} and a pH of 2.7.

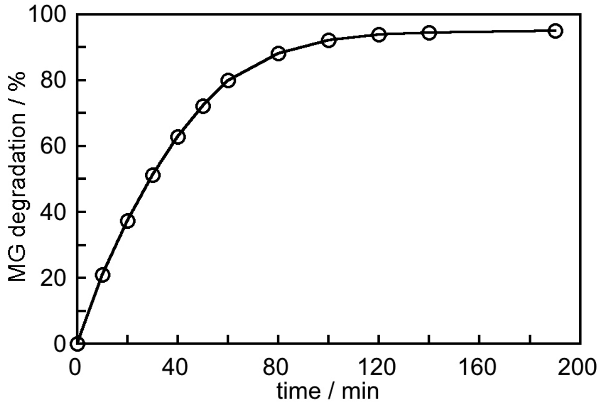


Figure 1. Degradation of MG (10 mg L^{-1}) using the Fe^{III}/H_2O_2 system under UVA light irradiation. Initial conditions were: $[Fe^{III}] = 2$ mg L^{-1}, $[H_2O_2] = 30$ mg L^{-1}, pH = 2.7.

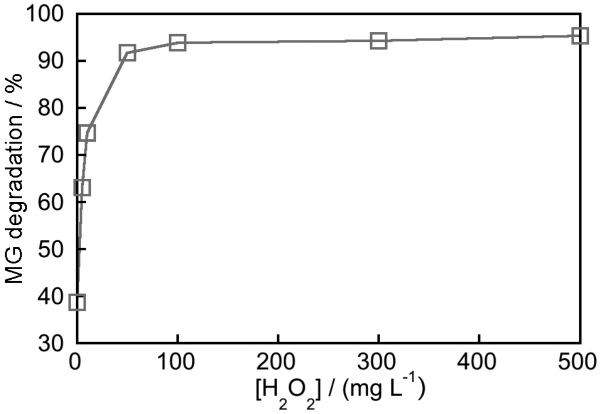


Figure 2. Effect of the initial concentration of H_2O_2 on the degradation of MG (10 mg L^{-1}) using the Fe^{III}/H_2O_2 system under UVA light irradiation. The concentration of Fe^{III} and the pH of the solution were kept constant for all the measurements ($[Fe^{III}] = 10$ mg L^{-1}, pH = 2.7). The total time for the each experiment was 100 min.

Figure 2 shows that the degradation of MG increased with the increase in the concentration of H_2O_2, reaching 94% at a concentration of 100 mg L^{-1} H_2O_2. Further increase of the concentration of the oxidant did not have an effect on the degradation efficiency. Therefore, the optimal concentration of H_2O_2 was taken as 100 mg L^{-1}. As seen from the initial point of the curve, an important degradation is observed in the absence of H_2O_2, suggesting that Fe^{III} itself can induce the degradation of MG, although with low efficiency. This result agrees with the fact that at pH 2.7, the predominant Fe^{III} specie is $Fe(OH)^{2+}$,[5,7,8] whose photolysis generates $OH^{\bullet}$ radicals as shown in equation 5, accounting for the partial degradation of MG. The presence of H_2O_2 allows Fe^{III} to be constantly regenerated, constituting a catalytic cycle that leads to removal of MG. No inhibition was observed due to the excess of H_2O_2 even up to 3000 mg L^{-1} (not shown) as opposed to the behavior described by other authors in the absence of UVA light, due to the scavenging of hydroxyl radicals by H_2O_2. The plateau observed at high concentrations of H_2O_2 is likely due to the amount of Fe^{III}, which limits the reaction.

Effect of initial Fe^{III} concentration for the Fe^{III}/H_2O_2/UVA system

Figure 3 shows the variation in the degradation efficiency of MG with the initial concentration of Fe^{III}. Experiments were conducted in the range 0-25 mg L^{-1} of Fe^{III}, keeping the concentration of H_2O_2 constant at 100 mg L^{-1} and pH 2.7.

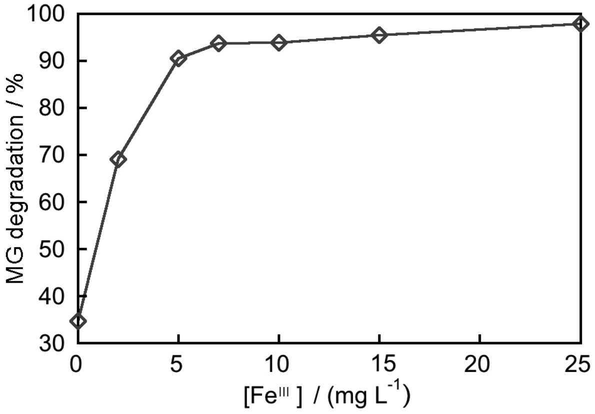


Figure 3. Effect of the initial concentration of Fe^{III} on the degradation of MG (10 mg L^{-1}) using the Fe^{III}/H_2O_2 system under UVA light irradiation. The concentration of H_2O_2 and the pH of the solution were kept constant for all the measurements ($[H_2O_2]$ = 100 mg L^{-1}, pH = 2.7). The total time for the each experiment was 100 min.

In the absence of Fe^{III}, the degradation of MG was 35%, increasing significantly as the initial concentration of Fe^{III} increased, reaching 94% at 7 mg L^{-1}. The reasons for the observed degradation of MG in the absence of Fe^{III} are not clear. The direct photolysis of H_2O_2 is a possibility,[23] although very unlikely, since this compound does not absorb light significantly above 260 nm.[7,10] An enhanced photodecomposition of MG in the presence of H_2O_2 could be a possibility considering that MG undergoes photoinduced electron-transfer if directly excited by the light,[39] and H_2O_2 could act as an electron acceptor.[40] In the range from 7 to 15 mg L^{-1} of Fe^{III}, the degradation of MG increased only slightly (95% at 15 mg L^{-1} Fe^{III}). Therefore, we used 7 mg L^{-1} Fe^{III} as the optimal concentration. At 25 mg L^{-1}, 98% of the MG is degraded. However, during the course of the irradiation, $Fe(OH)_3$ precipitates out of the solution, which could cause problems in the operation of the photo-reactor. The formation of this gel-like precipitate could account for the additional removal of MG from the solution through flocculation.

Effect of the initial pH for the Fe^{III}/H_2O_2/UVA system

Figure 4 shows the variation in the degradation of MG as a function of the initial pH. The studies were performed in a narrow range between pH 2.3 and 3.6, fixing the other parameters to the optimized values found in the previous studies. Below pH 2.3, the initial absorbance of MG was significantly decreased due to the formation of the colorless acidic form of MG,[41] and, hence, no studies were performed below this lower limit.

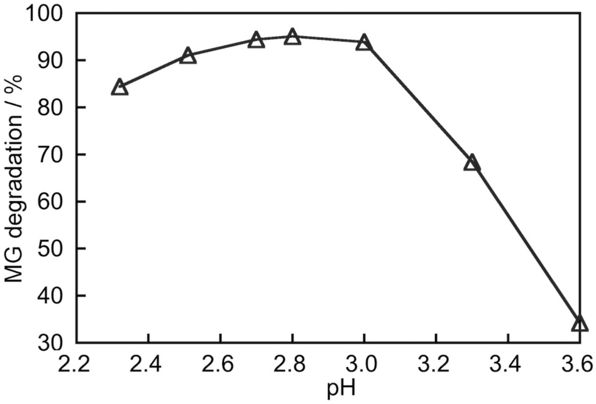


Figure 4. Effect of the initial pH of the solution on the degradation of MG (10 mg L^{-1}) using the Fe^{III}/H_2O_2 system under UVA light irradiation. The concentration of Fe^{III} and H_2O_2 were kept constant for all the measurements ($[Fe^{III}]$ = 10 mg L^{-1}, $[H_2O_2]$ = 100 mg L^{-1}). The total time for the each experiment was 100 min.

As seen in Figure 4, the degradation of MG reaches high values (> 94%) in a very narrow pH range between 2.7 and 3.0. The maximum was observed at pH 2.8 (95%). Above pH 3.0 the degradation decreases abruptly due the precipitation of Fe^{III}; for instance, only 34% of MG is degraded at pH 3.6. Below pH 2.7, the degradation of MG decreases slightly probably due to the formation of unreactive species such as $Fe(H_2O)_6^{3+}$ as has been proposed before.[7,13] The optimum initial pH for the reaction was well within the range reported by others.[5-8,10] Even though only the initial pH was measured for the reaction, the pH usually drops during the degradation as carboxylic acids form as oxidation products.

Optimized parameters for the degradation of a 10 mg L^{-1} MG solution using the Fe^{III}/H_2O_2/UVA system were 7 mg L^{-1} Fe^{III}, 100 mg L^{-1} H_2O_2 and pH 2.8. This is equivalent to a mass ratio of 1:0.7:10 for MG:Fe^{III}:H_2O_2.

Effect of UVA light irradiation for the Fe^{III}/H_2O_2 system

The irradiation of a Fenton-like system with UVA light has been shown to accelerate the decomposition of organic compounds considerably due to the enhanced generation of $OH^{\bullet}$ radicals (equation 5). To assess the role of UVA light on the degradation of MG, the experiments were conducted under optimized conditions and the degradation was followed in the absence of light (dark reaction) and under UVA light irradiation.

As shown in Figure 5, the irradiation of the system with UVA light considerably accelerates the degradation of MG. After 120 min of irradiation the degradation of MG reaches more than 99%. It is noteworthy that this percentage is higher than achieved before optimization (Figure 1). At the same time, the degradation of MG in the dark is only 43%. The degradation of MG observed in the dark can be explained by the slow formation of Fe^{II} by the reaction between Fe^{III} and H_2O_2 (equation 3), possibly enhanced by the generation of hydroperoxyl radicals (equation 4).[7,10] The formation of Fe^{II} in the presence of H_2O_2 results in the Fenton reaction (equation 1), explaining the degradation of MG even in the dark.[7,10]

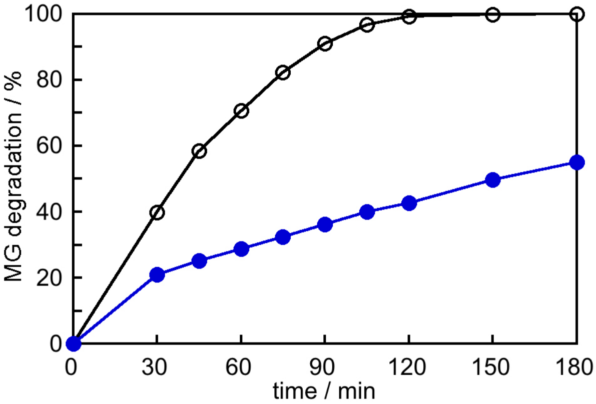


Figure 5. Degradation of MG (10 mg L^{-1}) using the Fe^{III}/H_2O_2 system in the presence (open black circles) and absence (closed blue circles) of UVA light under optimized conditions ($[Fe^{III}] = 7$ mg L^{-1}, $[H_2O_2] = 100$ mg L^{-1}, pH = 2.8).

Effect of added anions for the Fe^{III}/H_2O_2/UVA system

The presence of anions such as sulfate and chloride, often present in contaminated waters, can significantly inhibit the degradation of organic compounds by Fenton-like processes due to the formation of less reactive iron complexes.[17,27,42] Figure 6 shows the effect of different concentrations of SO_4^{2-} and Cl^- anions on the degradation of MG. Since MG is mostly used as a dye in industrial processes and as a fungicide in aquaculture, the concentrations of the anions were chosen in the range of the concentrations found in local tap water and/or seawater.

As shown in Figure 6, the presence of SO_4^{2-} decreased somewhat the degradation of MG. However, even at a high concentration of SO_4^{2-} the decrease is small and a high degradation percentage is achieved after 2.5 h. The decrease in the degradation rate observed in the presence of SO_4^{2-} anions is due to the formation of the non-reactive iron complexes $FeSO_4^+$ and $Fe(SO_4)_2^-$, decreasing the concentration of the active iron species.[17] On the contrary, the presence of Cl^- did not alter the degradation of MG. This result was not expected since a strong inhibition of the degradation of organic molecules by the Fenton reaction has been reported.[17,42-44] In the presence of Cl^-, Fe^{III} ions can be complexed forming the species $FeCl^{2+}$ and $FeCl_2^+$.[17,42-44] Additionally, Cl^- can scavenge $OH^\bullet$ radicals.[17,42-44] The photolysis of the $FeCl^{2+}$ complex generates $Cl^\bullet$ atoms leading to the formation of $Cl_2^{\bullet-}$ radicals according to equations 7 and 8, which are less reactive than hydroxyl radicals. It has been reported that the inhibition effect of chloride can be abated at pH around 3 for the photo-Fenton process,[44] which is close to the optimal pH used in this study.

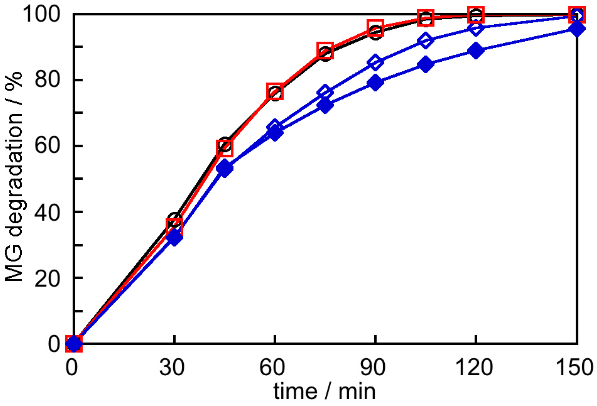


Figure 6. Degradation of MG (10 mg L^{-1}) using the Fe^{III}/H_2O_2 system under UVA light irradiation in the absence of added anions (black circles) and in the presence of added sulfate anions (blue diamonds, open for 275 mg L^{-1} and closed for 2700 mg L^{-1}) and chloride anions (red squares, 400 mg L^{-1}) under optimized conditions ($Fe^{III} = 7$ mg L^{-1}, $H_2O_2 = 100$ mg L^{-1}, pH 2.8).

$$FeCl^{2+} + h\nu \rightarrow Fe^{II} + Cl^\bullet \quad (7)$$

$$Cl^\bullet + Cl^- \rightarrow Cl_2^{\bullet-} \quad (8)$$

It is important to note that both sulfate and chloride do not have an important effect on the degradation of MG by the photo-Fenton process, which is opposed to the Fenton reaction, where these anions have a significant effect on the degradation of organic pollutants.[13,17,27,42] This fact might be an important reason to prefer light-assisted processes to the degradation in the dark.

Removal of the COD during the degradation of MG

There is a large amount of evidence for the mineralization of organic compounds by the photo-Fenton process.[7,8,10] To assess the mineralization of MG, the COD removal was determined. Discrepancies between the disappearance of MG by the Fenton oxidation and the decrease in the COD have been reported due to the formation of refractory compounds.[27]

The COD removal was determined simultaneously with spectrophotometric measurement of MG.

Figure 7 shows that the COD removal increases as the solution is being discolored, indicating that MG is being mineralized in the system. The fact that the COD removal is lower than the disappearance of the color is likely due to the formation of colorless degradation products.[27,45] The products of degradation of MG by $OH^{\bullet}$ radicals have been reported in the past and include *N*,*N*-dimethylaniline, 4-dimethylaminophenol, 4-methylamino benzophenone, 4-dimethylaminobenzophenone, benzeneacetic acids and 4-hydroxybenzoic acid.[32,34,45] Between 1 h and 2 h of irradiation, the COD does not change very much, possibly indicating the formation of refractory compounds. After this point, the COD removal increases, with a tendency to reach the levels achieved for the degradation of MG. Complete discoloration of a highly colored 50 mg L^{-1} MG solution (A >> 2) is achieved under 2 h with relatively mild reaction conditions, while the COD reduction reaches 70% after 3 h, which is relatively high considering the formation of intermediate products that are usually harder to oxidize.

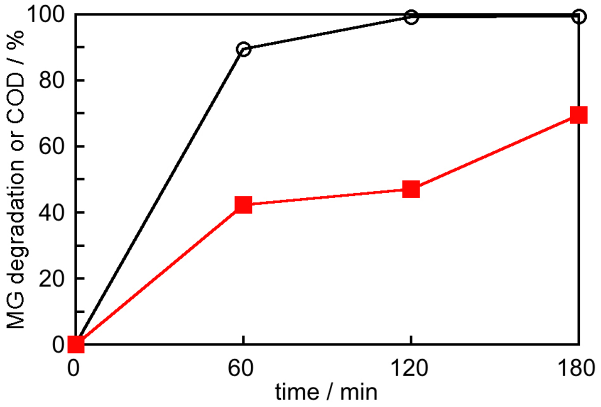


Figure 7. Comparison between the degradation of MG (black circles) and the removal of the COD (red squares) using the Fe^{III}/H_2O_2 system under UVA light irradiation. The conditions of the experiment were modified to optimize the determination of the COD ([MG] = 50 mg L^{-1}, [Fe^{III}] = 15 mg L^{-1}, [H_2O_2] = 300 mg L^{-1}, pH = 2.8).

Optimization of the degradation of MG using Fe^{II}/H_2O_2/UVA

The optimization of the degradation of MG using the Fe^{II}/H_2O_2/UVA system was carried out in the same manner as the experiments shown above for Fe^{III} (see Figures S1, S2 and S3 on the Supplementary Information). The trends in the effect of Fe^{II}, H_2O_2 and pH were the same as those described for Fe^{III} and are consistent with the literature discussed above. Optimized parameters for the degradation of a 10 mg L^{-1} MG solution using the Fe^{II}/H_2O_2/UVA system were 10 mg L^{-1} Fe^{II}, 100 mg L^{-1} H_2O_2 and pH 2.7. This is equivalent to a 1:1:10 mass ratio for MG:Fe^{II}:H_2O_2.

Comparison between Fe^{III} and Fe^{II} systems under optimized conditions

Classic Fenton reaction uses Fe^{II} as a catalyst to generate the hydroxyl radicals, although several sources of iron ions have been used in the past.[17,46] To compare the relative efficiencies of the degradation of MG by using Fe^{II} and Fe^{III} salts, we used the optimized parameters found in the experiments above. It must be noted that the mass ratios and the pH were only slightly different for Fe^{III} and Fe^{II} processes. As discussed above, there are few studies where these two processes have been compared, especially for the photo-Fenton process under UVA light irradiation.

Figure 8 shows that the degradation of MG under optimized conditions using Fe^{II} is twice as fast as the system with Fe^{III}. The difference is noticeable from the beginning of the reaction, for instance, at 30 min the degradation achieved with Fe^{II} is 69%, while at the same time the degradation using Fe^{III} is 40%. When using Fe^{II}, the complete degradation of MG is achieved in 1 h, compared to 2 h for Fe^{III}. This is due to the fact that the rate of reaction with hydrogen peroxide is faster for Fe^{II} (equation 1) compared to Fe^{III} (equation 3). It must be pointed out that the optimized process with Fe^{II}, although faster, requires a 30% increase in iron mass. This may be an important factor to consider when scaling up the degradation process. Additionally, the fact that the reaction with Fe^{III} is slower might allow a more homogeneous mixing with the contaminated effluent. In this context, the combination of Fe^{III} process with UVA light irradiation is fundamental to achieve a high degree of degradation and mineralization. As shown here, the implementation of a flow photo-reactor allows treating larger volumes and the UVA light irradiation (if needed) could be easily replaced with solar irradiation.

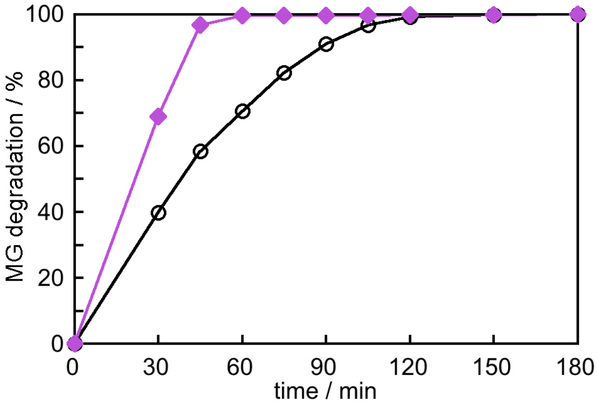


Figure 8. Comparison between the degradation of MG (10 mg L^{-1}) using the Fe^{III}/H_2O_2/UVA (black circles) and the Fe^{II}/H_2O_2/UVA (purple diamonds) systems under optimized conditions ([Fe^{III}] = 7 mg L^{-1} or [Fe^{II}] = 10 mg L^{-1}, [H_2O_2] = 100 mg L^{-1}, pH = 2.8 for Fe^{III} or pH = 2.7 for Fe^{II}).

Conclusions

The degradation of MG by the photo-Fenton process using Fe^{III} and Fe^{II} salts was very efficient, resulting in a high degree of decoloration and mineralization of the dye. It must be pointed out that the use of a flow reactor allowed the irradiation of a higher volume of solution than in regular lab-scale experiments, which points to the applicability of this method to real contaminated effluents. Optimized parameters for the degradation of MG using Fe^{III} and Fe^{II} salts were similar, indicating that the source of iron ions can be switched depending on the application. Although the system with Fe^{II} requires slightly higher masses of reagents than Fe^{III}, the degradation is twice as fast, indicating that the ferrous salt is a better choice for faster degradations. Even so, the efficiency of the Fe^{III} system is still high compared with other available wastewater treatments, allowing the degradation of a highly colored solution in 2 h under mild reagent and irradiation conditions.

Supplementary Information

Effect of pH, Fe^{II} and H_2O_2 concentration for the Fe^{II}/H_2O_2/UVA system are available free of charge at http://jbcs.sbq.org.br as PDF file.

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