

DEGRADATION OF 3-METHYLPHENOL PHOTOINDUCED BY THE COMPLEX Fe (III)-CITRATE IN THE PRESENCE OF HYDROGEN PEROXIDE

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Abstract

The study of 3-methylphenol (m-cresol) photodegradation has been achieved in two system, UV / Fe(III)-Cit and UV / Fe(III)-Cit / H₂O₂ in natural (pH = 6.5). The presence of H₂O₂ in UV / Fe(III)-Cit system reduce the efficiency of m-cresol degradation at low concentration, however for the high level of H₂O₂ the process is improved. The optimal concentration of H₂O₂ was found to be 5 mM. This can be probably explained by a low Fe(II) formation of in this system. The result shows in the both systems that the acidic media is favorable for this kind of reaction. The Comparison between the aquacomplexes and Fe(III)-Cit complex in the presence or absence of H₂O₂ have confirmed that the best condition of m-cresol degradation was achieved with the addition of H₂O₂. Additionally, the use of 1.0 % of tertibutanol as a scavenger confirmed the intervention of hydroxyl radicals in the m-cresol photodegradation.

Keywords: Fe(III)-Cit Complex, H₂O₂, m-cresol, [•]OH radical, photodegradation.

Résumé

La dégradation du m-crésol (3-méthylphénol) photoinduite par le complexe organique Fe(III)-Cit en solution aqueuse a été réalisée dans deux systèmes UV / Fe(III)-Cit et UV / Fe(III)-Cit / H₂O₂. La présence de H₂O₂ dans le système UV / Fe(III)-Cit réduit l'efficacité de la dégradation de m-crésol à pH naturel (pH = 6,5) à faible concentration cependant pour des concentrations plus forte le processus est amélioré. La concentration optimale de H₂O₂ est évalué à 5 mM. Ceci peut être expliqué par la faible formation de Fe(II) dans le système UV / Fe(III)-Cit / H₂O₂. La photodégradation de m-crésol dépend également du pH, elle est nettement meilleure en milieu acide dans les deux systèmes. La comparaison entre les aquacomplexe de Fe(III) et le complexe Fe(III)-Cit en présence et en absence du H₂O₂ a montré que la meilleure dégradation du m-crésol est obtenue en présence du H₂O₂. Outre cela, l'utilisation de 1,0 % du tertibutanol en tant que piège à radicaux hydroxyle a confirmé l'intervention de [•]OH dans la photodégradation du m-crésol.

Mots clés : Complexe Fe(III)-Citrate, H₂O₂, m-crésol, Radicaux hydroxyle, Photodégradation.

ملخص

التخلص من 3- ميثيل فينول باستعمال تقنية التحفيز الضوئي في وجود الانظمة UV / Fe(III)-Cit و UV / Fe(III)-Cit / H₂O₂ والتي تمت دراستها في وسط مائي. لقد أظهرت النتائج أن سرعة تفكك و اختفاء الملوث تتحسن بوجود المعقد Fe(III)-Cit إضافة H₂O₂ إلى هذا المعقد ينقص من فعالية تفكك الملوث عند درجة الحموضة الطبيعية (pH = 6.5). وهذا يمكن أن يفسر على الأرجح إلى كمية الحديد الثنائي القليلة الناتجة التركيز الأفضل لبيروكسيد الهيدروجين هو 5 ميلي مول. كما وجد أن عملية التفكك الضوئي مرتبطة بدرجة الحموضة. ولقد أكدت النتائج أن تفكك 3- ميثيل فينول يكون سريع في الوسط الحمضي بالنسبة للنظامين. إضافة H₂O₂ إلى كل من المعقد Fe(III)-Cit و Fe(III) يحسن من سرعة تفكك و اختفاء 3- ميثيل فينول عند pH = 2.8. إضافة 1 % من الترسبيوتانول يؤكد تدخل الجذور الهيدروكسيلية في التفكك الضوئي لهذا الملوث.

الكلمات المفتاحية : المعقد Fe(III)-Cit، 3- ميثيل فينول، جذور الهيدروكسيل، التفكك الضوئي.

1. Introduction

Iron is present under a variety of forms in water ranging from soluble to colloidal and particulate species. But, most of the iron in natural waters exists in the form of insoluble ferric oxides and (hydr)oxides [1]. The concentration of dissolved iron is very low and most of the dissolved iron is associated with strong organic ligands in natural waters.

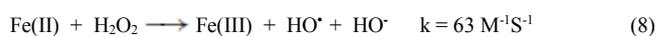
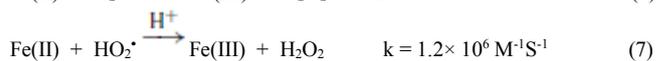
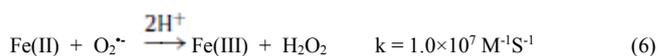
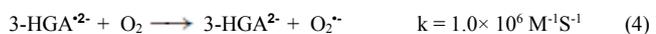
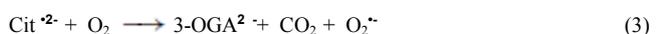
Iron dissolution will depend upon the pH of the medium, but also the presence of iron complexing agent such as (poly) carboxylic acid, which are ubiquitous chemical species in the environment. Their concentrations can reach several milligrams per liter of soil solution. Organic acids can increase the dissolution of iron in natural aquatic environment. Fe(III)-polycarboxylate complexes typically have higher molar absorption coefficients in the near UV and visible regions, higher quantum yields and broader working pH ranges than simple aquacomplexes (Fe(III)-OH) [2-5]. Fe(III) is capable of being present as the Fe(III)-carboxylate species at pH > 4 in the presence of carboxylate ligand, which outcompetes the complexation of hydroxide ions with Fe(III) in aqueous solution [6].

It is well known that Fe(III)-carboxylate complexes undergo ligand-to-metal charge transfer (LMCT) process upon irradiation and photochemically generate reactive oxygen species (ROS) such as HO₂[•]/O₂^{•-}, H₂O₂, and [•]OH [7-9]. It is known that organic pollutants were attacked by hydroxyl radical and mineralized efficiently in above photochemical system.

Literature reports that the presence of carboxylic acids such as oxalic, citric or tartaric acids with Fe(III) and UVA radiation improves the water elimination rates of organics such as dyes [10-12], herbicides [13-15], pesticides [16,17], surfactants [18,19], benzene [20], phenols [21,22] and other hydrocarbons [23] among other [24].

Due to its strong UV absorption and high cumulative stabilization constants (log β = 14.29), Fe(III)-citrate exhibits appreciable photoreactivity at near neutral pH and it has the potential for application in wastewater treatment [25]. In addition, Fe(III)-cit complexes have been demonstrated to be excellent Fe(III)-photocatalysts with low toxicity and high photoreactivity [26-28].

Photolysis of Fe(III)-citrate complex may result in oxidative degradation of the citrate ligand and reduction of the metal center to Fe(II). In addition, the Fe(III)-citrate complex may play a significant role in the photochemical generation of reactive species such as O₂^{•-}, HO₂[•], [•]OH and H₂O₂ (Eqs. (1)-(7))[2]. The Fe(II) and H₂O₂ so produced may react via the so-called Fenton reaction to produce hydroxyl radicals (Eq. (8)).



OGA: 1,3-acetonedicarboxylic acid and
HGA: 3-hydroxyglutaric acid.

The degradation of a variety of organic contaminants has been examined and attributed to attack by hydroxyl radicals generated on photolysis of Fe(III)-citrate species [25,26,29-32].

In the present study, we have investigated the degradation of m-cresol in water using Fe(III)-Citrate / UV system, focusing on the role of H₂O₂ whether it is initially added or not. Many factors, such as pH value and initial concentrations of H₂O₂, affected on the degradation were evaluated.

2. Materials and methods

2.1. Materials

Ferric perchlorate nonahydrate (Fe(ClO₄)₃ · 9H₂O), Carlo Erba, pur and citric acid (Synth) was used as ligand. 3-Methylphenol (m-cresol) was supplied by Prolabo (purity greater than 99 %). NaOH (98 %) and methanol (99 %) was provided by Carlo Erba Reagenti. HCl (37 %) Merck, ammonium acetate (98 %), acetate sodium (99 %), acetic acid (99.5 %) and sulfuric acid (98 %) provided by Panreac. 1,10 phenantroline Fluka (> 99 %), perchloric acid (98 %), tertiobutanol, (99 %) and hydrogen peroxide (30 %), were provided by Prolabo, All chemicals were of analytical grade and used without further purification. The solutions were prepared using ultrapure water.

2.2. Irradiation procedure

The irradiation experiments were carried out in a self-constructed Pyrex photoreactor (diameter of 3 cm) with a cooling water jacket placed in an elliptical stainless steel chamber. A fluorescent lamp (Philips HPW 125), which dominantly emits radiation at 365 nm was used. The lamp and the reactor are on both focal axes of the elliptical chamber. The solution (usually 50 mL) was continuously magnetically stirred with a magnetic bar during irradiation to insure its homogeneity. Control experiments showed that no degradation of m-cresol occurred in Fe(III)-Cit complex without irradiation in this reactor. The reaction temperature was kept at 20 ± 1 °C by cycling water. The pH was measured with a pH-meter type (HANNA) equipped with a combined glass electrode. The pH meter is first calibrated with buffer solutions (pH = 4, pH = 7 and pH = 10).

2.3. Analytical methods

The disappearance of 3-Methylphenol was monitored by high-performance liquid chromatography using a Shimadzu HPLC equipped with a controller model SCL-10A VP, photodiode-array UV-Vis detector model

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SPD-M10A VP and two pumps model LC 8A. The system is controlled by software "Class VP5" for storing and processing of chromatograms. The analytical column is a C18 Supelco (5 m, 250 mm × 4.6 mm i.d). The mobile phase was a mixture of methanol/water (60/40 v/v) was operated at a flow-rate of 1 mL.min⁻¹. The detection wavelength was at 272 nm. The UV-Vis absorption spectra were recorded employing a Unicam « Helios α » spectrophotometer controlled by software "Vision". The ferrous ion can easily be determined by the formation of a red complex with 1,10-phenanthroline. The molar absorption coefficient at 510 nm of the complex Fe (II)-phenanthroline is equal to 11040 M⁻¹ cm⁻¹ [33]. Hydrogen peroxide was determined by formation of a yellow complex with titanium chloride TiCl₄ by measuring the absorbance at 410 nm of the complex (the molar absorption coefficient: 720 M⁻¹ cm⁻¹ [34]).

3. Results and discussion

3.1 Formation the H₂O₂ upon irradiation of m-cresol in UV / Fe(III)-Cit system

Upon irradiation at 365 nm of a solution containing a mixture of m-cresol / Fe(III)-Cit (0.1 mM, 0.3 mM) in the natural conditions of pH and temperature, there is a decrease in the concentration of m-cresol. As is shown in (Fig.1), m-cresol disappear rapidly from the beginning of the reaction. This greatly slows down after 20 minutes of irradiation is explained by deficiency in Fe(III)-Cit complex.

As is reported in literature, H₂O₂ is mainly generated by the reaction of Fe(II) with O₂^{•-} and HO₂[•] (Eq 6 and 7) are insufficient for the Fenton reaction to occur, even though Fe(II) is continuously regenerated by the photolysis of Fe(III)-Cit (Eq 1) in the UV / Fe(III)-Cit system. To this end, the formation of total H₂O₂ at pH naturel (pH = 6.5) in the UV / Fe(III)-Cit system was measured using the method of Frew with titanium chloride TiCl₄ [34]. As is presented in (Fig. 1) the H₂O₂ formed upon irradiation in the UV / Fe(III)-Cit system increased with increasing reaction time up to 20 min. The maximum level is 4.5 × 10⁻² mM. This fact is consistent with m-cresol maximum disappearance obtained after 30 minutes. For longer time it reached a relatively stable value that lasted at least 5 h.

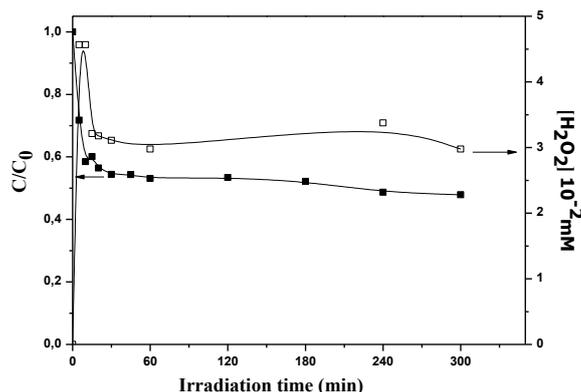


Fig.1. Kinetics disappearance of m-cresol in the mixture m-cresol / Fe(III)-Cit (0.1 mM, 0.3 mM) upon irradiation at $\lambda_{\text{irradiation}} = 365\text{nm}$ and H₂O₂ formation.

3.2. comparative study of m-cresol Degradation in UV / Fe(III)-Cit and UV / Fe(III)-Cit / H₂O₂ systems

In the UV / Fe(III)-Cit system, the major pathway for [•]OH production, is the reaction of Fe(II) with H₂O₂, i.e. the so-called Fenton reaction. We find useful to study the effect of H₂O₂ levels added in this system. The result shows that the addition of H₂O₂ in the UV / Fe(III)-Cit system could inhibit the rates of m-cresol degradation, as compared to those in the absence of H₂O₂ (Fig. 2). In fact, the generation of Fe(II) was not observed while H₂O₂ was present which lowers the production of [•]OH in comparison with the UV / Fe(III)-Cit systems (Fig. 3). While in the UV / Fe(III)-Cit, only (0.062 mM) of the Fe(III) initially added was reduced to Fe(II) obtained in 20 minutes.

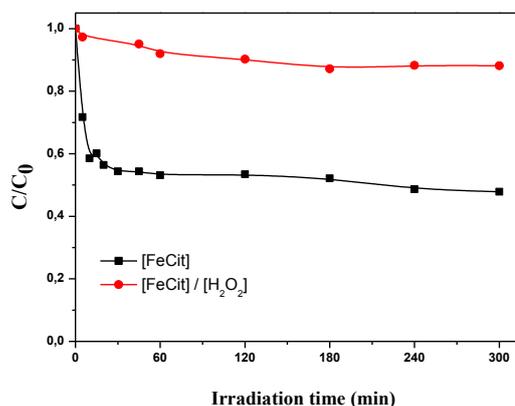


Fig.2. photodegradation the m-cresol in the both systems UV / Fe(III)-Cit and UV / Fe(III)-Cit / H₂O₂ at pH naturel. [m-crésol] = 0.1 mM, [Fe(III)-Cit] = 0.3 mM, [H₂O₂] = 5 mM (if any).

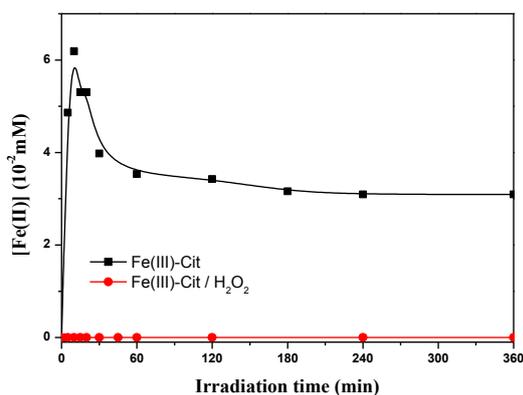


Fig.3. The formation of Fe(II) during m-cresol photodegradation in the both systems UV / Fe(III)-Cit and UV / Fe(III)-Cit / H₂O₂ pH naturel. [m-crésol] = 0.1 mM, [Fe(III)-Cit] = 0.3 mM, [H₂O₂] = 5 mM (if any).

3.3. The effect of the initial concentration of H₂O₂

Contrary to what was expected, the presence of H₂O₂ in UV / Fe(III)-Cit system could reduce efficiency of m-cresol degradation as compared to those in the absence of H₂O₂. When H₂O₂ was initially added, the degradation rate of m-cresol increased with increasing the initial concentration of H₂O₂ up to 5 mM (Fig. 4). This can be explained by the fast Fe(II) reoxydation generating Fe(III) and hydroxyl radicals. Addition of H₂O₂ beyond 5 mM did not drastically improve the maximum degradation percentage. Such trend could be explained by the scavenging effect of hydrogen peroxide toward generated hydroxyl radicals via reaction (Eq 9).

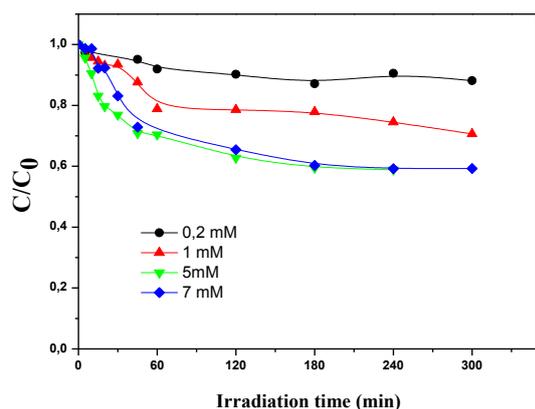
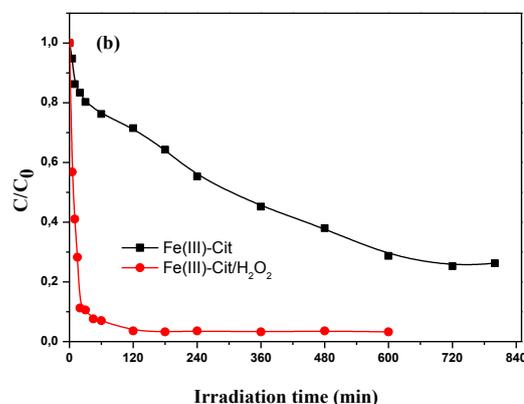
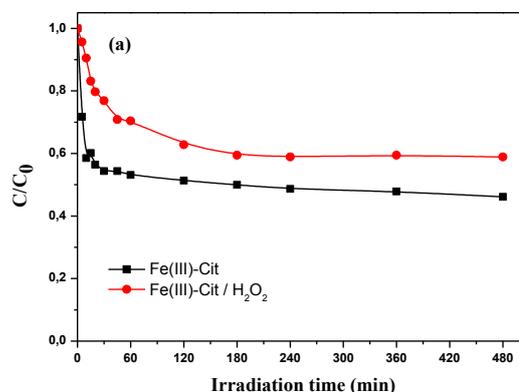


Fig.4. m-cresol degradation in the presence of different H₂O₂ concentrations. Initial concentrations were 0.1 mM m-cresol and 0.3 mM Fe(III)-Cit.

3.4. The effect of initial pH value

In the Fenton and photofenton processes, pH is one of the critical operating parameters, due to the fact that the

Fenton reaction can work only under acidic pH conditions. the ferric iron complex (Fe(III)-Cit) will provide an alternative to the traditional Fenton process with its limited range of pH conditions, since its high solubility in aqueous media can broaden the available pH range of the Fenton reaction up to the near neutral pH regime. It is for that we investigated the effect of initial pH in the degradation of m-cresol in the UV / Fe(III)-Cit system (Fe(III)-Cit = 0.3 mM) at two pH (2.86 and 6.50) in the presence or absence of H₂O₂ (Fig. 5). The photodegradation of m-cresol is seen to depend strongly on pH. The degradation of m-cresol increases with decreasing pH in the both systems. Moreover, the best condition of m-cresol degradation was achieved with the addition of H₂O₂ to the Fe(III)-Cit complex at pH acid (pH = 2.86). Their degradation reached 92 % after 120 min of irradiation. However, in the absence of H₂O₂, the behavior of the m-cresol degradation included a significant phase at the beginning of the reaction, as shown in (Fig. 5b). However, in the presence of H₂O₂, the degradation of m-cresol proceeded more rapidly and the initial phase disappeared (Fig. 5b). The initial phase of m-cresol degradation, shown in (Fig. 5b), means that in the absence of H₂O₂, the Fenton reaction is limited. In the initial stages of irradiation, the H₂O₂, which is formed is insufficient for the Fenton reaction to occur, even though Fe(II) is continuously regenerated by the photolysis of Fe(III)-Cit (Eq 1) in the UV / Fe(III)-Cit system.



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Fig.5. m-cresol degradation in different systems and at different pH. a) pH = 6.5 and b) pH = 2.86

Initial concentrations: 0.1mM m-cresol, 0.3 mM Fe(III)-Cit, 5 mM H₂O₂.

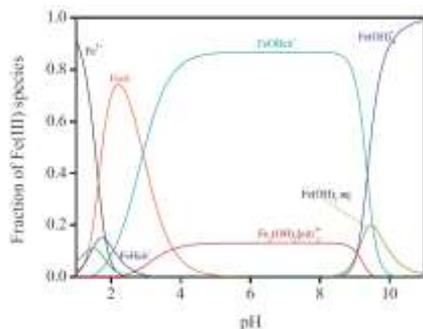


Fig.6. The fraction of Fe(III) species based on the stability constants of Fe(III)-cit and Fe(III)-hydroxo species as a function of pH ($[Fe(III)]_0 / [cit]_0 = 10 / 150$; data of stability constants is from Medusa soft, formation of iron precipitation was omitted) [25].

The effect of pH may be explained by two main reasons, the speciation of different complex Fe(III)-Cit function of pH and the reactivity of radical species generated. It has reported that the most important Fe(III)-Cit species were FeCit and FeOHCit⁻ which have a considerable photoreactivity when the pH was at around 3 [25]. In our study at acid pH (pH = 2.86) the FeCit and FeOHCit⁻ species might exist in a higher concentration in the solution, but in pH = 6.5 the Fe(III)-Cit species are present as FeOHCit⁻ and Fe₂(OH)₂(Cit)₂⁻² (Fig. 6). Probably, the degradation of m-cresol was attributable to the formation of FeOHCit⁻ because of the high photoreactivity which is predominant at thipH.

3.5. The effect of tertibutanol

In order to elucidate the formation of [•]OH radicals, 1.0 % of tertibutanol was added to cresol-Fe(III)-Cit / UV in the presence of H₂O₂ and under light irradiation. tertibutanol is used as a hydroxyl radicals scavenger. The results showed that the photodegradation of m-cresol was totally inhibited compared to the photodegradation of m-cresol in absence of tertibutanol in this system (Fig. 7). It can be seen that the kinetic of disappearance of m-cresol in presence of 1.0 % of tertibutanol was similar to the kinetic of disappearance obtained from UV direct photolysis of m-cresol at 365 nm. This inhibition confirms the involvement of radical [•]OH in degradation of m-cresol induced by the Fe(III)-Cit complex in presence of H₂O₂.

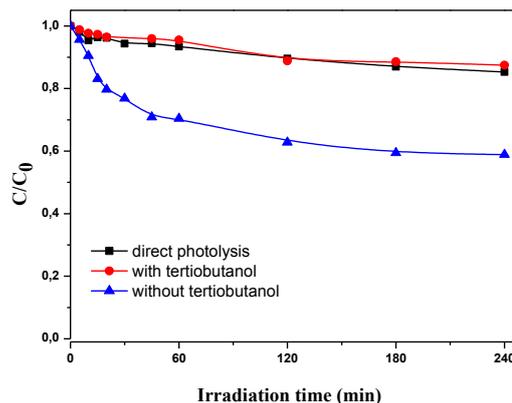


Fig.7. Effect of isopropanol on the photodegradation of m-cresol in different system UV / Fe(III)-Cit / H₂O₂ (m-cresol = 0.1 mM, Fe(III)-Cit = 0.3 mM, H₂O₂ = 5 mM)

3.6. Comparative study of the degradation of m-cresol between aquacomplex and Fe(III)-cit complex in the presence and absence of H₂O₂

The degradation of m-cresol at pH 2.86 in the presence of light using Fe(III), Fe(III) / H₂O₂, Fe(III)-Cit and Fe(III)-Cit / H₂O₂, is shown in (Fig. 8). In the presence of Fe(III)-Cit, over 75 % of the m-cresol was transformed, due to the rapid photochemical reactions involving Fe(III)-Cit complexes under UV light, but we can estimate that in the presence of Fe(III) alone the m-cresol disappearance was about 40 % in this system. Moreover, with the addition of H₂O₂ to the both systems (Fe(III)-Cit complex, Fe(III)) the m-cresol degradation is faster and the complete m-cresol transformation is reached after 60 minutes. Although the m-cresol degradation in the system of Fe(III) / H₂O₂ was almost the same as in the system of Fe(III)-Cit / H₂O₂, the initial reaction rate in the system of Fe(III)-cit / H₂O₂ was obviously faster, which may be due to the high photoreactivity of Fe(III)-Cit leading to the faster [•]OH radical generation in Fe(III)-Cit / H₂O₂ system. However, it is important to the m-cresol degradation in Fe(III) / H₂O₂ system can be attributed to Fenton process.

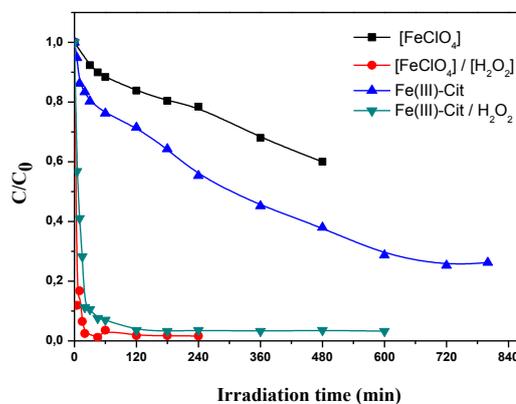


Fig.8. Comparison between Fe(III) aquacomplex and Fe(III)-Cit in presence or absence of H₂O₂ ($[Fe(III)-Cit] = 0.3 \text{ mM}$, $[Fe(III)] = 0.3 \text{ mM}$, $[H_2O_2] = 5 \text{ mM}$)

4. Conclusion

In this study, the photodegradation of m-cresol is seen to depend strongly on pH in the UV / Fe(III)-Cit system in the presence or absence of H₂O₂. The degradation of m-cresol increases with decreasing pH in the both systems. The best condition of m-cresol degradation was achieved with the addition of H₂O₂ to the Fe(III)-Cit complex in acidic pH. This contrast can be explained by two main reasons, the speciation of different complex Fe(III)-Cit function of pH and the reactivity of radical species generated (O₂^{•-} and HO₂[•]). On the other hand, when H₂O₂ was initially added, this reaction leads to a reduce efficiency of m-cresol degradation as compared to those in the absence of H₂O₂. However, in the presence of H₂O₂, the degradation rate of m-cresol increased with increasing the initial concentration of H₂O₂. In fact, the generation of Fe(II) was not observed in this system, which lowers the production of [•]OH, thus explaining the negative degradation of m-cresol.

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