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Fe(III) INVOLVEMENT IN THE PHOTODEGRADATION OF ASPIRIN IN HOMOGENEOUS AND HETEROGENEOUS PHASE

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Abstract

The photocatalytic degradation of Aspirin (ASP) induced by Fe(III) in homogeneous (ASP-Fe(III)-citrate complex) and heterogeneous phase (ASP-Goethite) was studied in aqueous solution up on irradiation at 365nm and by solar light. A dark investigation of system containing a mixture of aspirin and Fe (III) reveals no interaction in homogeneous phase but in heterogeneous phase, the interaction observed was traduced by aspirin adsorption on Goethite in aqueous solution. Under irradiation, Fe(III)-Citrate complex enhance the photooxidation of ASP; a pseudo-first order kinetic model was employed to discuss the results. Against in heterogeneous phase, kinetics is slower and the process is accelerated at acidic pH. The involvement of HO$^{\bullet}$ radicals has been established because of the influence of tertiobutanol used as a scavenger. The photodegradation of ASP in the mixture ASP-Fe(III)-Cit and ASP-Goethite under solar light was significantly accelerated in comparison with artificial irradiation at 365nm.

***Keywords**:* Goethite, Fe(III)-Cit Complex, Aspirin, $^{\bullet}$OH radical, photodegradation

Résumé

La dégradation photocatalytique de l'aspirine (ASP) induite par le Fe (III) en phase homogène (ASP- complexe Fe (III)-citrate) et en Phase hétérogène (ASP-Goethite) a été étudiée en solution aqueuse sous irradiation à 365 nm et par la lumière solaire. Une étude à l'obscurité du mélange d'aspirine et de Fe (III) ne révèle aucune interaction en phase homogène, par contre en phase hétérogène, une interaction traduite par une adsorption de l'aspirine sur la Goethite en solution aqueuse. Sous irradiation le complexe de Fe (III)-citrate améliore la photo-oxydation de l'ASP; une cinétique d'ordre un a été utilisé pour discuter les résultats. Par contre en phase hétérogène la cinétique est plus lente et le processus est accéléré à pH acide. L'implication des radicaux HO$^{\bullet}$ a été établie en raison de l'influence du tertiobutanol utilisé en tant que piège aux radicaux. La photodégradation de l'ASP dans le mélange ASP-Fe (III)-Cit et ASP-Goethite sous la lumière solaire est considérablement accéléré par rapport à l'irradiation artificielle à 365 nm.

***Mots clés** :* Goethite, Complexe Fe(III)-Citrate, Aspirin, Radicaux hydroxyle, Photodégradation.

ملخص

تفكك الأسبيرين باستعمال تقنية التحفيز الضوئي في الوسط المتجانس (ASP- complexe Fe(III)-citrate) و الغير متجانس (ASP-Goethite) تمت دراستها في وسط مائي تحت إشعاع ضوئي عند 365 ن م ، و تحت اشعة الشمس. الدراسة في غياب الضوء للمزيج ((ASP-Fe(III)) أثبتت عدم وجود اي تفاعل في الوسط المتجانس، لكن في الوسط الغير متجانس التفاعل ترجم بإدمصاص الأسبيرين على Goethite في المحلول المائي. في حالة التحفيز الضوئي، المعقد Fe (III)-citrate يحسن من الأكسدة الضوئية لل(ASP) ؛ وقد عبر عن هذه العملية بنموذج حركي من الرتبة الأولى. في حين الوسط الغير متجانس سرعة التفكك ابطأ ، و العملية تتحسن في الوسط الحمضي. إضافة 1 % من الترسيوبيوتانول يؤكد تدخل الجذور الهيدروكسيلية في التفكك الضوئي لهذا الملوث .التفكك الضوئي للأسبيرين في المزيجين (ASP- complexe Fe (III)-citrate) و(ASP-Goethite) يكون أحسن تحت اشعاع الطبيعي منه من الأشعاع الاصطناعي عند 365 ن م.

الكلمات المفتاحية **:** Goethite , المعقد Fe (III)-citrate, الأسبيرين, الجذور الهيدروكسيلية, التفكك الضوئي

1. Introduction :

Pharmaceuticals have been detected in trace concentrations in the natural aquatic environment at concentrations of ng L^{-1} to µg L^{-1} [1-4],many compounds that have been detected, such as, carbamazepine, diclofenac, and ibuprofen, are entirely synthetic and classed as xenobiotics [5].

Aspirin (ASP) was selected as drug model for it most popular painkiller mainly sold as 'over-the-counter' drug. In Germany,the total quantities of ASP sold per year havebeen estimated at >500 tons [6]. ASP was detectedat a median concentration of only 0.22µg.L^{-1} insewage effluents in Germany [7]. Inthe same study, the median concentration of ASPin surface water samples was below the detection limits.

Pharmaceuticals persist in the environment due to their inability to be degraded by natural physical or microbial processes [8]. Various technologies are in use to purify aqueous municipal and industrial effluents containing pharmaceutical substances, before entering surface waters. Among them, advanced oxidation processes (AOPs) have been of major interest in recent years. [9, 10].

Among all the Advance Oxidation Processes (AOPs), Titanium Dioxide (TiO2) photocatalytic oxidation holds a great deal of promise to address this issue due to the low cost of TiO2 and its chemical stability. It is also remarkably active and non-toxic over a wide range of pHs [11].

The literature has reported the degradation of Aspirin with (AOPs), **Ghajar** and **Sohrabi** have studied the optimization of the photo catalytic degradation of Aspirin with TiO_2 nano-particles, irradiated by ultraviolet light [12]. According some conditions, about 73% of Aspirin is decomposed after 60 min.

Iron (hydr)oxides, also semiconductors, are widespread in nature and can absorb a large amount of sunlight (200-800 nm). As compared to TiO_2, however, iron (hydr)oxides have been much less studied as photocatalysts for wastewater treatment[13-18].

Fe(III)-photocatalysis has been also extensively employed for the degradation of pharmaceutical products [19-24]. 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 such as $HO_2^{\bullet}/O_2^{\bullet-}$, H_2O_2, and $^{\bullet}OH$ [25-27]. Due to its strong UV absorption and high stabilization constants, Fe(III)-citrate exhibits appreciable photoreactivity at near neutral pH and it has the potential for application in wastewater treatment.

The aims of this study were as follows: (1) characterizing the photochemical activity of Goethite and Fe(III)-Cit complex, (2) studying the degradation of ASP in heterogeneous and homogenous system, and examining several factors that controlled the kinetics of ASP degradation.

The sunlight is using as light source for photodegradation of ASP in aqueous solutions containing Goethite and Fe(III)-Citrate complex. In order to test the efficiency of aspirin removal from the water, when the degradation is photoinduced by Goethite and Fe (III)-Citrate complex in environmental conditions, a comparative study in term of the kinetic and the pathway of photodegradation process in natural and artificial media was performed.

2-Experimental:

2-1- Chemicals :

A. O-Acetylsalicylic acid (>99%) was purchased from Flucka. Mohr salt $(NH_4)_2Fe\ (SO4)_2.6H_2O$ was purshased from Labosi (99 %). 1,10-phenanthroline (> 99%) was purshased from Fluka. Sodium acetate (> 99%) and Tertiobutanol (> 99%) were purchased from Prolabo products. Acetonitrile was HPLC grade was purchased from Carlo Erba. All solutions were prepared with deionized ultrapure water (ρ = 18MΩ cm). The pH of solution was adjusted by sodium hydroxide (> 97%) and perchloric acid (60 %) purchased from Prolabo and Merck respectively.

B. Preparation of Fe(III)-Citrate Complex.

A stock solution containing 13.0 mM citric acid was prepared with deionized water, and 2mL of this stock solution was diluted to 50 mL. Stock solutions were prepared containing 13.0mM.$(Fe(ClO_4)_3$, $9H_2O)$. The solution was maintained under anoxic conditions until further use. EquimolarFe(III)-Cit complexes were prepared by adding 2mL each of 13.0mM citric acid and (Fe(ClO4)3, 9H2O) solution and diluted to a final concentration of 0.52 mM. The ionic strength of the solution was not controlled, and the pH was adjusted to 6.1 by NaOH 0.1M[28]. All complexes were prepared under low light and kept in the dark to prevent photodecomposition.

2-2 Apparatus

The irradiation experiments were performed in a Pyrex cylindrical reactor with a double envelope with about 3 cm in diameter, open to air, was placed in the centre of the cylindrical stainless steel container. The photoreactor was exposed to the radiation sources composed of one low pressure mercury UV lamps type Philips HPW 125, (UV-A, λmax=365 nm). The solution (usually 50 ml) was continuous magnetically stirred with a magnetic bar during irradiation to insure its homogeneity.

HPLC was performed with a Shimadzu LC-8A gradient chromatograph equipped with two LC-8A pumps, controlled by a SCL-10A VP interface module, and SPD-M10A photodiode array detector (PAD) was used for peak purity test and analysis of compounds. Solvents were filtered using a Millipore system and analysis was performed on a Waters C18 µBODAPAK column (250 mm x 4.6 mm I.D.). The mobile phase was a mixture of water and methanol (v/v 95:5) (flow rate: 1 mL.min^{-1}). The injection volume was 20 µL and the samples were monitored at 228 nm.

All chromatographic experiments were performed at room temperature. UNICAM Heλios-α UV-visible spectrophotometer with 1 cm matched quartz cuvettes were used for all absorbance measurements.

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) and was adjusted when necessary by using $HClO_4$ acid 0.1M or NaOH 0.1M.

2-3- Analysis

The presence of iron (II) in the filtered aliquots was checked out by complexometry with 1,10-phenanthroline using ε_{510} = 11180 L.mol^{-1}.cm^{-1} for the iron(II)-phenanthrolinecomplex [29].ASP degradation was followed by spectrophotometer and quantified by HPLC.

3- Results

3-1- Characterization of ASP

Aspirin known as acetylsalicylic acid is often used as an analgesic, antipyretic and anti-inflammatory. It is a transparent, colorless, odorless crystals having acidic pH.The concentration of ASP used in the work (10^{-4} mol.L^{-1}).

A- Spectral properties of ASP

The UV-visible spectra of ASP (10^{-4} mol.L^{-1}) in aqueous solution pointed up in Fig.1 shows a strong absorption band at 228 nm corresponding to the transition of benzenic cycle π-π * (ε = 5677 L.mol-1. cm -1) and a second band of low intensity at 296 nm corresponding to the transition n-π * (ε = 491 L.mol^{-1}. cm $^{-1}$).

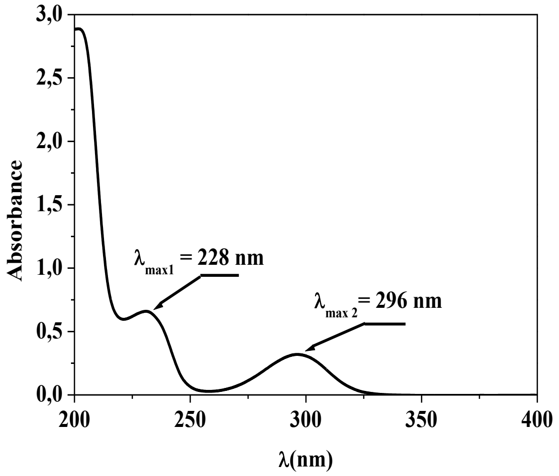


Fig. 1.UV-Visible spectrum of ASP (10^{-4} mol.L^{-1}) in aqueous solution

3-2 Photochemical behavior of ASP- Goethite system

The irradiations were carried out immediately after mixing the reactants. The contribution of the thermal processes is neglected since the time scale of these processes is much larger than the time of irradiation used during the study.
The evolution of ASP-Goethite system (10^{-4} mol.L^{-1}, 1 g.L^{-1}) under irradiation at 365 nm was followed at different times by UV-Visible and the loss of the pollutant in the mixture by HPLC.

A- Photo transformation of ASP-Goethite system at 365nm

When the mixture ASP-Goethite (10^{-4} mol L^{-1}, 1 g. L^{-1}) was irradiated at 365 nm, a decrease in absorbance was observed all along the spectrum Fig.3. The peak at 228 nm diminished illustrating the loss of ASP in the solution. Moreover, the presence of an isosbestic point at 220 and at 276 nm reflects changes in the component of the mixture.

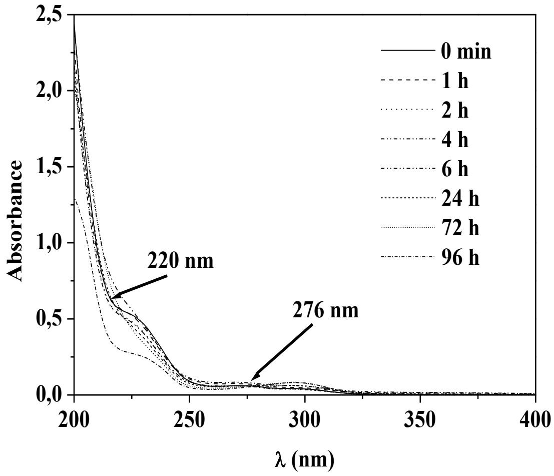


Fig. 4.UV–Visible spectral changes of ASP in the mixture ASP-Goethite (10^{-4} mol.L-1, 1 g.L^{-1}) under irradiation at 365 nm, initial pH = 4,3

- Disappearance of ASP

The concentration changes of ASP up on irradiation at 365 nm, followed by HPLC in solution containing a mixture ASP-Goethite (10^{-4}mol L^{-1}, 1 g.L^{-1}), reveal a drop off the ASP concentration **Fig. 5**.

The kinetics of disappearance shows that the reaction is slow.

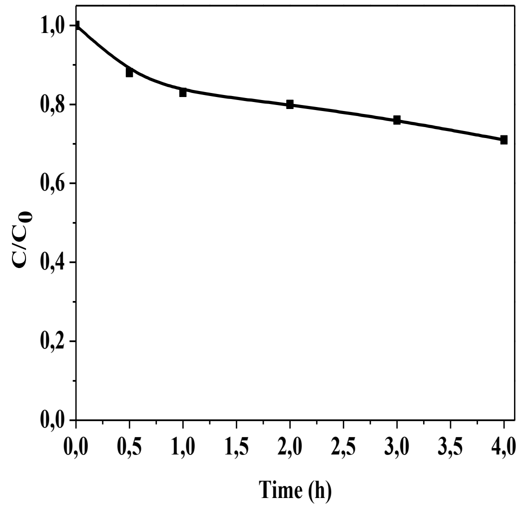


Fig. 5 ASP Disappearance in the solution up on irradiation at 365 nm, pH 4,3

- Influence of pH

The pH dependence is one of the most relevant parameters in the photocatalytic process because it may affect the catalyst surface properties and the substrate structure, changing the photocatalytic efficiency [30-32]. In this set of experiments the initial pH interval range from 3,5 to 4,3. Fig. 6.

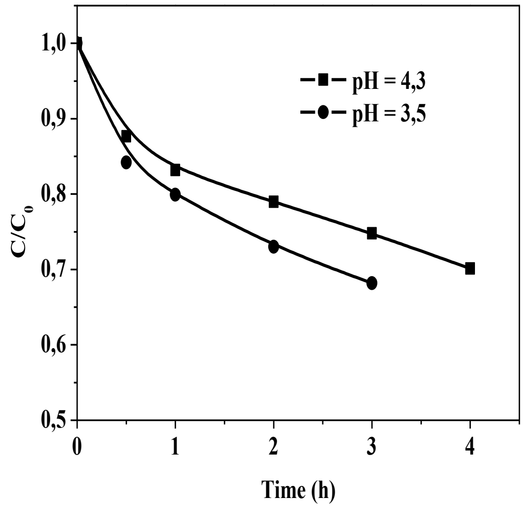


Fig. 6 ASP disappearance in the mixture ASP-Goethite (10^{-4} mol.L^{-1} , 1g.L^{-1}) under irradiation at 365 nm and at different pH

The results showed that the optimal initial pH value should be around 3. This can go well with the results obtained by authors who explained the phenomenon by relationship to PZC value [33]. Then as the pH is lower than PZC value, the Goethite surface becomes positively charged and becomes predominantly negative for a pH value above PZC.

- Fe(II) formation

The concentration of Fe(II) was also measured using complexometric method with 1,10-phenanthroline. Fe(II) concentration increases gradually as the reaction proceeds up to a maximum of 10^{-6} and 2.10^{-6} mol.L^{-1}at pH 4,3 and 3,5 respectively after 25 hours. However, for longer times, the concentration of Fe(II) decrease. Fig. 9

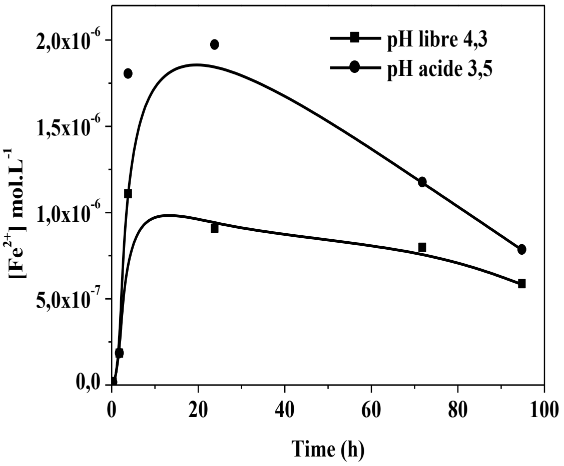


Fig. 7 Fe(II) formation in the mixture ASP–Goethite (10^{-4} mol.L^{-1} , 1 g.L^{-1}) upon irradiation at 365 nm ; pH=4,3 and 3,5 T= 22°C

This fact can be explained by the reoxidation of Fe(II) to Fe(III), probably through the different species present in the solution. The intervention of molecular oxygen is confirmed by the study in deoxygenated environment where we recorded a higher value of Fe(II).

- Irradiation in the presence of tertiobutanol

In order to give evidence for the involvement of $^{\bullet}$OH radicals in phototocatalytic reaction, tertiobutanol 1% (v/v) used as a hydroxyl radicals scavenger was added to some ASP-Goethite suspensions. In **Fig. 8**, the degradation of ASP under irradiation in ASP-Goethite system with (1%) tertiobutanol is inconsequential as compared at the same mixture without alcohol, and without alcohol and UV.

The photodegradation of ASP can be directly attributed to the attack of $^{\bullet}$OH radicals as demonstrated by the inhibition of the degradation during irradiation at 365 nm in the presence of tertiobutanol 1% (v/v): HO• radicals are the major radical species present in the early stages upon irradiation of such solutions [34].

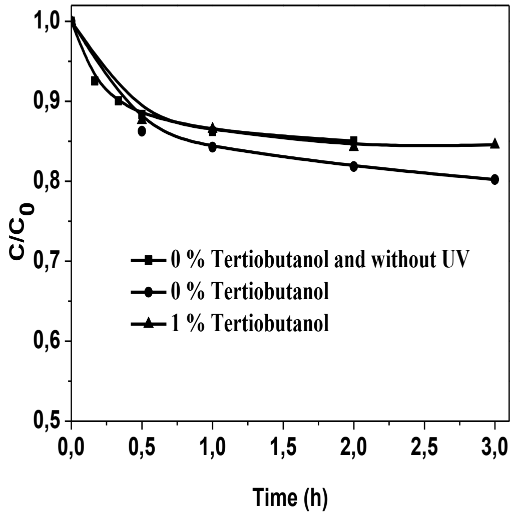


Fig. 8 ASP disappearance in the mixture ASP- Goethite (10^{-4} mol.L^{-1}–1g.L^{-1}) upon irradiation at 365 nm

- Phototransformation of ASP-Goethite-H_2O_2 system

During irradiation at 365 nm, the concentration of ASP was also measured by HPLC in the Goethite-H_2O_2-UV system, upon irradiation at 365 nm (**Fig. 9**).

The rate of disappearance of ASP in the absence of hydrogen peroxide is 12٪ after first hour of irradiation; however the addition of hydrogen peroxide increases the rate up to 56 ٪ during the same time.

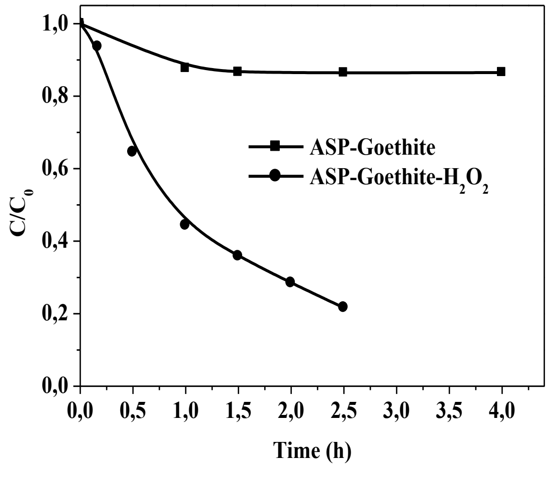


Fig. 9 ASP degradation upon irradiation at 365 nm of ASP-Goethite with and without H_2O_2. (10^{-4} mol.L^{-1}, 1g.L^{-1}) [H_2O_2] = 5.10^{-3} mol.L^{-1}

The successful degradation of ASP shows that the photodegradation process occurs via the photoexcitation of complex Goethite-H_2O_2 may produce HO$^•$ radicals. ***He et al*** proposed the mechanism of photodegradation of various aromatic compounds in Goethite-H_2O_2 system at neutral pHs as reactions (1)–(4) [35].

$$\equiv Fe(III)OH + H_2O_2 \rightarrow \equiv Fe(III)OOH + H_2O \quad (1)$$
$$\equiv Fe(III)OOH + h\upsilon \rightarrow \equiv Fe(IV){=}O + HO^• \quad (2)$$
$$\equiv Fe(IV){=}O + H_2O \bullet \rightarrow \equiv Fe(III)OH + HO^• \quad (3)$$
$$\text{Organic compound} + HO^• \rightarrow \text{degradation products} \rightarrow CO_2 + H_2O \quad (4)$$

The photo-decomposition of ASP is more quick in aqueous Goethite-H_2O_2, due to the efficient production of HO$^•$ by photolysis of the surface complex. The rate constants (k) are: k = 1, 26.10^{-5} h^{-1} and k = 5,76.10^{-5} h^{-1} respectively proving of this fact.

3-3 Comparative study of the degradation of aspirin in homogeneous and heterogeneous phase:

Aspirin was investigated in both homogeneous and heterogeneous systems, a comparative study under artificial and natural radiation is necessary to adopt the best technology.

A- Photodegradation of ASP in artificial radiation at 365 nm

In order to test the efficiency of ASP removal from the water, when the degradation is photoinduced by Goethite and Fe(III)-Cit complex under irradiation at 365 nm, a comparative study in term of the kinetic and the pathway of photodegradation process in artificial media was performed by HPLC **Fig. 10.**

TABLE 1. Initial velocity of asp disappearance

System	v_0 (mol.L^{-1}.h^{-1}) .10^{-5}
ASP-Goethite	5,9
ASP-Complex	18,3

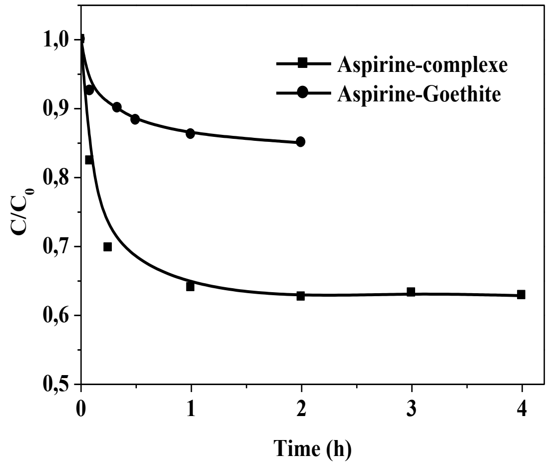


Fig. 10 ASP disappearance in the mixture ASP Fe(III)Cit (10^{-4}, 3.10^{-4} mol.L^{-1}), ASP –Goethite (10^{-4} mol.L^{-1}, 1g,L^{-1}) upon irradiation (365 nm)

The initial velocity deduced show clearly that the phenomenon is faster in homogenous system **Tab. 1**. The phenomenon is limited by the photolysis of complex.

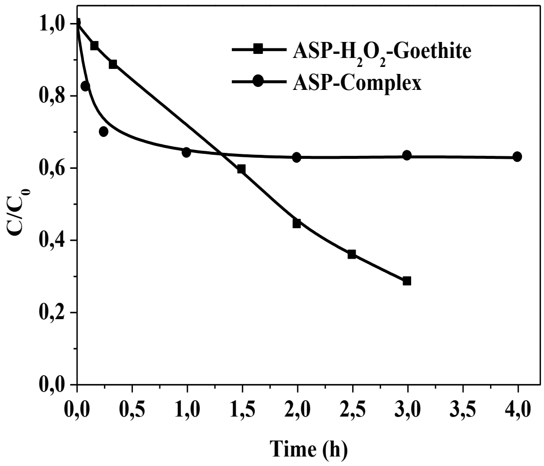
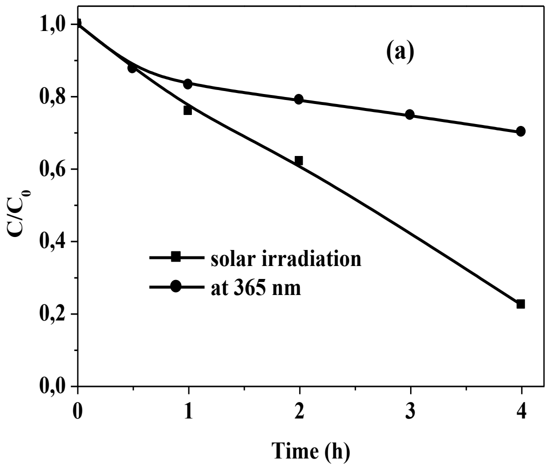


Fig. 11.ASP disappearance in the mixture ASP-Fe(III)Cit (10^{-4} mol.L^{-1}, 3.10^{-4} mol.L^{-1}), ASP-Goethite (10^{-4} mol.L^{-1}, 1g,L^{-1}) upon irradiation (365 nm)

However the addition of the peroxide does not significantly improve the reaction at the beginning, but for a longer time trend has reversed **Fig. 11**.

B- Photodegradation of ASP in natural radiation

Aqueous solutions of ASP with concentrations of 10^{-4} mol.L^{-1}in heterogeneous and homogenous system were exposed to solar irradiation(during a sunny day at Constantine (Algeria).



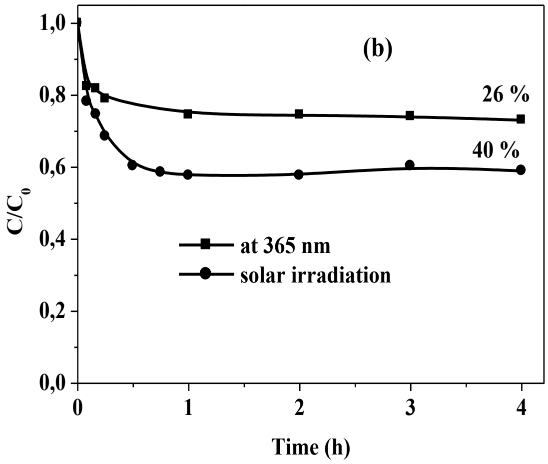


Fig. 12 ASP disappearance during natural and artificial irradiation

(a) The mixture ASP-Goethite (10^{-4}mol.L^{-1}, 1 g.L^{-1})

(b) The mixture ASP-Complex (10^{-4}mol.L^{-1}, 3.10^{-4}mol.L^{-1})

The average of solar irradiance in the experiment was 2.1 mW cm^{-2}). (latitude 36° 22'N, longitude 6° 40'E),a comparative study in term of kinetics of disappearance in natural irradiation and artificial light, it appears that the degradation rate is faster in sunlight **Fig. 12.**

4. Conclusion

The present work illustrates the efficiency of photochemical ASP degradation when the process is induced by Goethite or Fe(III)-Citrate complex in aqueous solution.

When the mixture ASP-Goethite was irradiated at 365 nm, the presence of an isosbestic point at 220 and 276 nm reflects transformation in the component of the mixture. Otherwise, the concentration changes of ASP followed by HPLC in mixture reveal a drop off the ASP concentration, the phodegradation of ASP by this system involves the attack by HO• radicals..

The photodegradation of ASP in aqueous solution by using Goethite has been studied in the pH range from 3.5 to 4,3, the acidic medium enhance the reaction.

The degradation of ASP was accelerate by adding H_2O_2 in ASP-Goethite suspension.

The experience shows that, in homogenous and heterogeneous system, the degradation rate constant was advanced under solar irradiation than under the UV light source.

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