

DECOLORIZATION OF BROMOCRESOL PURPLE (BCP) PHOTOINDUCED BY A Fe (III) OXYHYDROXYDE (GOETHITE)

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Résumé

Cette étude a porté sur la décoloration du bromocrésol pourpre (BCP) en présence de l'oxyhydroxyde de Fe (III) (goethite) comme photoinducteur. Le mélange du colorant avec Goethite à l'obscurité et à température ambiante, montre une réaction entre le colorant et le Fe (III). En effet, le suivi de la réaction par UV-visible montre une faible diminution de la bande principale du colorant. Cela révèle l'existence d'une interaction entre le substrat et la goethite particulièrement dans le milieu acide. L'irradiation à 365 nm du mélange de goethite-BCP ($1\text{g.L}^{-1}-10^{-4}\text{ M}$) conduit à une transformation du substrat. La diminution de la bande principale à 432nm et la présence d'un point isobestique 508 nm confirment la transformation du BCP. La cinétique de disparition du substrat est améliorée en milieu acide. L'addition de peroxyde d'hydrogène ($5.10^{-3}\text{ mol.L}^{-1}$) dans une suspension de goethite, accéléré de manière significative la vitesse de disparition du colorant. Des tests sous irradiations naturelles ont montré que le phénomène de photodégradation est accéléré. Les études sur la minéralisation par le biais de la DCO certifient que cette méthode, compatible avec l'environnement, peut être prise en compte dans le traitement des eaux usées

Mots clés : Colorant, goethite, dégradation photochimique, le peroxyde d'hydrogène

Abstract

This study focused on the decolorization of bromocresol purple (BCP) using Fe (III) oxyhydroxide (Goethite) as an inducer. The mixture dye- Goethite in dark condition and ambient temperature, shows a reaction between the dye and the Fe (III) oxyhydroxide. Indeed, the tracking of the reaction using UV-visible spectrophotometry showed a low decrease in the principal band of the dye. This reveal the existence of an interaction between the substrate and the Goethite which is important in acidic medium. The irradiation at 365 nm of mixture Goethite-BCP ($1\text{g.L}^{-1}-10^{-4}\text{ M}$) leads to a transformation of substrate. The decrease of the band at 432nm and the presence of an isobestic point at 508 nm support the transformation of BCP. The substrate kinetics disappearances are improved in acidic medium. The addition of hydrogen peroxide ($5.10^{-3}\text{ mol.L}^{-1}$) in a suspension of Goethite, accelerate significantly the rate of disappearance of the dye. Natural radiation tests showed that the degradation was faster than artificial one at 365 nm. Studies on mineralization using COD method certify that this method, compatible with the environment, may be considered in the treatment of wastewater

Keywords: dye, goethite, photochemical degradation, hydrogen peroxide.

ملخص

ركزت هذه الدراسة على إزالة صبغ البرومو كريزول بوربر باستخدام طريقة كيميائية ضوئية في وجود اكسيهيدروكسيد الحديد الثلاثي (Goethite) كمحفز. أثناء دراسة خليط الصبغ مع اكسيهيدروكسيد الحديد الثلاثي (Goethite) في عدم وجود الضوء ودرجة الحرارة العادية تبين وجود تفاعل بين الصبغ و اكسيهيدروكسيد الحديد الثلاثي (Goethite). في الواقع، تتبع التفاعل باستخدام القياس الطيفي للأشعة المرئية فوق البنفسجية أظهرت انخفاض في موجة الإمتصاص الرئيسية للصبغ. هذا مايكشف عن وجود تفاعل بين المحلول الصبغ وال-(Goethite) وبصفة خاصة في الوسط الحمضي. الإشعاع عند 365 نانومتر لخليط يحتوي على (Goethite) والصبغ ($1\text{g.L}^{-1}-10^{-4}\text{ M}$) يؤدي إلى تحول في مكونات الخليط. و النقص في الموجة الرئيسية عدة 432 نانومتر ووجود نقطة تساوي الامتصاصية عند 508 نانومتر تدعم فرضية تحول صبغ البرومو كريزول بوربر. تحت الظروف التجريبية لدينا حركية إختفاء الصبغ تتحسن في الوسط الحمضي. إدخال محفز في النظام اكسيهيدروكسيد الحديد الثلاثي (Goethite) وصبغ البرومو كريزول يحسن كفاءة إزالة الملوث ألا وهو الصبغ ويرجع ذلك إلى التحفيز الحاصل على سطح اكسيهيدروكسيد الحديد الثلاثي (Goethite) و إنتاج ايونات الحديد. إضافة بيروكسيد الهيدروجين ($5.10^{-3}\text{ mol.L}^{-1}$) في معلق اكسيهيدروكسيد الحديد الثلاثي (Goethite)، يسرع وبصفة ملحوظة في معدل إختفاء الصبغ. وأظهرت اختبارات الإشعاع الطبيعي إزالة أسرع للصبغ مقارنة مع الأشعة 365 نانومتر. دراسات التمعدين باستخدام طريقة DCO تحت الضوء الطبيعي تؤكد أن هذه الطريقة والمتوافقة مع البيئة، يمكن أن تؤخذ بعين الإعتبار في معالجة مياه الصرف الصحي وعموما في عملية في إزالة هذا النوع من الملوثات.

الكلمات المفتاحية: صبغ ، اكسيهيدروكسيد الحديد الثلاثي ، إزالة كيميائية ضوئية، بيروكسيد الهيدروجين.

Introduction :

Most of the colors in the effluent from dyes involve aromatic compounds which are chemically stable and harmful to human health when they enter into aquatic system [1– 4]. Physical methods, such as adsorption [5], biological methods (biodegradation) [6,7] and chemical methods (chlorination, ozonation [8]) are the most frequently used for the treatment of these dyes. Other methods such as flocculation, and reverse osmosis have also been tested [9–11]. We found also treatment using bacterial beds, this process was less adapted because of the fluctuations of the wastewater composition [12,13]. Since several years “Advanced Oxidation Processes” (AOP) have appeared, these techniques are based on the production of reactive species such as hydroxyl radicals ($\text{HO}\cdot$) by several ways [14,15], which are powerful oxidizing agents and capable of attacking a wide variety of organic molecules [16]. AOPs photocatalysis systems include combination of semiconductors and light. Heterogeneous photocatalysis is the most promising method of AOPs for wastewater treatments with low-organic contents [17,18]. Iron (hydr)oxides can also be used as semiconductors, they are widespread in nature and have an absorbency of sunlight (200-800nm).

Major iron oxides including hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), Goethite ($\alpha\text{-FeOOH}$), and lepidocrocite ($\gamma\text{-FeOOH}$) show semiconductor properties with a narrow band gap of 2.0–2.3 eV and could be photoactive under solar irradiation [19]. Several recent studies have taken the band model to explain the observed photodegradation of aminophenols [20,21], methylphenol[22], chlorophenols[23] and azo dyes[24] on $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ in the aerated aqueous suspension. Recently, the use of goethite with hydrogen peroxide was found as an effective oxidize organic compounds due to the catalysis on goethite surface and ferrous ion generation [25]-[26]. Ju He et al, reported that the combination of Goethite and hydrogen peroxide provide rapid degradation of azo dye Mordant Yellow 10 at neutral pH [article2]. Lu also indicated that 2 chlorophenol can be decomposed with H_2O_2 catalyzed by goethite [25]. Ming-Jer Liou et al studied the catalytic degradation of nitro aromatic explosives (picric acid and ammonium picrate) with goethite and hydrogen peroxide process [27]. We et dimethyl sulphoxide (DMSO) in the neutral pH [28].

A previous work study was carried out on the degradation of bromocresol purple (BCP) photoinduced by Goethite ($\alpha\text{-FeOOH}$) in aqueous solution. The aim of the experiments reported here on the photolysis of Goethite-BCP and Goethite-BCP- H_2O_2 systems using natural and artificial light irradiation was to test the efficiency of BCP decolorisation in aqueous medium. Dark experiences of Goethite-BCP and Goethite-BCP- H_2O_2 systems were performed before studying the photochemical behavior. These experiments are projected in order to detect an eventual interaction in absence of light.

2- CHEMICALS AND APPARATUS :

2-1- Chemicals :

Bromocresol purple was purchased from Fluka chemical company and used without further purification. Ortho-phenantroline, sodium hydroxide, Hydrogen peroxide was a Labosi product with a purity of 30% , Goethite ($\alpha\text{-FeOOH}$) was synthesized according to the procedure described by Atkinson et al [29]. All suspensions were prepared with ultra-pure water (Millipore simplicity-UV) and filtered through millipore filter 0.45 μm . The pH measurements were carried out with HANNA pH- meter to ± 0.1 pH unit. The pH of the solution was adjusted by adding NaOH (Prolabo, >97%) and HClO_4 (Merck, 60 %).The ionic strength was not controlled .

2-2- Apparatus :

Adsorption and photocatalytic experiments were carried out in a Pyrex cylindrical reactor with a double envelope with about 3 cm in diameter, open to air. The reactor assembly was placed on a magnetic stirring plate to maintain Goethite in suspension. The photoreactor was exposed to the radiation sources composed of one low pressure mercury UV lamps type Philips HPW 125, (UV-A, $\lambda_{\text{max}}=365$ nm). The mean value of flux intensity reaching the middle of the reacting suspension was measured with a radiometer type VLX 3 W.

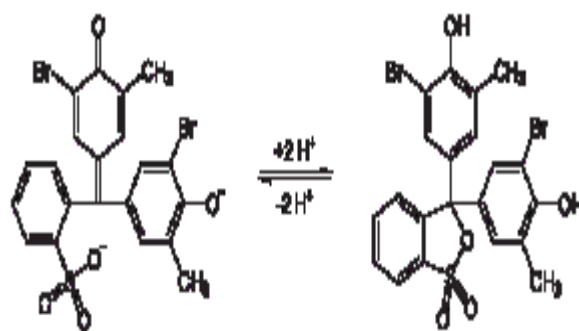
LC spectrophotometer Lambda–Max Model 481 was used to measure Bromocresol purple concentration with an accuracy of 3% (SD = 0,0030).

The crystal structure of the powdered Goethite samples was verified by X-ray diffraction analysis with diffractometer (Siemens) and using Nicolet 5 SXC FT-IR spectrometer by dusting on the KBr.

3- RESULTS AND DISCUSSION

3-1- Characterization of BCP

Bromocresol purple (abbreviation: BCP, molecular formula: $\text{C}_{21}\text{H}_{16}\text{Br}_2\text{O}_5\text{S}$, molecular weight = $540,222 \pm 0,026 \text{ g}\cdot\text{mol}^{-1}$ (C 46,69 %, H 2,99 %, Br 29,58 %, O 14,81 %, S 5,94 %) It is a well known acid–base indicator with a range that lies between pH 5.2 and 6.8, and is yellow at pH 5.2 to purple at pH 6.8 (pka =6.4). Its molecular structure is shown in the scheme



Molecular structure of Bromocresol purple (BCP). The spectra depicted in Fig.1 of BCP (10^{-5} mol/l, pH=4.4) in aqueous solution represents a maximum absorption band at 432 nm. The molar absorption coefficient was evaluated to $27100 \text{ M}^{-1}\text{cm}^{-1}$.

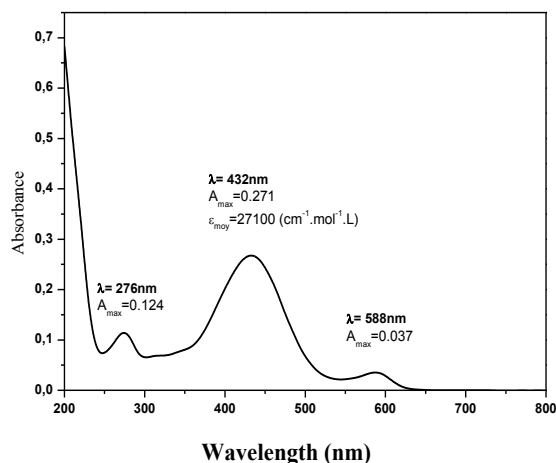


Fig. 1. UV-Visible spectrum of BCP (10^{-5} mol.L⁻¹, pH=4.4) in aqueous solution.

Effect of pH

The pH plays an important role in molecular and anionic forms of the studied compound. It therefore appeared to us, as a preliminary step for further work, to study the influence of this parameter on the form of the molecule and hence the behaviors of the mixture to better understand its behavior in the presence and absence of light. In Fig.2, we can observe the evolution of the absorption spectrum of a solution of the BCP (10^{-5} mol L⁻¹) under different pH values.

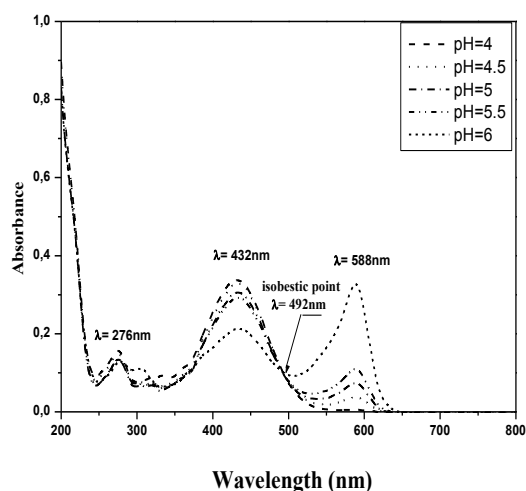


Fig. 2. UV-Visible spectrum of PCB (10^{-5} mol L⁻¹) in aqueous solution at different pH.

The increase in pH causes changes in the UV-Visible spectrum of the dye. Indeed the spectrum of BCP in acid medium is characterized by the absence of the 588 nm band. However in basic medium, it appears and become more intense when the pH increases. This is explained by the fact that in free and acidic pH the two forms are identical (molecular form), since we are in the interval of pH below the pKa.

3-2- Thermal behavior of BCP - Goethite system in aqueous solution

A dark investigation of the system was performed before studying the photochemical behavior. Under our experimental conditions [BCP] = 10^{-5} mol/l, [Goethite]=1g/l at pH=5.9, the UV-Visible spectrum of mixture in aqueous solution as a function of time presents diminution of band at 432nm and an equilibrium is reached after 20 min and the presence of an isobestic point at 492 nm of a transformation Fig.3. This could be attributed to adsorption on the goethite.

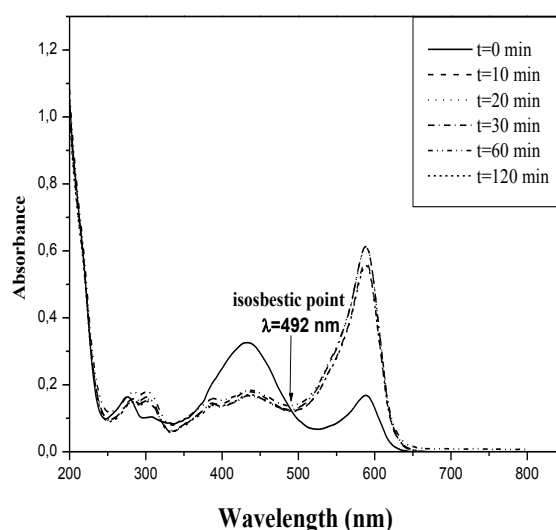


Fig. 3. UV-visible spectrum of BCP-Goethite mixture (10^{-5} mol/l, 1 g/l) in aqueous solution in the dark at T = 25 °C, pH = 5,9.

3-3- Photochemical behavior of BCP - Goethite system in aqueous solution

During irradiation at 365 nm, the temporal evolution of the UV-Visible spectra changes taking place in the studied system BCP- Goethite (10^{-5} mol/l, 1 g/l) is displayed in Fig 4.

DECOLORIZATION OF BROMOCRESOL PURPLE (BCP) PHOTOINDUCED BY A Fe (III) OXYHYDROXYDE (GOETHITE)

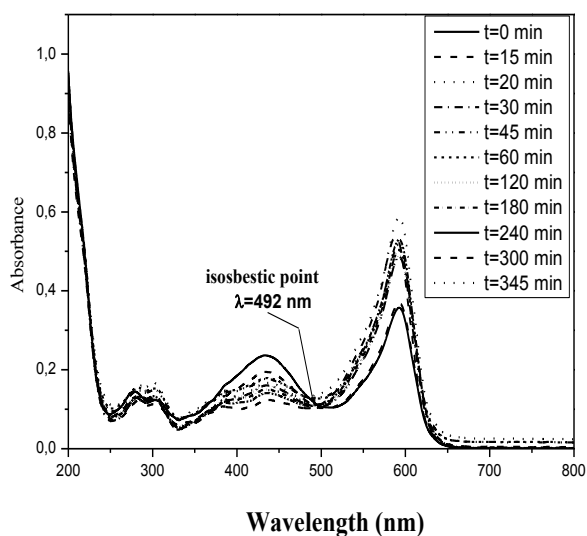


Fig. 4. UV-Visible spectral changes of BCP in the mixture BCP-Goethite (10^{-5} mol.L $^{-1}$, 1 g.L $^{-1}$) under irradiation at 365 nm, initial pH = 5,9

The results clearly showed a decrease in absorption at 432 nm located. Moreover, the band at 588 nm is marked by a greater increase in this case to reach a maximum after 6h. This shows that the presence of photoproducts absorb at this wavelength and the formation of isosbestic point illustrate that a transformation occurred between different constituents.

Effect of pH

Experiments were carried out to study the pH effect on the photodegradation of BCP in the solution with Goethite. Fig. 5 shows that the optimal photodegradation efficiency was observed at acidic Medium.

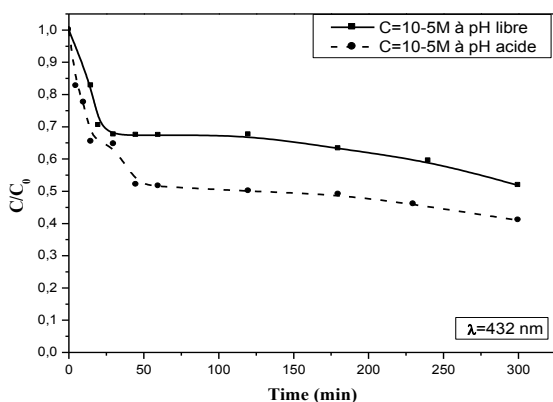


Fig. 5. BCP disappearance in the mixture BCP-Goethite (10^{-5} mol.L $^{-1}$, 1g.L $^{-1}$) under irradiation at 365 nm and at different pH

3-4- Phototransformation of BCP-Goethite-H₂O₂ system

- Thermal behavior

The experiments were carried out to study the effect of H₂O₂ on efficiency of BCP degradation. The dark investigation of the BCP-Goethite-H₂O₂ (10^{-5} mol/l, 1 g/l, 5×10^{-3} mol/l) system was performed at room temperature. The results obtained in the absence of irradiation (Fig. 6), showing a decrease of the band at 432nm and an increase in the 588nm band. A transformation of the components is the source of this variation of absorbance, the presence of an isosbestic point at 500 nm confirms that fact.

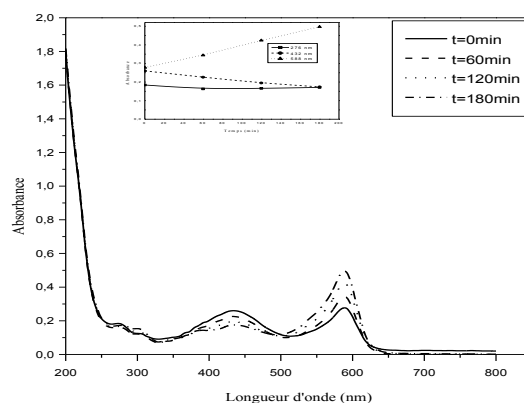


Fig. 6. UV-visible spectrum of BCP-Goethite-H₂O₂ mixture (10^{-5} mol/l, 1 g/l, $5 \cdot 10^{-3}$ mol/l) in aqueous solution in the dark.

Inset: Evolution of the optical density at 588 nm and 276nm and 432 nm

The comparative study of the Goethite-BCP system, in the presence and absence of hydrogen peroxide, shows that the degradation is greater in the absence of peroxide. This can be attributed to a competition adsorption of BCP and H₂O₂ on Goethite Fig. 7.

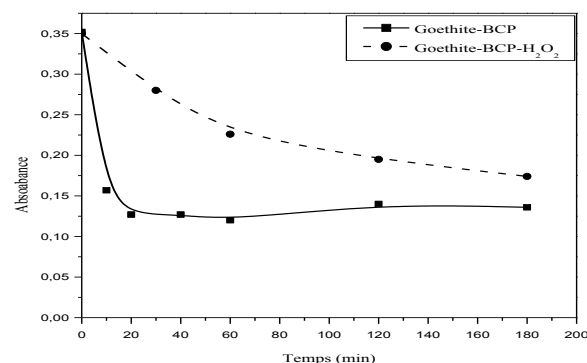


Fig. 7. Evolution of the optical density at 432 nm of the mixture Goethite-BCP (1g.L $^{-1}$, 10^{-5} mol.L $^{-1}$) and Goethite-BCP-H₂O₂ (1g.L $^{-1}$, 10^{-5} mol.L $^{-1}$, $5 \cdot 10^{-3}$ mol.L $^{-1}$) in absence of light.

Effect of pH

The pH value of solution is significant factor acting in the course of reaction. The Goethite-BCP-H₂O₂ (1g.L⁻¹, 10⁻⁵mol.L⁻¹, 5.10⁻³mol.L⁻¹, pH = 3.1).The results illustrate that BCP degradation seems to be the most efficient at acidic medium (pH=3) (Fig. 8).

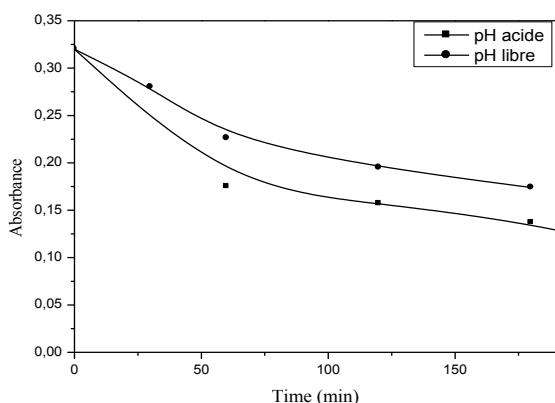


Fig. 8. Evolution of the optical density at 432 nm of the mixture Goethite-BCP-H₂O₂ (1g.L⁻¹, 10⁻⁵ mol.L⁻¹, 5.10⁻³mol.L⁻¹) in absence of light at different pH.

- Photochemical behavior

The results found in the absence of light showed a disappearance of the substrate when the solution ages. We are seated in the photochemical experiments under conditions where the thermal contribution is the weakest possible. The evolution of BCP-Goethite-H₂O₂ system (1g.L⁻¹, 10⁻⁵mol.L⁻¹, 5.10⁻³mol.L⁻¹) under irradiation at 365 nm was followed at different times by UV-Visible.

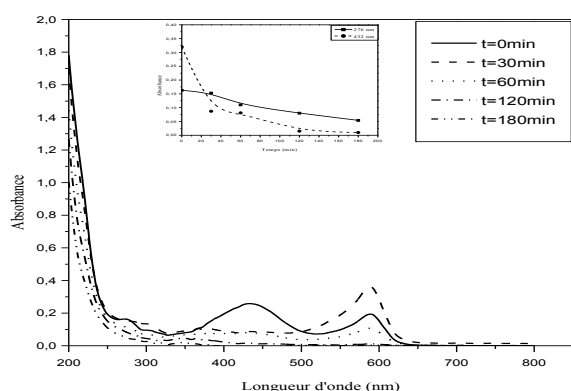


Fig. 9. UV-Visible spectral changes of BCP in the mixture BCP-Goethite-H₂O₂ (10⁻⁵ mol.L⁻¹, 1 g.L⁻¹, 5.10⁻³mol.L⁻¹) under irradiation at 365 nm.

Inset: Evolution of the optical density at 276 nm and 432 nm

The experimental results show a disappearance of the band at 432 nm after 30 min, whereas the band at 588 nm

disappears after 120 min. The comparative study of the BCP-Goethite mixture in the presence and absence of hydrogen peroxide shows that the best efficiency is obtained for the system containing hydrogen peroxide Fig. 10.

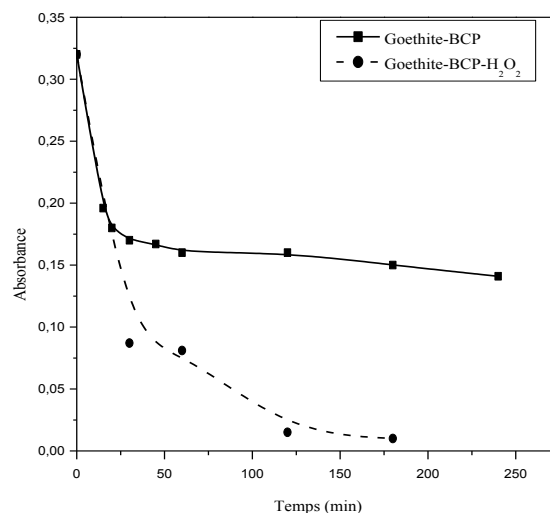


Fig. 10. Evolution of the optical density at 432 nm of mixtures Goethite-BCP (1g.L⁻¹, 10⁻⁵mol.L⁻¹), Goethite-BCP-H₂O₂ (1g.L⁻¹, 10⁻⁵mol.L⁻¹, 5.10⁻³mol.L) under irradiation at 365 nm.

Effect of pH

The pH dependence is one of the most relevant parameters in the photocatalytic process, so it is important to study this parameter in this new system. The evolution of the UV-Visible spectrum of the mixture Goethite-BCP-H₂O₂ (1g.L⁻¹, 10⁻⁵mol.L⁻¹, 5.10⁻³mol.L⁻¹, pH=2.9) is reported in Fig. 11. In this case the disappearance of all the bands is obtained in point is less than 120 min.

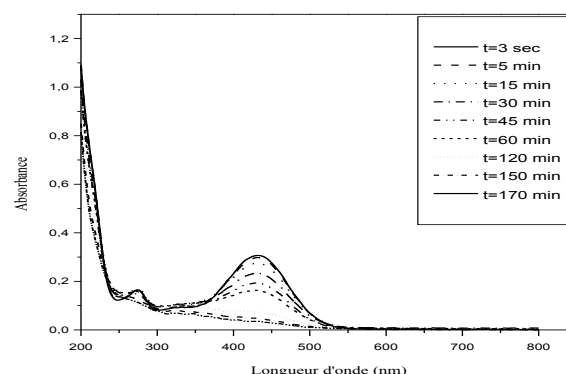


Fig. 11. UV-Visible spectral changes of BCP in the mixture Goethite-BCP-H₂O₂ (1g.L⁻¹, 10⁻⁵mol.L⁻¹, 5.10⁻³mol.L⁻¹, pH=2.9) under irradiation at 365 nm.

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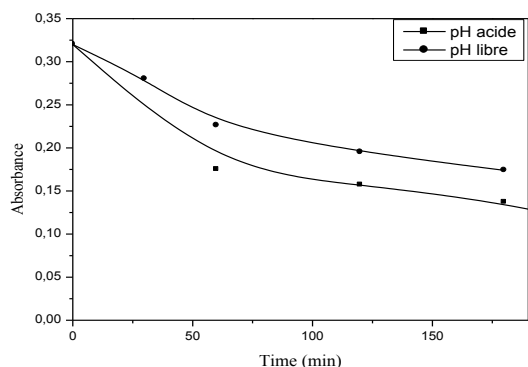


Fig. 12. Evolution of the optical density at 432 nm of the mixture Goethite-BCP-H₂O₂ (1g.L⁻¹, 10⁻⁵ mol.L⁻¹, 5.10⁻³ mol.L⁻¹) under irradiation at 365 nm at different pH.

The results illustrate that BCP degradation seems to be the most efficient at acidic medium (pH=3) (Fig.12).

This phenomenon is probably related to the PZC. Indeed since the point of zero charge (PZC) of goethite is about 8.0 [32], a lower pH value (<8) causes changes on the surface to be positively charged, this favors adsorption of the pollutant [33]. Moreover, it will be noticed that the photo-Fenton is more efficient in acidic media. This is in agreement with Ju et al which reported that the rate degradation of Mordant Yellow (MY10) was more rapid in acidic media (pH=5), in which [MY10] = 0.1 mM and [goethite] = 0.5 g/l and [H₂O₂] = 1 mM [33].

Effect of H₂O₂ concentration

The effect of H₂O₂ concentration on photodegradation of BCP in the BCP-goethite-H₂O₂ system is presented in Fig. 13.

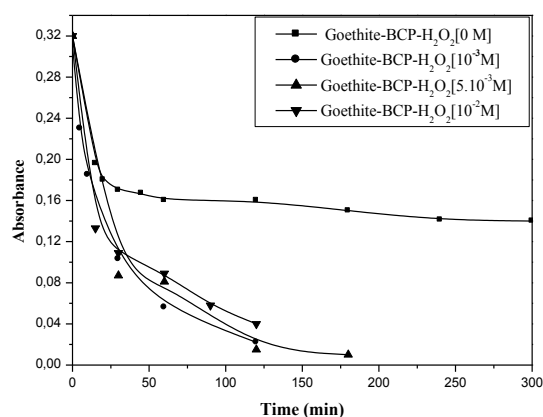
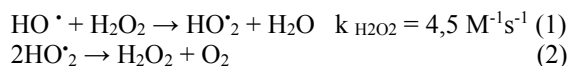


Fig. 13. BCP degradation upon irradiation at 365 nm of BCP-Goethite-H₂O₂ (10⁻⁵ mol/l-1g/l-[H₂O₂]) at different concentration of H₂O₂.

The reaction rate of BCP degradation accelerated by increasing the concentration of hydrogen peroxide. Thus, more hydroxyl radicals were produced when the concentration of H₂O₂ was increased from 10⁻³ to 5.10⁻³

mol/l. Nevertheless, further increase in the H₂O₂ concentration 10⁻² mol/l would result in the decrease of degradation of BCP. This fact is due to the scavenging effect of hydroxyl radicals by hydrogen peroxide existing at high concentration. The hydroperoxy radicals are predominantly produced in this case [30]. Moreover, these hydroperoxy radicals are much less reactive and do not contribute to oxidation of DMSO [31].



Wu et al also found that the degradation of DMSO was significantly improved by increasing the concentration of H₂O₂ to 2.9 x10⁻¹ mol/l [31].

3-5- Environmental significance

In order to test the efficiency of BCP removal from the water, when the degradation is photoinduced by Goethite and H₂O₂ in environmental conditions, a comparative study in term of the kinetic and the pathway of photodegradation process in natural and artificial media was performed by UV-Visible.

The process was experienced by using solar light irradiation where mixture of BCP- Goethite -H₂O₂ (1.0 × 10⁻⁵ mol L⁻¹; 1g.L⁻¹; 5.10⁻³ mol.L⁻¹) was exposed to natural sunlight during a sunny day at Constantine (Algeria). The average of solar irradiance in the experiment was 37 mW cm⁻².

Fig. 14. shows that OBS disappearance is faster in solar irradiation.

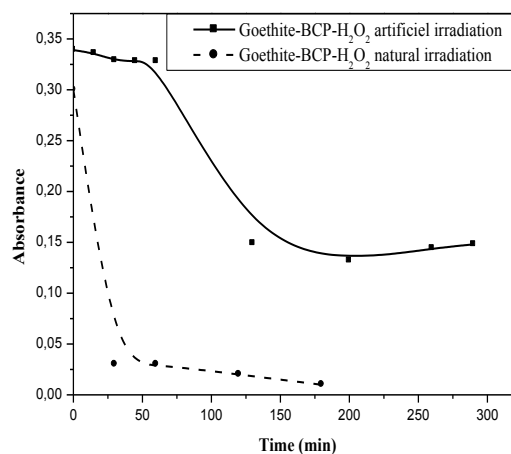


Fig. 14. BCP disappearance during natural and artificial irradiation in the mixture BCP-Goethite-H₂O₂ (10⁻⁴ mol.L⁻¹, 1 g.L⁻¹, 5.10⁻³ mol.L⁻¹)

Fe(II) formation

The Fe(II) formation shown in Fig. 15, is very fast at the beginning and then decreases after reaching a maximum after 15min.

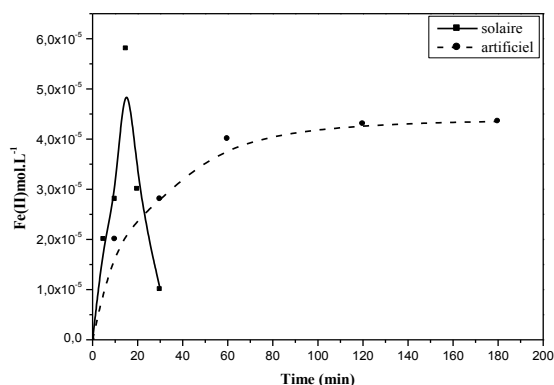


Fig. 15 Fe(II) formation in the mixture BCP–Goethite - H_2O_2 (10^{-4}mol.L^{-1} , 1g.L^{-1} , $5.10^{-3}\text{mol.L}^{-1}$) during natural and artificial irradiation.

3-6- Study of the mineralization

The result shows that the mineralization follows a slower than decolorization, however it should be noted that the dye is highly adaptable to a photocatalytic degradation kinetics (Fig. 16).

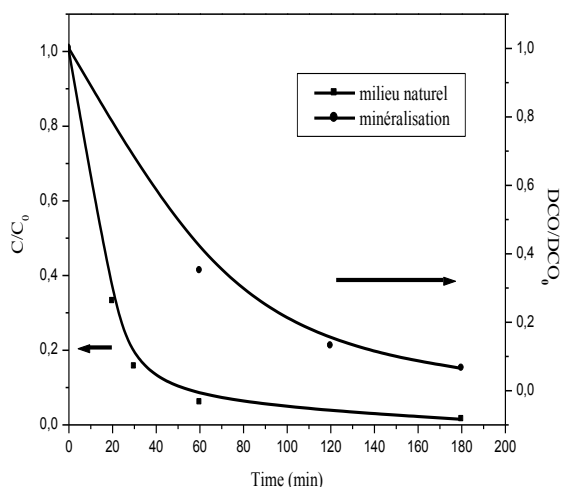


Fig. 16. Evolution of decolorization and minimization during solar irradiation Goethite-BCP- H_2O_2 system (1g.L^{-1} , 10^{-5}mol.L^{-1} , $5.10^{-3}\text{mol.L}^{-1}$).

CONCLUSION

The development of the mixture dye and Goethite in the dark and ambient temperature, causes a reaction between the dye and the oxide hydroxide Fe (III). This interaction was demonstrated by UV-visible spectrophotometry analysis where disappearance of the dye, particularly in the acidic medium is observed. This decolorization was attributed to the adsorption or complexation reactions occurring at the surface of the goethite.

Under monochromatic irradiation at 365 nm, the experiments in the heterogeneous phase showed the efficacy of this oxyhydroxide Fe (III) to degrade such dye.

The influence of important parameters such as pH, substrate concentration on the course of the reaction was stayed.

The introduction of activator in the heterogeneous phase system improves the efficiency of the degradation. Indeed, the addition of hydrogen peroxide ($5.10^{-3}\text{mol.L}^{-1}$) in a suspension of 1g.L^{-1} Goethite, accelerates significantly the rate of disappearance of the dye as a result of the intervention of OH^\bullet radicals generated by the Fenton and PhotoFenton reactions.

Natural irradiation tests shows more rapid degradation of the dye when excited by sunlight highlighting the effectiveness of Goethite- H_2O_2 -UV system.

This method, compatible with the environment, appears effective in the treatment of waste water and in general in the elimination process of dyes.

Studies on mineralization through COD with natural light certify that this method, compatible with the environment, appears to be effective in the treatment of wastewater.

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**DECOLORIZATION OF BROMOCRESOL PURPLE (BCP) PHOTOINDUCED BY A Fe (III)
OXYHYDROXYDE (GOETHITE)**

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