

EFFECT OF NATURAL IRON OXIDE, HYDROGEN PEROXIDE, AND OXALIC ACID ON PHOTOCHEMICAL DEGRADATION OF 2-CHLOROPHENOL

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Abstract

The voluntary or accidental release of chemical compounds in the environment is a major cause of pollution of natural waters. Most of chlorophenols are toxic and hardly biodegradable and are difficult to remove from the environment. Therefore, it is important to find innovative and economical methods for the safe and complete destruction. The objective of this work is to test the activity photocatalytic of natural iron oxide (NIO) in the photodegradation of 2-chlorophenol (2-CP). The analysis chromatographic with HPLC of solutions exposed under UV irradiation revealed that the degradation of 2-CP was negligible under the condition of using only natural iron oxide. The effect of wavelength on photoreactivity of NIO was also investigated in this process: at high wavelength thus at low energy the efficiency of degradation is important. We have also investigated the activation of NIO by hydrogen peroxide and oxalic acid, The results showed that the photodegradation of 2-CP under UVA irradiation could be enhanced greatly in the presence of oxalate. 2-CP was completely removed after 240 minutes of irradiation when the concentration of oxalic acid is equal to 2.10^{-3} M. The use of 2.0 % of isopropanol as a scavenger confirmed the intervention of hydroxyl radicals in the photodegradation of 2-CP.

keywords : Iron oxides , 2-Chlorophenol, Oxalic acid.

Résumé

Le rejet volontaire ou accidentel de composés chimiques dans l'environnement est une cause importante de pollution des eaux naturelles. Les dérivés phénoliques chlorés sont considérés comme des polluants toxiques et cancérigènes même à l'état de traces, leur persistance dans l'environnement correspond à leur degrés de chloration. C'est pourquoi, il est impératif de se préoccuper de l'impact de ces substances sur ce compartiment environnemental. L'objectif de ce travail est de démontrer la capacité d'hématite (minerai naturel Algérien) à photoinduire la dégradation d'un composé organique, dans le cas présent du 2-chlorophénol (2-CP). Les analyses chromatographiques par HPLC des solutions exposées à la lumière ultraviolette en présence d'hématite ont montré que la dégradation de 2-CP est insignifiante ainsi que sa disparition ne dépend pas ou peu du pH. L'effet de la longueur d'onde d'irradiation sur la photoréactivité d'hématite a été également étudié dans ce système, à grande longueur d'onde donc à plus faible énergie l'efficacité de dégradation de 2-CP est importante. Nous avons étudié également l'activation d'hématite par le peroxyde d'hydrogène et l'acide oxalique ce dernier est présent en quantité non négligeable dans le compartiment aquatique et adsorbé à leur surface, il peut induire la dissolution des oxy(hydroxy)des de fer. Le 2-CP a complètement disparu pour une concentration en acide oxalique de 2.10^{-3} M au bout de 240 minutes d'irradiation. La dégradation est attribuée aux radicaux hydroxyle générés via la réaction de Fenton.

Mots clés : oxy(hydroxydes) de fer, hématite, 2- chlorophénol, acide oxalique.

ملخص

الرمي الارادي للمواد الكيميائية في البيئة هو أحد الأسباب الرئيسية لتلوث المياه الطبيعية. تعتبر مشتقات الفينول الكلورية ملوثات سامة ومسببة للسرطان ولو بنسب قليلة. ثباتها في البيئة يوافق عدد درات الكلور الموجودة في تركيبها. لهذا السبب من الضروري الاهتمام بتأثير هذه المركبات على البيئة. الهدف من هذا العمل هو تبين قدرة أكسيد الحديد الطبيعي على تفكيك مركب عضوي يتمثل في 2-كلوروفينول. أظهرت التحاليل الكروماتوغرافية للمحاليل المعرضة للأشعة فوق البنفسجية أن نسبة تفكك الملوث ضئيلة جدا في وجود أكسيد الحديد الطبيعي كما أن اختفائها لا يتعلق بدرجة الحموضة. كما تبين أن طول الموجة تأثير على الفعالية الضوئية لأكسيد الحديد الطبيعي حيث أنه عند أطوال الموجة العالية اذن الموافقة لقيم طاقة أقل عملية التفكيك تكون أحسن.

من أجل زيادة فعالية أكسيد الحديد قمنا باضافة بيروكسيد الهيدروجين و حمض الأوكساليك، هذا الأخير موجود بكثرة في الطبيعة و ادمصاصه على أكسيد الحديد يقوم بتفكيكه. أظهرت النتائج أن الملوث اختفى تماما عند استعمال حمض الأوكساليك بتركيز 2.10^{-3} مول / لتر في مدة 240 دقيقة من الاشعاع. هذا التحسن راجع الى تدخل الجذور الهيدروكسيلية الناتجة من عملية الفنتون الضوئي.

الكلمات المفتاحية: أكسيد الحديد الطبيعي، 2-كلوروفينول ، حمض الأوكساليك.

1. Introduction :

Phenolic compounds are considered priority contaminants because of their high toxicity at low concentrations. Their low biodegradability poses serious risks to the environment once they are discharged into natural water. The process of photocatalysis using semiconductor suspension is a method widely used in environmental protection. The use of iron oxides as photocatalysts is recommended due to their abundance on earth and their ability to limit the migration of pollutants in many ecosystem. The iron oxides are found in soils and rocks, lakes and rivers, on the seafloor, in air and organism [1]. Major iron oxides include goethite (α -FeOOH), hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), lepidocrocite (γ -FeOOH) and magnetite (Fe₃O₄) show semiconductor properties with a narrow band gap of 2.0–2.3 eV and could be photoactive under solar irradiation [2]. The photocatalytic degradation of organic pollutants on the surface of iron oxides is very feasible and useful for removal of organic pollutants from contaminated soils and waters [3]. When a semiconducting material absorbs light energy equal to (or) greater than its band gap energy, electrons and holes that are responsible for the generation of free radicals in the system to oxidize the organic moiety are produced. In Fenton and Fenton-like systems, hydrogen peroxide (H₂O₂) is the most important factor because it is the direct source of \cdot OH [4]. Sufficient hydrogen peroxide has to be added so as to make the system be efficient [5,6]. The process is based on the formation of hydroxyl radical (\cdot OH) able to oxidize almost all organic matters and mineralize them to carbon dioxide and water owing to its high oxidation potential ($E_0 = +2.80$ V versus NHE) [7]. When light was introduced into Fenton or Fenton-like system, as called photo-Fenton and photo-Fenton-like reactions, more \cdot OH could be generated [8].

Iron oxides and oxalic acid, which coexist together in aquatic environment, can set up a so called photo-Fenton system under light irradiation to degrade organic pollutants [9–11]. It is known that the photoexcitation of Fe (III)–carboxylate complexes results in the formation of Fe(II) and carboxylate radicals through a ligand-to-metal charge transfer (LMCT) path [12]. In the presence of dissolved oxygen, H₂O₂ is formed from the photodegradation of organic carboxylic acid. The formation of Fe (II) and H₂O₂ sets up a photo-Fenton system, which can be used to effectively degrade the organic pollutants present in the system [13]. This study selected a natural iron oxide which is provided from the iron deposits from Chaabet-El-Ballout which is located in North-East Algerian. XRD results revealed that iron deposits are mostly composed of hematite [14]. The photocatalytic activity of this catalyst was investigated on the photodegradation of 2-chlorophenol

(2-CP). The effects of different parameters such as wavelength, oxalic acid and H₂O₂ concentration were evaluated in order to study their influence on the photocatalytic activity. We focused also on the explanation of the effects of pH on 2-CP photodegradation in photo-

Fenton system because pH is an important factor affecting the activity of photo-Fenton systems.

2. Materials and methods

2.1. Materials

2-CP was supplied by Reidel-de Haën (purity greater than 99%). NaOH (98%) and acetonitril (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%, and Oxalic acid (99.5%), Prolabo, Hydrogen peroxide (30%), Prolabo. The natural iron oxide (NIO) was washed several times with distilled water and dried at 45 °C.

2.2. Irradiation procedure

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, $\lambda_{max}=365$ nm). The reaction suspension was formed by adding given dosage of iron oxide powder into 50 mL of aqueous 2-CP solution. In all experiments here the initial concentration of 2-CP was 10⁻⁴ M. Prior to the photoreaction, the suspension was magnetically stirred in the dark for 30 min to establish adsorption/desorption equilibrium. The samples taken from the solution at certain time intervals were filtered through 0.45 μ m membrane filters to separate iron oxide particles from the solutions. All solutions were prepared with ultra-pure water (MILIPORE).

2.3. Analytical methods

At different time intervals during the irradiation, samples were collected and analyzed by HPLC. 2-CP was monitored at 272 nm by HPLC (shimadzu) equipped with a controller model SCL-10A VP, photodiode-array UV-Vis detector model SPD-M10A VP and two pumps model LC8A. The system is controlled by software “Class VP5” for storing and processing of chromatograms. The mobile phase was a mixture of Acetonitril/water (60/40 v/v) was operated at a flow-rate of 1.0 mL min⁻¹ using Supelco, C18 column (5 μ m, 250 mm×4.6 mm i.d). The UV-Vis absorption spectra were recorded employing a Unicam «Helios α » spectrophotometer controlled by software “Vision”. Fe(II) concentration was determined by the method of Zuo[15] with o-phenanthroline by measuring the absorbance at 510 nm of the complex (the molar absorption coefficient: 11040 M⁻¹ cm⁻¹).

3. Results and discussion

3.1. Photocatalytic degradation kinetics

The first step to study in these processes is to check the influence of direct photolysis.

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photolysis when exposed to UV irradiation is negligible. When NIO was added into the reaction the removal percentage of 2-CP was at 8% level under UV light irradiation (365 nm) and at 11% level at 360 min under (300 nm < λ < 450 nm). However when NIO was exposed to solar light 50% of 2-CP was removed after 4 hours. In fact solar spectrum which consists of UV, Visible light and infrared radiation creates photons able to excite and generate electron-hole pairs in NIO.

When a photon, energy which is above or equal to that of the band gap of a semiconductor impinges on a photocatalyst, an electron is excited from the valence band to the conduction band, leaving a positive hole. The excited electrons are further transferred to oxygen to form hydroxyl radicals as described by Eqs. (1)–(3). 2-CP in the reaction solution is then attacked by the hydroxyl radicals to be degraded.

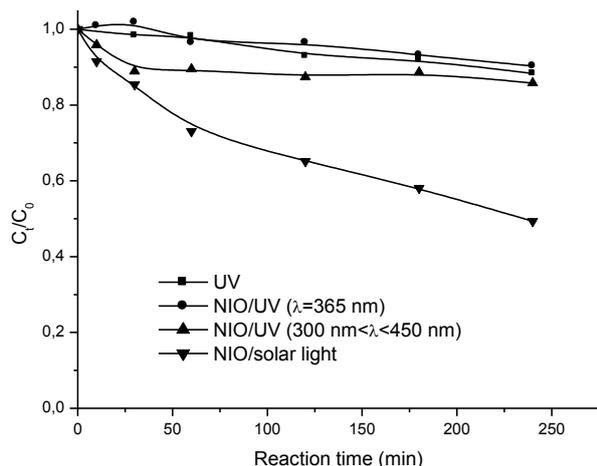
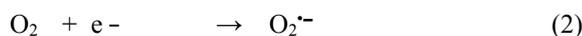
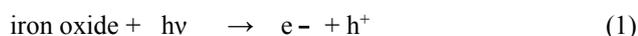


Fig. 1. The effect of wavelength on the photodegradation of 10^{-4} M 2-CP by using 1.0 g L^{-1} NIO at natural pH (pH=8.5).

3.2. The dependence of the photodegradation of 2-CP on the initial concentration of oxalate

To examine the effect of the initial oxalic acid concentration a series of experiments were performed under the following conditions; initial 2-CP concentration = 10^{-4} M, NIO content = 1 g L^{-1} and UV light irradiation. The change in 2-CP concentration at various oxalate concentrations are shown in Fig.2.

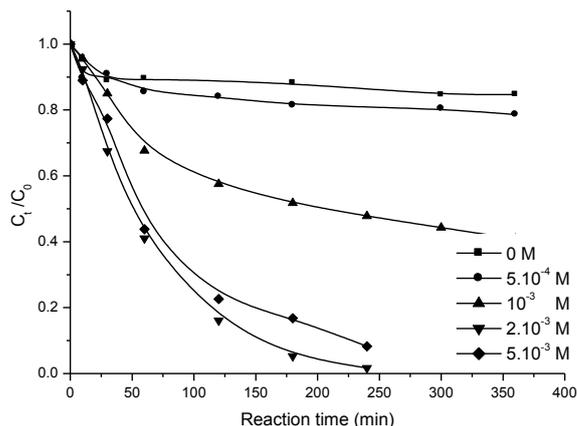


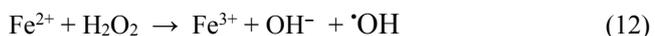
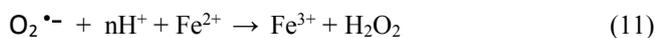
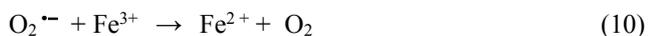
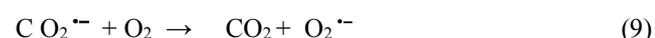
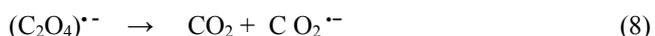
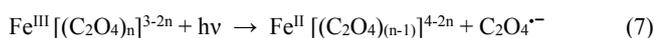
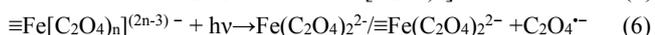
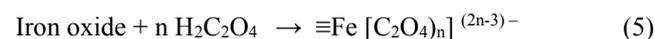
Fig.2. Effect of the initial concentration of oxalic acid on the 2-CP degradation with the initial concentration of 10^{-4} M under UV irradiation by using NIO (1 g L^{-1}).

It can be seen from Fig.2. that the presence of NIO and oxalate in cooperation can greatly accelerate the degradation of 2-CP. In the presence of oxalate, iron oxide-oxalate complex formed and a photo-Fenton-like system was set up (Eqs. 5-12). The experimental data were well fitted by the first-order kinetic model and the first order kinetic constant (k) for the photodegradation of 2-CP are listed in **Table 1**. The result indicates that 2-CP transformation is sensitive to oxalate concentration. The optimal concentration of oxalic acid is 2.0 mM for a maximal k value for 2-CP transformation. However, any excess oxalic acid will occupy the adsorption sites on the surface of iron oxide, and the excess oxalic acid will also compete with 2-CP in reaction with the generated $\cdot\text{OH}$ radicals competitively with 2-CP (Eq. 4). Thus, under these conditions, less of the generated hydroxyl radicals would be available for 2-CP photodecomposition.



Table 1 : The apparent first-order kinetic constant K (min^{-1}) and relation coefficient (R^2) for degradation of 2-CP with different initial concentration of oxalic acid.

C_{ox} (M)	K	R^2
5.10^{-4}	-	-
10^{-3}	0.004	0.955
2.10^{-3}	0.015	0.991
5.10^{-3}	0.0127	0.982



3.3. Formation of Fe²⁺

The concentration of Fe(II) was also measured using complexometric method with 1,10-phenanthroline. Fig. 3. showed the change of the concentration of Fe²⁺ in the presence of different initial concentration of oxalic acid by using NIO with the dosage of 1 g L⁻¹ under UV light irradiation.

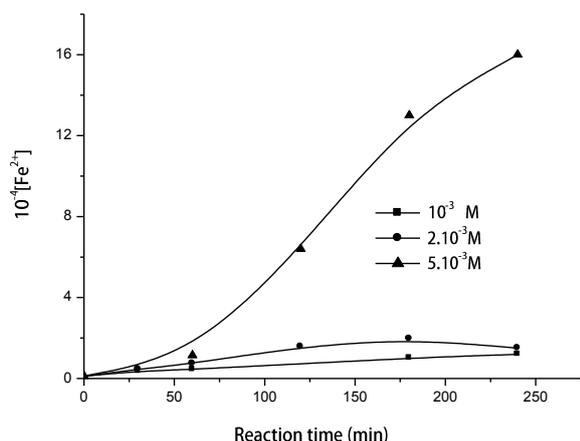


Fig. 3. The concentration of the dissolved Fe²⁺ vs. reaction time with different initial concentration of oxalic acid by using 1.0 g L⁻¹NIO under UVA irradiation.

Since the photoreaction, natural iron oxide would be photodissolved. The results indicated that generation of Fe²⁺ under UVA irradiation depended strongly of oxalate concentration. Obviously, the higher oxalate concentration leads to the more Fe²⁺ concentration. Fe(III)–oxalate complexes could generate Fe²⁺ species by the photo-reduction of dissolved Fe³⁺ species.

3.4. The effect of isopropanol

In order to determine if hydroxyl radicals are involved in the phototransformation of the 2-CP, 2.0% of isopropanol was added to NIO/2-CP suspension in the presence of oxalate and under light irradiation. Actually, isopropanol is usually used as a hydroxyl radicals scavenger, the rate constant of reaction of these radicals on isopropanol being close to 2×10⁹ M⁻¹ s⁻¹ [16].

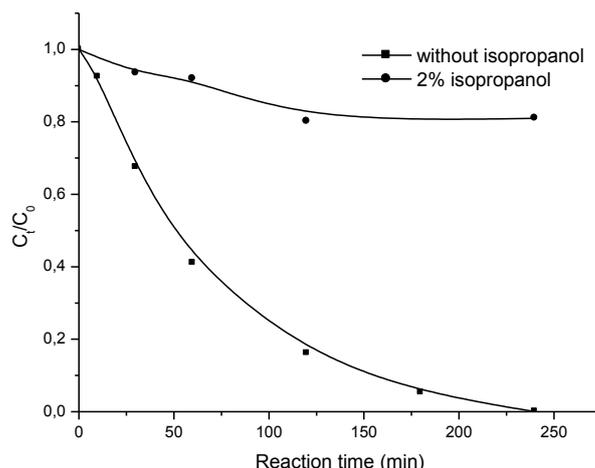


Fig. 4. Effect of isopropanol on the photodegradation of 2-CP in presence of NIO (1 g L⁻¹) and oxalic acid (2× 10⁻³M).

The photodegradation of 2-CP can be directly attributed to the attack of ·OH radicals as demonstrated by the inhibition of the degradation during irradiation at 365nm in the presence of isopropanol 2% (v/v) : ·OH radicals are the major radical species present in the early stages upon irradiation of such solutions.

3.5. Activation of NIO by H₂O₂

3.5.1. Effect of H₂O₂ dosage at natural pH

In order to investigate the effect of H₂O₂ concentration during the photo-Fenton system, experiments in the presence of 1 g L⁻¹ NIO with three different H₂O₂ concentrations (10⁻³, 10⁻² and 10⁻¹ M) at natural pH (8.2) were carried out.

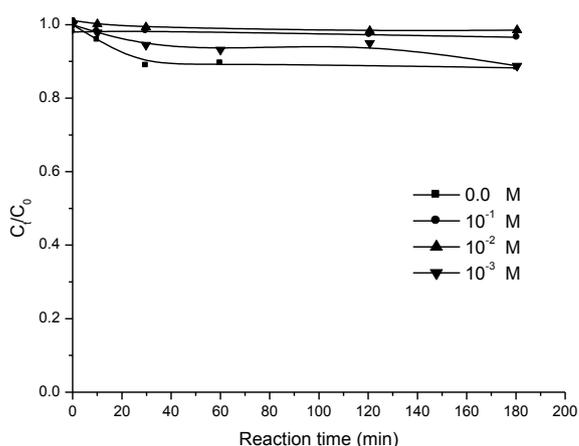


Fig. 5. Effect of initial H₂O₂ concentration on the photodegradation of 2-CP (10⁻⁴ M) in the system 2-CP-NIO under pH = 8.2.

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In the presence of hydrogen peroxide alone (not shown) the 2-CP degradation is negligible. When NIO and hydrogen peroxide were added into the suspension almost no 2-CP degradation was observed in the same degradation time period. This result proved that at neutral and alkaline pH, the interaction between iron species and H₂O₂ will be weakened due to the precipitation of iron. Thus oxidative intermediate species (mainly hydroxyl radicals) are not generated under irradiation.

3.5.2 Effect of H₂O₂ dosage at acidic pH

It is known to all that Fenton or photo-Fenton process is affected by pH value of the environment largely. Usually in traditional Fenton and photo-Fenton systems, the best efficiency of the system is achieved at around pH 3. In order to examine the effect of H₂O₂ on heterogeneous photo-Fenton system at acidic pH (pH = 2) the experiments with fixed NIO dosage (1 g L⁻¹), and 2-CP (10⁻⁴ M) at different concentration of H₂O₂ were conducted.

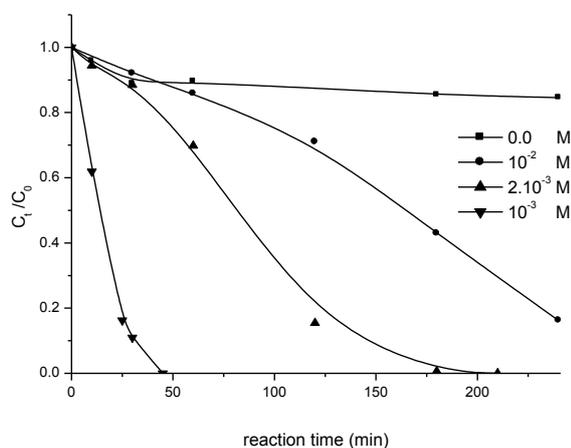
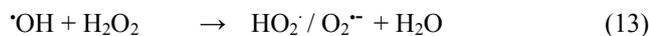


Fig. 6. Effect of initial H₂O₂ concentration on the photodegradation of 2-CP (10⁻⁴ M) under pH = 2.

From the results shown in Fig. 6. it is obviously that the 2-CP photodegradation was very effective in the presence of NIO- H₂O₂ at pH 2. 2-CP was completely removed after 45 minutes of irradiation when the concentration of H₂O₂ is equal to 10⁻³ M.

At acidic pH hydroxyl radical can be generated by the reaction between hydrogen peroxide and iron surface leading to 2-CP degradation. The [•]OH radicals attack the 2-CP molecules at low H₂O₂ concentration, whereas at much higher H₂O₂ concentration, there is a competitive reaction between the 2-CP and H₂O₂. The occurrence of this maximum H₂O₂ concentration for the effective degradation of 2-CP could be explained by the scavenging effect of hydroxyl radicals by hydrogen peroxide (Eq. 13).



Recently, Kwan (2003) have suggested a mechanism to explain the formation of hydroxyl radicals on an iron oxide surface (Eqs. 14-16) whose rate-limiting step involves H₂O₂

adsorbed onto the iron surface (Eq. 15). In this case the rate of [•]OH production would be proportional to the concentration of H₂O₂ adsorbed on the solid.



Conclusion

2-CP was not removed under the condition of using only iron oxide under UV irradiation. The degradation of 2-CP was enhanced under solar light. This can be due to the higher absorptivity of NIO in the solar system.

2-CP can be effectively photodegraded in natural iron oxide /oxalate/UV systems. The reason of this is due to the formation of Fe(III)-oxalate that photolyse to yield free radicals [•]OH.

The degradation of 2-CP in the presence of NIO-H₂O₂ in the like photo -Fenton system was very low and negligible at neutral pH, the reaction rate of reduction from Fe(III) to Fe(II) is important to the whole reaction process. However under acidic conditions, the oxidation of 2-CP during H₂O₂ decomposition has been attributed to hydroxyl radical ([•]OH) production from the reaction of H₂O₂ with reduced surface iron ($\equiv\text{Fe}^{2+}$).

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