



## Removal of 4-Chlorophenols from Simulated Wastewater by Advanced Oxidation Processes

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### Abstract

The degradation and mineralization of 4-chlorophenol (4-CP) by advanced oxidation processes (AOPs) was investigated in this work, using both of UV/H<sub>2</sub>O<sub>2</sub> and photo-Fenton UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> systems. The reaction was influenced by the input concentration of H<sub>2</sub>O<sub>2</sub>, the amount of the iron catalyst, the type of iron salt, the pH and the concentration of 4-CP.

A colored solution of benzoquinone can be observed through the first 5 minutes of irradiation time for UV/H<sub>2</sub>O<sub>2</sub> system when low concentration (0.01mol/L) of H<sub>2</sub>O<sub>2</sub> was used. The colored solution of benzoquinone could also be observed through the first 5 minutes for the UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system at high concentration (100ppm) of 4-CP. The results have shown that adding Fe<sup>+3</sup> to the UV/H<sub>2</sub>O<sub>2</sub> system enhanced the rate of 4-CP oxidation at a molar ratio of H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup>/4-CP equals to 13/0.4/1 by a factor of 7. This reduced the consumption of H<sub>2</sub>O<sub>2</sub> by a factor of 6 and the irradiation time required for complete degradation was reduced by a factor of 6. The experimental results have shown that the optimum reagents for a complete degradation of 4-CP(50ppm) were H<sub>2</sub>O<sub>2</sub>=0.005mol/L, Fe<sup>+3</sup>=0.16\*10<sup>-3</sup> mol/L under acidic condition (pH=3) and irradiation time of 15 min for the UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system with a molar ratio of H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup>/4-CP equals to 13/0.4/1.

**Keywords:** 4-chlorophenol; advance oxidation process; Fenton process; photo-Fenton process; UV photolysis.

### الخلاصة

تم التحقق من فاعلية استخدام طرق الأكسدة الحديثة (AOPs) للنظامين UV/H<sub>2</sub>O<sub>2</sub> و UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> لأكسدة وتحلل مادة الكلوروفينول (4-CP). التفاعل تأثر باختلاف الكميات المضافة من بيروكسيد الهيدروجين (H<sub>2</sub>O<sub>2</sub>)، كمية الحديد كعامل مساعد، نوعية العامل المساعد Fe<sup>+3</sup> و Fe<sup>+2</sup>، pH و تراكيز المحلول للكلوروفينول. المواد الملونة متمثلة بال (benzoquinone) تم ملاحظتها بعد 5 دقائق من بدأ التجربة لنظام UV/H<sub>2</sub>O<sub>2</sub> عند استعمال تركيز قليل لبيروكسيد الهيدروجين (0.01 mol/L). كذلك تم ملاحظة ظهور المواد الملونة بعد 5 دقائق من بدأ التجربة لنظام UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> عند استعمال تراكيز عالية من الكلوروفينول (100ppm). النتائج بينت ان إضافة الحديد (Fe<sup>+3</sup>) كعامل مساعد الى نظام UV/H<sub>2</sub>O<sub>2</sub> وبنسبة مولارية 1/0.4/13 ل H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup>/4-CP أعطت تحلل أعلى بمقدار 7 مرات وأدت إلى تقليل مادة H<sub>2</sub>O<sub>2</sub> المضافة بمقدار 6 مرات وان الزمن اللازم للوصول الى التحلل الكامل انخفض بمقدار 6 مرات. التراكيز المثلى اللازمة للحصول على تحلل كامل للكلوروفينول بتركيز 50 ppm هي H<sub>2</sub>O<sub>2</sub>=0.005mol/L، Fe<sup>+3</sup>=0.16\*10<sup>-3</sup>mol/L عند وسط حامضي pH = 3 و بزمن 15 دقيقة للنظام UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> وبنسبة مولارية 1/0.4/13.

## 1. Introduction

The need to restore contaminated sites to avoid further damage to the environment has raised the development of effective methods for pollutants removal in the last years. The treatment processes for different types of effluents must guarantee the elimination or recuperation of the pollutants in order to reach the strict authorized levels for their discharge, (Weber and Smith, 1986).

An ideal waste treatment process must completely mineralize the toxic species present in the waste streams without leaving behind any hazardous residues and should be cost-effective as well, (Stoyanova et al., 2003).

Chlorophenols are highly toxic and cause considerable damage to the ecosystem and human health. They are notified as potential toxic compounds by United State Environmental Protection Agency (USEPA) and their maximum allowable concentrations in drinking-water as total chlorophenols are 0.1ppb (WHO, 2008).

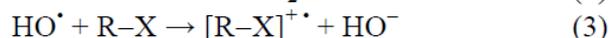
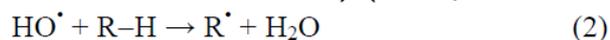
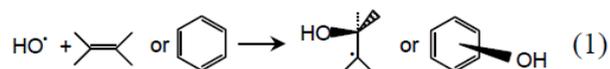
They are introduced into the environment as a result of several man-made activities, e.g. water disinfection, waste incineration, uncontrolled used of pesticides and herbicides, as well as by-products in bleaching of paper pulp with chlorine (Pera-Titus et al., 2004).

Chlorophenols are designated as the priority pollutants by the USEPA and European Commission (Kralik et al., 2009). All chlorophenols possess bactericidal activities that increase with the degree of chlorination. Chlorophenols are highly toxic to algae. Most plants are very sensitive to the phytotoxicity of chlorophenols. As for aquatic organisms, fish and other aquatic organisms absorb chlorophenols through their gills, gastrointestinal tract or skin (WHO, 1998).

The conventional pollutant destructive technologies include biological, thermal and physiochemical treatments. On most occasions, biological treatments require long residence time for microorganisms to degrade the pollutant because they are affected by the pollutant toxicity. Thermal treatments present considerable emission of other hazardous compounds. Other techniques such as flocculation, precipitation, adsorption, air stripping or reverse osmosis (RO) require post-treatment to remove the pollutant from the newly

contaminated environment. Alternative methods to these well-established techniques are the so-called advanced oxidation processes. AOPs are based on the initial formation of radicals, i.e., hydroxyl radicals ( $\text{OH}\cdot$ ) that later act as non-selective oxidation agents.

The possible reaction pathways involving the attack of hydroxyl radicals onto organic compounds are: the electrophilic addition of a hydroxyl radical to organic compounds (unsaturated or aromatic) leading to the formation of organic radicals (Equation 1), the hydrogen abstraction by reacting the hydroxyl radical with a saturated aliphatic compound (Equation 2) and electron transfer with reduction of the hydroxyl radical into a hydroxyl anion by an organic substrate (Equation 3), (Tang, 2004).



Several technologies are included in the AOPs like Fenton, photo-Fenton, wet oxidation, ozonation, photo catalysis...etc. and the main difference between them is the manner to form the radicals. Even though these techniques can provide the conversion of contaminants to less harmful compounds, on most occasions, oxygenated organic products and low molecular weight acids are formed throughout the process. In addition, advanced oxidation processes are limited to treat waters which contain low concentrations of organic or inorganic scavenging substances. Experiences with different oxidation technologies and substrates have shown that partial oxidation of toxic water may increase its biodegradability up to high levels (Pera-Titus et al., 2004).

Advanced oxidation technologies (AOPs) have received increased interest (Kralik et al., 2009). Alnaizy et al., (2000) studied phenol degradation with a UV/ $\text{H}_2\text{O}_2$  process in a completely mixed, batch photolytic reactor, the UV irradiation source was a low-pressure mercury lamp. The study indicates that there is an optimum  $\text{H}_2\text{O}_2$  /phenol molar ratio for efficient degradation in the range of 100-250.



Hirvonen et al., (2000) made a comparison between 2, 4-dichlorophenol degradation rate by UV/H<sub>2</sub>O<sub>2</sub> process and direct UV (20-W 254 nm lamp) irradiation, in the study they reported that the addition of hydrogen peroxide at acidic pH increased the reaction rate by one order of magnitude.

Munter (2001) used AOP to oxidize inorganic contaminants such as cyanide, sulphide and nitrite.

Carneiro et al., (2006) show that typical Fenton catalyst/H<sub>2</sub>O<sub>2</sub> ratios range is 1:5 to 1:25; they proven that the optimal pH range for Fenton process is between 2.8 and 3.0.

Matilainen and Sillanp (2010) noted that the degradation of target compounds with UV/ H<sub>2</sub>O<sub>2</sub> and VUV ( $\lambda=172\text{nm}$ ) occur about eight times more effectively than with direct UV-photolysis.

Kuo and Wu, (2010) investigate the effect of solar irradiation on Fenton degradation of 4-chlorophenol. The results indicated that solar assisted photo-Fenton process was effective for complete removal of 4-chlorophenol in water. More than 90% of 4-chlorophenol was mineralized to CO<sub>2</sub> in solar assisted process while only 25% carbon mineralization was observed in Fenton process.

Bogatu et al., (2005); Nogueira et al., (2008); Murcia et al. 2009; and Elghniji et al., (2011) identified the intermediate generated during the photocatalytic process of phenolic compounds. The major intermediates are benzoquinone and hydroquinone. The concentrations reach a maximum and then tend to decrease gradually for longer irradiation time indicating the mineralization of these compounds.

The objective of this work is to study the effectiveness of the AOPs in the degradation of 4-chlorophenol as one of the main compounds of the chlorophenols, using pilot plant scale. The AOPs selected to carry out this study were, UV/H<sub>2</sub>O<sub>2</sub> and photo-Fenton (UV /H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup>) systems. To achieve the experimental objectives, different variables were chosen to be followed throughout the treatment: 4-chlorophenol concentration, pH, H<sub>2</sub>O<sub>2</sub> and Fe<sup>+3</sup> concentrations.

## 2. Materials and Methods

### 2.1. Reagents

4-Chlorophenol (4-CP) was used as a model substance employed in this research. The physical, chemical, UV-visible absorption spectra and molecular structure of 4-CP are shown in Table 1 and Fig.1, (Thomas and Burgess, 2007). Table 2 shows all the chemicals that were used in the experimentation. All were analytical grade and used as received. All the solutions were prepared by dissolving requisite quantity in distilled water. The pH of the solution was adjusted using H<sub>2</sub>SO<sub>4</sub> solution. Initial pH of solution was monitored using a pH meter from (WTW Co., Germany, INOLAB 720).

### 2.2. Equipments

A laboratory scale set up of AOPs system applied in this study is presented in Fig. 2, (Shihab, 2011). The reactor (1) was made entirely of aluminum with an effective volume of 37.5L. A feed tank (5) of 24L volume was used to prepare the solutions. The solution was circulated at flow rate of 3L/min by using a water pump (3) of 0.5Hp and 0.37kw (Marquis Co., China). To measure the flow rate, a calibrated flow meter (4) of Hidrotek type with flow range (3 to 20L/min) was used. This flow meter was installed vertically and the flow direction was upward. Valves were utilized for sampling, washing, drain and control in the AOPs system as illustrated in Fig.2. A photograph of the photo reactor is shown in Fig. 3. The inlet and outlet pipes were 1.8cm diameter. Vertical baffles were fixed after the inlet zone to let the water overflow to increase the mixing. Two vertical plates with ten rectangular openings (13x1cm) were used as distributors. Three removable side baffles were fixed vertically at the reactor side walls. These baffles are with square cross sectional area with a side length of 5 cm. These baffles reduce the presence of low radiation zones near the reactor walls. UV radiation was generated from three UV lamps TUV 11W 4P-SE (4-Pin single ended), these lamps emit output power at a wavelength of 253.7nm and each was sheathed in a quartz sleeve for protection. These lamps were fixed in a staggered form in the reactor. The spacing between two adjacent lamps should be in a range between (5-12) cm. If this distance is less than 5cm then the

UV energy will be absorbed by the adjacent UV lamp, if the spacing is more than 12cm, there will be a formation of a zone with low UV intensity between the lamps (Chiu et al., 1999; Lyn and Blatchley, 2005). In this study 10cm spacing was used.



Fig.3: A photograph of the AOPs reactor.

Table 1: 4-CP properties (Thomas and Burgess, 2007)

General	
Name	4-Chlorophenol
CAS No.	106-48-9
Formula	C <sub>6</sub> H <sub>4</sub> ClO
Molecular weight	128.57 g
Solubility (H <sub>2</sub> O)	27 g/L (20°C)
pKa	9.4 (25°C)
Refractive index	1.55
Spectra acquisition	
Solvent	H <sub>2</sub> O
Concentrations	20.0 mg/L (pH = 1.5) and 19.5 mg/L (pH = 12.2)
Pathlength	10 mm
Reference product	FLUKA
Purity	GC > 99%

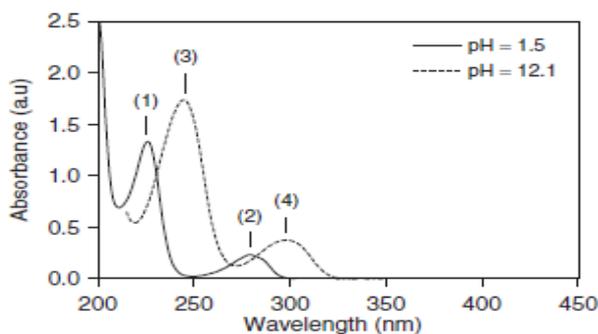
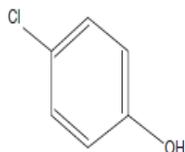


Fig.1: UV-visible spectra for the 4-CP at different pH values (Thomas and Burgess, 2007).

Table 2: List of chemicals used

Compound	Formula	Vendor
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	Scharlau (50 % wt/wt)
Ferrous sulphate heptahydrate	FeSO <sub>4</sub> ·7H <sub>2</sub> O	Thomas Baker (98 % purity)
Ferric sulphate heptahydrate	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	Thomas Baker (99.5 % purity)
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	BDH (97 % purity)
Sodium thiosulfate pentahydrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	Riedel Seelze Hannover (99 % purity)

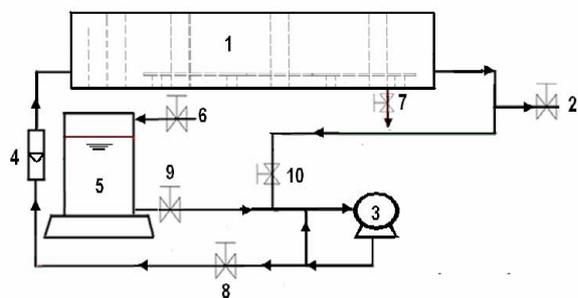


Fig.2: A laboratory scale set up of AOPs system. (1) AOPs reactor, (2) sample extraction valve (3) water pump (4) flow meter (5) feed tank (waste water) (6) washing water inlet valve, (7) drain valve, and (8, 9 and 10) control valves.

### 2.3. Experimental Procedure

The experimental procedure used in this research was as follows:

- The desired concentration of 4-CP was prepared and the pH was adjusted by adding a dilute H<sub>2</sub>SO<sub>4</sub> solution in the feed tank.
- well mixing was maintained by using a mechanical stirrer for 5min.
- Initial sample (sample at time zero) was taken for analysis.



-The pump was switched on and the solution was allowed to flow from the feed tank through the pump to the photoreactor. Valves No. 2, 7 and 6 were closed and all the other valves were opened.

-The head in the photoreactor was maintained at 15cm by controlling the flow through valve No. 8.

-The desired quantity of H<sub>2</sub>O<sub>2</sub> (0.01-0.05) mol/L was added to the feed tank. Circulation was allowed for few minutes then valve No.9 was closed.

-The UV light source was switched on.

-Samples were taken every 15 minutes through valve No.2 until the end of run. Samples were stored in 10 ml vials before analysis. One drop of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O(0.1N) was added to each sample to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with 4-CP during the analysis.

-For UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system, the same procedure was followed and the desired quantity of ferric sulphate was added in the feed tank before adding H<sub>2</sub>O<sub>2</sub>.

-The system was cleaned after the end of each run as follows:

The UV light source was turn off, the valves No.7 and 9 were opened leaving valves No.2,10 and 6 closed to drain the reactor and feeding tank. The system was washing by a tap water through valve No.6, by maintaining valve No.10 and 2 closed and valve No.7 opened for drainage.

UV-visible spectrophotometer (Model SP-3000 plus, Optima Co., 2003, Japan) was used to analyze the samples.

### 3. Results and Discussion

#### 3.1. UV/H<sub>2</sub>O<sub>2</sub> System

The combination of UV radiation and a little amount of H<sub>2</sub>O<sub>2</sub> enhanced strongly the efficiency of degradation of 4-CP. Experiments were carried out at different doses of H<sub>2</sub>O<sub>2</sub> (0.01-0.05) mol/L to study its effect on the degradation and mineralization of 4-CP. Fixed 4-CP concentration at 0.39\*10<sup>-3</sup>mol/L (50ppm) was maintained during the experiments.

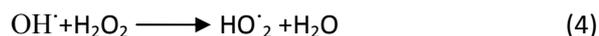
#### 3.1.1. Effect of initial H<sub>2</sub>O<sub>2</sub> concentration on UV/H<sub>2</sub>O<sub>2</sub> system

Different concentrations of H<sub>2</sub>O<sub>2</sub> (0.02, 0.03, 0.04 and 0.05) mol/L were used to show the percent degradation of 4-CP as a function of the irradiation time. The results are plotted in Fig.4. From this figure, it can be noticed that the degradation rate of 4-CP increased as the concentration of H<sub>2</sub>O<sub>2</sub> increased from 0.02 to 0.03mol/L, and achieve 100% degradation at 0.03mol/L after 90 min of irradiation time. Then the degradation decreased as the H<sub>2</sub>O<sub>2</sub> increased to 0.04 and 0.05 mol/L.

Fig.5 shows the degradation of 4-CP at different concentrations of H<sub>2</sub>O<sub>2</sub> at irradiation time of 90 minutes. The percent of degradation increased to 100% at 0.03 mol/L of H<sub>2</sub>O<sub>2</sub> then decreased to 45% at 0.05mol/L of H<sub>2</sub>O<sub>2</sub>.

Investigators gave more than one explanation for these phenomena, among them:

-Hydroxyl radicals generated from the direct photolysis of hydrogen peroxide were the main responsible species of 4-CP elimination. It was expected that increasing the concentration of H<sub>2</sub>O<sub>2</sub> reduces the rate of degradation of 4-CP, due to the reaction of hydrogen peroxide with these radicals, and hence acts as an inhibiting agent of 4-CP degradation (i.e. self-scavenging of OH<sup>·</sup> by H<sub>2</sub>O<sub>2</sub>)



-Hydroxyl radical may recombine and participate in radical-radical reactions to form H<sub>2</sub>O<sub>2</sub>

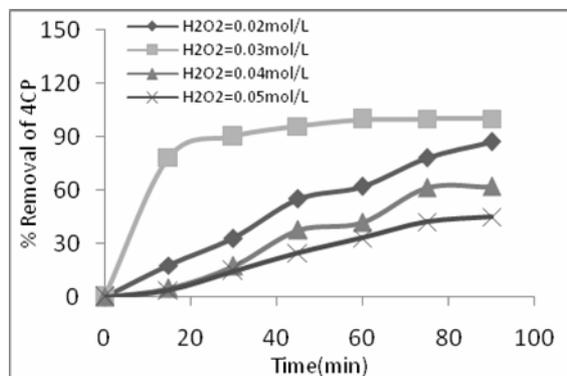


-At higher H<sub>2</sub>O<sub>2</sub> concentrations there is lower light intensity available for 4-CP degradation, since H<sub>2</sub>O<sub>2</sub> also absorb light in the system. This can possibly be attributed to low degradation of 4-CP.

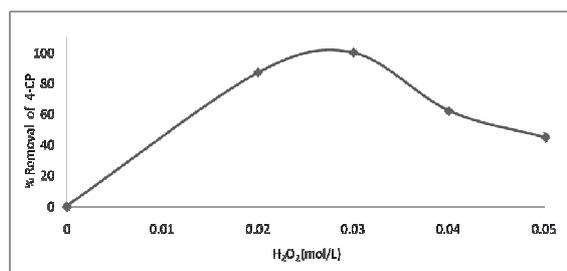
-Hydroxyl radical efficiently reacts with H<sub>2</sub>O<sub>2</sub> and produces HO<sub>2</sub><sup>·</sup> (equation 4). Since HO<sub>2</sub><sup>·</sup> radicals are not as reactive as OH<sup>·</sup>, and then low degradation may be obtained. H<sub>2</sub>O<sub>2</sub> is OH<sup>·</sup> scavenger and so an excess H<sub>2</sub>O<sub>2</sub> can result in a net decrease in the treatment efficiency (Kutschera et al., 2009).

However, if H<sub>2</sub>O<sub>2</sub> dose is low, OH<sup>·</sup> formation will also be low, decreasing the treatment efficiency.

Therefore, a balance must be maintained between excess and low levels of H<sub>2</sub>O<sub>2</sub>.



**Fig. 4:** Degradation of 4-CP by UV/H<sub>2</sub>O<sub>2</sub> system, 4-CP=0.39\*10<sup>-3</sup> mol/L, pH=3. The effect of initial H<sub>2</sub>O<sub>2</sub> concentration.



**Fig.5:** Degradation of 4-CP as a function of H<sub>2</sub>O<sub>2</sub> initial concentration by UV/H<sub>2</sub>O<sub>2</sub> system, 4-CP=0.39\*10<sup>-3</sup> mol/L, pH=3, irradiation time 90 min.

### 3.1.2. Reaction rate constant for UV/H<sub>2</sub>O<sub>2</sub> system

The experimental data obtained for 4-CP degradation can be fitted according to a pseudo-first-order reaction as follows:

$$-\frac{dc}{dt} = KC \quad (6)$$

The integration leads to

$$\ln C/C_0 = -K * t \quad (7)$$

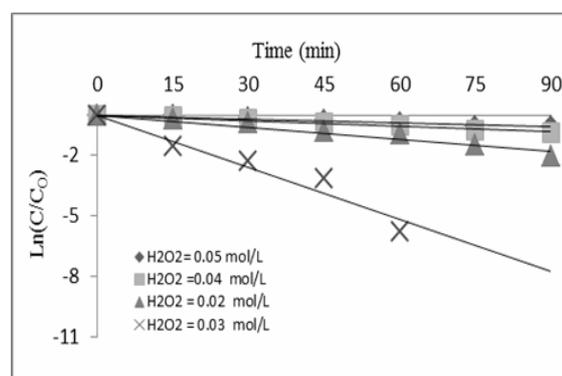
where C<sub>0</sub> and C are the concentration of 4-CP at irradiation times 0 and t, K is a pseudo-first-order rate constant (in min<sup>-1</sup>) and t is the irradiation

time (in min). The regression analysis of the concentration curves versus reaction time indicates that the decomposition rate of this compound could be described by first order kinetics, Fig.6. A high increase in K was observed for 0.03mol/L H<sub>2</sub>O<sub>2</sub> (0.086 min<sup>-1</sup>) compared with other concentrations, Fig. 7.

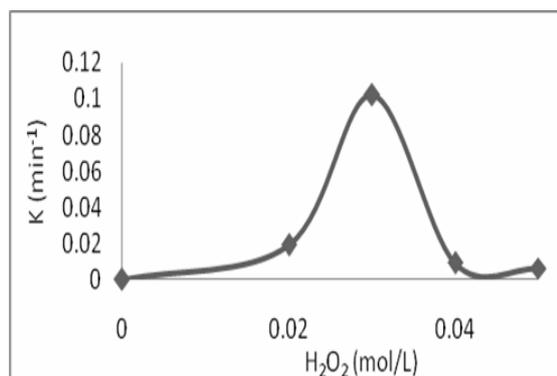
## 3.2 UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> (photo-Fenton) systems

### 3.2.1. The effect of initial H<sub>2</sub>O<sub>2</sub> concentration on UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system

In the photo-Fenton system both Fe<sup>+3</sup>(Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·7H<sub>2</sub>O) and H<sub>2</sub>O<sub>2</sub> were used to attain the desirable degradation. First Fe<sup>+3</sup> is fixed at constant concentration while H<sub>2</sub>O<sub>2</sub> changed until high degradation was obtained.

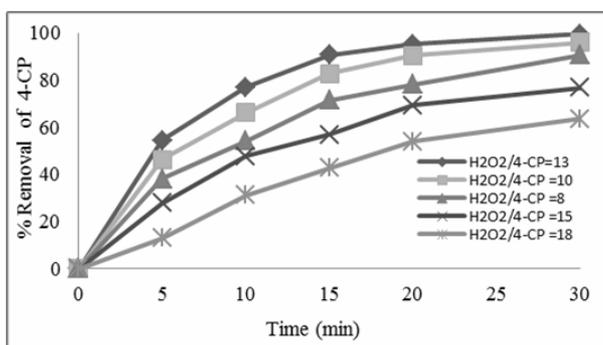


**Fig.6:** Pseudo-first-order rate constant for 4-CP degradation by UV/H<sub>2</sub>O<sub>2</sub> system, 4-CP=0.39\*10<sup>-3</sup> mol/L, pH=3.

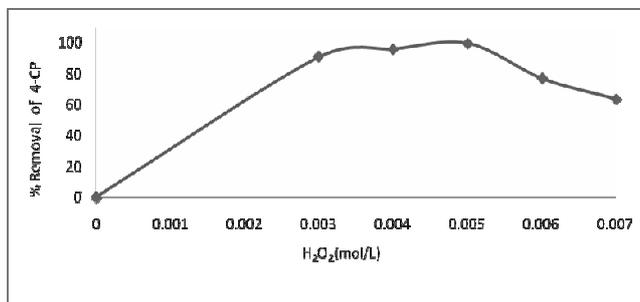


**Fig.7:** Pseudo-first-order rate constant for 4-CP degradation as a function of H<sub>2</sub>O<sub>2</sub> initial concentration by UV/H<sub>2</sub>O<sub>2</sub> system, 4-CP = 0.39\*10<sup>-3</sup> mol/L, pH=3, irradiation time 90 min.

In this sense, a series of experiments were carried out in order to determine the optimum ratio of H<sub>2</sub>O<sub>2</sub>/4-CP. Different concentrations of H<sub>2</sub>O<sub>2</sub> (0.003 , 0.004 , 0.005 , 0.006 and 0.007 mol/L) were used in the presence of fixed Fe<sup>+3</sup> concentration 0.078\*10<sup>-3</sup> mol/L . H<sub>2</sub>O<sub>2</sub>/4-CP ratios for these concentrations were 8,10,13,15 and 18 respectively, while the ratio of Fe<sup>+3</sup>/4-CP was 0.2. The results are plotted in Figs. 8 and 9. From these figures it can be noticed that a significant enhancement of degradation efficiency was observed when the H<sub>2</sub>O<sub>2</sub> concentration was increased to 0.005 mol/L. (i.e. the ratio of H<sub>2</sub>O<sub>2</sub>/4-CP =13). Above this concentration, the oxidation rate seems to be negatively affected by the increase of H<sub>2</sub>O<sub>2</sub> up to 0.007 mol/L (i.e. the molar ratio of H<sub>2</sub>O<sub>2</sub>/4-CP =18). This is due to both the auto-decomposition of H<sub>2</sub>O<sub>2</sub> into oxygen and water, and the scavenging effect of hydroxyl radicals by H<sub>2</sub>O<sub>2</sub>. Excess of H<sub>2</sub>O<sub>2</sub> will react with HO<sup>•</sup> competing with organic pollutants and consequently reducing the efficiency of the treatment.



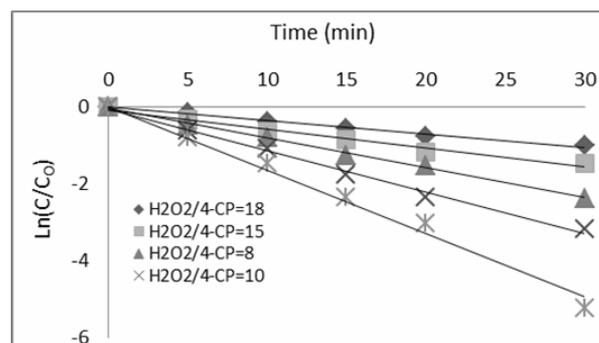
**Fig.8:** Degradation of 4-CP by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system, Fe<sup>+3</sup> = 0.078\*10<sup>-3</sup> mol/L , 4-CP = 0.39\*10<sup>-3</sup> mol/L (Fe<sup>+3</sup>/4-CP=0.2) , pH=3. The effect of initial H<sub>2</sub>O<sub>2</sub> concentration.



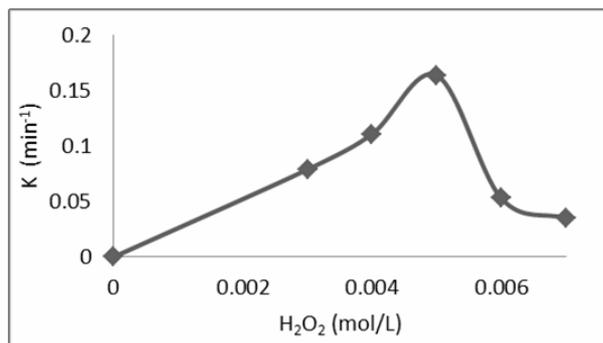
**Fig.9:** Degradation of 4-CP as a function of H<sub>2</sub>O<sub>2</sub> initial concentration by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system, Fe<sup>+3</sup>=0.078\*10<sup>-3</sup> mol/L ,4CP=0.39\*10<sup>-3</sup> mol/L (Fe<sup>+3</sup> /4-CP= 0.2), pH=3, irradiation time 30 min.

### 3.2.2. Reaction rate constant for UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system at constant Fe<sup>+3</sup>

The experimental data obtained for 4-CP degradation can be fitted according to a pseudo-first-order reaction; the results are plotted in Figs. 10 and 11. From these results it can be observed that addition of Fe<sup>+3</sup> to UV/ H<sub>2</sub>O<sub>2</sub> system with ratio of H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup>/4-CP equal to 13/0.2/1 enhanced the rate of 4-CP degradation by a factor of 1.9 (from 0.086 to 0.164 min<sup>-1</sup>) and decrease the amount of H<sub>2</sub>O<sub>2</sub> by a factor of 6 (from 0.03 to 0.005 mol/L).



**Fig.10:** Pseudo-first-order rate constant for 4-CP degradation by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system ,Fe<sup>+3</sup>=0.078\*10<sup>-3</sup> mol/L, 4-CP = 0.39\*10<sup>-3</sup> mol/L (Fe<sup>+3</sup> /4-CP= 0.2), pH=3.



**Fig.11:** Pseudo-first-order rate constant for 4-CP degradation as a function of H<sub>2</sub>O<sub>2</sub> initial concentration by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system, 4-CP=0.39\*10<sup>-3</sup> mol/L, Fe<sup>+3</sup>=0.078\*10<sup>-3</sup> mol/L (Fe<sup>+3</sup>/4CP=0.2), pH=3, irradiation time=30min.

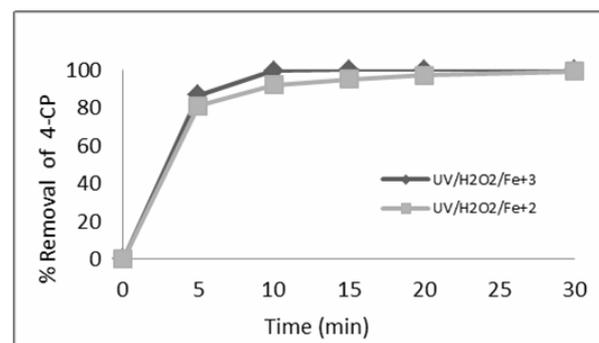
### 3.2.3. Effect of using Fe<sup>+2</sup> or Fe<sup>+3</sup> on UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system

Iron in its ferrous Fe<sup>+2</sup> (FeSO<sub>4</sub>·7H<sub>2</sub>O) and ferric Fe<sup>+3</sup> (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·7H<sub>2</sub>O) form was used as photocatalyst in the photo-Fenton system. Experiments with 4-CP concentration of 0.39\*10<sup>-3</sup> mol/L, H<sub>2</sub>O<sub>2</sub> of 0.005 mol/L, Fe<sup>+2</sup> or Fe<sup>+3</sup> of 0.078\*10<sup>-3</sup> mol/L and pH =3 were carried out in order to study the influence of using Fe<sup>+2</sup> or Fe<sup>+3</sup> on the degradation process. The results are plotted in Fig. 12. It can be seen from this figure, a slight increase in degradation was obtained for Fe<sup>+3</sup> photocatalyst. This may be illustrated as, the Fenton process is carried out in presence of Fe<sup>+2</sup> as catalyst; however the mineralization step appears to be driven by Fe<sup>+3</sup> catalyzed processes, especially in the presence of light (Pignatello et al., 1999). In the light of the experimental results besides the fact that degradation appears to be driven by Fe<sup>+3</sup>, Fe<sup>+3</sup> has been selected as catalyst to be used in the photo-Fenton experiments.

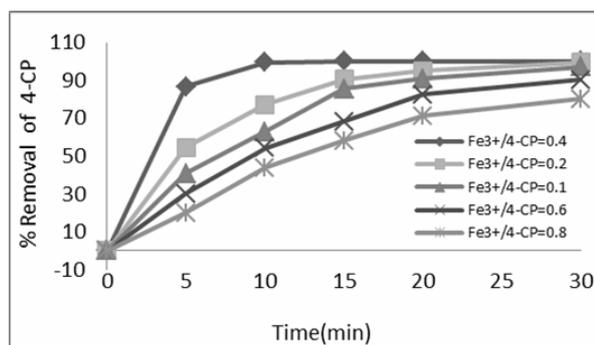
### 3.2.4. The effect of initial Fe<sup>+3</sup> concentration on UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system

The effect of initial Fe<sup>+3</sup> concentrations on photo-Fenton process was tested by carrying out experiments with various amounts of Fe<sup>+3</sup> (0.04, 0.078, 0.16, 0.23 and 0.31)\*10<sup>-3</sup> mol/L. Fe<sup>+3</sup>/4-CP ratios for these concentrations were 0.1, 0.2, 0.4, 0.6 and 0.8 respectively. The optimum H<sub>2</sub>O<sub>2</sub> concentration 0.005 mol/L (i.e. the ratio of H<sub>2</sub>O<sub>2</sub>/4-

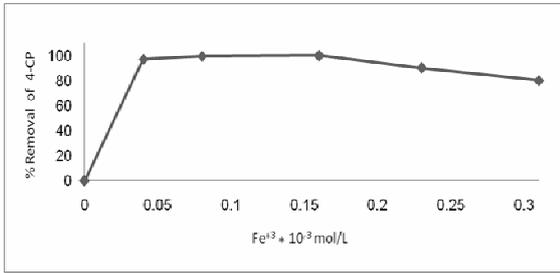
CP =13) was used in these experiments. The results are plotted in Figs. 13 and 14. From these figures it can be noticed that the addition of Fe<sup>+3</sup> enhanced the efficiency of UV/H<sub>2</sub>O<sub>2</sub> system for 4-CP degradation. The degradation rate of 4-CP distinctly increased with increasing amounts of the iron salt. It reached its maximum value at 0.16\*10<sup>-3</sup> mol/L Fe<sup>+3</sup> (Fe<sup>+3</sup>/4-CP ratio =0.4) after about 10min of irradiation time. The addition of the iron salt above this value did not affect the degradation, and had a negative effect.



**Fig.12:** The effect of Fe<sup>+2</sup> and Fe<sup>+3</sup> on the 4-CP degradation by UV/H<sub>2</sub>O<sub>2</sub>/Fe system, 4-CP=0.39\*10<sup>-3</sup> mol/L, H<sub>2</sub>O<sub>2</sub>= 0.005 mol/L (H<sub>2</sub>O<sub>2</sub>/4-CP=13), Fe<sup>+2</sup> = Fe<sup>+3</sup> = 0.078\*10<sup>-3</sup> mol/L (Fe/4-CP=0.2), pH=3.



**Fig.13:** Degradation of 4-CP by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system, H<sub>2</sub>O<sub>2</sub>=0.005mol/L, 4-CP = 0.39\*10<sup>-3</sup> mol/L (H<sub>2</sub>O<sub>2</sub>/4-CP=13), pH=3. The effect of initial Fe<sup>+3</sup> concentration.



**Fig.14:** Degradation of 4-CP as a function of Fe<sup>3+</sup> initial concentration, H<sub>2</sub>O<sub>2</sub>= 0.005 mol/L, 4-CP=0.39\*10<sup>-3</sup> mol/L (H<sub>2</sub>O<sub>2</sub>/4-CP=13), pH=3, irradiation time 30 min.

### 3.2.5. Reaction rate constant for UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> system at constant H<sub>2</sub>O<sub>2</sub>

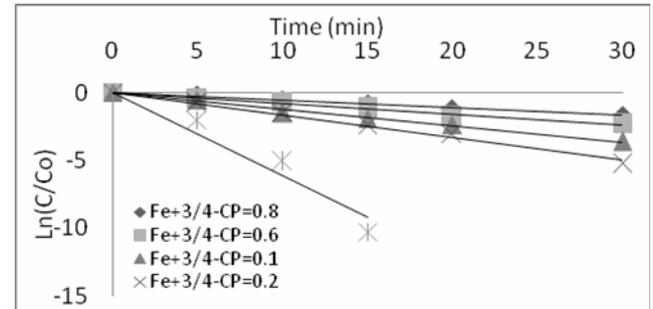
The experimental results in Figs. 15 and 16 show that the reaction rate was of a first order and the photo-Fenton process had a significant accelerating effect on the rate of oxidation of 4-CP. The reaction rate constant reaches its maximum value at 0.16\*10<sup>-3</sup>mol/L Fe<sup>3+</sup>(i.e. H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>/4-CP ratio =13/0.4/1). It can be observed that the photo-Fenton process enhanced the rate of 4-CP oxidation by a factor of 7 compared with UV/H<sub>2</sub>O<sub>2</sub> system (i.e. K increased from 0.086 to 0.614 min<sup>-1</sup>). The optimum ratio for H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> /4-CP was 13/0.4/1 which represents a ratio of 31 for H<sub>2</sub>O<sub>2</sub>/ Fe<sup>3+</sup>. This result is in a good agreement with Kavitha and Palanivelu (2004) , they reported that the optimal ratio was 20–40 and also with Kuo and Wu (2010) ,they showed that the optimal ratio of H<sub>2</sub>O<sub>2</sub>/ Fe<sup>3+</sup> was 40.

### 3.3.Effect of the pH value on UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> system

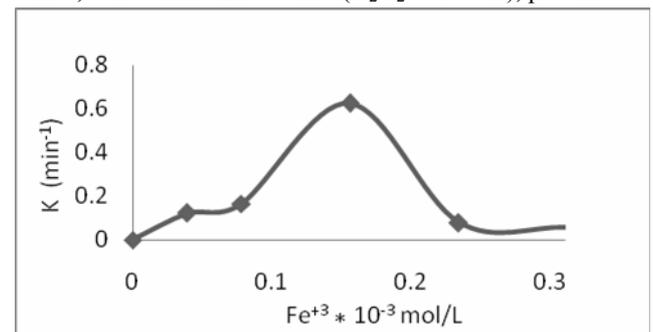
The photo-Fenton reaction is strongly affected by the pH-dependence. The pH value influences the generation of OH radicals and thus the oxidation efficiency. Different values of pH (2, 3, 4 and 5) were used to show its influence on the degradation of 4-CP. The results are plotted in Figs. 17 and 18. From these figures, it can be noticed that the maximum degradation was obtained with the system UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> at pH=3. For pH values above 3 the degradation strongly decreases, that is because at higher pH values iron precipitates as hydroxide and that reduces the transmission of the radiation. At lower levels of pH

self-decomposition of hydrogen peroxide is promoted (Meric et al.,2004) .

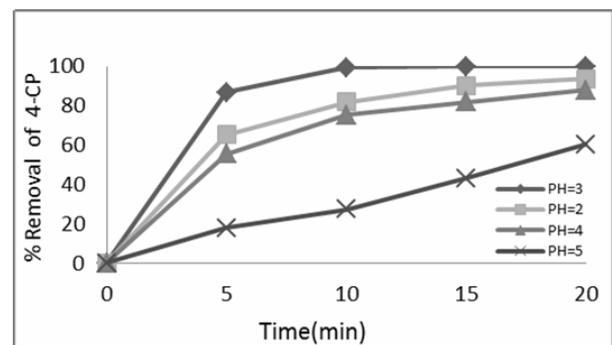
Therefore, a balance must be maintained to get an optimum condition. Figs. 19 and 20, illustrate the influence of pH values on the reaction rate of 4-CP.



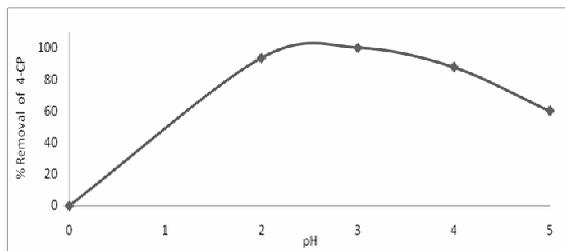
**Fig.15:**Pseudo-first-order rate constant for 4-CP degradation by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> system, H<sub>2</sub>O<sub>2</sub> = 0.005 mol/L, 4-CP=0.39\*10<sup>-3</sup> mol/L (H<sub>2</sub>O<sub>2</sub>/4-CP=13), pH=3.



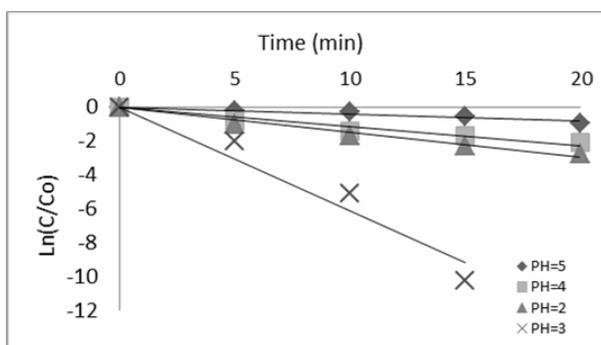
**Fig.16:**Pseudo-first-order rate constant for 4-CP degradation as a function of Fe<sup>3+</sup> initial concentration by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> system, H<sub>2</sub>O=0.005 mol/L, 4- CP=0.39\* mol/L (H<sub>2</sub>O<sub>2</sub>/4-CP=13), pH=3, irradiation time 30 min.



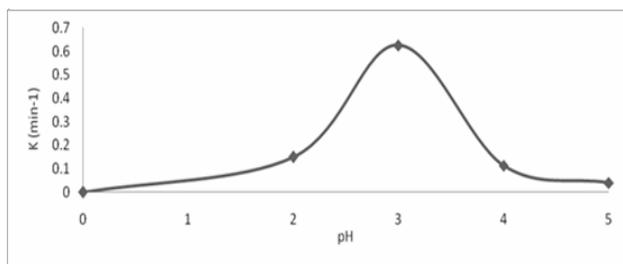
**Fig.17:** Degradation of 4-CP at different pH values by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> system, Fe<sup>3+</sup>=0.16\*10<sup>-3</sup>mol/L, H<sub>2</sub>O<sub>2</sub> = 0.005 mol/L, 4-CP=0.39\*10<sup>-3</sup> mol/L.



**Fig.18:** Degradation of 4-CP as a function of pH values by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system, Fe<sup>+3</sup> = 0.16\*10<sup>-3</sup> mol/L, H<sub>2</sub>O<sub>2</sub> =0.005mol/L,4CP=0.39\*10<sup>-3</sup> mol/L, irradiation time 20 min.



**Fig.19:**Pseudo-first-order rate constant for 4-CP degradation by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system at different values of pH, Fe<sup>+3</sup>=0.16\*10<sup>-3</sup> mol/L, H<sub>2</sub>O<sub>2</sub>=0.005 mol/L, 4-CP=0.39\*10<sup>-3</sup> mol/L.



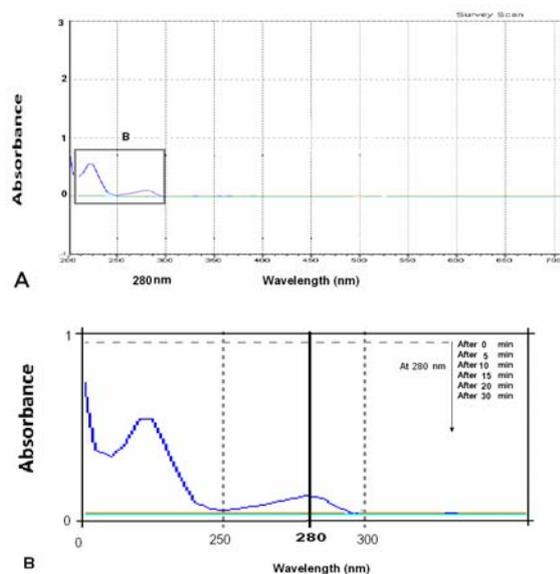
**Fig.20:**Pseudo-first-order rate constant for 4-CP degradation by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system as a function of pH, Fe<sup>+3</sup>=0.16\*10<sup>-3</sup> mol/L, H<sub>2</sub>O<sub>2</sub>=0.005 mol/L, 4-CP=0.39\*10<sup>-3</sup> mol/L, irradiation time 20 min.

### 3.4. Effect of initial 4-CP concentration on UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system

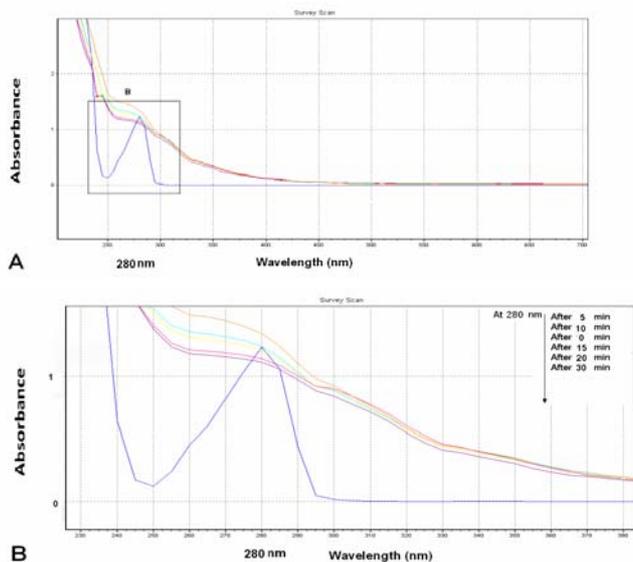
Experiments with 10ppm (0.078 \*10<sup>-3</sup> mol/L) and 100ppm (0.78 \*10<sup>-3</sup> mol/L) of 4-CP in the UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system were performed to see the

effect of initial concentration change on the degradation process. Figs. 21 and 22, show the UV-vis spectra for 4-CP degradation and its products at different irradiation time at 10 and 100ppm respectively. Referring to Figs. 21A and B, a high powerful oxidization ability for photo-Fenton system toward low level concentration of 4-CP (10ppm) was observed.

No absorbance in the region of intermediate degradation products was observed for hydroquinone (221 and 290 nm) and benzoquinone (247 and 500nm). After only 5 min of irradiation time a complete degradation of 4-CP was observed. Referring to Figs. 22A and B, for high 4-CP concentration (100ppm), a gradual rise in the base line over time was observed .The base line reached a maximum and then tended to decrease gradually for longer irradiation times. This can be the result of the accumulation of degradation products such as hydroquinone which absorb light at about the same wavelength range (221 and 290) nm as 4-CP and benzoquinone (at 247nm). In the visible spectrum, the signal of benzoquinone (at 500nm) is small, but it can be observed at all the times of the experiment.



**Fig.21(A and B):** UV-visible spectra for 4-CP degradation by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system , Fe<sup>+3</sup> =0.16\*10<sup>-3</sup> mol/L , H<sub>2</sub>O<sub>2</sub> = 0.005,4-CP= 0.078 \*10<sup>-3</sup> mol/L (10ppm), pH=3, irradiation time 30min.



**Fig.22(A and B):** UV-visible spectra for 4-CP degradation by UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system, Fe<sup>+3</sup> = 0.16 \* 10<sup>-3</sup>

mol/L, H<sub>2</sub>O<sub>2</sub> = 0.005 mol/L, 4-CP = 0.78 \* 10<sup>-3</sup> mol/L (100ppm), pH= 3, irradiation time 30 min.

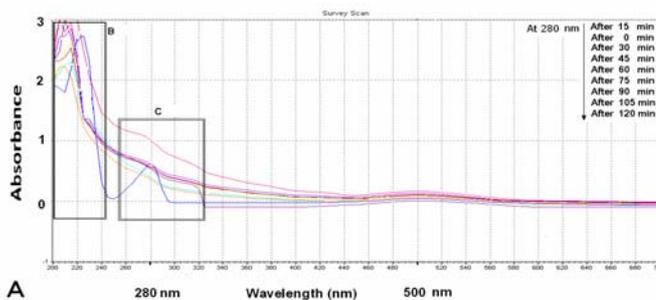
### 3.5. Evolution of color due to intermediate formation

The main intermediates that were generated during the 4-CP degradation are hydroquinone and benzoquinone. Hydroquinone was the primary formed product from the degradation of 4-CP. A colored solution of benzoquinone could be observed through the first 5 minutes of irradiation time for UV/H<sub>2</sub>O<sub>2</sub> system when low concentration (0.01mol/L) of H<sub>2</sub>O<sub>2</sub> was used. This can be indicated from the absorption peaks that appear at 500nm, Fig.23. The initial colorless of the solution became green in first 5 minutes of reaction and then dark green after 15 minutes, and gradually the color intensity decreased, finally disappeared, Fig 24. Also the colored solution of benzoquinone could be observed through the first 5 min for the UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system at high concentration (100ppm) of 4-CP. It can realized that when there is insufficient amount of reagents required to degraded the 4-CP, intermediate compounds from the degradation product were formed and remain in the

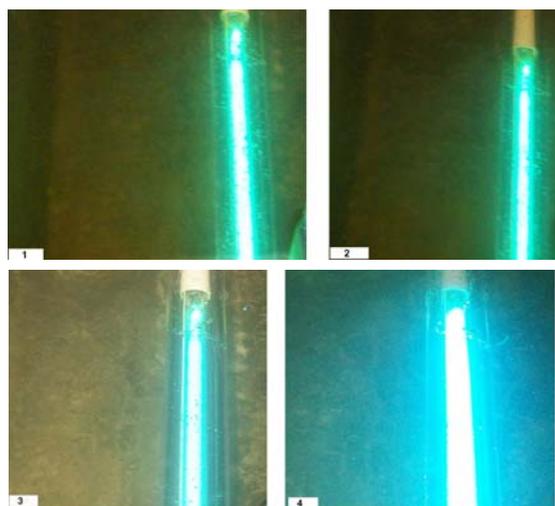
solution where longer irradiation time for complete degradation and mineralization of 4-CP is required.

### 3.6. Comparison between UV/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> systems

The photo degradation of 4-CP was investigated in both systems UV/H<sub>2</sub>O<sub>2</sub> and photo-Fenton UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup>. The optimum results are listed in Table 3. It can be indicated that the photo-Fenton system had a significant accelerating effect on the rate of oxidation of 4-CP. The data in Table 3 show that adding Fe<sup>+3</sup> to the UV/H<sub>2</sub>O<sub>2</sub> system enhanced the rate of 4-CP oxidation by a factor of 7, reduce the consumption of H<sub>2</sub>O<sub>2</sub> by a factor of 6 and the irradiation time required for complete degradation was reduced by a factor of 6. The intermediate products were also minimized.



**Fig.23:** UV-visible spectra for the 4-CP degradation and its photoproducts, 4-CP = 0.39\*10<sup>-3</sup>mol/L, H<sub>2</sub>O<sub>2</sub>=0.01 mol/L, pH= 3.



**Fig.24:** Closer photos inside the reactor for the color evolution in 4-CP solution, H<sub>2</sub>O<sub>2</sub> = 0.01mol/L, 4-CP = 0.39\*10<sup>-3</sup> mol/L, pH=3, irradiation time 120 min.

**Table 3**

A comparison between UV/H<sub>2</sub>O<sub>2</sub> and UV /H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> systems

System	H <sub>2</sub> O <sub>2</sub> (mol/L)	Fe <sup>+3</sup> (mol/L)	p H	Irradiation time(min)	K (min <sup>-1</sup> )
UV/H <sub>2</sub> O <sub>2</sub>	0.03	--	3	90	0.086
UV/H <sub>2</sub> O <sub>2</sub> /Fe <sup>+3</sup>	0.005	0.16*10 <sup>-3</sup>	3	15	0.614

#### 4. Conclusions

The main conclusions that can be drawn from the experimental work of this study are as follows:

1. When there is insufficient amount of reagents required to degrade 4-CP, intermediate compounds from the degradation product are formed, remain in the solution and need longer irradiation time for complete degradation and mineralization. The intermediate products are identified:

- At low concentration of H<sub>2</sub>O<sub>2</sub> (0.01mol/L) in UV/H<sub>2</sub>O<sub>2</sub> system for 4-CP at concentration of 50ppm.
- At high concentration of 4-CP (100ppm) for UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system at H<sub>2</sub>O<sub>2</sub> concentration of 0.005mol/L.

2. When insufficient amounts of reagents are used, a colored substance (benzquinone) was formed in the above systems (smaller signal of benzquinone for UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system) after 5 min of irradiation time then the color intensity are decreased and disappeared at longer irradiation time ,120min for UV/H<sub>2</sub>O<sub>2</sub> and 30min in UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> systems.

3. The study showed that the photo-Fenton process, was the most effective treatment process under acidic conditions pH=3 and produced a higher rate of degradation of 4-CP at a short irradiation time. The results show that adding Fe<sup>+3</sup> to the UV/H<sub>2</sub>O<sub>2</sub> system with a molar ratio of H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup>/4-CP equal to 13/0.4/1 enhanced the rate of 4-CP oxidation by a factor of 7, reduce the consumption of H<sub>2</sub>O<sub>2</sub> by a factor of 6 and the irradiation time required to complete degradation was reduced by a factor of 4.5. The intermediate and colored products were also minimized.

4. The experimental results showed that the optimum reagents for a complete degradation of 4-CP (50ppm) were obtained at pH=3, H<sub>2</sub>O<sub>2</sub>=0.005 mol/L, Fe<sup>+3</sup> =0.016 mol/L and irradiation time of

15 min for UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup> system with a molar ratio of H<sub>2</sub>O<sub>2</sub>/Fe<sup>+3</sup>/4-CP equal to 13/0.4/1.

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