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Removal of 4-chlorophenol from wastewater using a pilot-scale advanced oxidation process

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ABSTRACT

Advanced oxidation processes utilizing both UV/H_2O_2 and photo-Fenton UV/H_2O_2/Fe^{+3} systems were investigated using pilot-scale experiments for the degradation and mineralization of 4-chlorophenol (4-CP). The experiments were conducted by using a photoreactor, which consists of three UV lamps fixed in staggered form. Three baffles were fixed vertically at the reactor side walls. These baffles reduce the presence of low radiation zones near the reactor walls. The study shows 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 very short irradiation time. The reaction was found to follow the first order through both systems. A colored solution of benzoquinone can be observed through the first 5 min of irradiation time for the UV/H_2O_2 system when a low concentration (0.01 mol/L) of H_2O_2 was used. The colored solution of benzoquinone can also be observed through the first 5 min for the UV/H_2O_2/Fe^{+3} system at a high concentration (100 ppm) of 4-CP. The experimental results show that the optimum reagents for complete degradation of 4-CP (50 ppm) were $H_2O_2 = 0.005$ mol/L, $Fe^{+3} = 0.16 \times 10^{-3}$ mol/L under acidic conditions (pH = 3), and irradiation time of 15 min for the UV/H_2O_2/Fe^{+3} system with a molar ratio of H_2O_2/Fe^{+3}/4-CP equals 13/0.4/1.

Keywords: 4-chlorophenol; Advance oxidation process; Fenton process; Photo-Fenton process; UV photolysis

1. Introduction

Chlorophenols (CPs) constitute a group of organic substances that are introduced into the environment as a result of quite a lot of actions. CPs are highly toxic and cause considerable damage to the ecosystem and human health. They are notified as potential toxic compounds by the United States Environmental Protection Agency [1]. The European Community issued a pollutant list including many CPs, and established their maximum allowable concentration in drinking water at (0.5 μg/L) [2]. They are introduced into the environment as a result of several human activities, e.g. water disinfection, waste incineration, uncontrolled used of pesticides and herbicides, as well as through the by-products of bleaching of paper pulp with chlorine [3].

All CPs possess bactericidal activities that increase with the degree of chlorination. CPs are highly toxic to algae. Most of the plants are highly sensitive to the phytotoxicity of CPs. As for aquatic organisms, fish and other aquatic organisms absorb CPs through their gills, gastrointestinal tract, or skin.

4-Chlorophenol (4-CP) was chosen as a model pollutant in the present research. The acute (short-term) health effects may occur immediately or shortly after

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exposure to 4-CP. It is very hazardous in case of skin contact (irritant) and of eye contact (irritant). Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Severe over-exposure can produce lung damage, choking, unconsciousness, or death. The chronic (long-term) health effects can occur at some time after exposure to 4-CP, and can last for months or years. The substance may be toxic to the liver, brain, gastrointestinal tract, upper respiratory tract, and central nervous system [4].

Most CPs are barely biodegradable and also difficult to remove from the environment, thus increasing their hazardous potential to the environment due to the proven toxicity and suspected carcinogenicity as well. Due to the low biodegradability of CPs, as well the shortcomings of insufficiently effective common wastewater treatment technologies, particularly physical and chemical–physical methods transferring the pollution from one phase to another causing a demand for secondary treatment, alternative treatment technologies, such as advanced oxidation technologies, have received increased interest [1].

Several technologies are included in the advanced oxidation processes (AOPs), such as Fenton, photo-Fenton, wet oxidation, ozonation, photo catalysis, etc. The main difference among them is the manner used to form the radicals. Even though these techniques can convert contaminants to less harmful compounds, on most occasions oxygenated organic products and low molecular weight acids are formed throughout the process; in addition, AOPs are limited to treating water which contains low concentrations of organic or inorganic scavenging substances [5].

The photochemical AOPs, including photolysis and photocatalysis, are attractive environmental remediation technologies. They are gaining increasing importance for the degradation of most organic pollutants. A combination of H_2O_2 and UV radiation with Fe^{+2}or Fe^{+3}, the so-called photo-Fenton process, is a promising process in which iron salts serve as photocatalysts and H_2O_2 as an oxidizing agent. It represents an efficient and cheap method for wastewater treatment, and produces more hydroxyl radicals in comparison with the systems UV/H_2O_2, thus promoting the degradation of various organic pollutants [6].

Experiences with different oxidation technologies and substrates have shown that partial oxidation of toxic water may increase its biodegradability, up to high levels. The use of AOPs as a pretreatment step to enhance the biodegradability of wastewater containing recalcitrant or inhibitory pollutants can be justified if the resulting intermediates are readily degradable by micro-organisms in further biological treatment. Consequently, photo-Fenton processes, and AOPs in general, have been proposed as a pretreatment to biological treatment for toxic wastewater streams [7].

Different intermediate products have been identified during the oxidation process of 4-CP and phenolic compounds [8]. The major intermediates are benzoquinone, hydroquinone, 4-chlorocatechol, and catechol. Some of these identified intermediates were more toxic than the primary compound [9].

Elghniji et al. [10] showed that the concentration of hydroquinone initially increased nearly linearly with the degradation of 4-CP, and after 180 min of irradiation, the concentration of this major intermediate underwent a fast drop, indicating the mineralization of 4-CP.

The objective of this work is to study the effectiveness of the AOPs in the degradation of 4-CP as one of the main compounds of the CPs, using a pilot-plant scale. The AOPs selected to carry out this study were UV/H_2O_2 system and photo-Fenton ($UV/H_2O_2/Fe^{3+}$) system. To achieve the experimental objectives, different variables were chosen throughout the treatment: 4-CP concentration, pH, H_2O_2, and Fe^{3+} concentrations.

2. Materials and methods

2.1. Materials

The materials used in the experimental setup involve 4-CP C6H5CLO (Fluka), hydrogen peroxide H_2O_2 50% wt./wt. (Scharlau), ferrous sulphate heptahydrate $FeSO_4.7H_2O$ (Thomas Baker), ferric sulphate heptahydrate $Fe_2(SO_4)_3{\cdot}7H_2O$ (Thomas Baker), sodium thiosulfate pentahydrate $Na_2S_2O_3{\cdot}5H_2O$ (Riedel Seelze Hannover), and sulfuric acid H_2SO_4 (BDH). All materials were analytical grade and used as received. The solutions were prepared by dissolving the requisite quantity in distilled water. The pH of the solution was adjusted by using a sulfuric acid solution. Initial pH of the solution was monitored using a pH meter (WTW Co., Germany, INOLAB 720).

2.2. Equipment

A laboratory-scale setup of the AOPs system applied in this study is presented in Fig. 1(A). The reactor (1) was made entirely of aluminum with an effective volume of 37.5 L. A feed tank (5) of 24 L volume was used to prepare the solutions. The solution was circulated at a flow rate of 3 L/min by using a water pump (3) of 0.5 hp and 0.37 kw (Marquis Co., China). To measure the flow rate, a calibrated flow

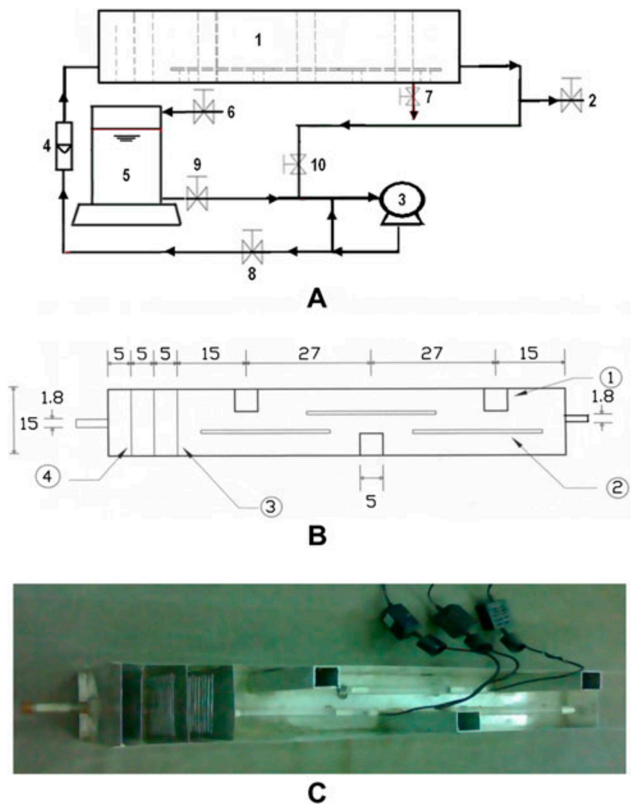

Fig. 1. (A): A laboratory scale set up of AOPs system. (1) AOPs reactor, (2) sample extraction valve, (3) water pump, (4) flow meter, (5) feed tank (waste water), (6) washing water inlet valve, (7) drain valve, and (8, 9 and 10) control valves; (B): AOPs reactor dimensions; and (C): A photograph of the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

meter (4) of the Hidrotek type with a flow range of 3–20 L/min was used. This flow meter was installed vertically, and the flow direction was upward. Valves were utilized for sampling, washing, draining, and control in the AOPs system as illustrated in Fig. 1(A). The reactor dimensions are illustrated in Fig. 1(B). All dimensions (in cm) schematically depict the experimental system employed in this investigation. A photograph of the photo reactor is shown in Fig. 1(C). The inlet and outlet pipes were 1.8 cm in diameter. Two vertical plates with 10 rectangular openings (13 × 1 cm) were used as distributors. Three removable side baffles were fixed vertically at the reactor side walls. These baffles have a 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, Philips, England), 4-pin single ended, these lamps emit output power at a wavelength of 253.7 nm, and each one 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 and 12 cm. If this distance is less than 5 cm, then the UV energy will be absorbed by the adjacent UV lamp, and if the spacing is more than 12 cm, there will be a formation of a zone with low UV intensity between the lamps [11,12]. In this study 10 cm spacing was used.

2.3. Experimental procedure

The desired concentration of 4-CP was prepared, and the pH was adjusted by adding a dilute H_2SO_4 solution in the feed tank. Mixing was maintained by using a mechanical stirrer for 5 min. An initial sample (sample at time zero) was taken for analysis. The solution was allowed to flow from the feed tank through the pump to the photoreactor. The desired quantity of H_2O_2 was added to the feed tank. Circulation for few minutes was allowed, and then the UV light source was switched on.

Samples were taken every 15 min until the end of the run. Samples were stored in 10 ml vials before analysis. One drop of $Na_2S_2O_3.5H_2O$ (0.1 N) was added to each sample to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with 4-CP during the analysis.

For the $UV/H_2O_2/Fe^{+3}$ system, the same procedure was followed, the desired quantity of ferric sulphate was added in the feed tank before adding H_2O_2.The system was cleaned after the end of each run.

AUV-visible spectrophotometer (Model SP-3,000 plus, Optima Co., 2003, Japan) was used to analyze the samples.

3. Results and discussion

3.1. UV/H_2O_2 system

The combination of UV radiation and a small amount of H_2O_2 strongly enhanced the efficiency of degradation of 4-CP. Experiments were carried out at different doses of H_2O_2 (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^{-3} mol/L (50 ppm) was maintained during the experiments.

3.1.1. Spectrophotometric analyses for UV/H_2O_2 system

Both concentration variation for H_2O_2 and recording of corresponding ultraviolet-visible spectra allowed identification of oxidation reaction steps. Analyses were performed at different times with

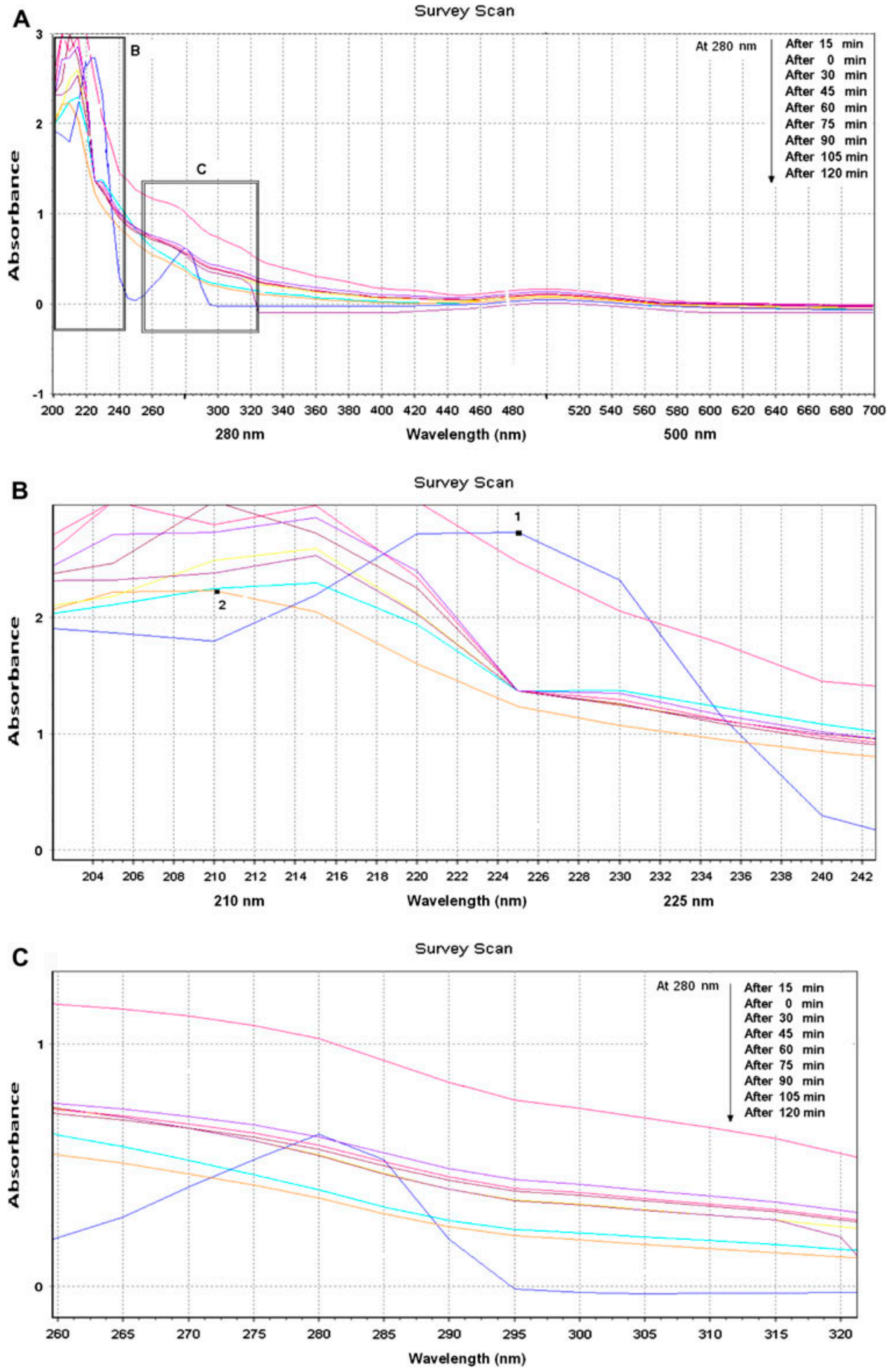

Fig. 2. (A) UV–visible spectra for the 4-CP degradation at $H_2O_2 = 0.01$ mol/L, 4-CP concentration = 0.39×10^{-3} mol/L, pH = 3; (B) illustration for the region B in A; and (C) illustration for the region C in A.

different H_2O_2 concentrations (0.01, 0.02, 0.03 and 0.04 mol/L). The evolution of absorption spectra vs. time is shown in Figs. 2–5. Fig. 2(A) shows the UV-visible absorption spectra for 0.01 mol/L H_2O_2 concentration. From this figure, it can be seen that the absorbance spectra at time = 0 for 4-CP appears at 225 and 280 nm, and absorption in the visible region of benzoquinone (intermediate degradation product) at 500 nm was presented. Fig. 2(B) shows the moving of 225 nm maximum at time = 0 to 210 nm at time = 120 min (point 1 and point 2), and a gradual rise in the baseline over time was also observed. This is the result of accumulation of some intermediate degradation products such as hydroquinone, which absorb light at about the same wavelength range (221 and 290 nm) of 4-CP. The baseline reached a maximum and then tended to decrease gradually for longer irradiation time because of the degradation of the intermediate products. Fig. 2(C) illustrates the disappearance of the 280 nm maximum. This is possibly associated with 4-CP degradation.

Figs. 3–5 show the analysis at higher H_2O_2 concentration, 0.02, 0.03, and 0.04 mol/L, respectively. The peaks at 225 and 280 nm gradually diminished with increasing irradiation time, and reached zero at Fig. 4 after 90 min at an H_2O_2 concentration of 0.03 mol/L, meaning complete mineralization and degradation of 4-CP were achieved.

3.1.2. *The effect of initial H_2O_2 concentration on the UV/H_2O_2 system*

Different concentrations of H_2O_2 (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 were plotted in Fig. 6. From this figure, it can be noticed that the degradation rate of 4-CP increased as the concentration of H_2O_2 increased at 0.02 and 0.03 mol/L, and achieve 100% degradation at 0.03 mol/L after 90 min of irradiation time. Then, the degradation decreased as the H_2O_2 increased at 0.04

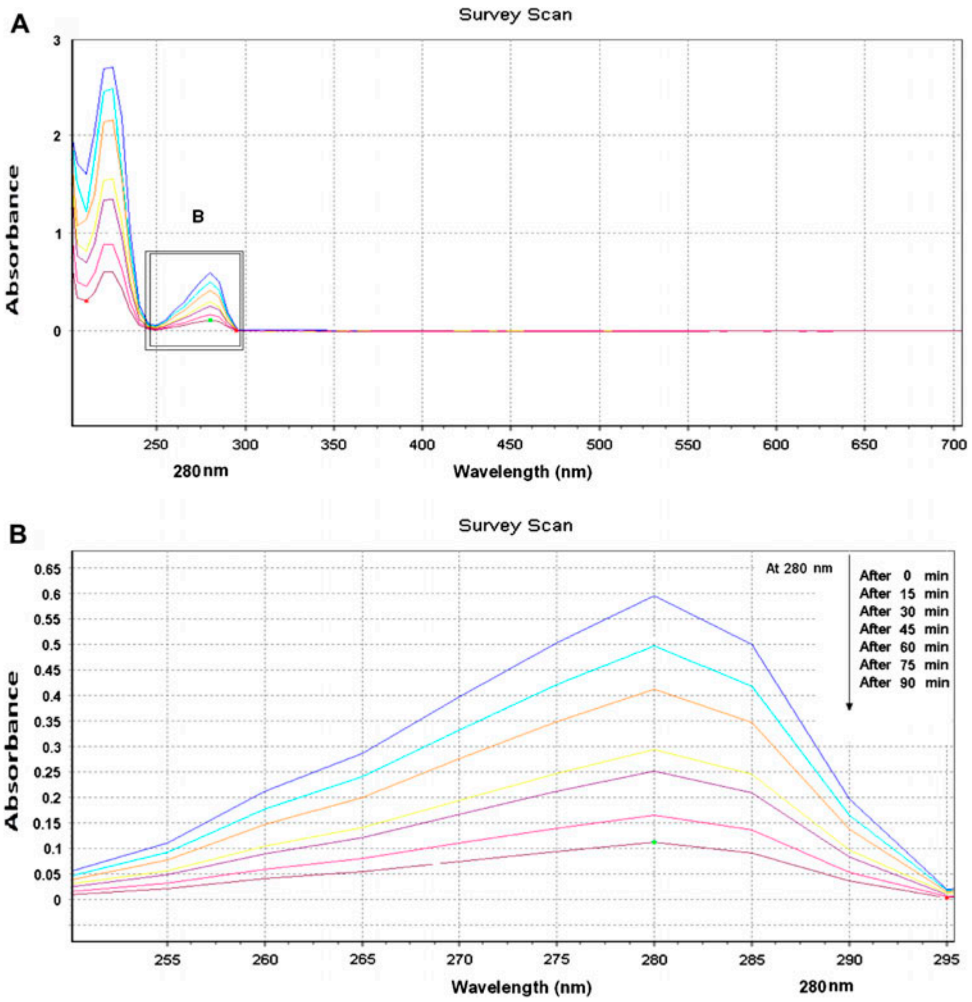

Fig. 3. (A and B) UV–visible spectra for 4-CP degradation at $H_2O_2 = 0.02$ mol/L, 4-CP concentration = 0.39×10^{-3} mol/L, pH = 3.

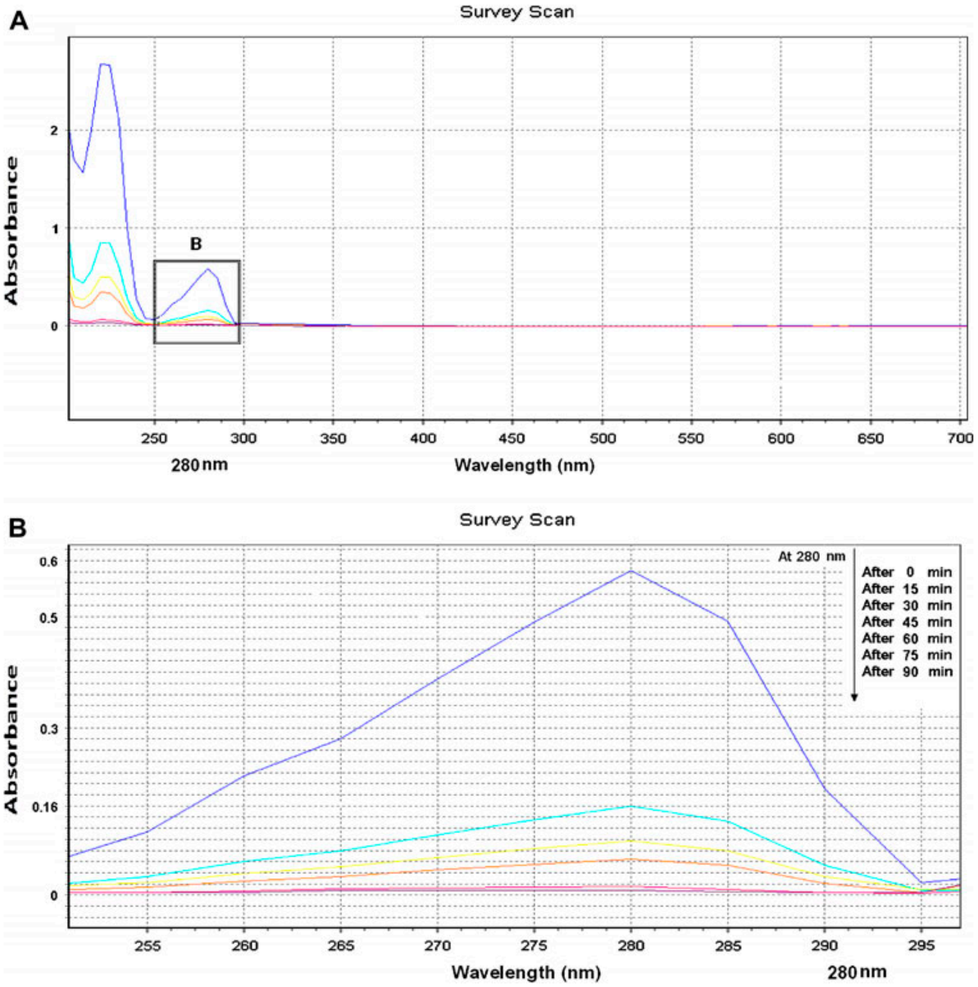

Fig. 4. (A and B) UV-visible spectra for 4-CP degradation at $H_2O_2 = 0.03$ mol/L, 4-CP concentration = 0.39×10^{-3} mol/L, pH = 3.

and 0.05 mol/L, reaching 45% of degradation at 0.05 mol/L.

Many investigators give 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_2O_2 reduces the rate of degradation of 4-CP, due to the reaction of hydrogen peroxide with these radicals, and hence acting as an inhibiting agent of 4-CP degradation (i.e. self scavenging of OH by H_2O_2). Hydroxyl radicals may recombine and participate in radical–radical reactions to form H_2O_2. At higher H_2O_2 concentrations, lower light intensity is available for 4-CP degradation; since H_2O_2 also absorbs light in the system, this can be attributed to low degradation of 4-CP. A hydroxyl radical efficiently reacts with H_2O_2 and produces HO_2, since HO_2 radicals are not as reactive as OH, and then low degradation may be obtained. H_2O_2 is an OH scavenger, so an excess of H_2O_2 can result in a net decrease in the treatment efficiency [5]. However, if H_2O_2 dose is low, OH formation will also be low, decreasing the treatment efficiency. Therefore, a balance must be maintained between excess and low levels of H_2O_2.

3.2. *UV/H_2O_2/Fe^{+3} (photo-Fenton) system*

3.2.1. *The effect of initial H_2O_2 concentration on UV/H_2O_2/Fe^{+3} system*

In a photo-Fenton system, both Fe^{+3} ($Fe_2(SO_4)_3{\cdot}7H_2O$) and H_2O_2 were used to attain the desirable degradation. First, Fe^{+3} is fixed at a constant concentration while H_2O_2 is changed until the best degradation was obtained. In this sense, a series of

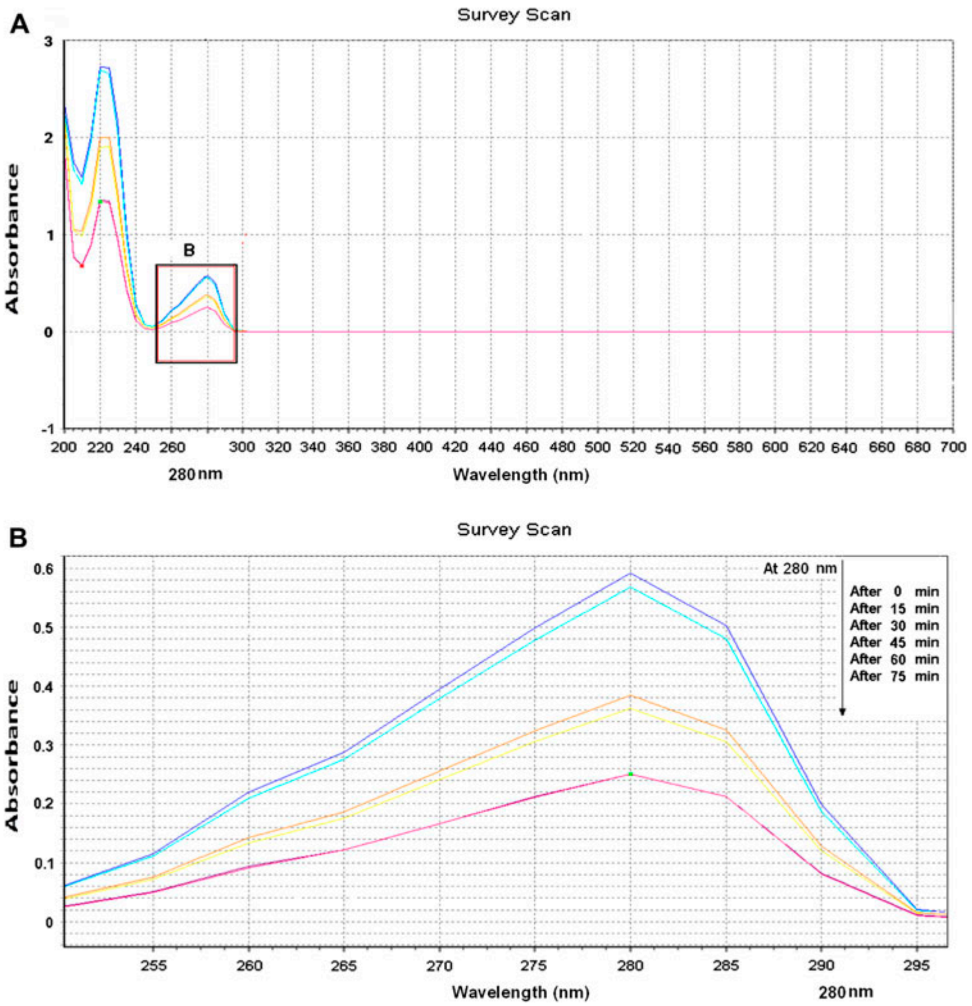

Fig. 5. (A and B) UV–visible spectra for 4-CP degradation at $H_2O_2 = 0.04$ mol/L, 4-CP concentration = 0.39×10^{-3} mol/L, pH = 3.

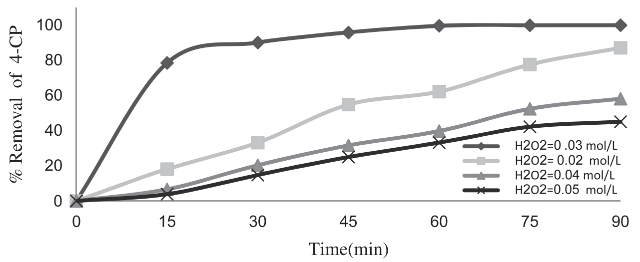

Fig. 6. Degradation of 4-CP by UV/H_2O_2 system, 4-CP = 0.39×10^{-3} mol/L, pH = 3. The effect of initial H_2O_2 concentration.

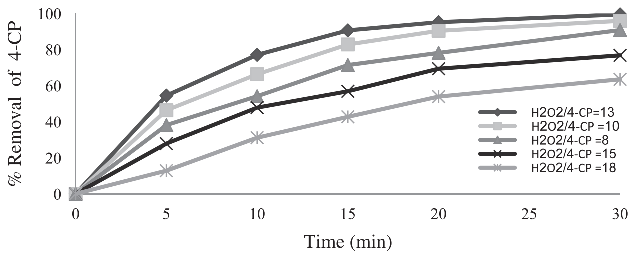

Fig. 7. Degradation of 4-CP by UV/H_2O_2/Fe^{+3} system, $Fe^{+3} = 0.078 \times 10^{-3}$ mol/L, 4-CP = 0.39×10^{-3} mol/L (Fe^{+3}/4-CP = 0.2), pH = 3. The effect of initial H_2O_2 concentration.

experiments were carried out in order to determine the optimum ratio of H_2O_2/4-CP. Different concentrations of H_2O_2 (0.003, 0.004, 0.005, 0.006, and 0.007 mol/L) were used in the presence of a fixed Fe^{+3} concentration (0.078×10^{-3} mol/L). H_2O_2/4-CP ratios for these concentrations were 8,10,13,15, and 18, respectively. The ratio of Fe^{+3}/4-CP is equal to 0.2. The results were plotted in Fig. 7. From this figure, it can be noticed that a significant enhancement of degradation efficiency was observed when the H_2O_2 concentration was increased to 0.005 mol/L (i.e. the ratio of H_2O_2/4-CP = 13). Above this concentration,

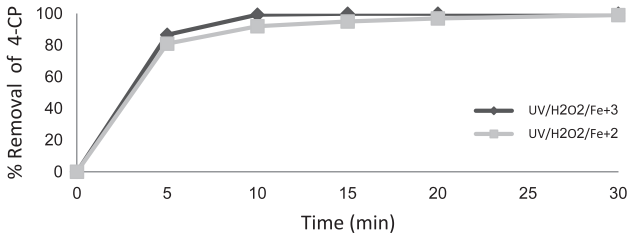

Fig. 8. The effect of Fe^{+2} and Fe^{+3}on the 4-CP degradation by $UV/H_2O_2/Fe$ system, $4\text{-CP} = 0.39 \times 10^{-3}$ mol/L, $H_2O_2 = 0.005$ mol/L ($H_2O_2/4\text{-CP} = 13$), $Fe^{+2} = Fe^{+3} = 0.078 \times 10^{-3}$ mol/L (Fe/4-CP = 0.2), pH = 3.

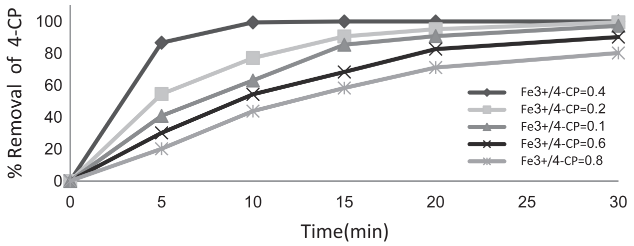

Fig. 9. Degradation of 4-CP by $UV/H_2O_2/Fe^{+3}$ system, $H_2O_2 = 0.005$ mol/L, $4\text{-CP} = 0.39 \times 10^{-3}$ mol/L (H_2O_2/4-C$p = 13$), pH = 3. The effect of initial Fe^{+3}concentration.

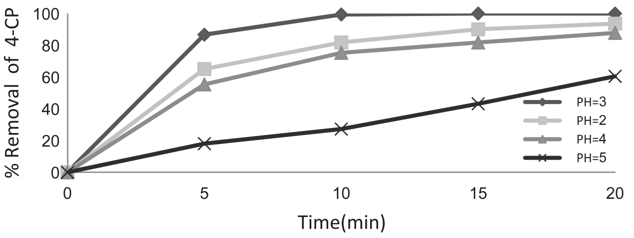

Fig. 10. Degradation of 4-CP at different pH values by $UV/H_2O_2/Fe^{+3}$ system, $Fe^{+3} = 0.16 \times 10^{-3}$ mol/L, $H_2O_2 = 0.005$ mol/L, $4\text{-CP} = 0.39 \times 10^{-3}$ mol/L.

the oxidation rate seems to be negatively affected by the increase of H_2O_2, up to 0.007 mol/L (i.e. the molar ratio of $H_2O_2/4\text{-CP} = 18$). This is due to the auto-decomposition of H_2O_2 into both oxygen and water, and the scavenging effect of hydroxyl radicals by H_2O_2. Excess H_2O_2 will react with OH competing with organic pollutants, consequently reducing the efficiency of the treatment.

3.2.2. The effect of using Fe^{+2} or Fe^{+3} on a $UV/H_2O_2/Fe^{+3}$ system

Iron in its ferrous Fe^{+2} ($FeSO_4.7H_2O$) and ferric Fe^{+3} ($Fe_2(SO_4)_3.7H_2O$) forms was used as a photocatalyst in the photo-Fenton system. Experiments with a 4-CP concentration of 0.39×10^{-3} mol/L, H_2O_2 of 0.005 mol/L, Fe^{+2} or Fe^{+3} of 0.078×10^{-3} mol/L, and pH = 3 were carried out in order to study the influence of using Fe^{+2} or Fe^{+3} on the degradation process. The results were plotted in Fig. 8. It can be seen from this figure that a slight increase in degradation degree was obtained for the Fe^{+3} photocatalyst. This can be illustrated as the Fenton process is carried out in the presence of Fe^{+2} as a catalyst; however, the mineralization step appears to be driven by a Fe^{+3} catalyzed processes, especially in the presence of light [13]. In light of the experimental results, besides the fact that degradation appears to be driven by Fe^{+3}, Fe^{+3} has been selected as the catalyst to be used in the photo-Fenton experiments.

3.2.3. The effect of initial Fe^{+3} concentrations on $UV/H_2O_2/Fe^{+3}$ system

The effect of initial Fe^{+3} concentrations on the photo-Fenton process was tested by carrying out experiments with various amounts of Fe^{+3} (0.04, 0.078, 0.16, 0.23, and 0.31×10^{-3} mol/L). Fe^{+3}/4-CP ratios for these concentrations were 0.1, 0.2, 0.4, 0.6, and 0.8, respectively. The optimum H_2O_2 concentration of 0.005 mol/L (i.e. the ratio of $H_2O_2/4\text{-CP} = 13$) was used in these experiments. The results were plotted in Fig. 9, from which it can be noticed that the addition of Fe^{+3} enhanced the efficiency of the UV/H_2O_2 system for 4-CP degradation. The degradation rate of 4-CP distinctly increased with increasing amounts of iron salt. It reached its maximum value at 0.16×10^{-3} mol/L Fe^{+3} (Fe^{+3}/4-CP ratio = 0.4) after about 10 min of irradiation time. The addition of the iron salt above this value did not affect the degradation; it has a negative effect. The negative effect can be explained as follows: the addition of ferric salt increases wastewater brown turbidity during the photo-treatment, which hinders the absorption of the UV light, required for the photo-Fenton process, and excess ferric ions can react with hydroxyl radicals, decreasing the attack of hydroxyl radicals on organic substrates. Also, the excess of ferric ions can react with OH radicals producing compounds that inhibit the reaction rate [6]. It is desirable that the ratio of H_2O_2 to Fe^{+3} should be as small as possible so that recombination can be avoided and the sludge production from the iron complex is also reduced.

3.2.4. Effect of the pH value on $UV/H_2O_2/Fe^{+3}$ system

The photo-Fenton reaction is strongly affected by 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

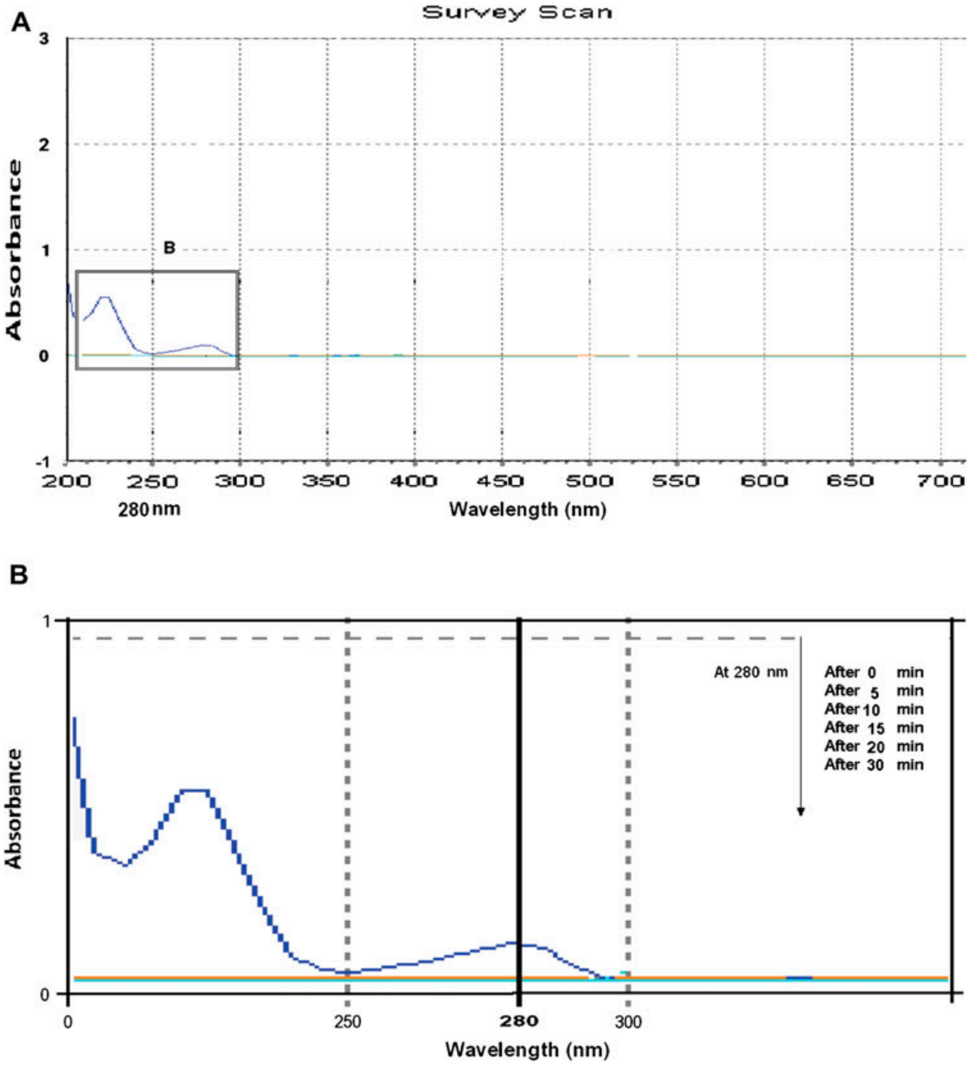

Fig. 11. (A and B) UV–visible spectra for 4-CP degradation by UV/ H_2O_2/Fe^{+3} system, $Fe^{+3} = 0.16 \times 10^{-3}$ mol/L, $H_2O_2 = 0.005$, 4-CP $= 0.078 \times 10^{-3}$ mol/L (10 ppm), pH = 3, irradiation time 30 min.

show its influence on the degradation of 4-CP. The results were plotted in Fig. 10. From this figure, it can be noticed that the maximum degradation was obtained with the system $UV/H_2O_2/Fe^{+3}$ at pH = 3. For pH values above 3, the degradation strongly decreases. This happens 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 [14]. Therefore, a balance must be maintained to get an optimum condition.

3.2.5. Effect of initial 4-CP concentration on a UV/H_2O_2/Fe^{+3} system

Experiments with 10 ppm (0.078×10^{-3} mol/L) and 100 ppm (0.78×10^{-3} mol/L) of 4-CP in the $UV/H_2O_2/Fe^{+3}$ system were performed to see the effect of concentration change on the degradation process. Figs. 11 and 12 show the UV-visible spectra for 4-CP degradation at different irradiation time at 10 and 100 ppm respectively. Referring to Fig. 11(A) and (B), a highly powerful oxidization ability for the photo-Fenton system toward a low-level concentration of 4-CP (10 ppm) was observed. No absorbance in the region of intermediate degradation products was noticed for hydroquinone (221 and 290 nm) and benzoquinone (247 and 500 nm). After only 5 min of irradiation time, complete degradation of 4-CP was seen. Referring to Fig. 12(A) and (B), for high 4-CP concentration (100 ppm), a gradual rise in the baseline over time was observed. The baseline reached a maximum and then tended to decrease gradually for longer irradiation times. This can be the result of the accumulation

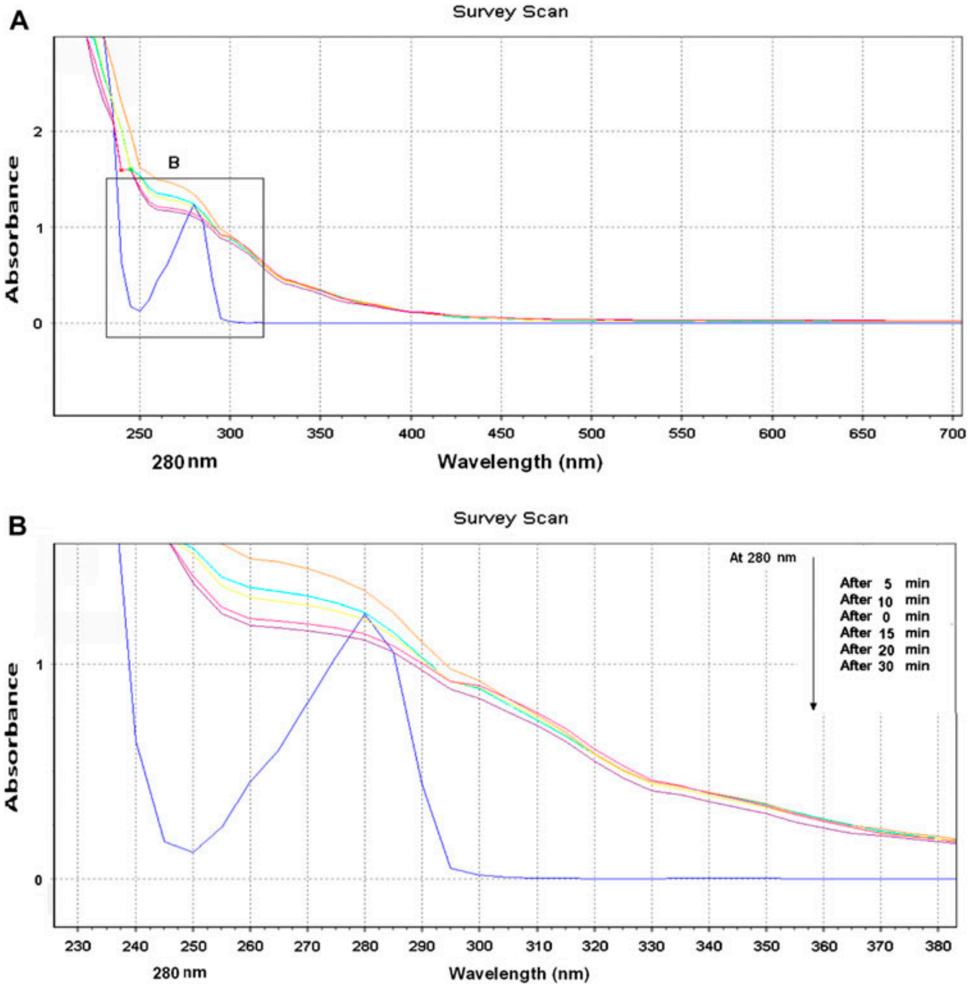

Fig. 12. (A and B) U-visible spectra for 4-CP degradation by UV/H_2O_2/Fe^{+3}system, $Fe^{+3} = 0.16 \times 10^{-3}$ mol/L, $H_2O_2 = 0.005$ mol/L, 4-CP = 0.78×10^{-3} mol/L (100 ppm), pH = 3, irradiation time 30 min.

of degradation products such as hydroquinone, which absorbs light at about the same wavelength range (221 and 290 nm) as 4–CP, and benzoquinone (at 247 nm). In the visible spectrum, the signal of benzoquinone (at 500 nm) is small, but it can be recognized at all times of the experiment.

3.3. Reaction rate constant for UV/H_2O_2 and UV/H_2O_2/Fe^{+3} systems

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

$$-\frac{dC}{dt} = KC \tag{1}$$

The integration leads to

$$\ln\frac{C}{C_O} = -K \times t \tag{2}$$

where C_o and C are the concentration of 4-CP at irradiation times 0 and t, K is a pseudo-first-order rate constant (in min^{-1}), and t is the irradiation time (in min). The regression analysis of the concentration curves vs. reaction times indicates that the decomposition rate of this compound could be described by first-order kinetics. The results are shown in Table 1. A correlation coefficient R^2 ranging from 0.94–0.99 can be seen, revealing that the rate of degradation was directly proportional to the concentration of 4-CP in aqueous solution. The highest K, equal to 0.086 min^{-1}at 0.03 mol/L H_2O_2 in the UV/H_2O_2 system, was gained.

The addition of Fe^{+3} to the UV/H_2O_2 system with a ratio of H_2O_2/Fe^{+3}/4-CP equal to 13/0.2/1 (i.e. $H_2O_2 = 0.005$, $Fe^{+3} = 0.078 \times 10^{-3}$ and 4-C$p = 0.39 \times 10^{-3}$ mol/L)

Table 1
Pseudo-first-order rate constant for 4-CP degradation

$Fe^{+3} = 0$ mol/L, 4-CP concentration = 0.39×10^{-3} mol/L, pH = 3			
H_2O_2 (mol/L)	Removal efficiency %	Pseudo-first-order constant	
		K (min^{-1})	R^2
0.02	87	0.019	0.946
0.03	100	0.086	0.945
0.04	62	0.009	0.976
0.05	45	0.006	0.976
$Fe^{+3} = 0.078 \times 10^{-3}$ mol/L, 4-CP concentration = 0.39×10^{-3} mol/L, pH = 3			
H_2O_2 (mol/L)	Removal efficiency %	Pseudo-first-order constant	
		K (min^{-1})	R^2
0.003	91.0	0.079	0.995
0.004	96.0	0.111	0.993
0.005	99.5	0.164	0.988
0.006	77.0	0.053	0.964
0.007	63.0	0.035	0.986
$H_2O_2 = 0.005$ mol/L, 4-CP concentration = 0.39×10^{-3} mol/L, pH = 3			
$Fe^{+3} \times 10^{+3}$ (mol/L)	Removal efficiency %	Pseudo-first-order constant	
		K (min^{-1})	R^2
0.04	97.25	0.122	0.987
0.08	99.47	0.165	0.990
0.16	100.00	0.614	0.961
0.23	90.21	0.079	0.991
0.31	80.23	0.056	0.988
$H_2O_2 = 0.005$ mol/L, $Fe^{+3} = 0.16 \times 10^{-3}$ mol/L, 4-CP concentration = 0.39×10^{-3} mol/L			
pH	Removal efficiency %	Pseudo-first-order constant	
		K (min^{-1})	R^2
2	94	0.149	0.958
3	100	0.614	0.961
4	88	0.114	0.943
5	76	0.041	0.956

Table 2
Optimum values obtained in the present study by UV/H_2O_2 and $UV/H_2O_2/Fe^{+3}$systems

System	H_2O_2 (mol/L)	Fe^{+3} (mol/L)	pH	Irradiation time (min)	Removal efficiency %	K (min^{-1})
UV/H_2O_2	0.03	–	3	90	100	0.086
$UV/H_2O_2/Fe^{+3}$	0.005	0.16×10^{-3}	3	15	100	0.614

enhanced the rate of 4-CP degradation by a factor of 1.9 (i.e. K increased from 0.086 to 0.164 min^{-1}) and decreased the amount of H_2O_2 by a factor of 6 (from 0.03 to 0.005 mol/L).

The reaction rate constant reaches its maximum value (0.614 min^{-1}) at H_2O_2/Fe^{+3}/4-CP ratio = 13/0.4/1 (i.e. $H_2O_2 = 0.005$, $Fe^{+3} = 0.16 \times 10^{-3}$, and 4-CP = 0.39×10^{-3} mol/L).It can be observed that the photo-Fenton process enhanced the rate of 4-CP oxidation by a factor of 7 as compared with the UV/H_2O_2 system (i.e. K increased from 0.086 to 0.614 min^{-1}).

The optimum ratio of H_2O_2/Fe^{+3} represents a value of 31. This result was in a good agreement with Kavitha and Palanivelu [15], they reported that the optimal ratio was 20–40, and also with Kuo and Wu [16], they showed that the optimal ratio of H_2O_2/Fe^{+3} was 40.

3.4. Evolution of color due to intermediate formation

The main intermediates that were generated during the 4-CP degradation are hydroquinone and benzoquinone. Hydroquinone was a primary formed product from the degradation of 4-CP. A colored solution of benzoquinone can be observed through the first 15 min of irradiation time for the UV/H_2O_2 system when a low concentration (0.01 mol/L) of H_2O_2 was used. This is indicated from the absorption peaks that appear at 500 nm, Fig. 2(A). The initially colorless solution became green in the first 5 min of reaction, and then dark green after 15 min, and gradually the color intensity decreased, finally disappearing. Also, the colored solution of benzoquinone can be observed through the first 15 min for the $UV/H_2O_2/Fe^{+3}$ system at a high concentration (100 ppm) of 4-CP. It can be realized that when there is an insufficient amount of reagents required to degrade the 4-CP, intermediate compounds from degradation product were formed. It remains in the solution and needs longer irradiation time for complete degradation and mineralization of 4-CP.

3.5. Comparison between UV/H_2O_2 and $UV/H_2O_2/Fe^{+3}$ systems

The photodegradation of 4-CP was investigated in both UV/H_2O_2 and photo-Fenton $UV/H_2O_2/Fe^{+3}$ systems. The optimum results are listed in Table 2. 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 2 show that adding Fe^{+3} to the UV/H_2O_2 system enhanced the rate of 4-CP oxidation by a maximum factor of 7, reduced the consumption of H_2O_2 by a maximum factor of 6, and that the irradiation time required for complete degradation was reduced by a factor of 6. Intermediate products were also minimized.

Ghaly et al. [6] show in their experiments on photodegradation of 4-CP using a bench-scale batch reactor (0.85 L volume) with UV lamp (256 nm) that adding Fe^{+3} to the UV/H_2O_2 system enhanced the rate of 4-CP oxidation by a maximum factor 9, over the UV/H_2O_2 system. They obtained a maximum $k = 1.32\ min^{-1}$ at 0.01 mol/L H_2O_2 and 0.4×10^{-3} mol/L Fe^{+3}. Comparing Ghaly et al.'s results with the present results, it can be observed that a lower rate constant of 0.614 min^{-1} was obtained for the $UV/H_2O_2/Fe^{+3}$ system, but with a lesser dose of materials 0.005 mol/L H_2O_2 and 0.16×10^{-3} mol/L Fe^{+3} using a pilot-scale reactor.

4. Conclusions

UV/H_2O_2 and photo-Fenton ($UV/H_2O_2/Fe^{+3}$) systems were used to examine the performance of AOPs for the degradation of 4-CP in wastewater. The results indicated that when there is an insufficient amount of reagents required to degrade 4-CP, intermediate compounds from the degradation product were formed. They remained in the solution and needed longer irradiation times for complete degradation and mineralization. The intermediate products were identified at low concentration of H_2O_2 (0.01 mol/L) in UV/H_2O_2 system at a 4-CP concentration of 50 ppm. They were also identified in a high concentration of 4-CP (100 ppm) for a $UV/H_2O_2/Fe^{+3}$system at an H_2O_2 concentration of 0.005 mol/L. A colored substance (benzoquinone) was formed in the above systems after 5 min of irradiation time, and then the color intensity was decreased and disappeared at longer irradiation times.

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 experimental results showed that the optimum reagents for complete degradation of 4-CP (50 ppm) were obtained at $pH = 3$, $H_2O_2 = 0.005\,mol/L$, $Fe^{+3} = 0.016 \times 10^{-3}\,mol/L$, and an irradiation time of 15 min for a $UV/H_2O_2/Fe^{+3}$ system with a molar ratio of H_2O_2/Fe^{+3}/4-CP equal to 13/0.4/1.

References

[1] P. Kralik, H. Kusic, N. Koprivanac, A.L. Bozic, Degradation of chlorinated hydrocarbons by UV/H2O2: The application of experimental design and kinetic modeling approach, Chem. Eng. J. 158 (2010) 154–166.

[2] Directive 80/77/CE 157-1990, Diario Oficial delas Comunidades Europeas, 30-8-1990, European Community, Brussels, 1990.

[3] M. Pera-Titus, V. Garcia-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: A general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

[4] M. Czaplicka, Sources and transformations of chlorophenols in the natural environment, J. Sci. Total Environ. 322 (2004) 21–39.

[5] K. Kutschera, H. Brnick, E. Worch, Photoinitiated oxidation of geosmin and 2-methylisoborneol by irradiation with 254 nm and 185 nm UV light, J. Water Res. 43 (2009) 2224–2232.

[6] M.Y. Ghaly, G. Härtel, R. Mayer, R. Haseneder, S. Esplugas, Photochemical oxidation of p-chlorophenol by UV/H_2O_2 and photo-Fenton process, A comparative study, Waste Manage. 21 (2001) 41–47.

[7] D. Mantzavinos, E. Psillakis, Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment: Review, J. Chem. Technol. Biotechnol. 79 (2004) 431–454.

[8] K.R.B. Nogueira, A.C.S.C. Teixeira, C.A.O. Nascimento, R. Guardani, Use of solar energy in the treatment of water contaminated with phenol by photochemical processes, Braz. J. Chem. Eng. 25 (2008) 671–682.

[9] C.Y. Kuo, S.L. Lo, M.T. Chan, Oxidation of aqueous chlorophenols with the photo-Fenton process, J. Environ. Sci. Heal. 33 (1998) 723–747.

[10] K. Elghniji, O. Hentati, N. Mlaik, A. Mahfoudh, M. Ksibi, Photocatalytic degradation of 4-chlorophenol under P-modified TiO_2/UVsystem: Kinetics, intermediates, phytotoxicity and acute toxicity, J. Environ. Sci. 23 (2011), doi: 10.1016/S1001-0742(10)60659-6.

[11] K. Chiu, D.A. Lyn, P. Savoye, E.R. Blatchley, Integrated UV disinfection model based on particle tracking, J. Environ. Eng. 125 (1999) 7–16.

[12] D.A. Lyn, E.R. Blatchley, Numerical computational fluid dynamics-based models of ultraviolet disinfection channels, ASCE J. Environ. Eng. 131 (2005) 838–849.11.

[13] J. Pignatello, D. Liu, P. Huston, Evidence for an additional oxidant in the photoassisted Fenton reaction, J. Environ. Sci. Technol. 33 (1999) 832–1839.

[14] S. Meric, D. Kaptan, T. Olmez, Colour and COD removal from wastewater containing reactive black 5 using Fenton's oxidation process, Chemosphere 54 (2004) 435–441.

[15] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, Chemosphere 55 (2004) 1235–1243.

[16] W.S. Kuo, L.N. Wu, Fenton degradation of 4-chlorophenol contaminated water promoted by solar irradiation, Sol. Energy 8 (2010) 459–465.