EFFECT OF OPERATIONAL CONDITIONS ON REMOVAL OF 4-CHLOROPHENOL IN WATER USING UV/NiO PROCESS

ASSADI A.[1]
ALIMORADZADEH R.[1,*]
NASSERI S.[2]
MEHRASBI M.R.[1]

[1]Department of Environmental Health Engineering
Zanjan University of Medical Sciences, Zanjan, Iran
[2]Department of Environmental Health Engineering
School of Public Health and Center for Water Quality Research
Institute for Environmental Research
Tehran University of Medical Sciences, Tehran, Iran

*to whom all correspondence should be addressed:
e-mail: r.alimoradzade@gmail.com

ABSTRACT

This study present the removal of 4-chlorophenol (4-CP) from water by nickel oxide (NiO) nanoparticles. Photodegradation was compared using different processes in a batch reactor with medium-pressure mercury lamp irradiation. The effects of operating conditions such as feed concentration of reactants, catalyst load, pH, and half-life time on photodegradation system were evaluated. The results showed that photodegradation using UV/NiO system in the presence of H_2O_2 were much more effective than using either UV/H_2O_2 or UV/NiO processes. The optimum conditions for the complete degradation of 4-CP were achieved at a neutral pH, with 0.2 mol l^{-1} H_2O_2, and 0.05 g l^{-1} of NiO. However, no significant pH effects were observed in the range of 4-10. Also, the best TOC removal and Cl^- ions formation results were achieved by combined system with 48 and 80%, respectively. The illuminated NiO nanoparticles had lower influence on the degradation of 4-CP but dramatically promoted the mineralization of 4-CP. For all these reactions, the degradation rates are evaluated by determining their first-order rate constants and half-life times. The reaction rate constants ranged from 0.0003 min^{-1} by direct photolysis to 0.029 min^{-1} and 0.083 min^{-1} using UV/NiO in absent and presence of H_2O_2, respectively.

Keywords: 4-chlorophenol, UV light, Nickel oxide, Hydrogen peroxide

1. Introduction

Increasing demand and shortage of water sources due to the rapid development of industrialization, population growth and long-term droughts have become an issue worldwide. With this growing demand, there is a need to increase new water and wastewater treatment processes to reduce negative effects on water bodies.

Among the methods considered, heterogeneous photocatalytic oxidation systems (HPOs) can efficiently eliminate persistent organic pollutants at a low cost energy (Stasinakis, 2008; Catrinescu *et al.*, 2011). Photocatalytic oxidation processes concern with photoactivated metal oxides as semiconductors to remove contaminants in aqueous environment (Lo *et al.*, 2004). In the photocatalytic systems, the UV irradiation of metal oxides upon incidence of photon with an energy higher than its band gap energy results in the formation

of electrons (e^-) in the conduction band and positive holes (h^+) in the valence band. The hole can either oxidize a compound directly or react with electron donors like water to form OH radicals, which react with pollutants and mineralize them to CO_2 and H_2O_2 (Aguedach *et al.*, 2005; Goel *et al.*, 2010).

Chlorophenols are hazardous chemicals and generally categorized as non-biodegradable pollutants. Continuous consumption of drinking water contaminated with chlorophenols can affect human health. A representative of this class of compounds is 4-chlorophenol (4-CP). Sources of this compound include industrial effluents, such as petroleum refining, and production of pesticides, paint, plastic, resin, textile, iron, solvent, pharmaceutics and wood preserving chemicals and named as one of the priority pollutants by the US Environmental Protection Agency (EPA) and the European Union (EU). The permissible limit of 4-CP in drinking water supply is 0.5 mg l^{-1} (Pera-Titus *et al.*, 2004; Pi *et al.*, 2007; Movahedyan *et al.*, 2008; Gomez *et al.*, 2009; Neppolian *et al.*, 2011; Olaniran and Igbinosa, 2011). Due to 4-CP high toxicity and persistence in the environment, attention has been focused on its removal from the aqueous media.

Titanium dioxide (TiO2) has received the greatest interest in research of photocatalytic process due to chemical and thermal stability or resistance to chemical breakdown, low cost and their strong mechanical properties have promoted its wide application in photocatalytic water treatment (Laoufi *et al.*, 2008; Gaya *et al.*, 2009; Ghosh *et al.*, 2009). The main pitfall of TiO_2 is based on the economy of the extensive use for large-scale facilities, and, in some cases, on the low mineralization level achieved, requiring a final polishing stage (Gimeno *et al.*, 2005). There is renewed effort to study for more reliable semiconductors (Li *et al.*, 2009). Other semiconductor catalsts has demonstrated its efficiency in degrading a wide range of chlorophenols. (Stoyanova *et al.*, 2003; Lai *et al.*, 2008; Stoyanova and Christoskova, 2011). NiO is a vital semiconductor widely used as a catalyst with extraordinary electrical, thermal, catalytic, and redox properties (Stoyanova *et al.*, 2006; Devulapelli and Sahle-Demessie, 2008).

Most attracting features of NiO are excellent durability and electrochemical stability. Reported band gap energy value for the nickel oxide is in the range of 3.4-3.8 eV. This suggests that the optical transition in NiO takes place through direct inter-band transition (Patil and Kadam, 2002). Also, NiO can act as a promoter for the generation of OH radicals (Zhang *et al.*, 2009). The results of research work have proved that the recovered nickel oxides particles had a catalytic activity as well as the properties of the product before use (He *et al.*, 2010). Recently, photocatalytic degradation of organic pollutants using NiO particles has gained considerable attention (Stoyanova *et al.*, 2003; Lai *et al.*, 2007; Lai *et al.*, 2011). The drawback of NiO particles might be the influence on the amount of mineralization and the presence of nanoparticles in the effluent. The main aim of this study was to examine effects of operational parameters for the removal of 4-CP under different irradiation processes such as direct photolysis (UV alone), UV/H_2O_2, UV/NiO, and $UV/NiO/H_2O_2$ in the presence and absent of NiO nanoparticles. Also, the mineralization of 4-CP and the first-order rate constants were determined under different conditions.

2.   Materials and methods

2.1 Material

4-CP (purity 99%) and H_2O_2 (30%, w/v) reagents were purchased from Merck Co. NiO nano powder (99.8% purity and <50 nm particle size) was obtained from Sigma–Aldrich. Other chemicals were of analytical grade and were used without further purification. Deionized water was used throughout this present study. The pH of solution was adjusted using NaOH and H_2SO_4, where needed.

2.2 Experimental Set-up

The photocatalytic experiments were performed in a batch reactor. It consisted of a cylindrical glass reactor (2 l total volume) with an inner diameter and height of 11cm and 16 cm, respectively. In each experiment, the

reactor was filled with 1000 mL of an aqueous solution of 4-CP with predetermined pH value. Irradiation was achieved by using UV lamp of 150 W (medium-pressure lamp) with main emission wavelength at 247 nm. Also, the intensity of it is 1020 μW cm^{-2} in the distance of 15 cm. The UV lamp was located vertically in the center of reactor within a double-wall cooling system.

The reactor was filled with the reaction mixture containing constant concentration of 100 mg l^{-1} 4-CP. The reaction was performed at neutral pH except for a few runs to evaluate pH effects on the reaction rate. For runs UV/H_2O_2, UV/NiO, UV/NiO/H_2O_2 system, the pH value of solution was adjusted at the desired value before start-up, and then a given amount of NiO was added. The nanocatalyst was mixed very well with 4-CP before the addition of given volume ofoxidant. The time at which UV lamp was turned on was considered time zero. All experiments have been done in 60 min. The initial concentrations of H_2O_2 and NiO varied in the range of 0.005- 0.4 mol l^{-1} and 0.025- 0.2 g l^{-1}, respectively.

2.3 Analysis

Samples were taken from the sample port of the reactor at predetermined time intervals. Potential reactions with hydrogen peroxide and hydroxyl radicals in the samples were quenched by using 6M NaOH solution. The samples were filtered by syringe membrane filter (0.45 μm pore-size) to remove NiO particles. Analyses of initial and remaining concentrations of 4-CP were determined with a Knauer HPLC instrument with a reversed phase C18 column (Erouphere 250×4.6 mm). The injected volume of reaction solution was 20 μL. The mobile phase was prepared by methanol and deionized water (containing 2 percent acetic acid) in 52/48 (V/V) ratio at a flow rate of 1 ml min^{-1}. The UV detector was set to 278 nm (Du *et al.*, 2011; Alimoradzadeh *et al.*, 2012).

Ion chromatography (881 Compact IC pro, Metrohm) equipped with a Metrosep ASUPP4 column (250×4.0 mm) was employed for the analysis of chloride ion concentrations in aqueous solution using NaCl as a standard. The mobile phase of a mixture of 2.5 mM Na_2CO_3 and 2.4 mM $NaHCO_3$ was used at a flow rate of 0.7 ml min^{-1}. The volume of each sample was 20 μL. The level of quantitation (LOQ) for determination of chloride ion was 25 μg l^{-1}. The total organic carbon (TOC) was measured by means of a Dohrmann DC-190 (Rosemount Analytical Inc., Santa Clara, CA, USA) high-temperature TOC analyzer based on the combustion-infrared method. All experiments have been performed once except for quality analysis and pretests. Calibration curve at six concentration levels were prepared from working solutions containing the 4-CP in the range of 0.1-100 mg l^{-1} (R^2= 0.999). Detection limit of this method for determination of 4-CP is 0.02 mg l^{-1} and the relative standard error (RSD) did not exceed more than 0.2 percent based on triplicate.

The surface of NiO particles was observed with a scanning electron microscopy (SEM). It demonstrates almost uniform morphologies with size in the range of 53-117 nm that had been used in our previous work (Alimoradzadeh *et al.*, 2012).

3.   Results and discussion

3.1 Effect of operational conditions on 4-CP removal

Several blank tests were carried out in constant concentration of 4-CP to show the removal options rather than photocatalytic processes. The data in Fig.1 presents that there is little adsorption of 4-CP (less than 4.5%) by NiO alone in the absence of UV illustration. The contribution of volatilization was negligible in the removal of 4-CP from reactor. Nevertheless, all parts used in the reactor were glassware to minimize the impact of adsorption (Chiou *et al.*, 2008). Also, it is found that H_2O_2 could not remove 4-CP alone. Similarly, Zhihui *et al.* (Zhihui *et al.*, 2005) showed that the degradation of 4-CP was not affected by H_2O_2 alone. Direct photolysis of 4-CP whit UV alone leads to a moderately 4-CP removal.

It is necessary to mention that about 82% of 4-CP is degraded within 60 min when 0.05 g l^{-1} NiO is added using UV/NiO process. Also, approximately complete 4-CP removal is obtained when the solution is treated

with 0.2 M H_2O_2 under UV irradiation.
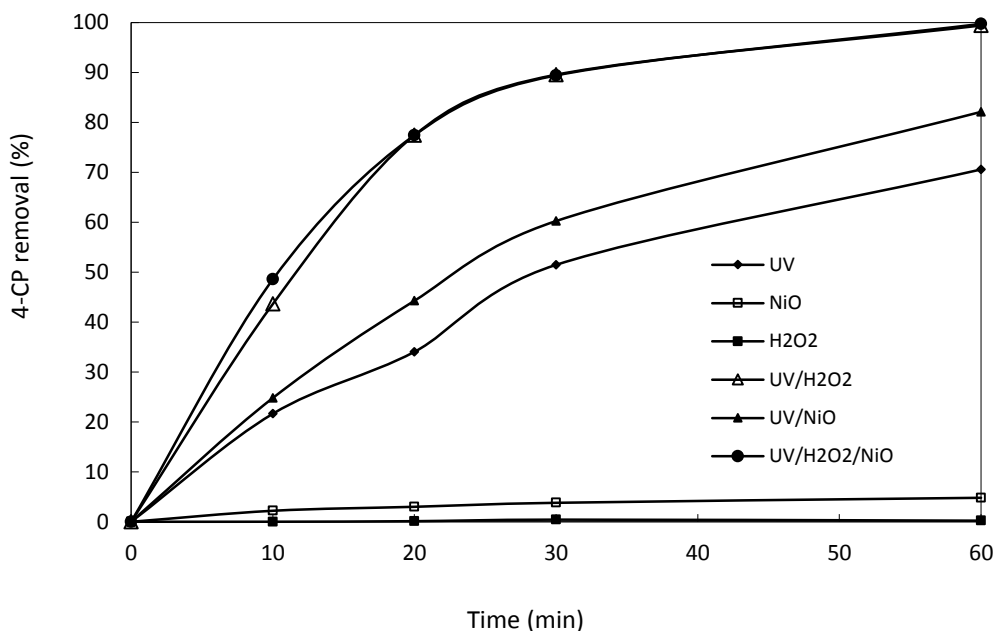
Figure 1. The effect of different reaction conditions on 4-CP removal
(C_o=100 mg l^{-1}, H_2O_2=0.2 mol l^{-1}, NiO= 0.05 g l^{-1}, pH=7)

On the other hand, the combination of such two processes (that is, the UV/NiO/H_2O_2 system) further improves 4-CP removal (Fig.1). The results of study showed that photodegradation of phenol using UV/TiO$_2$/H_2O_2 process was much more effective than using either UV/H_2O_2 or UV/TiO$_2$ process (Chiou *et al.*, 2008). Similar results by different catalysts for 4-CP removal were observed with those reported by other studies (Stoyanova *et al.*, 2003; Lai *et al.*, 2008; Wang *et al.*, 2009; Lai *et al.*, 2011).

3.2 Mineralization of 4-CP

Mineralization of xenobiotics is the main goal in industrial wastewater treatment facilities. Therefore, It is important to follow not only disappearance of the initial pollutant but also its mineralization into CO_2, H_2O, and inorganic ions (Goel *et al.*, 2010). Figure 2 illustrates the mineralization profile of 4-CP by variations of TOC in the different processes. The TOC data presented that the mineralization of 4-CP by UV/NiO and UV/H_2O_2 at a reaction time of 60 min are 29.6 percent and 34.9 percent, respectively. The reduction of TOC was firstly slow and then a relatively faster degradation followed after 30 minutes in the UV/NiO system. This provides further support to previous work that 4-CP photodegradation is likely initiated by branch dissociations, benzene rings remain intact and the hydroxyl radicals produced by the system tend to react with organic molecules over the catalyst surface or in the solution released from the catalyst surface (Chiou *et al.*, 2008). In contrast, the UV/H_2O_2 system begins with a fast degradation and follows by retarded degradation rate. But in the UV/NiO/H_2O_2 system, TOC removal is enhanced; with 48% of the TOC being mineralized after 60 min of reaction. Thus, combining UV/H_2O_2 with UV/NiO further promotes photodegradation for 4-CP than UV/H_2O_2 or UV/NiO alone. In agreement with results of our previous work (Alimoradzadeh *et al.*, 2012), the researchers have main reasons to consider that the NiO may be a good catalyst in UV/NiO/H_2O_2 system.

As shown in Fig.2, the formation of Cl$^-$ ions during UV/NiO, UV/H_2O_2, and UV/NiO/H_2O_2 systems were 16.39,

20.89, and 21.4 mg l^{-1}, respectively, whereas the stoichiometric concentration of Cl$^-$ atoms initially present in the molecule of 100 mg l^{-1} 4-CP are 27.6 mg l^{-1}. It is seen that, by addition NiO catalyst to UV/H$_2$O$_2$ process, the formation of Cl$^-$ ions rose to reach 80%. This was due to the higher decomposition of 4-CP. On the other hand, about 52% of TOC still remained after 60 min irradiation while 4-CP was more dechlorinated and subsequent the Cl$^-$ ions were generated. It seems that the Cl$^-$ ions accounted for its inhibitory effect on NiO photocatalysis through a preferential adsorption displacement mechanism over the surface bound OH$^-$ ions. This reduces the number of OH$^-$ ions available on the NiO surface, and the substituted Cl$^-$ further increases the recombination of electron-hole pairs. In other words, the presence of Cl$^-$ as a scavenger may decrease mineralization rate (Chong *et al.*, 2010).
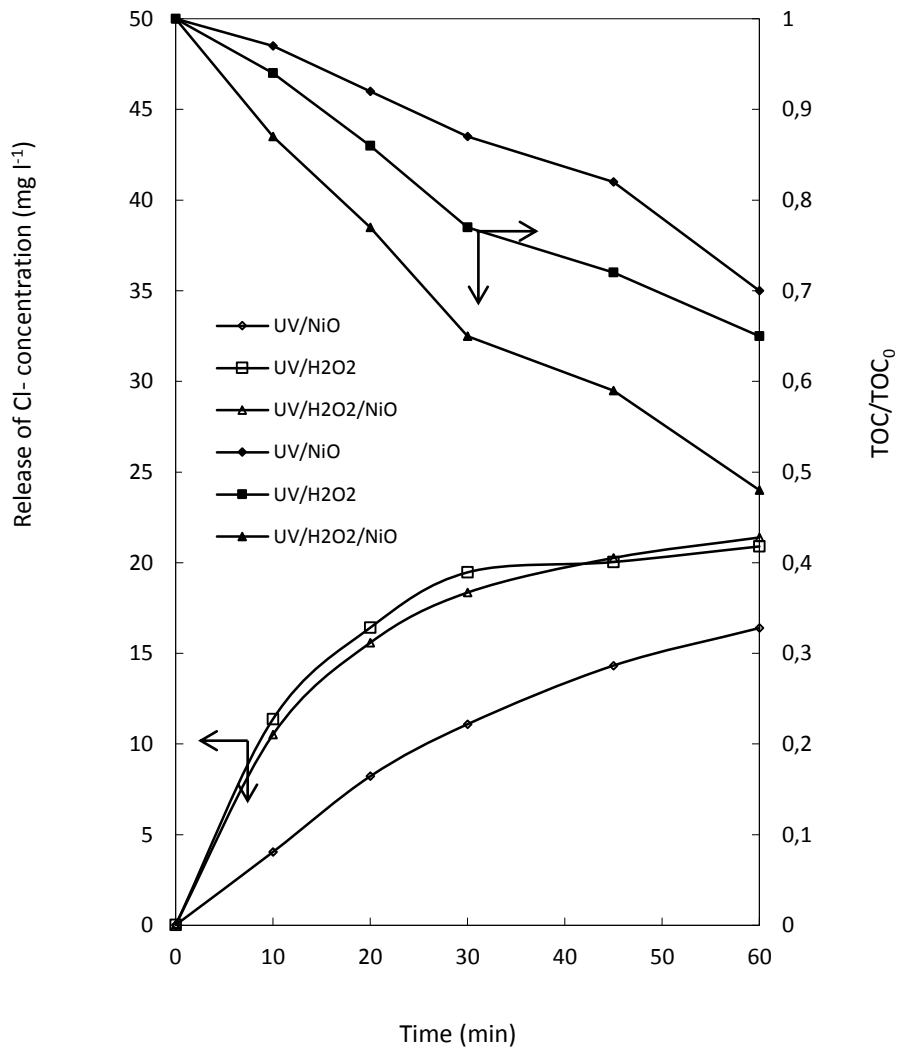
Figure 2. The effect of various oxidation processes on TOC removal and release of Cl$^-$ ions during 4-CP degradation (C$_o$=100 mg l^{-1}, H$_2$O$_2$=0.2 mol l^{-1}, NiO= 0.05 g l^{-1}, pH=7).

The variations of pH as other aspect of 4-CP mineralization clearly have presented in Fig. 3.
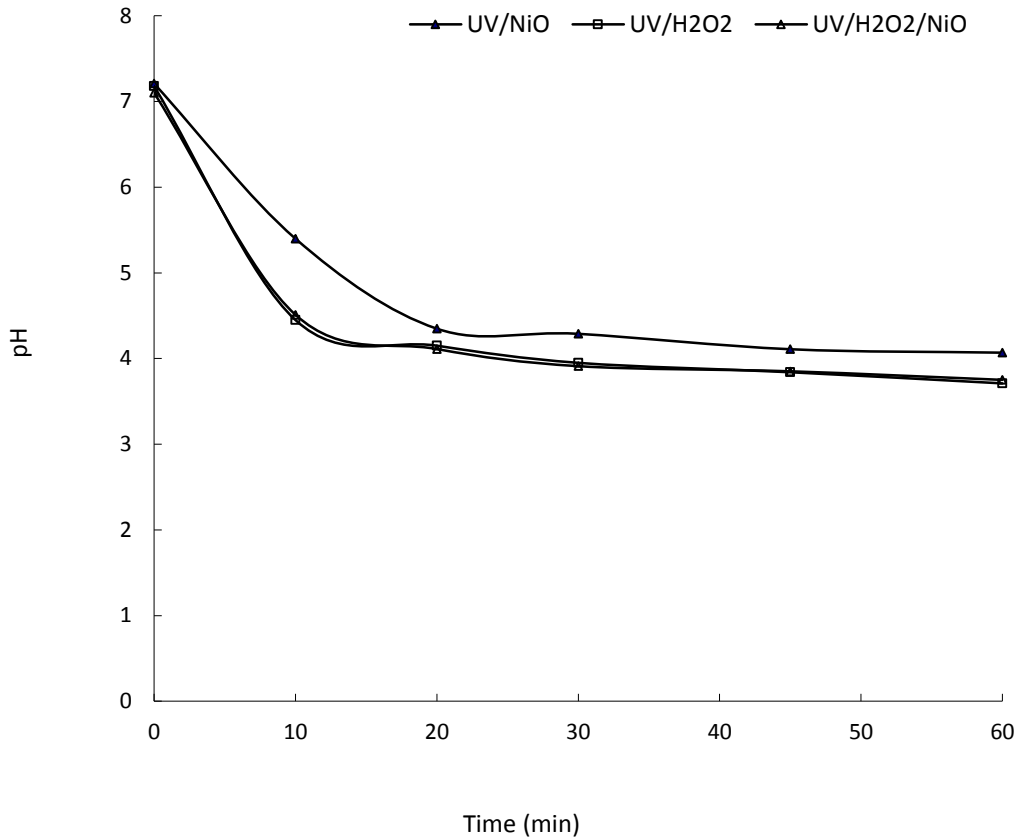
**Figure 3.** The variation of the initial solution pH on 4-CP removal using UV/NiO, UV/H$_2$O$_2$, UV/NiO/H$_2$O$_2$ processes (C$_o$=100 mg l^{-1}, H$_2$O$_2$=0.2 mol l^{-1}, NiO= 0.05 g l^{-1}, pH=7).

Since pH is a main operation parameter for catalyst surface properties in aqueous solution, it is important to examine the effect of pH. Also, the profile of pH variation in the reactor shows two fast and slow reduction trends at 60 min. The most likely explanation for the variation of pH value could be attributed to two factors. H$^+$ is generated when water is illuminated and the Cl$^-$ ions were produced during mineralization process. It is obvious that the decrease of the pH value could be attributed to the generation of HCl. The amount of organic Cl decreases with increasing of absorbed dose and thereby the HCl formation rate also decreases (Yang *et al.*, 2007).

The loss of 4-CP was observed as function of irradiation time and data fitted to a first-order rate model according to following equation with an apparent rate constant (*k*):

$$\ln\left(\frac{C}{C_o}\right) = -kt$$

A plot of −ln(*C/Co*) versus reaction time *t* yields a straight line, and the slope is the apparent rate constant (*k*). It was also confirmed in this study that 4-CP photodegradation using UV/NiO/H$_2$O$_2$ system follows the first-order kinetics as shown in Fig.4.
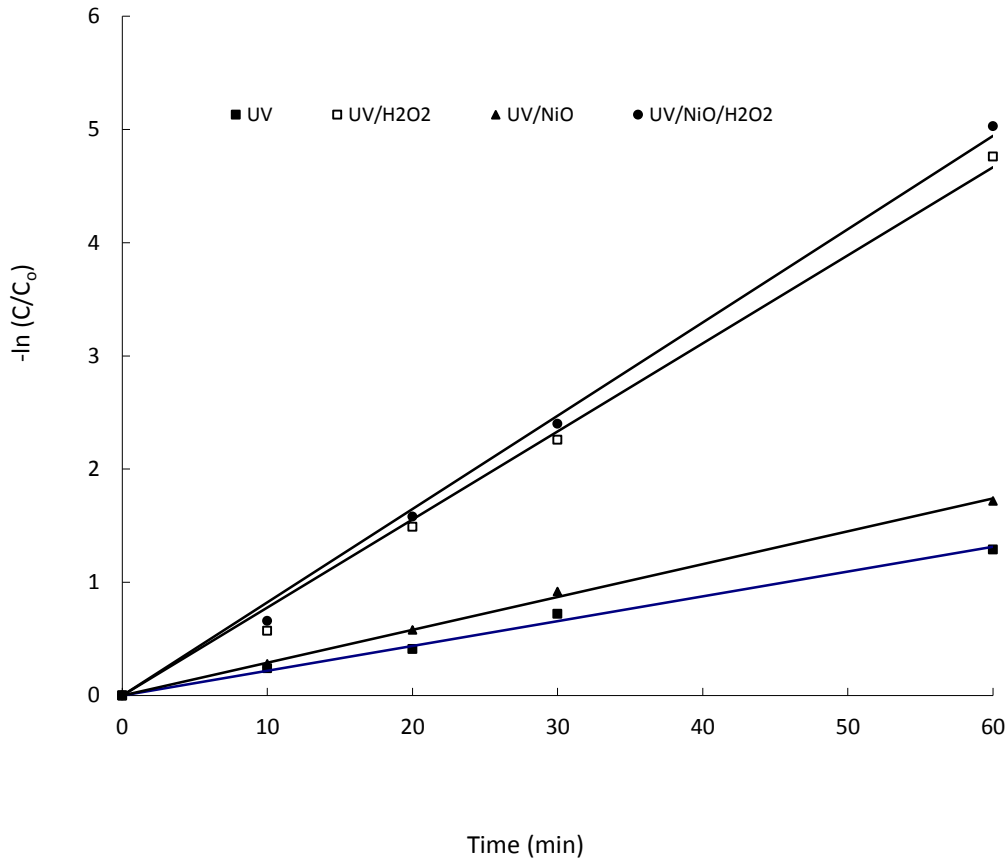
Figure 4. Comparison of reaction rates on different oxidation processes
(C_o=100 mg l^{-1}, H_2O_2=0.2 mol l^{-1}, NiO= 0.05 g l^{-1}, pH =7).

Table 1 lists the kinetic parameters for 4-CP photodegradation under various oxidation conditions. The process indicating highest k is UV/NiO/H_2O_2, approximately 2.9 times higher than the UV/NiO and 1.1 times higher than UV/H_2O_2 and the half-life time is related to the rate constant.

Table 1. First-order rate constant (k) and half-life for 4-CP removal in various oxidation processes.

process	k (min^{-1})	Initial rate (mg min^{-1})	Half-life (min)	R^2
UV	0.0003	1.22	30	0.994
UV/NiO	0.029	1.38	23	0.998
UV/H_2O_2	0.077	1.65	12.5	0.987
UV/NiO/H_2O_2	0.083	1.66	10	0.967

3.3 Effect of NiO dosage on 4-CP removal

To obtain the optimal NiO dosage, the investigation was performed with various amount of catalyst. Figure 5 shows the percent degradation of 4-CP as a function of the added NiO and the degradation rate of 4-CP distinctly increased with increasing of NiO. It is found that UV irradiation in the absence of NiO catalyst shows low 4-CP removal (about 70%). When NiO dosage increased to 0.05 g l^{-1}, removal of 4-CP increased to 83%.
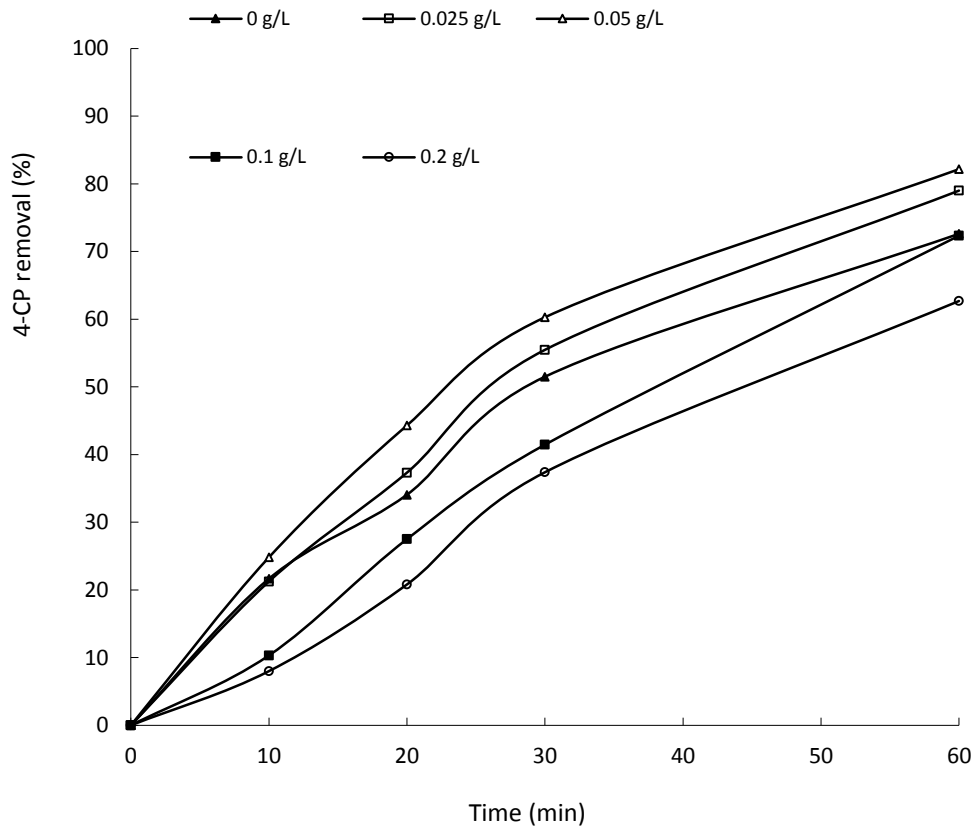
Figure 5. The effect of the dosage of NiO catalyst on 4-CP removal using UV/NiO process
(C_o=100 mg l^{-1}, NiO= 0.05 g l^{-1}, pH=7).

This indicates that 4-CP photodegradation by direct photolysis (using UV alone) is much lower than that of photocatalytic degradation by NiO. In other words, NiO is capable of promoting the interaction between hydroxyl radicals and 4-CP. Many works have proved that the rates of photodegradation are strongly affected by the number of active sites and the photo-absorption ability of the catalyst used (Lathasree *et al.*, 2004). Adequate dosage of the catalyst increases the generation rate of electron/hole pairs; therefore, the formation of OH radicals for promoting photodegradation. However, an overdose of the catalyst decreases the UV penetration due to opacity caused by excess catalyst clusters and at the same time increases the scattering effect (Gaya *et al.*, 2009).
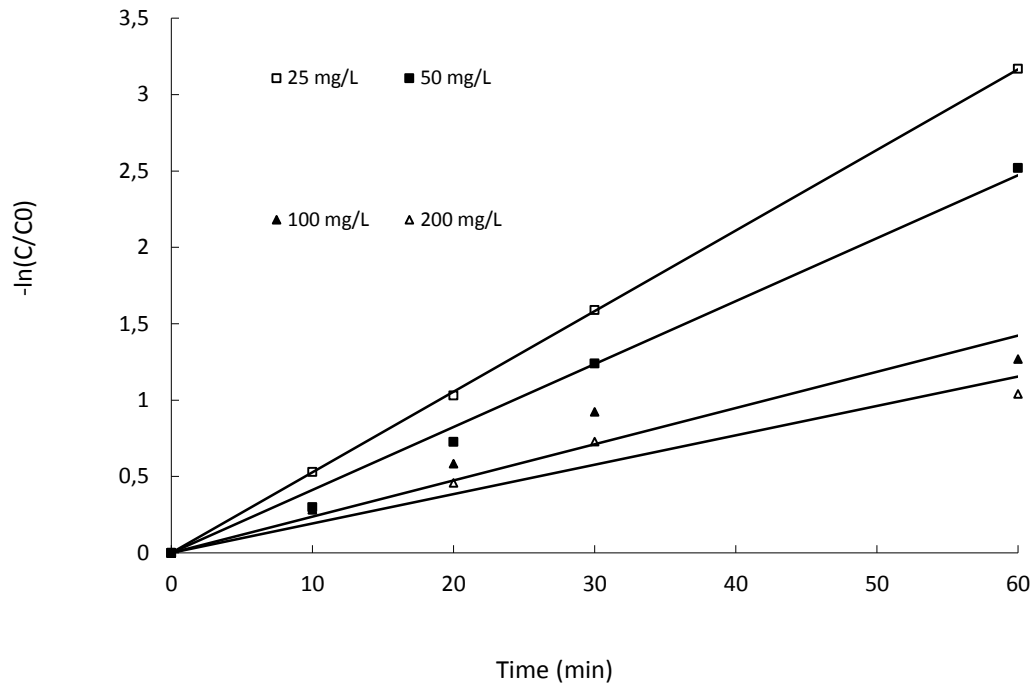
3.4 Effect of the initial 4-CP concentration

The effects of different 4-CP concentrations on the reaction constant rates of UV/NiO system are shown in Fig. 6.

The removal rates of 4-CP decrease with increasing C_0 under the conditions studied. At a 4-CP concentration below 25 mg l^{-1}, more than 90% of 4-CP is removed within 60 min. A first-order type of kinetic expression is still adopted here to describe the concentration effect on its photodegradation rate. The rate constants are 0.052, 0.041, 0.023 and 0.019 min^{-1} at C_0 of 25, 50, 100, and 200 mg l^{-1}, respectively. The present results indicate that photocatalytic oxidation is rather promising at low organic pollutant concentrations. This is also the case for heterogeneous catalytic processes where the reaction occurs at the interface between the two

phases (Cheng *et al.*, 2007). The main reason is that the formation of hydroxyl radical is constant for a given amount of the catalyst. Hence, the available OH radical are insufficient for 4-CP degradation at higher concentrations (Wang *et al.*, 2009). Moreover, the higher the 4-CP concentration, the higher concentrations of intermediate products are produced which compete for reacting with OH radicals generated from surface-trapped photogenerated holes (Gaya *et al.*, 2009).


Figure 6. The effect of initial 4-CP concentration on constant reaction rate (k) using UV/NiO process (pH=7, NiO= 0.05 g l^{-1}).

3.5 Influence of solution pH

Figure 7 shows the effect of pH on the degradation of 4-CP (C_0 = 100 mg l^{-1}) in the UV/NiO system. The pH of the solution dominates photodegradation process due to the strongly pH dependent of the properties such as semiconductor's surface charge state, flat band potential, and dissociation of the solution (Doong *et al.*, 2001). The UV/NiO process demonstrates that the degradation of 4-CP is independent of pH and relatively low effect was observed in the range of 4-10 at 60 min reaction time. Although, little decreasing was observed in acidic pH. The best results were obtained at basic pH.

As shown in Fig.7, the fastest rate of 4-CP degraded occurs within 10 min under different pH values (degree of conversion obtains 33.2% for pH 10 but 24.8% for pH 7 and 12.7% for pH 4). The most likely reason for this observation is the very low substantial loss of NiO to Ni^{+2} at low pH value (Stoyanova *et al.*, 2003). The removal rate increase at higher pH value due to NiO stability is less disturbed. This provide further support to earlier work that 4-CP can be totally removed in the pH range of 4-10 in 30 min by MW/NiO system (Lai *et al.*, 2007). In contrast, the findings of other works with different catalyst, ZnO (Gaya *et al.*, 2009), P-25 TiO$_2$, TiO$_2$ nanofibers, tin-doped TiO$_2$ nanofibers, and coumarin (C-343) coated TiO$_2$ nanofibers (Ghosh *et al.*, 2009),

TiO_2, WO_3, SnO_2, TiO_2/WO_3 and TiO_2/SnO_2 systems have shown that pH affects significantly the photocatalytic degradation of 4-CP or production of hydroxyl radical (Lin *et al.*, 2008).
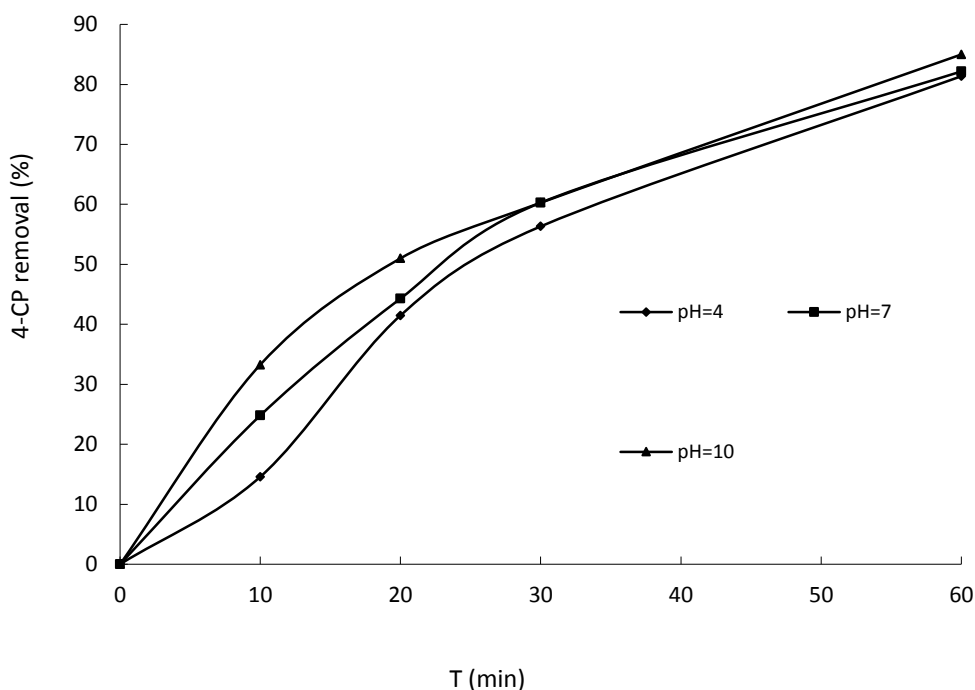
Figure 7. 4-CP degradation as a function of the pH value in the UV/NiO system
($Co=100$ mg l^{-1}, NiO= 0.05 g l^{-1}).

4.   Conclusions

Photodegradation with UV/NiO process was indicated that the complete removal of 4-CP could be achieved at different operating condition. The first-order rate constant increased nearly three-fold compared to the absence of H_2O_2. The present results indicated that photodegradation of 4-CP using NiO was best achieved near neutral pH. Unlike the complete degradation of 4-CP by 0.05 g l^{-1} NiO and 0.2 M H_2O_2 within 60 min based on 4-CP concentration data, the TOC of the solution was reduced by 48% only within 60 min. Moreover, the results of mineralization and chloride ions studies indicated that dechlorination was better accomplished, but more time was required to completely mineralize 4-CP into H_2O and CO_2. Finally, the efficient degradation of 4-CP observed in this study suggests that the UV/NiO process is a potentially useful method for the removal of xenobiotics in aqueous environment.

References

Aguedach A., Brosillon S., Morvan J. and Lhadi E.K. (2005), Photocatalytic degradation of azo-dyes reactive black 5 and

reactive yellow 145 in water over a newly deposited titanium dioxide, *Applied Catalysis B: Environmental*, **57**(1), 55-62.

Alimoradzadeh R., Assadi A., Nasseri S. and Mehrasbi M.R. (2012), Photocatalytic degradation of 4-chlorophenol by UV/H2O2/NiO process in aqueous solution, *Iranian Journal of Environmental Health Science & Engineering,* **9**(1), 1-8.

Catrinescu C., Arsene D. and Teodosiu C. (2011), Catalytic wet hydrogen peroxide oxidation of para-chlorophenol over Al/Fe pillared clays (AlFePILCs) prepared from different host clays, *Applied Catalysis B: Environmental*, **101**(3–4), 451-460.

Cheng Y., Sun H., Jin W. and Xu N. (2007), Photocatalytic degradation of 4-chlorophenol with combustion synthesized TiO2 under visible light irradiation, *Chemical Engineering Journal*, **128**(2–3), 127-133.

Chiou C.-H., Wu C.-Y. and Juang R.-S. (2008), Influence of operating parameters on photocatalytic degradation of phenol in UV/TiO$_2$ process, *Chemical Engineering Journal,* **139**(2), 322-329.

Chong M.N., Jin B., Chow C.W.K. and Saint C. (2010), Recent developments in photocatalytic water treatment technology: A review, *Water Research*, **44**(10), 2997-3027.

Devulapelli V.G. and Sahle-Demessie E. (2008), Catalytic oxidation of dimethyl sulfide with ozone: Effects of promoter and physico-chemical properties of metal oxide catalysts, *Applied Catalysis A: General*, **348**(1), 86-93.

Doong R.-A., Chen C.-H., Maithreepala R.A. and Chang S.-M. (2001), The influence of pH and cadmium sulfide on the photocatalytic degradation of 2-chlorophenol in titanium dioxide suspensions, *Water Research*, **35**(12), 2873-2880.

Du Y., Fu Q.S., Li Y. and Su Y. (2011), Photodecomposition of 4-chlorophenol by reactive oxygen species in UV/air system, *Journal of Hazardous Materials*, **186**(1), 491-496.

Gaya U.I., Abdullah A.H., Zainal Z. and Hussein M.Z. (2009), Photocatalytic treatment of 4-chlorophenol in aqueous ZnO suspensions: Intermediates, influence of dosage and inorganic anions, *Journal of Hazardous Materials,* **168**(1), 57-63.

Ghosh J.P., Sui R., Langford C.H., Achari G. and Berlinguette C.P. (2009), A comparison of several nanoscale photocatalysts in the degradation of a common pollutant using LEDs and conventional UV light, *Water Research*, **43**(18), 4499-4506.

Gimeno O., Carbajo M., Beltrán F.J. and Rivas F.J. (2005), Phenol and substituted phenols AOPs remediation, *Journal of Hazardous Materials*, **119**(1–3), 99-108.

Goel M., Chovelon J.-M., Ferronato C., Bayard R. and Sreekrishnan T.R. (2010), The remediation of wastewater containing 4-chlorophenol using integrated photocatalytic and biological treatment, *Journal of Photochemistry and Photobiology B: Biology*, **98**(1), 1-6.

Gomez M., Matafonova G., Gomez J.L., Batoev V. and Christofi N. (2009), Comparison of alternative treatments for 4-chlorophenol removal from aqueous solutions: Use of free and immobilized soybean peroxidase and KrCl excilamp, *Journal of Hazardous Materials*, **169**(1–3), 46-51.

He H., Yang S., Yu K., Ju Y., Sun C. and Wang L. (2010), Microwave induced catalytic degradation of crystal violet in nano-nickel dioxide suspensions, *Journal of Hazardous Materials*, **173**, 393-400.

Lai T.-L., Liu J.-Y., Yong K.-F., Shu Y.-Y. and Wang C.-B. (2008), Microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides under low temperature, *Journal of Hazardous Materials*, **157**(2–3), 496-502.

Lai T.-L., Wang W.-F., Shu Y.-Y., Liu Y.-T. and Wang C.-B. (2007), Evaluation of microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides, *Journal of Molecular Catalysis A: Chemical*, **273**(1–2), 303-309.

Lai T.-L., Yong K.-F., Yu J.-W., Chen J.-H., Shu Y.-Y. and Wang C.-B. (2011), High efficiency degradation of 4-nitrophenol by microwave-enhanced catalytic method, *Journal of Hazardous Materials*, **185**(1), 366-372.

Laoufi N., Tassalit D. and Bentahar F. (2008), The degradation of phenol in water solution by TiO$_2$ photocatalysis in a helical reactor, *Global NEST Journal,* **10**(3), 404-418.

Lathasree S., Rao A.N., SivaSankar B., Sadasivam V. and Rengaraj K. (2004), Heterogeneous photocatalytic mineralisation of phenols in aqueous solutions, *Journal of Molecular Catalysis A: Chemical*, **223**(1–2), 101-105.

Li J.-M., Meng X.-G., Hu C.-W., Du J. and Zeng X.-C. (2009), Oxidation of 4-chlorophenol catalyzed by Cu(II) complexes under mild conditions: Kinetics and mechanism, *Journal of Molecular Catalysis A: Chemical*, **299**(1–2), 102-107.

Lin C.-F., Wu C.-H. and Onn Z.-N. (2008), Degradation of 4-chlorophenol in TiO_2, WO_3, SnO_2, TiO_2/WO_3 and TiO_2/SnO_2 systems, *Journal of Hazardous Materials*, **154**(1–3), 1033-1039.

Lo S.-C., Lin C.-F., Wu C.-H. and Hsieh P.-H. (2004), Capability of coupled CdSe/TiO2 for photocatalytic degradation of 4-chlorophenol, *Journal of Hazardous Materials*, **114**(1–3), 183-190.

Movahedyan H., Assadi A. and Amin M.M. (2008), Effects of 4-chlorophenol loadings on acclimation of biomass with optimized fixed time sequencing batch reactor, *Iranian Journal of Environmental Health Science and Engineering*, **5**(4), 225-234.

Neppolian B., Ciceri L., Bianchi C.L., Grieser F. and Ashokkumar M. (2011), Sonophotocatalytic degradation of 4-chlorophenol using $Bi_2O_3/TiZrO_4$ as a visible light responsive photocatalyst, *Ultrason. Sonochem.*, **18**(1), 135-139.

Olaniran A.O. and Igbinosa E.O. (2011), Chlorophenols and other related derivatives of environmental concern: Properties, distribution and microbial degradation processes, *Chemosphere*, **83**(10), 1297-1306.

Patil P.S. and Kadam L.D. (2002), Preparation and characterization of spray pyrolyzed nickel oxide (NiO) thin films, *Applied Surface Science*, **199**(1–4), 211-221.

Pera-Titus M., García-Molina V., Baños M.A., Giménez J. and Esplugas S. (2004), Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Applied Catalysis B: Environmental*, **47**(4), 219-256.

Pi Y., Zhang L. and Wang J. (2007), The formation and influence of hydrogen peroxide during ozonation of para-chlorophenol, *Journal of Hazardous Materials*, **141**(3), 707-712.

Stasinakis A. (2008), Use of selected advanced oxidation processes (AOPs) for wastewater treatment—a mini review, *Global NEST Journal*, **10**(3), 376-385.

Stoyanova M. and Christoskova S. (2011), Catalytic degradation of methylene blue in aqueous solutions over Ni- and Co-oxide systems, *Central European Journal of Chemistry*, **9**(6), 1000-1007.

Stoyanova M., Christoskova S. and Georgieva M. (2003), Mixed Ni-Mn-oxide systems as catalysts for complete oxidation: Part I. Preparation and characterization, *Applied Catalysis A: General*, **249**(2), 285-294.

Stoyanova M., Konova P., Nikolov P., Naydenov A., Christoskova S. and Mehandjiev D. (2006), Alumina-supported nickel oxide for ozone decomposition and catalytic ozonation of CO and VOCs, *Chemical Engineering Journal,* **122**(1–2), 41-46.

Wang N., Li X., Wang Y., Quan X. and Chen G. (2009), Evaluation of bias potential enhanced photocatalytic degradation of 4-chlorophenol with TiO_2 nanotube fabricated by anodic oxidation method, *Chemical Engineering Journal,* **146**(1), 30-35.

Yang R., Wang M., Shen Z., Wang W., Ma H. and Gu J. (2007), The degradation and mineralization of 4-chlorophenol in aqueous solutions by electron beam irradiation in the presence of TiO_2 nanoparticles, *Radiation Physics and Chemistry*, **76**(7), 1122-1125.

Zhang X., Li X. and Qin W. (2009), Investigation of the catalytic activity for ozonation on the surface of NiO nanoparticles, *Chemical Physics Letters*, **479**(4–6), 310-315.

Zhihui A., Peng Y. and Xiaohua L. (2005), Degradation of 4-Chlorophenol by microwave irradiation enhanced advanced oxidation processes, *Chemosphere*, **60**(6), 824-827.