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Kinetic and mechanistic study of photochemical degradation of 4-chlorophenol using peroxy acetic acid (PAA)

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ABSTRACT

In this work, kinetic and mechanistic study of photochemical degradation of 4-chlorophenol (4-CP) with UV lamp of 6 W, 12 W, 18 W, and peroxy acetic acid (PAA) oxidant was estimated. The differential method was evaluated by fractional order of reaction for both UV and UV/PAA processes. Overall and initial reaction rate constants were evaluated using integral method. Reaction rate increases with UV input and PAA concentration and it decreases with the increase in 4-CP concentration. Samples were analyzed by HPLC, UV spectrophotometer, and GC-MS for residual concentration and identification of degraded products. The degradation compounds are identified and probable mechanism of reaction is established.

Keywords: 4-Chlorophenol (4-CP); Kinetic study; Mechanism; PAA; UV

1. Introduction

4-Chlorophenol (4-CP) is a well-known organic pollutant because of its widespread application and potential adverse health effects. 4-CP may accumulate in the human body and cause negative health effects, like carcinogenicity and acute toxicology [1]. It also occurs in the environment in both dissociated and undissociated form [2]. 4-CP is widely used as preservative for wood [3], refining solvent, disinfectant, denaturant, and antifungal agent. It is also used in the production of dyes, drugs, and fungicides. Due to toxic and refractory (resist natural breakdown) nature of 4-CP, its removal from the environment is a very essential aspect [4]. Conventional methods are available for the degradation of 4-CP which includes biological treatment, chlorination, and adsorption [5]. All these processes are required long treatment period and produce more harmful byproducts [6]. At present, advance oxidation processes (AOPs) are well known and proved as an efficient process to facilitate the degradation of 4-CP by producing highly reactive hydroxyl radical [7]. Among different AOPs, the photochemical processes are reported to be an effective means of 4-CP degradation [7]. The main advantage of this process is to convert 4-CP to less harmless compound at mild conditions of temperature [8]. During UV irradiation 4-CP reaches to an excited electronic state that is more susceptible to oxidation [9]. Rate of photooxidation is strongly influenced by oxidant concentration, input of irradiation, and pH of solution [2]. It is not possible to complete any study

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without understanding the reaction mechanism and kinetic aspects of the process.

Abundant literatures are available for 4-CP degradation kinetics by micro-organism [10], adsorption [11], UV/Fenton [12], and with inorganic oxidants [1,13]. However, reported data of kinetic study with organic oxidant are limited [14].

In this study, kinetic and mechanistic study of photochemical degradation of 4-CP are carried out with UV and peroxy acetic acid (PAA). The objective of this work is to investigate the effect of various parameters, such as UV input, pH, PAA, and 4-CP concentration on reaction kinetics of the process and to determine rate parameters for both UV and UV/PAA processes. In this work differential and integral methods are used to determine kinetic parameters of the process. Samples are analyzed by HPLC, UV spectrophotometer, and GC-MS for residual concentration and identification of degraded products. The compounds of degradation are identified and probable mechanism of reaction is proposed.

2. Experimental

2.1. Materials

4-CP (purity, 99%), PAA (40%) (National Chemical, Vadodara, India), and acetone (Merck, Mumbai) were purchased. Solutions were prepared with distilled water (Millipore, Elix, Banglore, India) produced in the laboratory. The radiation was provided by 6 W, 12 W, and 18 W low-pressure mercury lamp (254 nm) purchased from Zahabi Marketers (Surat, India). Other chemicals like NaOH and H_2SO_4 and potassium dichromate were of analytical grade and used without further purification.

2.2. Method

All the experiments were carried out in a batch reactor (figure not shown here). The reactor was cylindrical with 250 ml capacity made up of quartz glass. The UV lamp was (6 W, 12 W, and 18 W) axially centered in the reactor containing 4-CP solution. The reaction mixture (PAA/4-CP, UV/4-CP, or UV/PAA/4-CP) was filled in reaction chamber (between the reactor wall and UV lamp) and continuously stirred by magnetic stirrer. Reaction vessel was wrapped with aluminum foil to avoid the adverse effect of UV irradiation. The radiation intensity at the reactor wall or inside the reaction mixture was not measured. However, only the consumption power of the mercury lamp varied. Cooling was provided to the immersion vessel through water cooler pump. Experiments were performed with PAA/4-CP, UV/4-CP, and UV/PAA/4-CP processes at various pH with initial concentration of 4-CP as 51.4 ppm. The results obtained by UV/4-CP, PAA/4-CP processes were used as reference for experiment with UV/PAA process. For UV/PAA process, initially different concentrations of PAA were used. Initial concentration in parts per million (ppm) were as follows: 4-CP, 51.4, PAA: 510, 1020, 2040, 3040, and 4053. Remaining experiment of UV/PAA process was conducted with optimized PAA concentration. The pH maintained for the experiment were 4, 6.5, and 9.5 and controlled by adding 0.1 N/1.0 N NaOH and 0.1 N/1.0 N H_2SO_4 and measured on digital pH meter (ME-962P, Chandigarh, India). All the experiments of UV and UV/PAA system were run for 50 min. Samples were collected and analyzed for residual concentration immediately. The reproducibility study was carried out for several tests thrice. The results were found to be within 5% error.

2.3. Analysis

Sample analysis was done by HPLC (Shimurzu LC-2010 AHT, Kyoto, Japan) and UV spectrophotometer (DR 5000, HACH, USA) [15]. GC-MS analysis was carried out under following experimental condition: electron impact (EI) ionization, temperature programmed: SPLIT-50,60-8-260-30-280-3; carrier gas, helium; flow rate, 1 mL/min; injection volume, 1 μL; solvent delay, 3 min; column HP5MS; column length, 30 m; internal diameter, 0.25 mm; film thickness, 0.2 μm; detector mass spectrometer; mass range scanned, 50–2000 amu.

3. Result and discussions

The kinetics and mechanism of the reaction are extremely depended on operating parameters [2]. To evaluate the kinetic parameters, 4-CP is subjected to UV irradiation and oxidant PAA. Results on UV/4-CP and PAA/4-CP are used as a reference for other experiments with UV/PAA/4-CP system. PAA, itself initialized the decomposition reaction without the help of UV irradiation but degradation efficiency is not significant Only 4 to 5% reduction is possible after 50 min of treatment with only PAA. For further degradation of 4-CP, UV radiation is essential. Hence, remaining experiments are carried out with UV and UV/PAA process.

3.1. UV/PAA Process

Rate of photolysis is dependent on the pH of solution and input of the UV lamp. To evaluate the effect of UV input and pH, all the experiments on UV/4-CP are performed with an initial concentration of 4-CP as 51.4 ppm. The UV lamp and pH values used for the experiment are 6 W, 12 W, 18 W, and pH 4, 6.5, and 9.5, respectively. In case of direct photolysis, initial degradation rate is found to be high and gradually decreases with time. Maximum degradation of 4-CP is accomplished with 18 W UV lamp. Solution pH has significant role in UV/4-CP process. At the end of the reaction it is observed that pH 9.5 shows more reduction of 4-CP compared to all pH conditions used. The percent degradation is maximum at pH 9.5 at all UV sources, because hydroxyl radical formation is favorable in the basic medium. It is also observed (Fig. 1) that during UV/4-CP initial reaction rate is high and more than 80% 4-CP is degraded within 18 min of reaction.

An Addition of oxidant increases the reaction rate as well as the reaction efficiency of the process due to generation of more reactive hydroxyl ions. Degradation of 4-CP in aqueous solution by UV/PAA process resulted in the formation of various secondary products. The addition of hydroxyl radicals to the aromatic compound by hydroxylation of aromatic ring and/or replacement of chlorine atom by OH^* radical [16] is formed the degraded products. In UV/PAA process, intermediate compounds may further mineralized to CO_2 and H_2O as final compounds by following reaction mechanism.

$$\text{4-CP} + \text{PAA} + \text{UV} \xrightarrow{k1} \text{Intermediates} \xrightarrow{k2} CO_2 + H_2O \qquad (1)$$

where k_1 and k_2 indicates decomposition rate constant of 4-CP and mineralization rate constant for intermediate compounds. From GC-MS analysis results, decomposition and mineralization of 4-CP is assume to be irreversible reaction.

OH^* radical are highly reactive electrophills that react instantly and nonselectively with all type of organic species. Based on the nature of organic compounds OH^* radicals attack either by electron transfer, H^* abstraction, or $^*OH$ addition to aromatic ring. PAA is directly attack on the electron dense structures of the aromatic rings, double and triple bonds, and ether bonds [17]. To evaluate the effect of PAA concentration on 4-CP degradation in UV/PAA processes, experiments are performed with different PAA concentrations between 510 and 4,053 ppm. It is observed that (figure not shown here) 4-CP degradation increases with increasing PAA concentration because of more OH radical generation, but up to certain concentration. Further increase in PAA concentration decreases degradation efficiency of 4-CP. The degradation of 4-CP removal with PAA followed the order as 3,040 ppm > 2,010 ppm > 1,020 ppm > 510 ppm > 4,053 ppm. Therefore, the optimum PAA concentration for PAA/UV process is considered as 3,040 ppm. Hence, remaining experiments are carried out with 3,040 ppm PAA concentration.

Rate of photochemical degradation of 4-CP depends upon intensity of UV input and directly proportional to it. To find out the effect of UV irradiation in UV/PAA process experiments are performed with different UV lamps, such as 6 W, 12 W, and 18 W. It is found that the degradation rate of UV/PAA process increases with increase in UV input from 6 W to 18 W. The availability of photons in the system increases with intensity of UV light which generates more hydroxyl radicals. The degradation percent obtained at pH 9.5 by 6 W, 12 W, and 18 W UV lamps are 86, 88, and 90% after 18 min of reaction. Fig. 2 shows that the degradation rate of UV/PAA process at pH 9.5 by 18 W UV lamp. To evaluate the effect of pH on 4-CP degradation kinetics, the pH of the solution is

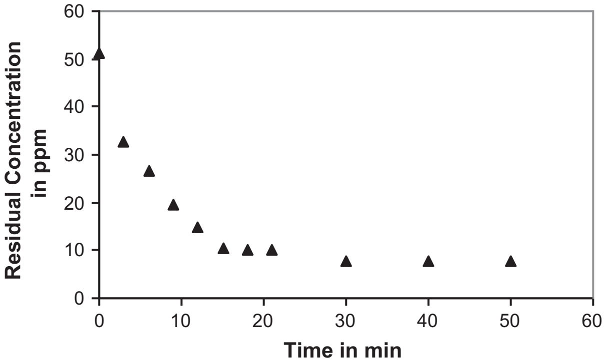

Fig. 1. Residual concentration vs. time for 4-CP in direct photolysis at pH 9.5 (4-CP: 51.4 ppm, 18 W).

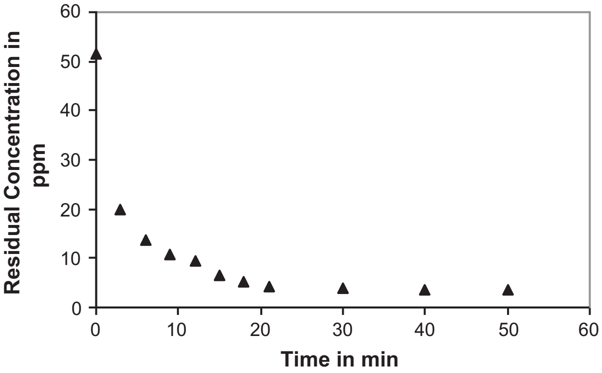

Fig. 2. Reduction vs. time for 4-CP in UV/PAA process at pH 9.5 (4-CP: 51.4 ppm, PAA: 3,040 ppm, 18 W).

Table 1A
Order of reaction by the differential method of analysis (for initial reaction period)

Process	UV source	Parameter	Rate constant, *k*	Order of reaction
UV	6 W	pH = 4	$1.26 \times 10^{-3}\,\mathrm{M}^{-1.15}\,\mathrm{min}^{-1}$	2.15
		pH = 6.5	$1.80 \times 10^{-4}\,\mathrm{M}^{-1.5}\,\mathrm{min}^{-1}$	2.50
		pH = 9.5	$4.09 \times 10^{-4}\,\mathrm{M}^{-1.5}\,\mathrm{min}^{-1}$	2.50
	12 W	pH = 4	$1.36 \times 10^{-3}\,\mathrm{M}^{-1.14}\,\mathrm{min}^{-1}$	2.14
		pH = 6.5	$4.21 \times 10^{-3}\,\mathrm{M}^{-0.75}\,\mathrm{min}^{-1}$	1.75
		pH = 9.5	$2.71 \times 10^{-3}\,\mathrm{M}^{-0.97}\,\mathrm{min}^{-1}$	1.97
	18 W	pH = 4	$5.62 \times 10^{-3}\,\mathrm{M}^{-0.81}\,\mathrm{min}^{-1}$	1.81
		pH = 6.5	$4.08 \times 10^{-3}\,\mathrm{M}^{-0.79}\,\mathrm{min}^{-1}$	1.79
		pH = 9.5	$0.056\,\mathrm{M}^{-0.13}\,\mathrm{min}^{-1}$	1.13
UV/PAA	6 W	pH = 4	$7.44 \times 10^{-3}\,\mathrm{M}^{-0.83}\,\mathrm{min}^{-1}$	1.83
		pH = 6.5	$0.011\,\mathrm{M}^{-0.67}\,\mathrm{min}^{-1}$	1.67
		pH = 9.5	$0.018\,\mathrm{M}^{-0.74}\,\mathrm{min}^{-1}$	1.74
	12 W	pH = 4	$8.65 \times 10^{-3}\,\mathrm{M}^{-0.81}\,\mathrm{min}^{-1}$	1.81
		pH = 6.5	$0.011\,\mathrm{M}^{-0.64}\,\mathrm{min}^{-1}$	1.64
		pH = 9.5	$0.014\,\mathrm{M}^{-0.65}\,\mathrm{min}^{-1}$	1.65
	18 W	pH = 4	$0.019\,\mathrm{M}^{-0.60}\,\mathrm{min}^{-1}$	1.60
		pH = 6.5	$0.010\,\mathrm{M}^{-0.72}\,\mathrm{min}^{-1}$	1.72
		pH = 9.5	$0.019\,\mathrm{M}^{-0.58}\,\mathrm{min}^{-1}$	1.58

Table 1B
Order of reaction by the differential method of analysis for UV/PAA process (for initial reaction period), (pH: 9.5, 18 W)

4-CP conc., ppm	PAA conc., ppm	Rate constant, *k*	Order of reaction
51.4	510	$8.5 \times 10^{-4}\,\mathrm{M}^{-1.39}\,\mathrm{min}^{-1}$	2.39
51.4	1,020	$1.09 \times 10^{-3}\,\mathrm{M}^{-1.36}\,\mathrm{min}^{-1}$	2.36
51.4	2,040	$6.09 \times 10^{-3}\,\mathrm{M}^{-0.89}\,\mathrm{min}^{-1}$	1.89
51.4	3,040	$0.019\,\mathrm{M}^{-0.58}\,\mathrm{min}^{-1}$	1.58
51.4	4,053	$0.060\,\mathrm{M}^{-0.1}\,\mathrm{min}^{-1}$	0.10
25	3,040	$0.021\,\mathrm{M}^{-0.84}\,\mathrm{min}^{-1}$	1.84
75	3,040	$0.015\,\mathrm{M}^{-0.51}\,\mathrm{min}^{-1}$	1.51
100	3,040	$0.120\,\mathrm{M}^{\,0.25}\,\mathrm{min}^{-1}$	0.75

maintained in the range of 4–9.5 pH. The pH is an essential factor for maximizing the efficiency and the degradation rate of the process. The optimized pH for UV/PAA process is 9.5. Further experiments are carried out at pH 9.5.

To evaluate the effect of initial concentration of 4-CP on its degradation kinetics, the concentration of 4-CP is used in the range of 25–100 ppm. The initial 4-CP concentration is the function of degradation rate (graph not shown here). The chloride ion is one of the important free radical scavenger and the chloride ions increases at high 4-CP concentration. Chloride ions formed may react with hydroxyl radicals to produce hypochlorite anion [18] radicals that lead generation of atomic chlorine radicals as in Eqs. (2) and (3). The attack by the OH radical initiates a complex cascade of oxidative reactions leading to mineralization of the organic compound.

$$\mathrm{HO}^{*} + \mathrm{Cl}^{-} \rightarrow \mathrm{HOCl}^{*-} \tag{2}$$

$$\mathrm{HOCl}^{*-} + \mathrm{H}^{+} \rightarrow \mathrm{Cl}^{*} + \mathrm{H_2O} \tag{3}$$

3.2. Kinetic study

To determine the kinetic parameter for both UV and UV/PAA process, differential method of analysis

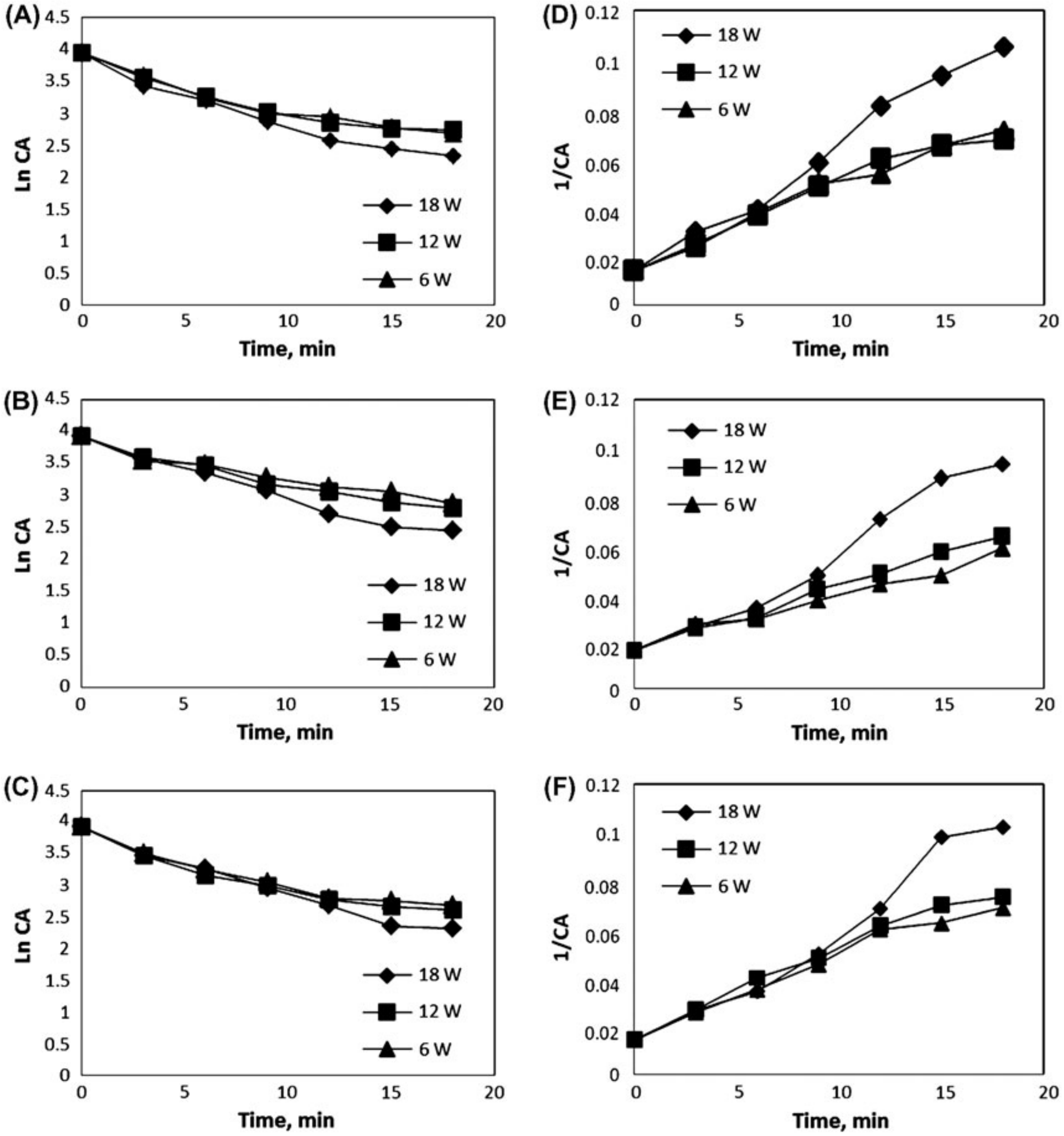

Fig. 3. First-order (A, B and C) and second-order (D, E and F) plots of 4-CP degradation in direct photolysis at pH 4(A, D), pH 6.5(B, E), and pH 9.5 (C, F); (4-CP: 51.4 ppm).

was applied as in Eqs. (4) and (5) [19]. Order of reaction and rate constant were calculated from the slope and intercepts of the straight line.

$$\text{Rate} = -\mathrm{d}C_\mathrm{A}/\mathrm{d}t = kC_\mathrm{A}^n \quad (4)$$

$$\ln(-\mathrm{d}C_A/\mathrm{d}t) = \ln k + n \ln \mathrm{C_A} \quad (5)$$

Rate constants were also evaluated using integral method using first-order and second-order rate equations as in Eqs. (6) and (7) [19].

$$\text{First-order } \ln\ \mathrm{C_A} = -kt + \ln\ \mathrm{C_{A0}} \quad (6)$$

$$\text{Second-order } 1/C_\mathrm{A} = 1/C_\mathrm{A0} + kt \quad (7)$$

The first-order and second-order reaction rate constants, k were determined (from slope) by plotting graph of ln (C_A) vs. time and $1/C_\mathrm{A}$ vs. time.

As observed, from Figs. 1 and 2, the initial rate of degradation of 4-CP is fast. Almost 80% for direct photolysis and 90% for UV/PAA process of 4-CP degraded within 18 min of initiation of reaction.

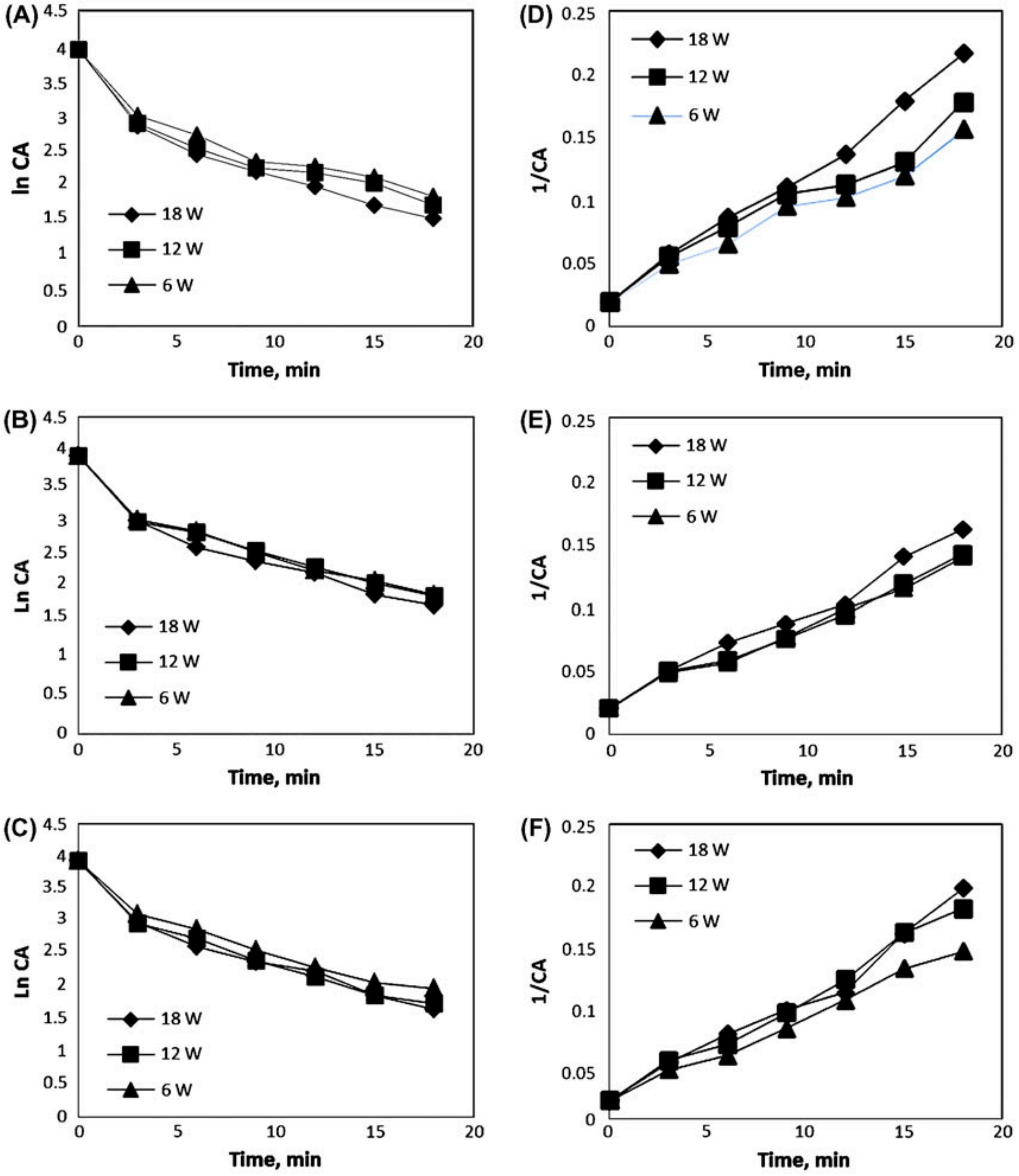

Fig. 4. First-order (A, B and C) and second-order (D, E and F) plots of 4-CP degradation in UV/PAA process at pH 4(A, D), pH 6.5 (B, E), and pH 9.5 (C, F); (4-CP: 51.4 ppm, PAA: 3,040 ppm).

Thereafter degradation rate is slow till 50 min. The intermediates formed react with available hydroxyl radicals and due to this, concentration of hydroxyl radicals required for 4-CP degradation decreases; as a result degradation rate decreases. Therefore, initial reaction rate is considered for further investigation of rate parameter by differential method. The order of reaction is calculated from the slope of the straight line. The rate constant and order of reaction for initial reaction rate by differential method for both direct photolysis and UV/PAA process are reported in Tables 1A and 1B. It is observed that the order of reaction for both UV and UV/PAA processes are fractional. Concentration of PAA and 4-CP also influences the order of reaction as observed in Table 1B.

Table 2A
Comparison of rate parameter for UV and UV/PAA process (for initial reaction period)

Process	UV lamp	Parameter	First order		Second order	
			Rate constant, *k*, min^{-1}	R^2	Rate constant, *k*, $\text{L mg}^{-1}\,\text{min}^{-1}$	R^2
UV	6 W	pH = 4	0.080	0.88	0.002	0.98
		pH = 6.5	0.062	0.91	0.001	0.98
		pH = 9.5	0.081	0.87	0.003	0.98
	12 W	pH = 4	0.080	0.85	0.002	0.96
		pH = 6.5	0.069	0.94	0.001	0.99
		pH = 9.5	0.086	0.85	0.003	0.98
	18 W	pH = 4	0.102	0.92	0.004	0.98
		pH = 6.5	0.086	0.96	0.003	0.97
		pH = 9.5	0.104	0.96	0.004	0.98
UV/PAA	6 W	pH = 4	0.133	0.74	0.007	0.98
		pH = 6.5	0.125	0.80	0.006	0.99
		pH = 9.5	0.129	0.82	0.007	0.99
	12 W	pH = 4	0.141	0.67	0.007	0.96
		pH = 6.5	0.126	0.78	0.006	0.98
		pH = 9.5	0.143	0.81	0.008	0.99
	18 W	pH = 4	0.143	0.75	0.010	0.99
		pH = 6.5	0.136	0.77	0.007	0.98
		pH = 9.5	0.156	0.81	0.011	0.97

Table 2B
Comparison of rate parameter for UV/PAA process (for initial reaction period), (pH: 9.5, 18 W)

4-CP conc., ppm	PAA conc., ppm	First order		Second order	
		k, min^{-1}	R^2	*k*, $\text{L mg}^{-1}\,\text{min}^{-1}$	R^2
51.4	510	0.109	0.50	0.003	0.92
51.4	1,020	0.117	0.55	0.004	0.94
51.4	2,040	0.129	0.68	0.006	0.98
51.4	3,040	0.156	0.81	0.011	0.99
51.4	4,053	0.115	0.78	0.004	0.90
25	3,040	0.268	0.64	0.055	0.94
75	3,040	0.100	0.93	0.004	0.99
100	3,040	0.062	0.96	0.002	0.97

Table 3A
Comparison of rate parameter for UV and UV/PAA process (for overall reaction period)

Process	UV lamp	Parameter	Second order	
			Rate const., *k* $\text{L mg}^{-1}\,\text{min}^{-1}$	R^2
UV	6 W	pH = 4	0.001	0.77
		pH = 6.5	0.001	0.82
		pH = 9.5	0.001	0.82
	12 W	pH = 4	0.001	0.82
		pH = 6.5	0.001	0.82
		pH = 9.5	0.001	0.81
	18 W	pH = 4	0.001	0.76
		pH = 6.5	0.001	0.70
		pH = 9.5	0.002	0.83
UV/PAA	6 W	pH = 4	0.004	0.83
		pH = 6.5	0.003	0.85
		pH = 9.5	0.004	0.86
	12 W	pH = 4	0.004	0.83
		pH = 6.5	0.003	0.85
		pH = 9.5	0.004	0.81
	18 W	pH = 4	0.005	0.83
		pH = 6.5	0.003	0.82
		pH = 9.5	0.005	0.89

For the entire time span either first-order or second-order linearity is not observed [14]. First- and second-order plots for direct photolysis and UV/PAA process are shown in Figs. 3 and 4. The value of rate constant (*k*) for initial reaction period (18 min) is evaluated by first- and second-order rate equations, Eqs. (6) and (7) for different UV sources and compared as in Tables 2A and 2B. It is observed that initial rate

Table 3B
Comparison of rate parameter for UV/PAA process (for overall reaction period), (pH: 9.5, 18 W)

4-CP conc., ppm	PAA conc., ppm	Second order	
		Rate const., k, L mg^{-1} min^{-1}	R^2
51.4	510	0.001	0.64
51.4	1,020	0.001	0.70
51.4	2,040	0.002	0.75
51.4	3,040	0.005	0.89
51.4	4,053	0.001	0.47
25	3,040	0.018	0.62
75	3,040	0.002	0.78
100	3,040	0.001	0.74

constants (k, L mg^{-1} min^{-1}) follows second-order rate equation for 6 W, 12 W, and 18 W at all pH (pH 4, 6.5, and 9.5). Decomposition of 4-CP generates secondary products that may be responsible for low k value. The initial reaction rate is high at both pH 4 and pH 9.5. Both alkaline and acidic condition is favorable for free radical release (Table 2A). Several researchers reported that basic pH is favorable for 4-CP degradation because at basic pH hydroxyl radical formation is found to be more [7]. Few studies show that degradation efficiency decreases at high pH [16]. Stable and aliphatic compounds are detected by GC-MS. During oxidation reaction, pH of the solution decreases by 1 and 2 units due to formation of acidic intermediates. From Table 2B and itis observed that reaction rate of

Table 4
Comparison of rate parameter for different oxidants as reported for 4-CP degradation

Sr no.	Oxidant	Process condition	Rate constant, k	Reference
1	PAA	UV: 6 W, 12 W and 18 W pH: 9.5	For UV: 0.004 L mg^{-1} min^{-1} For UV/PAA: 0.007,0.008 and 0.011 L mg^{-1} min^{-1}	This work
		4-CP (ppm): 25, 51.4, 75 and 100	For 4-CP: 0.055,0.04 and 0.02 L mg^{-1} min^{-1}	
		PAA (ppm): 510,1,020, 2040, 3,040 and 4,053	PAA: 0.003, 0.004, 0.006, 0.011, 0.04 L mg^{-1} min^{-1}	
2	PAA, PNBA, MEKP	UV: 254 nm 4CP: 0.4 mM	0.029 s^{-1}, 0.019 s^{-1} 0.011 s^{-1}, 23.4 s^{-1}	[14]
1	UV/TiO_2	UV: 100 W pH: 10 Bias potential: 0.5 V 4 CP: 200 μM	For UV: 2.75×10^{-3} min^{-1} Bias potential: 7.49×10^{-4} min^{-1} For combine; 9.26×10^{-3} min^{-1}	[16]
2	UV/ZnO UV/ZnO/SnO_2	UV: 8 W pH: 11	UV/ ZnO; 0.78 $^{h-1}$ UV/ZnO/SnO_2: 0.95 $^{h-1}$	[20]
3	CdSe/TiO_2	UV: 254 and 365 nm	For 254 nm: 1.35×10^{-2} min^{-1}, 4×10^{-2} min^{-1}	[21]
		pH: 7 and 11	For 365 nm; 2.0×10^{-3} min^{-1}, 1.9×10^{-3} min^{-1}	
4	Pulse arc discharge (PAED)	Energy: 588 J/discharge 4 CP(μM): 50,100,200 and 300	2.7×10^{-2} min^{-1}, 1.2×10^{-2} min^{-1} 7.6×10^{-3} min^{-1}, 5.0×10^{-3} min^{-1}	[22]
5	Ozone	UV: 254 nm, pH: 2.5 4 CP(mM): 0.1 and 0.4	1.86×10^{-3} s^{-1} 6.06×10^{-4} s^{-1}	[23]
6	UV/Kaolinite	UV: 589.44 nm Kaolinite: 0.06 wt.% pH: 6.08, 7, 8, 9 and 11	0.0055 min^{-1} 0.0059 min^{-1} 0.0079 min^{-1} 0.0087 min^{-1} 0.0100 min^{-1}	[24]
7	UV/H_2O_2	UV: 254 nm pH: 7 4-CP (ppm): 100 H_2O_2: 0.05 M	For UV: 0.02 min^{-1} For UV/H_2O_2: 0.137 min^{-1}	[25]

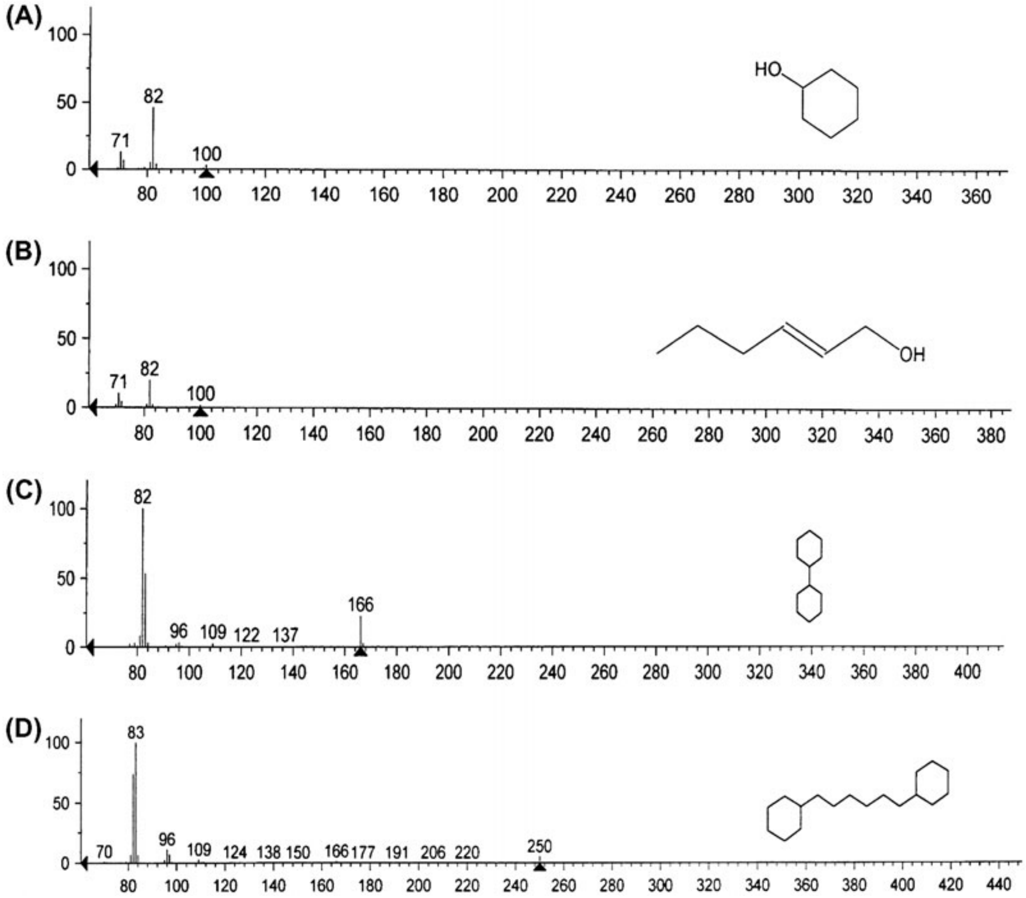

Fig. 5. Mass spectra of cyclohexanol (A) 2-Hexen-1-ol (B) 1,1´Bicyclohexyl (C) 1,6-dicyclohexyl-hexane (D).

4-CP degradation increases with increase in initial PAA concentration but up to certain limit. Excess of PAA inhabited the production of OH radical generation which ultimately lowers the degradation rate of 4-CP decomposition.

The rate constants (k) for different PAA concentration by second-order rate equation are in the range of 0.003–0.011 $\mathrm{L\,mg^{-1}\,min^{-1}}$. Reaction rate of 4-CP oxidation is rapid with PAA concentration, 3,040 ppm, compared to other concentrations. The rate constant obtained by second-order rate equation are in the range of 0.055–0.002 $\mathrm{L\,mg^{-1}\,min^{-1}}$ for 4-CP concentration of 25–100 ppm. The value of rate constant decreases with the increase in 4-CP concentration.

The value of rate constant (k) for overall reaction period (50 min) is evaluated by first- and second-order rate equations, Eqs. (6) and (7) for different UV sources are compared in Tables 3A and 3B. For overall reaction period, the reaction is more likely to follow second-order rate equation but with poor correlation coefficient (R^2) value. Rate parameters of photochemical degradation of 4-CP with different oxidants under varied experimental conditions are compared and reported in Table 4.

3.3. Reaction mechanism and degraded products

The mass spectra of intermediate product formed by PAA/4-CP, UV/4-CP, and UV/PAA/4-CP are shown in Fig. 5 (A), (B), (C), and (D). The degraded compounds for PAA/4-CP, cyclohexanol, and 2-Hexen-1-ol, for UV/4-CP 1,1´Bicyclohexyl, and 1,6-dicyclohexyl-hexane and for UV/PAA/4-CP 4-methyl-3-pentene-2-one [7] are identified by GC-MS. GC-MS results which confirm the absence of 4-CP and no trace of PAA. Based on the identified degraded compounds reaction mechanism is proposed as in Fig. 6.

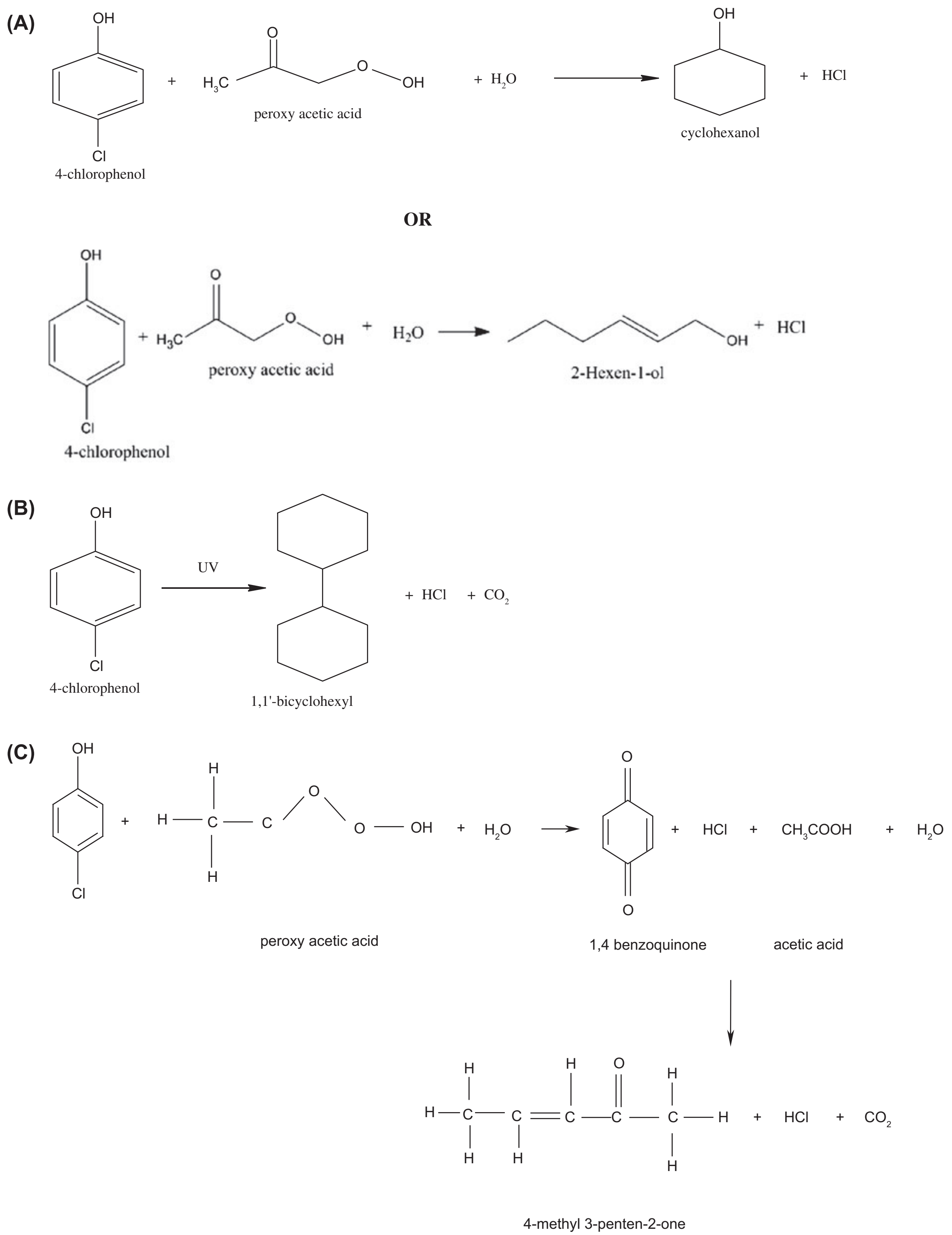

Fig. 6. Proposed reaction mechanism for [A] PAA/4-CP, [B] UV/4-CP and [C] UV/PAA/4-CP [7] mediated degradation of 4-CP.

4. Conclusions

In this study, kinetic parameters for 4-CP degradation is determined by differential and integral method of analysis for both UV and UV/PAA process. The oxidation rate for both UV and UV/PAA processes are affected by operating parameters, such as UV input, pH, PAA, and 4-CP concentration. The kinetic parameter is investigated for initial reaction period (18 min.). Order of reaction by differential method is in fractional order. Therefore, rate constant is determined by using first-order and second-order reaction rate equation. The overall reaction rate is more likely to follow second-order but with poor correlation coefficient (R^2) value. The initial reaction rate followed the second-order rate constants ($R^2 < 0.95$). The degraded compounds of 4-CP photochemical degradation are identified and probable mechanism of reaction is established.

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References

[1] N. Wang, X. Li, Y. Wang, X. Quan, G. Chen, Evaluation of bias potential enhanced photocatalytic degradation of 4-chlorophenol with TiO_2 nanotube fabricated by anodic oxidation method, Chem. Eng. J. 146 (2009) 30–35.

[2] M. Mukhopadhyay, D.P. Daswat, Photochemical degradation of 4-chlorophenol in aqueous phase using peroxy acetic acid (PAA), Water Sci. Technol. 67 (2013) 440–445.

[3] M. Gomez, M.D. Murcia, N. Christofi, E. Gomez, J.L. Gomez, Photodegradation of 4-chlorophenol using XeBr, KrCl and Cl2 barrier-discharge excilamps: A comparative study, Chem. Eng. J. 158 (2010) 120–128.

[4] A. Mesdaghinia, M. Rafiee, M.H. Ghahremani, S. Nasseri, R. Nabizadeh, 4-Chlorophenol inhibition on flocculent and granular sludge sequencing batch reactors treating synthetic industrial wastewater, Desalin. Water Treat 49 (2012) 307–316.

[5] M. Gomez, M.D. Murcia, E. Gomez, J.L. Gomez, N. Christofi, Degradation of phenolic pollutants using KrCl and XeBr excilamps in the presence of dye: A comparative study, Desalination 274 (2011) 156–163.

[6] J. Theurich, M. Lindner, D.W. Bahnemann, Photocatalytic degradation of 4-chlorophenol in aerated aqueous titanium dioxide suspensions: A kinetic and mechanistic study, Langmuir 12 (1996) 6368–6376.

[7] S. Sharma, M. Mukhopadhyay, Z.V.P. Murthy, Degradation of 4-chlorophenol in wastewater by organic oxidants, Ind. Eng. Chem. Res. 149 (2010) 3094–3098.

[8] W.H. Glaze, F. Beltran, T. Tuhkanen, J.W. Kang, Chemical models of advanced oxidation processes, Water Pollut. Res. J. Can. 27 (1992) 23–42.

[9] A. Antoniadis, V. Takavakoglou, G. Zalidis, I. Poulios, Development and the evaluation of an alternative method for municipal wastewater treatment using homogeneous photocatalysis and constructed wetlands, Catal. Today 124 (2007) 260–265.

[10] M. Gomez, G. Matafonova, J.L. Gomez, V. Batoev, N. Christofi, Comparison of alternative treatments for 4-chlorophenol removal from aqueous solutions: Use of free and immobilized soybean peroxidase and KrCl excilamp, J. Hazard. Mater. 164 (2009) 46–50.

[11] B.H. Hameed, L.H. Chin, S. Rengara, Adsorption of 4-chlorophenol on activated carbon prepared from rattan sawdust, Desalination 225 (2008) 185–198.

[12] C.E. Catalkaya, U. Bali, F. Sengul, Photochemical degradation and mineralization of 4-chlorophenol, Environ. Sci. Pollut. Res. 10 (2003) 113–120.

[13] J.S. Levitt, A.L. N'Guessan, K.L. Rapp, M.C. Nyman, Remediation of R methylnaphthalene-contaminated sediments using peroxy acid, Water Res. 37 (2003) 3016–3022.

[14] S. Sharma, M. Mukhopadhyay, Z.V.P. Murthy, Rate parameter estimation for 4-chlorophenol degradation by UV and organic oxidants, J. Ind. Eng. Chem. 18 (2012) 249–254.

[15] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, and WEF (American Public Health Association, American Water Works Association, and Water Environment Federation), APAH, 19th ed., Washington, USA, 1995.

[16] J. Yang, J. Dai, C. Chen, J. Zhao, Effects of hydroxyl radicals and oxygen species on the 4-chlorophenoldegradation by photoelectrocatalytic reactions with TiO_2-film electrodes, J. Photochem. Photobiol., A 208 (2009) 66–77.

[17] G. Cleriti, D. Zingaretti, R. Baciocchi, Kinetics of peroxyacetic acid formation and decomposition in soil-slurry systems, Sep. Sci. Technol. 45 (2010) 1610–1616.

[18] V.V. Goncharuk, N.M. Soboleva, A.A. Nosonovich, Photooxidative destruction of organic compounds by hydrogen peroxide in water, J. Water Chem. Technol. 32 (2010) 17–32.

[19] O. Levenspiel, Chemical Reaction Engineering, Wiley, India, 2007.

[20] X.-H. Ou, C.-H. Wub, S.-L. Lo, Photodegradation of 4-chlorophenol by UV/photocatalysts: the effect of the interparticle electron transfer process, React. Kinet. Catal. Lett. 88 (2006) 89–95.

[21] S.-C. Lo, C.-F. Lin, C.-H. Wub, P.-H. Hsieh, Capability of coupled CdSe/TiO_2 for photocatalytic degradation of 4-chlorophenol, J. Hazard. Mater. 114 (2004) 183–190.

[22] L.V. Hoang, B. Legube, Degradation of 4-chlorophenol by pulsed arc discharge in water estimation of the energy consumption, IEEE Trans. Dielectr. Electr. Insul. 16 (2009) 1604–1608.

[23] M. Trapido, A. Hirvonen, Y. Veressinina, J. Hentunen, R. Munter, Ozonation, ozone/UV and UV/H_2O_2 degradation of chlorophenols, Ozone Sci. Eng. 19 (1997) 75–96.

[24] S.-L. Kuo, C.-J. Liao, Solar photocatalytic degradation of 4-chlorophenol in kaolinite catalysts, J. Chin. Chem. Soc. 53 (2006) 1073–1083.

[25] H. Movahedyan, A.M. Seid Mohammadi, A. Assadi, A comparison of different advance oxidation processes degrading p-chlorophenol in aqueous solution, Iran. J. Environ. Health Sci. Eng. 6 (2009) 153–160.