Photocatalytic degradation of chlorfenapyr in aqueous suspension of TiO2

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Abstract

The direct photolysis and the photocatalytic degradations of chlorfenapyr in TiO2 suspensions with and without the use of hydrogen peroxide were studied using two different monochromatic UV irradiations (300 and 350 nm). Both the direct photolysis and photocatalytic degradations of chlorfenapyr follow pseudo-first-order degradation kinetics ($C_t = C_0 e^{-kt}$). Photolysis reactions were slow, and the corresponding photocatalysis rates were increased by about 2.5 and 3 times in the presence of TiO2 at 300 and 350 nm of UV, respectively. Photocatalytic rates were increased with the pH at neutral to alkaline ranges because of the increase of hydroxide ions. However, the reaction was gradually retarded at the neutral medium. The half times of degradation ($t_{1/2}$) were 13.7, 16.2, 16.2, 10.7 and 8.7 min, respectively, at pH 4, 6, 7, 9 and 11. The effect of temperature is helpful to the photocatalytic degradation of chlorfenapyr. The photocatalytic degradation rates were found to increase with TiO2 dosages, and the reaction was retarded at higher TiO2 dosages. The fastest degradation occurred when 1200 mg L^{-1} TiO2 was used, the rate increased slowly with increasing catalyst concentration up to 800 mg L^{-1} and more rapidly when the concentration was increased from 800 to 1200 mg L^{-1}, and decreased at 1600 mg L^{-1}. A much faster degradation rate at lower chlorfenapyr concentrations was achieved. The results of H2O2-assisted photocatalysis experiments showed that a low H2O2 dosage in photocatalysis would enhance the degradation rate of chlorfenapyr, however, an overdose of H2O2 will retard the rate because of the expenditure of hydroxyl radicals.
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1. Introduction

Semiconductor photocatalysis is an advanced oxidation process to eliminate organic pollutants from water. The semiconductor photocatalytic process is based on the combined use of low-energy UV light and semiconductor photocatalysts of which the anatase form of TiO2 is the most suitable [1,2]. TiO2 in the anatase form appears to be the most efficient semiconductor for environmental applications and has been studied as a photocatalyst for potential use in wastewater treatment. The use of TiO2 photocatalysts for environmental cleanup has been of interest, because TiO2 is stable, harmless, inexpensive, and solar-activated [3]. Therefore, TiO2 photocatalysis has been widely established as an alternative

physical–chemical process for environmental remediation in the last two decades [4,5]. The use of low-energy UV light and semiconductor photocatalysts such as the anatase form of TiO2, in suspension [6–8] or immobilized [9–12] can degrade and even mineralize these organic pollutants.

The TiO2 photocatalysis mechanism has been described by Robert and Malato [13]. The basic process of photocatalysis consists of ejecting an electron from the valence band to the conduction band of the TiO2 semiconductor, creating a hole in the valence band. This is due to UV irradiation of TiO2 with an energy equal or superior to the bandgap (3.2 eV). This is followed by the formation of reactive radicals at the semiconductor surface and/or a direct oxidation of the polluting species. The ejected electrons react with electron acceptors such as oxygen adsorbed or dissolved in water.

Insecticides are considered cumulative and toxic compounds. Their presence as contaminates in aquatic environments may cause serious problems to human beings

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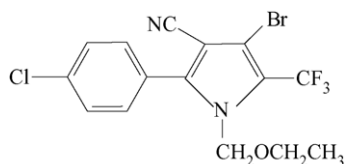*E-mail address:* ytlu@sjtu.edu.cn (Y. Lu).

Fig. 1. The structure of chlorfenapyr.

and other organisms [14–17]. Pesticide photocatalysis with TiO$_2$ has been conducted with fine TiO$_2$ particles (Degussa P-25, mean diameter 30 nm) suspended in an aqueous phase, such as powdered TiO$_2$-enhanced photocatalytic degradation of propachlor, metobromuron, isoproturon, chlortoluron, chlorbromuron, cinosulfuron, triasulfuron, atrazine, cyanazine, propazine, prometryne, irgarol, dicamba, MCPA, 2,4-D, 2,4,5-T, 3,4-xylylmethyl-carbamate, 3,5-xylylmethylcarbamate, propanil and molinate [6,18–26].

Chlorfenapyr was developed by American Cyanamid, IUPAC name: 4-bromo-2-(4-chlorophenyl)-1-ethoxymethyl-5-(trifluoromethyl)pyrrole-3-carbonitrile, Formula: C$_{15}$H$_{11}$BrClF$_3$N$_2$O, is a white to tan crystalline solid, belonging to the pyrrole group of pesticides (Fig. 1). Chlorfenapyr is a novel broad-spectrum insecticide–miticide currently registered in 19 countries for the control of various insect and mite pests on cotton, ornamentals and a number of vegetable crops. This specific acaricide/insecticide has generally no effect on beneficial insects including predaceous mites and thus offers a desirable reason for its use in developing new strategies of integrated pest management in vegetable [27–29].

In this paper, we report the results of the photocatalytic degradation of chlorfenapyr by TiO$_2$ in aqueous suspension. The effects of initial concentration of chlorfenapyr and pH on the degradation rate were investigated because the contaminant concentration and the pH are relevant parameters in wastewater treatment. The effects of TiO$_2$ amount, of hydrogen peroxide addition, of radiation source and of temperature were also examined for enhancement of chlorfenapyr degradation.

2. Materials and methods

2.1. Chemicals

An analytical standard of chlorfenapyr was friendly supplied by American Cyanamid, USA. Titanium dioxide (P-25), a known mixture of 65% anatase and 35% rutile form with an average particle size of 30 nm, nonporous with a reactive surface area (BET) of 50 m^2 g^{-1}, obtained from Degussa was used in this study. Chlorfenapyr standard solution (1294 mg L^{-1}) was prepared in methanol and the solutions required for preparing a standard curve (0.1294, 0.6470, 1.294, 3.235, 6.470 mg L^{-1}) were prepared from the stock solution by serial dilutions. Methanol was chromatograph reagent, all other solvents and chemicals used were of analytical grade

(Shanghai Experiment Reagent Co. Ltd., China). All solutions were prepared using distilled, deionized water.

2.2. Apparatus

All direct photolysis and photocatalysis experiments were conducted using an SGY-II photochemical reactor purchased from Nanjing Stonetech. EEC Ltd., Nanjing, China. A quartz cylinder (50 mm × 450 mm) filled with 500 ml sample solutions was placed inside the reactor and illuminated with monochromatic UV lamps and special glass filters restricting the transmission of wavelengths at either 300 or 350 nm which are available with the photoreactor. A magnetic stirrer was located at the base such that a homogenous TiO$_2$ suspension could be maintained throughout the reaction; a thermostat was also installed in the reactor to adjust the experimental temperature. HA0.45 μm filters were supplied from Millipore (Bedford, USA).

The HPLC system consisted of a Shimadzu (Kyoto, Japan) Model LC-10AT pump associated with a 7125 Rheodyne (Cotati, CA, USA), six-port valve with a 20-μl loop, and a UV–Vis absorbance detector connected to a Shimadzu Model C-R6A integrator for data acquisition. The analytical column was a Kromasil C$_{18}$5 μm (250 × 4.6 mm I.D.).

2.3. HPLC condition and working curve

Samples taken at different times of irradiation were filtered through 0.45-μm filters to remove TiO$_2$ particles before analyses by HPLC-UV at 260 nm. The mobile phase was methanol–water (80:20, v/v) with 1 mL min^{-1} flow rate. The column oven was kept at 30 °C. The volume of the injection was 20 μl. External standard method was adopted. Under the chosen conditions, chlorfenapyr showed a retention time of 14.50 min, allowing a complete separation of its signal from those of foreign substances present in the samples. Concentrations of chlorfenapyr were determined and the peak areas of the standards were recorded. The slope and intercept of the calibration graph were obtained by linear regression of peak area versus concentration: $y = ax + b$, where a is the slope, b the intercept, x the concentration and y the peak area. The parameters obtained by the selected chromatographic conditions for chlorfenapyr calibration correspond to: $y = 2765.3 + 61816x$, $R^2 = 0.9997$. The accuracy and precision of analytical method were 99.3 and 99.6%, respectively; the minimum detectable amount of chlorfenapyr was 6.5×10^{-10} g, the minimum detectable concentration was 0.0162 mg kg^{-1}.

2.4. Statistical analysis

The study was a completely randomized design, with three replications per treatment, chlorfenapyr concentrations were fit to a pseudo-first-order degradation equation $C_t = C_0 e^{-kt}$, where C_t is the chlorfenapyr concentration at time t, C_0 the initial concentration of chlorfenapyr, k the degradation rate

and t the time. To determine the half-lives and degradation rates from the data, the linear form of the equation was used as $\ln(C_t/C_0) = -kt$, in this form, k is the slope. Analysis of covariance of the linearized equations was done within the general linear models (GLM) procedure in SAS (Statistical Analysis Systems, Cary, NC). This procedure was used to determine slope differences among treatments. To accurately assess slopes, data were truncated after the first instance where the chlorfenapyr concentration reached zero for a specified treatment. Estimations of $t_{1/2}$ were made based on the equation $t_{1/2} = 0.693/k$, where k is the estimated pseudo-first-order degradation rate constant determined from the GLM procedure in SAS.

3. Results and discussion

3.1. Direct photolysis and photocatalytic degradation of chlorfenapyr at different UV wavelengths

The degradation of chlorfenapyr by either 300 or 350 nm UV irradiation, with and without the presence of TiO$_2$ at 25 °C, was investigated. The experiments were designed as follow: the initial concentrations of TiO$_2$ and chlorfenapyr were 800 and 50 mg L^{-1}, respectively, pH 6. All the reactions were found to follow a pseudo-first-order kinetic, as shown in Fig. 2. There was an excellent linear relationship between $\ln C$ (concentration of chlorfenapyr) and t (time). The photocatalysis rate constants (K) (with TiO$_2$) for 300 and 350 nm were 0.0427 and 0.0355 min^{-1}, which were higher than their corresponding direct photolysis rates (without TiO$_2$) by about 2.5, 3 times, respectively. This indicates that the chlorfenapyr is mainly oxidized by the hydroxyl radicals that are generated through the process of photocatalysis or by h$^+$ through the direct oxidation. The low direct photolysis rates were apparently due to the low molar absorptivity of chlorfenapyr at 300 and 350 nm, and the lower energy of the UV irradia-
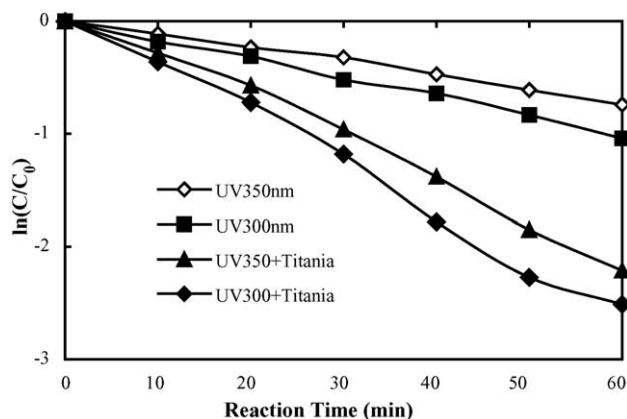

Fig. 2. Direct photolysis and photocatalytic degradation of chlorfenapyr using two different monochromatic UV irradiations: 300 and 350 nm. The initial concentrations of chlorfenapyr and TiO$_2$ were 50 and 800 mg L^{-1}, respectively; pH 6, $T = 25$ °C.
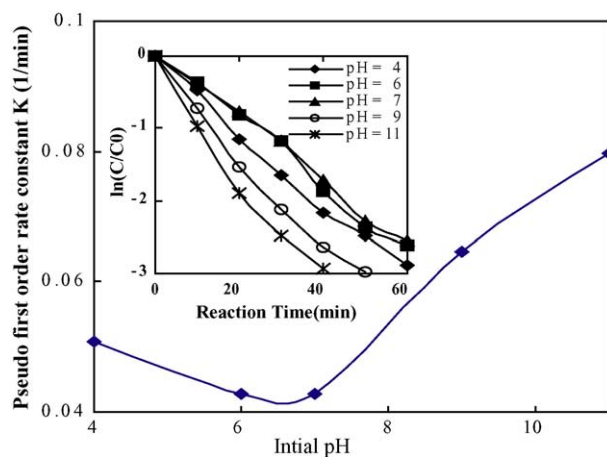

Fig. 3. Variation of pseudo-first-order rate constants with initial pH in photocatalysis reaction at 300 nm. The initial concentrations of chlorfenapyr and TiO$_2$ were 50 and 800 mg L^{-1}, respectively; $T = 25$ °C.

tion. Besides, the test of chlorfenapyr degradation in the dark (with TiO$_2$, but without the exposure to UV light) showed that variations in chlorfenapyr concentrations during 60 min of mixing was insignificant, suggesting that the adsorption (or loss) of chlorfenapyr onto the surface of the TiO$_2$ particles could be neglected.

3.2. Effect of pH on the photocatalytic degradation of chlorfenapyr

The effect of different initial pH levels on the photocatalytic degradation rates of chlorfenapyr under 300 nm irradiation at 25 °C was also investigated. The experiments were designed as 3.1 with variation of pH levels. The photocatalytic degradation rate (k) was found to increase quickly with the initial pH, from neutral (pH 7) condition to an alkaline medium (pH 11), and decrease slowly from an acid condition (pH 4) to a neutral (pH 7) medium, as shown in Fig. 3. The linear regression equations are described in Table 1. The half times of degradation ($t_{1/2}$) were 13.7, 16.2, 16.2, 10.7 and 8.7 min, respectively, at pH 4, 6, 7, 9 and 11. Thus, chlorfenapyr was less stable in acid and alkaline environments, but relatively more stable at neutral conditions. About 58% increase in rate constants were observed as pH increased from pH 4 to 11. At high initial pH, more hydroxide ions (OH$^-$) in the solution induced the generation of hydroxyl free radicals

Table 1
The effect of different initial pH levels on the photocatalytic degradation rates of chlorfenapyr

pH value	Linear regression equation	$t_{1/2}$ (min)	R^2
4	$\ln(C/C_0) = -0.0507t$	13.7	0.9884
6	$\ln(C/C_0) = -0.0427t$	16.2	0.9894
7	$\ln(C/C_0) = -0.0428t$	16.2	0.9922
9	$\ln(C/C_0) = -0.0647t$	10.7	0.9760
11	$\ln(C/C_0) = -0.0797t$	8.7	0.9648

The initial concentrations of TiO$_2$ and chlorfenapyr were 800 and 50 mg L^{-1}, respectively; $T = 25$ °C.
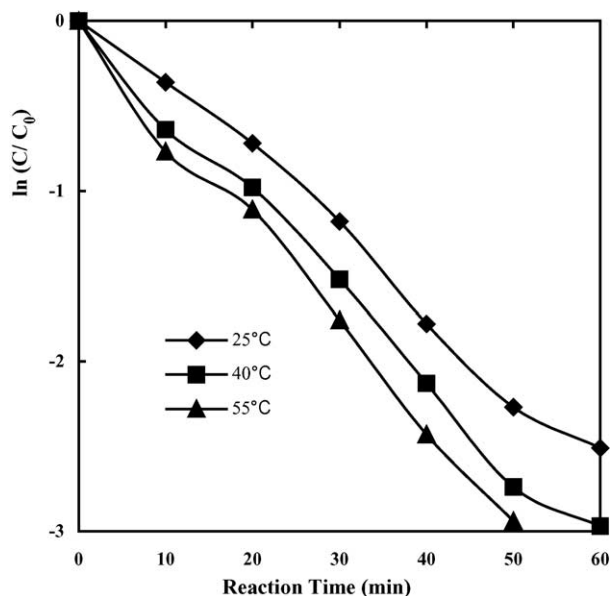
Fig. 4. Comparison of the photocatalytic degradation of chlorfenapyr at 300 nm of UV at different temperature. The initial concentrations of chlorfenapyr and TiO$_2$ were 50 and 800 mgL^{-1}, respectively; pH 6.

(HO$^\bullet$), which came from the photooxidation of OH$^-$ by holes forming on the titanium dioxide surface. Since hydroxyl-free radical is the dominant oxidizing species in the photocatalytic process, the photodegradation of chlorfenapyr is therefore accelerated in an alkaline medium. On the other hand, the point of zero charge (PZC) (pHPZC) for TiO$_2$, or pH at which the surface of this oxide is uncharged, is around 6.3 [30]. Above and below this value, the catalyst is negatively or positively charged. Similar reaction has been suggested by a number of researchers such as Ollis et al. [2], Sánchez et al. [31], Bianco-Prevot et al. [32] and Wong and Chu [33].

3.3. Effect of temperature on the photocatalytic degradation of chlorfenapyr

Three groups of experiments were carried out to study the effect of temperature on photocatalytic degradation of chlorfenapyr under pH 6 solution. The experiments were designed as 3.1 with variation of temperature. In all cases, the degradation rate of chlorfenapyr increased with temperature (Fig. 4). The photocatalysis rate constants (K) were 0.0427, 0.0519 and 0.0594 min^{-1}, respectively; the half times of degradation ($t_{1/2}$) were 16.2, 13.4 and 11.7 min, respectively, at $T = 25$, 40, 55 °C. The effect of temperature is helpful to the photocatalytic degradation of chlorfenapyr. However, the effect of temperature on photocatalytic degradation of chlorfenapyr was less than the effect of pH variation.

3.4. Effect of TiO$_2$ dosages

The effect of different dosages of TiO$_2$ on the photocatalytic degradation rates of chlorfenapyr was also exam-
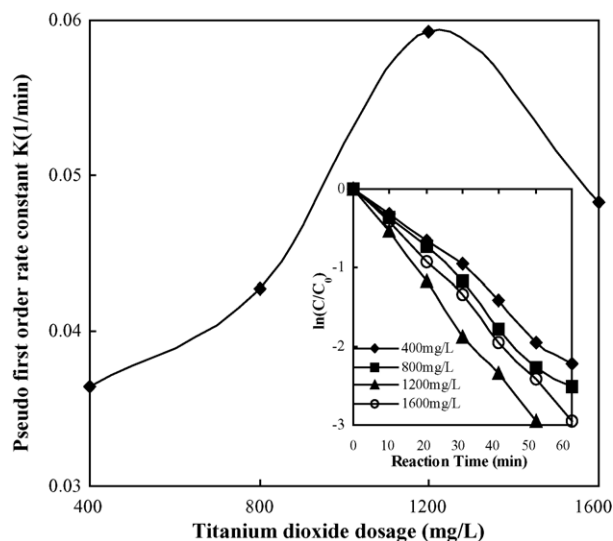

Fig. 5. The pseudo-first-order photodegradation rates of chlorfenapyr at various dosages of TiO$_2$, where the initial pH level is 6, the initial concentrations of chlorfenapyr was 50 mg L^{-1}, $T = 25$ °C, irradiated by UV 300 nm.

ined. The experiments were designed as 3.1 with variation of TiO$_2$ dosages. Experiments were carried out varying the TiO$_2$ amount from 400 to 1600 mg L^{-1}. Fig. 5 shows the variation of pseudo-first-order rate constants with four different TiO$_2$ dosages at 400, 800, 1200 and 1600 mg L^{-1} under UV illumination at 300 nm, in which the photocatalytic degradation rates were found to increase with TiO$_2$ dosages, but the reaction was retarded at higher TiO$_2$ dosages. The fastest degradation occurred when 1200 mg L^{-1} TiO$_2$ was used, the rate increased slowly with increasing catalyst concentration up to 800 mg L^{-1} and more rapidly when the concentration was increased from 800 to 1200 mg L^{-1}, and decreased at 1600 mg L^{-1}. The increase in the rates is likely due to the increase in the total surface area (or number of active sites) available for photocatalytic reaction as the dosage of TiO$_2$ increased. However, when TiO$_2$ was overdosed, the intensity of incident UV light was attenuated because of the decreased light penetration and increased light scattering, which embedded the positive effect coming from the dosage increment and therefore the overall performance reduced.

3.5. Effect of initial chlorfenapyr concentration

The effect of initial chlorfenapyr concentration was investigated over the range of 10–90 mg L^{-1}. The experiments were designed as 3.1 with variation of initial chlorfenapyr concentration dosages. The rate constants obtained in a suspension containing 800 mg L^{-1} of TiO$_2$ decreased significantly with the increase in initial concentration, as shown in Fig. 6. A much faster degradation rate at lower chlorfenapyr concentrations may be justified by the fact that the high number of available TiO$_2$ molecules is able to adsorb most of the molecules in suspension. On the other hand, the process is inverted at higher substrate concentrations, since a
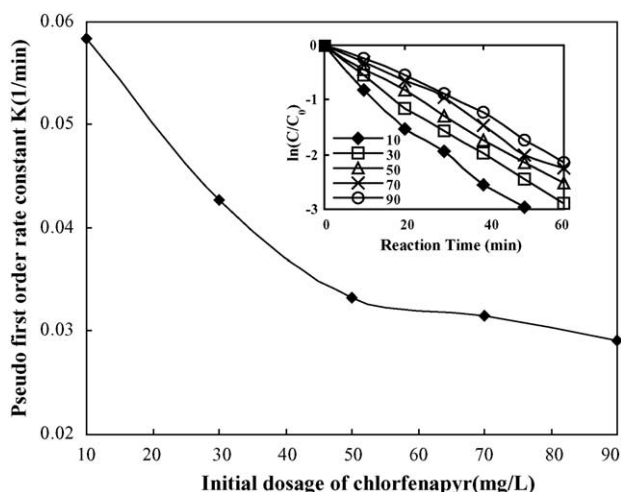
Fig. 6. The pseudo-first-order photodegradation rates of chlorfenapyr at various initial dosages of chlorfenapyr, where the initial pH level is 6, the initial concentrations of TiO_2 was 800 mg L^{-1}, $T = 25\,°C$, irradiated by UV 300 nm.

large number of substrate molecules compete for the adsorption sites with some intermediates such as carboxylic acids, aldehydes and aromatics [34]. As a consequence, there is a decrease in the rate constant because the number of available active sites is diminished for redox reaction [35,36].
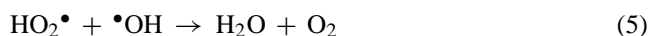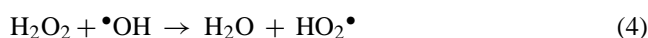
3.6. Effect of H_2O_2 addition

To investigate the effect of adding H_2O_2 to the photocatalysis of chlorfenapyr, experiments were carried out as 3.1 with adding five different dosages of H_2O_2 (0, 2, 20, 200 and 2000 mg L^{-1}), and the results are shown in Table 2. When irradiation was applied only in the presence of H_2O_2, the chlorfenapyr did not degrade satisfactorily, whereas in the presence of the semiconductor the rate increased significantly. The reaction rate was found to increase with low levels of H_2O_2 dosages. At maximum, a 2.1 times rate increment was achieved at the optimal H_2O_2 dosage of 200 mg L^{-1} compared to that of sole photocatalysis without H_2O_2. Above this optimal dosage, however, an overdose of H_2O_2 retards the chlorfenapyr photocatalytic rates. The rate improvement at lower H_2O_2 dosages is probably due to the enhancement of the initial concentration of hydroxyl radicals [37] produced

Table 2
Effect of hydrogen peroxide concentration on the chlorfenapyr degradation rate constant in the presence or absence of TiO_2

TiO_2 (mg L^{-1})	H_2O_2 (mg L^{-1})	K (min^{-1})	R^2	$t_{1/2}$ (min)
0	0	0.0035	0.9875	198
800	0	0.0427	0.9894	16.2
0	2000	0.0172	0.9834	40.3
800	2	0.0741	0.9926	9.4
800	20	0.0915	0.9858	7.6
800	200	0.0598	0.9861	11.6
800	2000	0.0482	0.9822	14.4

The initial concentrations of TiO_2 and chlorfenapyr were 800 and 50 mg L^{-1}, respectively; $T = 25\,°C$, pH 6.

by direct photolysis of H_2O_2 (1) and by reaction with $O_2^{\bullet-}$ (2). In addition, H_2O_2 can capture one electron of the conduction band and produce the hydroxyl radical, hindering the process of electron–hole recombination and increasing the rate of the photocatalytic process (3) [38]. In the presence of 200 and 2000 mg L^{-1} hydrogen peroxide, it may be suggested that the hydroperoxyl radical ($HO_2^{\bullet}$) produced by the reaction between H_2O_2 and the $OH^{\bullet}$ radical (4), as well as the neutral species generated between two radicals, $HO_2^{\bullet}$ and $^{\bullet}OH$ (5) [39] will contribute to the decrease in degradation rate. Similar behaviors were obtained for some contaminants such as organic phosphorus pesticides and 4-chlorobenzoic acid [40,41].

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \tag{1}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH^- + {}^{\bullet}OH + O_2 \tag{2}$$

$$H_2O_2 + e^- \rightarrow OH^- + {}^{\bullet}OH \tag{3}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \tag{4}$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \tag{5}$$

4. Conclusion

In this study, the direct photolysis and the photocatalytic degradations of chlorfenapyr in TiO_2 suspensions with and without the use of hydrogen peroxide were studied using two different monochromatic UV irradiations (300 and 350 nm). Both the direct photolysis and photocatalytic degradations of chlorfenapyr follow pseudo-first-order degradation kinetics ($C_t = C_0\, e^{-kt}$). Photolysis reactions were slow, and the corresponding photocatalysis rates were increased by about 2.5 and 3 times in the presence of TiO_2 at 300 and 350 nm of UV, respectively. Photocatalytic rates were increased with the pH at neutral to alkaline ranges because of the increase of hydroxide ions. However, the reaction was gradually retarded at the neutral medium. The half times of degradation ($t_{1/2}$) were 13.7, 16.2, 16.2, 10.7 and 8.7 min, respectively, at pH 4, 6, 7, 9 and 11. Thus, chlorfenapyr was less stable in acid and alkaline environments, and relatively more stable at neutral conditions. The effect of temperature is helpful to the photocatalytic degradation of chlorfenapyr. The photocatalytic degradation rates were found to increase with TiO_2 dosages, and the reaction was retarded at higher TiO_2 dosages. The fastest degradation occurred when 1200 mg L^{-1} TiO_2 was used, the rate increased slowly with increasing catalyst concentration up to 800 mg L^{-1} and more rapidly when the concentration was increased from 800 to 1200 mg L^{-1}, and decreased at 1600 mg L^{-1}. A much faster degradation rate at lower chlorfenapyr concentrations was achieved. The results of H_2O_2-assisted photocatalysis experiments showed that a low H_2O_2 dosage in photocatalysis would enhance the degradation rate of chlorfenapyr, however, an overdose of H_2O_2 will retard the rate because of the expenditure of hydroxyl radicals.

Acknowledgements

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