"Gheorghe Asachi" Technical University of Iasi, Romania

OPTIMIZATION OF ADVANCED OXIDATION PROCESSES FOR THE REMOVAL OF ACETAMIPRID FROM WASTEWATER

Puthenkattil Abdukunji Fasnabi[1]*, Gopal Madhu[2], Pooppana Antony Soloman[1]

[1]Government Engineering College, Thrissur, Kerala, India-680 009
[2]Cochin University of Science and Technology, Kochi, Kerala, India-682 022

Abstract

Advanced oxidation process is getting tremendous importance in the treatment techniques for the removal of nonbiodegradable organics from wastewater due to its ability to completely mineralize the pollutants. It uses different methods to produce hydroxyl radicals which are responsible for oxidation of pollutants. In this work, studies on Fenton, ultraviolet radiation (UV) and UV-hydrogen peroxide processes for removing acetamiprid, a neonicotinoid insecticide from aqueous solution are carried out. Acetamiprid is now finding wide use as a substitute for organophosphates. The effects of pH for UV, H_2O_2 concentration and Fe^{2+} concentration for Fenton process and pH and H_2O_2 concentration for UV-H_2O_2 process are studied for a simulated wastewater containing acetamiprid. The efficiency of the processes was evaluated by measuring acetamiprid concentration and total organic carbon concentration. The processes are optimized using central composite design of response surface methodology. A second order model has been suggested for the processes and the model is validated using statistical tools. The H_2O_2 and Fe^{2+} concentrations showed a positive effect on the removal of pesticide by Fenton process and the optimum conditions obtained are pH-3, H_2O_2- 190 mg/L and Fe^{2+} -19 mg/L. For UV-H_2O_2 process, the optimum pH is found to be 6 at a H_2O_2 concentration of 110 mg/l. Kinetic studies were conducted for Fenton, UV and UV-H_2O_2 processes at the optimized conditions, which show the applicability of first order kinetics.

Key words: acetamiprid, advanced oxidation process, optimization, response surface methodology, wastewater treatment

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1. Introduction

Pesticides have become the inevitable part of agriculture and modern life which results in pollution of ground as well as surface water. Neonicotinoids belong to the new classes of insecticides. Acetamiprid (E-N[1]-[(6-chloro-3-pyridyl) methyl]-N[2]-cyano-N[1]-methylacetamidine, Fig. 1) is a widely used neonicotinoid insecticide (Mateu-Sanchez et al., 2003). It is used for the control of insects which are of sucking type on cotton, leafy vegetables, fruits and ornamental plants and flowers. Being a systemic pesticide with special acting mechanism and high efficacy, acetamiprid has been widely used as an alternative to the organophosphate insecticides. It is

highly water soluble (solubility- 2.95 x 10^{+3} mg/L at $25°C$) which indicates the high potential to pollute both ground water and surface water. Acetamiprid is stable to hydrolysis at atmospheric temperatures, and photodegrades relatively slowly in water. It is classified as toxicity category rating II in acute oral studies with rats (U.S Environmental Protection Agency, 2002).
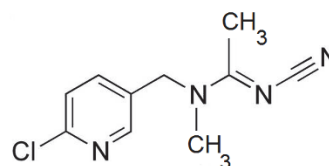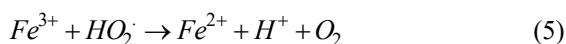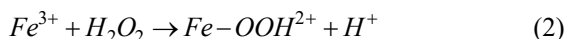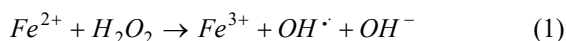

Fig. 1. Structure of acetamiprid

* Author to whom all correspondence should be addressed: e-mail: fasnasalah@gmail.com; Phone: +91 9495464599; Fax: +91 487 2336124

Advanced oxidation processes (AOPs) are used widely as a treatment technique for the removal of non biodegradable or slowly biodegradable compounds. They can be used for complete removal of compounds of high stability and/or low biodegradability. They can also be used as a pretreatment technique for biological treatment as it generally improves the biodegradability. It uses the oxidation potential of hydroxyl radicals for the mineralization of the pollutants. Different techniques are used for the generation of hydroxyl radicals (Andreozzi et al., 1999).

One of the oldest and simplest AOPs is Fenton's reaction. No sophisticated set up is needed for this process and it can be applied at room temperature. Its disadvantages include need of acidic environment and the formation of iron sludge. Fenton's reagent is catalyzed hydrogen peroxide; catalyst is a transition metal, normally ferrous iron. The major reactions taking place are the following (Chammaro et al., 2001; Jafari et al., 2017; Kang and Hwang, 2000; Neyens and Baeyens, 2003; Walling and Goosen, 1973).
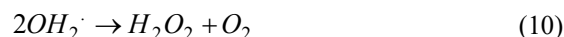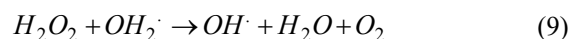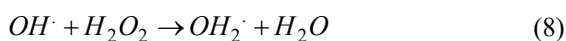
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe-OOH^{2+} + H^{+} \qquad (2)$$

$$Fe-OOH^{2+} \rightarrow Fe^{2+} + HO_2^{\cdot} \qquad (3)$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^{-} \qquad (4)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^{+} + O_2 \qquad (5)$$

Hydroxyl radicals can oxidize organics (RH) producing organic chemicals ($R^{\cdot}$) which are highly reactive and can be further oxidized (Chammaro et al., 2001; Grcic et al., 2017; Neyens and Baeyens, 2003; Walling, 1975).

$$RH + HO^{\cdot} \rightarrow H_2O + R^{\cdot} \qquad (6)$$

UV radiation has been the most widely used radiation method in initiating oxidation processes. This is based on supplying energy to the chemical compounds as radiation, which is absorbed by reaction molecules that can pass to excited states promoting further reaction (Esplugas et al., 2002).

UV-H_2O_2 process is very efficient in treating aqueous effluents. This process entails the formation of hydroxyl radicals by the photolysis of H_2O_2. The oxidation may be either due to direct photolysis or reaction with hydroxyl radicals (Poyatos et al., 2010).

$$H_2O_2 + h\nu \rightarrow 2OH^{\cdot} \qquad (7)$$

$$OH^{\cdot} + H_2O_2 \rightarrow OH_2^{\cdot} + H_2O \qquad (8)$$

$$H_2O_2 + OH_2^{\cdot} \rightarrow OH^{\cdot} + H_2O + O_2 \qquad (9)$$

$$2OH_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (10)$$

Despite the extensive use of acetamiprid, the use of AOP for the degradation of acetamiprid has been less frequently studied except some reports on photolysis (Xie et al., 2009) and photocatalysis (Guzsvany et al., 2009; Khan et al., 2010). The oxidation of acetamiprid by Fenton and Fenton like oxidation of acetamipirid is reported recently (Mistika et al., 2013). In this study, the use of AOPs: Fenton process, UV radiation and UV-H_2O_2 process for the acetamiprid removal from wastewater are investigated and compared. Optimization of the process parameters is done using response surface methodology. A comparison on the basis of operating cost is also attempted.

2. Experimental

2.1. Materials used

Acetamiprid (97%) was purchased from Rallis India. As a source of Fe^{2+}, Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) was used. Acetonitrile and water (HPLC grade), sulfuric acid, sodium hydroxide and hydrogen peroxide solution (30% w/w) used were from Merck. Distilled water was used throughout.

2.2. Set-up

1000 mL flat bottom borosilicate glass vessel was used for conducting experiments. The schematic diagram is shown in Fig. 2. Inside a glass reactor, an immersion well made of high purity quartz was placed and is fitted with a standard joint at the top. As a source of UV radiation, a 125 W medium pressure mercury vapor lamp was kept inside the immersion well. Thorough mixing of the content of the reactor was achieved by agitating the contents throughout the reaction using a magnetic stirrer. Cooling water was circulated through the annular space to maintain the temperature of the reaction at room temperature. The entire set up was housed in wooden chamber.

2.3. Procedures

50 ppm solution of acetamiprid was prepared in distilled water. 500 ml of the solution is taken in the reactor. 0.1 N sulfuric acid was used for adjusting the pH to desired level. Required amount of $FeSO_4.7H_2O$ (for Fenton process) was added after that and mixed well. Then required amount of hydrogen peroxide was added. As it is well known that favorable pH for Fenton reaction is 3, the experiments for Fenton process were conducted at pH 3 (Chitra et al., 2012). Reaction start for the Fenton reaction was the time when hydrogen peroxide added. Stable output was achieved by UV lamp after 2-3 minutes.

The content of the reactor was mixed using a magnetic stirrer throughout the reaction. The reaction time for the processes was selected so as to get at least 90% removal of acetamiprid. All the experiments were repeated three times and the average result is used for comparing the performance.
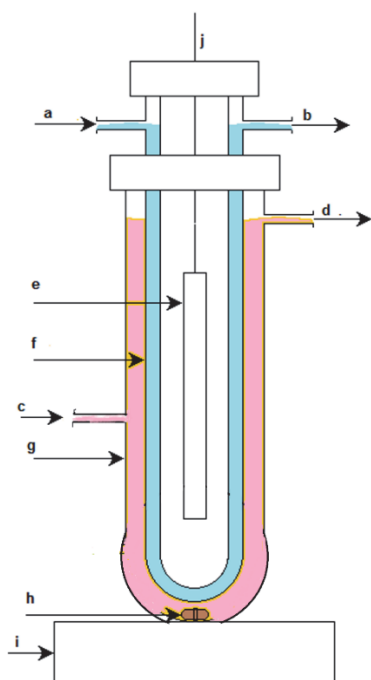

Fig. 2. Schematic diagram of reactor (a- cooling water inlet, b- cooling water outlet, c- sample inlet, d-sample outlet, e- UV lamp, f- Quartz immersion well, g-borosilicate glass vessel, h- magnetic stirrer bar, i- magnetic stirrer, j- power supply)

2.4. Analytical methods

Acetamiprid concentration and Total Organic Carbon (TOC) of the samples were analysed at required intervals. The pH of solution after Fenton reaction was increased to 10 to stop the reaction. One drop of 0.1 N $Na_2S_2O_3$ was added to decompose residual hydrogen peroxide in each sample (Badawy et al., 2006). The samples withdrawn were filtered through a 0.22μm syringe filters.

Modified iodometric method was used for detecting hydrogen peroxide concentration (APHA, 1998). High performance liquid Chromatograph (HPLC) was used for measuring acetamiprid concentration. Hitachi Elite Lachrom HPLC with C18 column (Shodex, 4.6 x150 mm) and UV detector was used for this purpose. Mixture of water and acetonitrile (70/30) was used as mobile phase. The samples of 20 μL were injected manually and it was eluted at a flow rate of 1 mL/min. The signal of acetamiprid was detected at 245nm and 4.4 min. Total organic carbon measurements (TOC) was carried out using a Schimadzu TOC-LCPH TOC analyzer.

2.5. Response Surface Methodology

One variable at a time was varied in conventional method of doing experiments. It is time consuming and labor intensive. The study of combined effects of two or more variables on the response is not possible by this method (Jiang et al., 2013). Response surface methodology (RSM) is a collection of mathematical and statistical tools useful for developing, optimizing and improving the processes (Baş and Boyacı, 2007; Bertea et al., 2013). It involves mainly three steps. First step is the design of the experiments statistically using the selected design and conducting the experiments, second is the determination of coefficients in the proposed model and the last step is the validation of the model (Montgomery, 2001). The central composite design (CCD) is the most popular second order class of RSM. This design is well suited for fitting quadratic surfaces and usually works well for process optimization .CCD helps to develop a model and optimize the effective parameters with a minimum number of experimental runs. In general, for k factors, CCD requires 2^k factorial runs with $2k$ axial or star runs and n_c center runs (Montgomery, 2001).

The effect of parameters on acetamiprid removal was determined using RSM. Central composite design with two factors at five levels was applied using Minitab 14 (PA, USA). Table 1 gives the operating parameters and the operating range covered for Fenton and UV-H_2O_2 processes in part *a* and *b* respectively. Range for experiments was fixed based on the results obtained from preliminary experiments.

The independent variables are converted into corresponding coded variables x_1, x_2, x_3 and x_4 between $-\alpha$ and $+\alpha$ in five levels as $-\alpha$, -1, 0. +1, and $+\alpha$ using the equation given below (Ahmed Basha et al., 2009).

Table 1. The level and range of variables chosen for the processes

Independent Variable	Symbols used	Coded levels				
		-α(1.2)	-1	0	+1	+ α(1.2)
		a)		Fenton process		
H_2O_2 (mg/L)	X_1	2	20	110	200	218
Fe^{2+} (mg/L)	X_2	0.2	2	11	20	21.8
		b)		UV-H_2O_2 process		
pH	X_3	2.4	3	6	9	9.6
H_2O_2 (mg/L)	X_4	2	20	110	200	218

$$x_i = \frac{2\alpha X_i - \alpha(X_{i,max} + X_{i,min})}{(X_{i,max} - X_{i,min})} \qquad (11)$$

where $X_{i,max}$ and $X_{i,min}$ are the maximum and minimum values of the variable X_i.

Experiments were conducted for thirteen runs (α=1.2) as given in Table 2.

Pure error is evaluated using the experimental responses at centre points. The Analysis of Variance (ANOVA) has been studied using RSM. The quality of the model suggested was tested using statistical parameters such as correlation coefficient (*R*), root mean square error (*RMSE*) and average absolute relative error (*AARE*) defined as follows.

$$R = \sum_{i=1}^{N} \frac{(E_i - \overline{E})(P_i - \overline{P})}{\sqrt{\sum_{i=1}^{N}(E_i - \overline{E})^2 \sum_{i=1}^{N}(P_i - \overline{P})^2}} \qquad (12)$$

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}(P_i - E_i)^2\right]^{1/2} \qquad (13)$$

$$AARE(\%) = \frac{1}{N}\sum_{i=1}^{N}\frac{(|E_i - P_i|)}{E_i} \times 100 \qquad (14)$$

where E is the experimental response, P is the predicted response obtained from the model. $\overline{E}$ and $\overline{P}$ represents the mean values of E and P, respectively. N refers to the number of experimental runs.

3. Results and discussion

3.1. Fenton process

The results of the experiments conducted for one hour are given in Table 2 part a. It is evident from the results that both factors influenced the removal of pesticide positively. An increase in removal of acetamiprid (%) from 17.5 to 62.5 is observed when H_2O_2 concentration was increased from 20 to 200 mg/L at Fe^{2+} concentration of 2 mg/L. (run no:1 and 2). Removal of acetamiprid increased with an increase in Fe^{2+} concentration also (run no: 2 and 4). This is due to the increase in hydroxyl radical formation with increasing H_2O_2 and Fe^{2+}concentration.

Acetamiprid removal of 99.5% was obtained when H_2O_2 concentration of 200 mg/L and Fe^{2+} concentration of 20 mg/L (run no: 4) was used. Use of optimum H_2O_2 and Fe^{2+} is important since excess use of H_2O_2 and Fe^{2+} results in scavenging of hydroxyl radicals as given in Eqs. (15) and (16) (Neyens and Baeyens, 2003). Excess use of H_2O_2 also results in auto decomposition (Eq. 17).

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \qquad (15)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^{-} \qquad (16)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (17)$$

Fig. 3a shows the combined effect of H_2O_2 concentration and a Fe^{2+} concentration on acetamiprid removal. Both factors show an increasing trend with increasing concentration because of the increase in hydroxyl radical formation (Badawy et al., 2006).

3.2. UV treatment

It was observed that acetamiprid is stable when protected from radiation and degrades slowly when exposed to light. Effect of pH on photodegradation was studied by varying the pH (not shown) .The rates of degradation was very close to each other when pH was increased from 4 to 9 and it is in agreement with the results reported in the literature (Xie et al., 2009). The maximum removal was obtained at pH of 4-5.

3.3. UV-H_2O_2 process

The results of the experiment are given in Table 2 part b. The increase in pesticide removal obtained is only from 80% to 84% at an initial H_2O_2 concentration of 20 mg/L when pH was increased from 3 to 9 (run no: 1 and 2). The percent increase is only from 95 to 96 when an initial H_2O_2 concentration of 200 mg/L was used (run no: 3 and 4). This increase in removal with pH can be due to the hydrolysis of acetamiprid at higher pH and it is not liable to hydrolyse at lower pH (Mistika et al., 2013). Acetamiprid removal of 99.9 % was obtained at a pH value of 6 and H_2O_2 concentration of 110 mg/L (run no: 9). Since the hydrolysis is insignificant at this pH, it can be concluded that degradation at this condition is due to the reaction with hydroxyl radicals. The use of higher pH is not recommended, since at higher pH, H_2O_2 photo-decomposes into oxygen and water (Ramesh et al., 2007). Increasing H_2O_2 concentration beyond optimum results in scavenging of hydroxyl radicals (Eq. 15) and it is evident in the Fig. 3b (Hernandez et al., 2002). The figure shows the combined effect of pH and H_2O_2 concentration on acetamiprid removal.

TOC removal in all the runs is comparatively lower. The presence of stable intermediates formed by degradation of pesticide may be the reason. The possible degradation intermediates of acetamiprid are 6-Chloro nicotinic acid, acetic acid, formic acid and acetaldehyde (Guzsvany et al., 2009).

3.4. Response Surface Methodology

This study reveals a mathematical relationship between the acetamiprid removal and the significant factors for the process which is of the form of Eq. (18). The coefficients of the model are given in Table 3.

Table 2. The design of experiment and experimental responses for Fenton and UV-H$_2$O$_2$ process

Run No.	H$_2$O$_2$ (mg/L)	Fe^{2+} (mg/L)	Acetamiprid removal (%)	TOC removal (%)
a)	*Fenton process, reaction time : 60 minutes*			
1	20	2	17.5	2.5
2	200	2	62.5	11.1
3	20	20	31.0	5.0
4	200	20	99.5	26.0
5	2	11	17.5	2.0
6	218	11	85.0	19.5
7	110	0.2	50.0	10.2
8	110	21.8	80.0	20.8
9	110	11	75.3	20.0
10	110	11	75.4	20.5
11	110	11	75.3	20.3
12	110	11	75.5	20.2
13	110	11	75.45	20.4

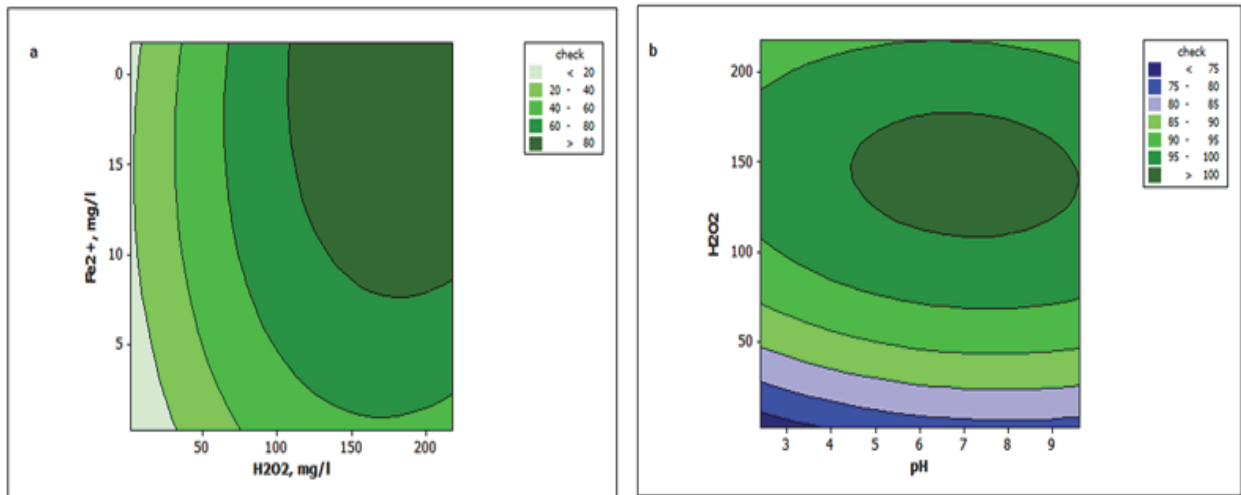| Run No.	pH	H$_2$O$_2$ (mg/L)	Acetamiprid removal (%)	TOC removal (%)
b) *UV-H$_2$O$_2$ process reaction time : 30 minutes*				
1	3.0	20	80.00	9.5
2	9.0	20	84.00	10.0
3	3.0	200	95.00	28.0
4	9.0	200	96.00	28.7
5	2.4	110	94.90	28.0
6	9.6	110	99.00	28.8
7	6.0	2	77.50	6.0
8	6.0	218	95.00	27.4
9	6.0	110	99.90	30.1
10	6.0	110	99.90	30.2
11	6.0	110	99.80	30.4
12	6.0	110	99.70	30.5
13	6.0	110	99.90	30.5

Fig. 3. a) Combined effect of H$_2$O$_2$ and Fe^{2+} concentration on acetamiprid removal for Fenton process; b) Combined effect of pH and H$_2$O$_2$ concentration on acetamiprid removal for UV-H$_2$O$_2$ process

The significance of the coefficients was analyzed by p- and t- test. The values *p* and *t* and the significance level (*1-p*) are given in the Table 3. From Table 3 it is clear that all the terms are significant in predicting the acetamiprid removal (%) for Fenton and UV- H$_2$O$_2$ process. The equation can be written as Eq. (19). For H$_2$O$_2$/UV process equation can be written as Eq. (20). The predicted optimum values by RSM for the Fenton process are 190 mg/L for initial H$_2$O$_2$

concentration and 19 mg/L for Fe^{2+} concentration. The predicted acetamiprid removal (%) is 97.65 while the experimental value obtained was 99.98. The TOC removal (%) was 26 at these conditions.

pH value of 6 and initial H$_2$O$_2$ concentration of 110 mg/L are the predicted optimum values for the UV- H$_2$O$_2$ process based on the criteria of achieving maximum removal by minimizing the cost of chemicals involved.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 \tag{18}$$

where y is the response variable of acetamiprid removal (%) in uncoded units, β_1, β_2 are regression coefficient for linear effects, β_{11}, β_{22} are quadratic coefficients, β_{12} is interaction coefficient.

$$Y_1 = -0.7662 + 0.6640X_1 + 2..63387X_2 - 0.00193X_1^2 - 0.08588X_2^2 + 0.00632X_1X_2 \tag{19}$$

where Y_1 is the acetamiprid removal (%) after Fenton process in uncoded units, X_1 and X_2 are the H_2O_2 concentration and Fe^{2+} concentration in mg/L respectively.

$$Y_2 = 64.5895 + 3.3641X_3 + 0.3497X_4 - 0.2099X_3^2 - 0.0012X_4^2 - 0.0030.X_3X_4 \tag{20}$$

where Y_2 is the acetamiprid removal (%) after UV- H_2O_2 process in uncoded units, X_3 and X_4 are initial pH and initial H_2O_2 concentration in mg/L, respectively.

Table 3. Estimated regression coefficients and corresponding *'t'* and *'p'* values for acetamiprid removal

Factor	Coefficient of the model in uncoded factors	't' value	'p' value	significance level (%)
a) Fenton Process				
β_0	-0.76662	-0.403	0.699	>30%
β_1	0.6640	27.813	0.000	>99%
β_2	2.63387	11.026	0.000	>99%
β_{11}	-0.00193	-20.952	0.000	>99%
β_{22}	-0.08588	-9.321	0.000	>99%
β_{12}	0.00632	6.487	0.000	>99%
b) UV-H_2O_2 process				
β_0	64.5895	110.952	0.000	>99%
β_1	3.3641	19.446	0.000	>99%
β_2	0.3497	77.903	0.000	>99%
β_{11}	-0.2099	-15.581	0.000	>99%
β_{22}	-0.0012	-76.865	0.000	>99%
β_{12}	-0.0030	-6.236	0.006	>99%

The pH value of 6 being the near free pH reduces the chemicals needed for pH adjustment. The acetamiprid removal (%) obtained from the experiment was 99.9 while the predicted removal is 99.8. The TOC removal obtained experimentally at these conditions was 31 %. The analysis of variance (ANOVA) for the models shows a higher F value for regression of 640.61 for Fenton and 2386.69 for UV-H_2O_2 compared to a tabulated value of 3.97. This shows that the quadratic model can navigate the design space well.

The model predictions and the experimental observation are compared and found that the variations are minimal. The R^2, *RMSE* and *AARE* (%) for the models are 0.99, 0.4015 and 0.72 for Fenton process and 0.99, 0.1883 and 0.17 for UV- H_2O_2 process. Hence the model accuracy is adequate to predict the system performance.

3.5. Kinetic study

The kinetic studies were conducted at the optimum values for the three processes. The degradation of acetamiprid using AOP can be expressed by a pseudo first order kinetic equation of the form (Eq. 21):

$$ln\frac{[C]}{[C]_0} = -kt \tag{21}$$

where *[C]* and *[C]₀* are the concentration of acetamiprid at *0* and *t* times and *k* is expected pseudo-first order rate constant

The change in concentration of acetamiprid with time for Fenton, UV and UV-H_2O_2 processes was monitored using HPLC. Fig. 4 shows the time dependent chromatograms for the UV treatment for duration of 60 minutes. The chromatograms are drawn at an interval of 10 min. The percentage degradation data of acetamiprid using the three processes are given in Fig. 5a. For a removal of 99.9 %, the time taken for Fenton process, UV treatment, UV-H_2O_2 process were 30, 120, 25 minutes respectively. he data obtained from the experiments for 30 minutes was used for plotting a pseudo first order plot and is shown in Fig. 5b. The rate constants and the R^2 value of plot are given in Table 4. The rate of removal is lowest for treatment with UV (rate constant of 0.0337 min^{-1}) followed by Fenton (0.1041 min^{-1}) and UV-H_2O_2 (0.1801 min^{-}1) process i.e. UV- H_2O_2 > Fenton > UV. This is similar to the results reported by Badawy et al. (2006) and Saritha et al. (2007).
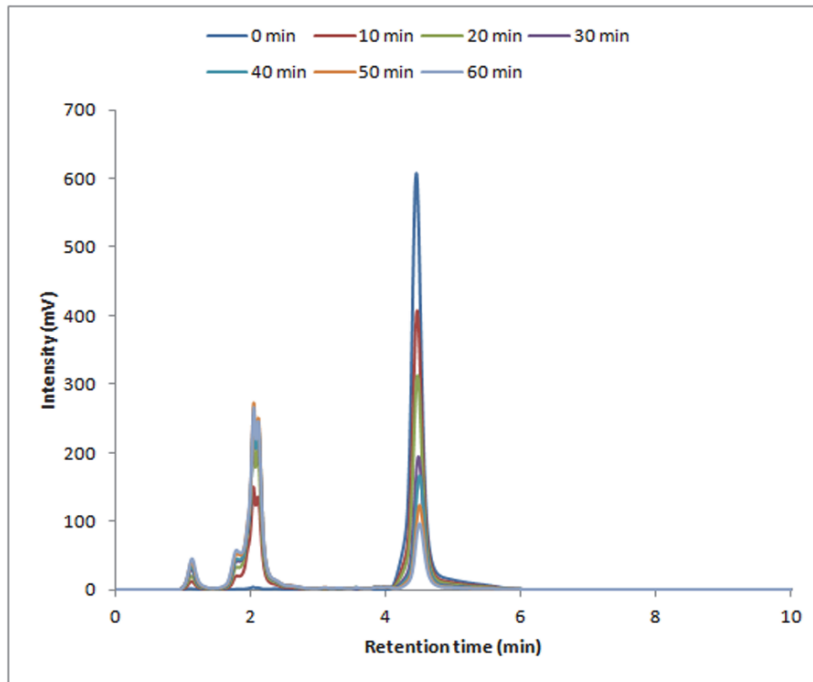
Fig. 4. Time dependent chromatograms of the UV treatment of acetamiprid between 0 and 60 minutes
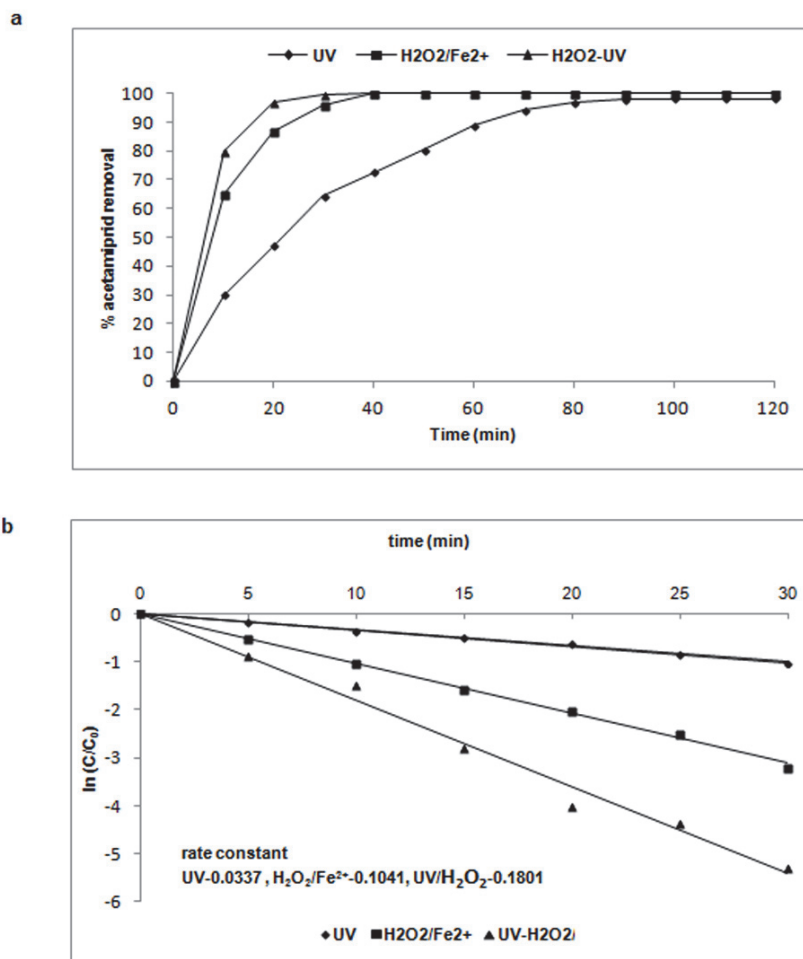

Fig. 5. a) Time percentage acetamiprid removal data for UV, Fenton and UV-H_2O_2 processes
b) Pseudo-first order plot for the removal of acetamiprid by UV, Fenton and UV-H_2O_2 processes

Table 4. Pseudo first order rate constants

Process	Rate constant (min $^{-1}$)	R^2 value
Fenton	0.1041	0.998
UV	0.0337	0.997
UV- H_2O_2	0.1801	0.987

In UV process the main mechanism of degradation is the photolysis of the compound which is governed by the absorption spectrum of compound and emission spectrum of UV lamp. In Fenton the main mechanism is the oxidation with hydroxyl radicals whose rate constant is higher. In UV- H_2O_2 process, the rate is increased because of the indirect photo-oxidation between the compound and the additional hydroxyl radicals formed in addition to the photolysis reaction (Chitra et al., 2012; Mamadou et al., 2011).

3.6. Cost estimation

The cost of full scale wastewater treatment plant depends on the nature and concentration of pollutant, the geometry of the reactor utilized, the lamp characteristics (if UV lamp is employed) and the flow rate of the wastewater (Esplugas et al., 2002). An attempt is made to calculate the approximate operating cost for the process based on the cost of materials used (Table 5 and 6). Calculation of cost for the processes utilizing UV is based on electrical energy per order (EE/O) (Saritha et al., 2007) using Eq. (22).

$$EE/O(kWh/m^3) = \frac{Ptx1000}{Vx60x\log(C_{init}/C_{fin})} \quad (22)$$

where P is rated power (kW), t is the time (min), V is the volume (liters), C_{init} and C_{fin} are initial and final concentration of the compound to be treated.

Table 5. Cost of the reagents

Reagent	Basis	Cost ($)
H_2O_2	Kg	0.76
$FeSO_4.7H_2O$	Kg	14
Electricity	kWh	0.0953

Table 6. Operating cost of the treatment methods

Process	Cost ($/m^3$)
Fenton	2
UV	376.8
UV- H_2O_2	75.38

It is evident from the cost data that the treatment with UV is costlier because of the high treatment time involved. Use of H_2O_2 along with UV reduces the cost since it produces more hydroxyl radicals reducing the reaction time requirement. Among the treatment methods studied, Fenton is the cheapest method but of course with a disadvantage of sludge formation. This can be minimized by using

Photo Fenton process ($H_2O_2/Fe^{2+}/UV$) and the cost can be further reduced if sunlight is made use of.

4. Conclusions

The results from this study revealed the viability of using Fenton, UV and UV- H_2O_2 processes for the acetamiprid removal from wastewater. The processes were optimized using RSM. Optimized conditions for Fenton process was found to be initial H_2O_2 concentration of 190 mg/L and Fe^{2+} concentration of 19 mg/L at a pH of 3. At this condition the rate constant for the process was found to be 0.1041 min^{-1} and a 99% removal of acetamiprid and a TOC removal of 26 % were obtained within 30 minutes. For UV treatment using 125 W medium mercury vapor lamp, the rate constant calculated was 0.0337 min^{-1} which had taken about 120 minutes for removal of acetamiprid. The addition of H_2O_2 to UV process showed a drastic improvement in the rate of UV process due to the generation of more hydroxyl radicals. The rate constant was increased to 0.1801 min^{-1}.

The process could remove 99.9% of the acetamiprid within 25 minutes at a pH of 6 and H_2O_2 concentration of 110 mg/L. The TOC removal at this condition was 32%. The low TOC removal in all the processes shows that intermediates formed are stable and the amount of reagents and/or the reaction time used were not sufficient to degrade the stable intermediates.

A model was predicted for the Fenton and UV- H_2O_2 process for acetamiprid removal. Statistical analysis was done to prove the adequacy of the model. A cost evaluation showed that Fenton is the cheapest of the three method studied

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