3.1 Introduction

Advanced oxidation process (AOP) is a class of oxidation techniques where oxidation by hydroxyl radicals is employed and there are a large number of methods for producing hydroxyl radicals. The AOPs selected should be capable of removing the pollutant to below the permissible limit and at low cost.

3.2 Selection of Model Compound for Study

Pollution of surface and ground water sources with pesticides has become the most discussed environmental issue at present.

Neonicotinoid insecticides are relatively a new class of insecticides. Because of the stringent environmental legislations and adverse effect of...
human and aquatic health, organophosphorous pesticides are now being replaced by neonicotinoids. Neonicotinoids are selective and attack nervous systems of target species. Because of this, their use is increasing widely and is increasingly found in the environment. Acetamiprid, the selected compound belongs to this class, has high solubility in water and potential to pollute surface and ground water. Important physical and chemical properties of acetamiprid are already discussed in chapter 2.

3.3 Processes and Operating Parameters Selected for Study

In this work following five methods were selected for the removal of acetamiprid from wastewater based on the literature survey and preliminary degradation studies conducted.

3.3.1 Fenton Process (Fe$^{2+}$/H$_2$O$_2$)

Fenton process is the simplest of all AOPs where H$_2$O$_2$ (reactant) and Fe$^{2+}$ (catalyst) are used. This process does not require any sophisticated set up and can be performed at room temperature. The main factors affecting the processes are found to be pH, H$_2$O$_2$ dosage and Fe$^{2+}$ dosage. The optimum pH for the Fenton process was reported as 2.8-3 in all literature studied and it was confirmed by conducting preliminary experiments. Hence a pH of 3 is used in this study. The experiments were conducted by varying H$_2$O$_2$ and Fe$^{2+}$ dosages at a pH of 3.

3.3.2 UV Treatment

Most of the organic pollutants in water undergo degradation by photolysis under natural sunlight. This can be enhanced by employing a
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powerful light source. This has the advantage of absence of chemical agents. The experiments were conducted using 125 W medium pressure mercury vapour lamp at different pH to study the effect of pH on degradation rate.

3.3.3 UV/ H₂O₂ Process

The photolysis of organic compounds under UV light is generally slow. The degradation can be enhanced by oxidation with hydroxyl radicals by the addition of hydrogen peroxide. This fact is made use in the UV/ H₂O₂ process. Effects of pH and initial H₂O₂ concentration on the removal of acetamiprid and TOC were studied by conducting experiments at different values of pH and H₂O₂ concentration in the presence of UV source.

3.3.4 Photo-Fenton Process (Fe²⁺/ H₂O₂/UV)

Fenton process has the disadvantage of sludge formation due to iron hydroxide. Use of UV light along with Fenton (photo-Fenton) reduces the formation of this sludge by converting the Fe³⁺ formed back to Fe²⁺, which will react again to form more hydroxyl radicals. This reduces the amount of reagents (H₂O₂ and Fe²⁺) required and sludge formed. In this work experiments were conducted at pH 3 for different H₂O₂ and Fe²⁺ dosages using a medium pressure mercury lamp of 125 W.

3.3.5 Photocatalysis Using Undoped and Cu, Fe Doped TiO₂

Photocatalysis using semiconductor materials such as TiO₂, ZnO₂, SnO₂ had been used for the removal of recalcitrant compounds from water/wastewater. TiO₂ being inexpensive, stable and inert material finds major application in the water and wastewater treatment. TiO₂ has a band
gap of 3.3 eV and hence it shows relatively high activity in the presence of ultraviolet light. Doping of TiO$_2$ with metals and non-metals are employed widely to enhance the photocatalytic activity of TiO$_2$. Here doping of TiO$_2$ with Cu and Fe has been attempted and used for the removal of acetamiprid from wastewater. TiO$_2$ has a neutral and stable state at a pH 6 (Cao et al., 2008). Hence degradation studies were conducted at pH 6 for different catalyst loading and dopant concentration.

3.4 Materials Used

Acetamiprid (Technical grade, 97%) was received from Rallis India and it was used as such without further purification. Ferrous sulphate heptahydrate (FeSO$_4$.7H$_2$O) was used in Fenton and photo-Fenton reactions as a source of Fe$^{2+}$. Acetonitrile (HPLC grade) received from Fisher Scientific. Ultrapure water was produced in situ using Millipore Direct-Q 3 UV system device. Sulphuric acid, sodium hydroxide used for pH adjustment and hydrogen peroxide solution (30% w/w) used were of analytical grade received from Merck. Acetamiprid of required concentrations were prepared by serial dilution of stock solution using double distilled water.

For preparation of titanium dioxide, titanium isobutoxide (Ti(OBu)$_4$) was purchased from Sigma Aldrich. CuCl$_2$ and FeCl$_3$ were used as the source of Cu an Fe for doping. Analytical grade isopropyl alcohol, Nitric acid, CuCl$_2$ and FeCl$_3$ were from Merck.

3.5 Experimental Set Up

The experiments were conducted in a 1000 ml flat bottom borosilicate glass vessel. The schematic diagram is shown in Fig. 3.1. An immersion
well made of high purity quartz was placed inside the glass reactor fitted with a standard joint at the top. A medium pressure mercury vapour lamp of 125 W was kept inside the immersion well as a source of UV radiation. The content of the reactor was kept agitated throughout the reaction using a magnetic stirrer. The temperature of the reaction mixture was maintained at room temperature (28±2°C) by circulating cooling water through the annular space of the immersion well. The entire set up was housed in wooden chamber to protect the operating personnel from UV radiation. The experimental set up is shown in Fig. 3.2.

![Fig. 3.1 Schematic diagram of reactor](image_url)
3.6 Preparation of Photocatalysts

TiO$_2$ was prepared by the controlled hydrolysis of titanium isobutoxide. The procedure was as follows. 20 ml of titanium isobutoxide was slowly added to 80 ml isopropyl alcohol with continuous stirring. 0.3 ml concentrated HNO$_3$ was added to the mixture followed by dropwise addition of 2 ml of water. The resulting mixture was sonicated for 5 minutes and then agitated vigorously for 30 minutes. The sol formed was kept for ageing at room temperature for 24 hours. The gel formed was dried at 80-100$^\circ$C for 2 hours to evaporate the solvent. The dried precipitate was
calcined at required temperature for 2 hours and ground to get fine TiO₂ powder. CuCl₂ and FeCl₃ solutions of required concentrations were used instead of water for preparing Cu doped and Fe doped TiO₂ respectively. The gel obtained after hydrolysis is shown in Fig. 3.3 and the fine powder obtained after calcination is shown in Fig 3.4.

Fig. 3.3  The gel obtained after hydrolysis a) undoped TiO₂ b) Cu doped TiO₂ c) Fe doped TiO₂

Fig. 3.4  TiO₂ obtained after calcination a) undoped TiO₂ b) Cu doped TiO₂ c) Fe doped TiO₂
3.7 Experimental Procedure

Synthetic solution of acetamiprid of 50 mg/L was prepared using distilled water to simulate the heavily loaded industrial wastewater. The reactor was filled with 500 ml of the solution. The desired pH was adjusted using 0.1 N sulphuric acid. Then the required amount of FeSO$_4$.7H$_2$O (for Fenton process and photo-Fenton process) was added and mixed well followed by addition of the required amount of hydrogen peroxide. In the case of photocatalysis required amount of catalyst was added after pH adjustment. Then the UV lamp was switched on. A preheating time of 1-2 minutes was given for UV lamp to achieve the stable output. Reaction start for the Fenton reaction was the time when hydrogen peroxide added while for the processes involving UV the time when the lamp achieved stable output was taken as time zero. The mixture was kept stirred throughout the experiment. The reaction time for the processes was selected so as to get at least 95% removal of acetamiprid. All the experiments were conducted in triplicate and the average result is used for representation.

3.8 Analytical Procedure

Samples were collected at required intervals and analysed for acetamiprid concentration and Total Organic Carbon (TOC). The pH of solution after Fenton and photo-Fenton processes was increased immediately to 10 to stop the reaction. Residual hydrogen peroxide in each sample was decomposed by adding one drop of 0.1 N Na$_2$S$_2$O$_3$ (Badawy et al., 2006). The samples collected in the photocatalysis experiments were filtered through 0.45 µm filters using a vacuum filtration assembly.
3.8.1 Pesticide Analysis

Pesticide analysis for preliminary studies was carried out using UV-VIS spectrophotometer (Hitachi U 900) with a band pass of 1.5 nm. The absorbance measurement was done at 245 nm. High Performance Liquid Chromatograph (HPLC) was used for determining the pesticide concentration in the detailed study. Hitachi Elite Lachrome HPLC with UV detector was used for the analysis and is shown in Fig 3.5.

![HPLC system used for pesticide analysis](image)

The samples collected were filtered through 0.22 µm filter paper and injected manually using Rheodyne injector. A mixture of acetonitrile and water (30:70) was used as the mobile phase. The samples were eluted through the C18 column (Shodex, 5 µm, 4.6 x150 mm) at a flow rate of 1 mL/min. The signals of acetamiprid were detected at 4.4 min at a wavelength of 245 nm. The concentration was calculated from the area of the peak at 4.4 min. Linear
relationship between area of the peak and concentration of the pesticide were confirmed by preparing a calibration curve (Annexure 1).

3.8.2 Total Organic Carbon Analysis

Total organic carbon (TOC) measurements were carried out using a Schimadzu TOC-L analyser. It is based on catalytic combustion of the organic material to CO$_2$ in an oxygen rich environment at $680^\circ$C with a platinum catalyst. The carbon dioxide generated is cooled and dehumidified, and then detected by the NDIR detector. The system used for the measurement is shown in Fig.3.6.

![Fig. 3.6 TOC system used for TOC analysis](image-url)
3.8.3 Characterisation of Undoped and doped TiO₂

X-ray diffraction patterns were recorded for the prepared photocatalysts to identify and determine the crystalline phase using X-ray diffractometer (Bruker, AXS D8 Advance). The patterns were recorded over a 2θ range 20 - 70°. The crystalline sizes could be calculated by Scherrer’s equation

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

(3.1)

Where D is the crystalline size, \( \lambda \) is the wavelength of the X-ray diffraction (1.5406 Å), \( K \) is the usually taken as 0.9 and \( \beta \) is the line width at half maximum height (Zhang et al., 2004). The micro structure examination was done using scanning electron microscope (SEM) (JEOL JSM- 6390LV).

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the obtained precipitate was carried out to understand the changes happened during heating and to study the thermal stability of catalysts. PerkinElmer system (STA 6000) was used for this purpose and is shown in Fig. 3.7. The samples were heated from 30-800 °C at rate of 6°C/ min. The change in weight of the sample and the amount of heat added/rejected was recorded.
3.9 Design of Experiments

The conventional method of conducting experiments is to vary one variable at a time and noting the response. It is time consuming and labour intensive. Moreover, it does not enable the study of combined effects or interaction of two or more variables on the response (Jiang et al., 2013; Montgomery, 2001). An interaction is the failure of one factor to produce the same effect on the response at different levels of another factor. The correct approach is to conduct factorial experiment if response is affected by several variables.

3.9.1 Response Surface Methodology

Response surface methodology (RSM) is a collection of mathematical and statistical tools useful for developing, optimising and improving the processes (Deniz et al., 2007).
RSM is extensively used when some performance measure or quality characteristic of a system (response) is influenced by several input variables (independent variables). The field of RSM consists of the experimental strategy for exploring the space of the process or independent variables, empirical statistical modeling to develop an appropriate approximating relationship between the response and the independent variables and optimisation methods for finding the values of the process variables that produce desirable values of the response. 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.

The general relationship between response and the independent variables can be written as

\[ y = f(x_1, x_2, \ldots, x_k) + \varepsilon \]  

where \( x_1, x_2, \ldots, x_k \) are independent variables affecting the system, \( y \) is the response and \( \varepsilon \) the error or noise in the system.

The surface represented by \( f(x_1, x_2, \ldots, x_k) \) is known as response surface.

Since the true functional relationship between the response and the independent variables is unknown an approximate relationship has to be found out from experimental data. Generally a first order or second order function is used. The first order model is used when the range of variable used is small and the probability of curvature in \( f \) is negligible. In the case of two independent variables, the first order function in coded variables can be written as
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\[ y = A_0 + A_1 x_1 + A_2 x_2 + \varepsilon \] ........................................(3.3)

The equation 3.3 is known as main effects model, since it considers only main effects of the variable \(x_1, x_2\) and interaction of the variable is not considered.

The equation can be modified by incorporating interaction between variables as

\[ y = A_0 + A_1 x_1 + A_2 x_2 + A_{12} x_1 x_2 + \varepsilon \] .......................... (3.4)

The interaction term introduces curvature in the response. When the curvature in the true response is strong, the first order model even with interaction is inadequate to represent in the system. A second order model may be required in such situations.

It can be written as

\[ y = A_0 + A_1 x_1 + A_2 x_2 + A_{11} x_1^2 + A_{22} x_2^2 + A_{12} x_1 x_2 + \varepsilon \] ...... (3.5)

The second order model is widely used in response surface methodology because of the following reasons (Carley et al., 2004)

1) The second-order model is very flexible. It can take on a wide variety of functional forms, so it will often work well as an approximation to the true response surface.

2) It is easy to estimate the parameters (the \(A\)’s) in the second-order model. The method of least squares can be used for this purpose.
3) There is considerable practical experience indicating that second-order models work well in solving real response surface problems.

In general the second order model for a response can be written as

\[ y = A_0 + \sum_{i=1}^{k} A_i x_i + \sum_{i=1}^{k} A_{ii} x_i^2 + \sum_{i=1}^{k} A_{ij} x_i x_j + \varepsilon \] ................................. (3.6)

To find out unknown \( A \)'s, the data systems has to be collected, generally by experiments. The data received are used to obtain an approximate model for the true response surface. It is usually done by multiple regression analysis.

### 3.9.2 Central Composite Design (CCD)

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 optimisation. CCD helps to develop a model and optimise 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).

A Box-Wilson central composite design, commonly called 'a central composite design', contains an imbedded factorial or fractional factorial design with centre points that is augmented with a group of 'star points' that allow estimation of curvature. If the distance from the centre of the design space to a factorial point is ±1 unit for each factor, the distance from the centre of the design space to a star point is ± \( \alpha \) with \( |\alpha| > 1 \). The precise value of \( \alpha \) depends on certain properties desired for the design and on the number of factors involved.
An illustration of central composite design is shown in Fig. 3.8. Central composite design always contains twice as many star points as there are factors in the design. The star points represent new extreme values (low and high) for each factor in the design. The value of $\alpha$ is chosen to maintain rotatability and its value depend on the number of experimental runs in the factorial portion of the central composite design:

In the present investigation the effect of parameters on acetamiprid removal and TOC removal was determined using RSM. Central composite design with two factors at five levels was applied using Minitab 14 (PA, USA).

The independent variables are converted into corresponding coded variables $x_1$ and $x_2$, between $-\alpha$ and $+\alpha$ in five levels as $-\alpha$, $-1$, $0$, $+1$, and $+\alpha$ using the equation given below (Ahmed Basha et al., 2009).
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\[ x_i = \frac{2\alpha X_i - \alpha (X_{i,\text{max}} + X_{i,\text{min}})}{(X_{i,\text{max}} - X_{i,\text{min}})} \] .........................................................(3.7)

Where \( X_{i,\text{max}} \) and \( X_{i,\text{min}} \) are the maximum and minimum values of the variable \( X_i \).

The value of \( \alpha \) used for Fenton, UV/ \( \text{H}_2\text{O}_2 \) and photo-Fenton processes was 1.2 while for photocatalysis it was 1.4. The change in value of \( \alpha \) was done to avoid negative values of the variables.

Operating ranges of the variables of the experiments were selected based on the results of the preliminary experiments. Operating parameters and ranges selected for the experiments are given in Table 3.1.

**Table 3.1 Operating parameters and ranges selected for the experiments**

<table>
<thead>
<tr>
<th>Independent Variable</th>
<th>Symbols used</th>
<th>Coded levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(-\alpha)</td>
</tr>
<tr>
<td>a) Fenton process and photo-Fenton process</td>
<td>( X_1, X_5^* )</td>
<td>2</td>
</tr>
<tr>
<td>H(_2)O(_2) (mg/L)</td>
<td>( X_2, X_6^* )</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe(^{2+}) (mg/L)</td>
<td>( X_3 )</td>
<td>2.4</td>
</tr>
<tr>
<td>pH</td>
<td>( X_4 )</td>
<td>2</td>
</tr>
<tr>
<td>b) UV-H(_2)O(_2) process</td>
<td>( X_7 )</td>
<td>300</td>
</tr>
<tr>
<td>Catalyst loading (mg/L)</td>
<td>( X_8 )</td>
<td>0.3</td>
</tr>
<tr>
<td>c) Photocatalysis</td>
<td>( X_{10} )</td>
<td>0.3</td>
</tr>
<tr>
<td>Dopant concentration (mol %)</td>
<td>( X_{12} )</td>
<td>0.3</td>
</tr>
</tbody>
</table>

* \( X_5 \) and \( X_6 \) are used for photo-Fenton process

Thirteen experiments were conducted including five replicates at centre point. Pure error is calculated based on the results at centre point. Analysis
Of Variance (ANOVA) has also been studied using RSM. A second order polynomial of the following form is fitted to the experimental data

\[ y = A_0 + A_1 x_1 + A_2 x_2 + A_{11} x_1^2 + A_{22} x_2^2 + A_{12} x_1 x_2 \quad \ldots (3.8) \]

where \( y \) is the response variable of acetamiprid removal (%) or TOC removal (%) in coded units, \( A_1, A_2 \) are regression coefficient for linear effects, \( A_{11}, A_{22} \) are quadratic coefficients, \( A_{12} \) is interaction coefficient.

The significance of regression coefficients are analysed by ‘\( p \)’ test.

The quality of fit of the model is represented by correlation coefficient (R), average absolute relative error (AARE), average root mean square error (RMSE) and scatter index (SI) expressed as follows.

\[
R = \frac{1}{\sqrt{\sum_{i=1}^{N} (E_i - \bar{E}) (P_i - \bar{P})}} \sum_{i=1}^{N} (E_i - \bar{E})^2 \sum_{i=1}^{N} (P_i - \bar{P})^2 \quad \ldots (3.9)
\]

\[
AARE(\%) = \frac{1}{N} \sum_{i=1}^{N} \left(\frac{|E_i - P_i|}{E_i}\right) \times 100 \quad \ldots (3.10)
\]

\[
RMSE = \left[ \frac{1}{N} \sum_{i=1}^{N} (P_i - E_i)^2 \right]^{1/2} \quad \ldots (3.11)
\]

\[
SI = \frac{RMSE}{E} \quad \ldots (3.12)
\]

where \( E \) is the response obtained from experiment, \( P \) is the predicted response obtained from the model, \( \bar{E} \) and \( \bar{P} \) are the mean values of \( E \) and \( P \) respectively. \( N \) refers to the number of experimental runs. The value of \( R \) is commonly used to represent the strength of linear relationship between the
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Experimental and predicted variables. But higher value of $R$ might not necessarily indicate the better performance of the model because of the tendency of a model to be biased towards higher or lower values. Hence $AARE$ and $RMSE$ are also computed for measuring the predictability of the model. Since $AARE$ and $RMSE$ are calculated through a term by term comparison, they represent unbiased statistics (Srinivasulu and Jain, 2006; Ahmed Basha et al., 2009).

3.10 Kinetic Modeling of Photo-Fenton Process

One of the commonly used methods for kinetic modeling of the process is description of the process using information from individual reactions. In this study, the model was developed based on the simplified reactions that take place in photo-Fenton treatment.

3.10.1 Proposed Reaction Scheme and Mass Balance Equations

The major reactions taking place in photo-Fenton process are given in Table 3.2.

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^+ + OH^{-}$</td>
<td>(3.13)</td>
<td></td>
</tr>
<tr>
<td>$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + OH^+ + H^+$</td>
<td>(3.14)</td>
<td></td>
</tr>
<tr>
<td>$Fe^{2+} + OH^+ \rightarrow Fe^{3+} + OH^-$</td>
<td>(3.15)</td>
<td></td>
</tr>
<tr>
<td>$H_2O_2 + OH^- \rightarrow H_2O + HO_2^-$</td>
<td>(3.16)</td>
<td></td>
</tr>
<tr>
<td>$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + O_2 + H^+$</td>
<td>(3.17)</td>
<td></td>
</tr>
<tr>
<td>$Fe^{2+} + HO_2^- \rightarrow Fe^{3+} + HO_2^-$</td>
<td>(3.18)</td>
<td></td>
</tr>
<tr>
<td>$HO_2^- + OH^- \rightarrow H_2O + O_2$</td>
<td>(3.19)</td>
<td></td>
</tr>
<tr>
<td>$AMP + OH^- \rightarrow AMP^*$</td>
<td>(3.20)</td>
<td></td>
</tr>
</tbody>
</table>
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The reaction (3.14) is responsible for the enhancement in the efficiency of removal by photo-Fenton process.

Kinetic schemes were written for the oxidation of the acetamiprid (AMP) and the mineralisation of the AMP to CO$_2$ and water was not considered. The reaction rate expressions and the mass balance equations written are given Table 3.3 and 3.4. Intensity of radiation used in photo-Fenton process is represented by the term ‘$I$’. The proposed model assumes eight processes and five species: - Fe$^{2+}$, H$_2$O$_2$, Fe$^{3+}$ AMP and radicals formed from peroxide –R, (in whatever form) (Cabrera Reina et al., 2012).

Table 3.3 Kinetics expressions for each reaction

<table>
<thead>
<tr>
<th>Kinetic expression</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1 = k_1[Fe^{2+}][H_2O_2]$</td>
<td>(3.21)</td>
</tr>
<tr>
<td>$r_2 = k_2[Fe^{3+}]I$</td>
<td>(3.22)</td>
</tr>
<tr>
<td>$r_3 = k_3[Fe^{2+}][R]$</td>
<td>(3.23)</td>
</tr>
<tr>
<td>$r_4 = k_4[H_2O_2][R]$</td>
<td>(3.24)</td>
</tr>
<tr>
<td>$r_5 = k_5[Fe^{3+}][R]$</td>
<td>(3.25)</td>
</tr>
<tr>
<td>$r_6 = k_6[Fe^{2+}][R]$</td>
<td>(3.26)</td>
</tr>
<tr>
<td>$r_7 = k_7[R][R]$</td>
<td>(3.27)</td>
</tr>
<tr>
<td>$r_8 = k_8[AMP][R]$</td>
<td>(3.28)</td>
</tr>
</tbody>
</table>
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Table 3.4 Mass balance equations for photo-Fenton process

<table>
<thead>
<tr>
<th>Mass balance equation</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{d}{dt}[\text{Fe}^{2+}] )</td>
<td>( -r_1 + r_2 - r_3 + r_5 - r_6 ) (3.29)</td>
</tr>
<tr>
<td>( \frac{d}{dt}[\text{H}_2\text{O}_2] )</td>
<td>( -r_1 - r_4 ) (3.30)</td>
</tr>
<tr>
<td>( \frac{d}{dt}[\text{Fe}^{3+}] )</td>
<td>( r_1 - r_2 + r_3 - r_5 + r_6 ) (3.31)</td>
</tr>
<tr>
<td>( \frac{d}{dt}[\text{AMP}] )</td>
<td>( -r_8 ) (3.32)</td>
</tr>
<tr>
<td>( \frac{d}{dt}[\text{R}] )</td>
<td>( r_1 + r_2 - r_3 - r_4 - r_5 - r_6 - r_7 - r_8 ) (3.33)</td>
</tr>
</tbody>
</table>

3.10.2 Modeling

The objective of the model was to predict the variation of acetamiprid concentration with time for different \( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+} \) concentration. For this, values of eight reaction constants used in the model (\( k_1, k_2, k_3, k_4, k_5, k_6, k_7 \) and \( k_8 \)) were to be obtained. The values of these parameters were to be optimised for the present study as these constants change within a wide range. The mass balance and rate expressions were solved using MATLAB® and the model parameters were optimised with error rate as objective function. The program will search for suitable values of the parameters within the range available in the literature. These values were used for finding simulated profiles for process variables (Carra et al., 2014). Then the simulated profiles were compared with experimental data obtained for the identification runs (Table 3.5). The error rate objective function is

\[
e_i = \alpha \left( \sum_{i=1}^{n} \sum_{t=0}^{t_{\text{end}}} \left( \frac{X_{\text{sim},i,t} - X_{\text{exp},i,t}}{X_{\text{exp},i,t}} \right)^2 \right) \tag{3.34}
\]
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The above function will calculate the sum of the errors for process variables. Where \( k \) represents the number of identification runs, \( t \) is the time when the variable was measured, \( \text{sim} \) stands for the simulated value, \( \text{exp} \) stands for experimental value and \( \alpha \) is the weighting parameter used to represent the importance and contribution of each parameter to the model.

Table 3.5 Identification and verification runs for photo-Fenton process modeling

<table>
<thead>
<tr>
<th>Sl No</th>
<th>( \text{H}_2\text{O}_2 ), mg/L</th>
<th>( \text{Fe}^{2+} ), mg/L</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>2</td>
<td>I</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>2</td>
<td>V</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>2</td>
<td>V</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>2</td>
<td>I</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>5</td>
<td>I</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>2</td>
<td>I</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>5</td>
<td>V</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>10</td>
<td>I</td>
</tr>
</tbody>
</table>

(I-Identification, V-Verification)

Model validation was done by comparing the simulated and experimental values for verification runs (Table 3.5).