Chapter 5

Summary and Conclusions

5.1 Summary

Conventional wastewater treatment systems based on biological treatment are not efficient to treat the wastewater containing recalcitrant compounds like pesticides. Advanced oxidation processes (AOPs) based on the oxidation of pollutant by hydroxyl radicals can effectively remove these pollutants. In AOPs hydroxyl radicals are produced in situ through different mechanisms. AOPs are showing success where biological treatment fails.

Acetamiprid is a neonicotinoid insecticide widely used to kill sucking type insects on crops such as leafy vegetables, citrus fruits, pome fruits, grapes, cotton, cole crops, and ornamental plants. It is recommended as a substitute for organophosphorous pesticides because of its efficacy and nervous system attacking mechanism. Because of its widespread use it is increasingly found in the environment. It has high water solubility and low
photolytic degradation rate. It is stable to hydrolysis at environmental temperature. It belongs to the toxicity category II based on the studies on rats. Even after its increased use, its removal methods are less frequently studied.

Five treatment methods (Fenton process, UV treatment, UV/H$_2$O$_2$ process, photo-Fenton process and photocatalysis using TiO$_2$) were selected for study to remove acetamiprid from wastewater, based on the preliminary experiments conducted and the literature survey. The influence of major operating parameters on the pesticide removal and TOC removal by the selected processes were investigated. Undoped TiO$_2$ and TiO$_2$ doped with Cu and Fe were prepared by sol-gel method. Characterisation of the prepared catalysts was done using XRD, SEM and DTA-TGA. All the experiments were designed using central composite design (CCD) of response surface methodology (RSM). Model equations were developed for the processes and were validated statistically as well as experimentally. Optimum operating conditions were found out for all the processes studied. Kinetic studies were carried out and the processes were compared based on reaction rate and approximate operating cost. Photo-Fenton was found to be the fastest method with lowest operating cost. A kinetic model was developed for photo-Fenton process using the elementary reaction constants available in the literature and the kinetic data collected through experiments. Using this model it is possible to predict the variation of acetamiprid concentration with time for different H$_2$O$_2$ and Fe$^{2+}$ concentrations.
5.2 Conclusions

The conclusions derived from the study are

- The selected AOPs viz. Fenton process, UV treatment, UV/H$_2$O$_2$ process, photo-Fenton and TiO$_2$ photocatalysis are viable options for the removal of acetamiprid from wastewater.

- The rate of removal with Fenton process increases with increase in initial H$_2$O$_2$ and Fe$^{2+}$ concentration.

- Effect of pH on the removal rate of acetamiprid by UV treatment is not much significant.

- Use of UV along with H$_2$O$_2$ increases the removal rate of acetamiprid.

- Removal of acetamiprid decreases when H$_2$O$_2$ concentration increases beyond a certain value due scavenging of hydroxyl radicals.

- Addition of Fe$^{2+}$ to UV/H$_2$O$_2$ process increases the reaction rate.

- There was almost 10 times reduction in the amount of reagents required when photo-Fenton was used instead of Fenton process.

- Doping of TiO$_2$ with Cu enhances the removal rate of acetamiprid by photocatalysis while with Fe doping removal decreases.

- Conducting the treatment at optimum operating conditions is important since excess use of reagents will result in reduction in removal rate and increase in operating cost.
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- All the processes follow pseudo-first order kinetics.

- The pseudo-first order reaction constants obtained for the processes at optimised conditions are Fenton- 0.1041 min⁻¹, UV – 0.0334 min⁻¹, UV/H₂O₂- 0.1801 min⁻¹, photo-Fenton- 0.3174 min⁻¹, UV/undoped TiO₂- 0.0445 min⁻¹ and UV/Cu doped TiO₂- 0.0532 min⁻¹

- Photo-Fenton process gives highest removal rate with lowest operating cost.

- The systems using UV require special experimental set up to enhance the UV lamps and capture the light output, whereas as for Fenton process no sophisticated set up is necessary. Hence total cost analysis should be done before selecting the treatment system.

5.3 Limitations of the study

- Effect of temperature on the removal of pesticide was not studied. All experiments were conducted at room temperature (28±2°C)

- Surface area determination and the composition analysis of prepared photocatalysts using EPS/EDX etc. were not carried out as the enhancement in the removal rate of acetamiprid with doped TiO₂ was not much significant.

- The improvement in the photocatalytic activity of doped TiO₂ under visible light was not investigated.

- Cost comparison of the processes was done based on operating cost. Initial capital cost was not calculated which depends on the design of the reactor employed.
5.4 Scope for future Research

- Possibility of coupling of two or more AOPs could be investigated to reduce the treatment time and to improve the mineralisation efficiency.

- Studies on the removal using TiO₂ doped with other metals/non-metals could be carried out.

- Pilot plant studies using real wastewater could be done using the optimal range of values for the operating parameters. Scaling up of the laboratory set up to pilot plant could be carried out.