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Degradation of Acetamiprid in Wastewater by Ozonation

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ABSTRACT

Pesticides belong to the class of persistent chemicals in the environment which cause serious health hazards. Advanced Oxidation Processes (AOPs) represent the fast developing area in water and wastewater treatment by which non biodegradable and difficult to biodegradable compounds can be removed. This paper discusses the use of ozonation for the removal of insecticide acetamiprid from water. Response surface Methodology was used for the optimisation of the process parameters: ozone flow rate and pH.

***Keywords* -** Acetamiprid, Advanced Oxidation Process, Ozonation

1. INTRODUCTION

Pesticides have become an unavoidable commodity in our modern life. The introduction of pesticides in the environment cause serious issues of which water pollution is of primary importance. Removal of these compounds from water is a challenge to the environmental engineers because most of them are nonbiodegradable [1]. Acetamiprid belongs to a new class of insecticides, neonicotinoids, The use of neonicotinoids is increasing tremendously because of their ability to replace most of the organophosphates. They are commonly applied to cotton, vegetables, flowers, fruits etc.

Most of the chemical treatment methods utilized for pesticides degradation cause the formation of secondary pollutants. Advanced oxidation processes employ different methods for generation of the hydroxyl radicals. Hydroxyl radicals are very reactive and not highly selective. They can convert the pollutants to CO_2 and water or atleast to degradable compounds [2-5]. Ozonation is a widely used technique for the removal of pollutants from water and wastewater[6-8]. The degradation of compounds occurs through the action of ozone itself as well as through the radicals generated in aqueous medium. The major reactions taking place are [9-11]:

$$O_3 + OH^- \rightarrow O_3.^- + OH^. \quad (1)$$

$$O_3^{.-} \rightarrow O_2 + O^- \quad (2)$$

$$O^- + H^- \rightarrow OH^. \quad (3)$$

Ozonation was utilized by Esplugas et al. for the removal of phenol from wastewater [9]. 100% degradation was obtained at a pH of 9.4 in 80 minutes. Degradation of carbofuran by ozone was studied by Benitez et al. He could obtain similar degradation at pH 2 and 9 which indicates the negligible contribution of the reaction with hydroxyl radical generated by the ozone self-decomposition at pH 9 [12]. K.lafi et al. could obtain 90% removal of the pesticide deltamethrin using ozonation in a period of 210 min [1]. Amat et al. treated a pair of commercial anionic surfactants with ozonation in an alkaline medium. After only 10 min of treatment, surfactants were almost completely eliminated [14]. The present work focuses on the degradation of acetamiprid by ozonation. The effect of parameters like ozone flow rate and pH were also studied. Response surface methodology was used for optimisation of the process.

2. EXPERIMENTAL

2.1 PROCEDURES

Acetamiprid (97%) was purchased from Rallis India. The properties of acetamiprid is given in Table 1. Sulphuric acid and sodium hydroxide were used for adjusting the pH. The reagents were not subjected to further purification. Distilled water was used for making the solutions throughout. Ozone generator of capacity 2g/hr was used as the source of ozone.

Table1. Properties of Acetamiprid

Common Name	Acetamiprid
Name (IUPAC):	(E)-N-[(6-chloro-3-pyridyl)methyl]-N-cyano-N-methyl acetamidin
Molecular Formula	$C_{10}H_{11}C_lN_4$
Molecular Weight	222.68
Pesticide Type	Insecticide
Chemical Family	Neonicotinoid Insecticide
Application Sites	Control of Sucking-Type Insects on Leafy Vegetables, Fruiting Vegetables, Cole Crops, Citrus Fruits, Pome Fruits, Grapes, Cotton, and Ornamental Plants and Flowers
Carrier	Water
Physical State	Solid, Powder
Color	White powder
Odour	Odorless
Solubility in Water	4.25 x 10^{+3} mg/L at 25°C

The stock solution of acetamiprid containing 0.5 mg /cm^3 was prepared using distilled water. 500ml of the solution was taken and pH was adjusted using H_2SO_4/ NaOH. The flow rate of ozone was adjusted to the desired level and it was passed through diffusers in to the solution for 2hours. After the treatment the solution was anlaysed for COD, TOC and concentration of the insecticide. TOC was measured using Shimadzu TOC-L-CPH analyzer. Concentration of pesticide was analysed by Hitachi Elite Lachrome High Performance Liquid Chromatograph equipped with UV detector. The mobile phase was a mixture of water /acetonitrile (70-30). It was eluted at a rate of 1 ml/min. COD was measured by standard methods [12].

2.2 RESPONSE SURFACE METHODOLOGY

Response surface methodology (RSM) is essentially a particular set of mathematical and statistical methods for designing experiments, building models, evaluating the effect of variables, and searching optimum conditions of variables to predict target responses [15-17]. Its important applications are in the designs, development, formulation of new processes, and in the improvement of existing designs. Its purpose is to determine the optimum operating conditions through experimental methods. In this work, central composite design with two factors at five levels was applied using Minitab 15 (Minitab Inc., State College, PA,trial version). The parameters used are ozone flow rate and pH which are denoted by A and B respectively. The levels of independent variables are given in Table 2.

Table 2: Independent variables and their levels for the central composite design

Variable	Coded Levels				
	-α	-1	0	+1	+α
pH	4.38	5.5	8.25	11	12.139
Ozone Flow rate (g/hr)	0.702	0.814	1.086	1.357	1.469

3. RESULTS AND DISCUSSION

3.1 RESPONSE SURFACE METHODOLOGY

A second-order polynomial model, as given in Equation 4 was fitted to the experimental data

$$Y = \text{Constant} + aA + bB + aaA^2 + bbB^2 + abAB \quad (4)$$

where Y is the response variable; a and b are the regression coefficients for linear effects; aa, bb are the quadratic coefficients and ab is the interaction coefficient. The significance of the regression coefficients was analyzed using p test. The values of p, and the significant level (1-p) are also given in the Tables 3-5. It can be observed from the tables 3 to 5 that all the terms except the interaction term of pH and ozone flow rate are highly influential in the model for the prediction of pesticide removal, COD and TOC from the waste water.

Table 3: Estimated Regression coefficients and corresponding p values for COD removal (%)

Factor	Coefficient of the model in uncoded factors	p value	Significance Level (%)
Constant	-266.109	0.003	>47%
A	834.206	0.002	>99%
B	313.705	0.006	>98%
Aa	-2.577	0.000	>99%
bb	-156.538	0.002	>99%
ab	6.268	0.194	>80%

Table 4: Estimated Regression coefficients and corresponding p values for Pesticide removal (%)

Factor	Coefficient of the model in uncoded factors	p value	Significance Level (%)
Constant	-7.4615	0.533	>47%
A	8.5787	0.000	>99%
B	44.5947	0.022	>98%
Aa	-0.5431	0.000	>99%
bb	-23.5968	0.007	>99%
ab	1.0447	0.239	>80%

Table 4: Estimated Regression coefficients and corresponding p values for TOC removal (%)

Factor	Coefficient of the model in uncoded factors	p value	Significance Level (%)
Constant	-34.1129	0.001	>47%
A	4.9307	0.000	>99%
B	38.4338	0.004	>98%
Aa	-0.3349	0.000	>99%
bb	-16.822	0.003	>99%
ab	0.2980	0.555	>45%

Equation 5 can be represented in terms of uncoded variables as

$$Y_1 = -266.109 + 34.20572A + 313.705B - 2.577A^2 - 156.538B^2 + 6.268AB \quad (5)$$

$Y_2 = -7.46154 + 8.57873A + 44.5947B - 0.5431A^2 - 23.5968B^2 + 1.0447AB$ (6)

$Y_3 = -34.1129 + 4.9307A + 38.4338B - 0.3349A^2 - 16.8222B^2 + 0.2980AB$ (7)

Where Y_1, Y_2, Y_3 correspond to response of COD, pesticide and TOC removal percentages respectively.

3.2 EFFECT OF VARIABLES

The results of the Experimental runs are given Figure 1-3. Contour plots shows that the maximum exists in the domain selected for study.

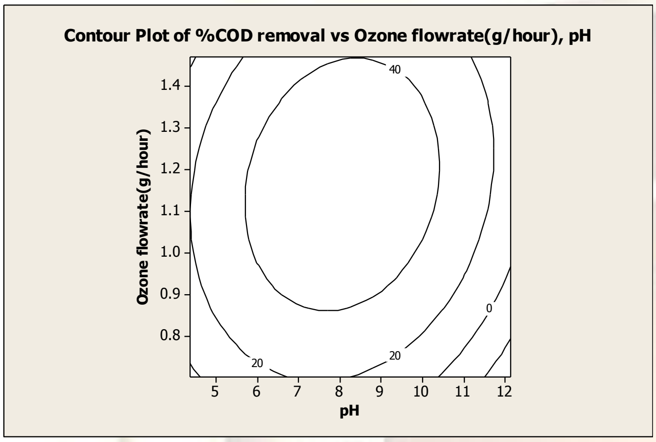

Fig 1: Combined Effect of pH and Ozone flow rate on COD removal

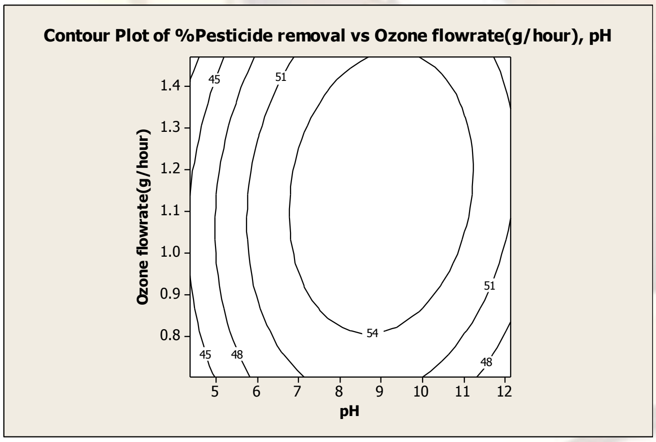

Fig 2: Combined Effect of pH and Ozone flow rate on Pesticide Removal

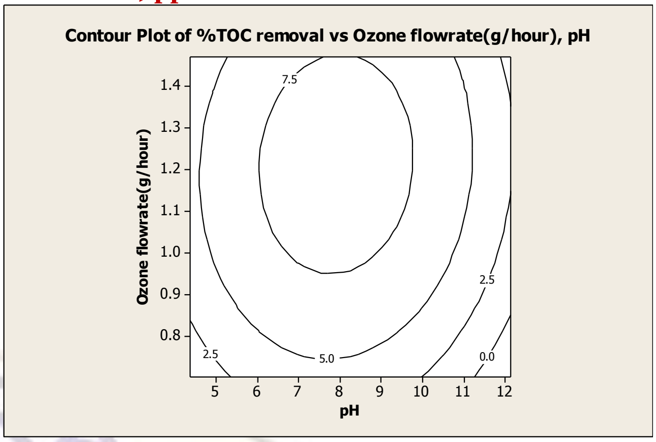

Fig 3: Combined Effect of pH and Ozone flow rate on TOC Removal

The optimum conditions predicted for the process were pH 8.2 and ozone flow rate of 1.18g/hr. The COD removal(%), pesticide removal (%) and TOC removal at this conditions were 53.9, 56.9 and 8.7% respectively. TOC removal is low since the degradation products of acetamiprid exist in the medium and mineralization was not complete. The optimum conditions were checked experimentally and results obtained were close to the predicted value.

4. CONCLUSION

The ozonation process for the removal of acetamiprid from aqueous solutions was investigated. As ozonation is normally used for disinfection, the removal of pesticide is an added advantage. Eventhough the degradation is not complete, a removal efficiency of 57% was obtained which shows that ozonation can be used as a first step in the treatment process. The optimum pH obtained was 8.1, which shows that the process is more effective in alkaline medium. This can be explained by the equations 1-3. Ozonation is a viable process for acetamiprid removal and it does not produce sludge as in Fenton process. Combination of Ozone with other reagents like H_2O_2 and UV can be tried for improving the removal of pesticide.

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