# PREFACE

Agriculture is the backbone of the economy in several countries, particularly India; therefore it is necessary to use pesticides for controlling pests. In India, the use of pesticides is high in some parts of the country in which, Andhra Pradesh (Seemandhra and Telangana) and Punjab consumes the largest amount of pesticides. Such high application of pesticides has resulted in an increase in the pesticide level in drinking water. There are many sources (water, fruit, vegetable, etc.) through which humans are exposed to pesticides which cause toxic effects on health. For this reason, it is very important to remove pesticides from water bodies. Various treatment technologies such as adsorption, coagulation-flocculation, photodegradation, Fenton oxidation, ozonation, biodegradation etc. are available for the removal of pesticides from water mass. The development of cost-effective methods for the removal of pesticides from contaminated waters offers a great challenge in the present scenario. In view of this the present work was initiated to evaluate the efficacy of (i) coagulation using conventional coagulants (alum and ferric chloride), (ii) Fenton oxidation and (iii) coagulation coupled with Fenton oxidation.

The present work was planned and executed to achieve above objectives in the following manner: (i) Simulated wastewater containing 30 mg/L pesticides − methyl parathion ($11.4 \times 10^{-5}$ M), chlorpyrifos ($8.65 \times 10^{-5}$ M) and carbofuran ($13.5 \times 10^{-5}$ M) was prepared separately to evaluate the reduction efficiencies, (ii) Batch experiments were carried out to evaluate the removal of COD and amount of pesticide using coagulation, Fenton oxidation and coagulation coupled with Fenton oxidation, (iii) Toxicity of residual pesticide and its degradation products, if any, was evaluated

using mammalian cells. The concentrations of samples were analyzed through the high performance liquid chromatography (HPLC) method at a wavelengths ($\lambda$) of 225, 220 and 276 nm, respectively, for methyl parathion, chlorpyrifos and carbofuran.

(i) *Removal through the coagulation-flocculation process:* Coagulation-flocculation in water treatment rely upon aluminium (Al) and iron (Fe) salts for the treatment of contaminants present in source waters containing dissolved organic compounds. In this study, removal of methyl parathion, chlorpyrifos and carbofuran was investigated through coagulation/flocculation using two commercial coagulants alum [$Al_2(SO_4)_3.18H_2O$] and ferric chloride ($FeCl_3$). For estimating the removal efficiency of absolute pesticide concentration and chemical oxygen demand (COD), the jar-test experiments were carried out by varying the initial pH (4-9), coagulant type and dose alum ($3 \times 10^{-5}$ to $18 \times 10^{-5}$ M), ferric chloride ($12.3 \times 10^{-5}$ to $7.40 \times 10^{-5}$ M), initial pesticide concentration and operating time. Response surface methodology (RSM) was used to design the jar-test experiments and central composite design (CCD) was used to analyze the effects of initial pH and coagulant dose on the removal of chlorpyrifos. Analysis of variance (ANOVA) showed that the coefficient of determination ($R^2$) value for chlorpyrifos removal was 0.971 and 0.981 with alum and ferric chloride, respectively. The present study also predicted that the obtained regression equations could be helpful as the theoretical basis for the coagulation process of pesticide wastewater. The COD removal for methyl parathion, chlorpyrifos and carbofuran simulated wastewater was 68.5, 79 and 65.98%, respectively, and the corresponding removal in terms of pesticide concentration was 79, 82 and 75.13%, respectively, with ferric chloride at optimum conditions (pH 5, ferric chloride dose $49.3 \times 10^{-5}$ M and operating time 30 min). Similarly, the COD removal for methyl parathion, chlorpyrifos and carbofuran simulated wastewater was 59, 64 and 59.95%, respectively, and

corresponding removal in terms of absolute pesticide concentration was 77.5, 79 and 71.86%, respectively, with alum at optimum conditions (pH 6, alum dose $12 \times 10^{-5}$ M and operating time 30 min). The SEM-EDX and FTIR studies were carried out to understand the sludge structure and composition, respectively. The sludge settling characteristics for alum and ferric chloride sludge were also studied. TGA/DTA analysis of the sludge showed the exothermic nature of the reactions.

(ii) *Removal using Fenton process:* The treatment of methyl parathion, chlorpyrifos and carbofuran bearing wastewater through Fenton oxidation using $Fe^{2+}$ as catalyst was investigated under batch mode. The aim of this part of the study was to investigate the role of different parameters such as initial pH, $Fe^{2+}$ dosage, $H_2O_2$ dosage, initial pesticide concentration, temperature and reaction time. The smearing response surface methodology (RSM) based central composite design (CCD) method and adaptive neuro-fuzzy inference system (ANFIS) was used to design the experiments, develop regression models, optimize and evaluate the effects of three independent parameters i.e. initial pH, $H_2O_2$ and catalyst concentrations on the chlorpyrifos removal efficiency and the enactment of the model was judged with the ANOVA for CCD. A quadratic model was used to represent the experimental data. The predicted and experimental values for chlorpyrifos were found to be in good agreement with $R^2 = 0.974$ for responses $Y_{conc}$, which define the propriety of the model. The efficacy of the ANFIS models was judged through the correlation coefficient (R), mean square error (MSE) and root mean square error (RMSE). The predictions of the RSM and ANFIS models were found to be in good agreement with experimental data for both the responses. It was observed that removal was faster at acidic pH

The recognized optimum conditions for maximum removal of methyl parathion and carbofuran were obtained as pH 3, $H_2O_2$ dose $6.53 \times 10^{-1}$ M, $Fe^{2+}$ dose $8.99 \times 10^{-3}$ M

and temperature 25 ℃. In the case of chlorpyrifos, maximum reduction efficiency was observed at optimum pH 3, $H_2O_2$ dose $5.71 \times 10^{-1}$ M and $Fe^{2+}$ dose $10.8 \times 10^{-3}$ M. Under optimum conditions, maximum degradation of methyl parathion, chlorpyrifos and carbofuran were obtained as 92, 94 and 89.34%, respectively, and the corresponding reduction in COD was 79.32, 83.15 and 76.28%, respectively. It was observed that complete conversion of $H_2O_2$ was attained at 0.571 M $H_2O_2$ dose in chlorpyrifos bearing wastewater. Three kinetic models have been used to study the degradation kinetics of pesticides. Regarding degradation kinetics of methyl parathion, chlorpyrifos and carbofuran, Behnajady–Modirshahla–Ghanbery model showed high correlation coefficient ($R^2$) as compared to first-order and second-order models at different operating conditions using Fenton oxidation.

(iii) *Removal through the coupled Fenton and coagulation process:* The experiments using coagulation coupled with Fenton oxidation were performed to achieve the permissible limit of these pesticides in treated solution. The maximum COD removal obtained was 96.36, 96.42 and 96.27% for methyl parathion, chlorpyrifos and carbofuran, respectively. The corresponding residual concentrations were 0.009, 0.003 and 0.066 mg/L for three pesticides, respectively.

(iv) *Toxicity studies:* The aim of this study was to determine the toxic effects of residual methyl parathion, chlorpyrifos and carbofuran on human cells and red blood count (RBC). Fenton treatment of methyl parathion, chlorpyrifos and carbofuran significantly increased the percent proliferation and decreased percent cytotoxicity towards U-87 cells. Also, treated samples were less toxic to the human dendritic cells (DC) and lymphocytes. Fenton treatment also improved the survival of RBC by preventing hemolysis. It was observed that carbofuran is more toxic compared to other two pesticides.