CONTENTS

CHAPTER – II : THEORY AND LITERATURE REVIEW

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 (11.4×10^{-5} M), chlorpyrifos (8.65×10^{-5} M) and carbofuran (13.5×10^{-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 (λ) 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 (3×10^{-5} to 18×10^{-5} M), ferric chloride (12.3×10^{-5} to 7.40×10^{-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 49.3×10^{-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 × 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 × 10^{-1} M, Fe^{2+} dose 8.99 × 10^{-3} M and temperature 25 ºC. In the case of chlorpyrifos, maximum reduction efficiency was observed at optimum pH 3, H_2O_2 dose 5.71 × 10^{-1} M and Fe^{2+} dose 10.8 × 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.

ABBREVIATIONS & NOTATIONS

Abbreviations	
AI	Artificial Intelligence
ANFIS	Adaptive Neuro Fuzzy Inference System
ANN	Artificial Neural Network
ANOVA	Analysis of Variance
APOs	Advanced Oxidation Processes
BDD	Boron-Doped Diamond
BFA	Bagasse Fly Ash
BHC	Benzene Hexachloride
BOD	Biological Oxygen Demand
CCD	Central Composite Design
CF	Carbofuran
CIBRC	Central Insecticides Board and Registration Committee
COD	Chemical Oxygen Demand
CPF	Chlorpyrifos
DC	Dendritic Cell
DDT	Dichloro-Diphenyl-Trichloroethane
DHS	Department of Health Services
DO	Dissolved Oxygen
DOE	Design of Experiment
DSAC	Date Seed Activated Carbon
DTA	Differential Thermal Analysis
EC	Emulsifiable Concentrates
EDX	Energy Dispersive X-ray Spectroscopy
EU	European Union
FAO	Food and Agriculture Organization
FSSAI	Food Safety and Standards Authority of India
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
GC	Gas Chromatography
GC–MS	Gas Chromatography–Mass Spectrometry
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
LC	Lethal Concentration
LD	Lethal Dose
MAC	Maximum Acceptable Concentration
MCL	Maximum Contamination Level
MDL	Minimum Detection Limits
MFs	Membership Functions
MOPs	Moringa Oleifera Pods
MP	Methyl Parathion
MRLs	Maximum Residue Limits
MSE	Mean Square Error
NOM	Natural Organic Matter
OD	Optical Density

Abbreviations

PAC	Powdered Activated Carbon
PBMC	Peripheral Blood Mononuclear Cell
RB	Rice Bran
RBC	Red Blood Cell
RfD	Reference Doses
RH	Rice Husk
RHBC	Rice Husk Biochars
RL	Reporting Limits
RMSE	Root Mean Square Error
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
SPE	Solid-Phase Extraction
TGA	Thermal Gravimetric Analysis
TLC	Thin Layer Chromatography
TMDI	Theoretical Maximum Daily Intake
TOC	Total Organic Carbon
TWBC	Tea Waste Biochars
UCIL	Union Carbide India Ltd.
US EPA	Environmental Protection Agency
WBC	White Blood Cell
WHO	World Health Organization

Notations

R^2	Regression coefficients
p	Number of experiments
n	Quadratic model parameters
Y	Responce
k	Number of patterns
X_i and X_j	Coded levels of input factors
b	Coefficient of quadratic model
A and B	Fuzzy sets
R	Correlation coefficient
C_i	Initial concentration and COD value
C_t	Concentration and COD after time t
k_1	Rate constants of first-order kinetic model
k_2	Rate constants of second order kinetic model
m and b	Characteristic constants of the B-M-G kinetic model
C_e	Equilibrium liquid phase concentration
q_e	Amount of pesticide adsorbed
K_L	Langmuir constant
K_F	Freundlich constant
u_c	Sedimentation velocity
v_f	Volumetric flow rate
σ	Residual mean square
μ_{Ai}	Membership functions of A_1
μ_{Bi}	Membership functions of B_1
Conc.	Concentration

ACKNOWLEDGEMENT

First and foremost I would like to express my heartiest gratitude to my research supervisor Dr. Pradeep Kumar, Department of Chemical Engineering and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi for his precious guidance, support, enthusiasm, stimulating suggestions and supervision at every level of this thesis. I shall be obliged forever for his kind inspiration, encouragement, useful criticism and constant support without which it has not been possible to complete this work. I have gained enormous knowledge from him during my research work that would be immensely useful to me for all my future endeavors.

I would like to take this opportunity to put on record my respects to Prof. P.K. Mishra, Head of Department, for providing me various facilities during the course of the present investigation. My sincere and grateful thanks are due to Research Progress Evaluation Committee (RPEC) member, Prof. Devendra Mohan, Department of Civil Engineering for his valuable time and encouragement during my research.

I wish to express my special thanks to Prof. M. K. Mondal for his constant motivation, support and guidance during my research work. He always helped me as RPEC member and by providing me lab facility.

I owe my sincere gratitude to Prof. S.N. Upadhyay for his constructive help and moral support during my research. My special thanks to Prof. A.S.K. Sinha for providing lab facility.

I am especially grateful Prof. P.P. Manna, Department of Zoology for his contribution to conduct my experimental work in his laboratory.

I owe grateful thanks to my friends V. Raghunath Ch., Dan Bahadur Pal, Chandradhwaj Nayak, Shailesh Kumar, Poornima Pandey, Parul Dohare, Bineeta Singh and many others who helped me at crucial moments.

My humble thanks to Shri Chandlal, Shri Ankit Kumar, Shri Arjun Prasad, Shri Umesh Pratap, Shri Shailendra K. Upadhyay, Shri Daya Ram Singh Yadav, Shri Surendra K. Verma and other staff of the department for their assistance during research work.

I gratefully acknowledge to Ministry of Human Resource Development (MHRD), Government of India for providing the financial assistance.

I would deeply appreciate my parents and father-in-law for their love, generous support, motivation and trust in me, without which it was not possible for me to complete my research work and most of all I put on record to express my love and affection to my loving, supportive and encouraging husband Mr. Avinash Singh whose faithful support during the entire journey of this work. I would highly appreciate to my brothers, sisters, and in-laws for their corporation and encouragement. I would like to acknowledge them for their prayers throughout this work.

I want to express my sincere thanks to all those who directly or indirectly helped me at various stages of this work.

Lastly, I bow to the 'Almighty God' that blessed me in the moments of need.

ROLI SAINI

LIST OF FIGURE

LIST OF TABLE