

Modeling of Coagulation Process for the Removal of Carbofuran in Aqueous Solution

Roli Saini, Pradeep Kumar

Abstract—A coagulation/flocculation process was adopted for the reduction of carbamate insecticide (carbofuran) from aqueous solution. Ferric chloride (FeCl_3) was used as a coagulant to treat the carbofuran. To exploit the reduction efficiency of pesticide concentration and COD, the jar-test experiments were carried out and process was optimized through response surface methodology (RSM). The effects of two independent factors; i.e., FeCl_3 dosage and pH on the reduction efficiency were estimated by using central composite design (CCD). The initial COD of the 30 mg/L concentrated solution was found to be 510 mg/L. Results exposed that the maximum reduction occurred at an optimal condition of $\text{FeCl}_3 = 80$ mg/L, and $\text{pH} = 5.0$, from which the reduction of concentration and COD 75.13% and 65.34%, 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.

Keywords—Carbofuran, coagulation, optimization, response surface methodology.

I. INTRODUCTION

MOST of the pesticides has either been banned or restricted by some countries, but in India these have been allowed to use on crops for large amount of production. Pesticides that have been used in India are regulated by Central Insecticides and Board and Registration Committee (CIBRC) and the Food Safety and Standards Authority of India (FSSAI). Carbofuran (2, 3-dihydro-2, 2-dimethyl-7-benzofuranyl N-methyl carbamate) was registered for 27 crops by CIBRC, i.e. jute, bajra, frenchbean, groundnut, potato, apple, tomato, maize, citrus fruits etc. Carbofuran is persistent carbamate insecticide from other carbamate or organophosphate insecticides [1]. The mode of action of carbamate insecticides is mostly similar to organophosphate insecticides.

Common pesticides, such as, carbofuran may appear as major pollutants in the soil, air, surface and water sources. Carbofuran is moderately toxic by dermal absorption and highly toxic by inhalation and ingestion. It is soluble in water. Several chemical and biological treatment methods have been suggested to reduce the concentration of carbofuran in water and wastewaters. Degradation of carbofuran in soil takes place by hydrolysis, microbial action and, to a lesser extent, photodecomposition. The persistence of carbofuran in the environment is dependent upon pH, soil type, temperature,

Roli Saini is with the Indian Institute of Technology (Banaras Hindu University), Varanasi – 221005, India (corresponding author, phone: +91-8765336478; e-mail: roli.6102@gmail.com).

Pradeep Kumar is with the Indian Institute of Technology (Banaras Hindu University), Varanasi – 221005, India (e-mail: pkumar.che@iitbhu.ac.in).

moisture content and the microbial population. The maximum concentration of carbofuran reported by the World Health Organization (WHO) in 3 $\mu\text{g/L}$ in potable water [2]. Carbofuran is very toxic to aquatic life with long lasting effects and fatal if swallowed or if inhaled. At extremely low doses, carbofuran can cause transient alterations in the concentration of many hormones in humans and animals.

Most of the techniques are ordinarily used for determination of pesticides in aqueous solutions such as gas chromatography–mass spectrometry, HPLC, HPLC-MS, double beam UV-Vis spectrophotometer. Pesticides which are insoluble in water (e.g. DDT), or which are easily decomposed, such as carbamate insecticides (carbofuran), can be effectively removed by the conventional methods. Various techniques have been used for the removal of insecticide carbofuran from wastewater such as, adsorption [3]-[7], Fenton [8], Photo-Fenton [9], electro-Fenton [10] and photo-degradation [11]-[14]. Pesticides polluted surface and ground water, therefore, can be treated very effectively by using one of these techniques. RSM was proposed as an efficient way to optimize the effects of individual factors and their responses. This statistical technique has been broadly used for the optimization of various experiments in material science, food chemistry, chemical engineering, biotechnology, and also used for building models [15], [16].

The main objective of the present study was to optimize the coagulation process (Jar-test experiment) by RSM. The CCD was chosen to analyze the effect of independent variables, i.e. initial pH and FeCl_3 dosage on two response concentration and COD.

II. MATERIALS AND METHODS

A. Materials

Technical grade carbofuran ($\text{C}_{12}\text{H}_{15}\text{NO}_3$) of 98% purity was supplied by Sigma–Aldrich (Mumbai). Ferric chloride was procured from Fisher Scientific (Mumbai, India). Water (HPLC grade) was procured from Merck, Mumbai and acetonitrile (HPLC grade) were procured from Fisher Scientific. Standard 1 M NaOH and 0.1 M H_2SO_4 solutions were used for pH modification. All reagents used in the present study were of analytical grade. All glassware of borosil was used for the experiment.

B. Analytical Methods

The pH meter was used for the measurement of pH in the solution. Characterization of sludge obtained during the coagulation process was analyzed through a Scanning Electron Microscope (SEM) to understand the surface morphology of

the sludge. Fourier Transform Infrared Spectroscopy (FTIR) analysis of the obtained sludge was carried out to check the functional group in the sludge. The concentration of the solution after treatment was analyzed by High performance liquid chromatograph (HPLC). COD values of samples, before and after treatment were measured by microwave digestion method using double wavelength (430 nm, 610 nm) photometer system.

C. Jar-Test Experiment

A stock solution of carbofuran (concentration = 30 mg/L) was prepared and stored at 4 °C. Batch studies in jar-test (Model: IK-155, IKON, Delhi, India) was conducted for the reduction of concentration and COD from the aqueous solution. The initial COD value of carbofuran solution was measured 510 mg/L. A jar-test apparatus comprising six thermostatic magnetic stirrers and beakers was set up at ambient temperature for each run. Each of the beakers of 1 L capacity was filled with solution for further studies. Different combinations of pH (4-9) and FeCl₃ dosage (20-120 mg/L) were tested. The initial pH of the samples was adjusted by either NaOH or H₂SO₄. After pH adjustment, FeCl₃ was added to the solution. The process was conducted at 120 rpm for 2 min, followed by a slow mixing of 40 rpm for 30 min. The flocs (precipitate) formed were allowed to settle down for 30 min. After settling, flocs were filtered with the help of Whatman No. 42 filter paper and precipitate-free liquid were taken for the analysis of concentration and COD.

The reduction efficiency of concentration (R₁) and COD (R₂) was determined by using the given equation:

$$R_1 (\%) = \frac{(\text{Initial conc.} - \text{Final conc.})}{\text{Initial conc.}} \times 100 \quad (1)$$

$$R_2 (\%) = \frac{(\text{Initial COD} - \text{Final COD})}{\text{Initial COD}} \times 100 \quad (2)$$

D. Design of Experiment

RSM was used for the modelling of the experiment. CCD in RSM has been extensively used. State-Ease Design Expert 9.0.5 was used for coagulation-flocculation process modelling. The independent key factors initial pH (X₁) and coagulant dose (X₂) was optimized by CCD. Equation (3) was used for statistical calculation to convert the actual value of an independent variable (X_i) to the coded form (x_i) [17], [18]:

$$x_i = \frac{(X_i - X_0)}{\delta X} \quad (3)$$

where, x_i, X_i, X₀ and δX are the coded value of ith independent variable, uncoded value, actual value at the center point and the step change, respectively. Concentration reduction and COD reduction were selected as a response variable. The response of the process was fitted by a second-order polynomial model:

$$Y = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k b_{ij} X_i X_j + \varepsilon \quad (4)$$

where, Y is the predicted response to be modeled; X_i and X_j are the coded variables; b₀ is offset terms; b_i is the linear

coefficient; b_{ii} is the quadratic coefficient for squared effects, b_{ij} is the interaction coefficient; and ε is the residual error. Operating range and coded levels of independent variables for the development of the model are shown in Table I. Analysis of variance (ANOVA) was used to investigate the data obtained from CCD.

TABLE I
OPERATING RANGE AND CODED LEVELS OF INDEPENDENT FACTORS

Factors	Symbols		Coded levels		
	Actual	Coded	-1	0	+1
Initial pH	X ₁	x ₁	4	6.5	9
FeCl ₃ dose	X ₂	x ₂	20	70	120

III. RESULT AND DISCUSSION

A. Effect of pH

The objective of this experiment was to examine the influence of pH on the reduction efficiency of the pre-determined operating condition, initial concentration 30 mg/L, initial COD 510 mg/L, coagulant dose 40 mg/L and agitation speed of 120 rpm. Initial pH of carbofuran containing solution was adjusted in the range of 4-9 by using 1M NaOH and 1M H₂SO₄. The obtained result expresses that the initial pH plays an important role on the both concentration and COD reduction efficiency. When the initial pH of the solution was increased, the reduction efficiency of concentration and COD increased markedly until the pH value of 5.0, but increasing the pH above 5.0 distinctly reduced the reduction efficiency in both cases. Therefore, the optimum pH value for concentration and COD reduction was 5.0, at which the concentration reduction was 73.12%; however, the COD reduction at this point was 64.13%. Based on this consideration, the optimum pH 5.0 was adopted for further experiment.

B. Effect of FeCl₃ Dose

Coagulant dose plays an important role in the coagulation process to determine the reduction efficiency. The purpose of this study to examine the influence of coagulant dosage on the pre-determined operating condition, initial concentration 30 mg/L, initial COD 510 mg/L, optimum pH 5 and agitation speed of 120 rpm. The coagulant dosages were investigated in the range of 20-120 mg/L. When FeCl₃ dosage was increased, the reduction efficiency of concentration and COD increased markedly up to the FeCl₃ dosage of 80 mg/L, but increasing the dose above 80 mg/L distinctly reduced the reduction efficiency in both cases. Therefore, the optimum coagulant dose for concentration and COD reduction was obtained 80 mg/L, at which the concentration reduction was 75.13%; however, the COD reduction at this point was 65.34%.

C. Statistical Analysis

The relationship between the independent factors (pH and coagulant dosage) and responses (concentration and COD) for the process was analyzed by using CCD of RSM. The CCD required significant model terms to obtain a best fit in a particular model. Thirteen run (13) required to develop the model. The CCD developed the mathematical equations in

terms of pH (X_1) and coagulant dose (X_2) according to (4). Then results obtained were analyzed by ANOVA to estimate the "goodness of fit". The coefficients of the polynomial model were estimated by ANOVA and values are given in Table II. The reduced quadratic model refers to (5) and (6), in terms of coded factors as:

$$Y_{Conc.(\%)} = 66.04 - 6.76 X_1 + 8.65 X_2 - 15.70 X_1^2 - 9.71 X_2^2 - 6.75 X_1 X_2 \quad (5)$$

$$Y_{COD} (\%) = 53.50 - 4.06 X_1 + 8.76 X_2 - 13.50 X_1^2 - 10.00 X_2^2 - 7.00 X_1 X_2 \quad (6)$$

The ANOVA confirms, adequacy of the model since P is less than 0.05. The Model F-value of 1.35 suggests that the model is significant. The "Lack of Fit F-test" describes that it is significant. Confidence intervals are 15.95-56 and 30.22-70.17 for COD and concentration reduction, respectively. The coefficient of determination (R^2) value is 0.903, and the accuracy of model is estimated.

TABLE II
ANOVA REGRESSION ANALYSIS FOR RESPONSE SURFACE QUADRATIC MODEL

Source	Degree of freedom	Sum of squares		Mean square		F value		p- value Prob>F	
		Conc.	COD	Conc.	COD	Conc.	COD	Conc.	COD
Model	5	3277.46	2690.10	655.49	538.02	12.38	20.13	0.0023 (significant)	0.0005 (significant)
X_1	1	365.46	131.91	365.46	131.91	6.90	4.93	0.0341	0.0618
X_2	1	598.30	613.96	598.30	613.96	11.30	22.97	0.0121	0.0020
$X_1 X_2$	1	182.25	196.00	182.25	196.00	3.44	7.33	0.1060	0.0303
X_1^2	1	1716.35	1267.83	1716.35	1267.83	32.41	47.43	0.0007	0.0002
X_2^2	1	655.55	695.65	655.55	695.65	12.38	26.02	0.0097	0.0014
Residual	7	370.70	187.13	52.96	26.73	-	-	-	-
Lack of Fit	3	2156.00	2692.00	431.20	545.30	31.05	23.15	< 0.0009 (significant)	< 0.0004 (significant)
Pure Error	4	69.43	0.81	0.69	0.81	-	-	-	-

D. Process Analysis

To observe the impact of pH and $FeCl_3$ dose on two responses, 3D response surface and contour plots are used. The response surface plots for coagulant $FeCl_3$ are shown in Fig. 1. Fig. 1 (a) indicates a maximum concentration reduction is 69%. Likewise, Fig. 1 (b) indicates that the maximum COD reduction is 55%. The plots are almost symmetrical in shape with circular contours and have a positive effect on reduction efficiency, shown in Figs. 2 (a) and (b).

All 3D plots show clear peaks, indicating the optimum conditions for maximum concentration and COD reduction in the design range of independent factors (pH and $FeCl_3$ dose). Standard deviation was found to be 7.28 and mean of responses became 53.40 using $FeCl_3$. The plots are almost symmetrical in shape with circular contours.

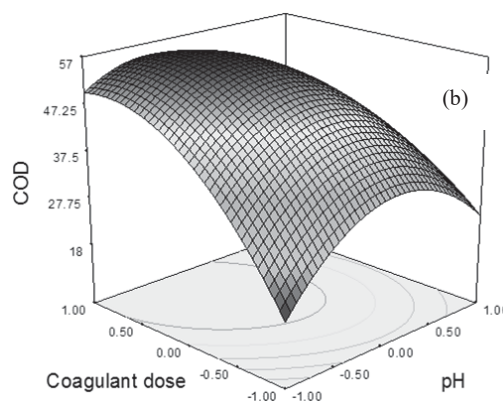
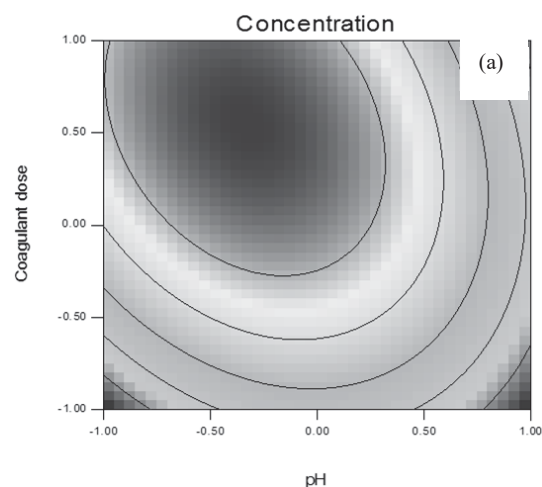
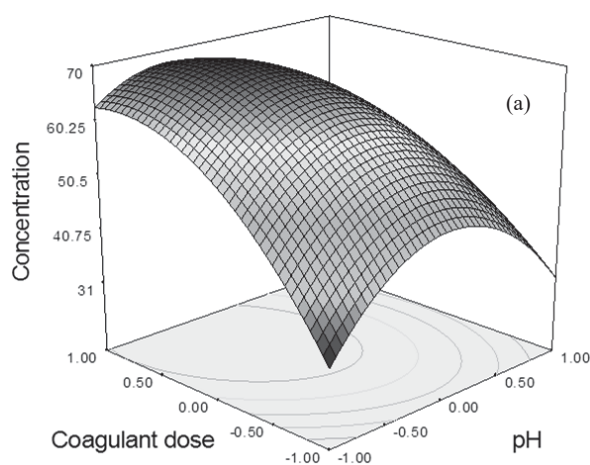


Fig. 1 Response surface plots for (a) concentration, (b) COD



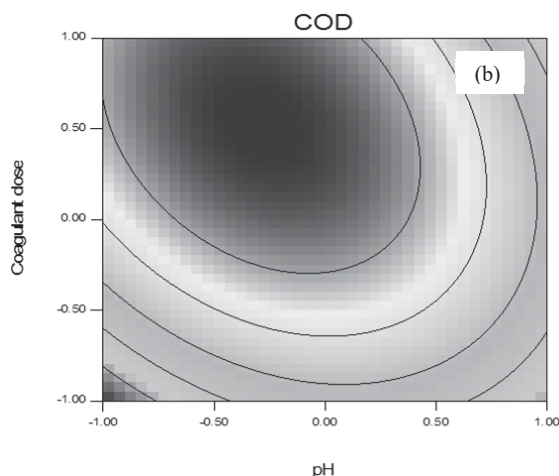


Fig. 2 Contour plots for (a) concentration, (b) COD

IV. CONCLUSION

Coagulation process was conducted for the treatment carbofuran containing aqueous solution. Statistical analysis was done by using RSM conducting CCD. The results indicated that the reduction efficiency was affected by initial pH and FeCl_3 dosage. ANOVA analysis exposed a high R^2 value of quadratic model, to ensure the accuracy of the model. Optimum pH and FeCl_3 dose was found to be 7.0 and 80 mg/L, respectively. At optimum pH, the concentration and COD reduction was 73.12% and 64.13%, respectively. At optimum dose, the concentration and COD reduction was 75.13% and 65.34%, respectively. The RSM demonstrated that predicted value has good agreements with measured values.

ACKNOWLEDGMENT

The authors are thanks to Department of Chemical Engineering and Technology, Indian Institute of Technology (BHU) Varanasi, India for providing facilities and support in doing experimental work.

REFERENCES

- [1] J. M. Salman and B. H. Hameed, "Adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon" *Desalination*, vol. 256, pp. 129–135, 2010.
- [2] J. M. Salman, V. O. Njoku and B. H. Hameed, "Bentazon and carbofuran adsorption onto date seed activated carbon: kinetics and equilibrium", *Chem. Eng. J.*, vol. 173, pp. 361–368, 2011.
- [3] M. Fernandez-Prez, M. Villafranca-Sanchez, F. Flores-Cspedes, J. Garrido-Herrera and S. Prez-Garca, "Use of bentonite and activated carbon in controlled release formulations of carbofuran", *J. Agric. Food Chem.*, vol. 53, pp. 6697–6703, 2005.
- [4] V. K. Gupta, I. Ali, Suhas and V. K. Saini, "Adsorption of 2,4-D and carbofuran pesticides using fertilizer and steel industry wastes", *J. Colloid Interface Sci.*, vol. 299, pp. 556–563, 2006.
- [5] G. Z. Memon, M. I. Bhangar and M. Akhtar, "The removal efficiency of chestnut shells for selected pesticides from aqueous solutions", *J Colloid Interface Sci.*, vol. 315, pp. 33–40, 2007.
- [6] K. L. Chang, C. C. Chen, J. H. Lin, J. F. Hsien, Y. Wang, F. Zhao, Y. H. Shih, Z. J. Xing and S. T. Chen, "Rice straw-derived activated carbons for the removal of carbofuran from an aqueous solution", *New Carbon Mater.*, vol. 29(1), pp. 47–54, 2014.
- [7] A. Bermudez-Couso, D. Fernandez-Calvino, I. Rodriguez-Salgado, J. C. Novoa-Munoz and M. Arias-Estevéz, "Comparison of batch, stirred flow chamber, and column experiments to study adsorption, desorption and transport of carbofuran within two acidic soils" *Chemosphere*, vol. 88, pp. 106–112, 2012.
- [8] J. H. Ramirez, F. J. Maldonado-Hodar, A. F. Perez-Cadenas, C. Moreno-Castilla, C. A. Costa and L. M. Madeira, "Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts", *Appl. Catal. B: Environ.*, vol. 75, pp. 312–323, 2007.
- [9] L. A. Lu, Y. S. Ma, M. Kumar and J. G. Lin, "Photo-Fenton pretreatment of carbofuran - analyses via experimental design, detoxification and biodegradability enhancement", *Sep. Purif. Technol.*, vol. 81, pp. 325–331, 2011.
- [10] A. Ozcan, Y. Sahin and M. A. Oturan, "Complete removal of the insecticide azinphosmethyl from water by the electro-Fenton method- A kinetic and mechanistic study", *Water Research*, vol. 47, pp. 1470-1479, 2013.
- [11] M. Mahalakshmi, B. Arabindoo, M. Palanichamy and V. Murugesan, "Photocatalytic degradation of carbofuran using semiconductor oxides", *J. Hazard. Mater.*, vol. 143, pp. 240–245, 2007.
- [12] F. J. Benitez, J. L. Acero and F. J. Real, "Degradation of carbofuran by using ozone, UV radiation and advanced oxidation processes" *J. Hazard. Mater.*, vol. B89, pp. 51-65, 2002.
- [13] H. Katsumata, K. Matsuba, S. Kaneco, T. Suzuki, K. Ohta and Y. Yobiko, "Degradation of carbofuran in aqueous solution by Fe(III) aquacomplexes as effective photocatalysts", *J. Photochem. Photobiol. A: Chemistry*, vol. 170, pp. 239–245, 2005.
- [14] B. Lopez-Alvarez, R. A. Torres-Palma and G. Penuela, "Solar photocatalytic treatment of carbofuran at lab and pilot scale: Effect of classical parameters, evaluation of the toxicity and analysis of organic by-products", *J. Hazard. Mater.*, vol. 191, pp. 196–203, 2011.
- [15] Y. Wang, K. Chen, L. Mo, J. Li and J. Xu, "Optimization of coagulation-flocculation process for papermaking-reconstituted tobacco slice wastewater treatment using response surface methodology", *J. Ind. Eng. Chem.*, vol. 20, pp. 391–396, 2014.
- [16] J. Wang, Y. Chen, Y. Wang, S. Yuan and H. Yu, "Optimization of the coagulation-flocculation process for pulp mill wastewater treatment using a combination of uniform design and response surface methodology", *Water research*, vol. 45, pp. 5633-5640, 2011.
- [17] R. Saini and P. Kumar, "Simultaneous removal of methyl parathion and chlorpyrifos pesticides from model wastewater using coagulation/flocculation: Central composite design", *J. Environ. Chem. Eng.*, Vol. 4, pp. 673–680, 2016.

R. Saini received the M.Tech degree from Indian Institute of Technology (Banaras Hindu University) Varanasi, India, in 2011, and pursuing Ph.D from Indian Institute of Technology (Banaras Hindu University) Varanasi, India, all degrees in Chemical Engineering.

She has two year teaching experience in Harcourt Butler Technological Institute, Kanpur, India from July 2007 to June 2009. She also worked as Assistant Professor in Mewar University, Chittorgarh, India from July 2011-April 2012. Her current research areas include environment.

P. Kumar received the Ph.D degree from Indian Institute of Technology Roorkee, India, in Chemical Engineering.

He worked as a Post doctoral fellow in University Sains Malaysia. At present he is working as an Assistant Professor in the Department of Chemical Engineering, Indian Institute of Technology (Banaras Hindu University) Varanasi, India. He is author/co-author of several national/international publications.