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Lantana trifolia ACTIVATED CARBON FOR REMOVAL OF 2-PHENOXYETHANOIC ACID: NEURAL NETWORK OPTIMIZATION APPROACH

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ABSTRACT

This study uses a low-cost *Lantana trifolia-activated* carbon and an artificial neural network (ANN) to predict wastewater having 2-phenoxyethanoic acid adsorption. To forecast 2-phenoxyethanoic acid elimination efficiency, MATLAB uses a three-layer feed-forward neural network, a Multilayer Perceptron (MLP), with backpropagation. The neural network is trained with three input parameters: 2-phenoxyethanoic acid concentration, adsorbent amount, and contact duration. Root mean square error and linear regression estimate the removal effectiveness of 2-phenoxyethanoic acid. The findings reveal that the generated ANN models for 2-phenoxyethanoic acid adsorption accurately match empirical data on pollutant removal efficacy. This suggests that low-cost *Lantana trifolia* activated carbon may be used to estimate 2-phenoxyethanoic acid absorption using the neural network technique.

Keywords: Adsorbent, 2-Phenoxyethanoic Acid, *Lantana trifolia*, Artificial Neural Network, Statistical Measures, Feed Forward Neural Network.

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INTRODUCTION

Wastewater from the chemical industry includes hazardous pollutants. Recently, the farming industry has needed various pesticides to control pests and raise crop yield and quality to meet the world's expanding food demand.[1,2] Phenoxyacetic acid (2-phenoxyethanoic acid), especially its salts or esters like 2, 4-Dichlorophenoxyacetic acid, is employed as a herbicide[3]. According to the IARC classification, 2, 4-D falls under Group 2B, indicating that it is reasonably anticipated to be a human carcinogen.[4] It's used to defoliate plants and suppress broadleaf weeds in crops. In addition to its toxicity and persistence in soil and water, 2-Phenoxyethanoic acid is a contaminant.[5] Herbicides, industrial discharges, and improper chemical waste management can release it into the environment. 2-Phenoxyethanoic acid has been studied for its implications on ecosystems and human health.[6] Studies have examined its toxicity to aquatic creatures, bioaccumulation in the food chain, and impacts on non-target organisms. 2-Phenoxyethanoic acid disinfects, anesthetizes and kills germs. It's used as animal medication. Environmental laws rank 2-phenoxyethanoic acid 11th out of 126 prioritized wastewater contaminants. It should be below 0.1 mg/L before being introduced into water sources.[7] Many 2-phenoxyethanoic acids cause cancer in small doses and it is documented.[8] The extensive usage of phenolic acidic compounds due to their elemental features - strong water miscibility, low acid dissociation constant, poor biodegradability, diminished absorptivity - requires its removal from aqueous effluents.[9] The numerous treatment techniques include ion exchange methods[10], biosorption[11], photo degradation[12], membrane separation processes[13], electrochemical processes[14], oxidation procedures[15–19], biodegradation[20], and extraction.[21] Because plant carbon compounds may adsorb various organic and inorganic substances, they are inexpensive. Bonding processes and adsorption strength depend on carbonaceous surface chemistry and adsorption solution parameters. The adsorption is improved due to the electrostatic forces, London dispersion forces, covalent bonding,

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hydrogen bonding, dipole interactions, surface area, etc., which adsorb organic molecules in activated carbon.[22]

Lantana trifolia

Lantana trifolia is also known as "Wild Sage" or "West Indian Lantana." It's a blooming Verbenaceae plant. "Thumbai" or "Kalliveli" are Tamil Nadu's names for *Lantana trifolia*. It's known for its tiny, brilliantly colored blooms and adaptability. *Lantana trifolia* (LT) is non-native in various countries, including India (Fig.-1). It may quickly spread and destroy local plants and animals.

Fig.-1: *Lantana Trifolia*

2-Phenoxyethanoic acid adsorption is best with LT plant carbon. First, plant carbon's porous nature and high surface area make it a good adsorbent for removing target compounds from aqueous solutions. This plant carbon has strong chemical stability and can resist a broad variety of pH levels, making it suitable for varied wastewater treatment situations. Using plant-based adsorbents like *Lantana trifolia* to remove 2-Phenoxyethanoic acid encourages the use of agricultural waste and the circular economy by turning a natural by-product into a useful resource.[23]

Mathematical Simulation

A proper experimental procedure is needed to examine relevant variables. The study design uses ANN and RSM. This method optimizes harmful effluent removal and generates optimal experiment modelling parameters.[24, 25] ANNs have demonstrated their capability in environmental modelling by accurately capturing the nonlinear interactions between various factors in intricate systems, such as medicines and calcium alginate beads.[26] The Central Composite Design (CCD) is a time-efficient experimental design that is part of the response surface approach. This design entails testing three levels for each element.[27] ANNs have input, output, and hidden layers, and neurons connect them.[28] RSM and ANN models use different Nanocomposite materials to remove heavy metals and dyes.[29] This study employed *Lantana trifolia* plant adsorbent (LTA) to batch-remove 2-phenoxyethanoic acid from wastewater.

EXPERIMENTAL

Preparation of 2-phenoxyethanoic Acid (PEA) as Adsorbate

Adding chloroacetic acid to phenol in the presence of sodium hydroxide and stirring it constantly at 70°C yielded 2-phenoxyethanoic acid, which was filtered and purified (Melting point, 97.5°C).

$C_6H_5OH + CH_2ClCO_2H + NaOH \rightarrow C_6H_5OCH_2CO_2H$

Preparation of *Lantana trifolia* Activated Carbon (LTAC) Adsorbent

Lantana trifolia was collected and dried for a week. The dry material was burnt without oxygen to generate charcoal. Chemical activation involved stirring charcoal with a suitable activating agent like sulphuric acid for 4 hours at 80 to 85 ^{0}C to make charcoal porous, increasing its active sites and adsorption capacity. pH was seven after three to four rinses. In an airtight container *Lantana trifolia* activated carbon (LTAC) powder was baked at 120 ^{0}C (248 degrees Fahrenheit) for eight hours.

Batch Studies to Characterise the Adsorbent and Remove 2-phenoxyethanoic Acid

The elimination of PEA by conventional adsorbents is recognized to be a costly endeavor. In the batch investigations, the pH was raised from 2.0 to 11.0 by adding 0.1M H_2SO_4. Adsorbents were introduced at concentrations ranging from 0.1 to 2.5 g, and temperatures were held constant between 20 and 60 degrees Celsius.

Experimental Design

Experimental statistics provide a foundation for conducting analysis of variance and developing regression models. Analysis input factors (Table-1) comprise the adsorbent dosage (0.1 to 1.5 g/ml), solution pH (1 to 5), starting concentration (1 to 25 ppm), and contact period (5 to 120 minutes). During optimization, the Central composite Design 20 separate trials, and their results were utilized to compute the lowest and greatest possible values.[30]

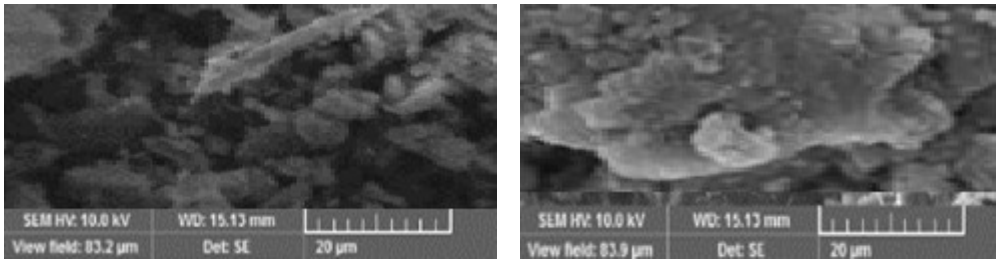
Table-1: Testing Variables

Variables		Various factor levels		
		-1	0	+1
Concentration (parts per million)	A	1	13	25
Time (mins)	B	5	62.5	120
Adsorbent dose (g/ml)	C	0.1	0.8	

RESULTS AND DISCUSSION

Morphology Studies

The plant-derived substance, unrefined adsorptive materials, and acid-processed adsorbents were examined using SEM by JOEL JSM 6360 machine at various magnifications in order to evaluate the features of each of these three types of adsorbents (Fig.-2 a and b). The image depicts a significantly porous framework, whereby subjecting it to acid treatment leads to the generation of supplementary pores, providing a visual representation of the inclusion of 2-phenoxyethanoic acid inside the LTAC. The non-uniform distribution of pores throughout the structure is apparent, with their dispersion observed across the entire system. As a consequence of the removal of organic volatiles during the adsorption process, the surface of the material will be left with enlarged pores (Fig.-3).



(a) Pre-treatment (b) Acidified carbon

Fig.-2: *Lantana trifolia*-Activated Carbon Scanning Electron Microscopy Visuals

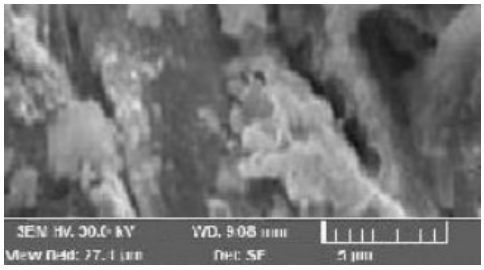
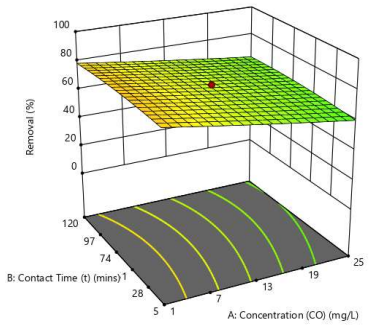
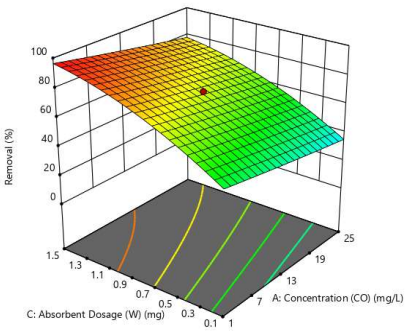


Fig.-3: PEA Adsorbed Carbon

Adsorbent Dose, Beginning Concentration, and Contact Time on 2-Phenoxyethanoic Acid Removal

As 2-phenoxyethanoic acid concentration increases, the active sites on the carbon surface interact more with it and hence the speed of adsorption at the initial time is more and later becomes constant owing to the blockage[31] of the active pores (Fig.-4). The removal of PEA is higher at 1.5 ppm of adsorbent load[21] due to more active centers on the acid-treated adsorbent and decreased at higher concentrations as shown in Fig.-5. The removal efficiency was higher for the adsorbent dosage (1 to 1.5 pm) and remained saturated over time[32] since 2-phenoxyethanoic acid entered the pores of the LTAC at a slower pace to attain equilibrium due to augmented repulsion from adsorbed herbicides making the remaining sites harder to access.





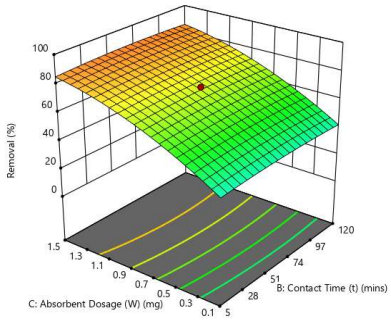


Fig.-4: PEA Removal vs Time and Concentration Fig.-5: PEA Removal vs Dosage and Concentration Fig.-6: PEA Removal vs Dosage and Time

Central Composite Design Trial Results

The results from DESIGN EXPERT experiments are in Table-2. The connection between input and output parameters is defined by a quadratic empirical equation.

$$Y= +71.52-8.52*A+0.4981*B+22.01*C+1.01*A*B-0.6025*A*C-0.0550*B*C+0.4273*A^2-1.50*B^2-6.68*C^2 \quad (1)$$

Where Y is the PEA elimination rate.

Table-2: Findings from 2-Phenoxyethanoic Acid Removal Employing Response Surface Methodology

Run	Concentration	Contact Time	Absorbent dosage	PEA removal		Relative Error
				Experimental	RSM Predicted	
1	1	5	1.5	95.39	95.475	0.09%
2	25	5	0.1	33.5	32.281	3.64%
3	13	62.5	0.8	71.43	71.518	0.12%
4	13	62.5	0.8	73.43	71.518	2.60%
5	13	62.5	0.8	73.43	71.518	2.60%
6	25	120	1.5	78.45	78.117	0.42%
7	1	120	1.5	90.95	94.338	3.72%
8	13	62.5	0.8	71.43	71.518	0.12%
9	-7.18	62.5	0.8	88.75	87.055	1.91%
10	25	5	1.5	71.67	75.206	4.93%
11	1	120	0.1	50.59	49.223	2.70%
12	13	159.2	0.8	69.32	68.124	1.72%
13	13	62.5	-0.377	15.78	15.638	0.90%
14	13	-34.2	0.8	68.32	66.449	2.74%
15	1	5	0.1	47.64	50.142	5.25%
16	33.18	62.5	0.8	59.77	58.398	2.30%
17	13	62.5	1.977	92.58	89.654	3.16%
18	13	62.5	0.8	68.43	71.518	4.51%
19	25	120	0.1	33.33	35.412	6.25%
20	13	62.5	0.8	70.43	71.518	1.54%

The Beta coefficient of the entire polynomial model is shown in Table-3. Table-4 demonstrates the outcome of ANOVA for the output to determine the model's accessibility. By employing F-value tests, the model's optimal fitness is defined, giving greater priority to the best-fit model with a higher F value. According to the thumb rule, a model parameter is considered significant if its $P < 0.05$. The selected configuration for 2-Phenoxyethanoic acid removal using the adsorbent defines the statistics based on ANOVA. The 0.9911 coefficient of regression (R^2) shows that the experimental and predicted values are well correlated as shown in Fig.-7. The closeness of the Adjacent R^2 to the coefficient of regression value suggests a higher level of agreement between the predictor variables and the response variable. The current statistical technique has

been efficiently used to investigate the impact of specific, cumulative, and contact process parameter effects. From CCD, the maximum adsorption of PEA was established to be 88.334% during the concentration of 10.84 mg/L, time 87.8 min at absorbent dosage 1.5 mg.

Table-3: Regression Coefficient Values

Regression Coefficient	Parameter estimate	P-Value
β_0	71.52	< 0.0001
β_1	-8.52	< 0.0001
β_2	0.50	0.515
β_3	22.01	< 0.0001
β_{12}	1.01	0.3183
β_{13}	-0.60	0.546
β_{23}	-0.06	0.9556
β_{11}	0.43	0.5651
β_{22}	-1.50	0.0639
β_{33}	-6.68	< 0.0001

Table-4: ANOVA Outcome Analysis

Source of Variation	Degrees of Freedom (df)	The sum of squares (ss)	Mean Square (ms)	F - Value	P – Value
Regression	9	8292.38	921.38	123.92	< 0.0001
Residual	10	74.35	7.44		
Total	19	8366.73			
R-Squared	0.9911				
Adj R-Squared	0.9831				

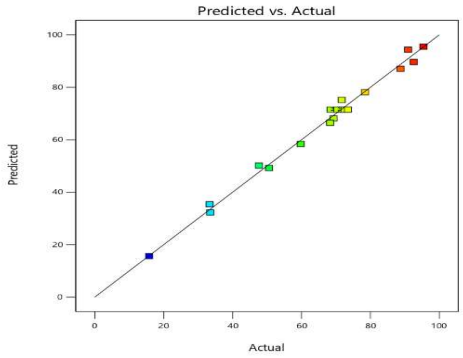


Fig.-7: Measured Values Compared to Predicted Results for the % Deletion of PEA from CCD

ANN Modelling

The adsorption mechanism is complex and non-linear, making modeling, and simulation challenging. A credible and representational model is needed to manage complexity and optimize processing parameters. ANNs simulate biological networks using artificial neurons as processing modules. Feed-forward ANN with 10 hidden layers was employed. An optimized ANN model is shown in Fig.-8. The hidden layer nodes were assigned sigmoid transfer functions, while a linear transfer function was opted for the output node. In the ANN training, the backpropagation technique was applied. The ANN model data was obtained using MATLAB software. The starting concentration of 2-phenoxyethanoic acid (over a range of 1-25 mg/L), the dosage of adsorbent (0.1-1.5 g/ml), and duration (5-120 min) were all employed as inputs to the ANN model. The outcome variable was the removal efficacy of 2-phenoxyethanoic acid. The test (15 data points) and training (5 data points) sets were both referenced to 20 experimental points. ANN topology was essential to ANN model creation due to the number of nodes in layers and transfer functions. MSE was used to count hidden layer neurons. According to MSE, the network's display was evaluated using the following equation:

$$MSE = \frac{1}{N}\sum_{i=1}^{i=N}\left(y_{i,pred} - y_{i,\exp}\right)^2 \quad (2)$$

N – number of data points, y_i, pred – predictive values, $y_{i, exp}$ – experimental values

The network achieved its lowest error when the hidden layer had at least 10 nodes, as seen in Fig.-8. A single-layer neural network with 10 hidden neurons and backpropagation was used to simulate the process, aiming for a modest MSE.

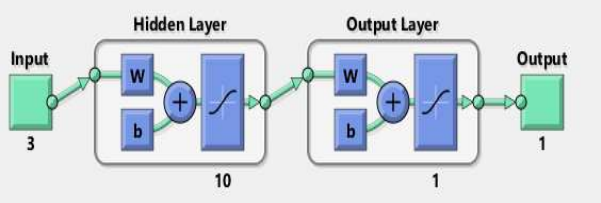


Fig.-8: ANN Structure

Table-5: Predicted Results of PEA Removal

Expt. No.	PEA Removal		% Deviation
	Experimental Values	Predicted Values	
1	95.39	95.42	0.03%
2	33.5	32.38	3.34%
3	71.43	71.49	0.08%
4	73.43	71.49	2.64%
5	73.43	71.49	2.64%
6	78.45	78.12	0.42%
7	90.95	94.36	3.75%
8	71.43	71.49	0.08%
9	88.75	87.06	1.90%
10	71.67	71.55	0.17%
11	50.59	49.24	2.67%
12	69.32	68.13	1.72%
13	15.78	15.64	0.89%
14	68.32	66.47	2.71%
15	47.64	48.15	1.07%
16	59.77	58.41	2.28%
17	92.58	89.68	3.13%
18	68.43	71.49	4.47%
19	33.33	34.46	3.39%
20	70.43	71.49	1.51%

The performance of evaluation was predicted by means of the MSE and is shown in Fig.-9. The weights are frozen after the training is completed, and the model is validated. The network is validated in this study based on how well it agrees with experimental results. The learning rate (η) was 0.95 and momentum (μ) was set to 0.5.

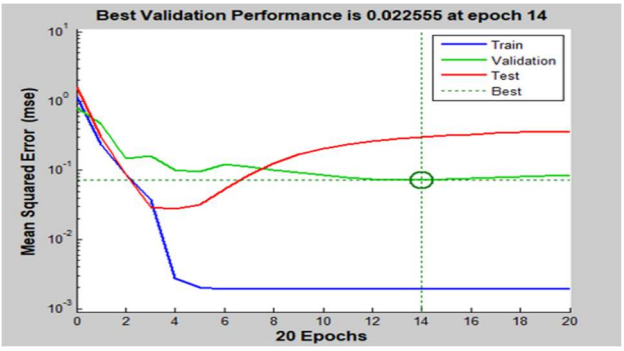


Fig.-9: Mean Squared Error

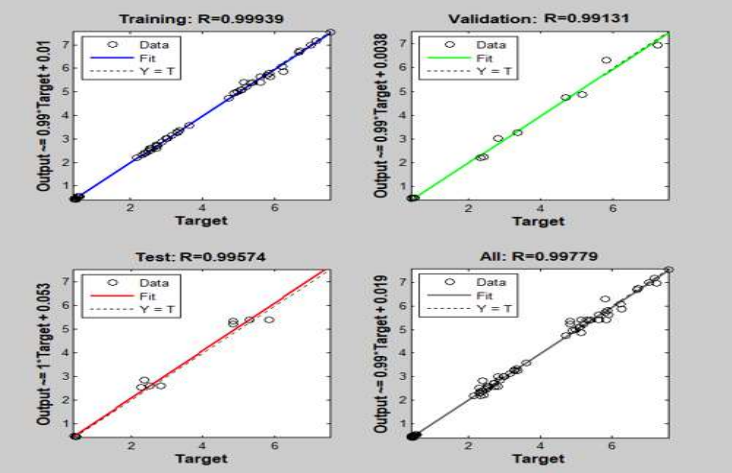


Fig.-10: Regression Co-efficient

For each input, the predicted value and respective experimentally measured value of the kerf width were compared, and the percentage deviation was found by the formula

$$\%\, Deviation = \frac{Experimental\, Value - ANN\, Predicted\, Value}{Experimental\, Value} \times 100 \qquad (3)$$

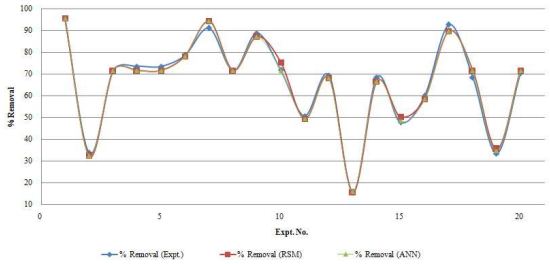


Fig.-11: Experimental and ANN-Predicted Removal Values of 2-Phenoxyethanoic Acid

In Fig.-11, the deviation between the experimental observations and the anticipated 2-phenoxyethanoic acid removal levels, as projected by the ANN, is visually depicted. The correlation coefficient between observed and predicted values is 0.90599, and the error percentage is less than 1% in all trials and approaching zero in some. The modeling seemed promising as the average error rate was 1.94 percent and several research had error percentages close to zero. The successful elimination of 2-phenoxyethanoic acid was achieved by the ANN model, which integrated three input variables: starting strength, time, and adsorbent dose.

CONCLUSION

The ideal process parameters for the greatest percent (%) removal of 2-phenoxyethanoic acid utilizing the adsorbent were established by both CCD in RSM and ANN. The Central Composite Design model, which had a regression coefficient (R^2) of 0.9831, was shown to be an efficient way to save time when examining the interactions among process elements on response. It was established that the greatest adsorption of PEA was established to be 88.334% during the concentration of 10.84 mg/L, time 87.8 min at an adsorbent dosage of 1.5 mg. This allowed for the greatest amount of adsorption that was predicted. A neural network with ten hidden layers, three inputs, and one output was trained using backpropagation to predict the elimination percentage of 2-phenoxyethanoic acid.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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