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Artificial neural network and response surface design for modeling the competitive biosorption of pentachlorophenol and 2,4,6-trichlorophenol to Canna indica L and analyzed by UV-Vis spectrometry in Aquaponia

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ABSTRACT

The continuous exposure of the environment to carcinogenic wastes and toxic chlorophenols such as pentachlorophenol (PCP) and 2,4,6-trichlorophenol (TCP) resulting from industrial production activities has become a great concern to research scientists and environmental policymakers. The search for a cost-efficient and eco-friendly approach to the phytoremediation of water will guarantee sustainability. The present research concerns the cost-benefit evaluation and the optimization modeling of the competitive biosorption of PCP and TCP from aqueous solution to Cana indica. L (CiL-plant) using response surface methodology (RSM) , artificial neural network (ANN) model, and UV-Vis Spectrometry. The predictive performances of the ANN model and the RSM were compared based on their statistical metrics. The antagonistic and synergetic effects of significant biosorption variables (pH, initial concentration, and exposure time) on biosorption were studied at p-values $\leq$0.005. The findings from the phytoremediation process confirmed that PCP and TCP removal rate reached equilibrium at the optimum conditions corresponding to predominantly acidic pH (4), required initial concentration of 50 mg L^{-1}, and exposure time of 25 days in aquaponia. The optimized output transcends to PCP and TCP removal rates of 90% and 87.99% efficiencies at predicted r-squared $\leq$0.9999 and a 95% confidence interval. The cost-benefit evaluation established that at the optimum conditions, the cost of operating the removal of TCP from the aqueous solution would save $ 7.72 compared to PCP. The optimization model's reliability based on the experiment's (DoE) design was more sustainable than the one-factor-at-a-time (OFAT) methodologies reported in previous research.

1. Introduction

Chlorinated phenols, such as Pentachlorophenol (PCP) and 2,4,6-Trichlorophenol (TCP), have been used since the 1930s in a variety of industries including wood preservation, pest control, and herbicide production [1,2]. As a result, wastewater from these industries can contain high levels of

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these chemicals, leading to the pollution of water resources and potential harm to ecosystems [3]. The use of pesticides on farms is a significant contributor to the contamination of water resources with chlorinated compounds. studies have shown the presence of significant amounts of organochlorines in water and fish samples [4,5,6]. TCP and PCP are classified as Group B2 probable human carcinogens and 1B highly hazardous; due to their high toxicity, carcinogenic potential, and environmental persistence [1,2]. These chemicals can cause serious health issues such as respiratory problems, cardiovascular disease, gastrointestinal issues, and cancer in humans and have been linked to an increased risk of lymphomas, leukemia, and liver cancer in animal studies [1,2]. Removing these chemicals from water resources or wastewater before they are released into the environment is essential to prevent potential harm to humans and ecosystems. Various methods are available for removing PCP and TCP from water, including biological and physicochemical approaches such as photochemistry, air stripping, incineration, and adsorption technologies using activated clay and plant-based carbons [7]. While some of these methods are effective, they can be challenging to implement. Using aquatic plants for wastewater treatment is a newer method for removing pollutants, and studies have shown that it can be effective when using constructed wetlands, pilot-scale systems, or hydroponic setups [7]. The efficiency of plant-based treatment systems can vary depending on the specific plant species and their productivity. In Nigeria and other tropical countries, various plants effectively remove pollutants from water. Canna lilies, a type of flowering plant, are a commonly used species for this purpose in Nigeria due to their wide distribution and dominance in aquatic environments. Additionally, canna lilies can effectively remove inorganic and organic pollutants such as PCP and TCP through phytoremediation [8-11] and can survive in polluted areas [12]. Central composite design and response surface methodology are statistical approaches used in pollutant removal studies to design experiments and optimize treatment conditions [13]. They allow selecting the most effective experimental conditions through statistical software, reducing the number of costly experiments and trials needed [14]. These methods have been applied to various processes, including coagulation to remove dyes from wastewater [15,16]. They can be helpful in predicting the behavior and outcomes of treatment systems and analyzing existing processes. Artificial neural networks (ANN), which utilize learning algorithms to evaluate the relationships between input and output variables, can also be used to model and predict the behavior of water management processes [17, 18]. While artificial neural networks require many data points to be effective, they are fast, adaptable, and can produce real-time predictions [18]. Both response surface methodology and artificial neural networks have been compared in their predictive capabilities for various processes [17]. This study examined the effectiveness of using *C. indica* L (CiL-plant), an aquatic plant, to remove PCP and TCP from water using response surface methodology and artificial neural networks. The use of aquatic plants for wastewater treatment, specifically for removing organic pollutants such as chlorophenols, is a relatively new method known as aquatic phytoremediation. This study aims to optimize the ability of C. indica to remove PCP and TCP from water using a hydroponic system, and to the best of our knowledge, is the first study of its kind. Furthermore, the removal behavior of C. indica for PCP and TCP has been predicted for the first time by a highly efficient developed ANN model. A techno-economic and cost-benefit evaluation of the phytoremediation process was also examined beyond removal efficiency to ascertain the suitability of the CiL-plant for Aquaponia.

2. Materials and methods

2.1. Preparation of plant material and pesticides solutions

We discussed how the plant material and pesticide solutions were manufactured in our earlier papers [8-10]. In a flood basin in Amakohia, Owerri, Imo state, Nigeria, Canna indica L. seeds and soil for growing the plant were collected. The plant was raised in nurseries with natural environmental conditions. To conduct the study, properly harvested seedlings with an average height of (14±1 cm) were employed. Without additional refinement, the PCP and TCP (analytical grade, 99.5%) was used after being acquired from FinLab in Owerri. Distilled water and ethanol were used to make the solutions for this experiment. An ethanol-water solution (10% v/v ethanol/distilled water) was used to dissolve 1.0 g of PCP/TCP per liter of solution in a 1.0 liter-volumetric flask while stirring continuously. The stock had a 1000 mg L^{-1} equivalent. By dilutions with distilled water, working solutions of 50, 100, 150, 200, and 250 mg L^{-1} were produced from the stock solution and labeled accordingly. Working solutions were made, and absorbance was measured at 220 nm for PCP and 296 nm for TCP using a UV spectrophotometer. The calibration curve (concentration vs. absorbance) was created using the recorded absorbance, and it was then utilized to calculate the amounts of PCP and TCP. With coefficients of determination more than 0.9995, the absorbance for PCP and TCP starting concentrations rose as the initial concentration increased. This indicates strong linearity of the regression line with good correlation, consequently, and satisfaction of the instrument calibration.

2.2. Batch studies

Uptake of PCP and TCP by *C. indica L.* in pesticide-contaminated water was studied in batch culture experiment using hydroponic, cylindrical (pots) containers with dimensions 18 cm in length, 37 cm in diameter (external) and 19 cm depth [9, 10]. The containers were filled with 500 mL working solutions. Then the plant was introduced into the solution and allowed to stand. This was done for four other pots, representing different time durations (i.e., 10 days, 15 days, 20 days, and 25 days). In total, 5 pots were prepared and at each interval of 5 days a plant was removed and the residue was analyzed by UV-vis spectrophotometer at 220 nm for PCP and 296 nm for TCP [9, 10]. The effect of pH on the removal of PCP and TCP by *C. indica* was determined in 500 mL of test solutions containing 100 mg L^{-1} of PCP and TCP at different pH (4- 9). 1 M nitric acid (HNO_3) and 1 M sodium hydroxide (NaOH) were used for pH adjustments. The pH of each solution was measured with a digital pH meter (Model Jenway 3510). The initial and final concentrations of PCP and TCP solutions were determined on a UV–visible spectrophotometer (Spectrum Lab 23A) at its maximum absorbance wavelength of 220 nm and 296 nm, respectively. All set-ups were conducted in triplicate (total pots were 80 for batch studies, including control and 90 for pH effect), each for PCP and TCP, and were placed randomly with position shifted once a week. After one week, all set-ups were supplemented with N.P.K. fertilizers (1%, i.e., 5 ml: 500 ml). For each treatment method mentioned, there was a corresponding control group that only consisted of deionized water; no pesticide was added, and only the nutrient needed for plant growth in water was provided.

2.3. Response surface design of Experiment

The Central Composite Design (CCD) is an empirical model used for multi-objective optimization of the adsorption or bio-sorption of microplastics from an aqueous solution [19,20]. The CCD optimization is based on the Response Surface Methodology (RSM) [15]. It is used to access and fit experimental data into a linear, cubic, quadratic, cubic, or polynomial model [21]. The model coefficients developed via the RSM can establish an optimal model equation and describe the antagonistic or synergetic interactions and relationship of experimental variables and their significance level with the response within the range studied [13]. In this study, the CCD matrices consisted of 20 experimental runs. The modeling of the bio-sorption of PCP and TCP to CiL-plant (Canna indica L.) in terms of actual values is shown in Table 1. The final model equation following the prediction of the optimum conditions for bio-sorption (pH, initial concentration, and time) for the removal of PCP and TCP is described by Equation 1.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} {x_i}^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon$$

(Eq.1)

Where x_{ij} experimental variable and β are ranked model coefficients, the summation symbols signify the interactive effect of the dependent and independent variables (pH, time, and concentration), ε is the model intercept, and Y is the response (PCP and TCP removal rate). The optimization modeling of the biosorption of TCP and PCP to the CIL plant was executed using Design Expert software v12.0. The experimental variables contact time (A) (days), initial concentration (B) (mg L^{-1}), and pH (C) shown in Table 1 were varied to 3-Levels with 5 replications. The toxicity was modeled following the CCD matrix. The initial concentration of the biosorbent and the contact time was varied to 5-Levels at an experimentally determined pH of 4.

2.4. Artificial Neural Network

Aside from RSM modeling, data modeling via artificial intelligence tools such as the artificial neural network (ANN) was implemented in this study to create a better understanding of the model validation of the bioremediation process. The neural network tool in MatLab 2018a was used to model the CiL-plant biosorption process. As input data, the experimental data set obtained from the experimental design supplied by CCD space (Table 2) via the RSM was employed. The network was trained using the Multi-Layer Perceptron (MLP) Levenberg-Marquardt (LM) method (*trainlm*) to fit the inputs and targets. The network was made up of the input layer (which included the five process parameters: time, concentration, and pH), neurons (the hidden layer), and the output layer (which contained the PCP or TCP removal efficiency, expressed in %) (Fig. 1). The input data with 20 samples were divided randomly (*dividrand*) into a training set (75%-14 points), validation (15%-3 points) and testing sets (15%-3 points). Based on R^2 and mean square error values, the ideal number of hidden layer neurons was determined by trial and error. More data for training decreases processing time and improves the model; testing provides an impartial evaluation of the network's performance. The training was stopped when the network generalization was improved indicated by the increase in MSE error of the validation samples. To eliminate network error, the input and output variables were normalized between 0 and 1 [17].

2.5. Cost estimation theory for the biosorption process

The techno-economic evaluation of the CiL-plant-driven bioremediation of the comparative removal of PCP and TCP from an aqueous solution was determined following the established cost-benefit analysis model [15]. The cost benefit and alternative cost models were used to describe the feasibility of CiL-plant biosorption of PCP and TCP beyond removal efficiency following the model equation described in Equations 2-5. The total cost for the biosorption of PCP, and TCP from 1.0 L of the aqueous solution to CiL-plant at optimum operating conditions was evaluated using

Table 1. Showing experimental factors in terms of coded values

Factor	Name	Units	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	Time	Days	5.00	25.00	-1 ↔ 5.00	+1 ↔ 25.00	14.50	8.87
B	Conc	mgL^{-1}	50.00	250.00	-1 ↔ 50.00	+1 ↔ 250.00	122.50	67.81
C	pH		4.00	9.00	-1 ↔ 4.00	+1 ↔ 9.00	5.85	2.06

Table 2. Design matrix in terms of actual and predicted values for the RSM and ANN optimization process

Factors					Response 1: %PCP Removal Efficiency			Response 1: %TCP Removal Efficiency		
Std	Run	A: Time (Days)	B: Concentration (mg L^{-1})	C: pH	Actual	RSM predicted values	ANN predicted values	Actual	RSM predicted values	ANN predicted values
11	1	25	250	4	78.31	77.91	78.04	78.74	78.70	78.76
14	2	15	100	6	52.70	54.81	52.64	66.19	64.97	61.62
18	3	5	100	9	7.56	12.20	7.56	4.81	8.34	5.78
8	4	5	100	6	50.37	33.52	50.32	32.33	21.30	31.17
16	5	25	100	4	82.00	77.11	81.96	85.71	81.89	85.75
13	6	15	100	9	36.33	27.88	36.33	52.29	33.60	48.70
1	7	5	50	4	34.64	35.65	34.6	9.04	9.15	9.07
17	8	25	100	9	49.26	48..85	49.19	53.00	53.81	52.85
10	9	15	100	6	52.70	54.81	52.64	66.19	64.97	61.62
12	10	25	100	6	73.00	81.40	76.81	81.05	83.45	80.53
3	11	15	100	6	52.70	54.81	52.64	52.70	64.97	61.62
15	12	5	250	4	13.24	13.58	12.71	3.85	3.89	3.81
2	13	25	50	4	90.00	87.99	85.37	82.09	81.87	82.18
7	14	5	100	9	7.56	12.20	7.56	4.81	8.31	5.78
9	15	5	100	4	16.86	21.75	27.52	5.00	8.73	2.12
6	16	15	100	6	52.70	54.81	52.64	66.19	64.97	61.62
4	17	5	250	4	13.24	13.58	12.71	3.85	3.89	3.81
19	18	25	100	9	49.26	48..85	49.19	53.00	53.81	52.85
5	19	5	50	4	34.64	35.65	34.60	9.04	9.049.15	9.07
20	20	25	250	4	78.31	77.97	78.04	78.74	78.70	78.76

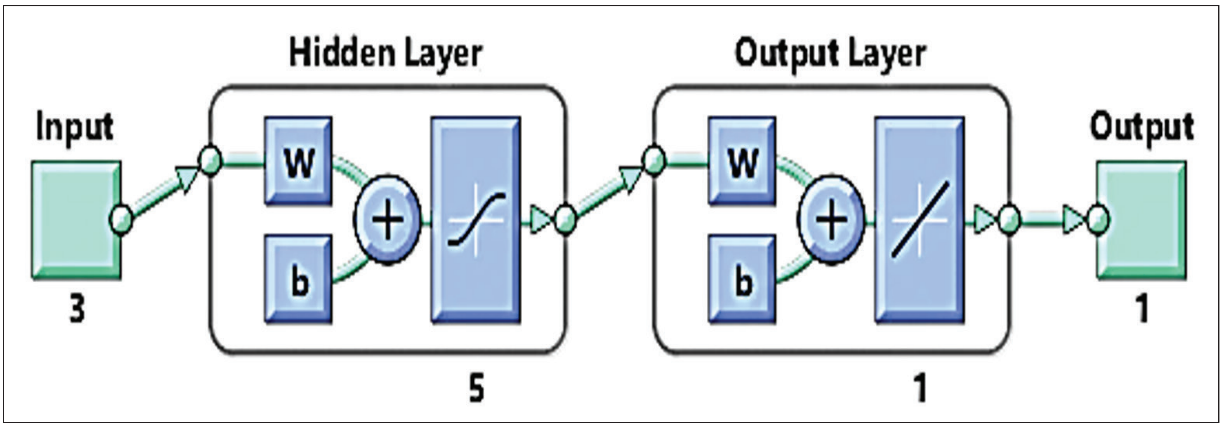


Fig. 1. ANN network of the PCP and TCP optimization sequence

the expression shown in Equation 3**.** The energy consumption (*EC*) was evaluated using Equation 2 [15, 23]. and given by:

$$E_C = P_C(f \times t \times C) \qquad \textbf{(Eq.2)}$$

Where P_C is the power consumption by the device (kW), f is the load factor. In a full mode, f =1, t is the time of usage of the device (hour), and C is the energy estimated cost ($) per (KWh) in Nigeria as of the month of April 9, 2021.

Total cost is a function of all costs, including biosorbent production, labour, and energy. C_m is the costs incurred from transportation, and renting [24].

$$T_C = C_P + C_L + C_m \quad \textbf{(Eq.3)}$$

$$C_B = F_O - C_O \quad \textbf{(Eq.4)}$$

Where F_O is the return on the selected and forgone option (PCP versus TCP), in this case, it's the performance of CiL-plant for the bioremediation of aqueous medium and C_O is the return on chosen option from PCP versus TCP, and C_B is the opportunity cost based derived based on environmental impact and regulatory risk (Eq. 4). In this case, the return on chosen option which defines the return on investment as a function of direct and indirect cost [15]. The parameter F_0 was evaluated following modified model Equation 5, expressed as:

$$F_0 = T_C + E_C + M_c \quad \textbf{(Eq.5)}$$

3. Result and Discussion

In our previous studies [8-10], the results for the removal of PCP and TCP have been presented. This current study is a step further in which removal processes are optimized and predicted using RSM and ANN, respectively, to determine the optimum operating variable for modeling the performance CiL-plant-driven bioremediation process. Furthermore, the techno-economic and cost-benefit analysis for the method was evaluated in the current study to ascertain the feasibility of the CiL-driven bioremediation of PCP and TCP in aquaponia beyond removal efficiency.

3.1. Central composite design modeling of the CiL-driven biosorption process

The findings from the CCD optimization modeling following the biosorption of PCP and TCP to CIL-plant from an aqueous solution follow a second-order quadratic model shown in the ANOVA (Tables 3 and 4). Tables 3 and 4 showed that the selected quadratic model recorded consistent outputs from the CCD that adequately describes the CiL-plant-driven biosorption of PCP and TCP from an aqueous solution. It was observed that model f-values PCP (30.55) and TCP (62.75) obtained a lack-of-fit value >3 recorded at a p-value less than 0.05. This statistical output indicates that there is only a 0.01% chance that f-values this large could occur in the optimization modeling of the phytoremediation process variables due to noise [19, 24]. A p-value $\leq$ 0.0500 obtained with the CCD space suggests that the quadratic model terms and subsequent assumptions on the phytoremediation process are significant at a 95% confidence level. The statistical output also suggests that the quadratic model results significantly describe the CiL-plant-driven biosorption of PCP and TCP from an aqueous medium [21]. The model fit statistics that describe the removal of PCP from the aqueous medium established that the predicted R^2 (0.8322), adjusted R^2 (0.9256), is in reasonable agreement with the correlation coefficient R^2 (0.9256) recorded from the central composite design space. Similarly, the model predicted R^2 (0.9329) was also in reasonable agreement with the adjusted R^2 (0.9630) reported for the CiL-plant biosorption of TCP from an aqueous solution. These r-squared values are close to unity (1), and their differences are less than 0.2, indicating that the selected quadratic model description of the CiL-plant-driven phytoremediation process is significant at a 95% confidence level [19, 21, 22]. However, where the adequacy of precision output >4 is desirable [15], the selected quadratic model recorded adequacy of precision (16.11) value measures the signal-to-noise ratio (16.11), and the model f-value (5.36) can be used to navigate design space for modeling the PCP removal rate [24]. The adequacy of precision (19.41), and signal ratio (19.41) recorded for the TCP biosorption modeling were > 4, confirming that the quadratic model following the design space adequately describes the modeling of the biosorption of PCP and TCP to CiL-plant. Few insignificant model terms are reported with the central composite design space, not counting those required to support hierarchy. Regarding PCP removal rate, the first-order phytoremediation variables such as; contact time, pH, and initial concentration, and the second-order degree of pH $(C)^2$ are significant model terms. This outcome indicated that contact time (A), initial concentration of CiL-plant (B), and pH (C) all have a significant antagonistic influence on CiL-plant biosorption of PCP from aqueous solution. The pH also has a second-order degree of significant impact on removing PCP from aqueous solution compliance to CiL-plant at p-values <0.100 [15]. The statistical outcome suggests model reduction was negligible, and the interactive effect of model factors A*B, and A*C which transcends to contact time*concentration (A*B), and contact time*pH (A*C) both have synergetic effects on the biosorption of PCP to Canna indica. L (CiL-plant) in the combined system. Comparatively, the quadratic model statistics and assumptions describing the CiL-plant-driven TCP removal rate established that contact time (A) and pH (C) of solution significantly affect on the phytoremediation process. However, the interactive effect of contact time*pH of solution (A*C) had a synergetic effect on the TCP removal from the aqueous solution. Also, the model assumption established that a higher order degree of contact time (A^2) and pH (C^2) are significant model terms for TCP biosorption to Canna indica L. (CiL-plant). This translates to both model terms having an antagonistic first and second-order impact on TCP biosorption to CiL-plant. The contact time-initial concentration (A*B) has a synergetic effect on the biosorption of TCP and PCP to *Canna indica* L. Consequently, the selected model assumption proved that sufficient contact time and optimized initial concentration of samples are consequential to the overall performance of CiL-plant in Aquaponia. The results from model fit statistics following the established design space also showed that the coefficient of estimate representing the expected change in TCP and PCP removal efficiency per unit change in the values of significant phytoremediation variables when non-significant factors are held constant [21] confirmed the range of variance inflation factors (VIFs) values (-2.91≤ VIFs ≤ 8.27) were recorded for the CiL-plant driven biosorption of PCP from aqueous solution. This range of VIFs output (1.22 ≤ VIFs ≤ 3.27) is consistent with the removal rate of TCP from an aqueous solution. The model-established VIFs outputs fell within the range 1≥ VIFs <10, suggesting that the intercept in an orthogonal design [17], while model coefficients are adjustments around that average based on the significant factors describing the efficacy of CiL-plant. The factors are orthogonal when the VIFs are equal to a unit (1); there is a situation of multi-collinearity at VIFs outputs >1 [17]. The moderate VIFs recorded with the CCD indicate a negligible level of severity of the correlation of factors [21]. Consequently, the VIFs <10 recorded for PCP and TCP are tolerable. The summary based on the VIFs obtained via the established quadratic model, the subsequent model hierarchy based on the level significance of the experimental factors following the biosorption of PCP, and TCP to Canna indica L. (CiL-plant) from an aqueous solution follows the Table order.

The established quadratic model equations describing the biosorption of PCP, and TCP to Canna indica L were obtained from the CCD optimization outputs. The outcome showed that the final model equation for the PCP removal rate is given by Equation 6, and the TCP removal rate is described by Equation 7.

*PCP ↔↔ Contact time > Initial Concentration > pH > Time*pH > Time*Initial Concentration*
*TCP ↔↔ Contact time > Initial Concentration > pH > Time*pH > Time*Initial Concentration*

$$Y_{PCP} = 47 + 25Time - 8Conc - 10pH + 3Time * Conc - 5Time * pH - 16pH^2 \quad \text{(Eq. 6)}$$

$$Y_{TCP} = 63 + 30Time - 7pH - 7Time * pH - 13Time^2 - 13pH^2 \quad \text{(Eq. 7)}$$

Table 3. ANOVA for the Quadratic modeling of PCP biosorption to CiL-plant

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	12028.39	8	1503.55	30.55	< 0.0001	**Significant**
A-Time	6707.47	1	6707.47	136.28	< 0.0001	
B-Concentration	421.62	1	421.62	8.57	0.0138	
C-pH	497.35	1	497.35	10.11	0.0088	
AB	66.62	1	66.62	1.35	0.2693	
AC	215.55	1	215.55	4.38	0.0604	
A^2	14.93	1	14.93	0.3034	0.5928	
B^2	97.68	1	97.68	1.98	0.1865	
C^2	450.18	1	450.18	9.15	0.0116	
Residual	541.40	11	49.22			
Lack of Fit	541.40	3	180.47			**Not significant**
Pure Error	0.0000	8	0.0000			
Cor Total	12569.79	19				

Pred R^2 = 0.832; Adj R^2 = 0.9256; R^2 =0.9565; stdv = 7.02; Adeq of Precision =16.105 and Mean value =46.27

Table 4. Showing ANOVA for Quadratic modeling of the TCP biosorption to CiL-plant

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	18743.53	8	2342.94	62.75	< 0.0001	**Significant**
A-Time	10015.46	1	10015.46	268.24	< 0.0001	
B-Concentration	29.10	1	29.10	0.7794	0.3962	
C-pH	284.22	1	284.22	7.61	0.0186	
AB	2.02	1	2.02	0.0540	0.8205	
AC	473.96	1	473.96	12.69	0.0045	
A^2	338.64	1	338.64	9.07	0.0118	
B^2	1.12	1	1.12	0.0301	0.8654	
C^2	300.46	1	300.46	8.05	0.0162	
Residual	410.71	11	37.34			
Lack of Fit	274.23	3	91.41	5.36	0.0257	**Not significant**
Pure Error	136.49	8	17.06			
Cor Total	19154.25	19				

Pred R^2 = 0.9329; Adj R^2 = 0.9630; R^2 =0.9786; stdv = 7.02; Adeq of Precision =19.41 and Mean value =44.43

3.2 Optimization outputs following the CiL-plant-driven biosorption process

The interpretation of the CiL-plant-driven biosorption of PCP, and TCP from an aqueous solution follows from the established model Equations 6-7. The results based on the interpretation of the optimization ramp (Fig. 2) confirmed that the optimum comparative conditions describing the best performance of the CiL-plant-driven biosorption of PCP and TCP from an aqueous solution correspond to pH (4), initial concentration (50 mg L^{-1}), and contact time (25 days). The predicted optimum based on the quadratic model output is confirmed from the optimization ramp shown in Figure 2. The predicted optimum outputs translate to a removal efficiency of 87.88 %, and 81.87 % for the biosorption of PCP, and TCP to CiL-plant as indicated in the optimization ramp in Figure 2. The optimum points transcend to a standard deviation of PCP (7.01), and TCP (6.80) from the actual observations practicable. The outcome is represented by the flag points shown on the 3-D plots in Figure 3 (a-b). The flag points confirmed that the predicted optimum points are located within the CCD design space [17, 24], and maintained within the range of the experimental values under investigation.

The predicted optimum indicates that the best biosorption of PCP, and TCP occurred via an active initial concentration of 50 mg L^{-1} of Canna indica L. plant. The phytoremediation progressed in a predominantly acidic medium (pH 4), and requires sufficient contact time (25 days) to drive the biosorption of PCP, and TCP to lower residual that guarantees sustainability. The optimization results established that under similar optimum operating conditions, the comparative biosorption rate of PCP to CiL-plant was most favorable compared to TCP with a significant difference of ≥6%.

3.3 Artificial neural network performance validation of the CiL-driven biosorption process

The validation performance in Figures 4 (a-b) shows how the number of epochs varied with the MSE for the optimal neural network. The best validation performance was 4.8753 and 2.8482 at epoch 3 for PCP and TCP biosorption. The scatter plots depicting the linearity of the output values of the network with the target values for the training, testing, validation, and overall data (as generated

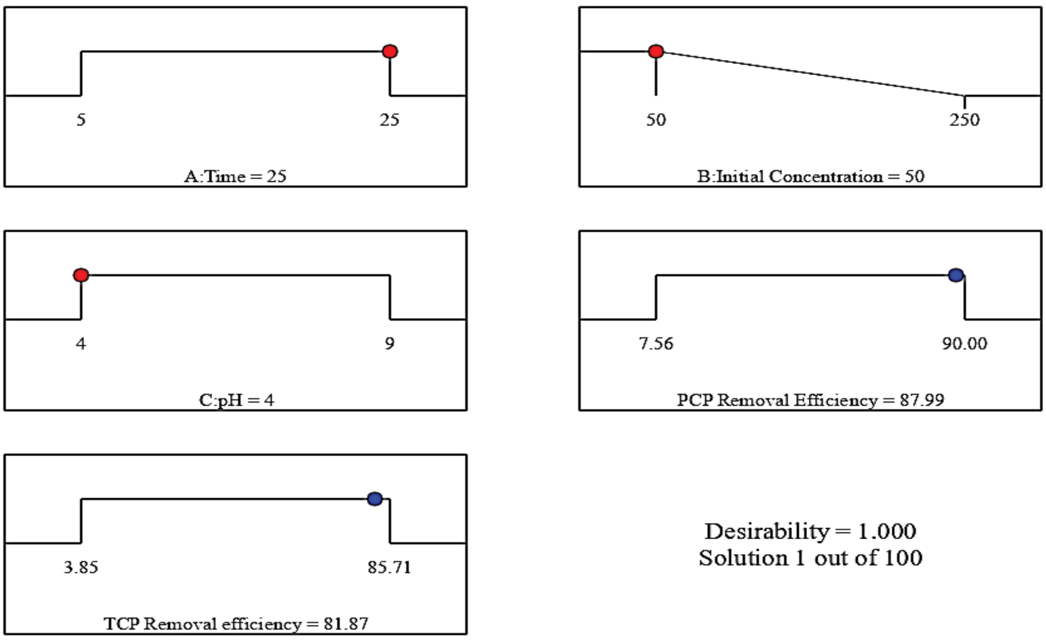


Fig 2. Optimization ramp for CiL-plant driven biosorption of PCP and TCP

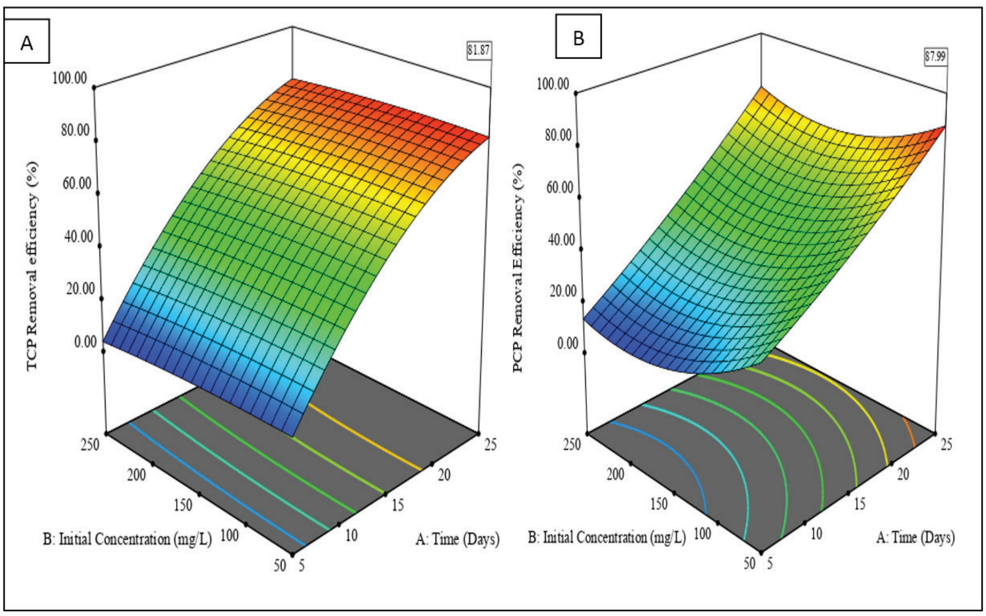


Fig. 3. 3D surfaces for the removal efficiency at different times and concentrations for (a) TCP and (b) PCP

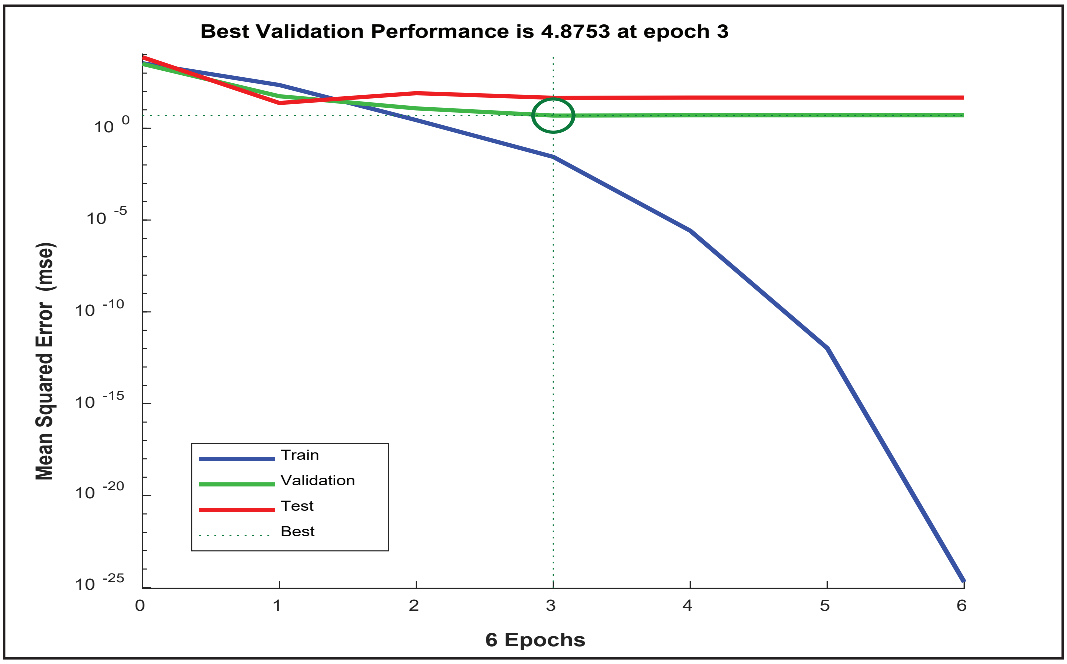
by the MLP platform) are illustrated in Figures 5 (a, b). The predicted R^2 values were used to indicate the linearity – with the training network having the highest value of 0.9999 and 0.9945 for the optimal neural network for PCP and TCP biosorption, respectively. The outputs design matrix in Table 2 (presented in section 2.4 above) displayed the anticipated responses at various experimental setups. It can be concluded from the outline of Figure 4 that the summary of the statistical and evaluation metrics from the ANN indicates an increase in model errors as the number of epochs increased. This outcome reasonably agrees with the optimization modeling procedure reported in the literature [16, 27]. The train and validation curves' curvature indicates that overfitting has been greatly minimized [27].

The performance of each model (ANN and RSM) was validated by evaluating their prediction accuracy using statistical tools (MSE, RSME, X^2 and SSE) [27, 28]. The mathematical equations representing the statistical tools are summarized in Table 5. A better predictive model has a high R^2 value (almost 1) and low statistical errors (close to 0) [11, 12]. The high R^2 values and statistical errors proved a good correlation with the actual observations practicable than the RSM. When compared to the RSM, the ANN outputs yielded significant statistics performance with minimal error (R^2 ≤0.9945, RMSE≤0.06, and X^2 ≤0.0001). The low statistical error indicates reliable adequacy of precession [25, 26], suggesting minimal error due to noise [27]. However, the statistical outcome from both optimization tools is in reasonable agreement with the actual values obtained from the experimentation with the RSM output indicating a ±0.005 deviation from the ANN output. The RSM performance evaluation has the benefit of providing a prediction equation, and demonstrating the influence of operational parameters and their interactions on the response [18]. The statistical model assumptions of the RSM have been ascertained for reliability, and the design space (CCD) has been tested based on the design of experiments (DoE). As a result, the predicted optimum reported for the RSM was employed to further optimize the CiL-plant driven biosorption process.

Table 5. Summary of the optimization fit statistics and errors factor

Error factor	Equation	RSM	ANN
MSE	$MSE = \frac{1}{N}\sum_{i=1}^{N}(y_i - y_i^*)^2$	0.0080	0.0036
RMSE	$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(y_i - y_i^*)^2}$	0.0894	0.0604
X^2	$X^2 = \sum_{i=1}^{N}\frac{(y_i - y_i^*)^2}{y_i^*}$	2.8478	0.0001
SSE	$SSE = \sum_{i=1}^{N}(y_i - y_i^*)^2$	0.1600	0.0729
Predicted R^2		0.9329	0.9954

Where yi, yi*, and y_m stand for the experimental, predicted, and mean value of the actual responses, *N* represents the number of experimental outcomes; MSE: mean squared error, RMSE: root mean square error, X^2: Chi-square and SSE: sum of squares errors



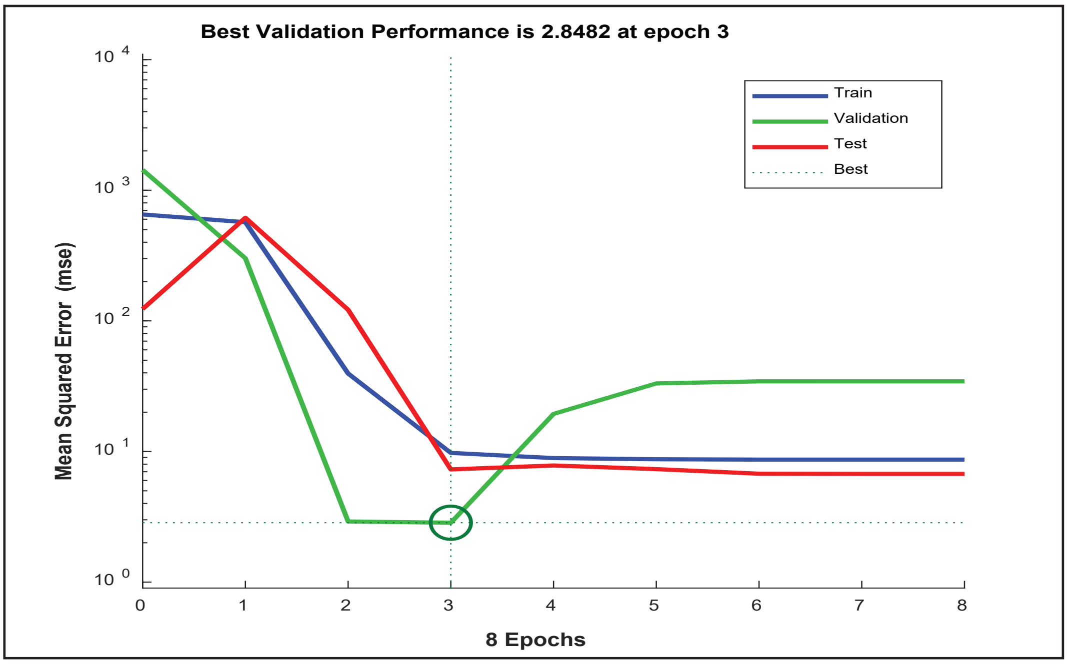


Fig. 4. Optimal neural network's validation performance graph for the **(a)** PCP, and **(b)** TCP biosorption processes

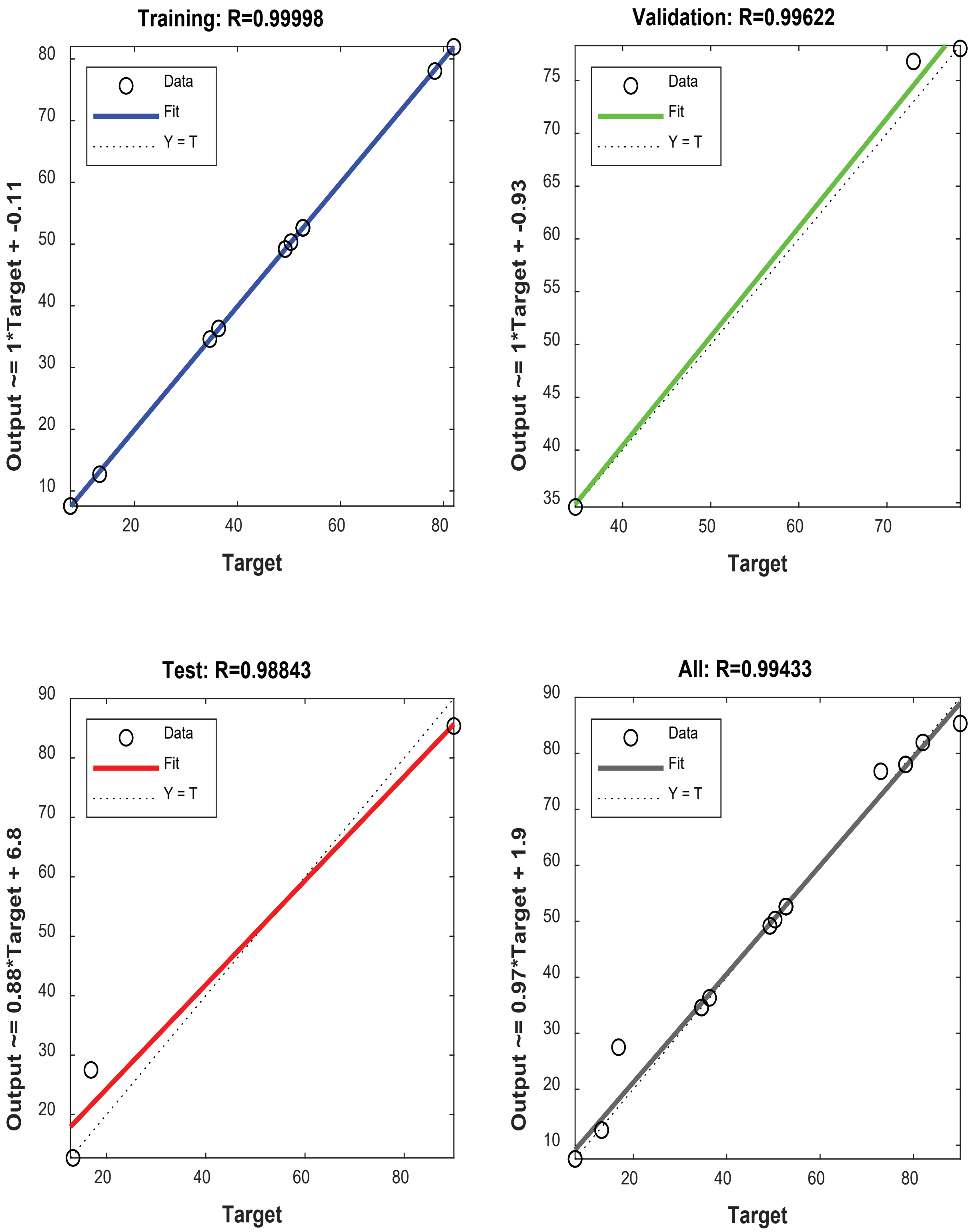


Fig. 5(a). The output/target values for the PCP biosorption processes' training, testing, validation, and overall data

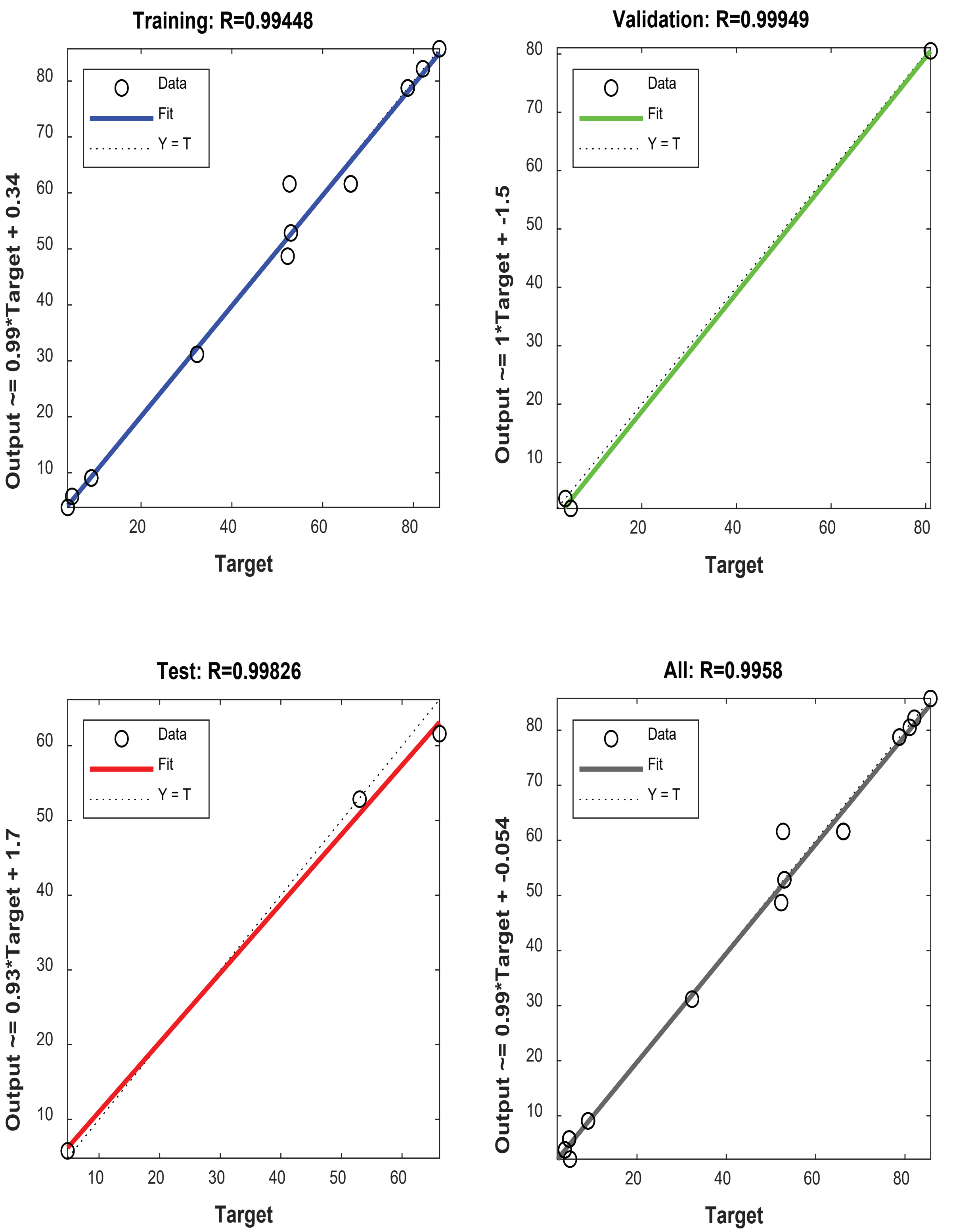


Fig. 5(b). The output/target values for the TCP biosorption processes' training, testing, validation, and overall data

3.4 Effects of experimental variables on the overall performance of the CiL-plant

The effects of the phytoremediation variables on the CiL-plant driven biosorption of PCP, and TCP from an aqueous solution were based on the CCD statistics (VIFs), and model hierarchy model parameters shown in section 3.1. The relative impact of significant model factors pH (C), and contact time (A) on the biosorption of PCP, and TCP aqueous solution compliance to CiL-plant in the single and interactive system when the significant variable is kept constant are presented in Figures 6 and 7.

3.4.1 Antagonistic effect of contact time on the Phytoremediation process

Figure 6 confirmed the antagonistic effect of contact time on the biosorption of PCP, and TCP to CiL-plant at the optimum concentration (50 mg L^{-1}). The graph showed that the CiL-plant-driven biosorption of PCP, and TCP from an aqueous solution increased significantly as the contact time increased in days. The overall performance under the influence of contact time corresponds to the maximum PCP removal rate (90%) recorded in 25 days and was consistent with the maximum removal rate recorded for TCP (87.99%). At contact time < 5 days removal efficiency was less than 10%; the outcome suggests biosorption of the chemical species (TCP) was slow on the CiL-plant surface or had not yet occurred for PCP. Comparatively, the antagonistic effect of contact time significantly favored the removal of PCP removal from the aqueous solution compared with the performance of CiL-plant biosorbent on the removal of TCP at maximum contact for 25 days. Sufficient time >20 days allowed for the biosorption of the contaminants (TCP and PCP) on CiL-plant from the solution to reach equilibrium [29]. The outline of the red and blue bars indicated that biosorption of TCP reached equilibrium faster than PCP. The finding suggests a relatively higher level of tolerance of the CiL-plant index to PCP-contaminated medium [8]. Overall performance was very satisfactory, confirming the potential of the CiL-plant as an active biosorbent for the sustainable removal of PCP and TCP to guarantee a tolerable residual contaminant level. The outcomes confirmed the influence of the optimum contact time on the removal of PCP and TCP from an aqueous solution recorded at a p-value of 0.0001 at a 95% confidence interval.

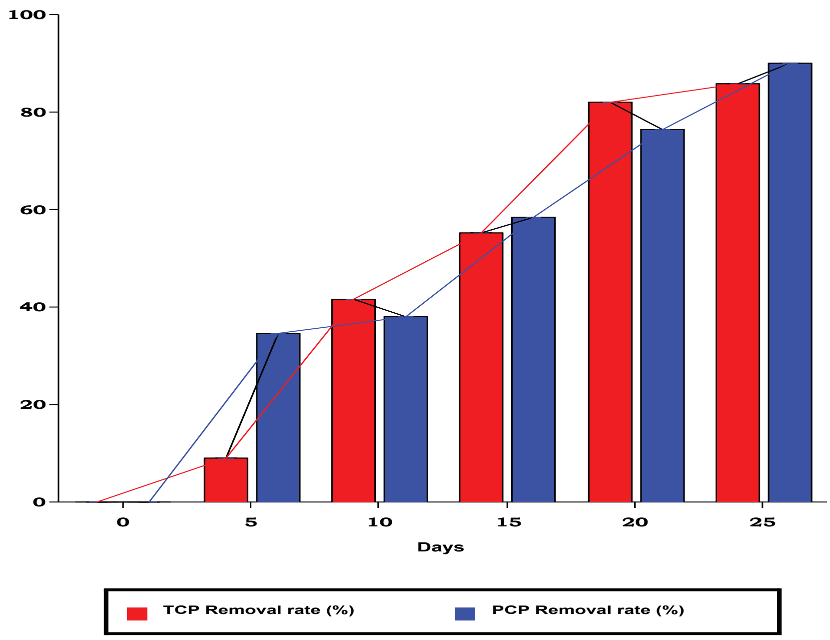


Fig 6. Effects of time on the removal of PCP and TCP to Canna indica L. at an optimum initial concentration (50 mg L^{-1}) and pH 4

3.4.2 Antagonistic impact of pH on the Phytoremediation process

The influence of pH on the CiL-plant drove biosorption of TCP from an aqueous solution at an initial concentration of 100 mg L^{-1} at pH 4 is shown in Figure 7. The graph showed that the biosorption of PCP and TCP to CiL-plant at varying pH decreased rapidly in an alkaline solution. The performance of the CiL-plant translates to a removal rate of 49.3% for PCP, and 53.2% for TCP at pH 9 and an optimum of 25 days, respectively. The removal rate increased significantly in a predominantly acidic medium transcending to 82% for PCP, and 85.7% for TCP at pH 4. The protonated chlorophenols were more absorbable [30], which accounted for the higher removal efficiency recorded for PCP and TCP at the lower pH value. The analysis of the significant impact of pH 4 on the treatment process confirmed that, irrespective of the pH window, the CiL-driven biosorption process favored TCP removal from an aqueous medium in an acidic medium compared to PCP at a p-value value of 0.0006 at 95% confidence interval. This outcome was consistent with the optimum pH 2 reported for the removal of PCP and TCP reported in the work of Radhika and Palanivelu et al. [29]. The outline of the figure also indicates that CiL-plant has a higher affinity for TCP at the optimum conditions than PCP [8], suggesting a superior solubility of 2,4,6-TCP in water than PCP at optimum pH 4 in aquaponia. Comparative evaluation of the maximum efficacy of CiL-plant under the effect of contact time of 25 days (90, 87.99%), and effect of pH (4) of solution corresponding (82, 85.7%) established that contact time had a significant main effect on the overall performance of CiL-plant-driven phytoremediation for sustainability.

3.4.3. Synergetic impact of Time-pH and concentration-pH on the Biosorption process

The significance of the synergetic effect of pH*Time and Time*initial concentration on the response PCP and TCP removal rate was confirmed based on the hierarchy from the VIFs at a p-value less than 0.005 and 95% CI. The 3-D surface plots in Figure 8 (a-d) were obtained from the response surface design space to understand better how the biosorption process works under the interactive influence of significant parameters [5, 8]. The red color gradient corresponds to higher removal efficiency of >87%. In comparison, the yellow contour gradient corresponds to moderate

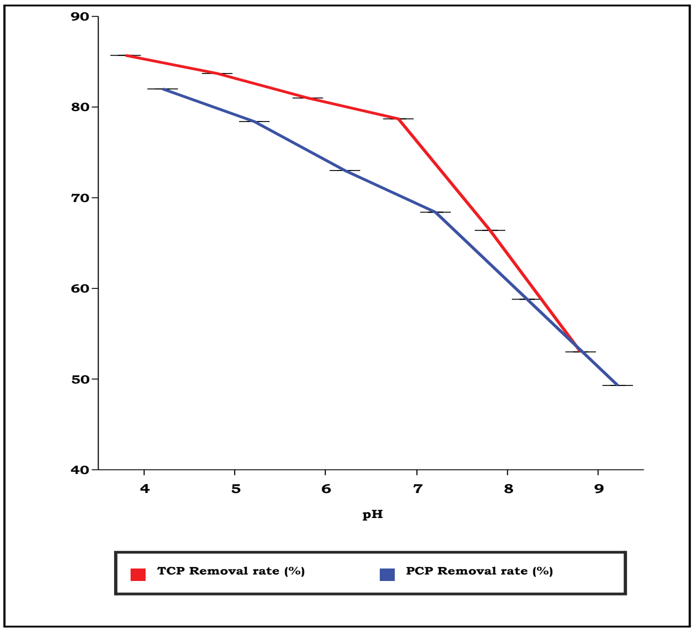


Fig 7. Effect of pH on the removal of PCP and TCP to Canna indica L. at optimum Time (25days) and initial concentration of 100 mg L^{-1} at pH 4

removal efficiency of less than 70%, and the dominant greenish-blue contour orientation translates to lower removal efficiency of less than 50%. The decrease in removal efficiency can be traced to possible charge reversal from surplus ions arising from the binary solution of PCP and TCP under changing pH in the medium. These excess negative charges contributed to the building up of the concentrations of the PCP and TCP molecules in an aqueous solution causing efficiency to drop significantly. The curvature of the red hue gradient on the base of the surfaces Figures 8 (a-b) show that the efficiency of removal of PCP and TCP increased significantly as the pH of the solution decreased from 9 to predominantly pH 4, as the exposure time of CiL-plant increased from 20 to 25 days. The phytoremediation performance of the biosorbent in aquaponia transcends to increase in PCP biosorption rate from 70 to 90%, while the TCP removal rate increased from 70 to 87.99%, as illustrated by the flag-point in the respective contour plots in Figure 8 (a,b). The pH depression from 7 to 4 yielded better performances that can be attributed to the synergetic influence of pH depression towards the acidic window and the prolonged exposure time of 25 days. This outcome is indicated by the curvatures of the dominant red contour deviation from the yellowish-green contour lines shown in Figure 8 (a,b). The basic tendency of CiL-plant-driven biosorption of PCP and TCP can be expressed from the plant's capability to drive the removal rate towards a dominantly acidic medium (pH 4) with no change in phase. The influence of the superior pH on the overall biosorption of PCP and TCP in aquaponia was attributed to the dissociation of most chlorophenol in the form of a salt which loses its negative charge easily when pH is increased [30], thus making it difficult to be adsorbed. The variation in the removal efficiency established that CiL-plant is tolerant in a solution of PCP, compared to TCP. This observation agrees with previous research works reported in the literature [8, 30] and confirms the optimization report in section 3.1. The synergetic effect of initial concentration*contact time is illustrated in the outline the contour plot in Figure 8 (c,d). The overall performance of the CiL-plant in the phytoremediation remediation of aquaponia is illustrated by the deviation of the green color contour from the dominant blue gradient on the base of the surfaces in Figure 8c and Figure 8d, respectively. The curvature of the light green from the dominant blue color orientation is attributed to areas of good performance of the biosorbent morphology and adaptation of Canna indica L for the removal of PCP and TCP. The data points and orientation of the dominant blue contour lines transcend to areas of poor performance of the biosorbent on PCP and TCP in solution. The intensity of the blue contour gradients in Figure 8 (c,d) confirmed that the best performance of the CiL-plant is adapted to an initial concentration of less than 100 mg L^{-1}. The PCP and TCP removal efficiency of the biosorbent decreased as the initial concentration was increased beyond 100 to 250 mg L^{-1}. The output reduces efficiency from 75% to 63% for PCP and <65% for TCP, as indicated by the curvature of the blue contour gradient in Figure 8 (c,d) and corresponding 3D surfaces in Figure 3. This outcome indicates that the initial concentration has a ceiling effect on the driving force of CiL-plant biosorption of PCP and TCP [30, 31]. In contrast, the contact time or exposure had a significant main effect on the phytoremediation process. The findings are consistent with the reports on TCP biosorption [29]. The authors reasoned that if the concentration was to be increased slightly beyond 100 mg L^{-1}, and a reduction in equilibrium exposure time below 25 days would decrease mass transfer to the surface of the biosorbent, would influence a reduction in PCP, and TCP removal efficiency significantly from 90% to 40%. This outcome established the significant impact of the interactive effect of initial concentration and exposure time on the overall performance of the CiL-plant-driven phytoremediation process in Aquaponia.

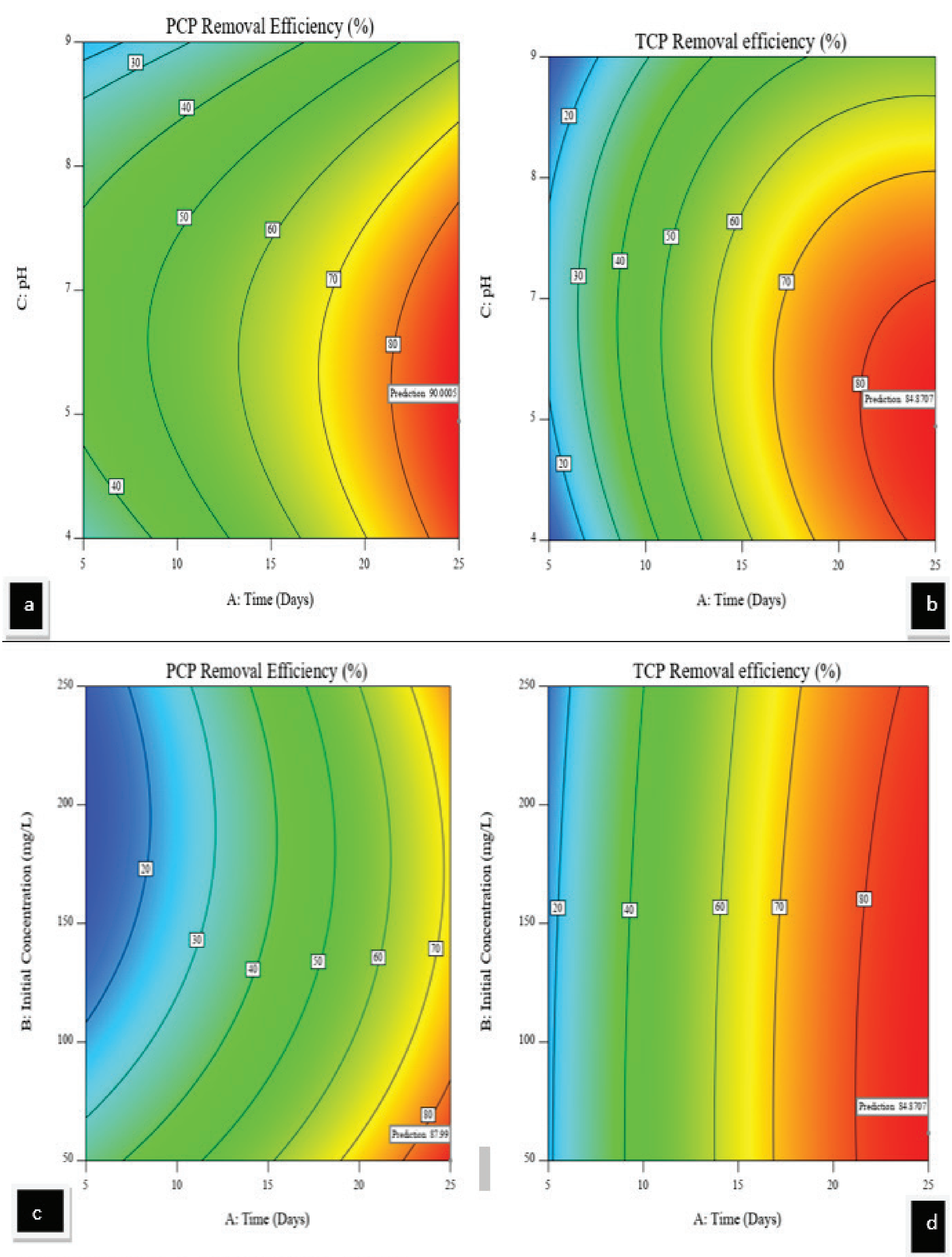


Fig. 8. Synergetic effect of process variables on Phytoremediation of Aquaponia **(a)** pH and Time on PCP, **(b)** pH-Time on TCP, **(c)** Conc-Time on PCP, **(d)** Conc-Time on TCP

3.5. Cost analysis of the treatment process

The authors explored the cost-benefit evaluation of the biosorption process as a decision-making tool to test the feasibility of the active CiL-plant as a biosorbent for removing PCP and TCP from an aqueous solution. The cost of the phytoremediation operation is based on the performance of the active CiL-plant, energy consumption, transportation to the remediation site, labor and technology used to remove contaminants [4, 8], and environmental and regulatory risk. The techno-economic feasibility of the biosorption process and phytotoxicity handling necessitates using low-cost materials (Canna indica L.) with negligible environmental impact and regulatory risk. The operating cost of treating 1.0 L of the aqueous solution was calculated by considering the cost of preparing the 100 mg L^{-1} initial concentration of the aqueous solution for CiL-plant as biosorbent. The labor cost was determined as a function of the number of working personnel on board for the treatment operation. The power consumption rate per unit of equipment utilized at full scale (f=1), and the time spent following the model report from previous research [15], were evaluated following equations 2-5 presented in section 2.5.

Analysis of Figure 9 confirmed that the operating cost of energy consumption corresponds to $ 27.80 for PCP, and $ 21.28 for TCP, respectively. It can be observed from Figure 9 that, the cost of operating the phytoremediation process for PCP removal was slightly higher than the cost of TCP removal in terms of energy consumption by $ 6.52. The preparation of 100 mg L^{-1} initial concentration of CiL-plant for removal of PCP from the aqueous solution cost $ 177.4 against $ 176.2 for removal of TCP from the aqueous solution under similar operating conditions. The labor cost was projected to be $ 100.2 per annum, while the cost of transportation of materials and personnel on board to the remediation site was $12.00, irrespective of operating with PCP or TCP. It can be concluded from the analysis of Figure 9 showed that the overall cost for using the biosorption of PCP from aqueous solution to CiL-plant at optimum conditions was computed as $ 321.20 and $ 313.48 for TCP, respectively. The analysis of the phytoremediation process proved that, at the established optimum condition, the opportunity cost of operating the biosorption of TCP from aqueous solution to CiL-plant would save $ 7.72 compared with PCP for sustainability. The authors reasoned that the outcome is largely due to higher solubility and rapid biosorption of TCP to the surface of the CiL-plant in aquaponia, irrespective of the longer exposure time required for the CiL-plant driven biosorption of PCP and TCP to reach equilibrium.

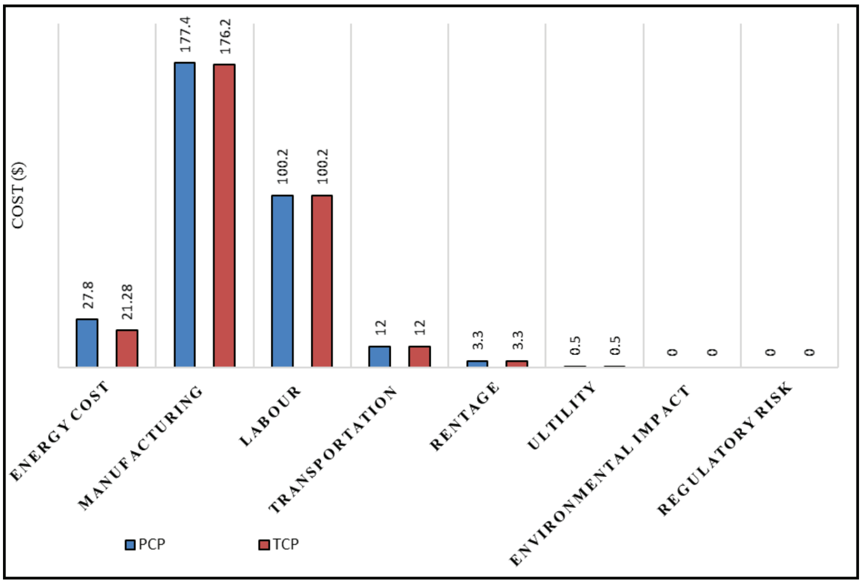


Fig. 9. Cost evaluation summary of the CiL-plant-driven biosorption treatment

Table 6. Comparative analysis of the optimization report

Methodology	DoE		OFAT	
	This study		Reference	
Parameter	(PCP)	(TCP)	(PCP)	(TCP)
pH		4		---
Initial Conc. (mg L^{-1})		50		100
Contact time (days)		25		25
optimum Efficiency %	90	81.87	87	80

OFAT: Reference [8]

3.6. Comparison of CiL-plant for the remediation of PCP and TCP from solution

The performance comparison of the biosorption of PCP, and TCP from aquaponia was analyzed and the report is summarized in Table 6 below. The previous research reports on the CiL-plant phytoremediation analysis applied the one-factor-at-a-time (OFAT) approach for determining the optimum PCP and TCP removal rate. The current study applied the design of experiment (DoE) approach via the RSM for the optimization modeling of the uptake of PCP and TCP to CiL-plant in aquaponia. The findings from the comparison of the results showed that with the RSM, the removal efficiency was higher than the optimum reported via the OFAT approach. The difference corresponds to ± 1.87 and ±3 for TCP and PCP, respectively.

4. Conclusion

The techno-economic evaluation and optimization modeling of the competitive biosorption of PCP and TCP from aqueous solution to the Cana indica plant have been investigated. The aqueous solution of fertilizer contaminated with PCP and TCP was prepared. The CiL-plant-driven phytoremediation of the aqueous medium was studied at varying pH, initial concentration, and constant time based on the design of experiments. The optimization modeling tools for ANN and RSM have yielded good statistical evaluation metrics for modeling the CiL-plant-driven phytoremediation process. The results confirmed that a statistical difference of ±0.005 was obtainable and adjusted $R^2 \leq 1.00$. The adopted RSM optimization outputs have to test their reliability based on DoE. The predicted optimum corresponds to pH, concentration, and exposure time of 4, 50 mg L^{-1}, and 25 days guaranteed PCP and TCP biosorption to CiL-plant ≤90%. The established optimum condition required $7.75 more for sustainable PCP removal than TCP.

5. Acknowledgement

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6. Conflict of interest

There are no conflicts of interest to declare

7. References

[1] USEPA, 2,4,6 Trichlorophenol. United states Environmental Protection Agency, 2000. https://www.epa.gov/sites/default/files/2016-09/documents/2-4-6-trichlorophenol.pdf

[2] WHO, The World Health Organization recommended classification of pesticides by hazard and guidelines to classification 2004, International Programme on Chemical Safety, pp.19-39, 2005. https://apps.who.int/iris/rest/bitstreams/1278712/retrieve

[3] ATSDR, Pentachlorophenol, Agency for Toxic Substances and Disease Registry, 2021. https://wwwn.cdc.gov/TSP/substances/ToxSubstance.aspx?toxid=70

[4] A.I. Olayinka, F.A. Ademola, I.A. Emmanuel, Assessment of Organochlorine and Organophosphorus pesticides residue in water and sediments from Ero River in South-Western Nigeria, J. Chem. Biol. Phys. Sci. D,

5 (2015) 4679–4690. https://www.jcbsc.org_
[5] A.W. Verla, J. E. Ejiako, E.N. Verla, I. G. Ndubuisi, C. E. Enyoh, Potential health risk index of polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in fish species from Oguta Lake, Nigeria, Int. J. Environ. Anal. Chem., (2021) 1946687. https://doi.org/10.1080/03067319.2021.1946687
[6] B. M. Obidike, A. W. Verla, C. E. Enyoh, E. N. Verla, O. N. Onyekachi, Fate and distribution of pesticides residues in water sources in Nigeria: A review, Int. J. Agrochem., 6 (2020) 29–48. https://chemical.journalspub.info/index.php?journal=IJCPD&page=article&op=view&path%5B%5D=1015
[7] B.O. Isiuku, C.E. Enyoh, Water pollution by heavy metal and organic pollutants: Brief review ofsources, effects and progress on remediation with aquatic plants, Anal. Methods Environ. Chem. J., 2 (3) (2019) 5-38. https://doi.org/10.24200/amecj.v2.i03.66
[8] C. E. Enyoh, B. O. Isiuku, Competitive biosorption and phytotoxicity of chlorophenols in aqueous solution to Canna indica L, Curr. Res. Green Sustain. Chem., 4 (2021) 100094. https://10.1016/j.crgsc.2021.100094
[9] C.E. Enyoh, B. O. Isiuku, Removal of pentachlorophenol (PCP) from aqueous solution using Canna indica L.: kinetics, isotherm and thermodynamic studies, Arab. J. Chem., 8(2) (2021) 193-213. http://www.mocedes.org/ajcer/volume8/AJCER-13-Enyoh-2021.pdf
[10] C.E. Enyoh, B.O. Isiuku, 2,4,6-Trichlorophenol (TCP) removal from aqueous solution using Canna iindica L.: kinetic, isotherm and Thermodynamic studies, Chem. Ecol., 37 (2020) 64-82. https://doi.org/10.1080/02757540.2020.1821673
[11] D.H. Tran, T.M.H. Vi, T.T.H. Dang, R. Narbaitz, Pollutant removal by Canna Generalis in tropicalconstructed wetlands for domestic wastewater treatment, Global J. Environ. Sci. Manage., 5 (3) (2019) 331-344. https://www.gjesm.net/article_35321_dc150b14811afe228b6bea1bcc85228f.pdf
[12] C.E. Enyoh, B.O. Isiuku, Determination and human health risk assessment of heavy metals in flood basin soils in Owerri, southeastern Nigeria, Chem. Africa, 3 (2020) 1059–1071. https://doi.org/10.1007/s42250-020-00171-2
[13] C.E. Enyoh, Q. Wang, P.E. Ovuoraye, Response surface methodology for modeling the adsorptive uptake of phenol from aqueous solution using adsorbent polyethylene terephthalate microplastics, Chem. Eng. J. Adv., 12 (2022) 100370. https://doi.org/10.1016/j.ceja.2022.100370
[14] S. Saini, J. Chawla, R. Kumar, Response surface methodology (RSM) for optimization of cadmium ions adsorption using C16-6-16 incorporated mesoporous MCM-41, SN Appl. Sci., 1 (2019) 894. https://doi.org/10.1007/s42452-019-0922-5
[15] P. E. Ovuoraye, V.I. Ugonabo, G.F. Nwokocha, Optimization studies on turbidity removal from cosmetics wastewater using Aluminum Sulfate and blends of fishbone, SN Appl. Sci., 3 (2021) 488. https://dio.org/10.1007/s42452-021-04458-y
[16] C. A. Igwegbe, L. Mohammed, S. Ahmadi, A. Rahdar, Modeling of adsorption of methylene blue dye on Ho-CaWO4 nanoparticles using response surface methodology and artificial neural network (ANN) techniques, Methods X, 6 (2019) 1779-1797. https://doi.org/10.1016/j.mex2019.07.016
[17] C.A. Igwegbe, O.D. Onukwuli, J.O. Ighalo, M.C. Menkiti, Bio-coagulation-flocculation (BCF) of municipal solid waste leachate using picralima nitida extract: RSM and ANN modelling, Curr. Res. Green Sustain. Chem. 4 (2021) 100078. https://doi.org/10.1016/j.crgsc.2021.100078
[18] C.E. Enyoh, C. E. Duru, P. E. Ovuoraye, Q.

Wang, Evaluation of nanoplastics toxicity to the human placenta in systems, J. Hazard. Mater., 446 (2023) 130600. https://doi.org/10.1016/j.jhazmat.2022.130600

[19] R. Hasanzadeh, M. Mojaver, T. Azdast, C. B. Park, Polyethylene waste gasification syngas analysis and multi-objective optimization using central composite design for simultaneous minimization of required heat and maximization of exergy efficiency, Energy Convers. Manag., 247 (2021) 114713. https://doi.org/10.1016/j.enconman.2021.114713

[20] L. Lujian, S. Tang, X. Wang, X. Sun, A. Yu, Adsorption of malachite green from aqueous solution by nylon microplastics: Reaction mechanism and the optimum conditions by response surface methodology, Process Saf. Environ. Prot., 140 (2020) 339-347. https://doi.org/10.1016/j.psep.2020.05.019

[21] C. E. Enyoh, Q. Wang, P. E. Ovuoraye, T. O. Maduka, Toxicity evaluation of microplastics to aquatic organisms through molecular simulations and fractional factorial designs, Chemosphere, 308 (2022) 136342. https://doi.org/10.1016/j.chemosphere.2022.136342

[22] C.E. Duru, C.E. Enyoh, I.A. Duru, M. Enedoh, Degradation of PET nanoplastic oligomers at the novel PHL7 target: insights from molecular docking and machine learning, J. Niger. Soc. Phys. Sci., 5 (2023) 1154. https://doi.org/10.46481/jnsps.2022.1154

[23] G. Aicha, I. Soumaya, E. Noureddine, A. T. Mohamed, G. Djamel, H. Ahmed, M. Abdelhakim, A. Badreddine, K. Lioua, Comparative study of chemical coagulation and electrocoagulation for the treatment of real textile wastewater: optimization and operating cost estimation, ACS Omega, 7(26) (2022) 22456–22476. https://doi.org/10.1021/acsomega.2c01652

[24] P.E. Ovuoraye, L.C. Okpala, V.I. Ugonabo, Clarification efficacy of eggshell and aluminum base coagulant for the removal of total suspended solids (TSS) from cosmetics wastewater by coag-flocculation, Chem. Pap., 75 (2021) 4759–4777. https://doi.org/10.1007/s11696-021-01703-x

[25] D. Wang, S. Thunell, L. Ulrika, A machine learning framework to improve effluent quality control in wastewater treatment plants, Sci. Total Environ., 784 (2021) 147138. https://doi.org/10.1016/j.scitotenv.2021.147138

[26] Y. Zhang, Y. Wu, Introducing machine learning models to response surface methodologies. Publisher: Intechopen, 270 pages, 2021. https://doi.org/10.5772/intechopen.9819

[27] P. E. Ovuoraye, V. I. Ugonabo, M. A. Tahir, P. A. Balogun, Kinetics-driven coagulation treatment of petroleum refinery effluent using land snail shells: An empirical approach to environmental sustainability, Clean. Chem. Eng., 4 (2022) 100084. https://doi.org/10.1016/j.clce.2022.100084

[28] H. Guo, Prediction of effluent concentration in a wastewater treatment plant using machine learning models, J. Environ. Sci., 32 (2015) 90-101. https://doi.org/10.1016/j.jes.2015.01.007.

[29] M. Radhika, K. Palanivelu, Adsorptive removal of chlorophenols from aqueous solution by low-cost adsorbent—Kinetics and isotherm analysis, J. Hazard. Mater., 138(1) (2006) 116-124. https://doi.org/10.1016/j.jhazmat.2006.05.045

[30] S.K. Nadavala, M. Asif, A. M. Poulos, M. Suguna, M. I. Al-Hazza, Equilibrium and kinetic studies of biosorptive removal of 2,4,6-trichlorophenol from aqueous solutions using untreated agro-waste pine cone biomass, Processes, 7 (2019) 757. http://doi:10.3390/pr7100757

[31] R. Bhutiani, N. Rai, P. K. Sharma, K. Rausa, F. Ahamad, Phytoremediation efficiency of water hyacinth (E. crassipes), canna (C. indica) and duckweed (L. minor) plants in treatment of sewage water, Environ. Conserv. J., 20 (2019) 143-156. https://doi.org/10.36953/ECJ.2019.1008.1221