



# Elimination of a Toxic Dye using *Avicennia Marina* Leaves: Optimization and Modeling

Rakesh Namdeti\*

Chemical Engineering, College of Engineering and Technology, University of Technology and Applied Sciences, Salalah, Sultanate of Oman.

(Received: 07 July 2023

Revised: 12 August

Accepted: 06 September)

## KEYWORDS

Methylene blue, Central composite design, Avicennia Marina, Artificial neural network.

## ABSTRACT:

In addressing the imperative need to treat toxic dyes in industrial effluent to prevent harm to human health and aquatic life, this study investigates the potential of *Avicennia marina* leaves as a biosorbent for removing methylene blue from synthetic solutions. Employing a central composite design, the study explores the influence of temperature, pH, sorbent dosage, and initial methylene blue concentration on the dye removal process. The optimal conditions identified include a temperature of 44.3°C, pH of 7.1, sorbent dose of 0.3 g, and an initial methylene blue concentration of 48.4 mg/L, resulting in an impressive 84.26% dye removal. The experimental biosorption percentage under these conditions is found to be 76.93%. The developed artificial neural network (ANN) model successfully predicts outcomes closely aligned with experimental results, showcasing the efficacy of *Avicennia marina* leaves as a promising biosorbent and the utility of ANN modeling for system optimization and prediction.

## 1. INTRODUCTION

The application of dyes in numerous industries, such as textiles, paper, rubber, plastic, food, leather, and cosmetics, results in the generation of substantial volumes of colorful aqueous waste, contributing to an estimated global production of around 0.7 million tons of industrial effluents annually (Zaharia C and Suteu D 2012a; Anjaneyulu Y et al 2005). These effluents undergo a weight loss of 10% to 15% during processing and manufacturing (Zaharia C and Suteu D 2012a). Discharging such wastewater with color to normal water flows poses significant danger threat, occurring various issues (Zaharia C 2012b). Even minimal dye concentrations, as minimum as ppm of 1 for all dyes, can adversely solubility of dissolved oxygen, aesthetics impact, clarity, sunrays penetration, subsequently affecting aquatic life and the food chain (Zaharia C 2012b). Certain dyes and their breakdown products, including aromatic amines, can pose risks to both aquatic life and human health (Latif A et al 2010; Suteu D 2009). Despite the availability of commercially accessible adsorbents, their cost remains a challenge (Zaharia C and Suteu D 2012a). To address this, the development of innovative and cost-effective

biosorbents is crucial for efficient color removal from wastewater. Recently, industrial byproducts and agricultural waste materials have been repurposed to create plant biomass, offering an affordable feedstock precursor (Zaharia C 2008; Latif A et al 2010; Suteu D 2009). This approach proves effective in removing various water-soluble dyes, including methylene blue (Zaharia C 2008; Latif A et al 2010; Suteu D 2009).

Methylene blue (MB) is represented by the chemical formula  $C_{16}H_{18}N_3SCl$  and manifests as an odorless, dark green powder when dissolved in water. As a basic dye, MB finds applications in coloring paper, hair dyes, paper coatings, tannin printing, cotton and leather dyeing, and serves as an antibiotic. Addressing the diverse characteristics of textile effluents, the removal of color involves various methods encompassing physical, chemical, and biological treatments. These techniques include membrane processes, flocculation, coagulation, activated carbon adsorption, electrochemical treatment, as well as aerobic or anaerobic biodegradation. An extensive examination of the advantages and disadvantages of each method has been conducted in prior studies (Han, Y 2011; Ubbe M. A 2012; Salleh M. A. M 2011).



Biosorption stands out as an effective and economically viable method for tackling dye-based industrial waste. This technique involves transferring a soluble dye, in liquid form, onto a solid surface using a porous material, known as the adsorbent, resulting in chemical or physical bonding. The appeal of adsorption lies in its attributes of low toxicity, making it the preferred choice for wastewater treatment due to its effectiveness, cost-efficiency, simplicity, and user-friendly nature. The versatility of adsorbent materials adds another layer of advantage, encompassing a range of natural sources like various clays, chitin, coal, wood, biomass, chitosan, and, peat along with industrial byproducts such as maize cob, red mud, sawdust, dye hydroxide sludge, ash, furnace blast slag, lignin, rice husks, bark, sunflower stalks, seashells, olive stones, and hazelnut shells. Importantly, these materials find utility in both batch and continuous processing conditions.

Surprisingly, there has been a notable gap in research exploring the optimization of *Avicennia marina* powder for the removal of methylene blue, particularly through the application of response surface methodology (RSM) or artificial neural network (ANN) approaches. Utilizing a central composite

design (CCD), which is a fundamental RSM design, encounters the optimization of parameters in a minimal number tests and facilitates the study of factors interactions. The efficacy of the modeling by ANN is gauged by the alignment in the predicted outcomes from the developed model and the experimental results. The investigation into achieving a substantial percentage of methylene blue removal from a synthetic solution involved a thorough exploration of factors such as temperature, pH, biosorbent dose, and initial dye concentration.

## 2. METHODOLOGY

### 2.1- Biosorbent

The *Avicennia Marina* plant as shown in Fig.1 was obtained from the Dhofar Region near Salalah in the Sultanate of Oman. Thorough cleaning of the leaves was conducted using distilled water to eliminate any impurities. Following this, the dried leaves underwent a grinding process, resulting in a fine powder with particle sizes ranging between 75 and 212 micrometers. This finely powdered substance was subsequently employed as a biosorbent for methylene blue biosorption, requiring no prior preparation.



**Fig.\_1:** Biosorbent preparation from *Avicennia marina* waste (Bozlur, R. M 2012).

### 2.2- Chemical

To create a methylene blue solution as showed in

Fig.2, an appropriate salt was dissolved in distilled water. The pH of the solutions was then carefully adjusted using 0.1 N HCl and NaOH.



**Fig. 2:** Preparation of Methylene Blue solution (Crini, G 2006).

Each test was repeated five times, and the outcomes were averaged. Blank experiments were performed to ensure that nil biosorption took place on the apparatus walls.

### 2.3 Equipment

To determine the methylene blue capacity, a UV spectrophotometer set at a wavelength of 665 nm was employed. The adsorbate pH and the adsorbent weight were measured using a Systronics pH meter and an electronic balance manufactured by Shimadzu.

### 2.4 Batch Study Biosorption

5.1 pH was adjusted by introducing sodium hydroxide and hydrochloric acid. Following this, experimental methylene blue solutions were prepared by diluting the stock solution to the desired concentrations. The impact of agitation duration on varying initial concentrations of methylene blue was explored by blending 30 ml of the solution with different methylene blue concentrations and 0.1 g of 75-micrometer-sized adsorbent at 180 rpm for 1 hour. After removing the adsorbent through centrifugation,

the remained methylene in the solution quantified at regular intervals using a UV spectrophotometer. Subsequent tests followed a spectrophotometric analysis. The quantity of metal adsorbed by *Avicennia marina* was calculated using an equation using the disparity with in the metal supplied to the adsorbent surface and the remaining metal quantity in supernatant.

$$q = (C_0 - C_f) * \frac{V}{M} \quad (1)$$

The metal adsorption, represented as "q" (mg/g), was computed utilizing the initial metal concentration "C<sub>0</sub>" and the final concentration "C<sub>f</sub>" in the solution (in ppm). This calculation involved the solution volume "V" (in mL) and the mass of the adsorbent "M" (in grams).

### 2.5- Experimental design for biosorption studies

As indicated in Table 1, four independent criteria were selected for the experiment to establish the optimal conditions for methylene blue removal at a%.

**Table.1. For methylene blue biosorption onto banana leaves, the experimental range and amounts of the independent factors were (Crini, G 2006):**

Independent Parameters	Range and Level				
	-2	-1	0	+1	+2
(X <sub>1</sub> ) Temperature, K	30	35	40	45	50
(X <sub>2</sub> ) pH	4	5	6	7	8
(X <sub>3</sub> ) Adsorbent Dosage, g/L	0.1	0.2	0.3	0.4	0.5
(X <sub>4</sub> ) Initial Concentration, mg/L	20	40	60	80	100

In the initial investigations, the ranges of (X<sub>1</sub>) temperature, (X<sub>2</sub>) pH, (X<sub>3</sub>) biosorbent dose, and (X<sub>4</sub>) initial dye concentration were determined. The relationship between these parameters and the response was established through the central

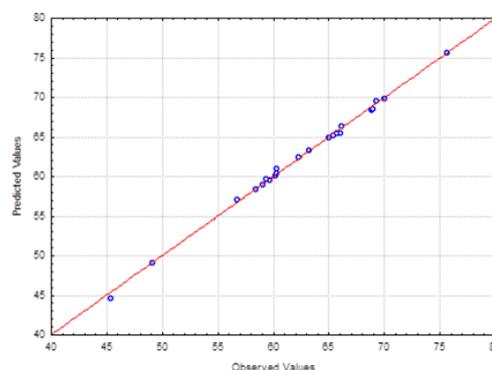
composite design (CCD) using Stat-Ease, Inc.'s Design Expert software (version 6.0.6), a United States-based company (as illustrated in Figure 3). The selection of CCD was based on its efficiency, adaptability, and robustness in this study [8]. As per



the CCD methodology [9], Table 1 represents the four parameter levels coded as -2, -1, 0, +1, and +2. Following the CCD approach, thirty trials were conducted, including 8 stars ( $\alpha=2$ ) and 6 replicates at the center point. The response in this experimental design was the percentage of methylene blue removed, denoted as (Y), and calculated accordingly:

$$(Y) \% \text{ Biosorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

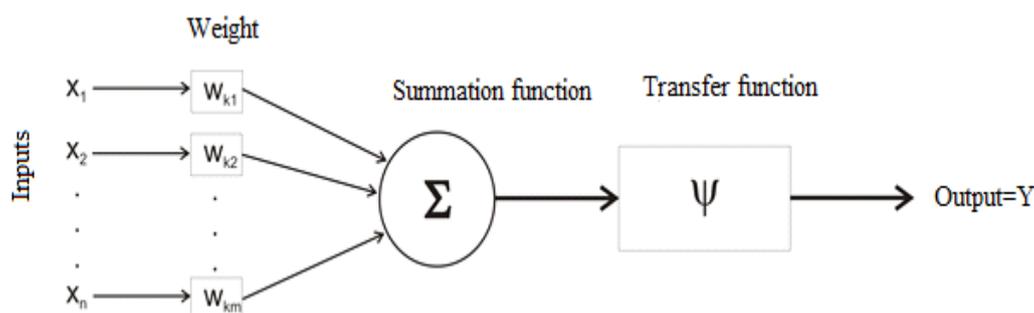
In each trial,  $C_i$  (mg/L) denotes the initial concentration, while  $C_f$  (mg/L) indicates the final or equilibrium concentration. Every experiment was replicated three times, and the averaged outcomes were documented. After the necessary incubation period, a UV spectrophotometer (Shimadzu Model AA 6650) was employed for sample analysis. Regression analysis, graphical evaluations, and analyses of variance (ANOVAs) were conducted utilizing Design Expert Software (version 6.0.6) by Stat-Ease, Inc., USA. To assess the statistical significance of the coefficients, Student's p-values and F-test were utilized. The degree to which the model explained the variance was determined by the multiple coefficients of determination, represented as  $R^2$ .



**Fig. 3:** A graph illustrating the distribution of observed vs. predicted methylene blue biosorption percentages using *Avicennia marina* (Enayatollahi I et al. 2013).

## 2.6 (ANN) Neural Network (Artificial)

A neural network functions as an intelligent system with the ability to predict an output pattern by identifying specific input patterns. The initial training of neural networks involves processing extensive datasets to enable accurate predictions. These networks utilize new input patterns to recognize similarities and generate predicted output patterns (Enayatollahi I et al. 2013). When it comes to predicting adsorption systems, empirical models paired with (ANNs) neural networks were acknowledged as potent alternatives to methods of numerical estimation.



**Fig. 4:** --\_ANN cell pattern (Chairez I 2009)

In this context, an artificial neural network (ANN) to model adsorption was utilized by employing information gathered from trials conducted under diverse conditions. The simplified architecture, illustrated in Figure 4, incorporates input variables denoted as  $x_1$ ,  $x_2$ , and so forth, with  $W_{k1}$ ,  $W_{k2}$ , and

$W_{kn}$  representing the weight coefficients associated with these inputs. Subsequently,  $x_n$  represents the input signals, while  $W_{kn}$  signifies their respective weight coefficients. The network's core calculates the weighted sum for all input signals, with the outputs denoted as  $Y$  (Yildiz S 2015). Depending on the



specific nature of the problem, the number of hidden layers in the ANN can be adjusted accordingly. The computations involving ANNs were executed using the software suite of MATLAB.

### 3.--\_RESULTS AND DISCUSSION

#### 3.1--\_ Analysis by Statistics

To pinpoint optimal conditions for methylene blue removal, it becomes crucial to discern the parameters

exerting the most substantial influence on the reaction. In this investigation, the model of quadratic aptly encapsulated the interaction between the four independent parameters and the percentage of dye removed. The percentage of methylene blue removed post-biosorption, assessed through central composite design (CCD), is articulated as a quadratic regression model when taking into account the coded factors.

$$Y (\text{percent dye biosorption}) = -212.740 + 12.065X_1 + 1.747X_2 + 67.310X_3 + 0.481X_4 - 0.171X_1^2 - 1.954X_2^2 + 34.332X_3^2 - 0.003X_4^2 + 0.574X_1X_2 - 2.085X_1X_3 - 0.005X_1X_4 + 0.949X_2X_3 + 0.007X_2X_4 - 0.118X_3X_4 \quad (3)$$

In this framework, X1 represents temperature, X2 denotes pH, X3 represents the biosorbent dosage, and X4 signifies the initial concentration. The Table 2 illustrates variations in the encoded values of these four parameters and their corresponding responses, comparing experimental results with the values predicted by the CCD design. The removal of dye from the source solution vary from 40.28% to 75.61%. The analysis of variance (ANOVA) for the model (Equation three shown in Table 3) was statistically required ( $P < 0.05$ ), with a 718.5 as F value. In this investigation, the coefficient of determination was 0.9985, indicating that 99.85% of the variation in the

data was explained by the model, and the remaining 0.15% was attributed to residues. The error calculated in this model was 0.263. Since the change was higher than 0.05, the quadratic model was considered valid for this study [11]. The first-order changes of temperature, biosorbent dose, pH, and initial blue concentration, as well as the second-order effects, were also found to be highly significant, as indicated in Table 4. The projected optimal conditions for achieving 75.86% methylene blue removal were as follows: a pH of 5.8, temperature of 39.4°C, an initial dye concentration of 53.07 mg/L, and, biosorbent dose of 0.27 g, as shown in Table 5.

**Table.2. For the biosorption of MB with Banana Leaves, showing observed and predicted data (Salleh, M. A. M. 2008)**

Run no.	Coded values				Real values				% Biosorption of methylene blue	
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	Observed	Predicted
1	-1	-1	-1	-1	35	5	0.2	40	69.2	69.50166
2	-1	-1	-1	1	35	5	0.2	80	58.38	58.39208
3	-1	-1	1	-1	35	5	0.4	40	68.13	66.44041
4	-1	-1	1	1	35	5	0.4	80	59.66	59.52833
5	-1	1	-1	-1	35	7	0.2	40	62.22	62.48542
6	-1	1	-1	1	35	7	0.2	80	60.12	60.19333
7	-1	1	1	-1	35	7	0.4	40	59.01	59.06167
8	-1	1	1	1	35	7	0.4	80	60.23	60.96708
9	1	-1	-1	-1	45	5	0.2	40	65.92	65.58542
10	1	-1	-1	1	45	5	0.2	80	60.21	60.40833
11	1	-1	1	-1	45	5	0.4	40	63.2	63.37667
12	1	-1	1	1	45	5	0.4	80	62.26	62.39708
13	1	1	-1	-1	45	7	0.2	40	59.29	59.67167
14	1	1	-1	1	45	7	0.2	80	63.22	63.31208
15	1	1	1	-1	45	7	0.4	40	56.71	57.10042
16	1	1	1	1	45	7	0.4	80	64.99	64.93833
17	-2	0	0	0	30	6	0.3	60	65.98	65.49625
18	2	0	0	0	50	6	0.3	60	65.72	65.55125
19	0	-2	0	0	40	4	0.3	60	49.12	49.11125
20	0	2	0	0	40	8	0.3	60	45.28	44.63625
21	0	0	-2	0	40	6	0.1	60	69.98	69.81125
22	0	0	2	0	40	6	0.5	60	68.86	68.37625
23	0	0	0	-2	40	6	0.3	20	68.93	68.48458
24	0	0	0	2	40	6	0.3	100	65.42	65.21291
25	0	0	0	0	40	6	0.3	60	75.82	75.82
26	0	0	0	0	40	6	0.3	60	75.82	75.82
27	0	0	0	0	40	6	0.3	60	75.82	75.82
28	0	0	0	0	40	6	0.3	60	75.82	75.82
29	0	0	0	0	40	6	0.3	60	75.82	75.82
30	0	0	0	0	40	6	0.3	60	75.82	75.82



**Table 3. ANOVA for the whole quadratic model of methylene blue onto adsorbent leaves (Enayatollahi I 2014).**

Source of variation	Sum of squares (SS)	Degrees of freedom (D.F)	Mean squares (MS)	F-value	Probe>F
Model	1689.912	14	120.708	718.5	0.000000
Error	2.518	15	0.168		
Total	1692.430	29			

$R^2 = 0.9985$ ; Adjusted  $R^2 = 0.9971$

$F_{0.01(14,15)} = S_r^2 / S_e^2 = 718.5 > F_{0.01(14,15)} \text{Tabular} = 2.46$

$P_{\text{model}} > F = 0.000000$

**Table.4. The model for biosorption of MB onto Adsorbent has coefficients, t- statistics, and probability (Zaharia, C, and Suteu, D 2012).:**

Term	Coefficient	Value	Standard error of coefficient	t-value	p-value
Constant	$b_0$	-267.206	13.30745	-20.0795	0.000000 <sup>a</sup>
$X_1$	$b_1$	6.723	0.40690	16.5229	0.000000 <sup>a</sup>
$X_1^2$	$b_{11}$	-0.101	0.00458	-22.0191	0.000000 <sup>a</sup>
$X_2$	$b_2$	76.544	1.75245	43.6781	0.000000 <sup>a</sup>
$X_2^2$	$b_{22}$	-7.184	0.11452	-62.7337	0.000000 <sup>a</sup>
$X_3$	$b_3$	51.063	14.28647	3.5742	0.004363 <sup>a</sup>
$X_3^2$	$b_{33}$	-162.906	11.45168	-14.2255	0.000000 <sup>a</sup>
$X_4$	$b_4$	-0.796	0.07143	-11.1402	0.000000 <sup>a</sup>
$X_4^2$	$b_{44}$	-0.005	0.00029	-19.1266	0.000000 <sup>a</sup>
$X_1 * X_2$	$b_{12}$	0.055	0.02392	2.3044	0.041709 <sup>a</sup>
$X_1 * X_3$	$b_{13}$	0.426	0.23922	1.7818	0.102366
$X_1 * X_4$	$b_{14}$	0.015	0.00120	12.3998	0.000000 <sup>a</sup>
$X_2 * X_3$	$b_{23}$	-0.906	1.19609	-0.7577	0.464566
$X_2 * X_4$	$b_{24}$	0.110	0.00598	18.4299	0.000000 <sup>a</sup>
$X_3 * X_4$	$b_{34}$	0.525	0.05980	8.7734	0.000003 <sup>a</sup>

$X_1$  stands for temperature,  $X_2$  for pH,  $X_3$  for biosorbent dosage, and  $X_4$  for initial concentration.

<sup>a</sup>Significant (p less than or equal to 0.05)

**Table.5. Optimum variable values derived from regression models for the removal of MB (Zaharia, C, and Suteu, D 2012):**

Variables	Value of optimum for zinc
Temperature, °C	39.42077
pH	5.86821
Bio sorbent dose, g	0.27744
Zinc initial concentration, mg/L	53.07435
% Predicted Biosorption	75.865
% Observed Biosorption	76.92



### 3.2 Adsorbent characterization

#### 3.2.1. --\_BET analysis

Table 6 presents information on the pore volume and BET surface area of the sorbents. *Avicennia Marina* demonstrated a surface area of 40 m<sup>2</sup>/g. It is

noteworthy that the BET surface area decreased as *Avicennia marina* particles occupied the pores. However, the pore volume of *Avicennia marina* was determined to be 0.265 cm<sup>3</sup>/g.

**Table-. \_6. --\_BET Area and BET pore volume of the adsorbent (Chairez I 2009):**

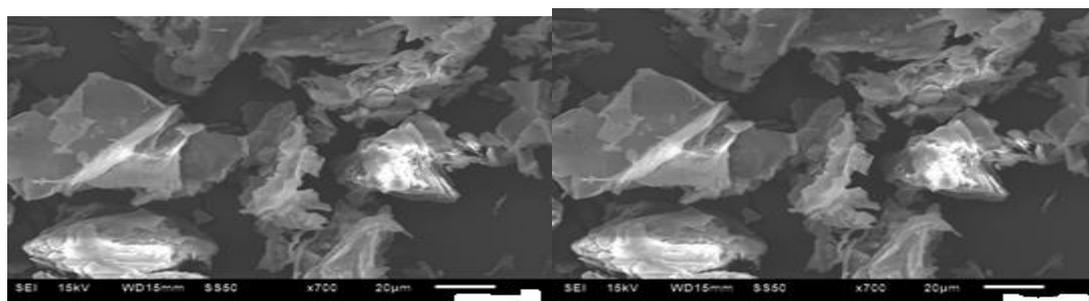
Adsorbent	BET Surface Area, m <sup>2</sup> /g	BET Pore Volume, cm <sup>3</sup> /g
<i>Avicennia Marina</i>	40	0.265

#### 3.2.2. SEM analysis

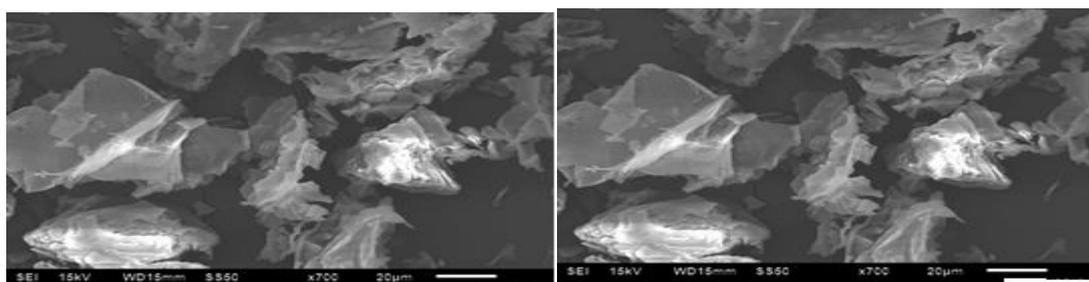
Utilizing scanning electron microscopy (SEM) proves to be an invaluable method for examining the morphology of natural sorbents and understanding their alterations resulting from interactions with sorbates. SEMs are microscopy techniques employing a high-energy electron beam to scan a sample's surface and generate detailed images. In this study, we employed Scanning Electron Microscopy (SEM) to investigate the potential mechanisms underlying the sorption of toxic elements in biomasses. Our goal was to discern variations resulting from the application of amendments.

Capturing images at a 10 kV voltage with various magnification settings provided a detailed view of the surface. As depicted in Figure 5, SEM images showcased the fibrous and superficial structures of untreated *Avicennia marina* leaf powder. The analysis uncovered an uneven and heterogeneous surface with pores on the leaf biomass.

After biosorption, as depicted in Figure 6, SEM analysis revealed an irregular texture on the surface characterized by globular and elongated grains, along with shiny particles enveloping the Methylene Blue-loaded biosorbent. The presence of these elongated grains implies that Methylene Blue particles adhere to the surface of the *Avicennia marina* leaf biosorbent.



**Fig.\_5. SEM micrograph of the *Avicennia marina* leaf biosorbent before biosorption.**



**Fig.\_6. SEM image depicting the *Avicennia Marina* leaves biosorbent after the adsorption of Methylene Blue (MB).**

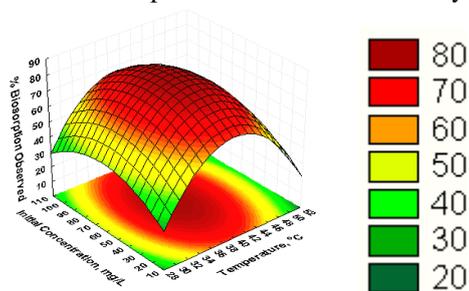


### 3.3--\_ Effects of the interaction among four parameters on the removal of Methylene Blue.

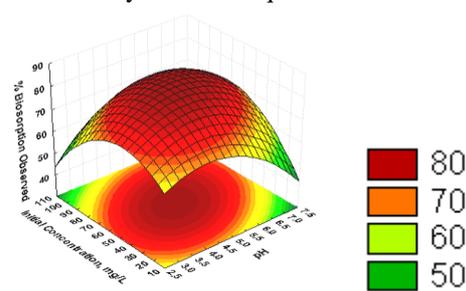
The biosorption capability of the current biosorbent for methylene blue ions was assessed using three-dimensional response surface plots, as shown in Figures 7–12. Figures 5-10 show the relationship between two components at a time, while the other factors remain constant. Interestingly, all response surface plots revealed negligible biosorbent capacity at both low and high concentrations, with no noticeable increase or reduction in biosorption capacity. This finding suggests the presence of an ideal range of biosorption parameters that improve methylene blue adsorption capability. Notably, temperature and starting dye concentration (X1 and X4), pH and initial dye concentration (X2 and X4), and biosorbent dosage and initial dye concentration (X3 and X4) all had direct proportional associations with dye uptake. The interaction of these parameters was extremely

significant ( $p < 0.05$ ) and played a vital role in generating the expected high dye uptake, as indicated by the model and response contour plots (Figures 3, 4, and 5).

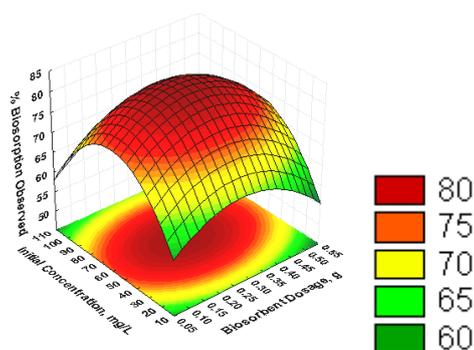
The curving contour lines show complex interactions between temperature and initial dye concentration (X1 and X4), pH and initial dye concentration (X2 and X4), and biosorbent dosage and initial dye concentration (X3 and X4) as showed in Fig 7 to 9. Furthermore, Fig. 10 to 12 show moderate interactions between temperature and pH (X1 and X2), temperature and biosorbent dosage (X1 and X3), and pH and biosorbent dosage (X2 and X3). The point prediction approach revealed the ideal biosorption variables with the maximum anticipated biosorption capacity, as shown in Table 5, which includes comprehensive surface response plots. A biosorption experiment done under these ideal conditions verified that the experimental data closely matched Equation 3 of the current model.



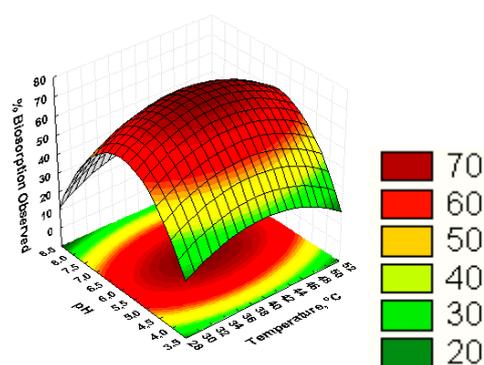
**Fig.7:** A response surface plot visually represents the influence of initial dye concentration and temperature on the percentage of Methylene Blue biosorption using *Avicennia Marina*.



**Fig.8:** A response surface plot provides a visual representation of how the percentage of Methylene Blue biosorption using *Avicennia Marina* is influenced by the initial dye concentration and pH.



**Fig.9:** A response surface plot illustrates how the percentage of methylene blue biosorption with

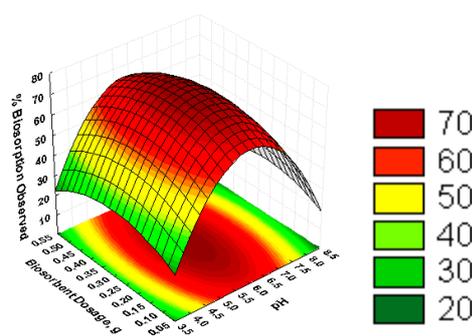
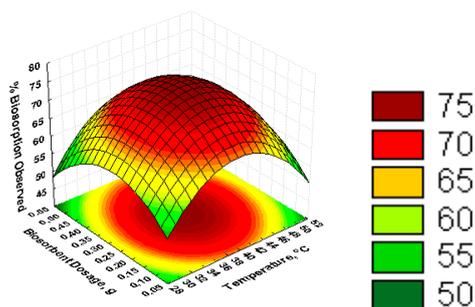


**Fig.10:** A response surface plot visually demonstrates how the percentage of methylene



Avicennia Marina is impacted by the initial dye concentration and the amount of biosorbent used.

blue biosorption with Avicennia Marina is influenced by the pH and temperature.



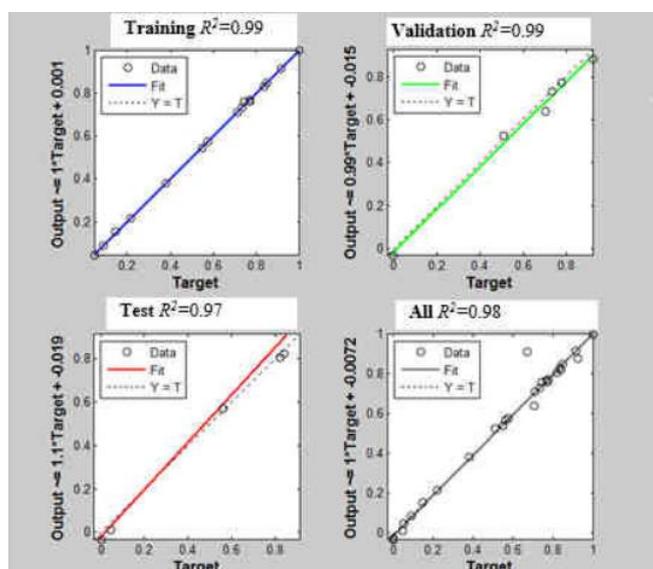
**Fig.11:** A response surface plot visually illustrates the influence of biosorbent dosage and temperature on the percentage of Methylene Blue biosorption using Avicennia Marina.

**Fig.12:** A response surface plot visually demonstrates the impact of biosorbent dosage and pH on the percentage of Methylene Blue biosorption using Avicennia Marina.

### 3.4--\_ANN

The neural network developed utilized input data derived from experimental variables, specifically initial pH, sorbent dosage, and starting concentration, to predict the quantities of adsorbed dye. Figure 13 presents a graphical representation of the verification, training, and test data for the ANN model, highlighting

its precision in making accurate predictions. In assessing the model's performance, various statistical parameters, such as standard error (SE), mean ( $\mu$ ), standard deviation ( $\sigma$ ), and regression coefficient ( $R^2$ ), were employed. Detailed statistical insights into the model's performance are provided in Table 7.



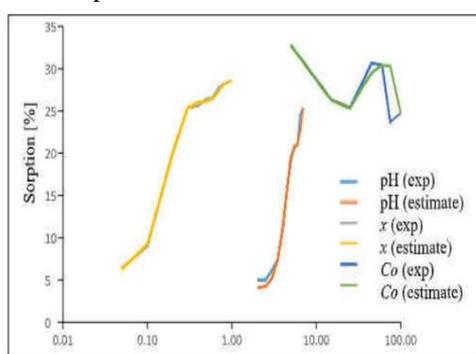
**Fig. 13:** The comparison between predicted and target values is conducted in terms of the percentage of dye elimination.



**Table-. \_7. The ANN Model's Statistical Performance (Zaharia, C, and Suteu, D 2012).**

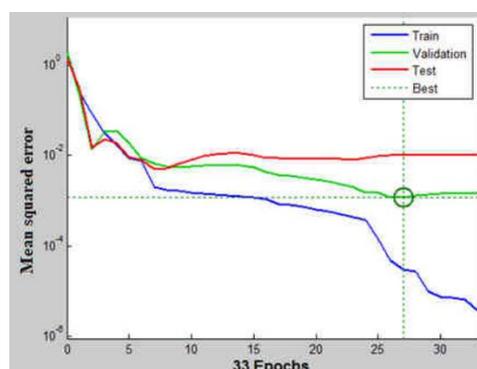
Model	Structure	$R^2$	$\sigma$	SE	$\mu$
I	3-6-1-1	0.99	8.4	2.16	1.01
II	3-5-1-1	0.97	8.4	2.24	0.99
III	3-4-1-1	0.96	8.3	1.64	1.00
IV	3-3-1-1	0.93	8.9	1.29	0.99
V	3-2-1-1	0.94	8.9	1.34	1.01

These findings highlight a strong correlation between the observed values in the generated models, as illustrated in the table. To evaluate the effectiveness of the ANN modeling as a valuable tool, the relationship between the prediction outputs of the developed ANN model and the experimental data was established.



**Fig.14:** The results of the experiment are compared with the predictions of the model.

Figure 14 presents a comparison of the experimental and predicted outcomes concerning initial pH, sorbent dosage (“x”), and initial concentration (co). The graph illustrates a close agreement between the experimental and projected results.



**Fig.15:** Mean Squared Error (MSE) of Methylene Blue Dye versus the number of epochs.

With robust  $R^2$  values of 0.97 for the test set, 0.99 for training, and 0.99 for validation, the artificial neural network (ANN) has demonstrated exceptional efficacy in modeling biosorption. The assessment of the ANN model's efficiency was based on achieving maximum  $R^2$  and minimizing the mean squared error (MSE) for the testing set. The exploration of the hidden layer involved varying the number of neurons from 1 to 20.

Notably, the method's performance exhibited no noticeable change after 27 epochs, as depicted in the graph showcasing the optimal ANN models. The most favorable validation performance was observed at epochs 27 and 28, attaining an MSE value of 0.0011846. Figure 15 offers insights into the effective training of the network through the resilient back-propagation technique.

## CONCLUSION

To enhance the efficiency of methylene blue elimination using *Avicennia marina* as a biosorbent, response surface methodology (RSM) was applied to pinpoint the optimal process parameters. The intricate interplay among pH, temperature, biosorbent dosage, and initial methylene blue concentration collectively exerted a significant influence on the dye removal process.

Under specific conditions, namely a pH of 5.8, temperature at 39.4°C, and a biosorbent dosage of 0.27 grams, *Avicennia marina* exhibited the removal of 75.86% of the initial 53.07 mg/L methylene blue. The characterization of *Avicennia marina* revealed a surface area of 40 m<sup>2</sup>/g and a pore volume of 0.265 cm<sup>3</sup>/g.

Utilizing a three-layered neural network featuring six neurons in the hidden layer, the predictive capability of



Avicennia marina in removing methylene blue from aqueous solutions was precisely determined. A meticulous examination of the experimental data and the forecasts generated by the developed ANN model revealed a robust agreement between them.

## ACKNOWLEDGEMENT

We would like to extend our sincere appreciation to the Head of School (HOS), the Head of Department (HOD) in the Department of Engineering, the (ADAA) Administrative and Academic Affairs, and the Dean of UTAS-Salalah, for their invaluable suggestions, support, and thoughtful recommendations. Furthermore, we are grateful for the provision of essential infrastructural facilities that played a crucial role in making this work possible.

## REFERENCES

1. Anjaneyulu, Y, Sreedhara, C. N, and Samuel, S.R.D. " Decolorization of industrial effluents-available methods and emerging technologies – A review, " *Rev. Environ. Sci. Biotechnol.* (2005); 4(4): 245-273.
2. Bozluur, R. M., Shibata, S., Diba, C. F., Uono, M." Low cost biodegradable adsorbent material for the removal of dissolved dyes from aqueous solutions:An economical process," *IACSIT Intern. J. Eng. & Technol.* (2012); 2(5): 468-473.
3. Chairez I, Garcia-Pena I, Cabrera A. Dynamic numerical reconstruction of a fungal biofiltration system using differential neural network. *J Process Control.* (2009); 19:1103-1110. DOI: 10.1016/j.jprocont.2008.12.009.
4. Crini, G., " Non -biodegradable low-cost adsorbent for dye removal. A review, " *Bioresour. Technol.* (2006); 97(9): 1061-1085.
5. Enayatollahi I, Bazzazi AA, Asadi A. Comparison between neural networks and multiple regression analysis to predict rock fragmentation in open-pit mines. *Rock Mech Rock Eng.*; (2014); 47:799-807. DOI: 10.1007/s00603-013-0415-6.
6. Han, Y., Zhang, W., Kan, X., Dong, L., Jiang Z, Li, H., Yang, H., and Chang, R. " Sorption of methylene blue by carboxymethyl cellulose and reuse process in a next procedure, " *Colloids and Surface A: Ohysicochem. Eng. Aspects* (2011), 380: 143-151.
7. Latif, A., Noor, S., Sharif, Q. M., and Najeebullah, M. " Different techniques recently used for the treatment of textile dyeing effluents: Areview, " *J. Chem. Soc. Pak.* (2010); 32(1): 115-124.
8. Salleh, M. A. M., Mahmoud, D. K., Karim, W. A. W. A., and Idris, A. " Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review," *Desalination* (2011); 280(1-3): 1-13.
9. Suteu, D., Zaharia, C., Muresan, R., and Popescu, A. " Using of industrial waste materials for textile wastewater treatment, " *Environ. Eng. Manage. J.* (2009); 8(5): 1097-1102.
10. Ubbe, M. A., Beck, K. R., ONeal, W. G., and Sharma, Y. Ch.." Cellulosic substrates for removal pollutants from a.queous system : A review. 2. Dyes," *BioResources* (2012); 7(2): 2592-2687.
11. Yildiz S, Değirmenci M. Estimation of oxygen exchange during treatment sludge composting through multiple regression and artificial neural networks. *Int J Environ Res.* (2015);9(4):1173-1182. DOI: 10.22059/IJER.2015.1007.
12. Zaharia, C, and Suteu, D. Organic Pollutants Ten Years After the Stockholm Convention Environmental and Analytical Update, T. Puzyn and A. Mostrage-Szlichtyng (eds.), InTech, Rijeka, Croatia. (2012a).
13. Zaharia, C. Environmental Legislation, Politehniun Publishing House, Iasi, Romania. (2008).
14. Zaharia, C., Suteu, D. "Coal fly ash as adsorptive material for treatment of a real textile effluent: Operating parameters and treatment efficiency," *Environ. Sci. pollute. Res.* (2012b; DOI 10. 1007/s11356-012-065-z.