Learnovate-International
An International Open-Access Journal Published By Lapain Press Publications[LPP]
Content Available at www.lapinjournals.com E-ISSN: 3049-1592
Research Article Open Access

STUDIES FOR SORPTION OF ANILINE BLUE DYE USING EUCALYPTUS LEAVES POWDER AND OPTIMIZATION USING CENTRAL COMPOSITE DESIGN

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Article History: Received: 28 Feb 2025, Revised: 06 Mar 2025, Accepted: 25 Mar 2025

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DOI: https://doi.org/10.70604/learnint.v2i1.17

Abstract
In this study, a novel biosorbent called Eucalyptus leaves powder is used in a batch biosorption process to remove the Aniline blue from aqueous solutions. Agitation time, biosorbent size, pH, initial dye concentration, biosorbent dosage, and temperature are among the characteristics that were examined. Lagergren first order and pseudo second order models were included in the kinetic investigation. The study also covered isotherms such as Temkin, Freundlich, and Langmuir as well as thermodynamics. Regression analysis revealed that the experimental data was highly well-fitting and correlated.
Keywords: Time, particle diameter, pH, Temperature, Kinetics, concentration.

1.0 Introduction

Water is undeniably one of the most essential and abundant substances in our environment, existing in all three physical states—liquid, solid, and vapor. Despite its abundance, only about 2.5% of the Earth's water is fresh, and just a tiny fraction of that around 0.26% is easily accessible for human and ecological use in rivers, lakes, and reservoirs [1]. Water resources are generally derived from three main sources:

- Rainwater
- surface water
- Groundwater

Each plays a critical role in meeting water demands, but challenges like climate change and human activities have significantly affected their availability and quality [2, 3]. Groundwater, for instance, is increasingly important because it helps buffer against drought, while surface water supports both human consumption and ecological balance [4, 10]. Unfortunately, water pollution remains a serious threat. It's caused by both point sources (like industrial discharges) and non-point sources (such as agricultural runoff). Many industries including sugar, glass, thermal power, and textile, discharge harmful substances such as heavy metals, dyes, and organic pollutants into water bodies. These contaminants not only degrade water quality but also pose risks to human health and aquatic life [11 - 17]. To address these issues, various water treatment technologies have been developed. Conventional methods like filtration, coagulation, and biological treatment are common but sometimes insufficient on their own [20, 21]. Advanced techniques such as membrane filtration, electrochemical separation, and ion exchange offer better efficiency, while emerging technologies like nanomaterials, carbon nanotubes (CNTs), and zeolite adsorption are gaining ground for their high effectiveness and sustainability [22 - 28]. Among these, adsorption stands out as a simple yet powerful method for removing pollutants. Both physical and chemical adsorption processes are influenced by factors like pH, temperature, and surface area, and they can be modelled using isotherms such as Langmuir, Freundlich, and Temkin to optimize performance [29 - 34]. This brings me to the focus of my current study: **exploring the use of Eucalyptus globulus leaf powder (ELP) as a biosorbent for the removal of Aniline Blue dye from aqueous solutions**. ELP is a natural, low-cost, and biodegradable material with a high adsorption capacity, making it a promising candidate for green water treatment technologies. The study investigates key parameters like contact time, biosorbent size, pH, concentration, adsorbent dosage and temperature to understand the adsorption kinetics and thermodynamics involved.

2.0 Experimental Procedure

The present experimentation is carried out both in batch-wise and column, on biosorption of Aniline blue dye from

aqueous solutions on them biosorbent -Eucalyptus Globulus leaves powder.

The experimental procedure consists of the following steps:

2.1. Reagents and materials

2.2. Preparation of the biosorbent

2.3. Preparation of the 1000 mg/L of Aniline blue solution

2.4. Studies on equilibrium biosorption process

2.5. Studies on biosorption isotherms, kinetics and thermodynamics

2.1. Reagents and materials

All the chemicals used in this investigation were of analytical grade and used without further purification. Solutions of Aniline blue dye were made from a stock solution containing 1000mg of Aniline blue powder in 1 litre. pH of Aniline blue dye solution was adjusted to the desired value by addition of 0.1 M HCL and 0.1M NaOH solutions.

2.2. Preparation of the biosorbent

Eucalyptus globulus leaves was taken from Eucalyptus plant and is dried under sun light in order to remove moisture content present in it. After that it is finely powdered and sized by passing it through a set of sieves ranging from 152 to 52 µm mesh sizes.

The powder of 52-152 µm fractions was separated and used as an adsorbent.

2.3. Preparation of the 1000mg/L of Aniline blue dye solution

Aniline blue dye stock solution of 1000 mg/L was prepared by dissolving 1 g of Aniline blue dye in 1000 ml of distilled water. It produces 1000 ppm dye solution.

From the dye stock solution (1000 ppm) various concentrations of dyes were prepared by suitable dilutions. 100 ppm dye solution was prepared by diluting 100 ml of 1000 ppm dye stock solution with distilled water in 1000 ml volumetric flask up to the mark. Similarly, solutions with different dye concentrations such as 20, 50, 100, 150 and 200 ppm were prepared.

2.4. Studies on equilibrium biosorption

The biosorption was carried out in batch process by adding a pre-weighed amount of Eucalyptus globulus leave powder to a known volume of aqueous solution for a predetermined time interval in an orbital shaker. The procedures adopted to evaluate the various parameters agitation time biosorbent size, biosorbent dosage, initial concentration of lead in aqueous solution, pH and temperature of the aqueous solution on the biosorption of Aniline blue dye were evaluated using single step optimization process.

Table 1: Experimental conditions for biosorption of Aniline blue dye

S.No.	Parameter	Values Investigated
1	Agitation time, t, min	3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180
2	pH of the aqueous solution	2, 3, 4, 5, 6, 7 and 8
3	Initial concentration, C_o, mg/L	20, 50, 100, 150 and 200
4	Initial biosorbent dosage, w, g/L	0.5, 1, 1.5, 2, 2.5 and 3
5	Temperature, K	283, 293, 303, 313 and 323

2.6. Studies on biosorption isotherms, kinetics and thermodynamics

2.6.1 Studies on isotherms

In order to determine the isotherms, 50 ml of known amount of dye concentration is taken in 250 ml conical flask and to this known amount of biosorbent is added and kept for shaking at room temperature at a speed of 180 rpm for optimum time. They are then settled, filtered and the filtrates are analyzed in UV-Spectrophotometer to find the final dye concentrations.

2.6.2 Studies on kinetics

In order to determine the order of the rate of biosorption, 50 ml of known amount of dye concentration is taken in fifteen flasks. To these known amounts of biosorbent is taken in each flask and shaken in orbital shaker at room temperature at a speed of 180 rpm for different time intervals (5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150, 180 min). They are then settled, filtered and the filtrates are analysed using UV-Spectrophotometer to find the final dye concentrations.

2.6.3 Studies on thermodynamics:

To estimate the enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG), 50 ml of aqueous solution containing known amount of dye concentration is taken in each of 250 ml flasks. Optimum amount of biosorbent is added to each of these flasks. These flasks are shaken in orbital shaker at room temperature at a speed of 180 rpm for optimum time. They are then settled, filtered and the filtrates are analysed in UV-Spectrophotometer to find the final dye concentrations.

3.0 Results and Discussion

3.1 Effect of agitation time

The following discussion examines the impact of various parameters on the biosorption of AB dye using Eucalyptus globulus leaf powder (ELP). The experiment was conducted by varying the agitation time from 3 to 180 minutes. As shown in Figure 3.1, the percentage of biosorption increased steadily up to 50 minutes. Maximum biosorption of 60% was achieved at 50 minutes, after which the rate remained constant, indicating that equilibrium had been reached at this point [35, 36].

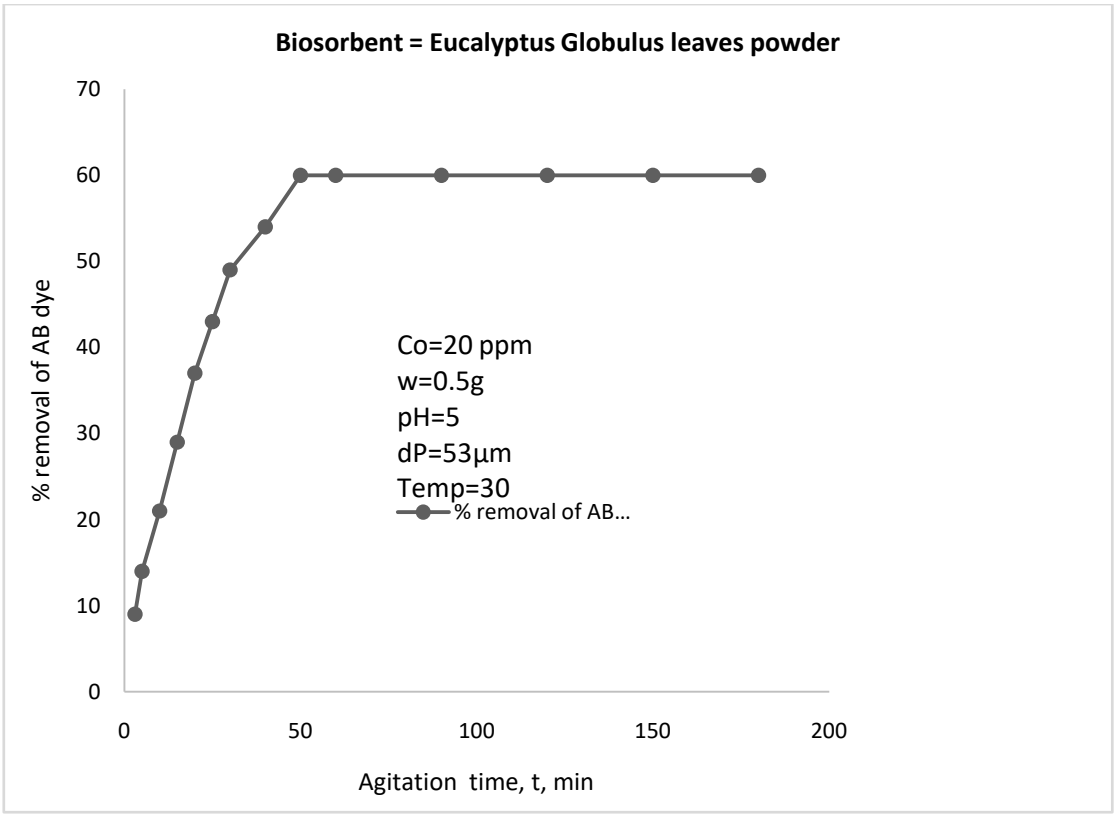

Fig. 3.1 Effect of agitation time on% biosorption of Aniline Blue dye

3.2 Effect of biosorbent size

Figure 3.2 illustrates the relationship between particle size and the percentage of AB dye biosorption using Eucalyptus globulus leaf powder. As the biosorbent particle size decreased from 152 µm to 53 µm, the biosorption efficiency increased from 46% to 60%. This suggests that smaller particle sizes, which offer a larger surface area and more active sites, enhance the interaction between the biosorbent and the bio sorbate [37-39].

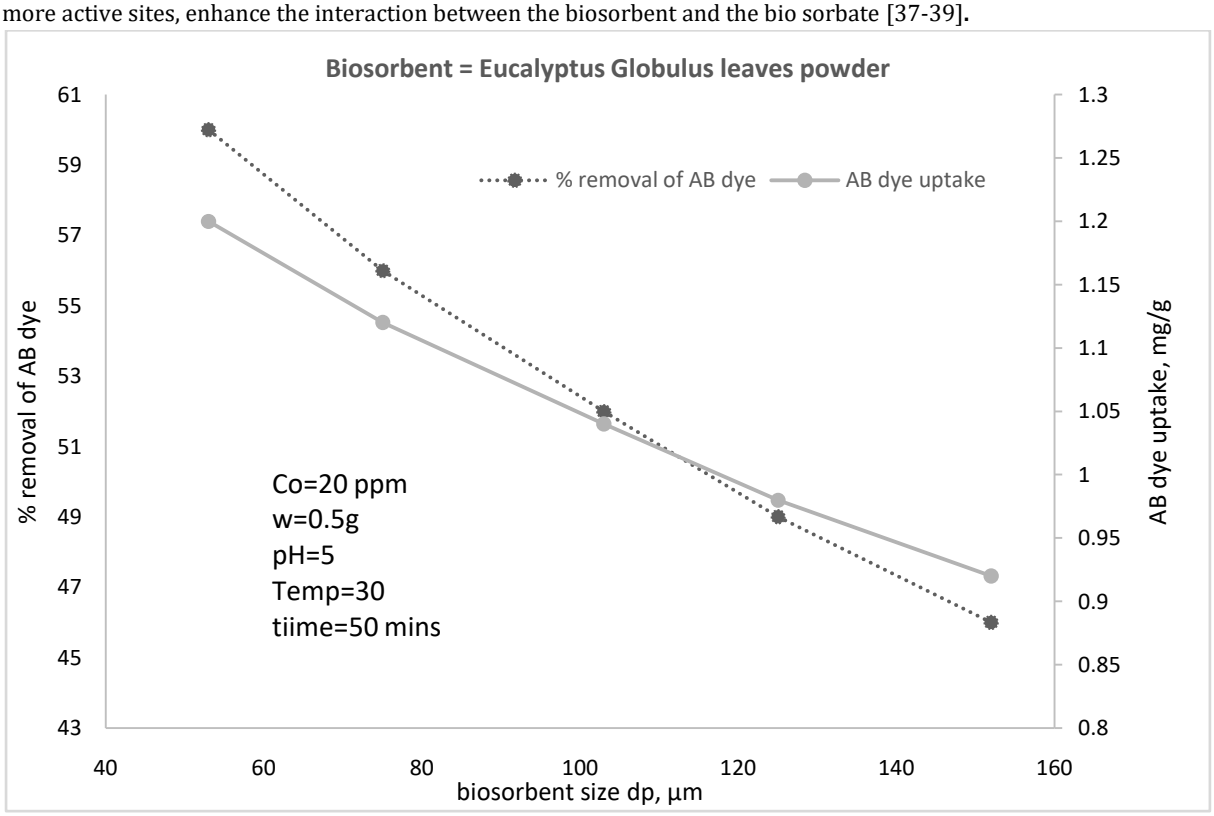

Fig. 3.2 % Biosorption of Aniline blue dye as a function of biosorbent size

3.3 Effect of pH

Figure 3.3 illustrates the effect of pH on the percentage biosorption of AB dye by *Eucalyptus Globulus leaves powder* in an aqueous solution. As the pH increases from 2 to 5, the biosorption efficiency rises from 45% to a peak of 60%, beyond the pH value of 5 it increased slowly and margin is also very less. This trend suggests that electrostatic interactions between the biosorbent and bio sorbate are the primary driving force behind dye biosorption. Stronger electrostatic attraction leads to higher biosorption efficiency.

During the biosorption process, AB dye molecules replace H^+ ions bound to the biosorbent's surface functional groups, facilitating interaction. Functional groups involved include =C–H from alkenes or aromatic rings, symmetric $–SO_3$ stretching, and symmetric CH_3 bending. Additionally, functional groups such as C=N from polyacrylonitrile and thiocyanate (–SCN) actively participate in biosorption. Other contributors include isothiocyanate, diazo, and aromatic combinations. Similar interactions were observed in studies involving orange peel as a biosorbent [40-42].

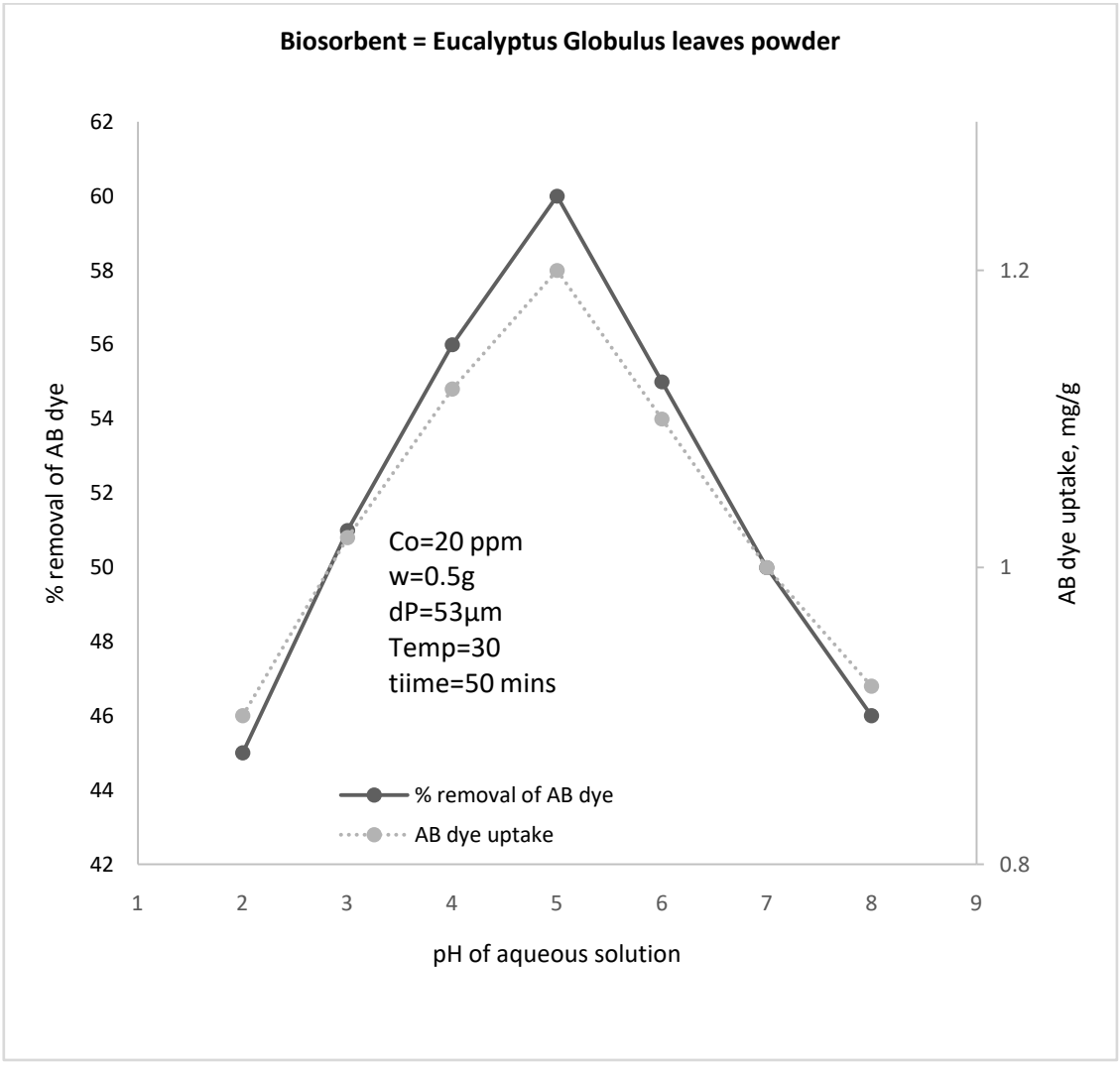

Fig. 3.3 Observation of pH along with % biosorption of AB dye

3.4 Effect of initial concentration of AB dye

The graph in Figure 3.4 illustrates the effect of the initial concentration of AB dye on the percentage biosorption by *Eucalyptus Globulus leaves powder*. As the dye concentration in the aqueous solution increases from 20 mg/L to 200 mg/L, the biosorption efficiency decreases from 60% to 44%. This decline can be attributed to the limited number of available active sites on the biosorbent, which become saturated as the concentration of the dye (bio sorbate) increases [43-45]

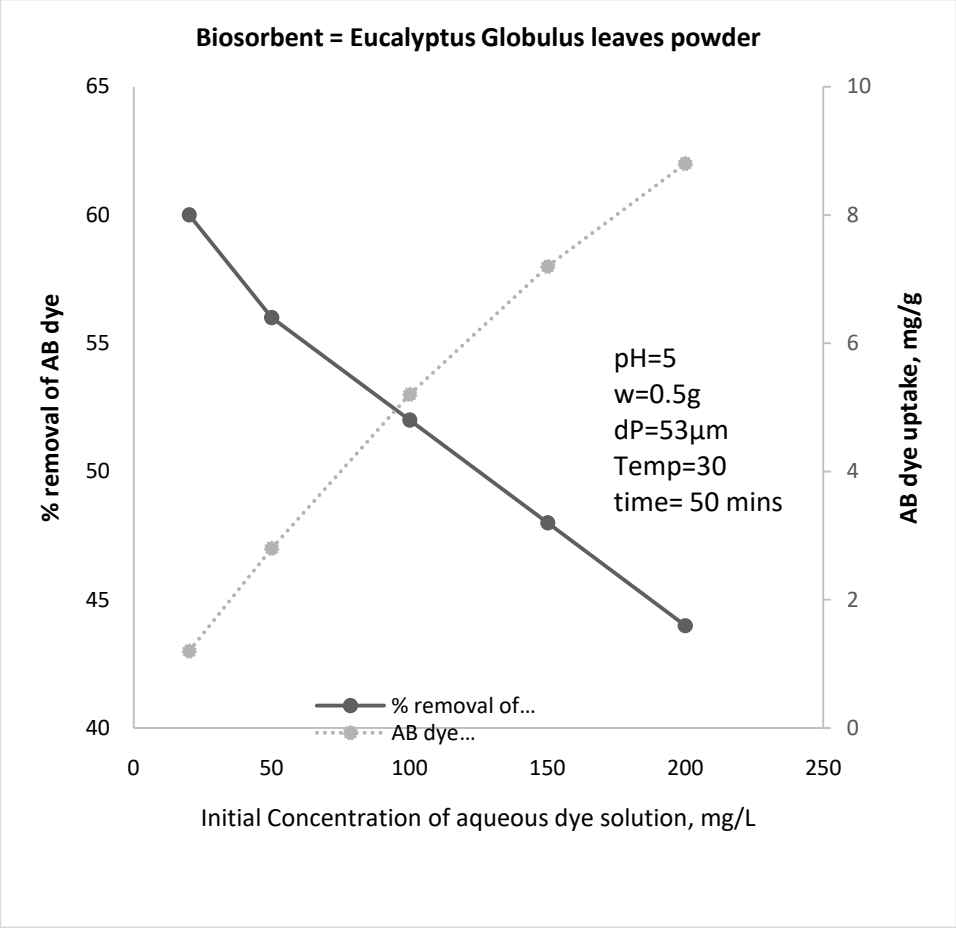

Fig. 3.4 Variation of initial concentration with % biosorption of AB dye

3.5 Effect of biosorbent dosage

Figure 3.5 illustrates the relationship between biosorbent dosage and the percentage biosorption of AB dye using *Eucalyptus Globulus leaves powder*. As the biosorbent dosage increases from 0.5 to 3 g/L, the biosorption efficiency rises from 61% to 91%, with an increase in biosorbent dosage from 10 to 40g/L. This enhancement in dye removal is attributed to the greater number of available active sites provided by the increased quantity of biosorbent, making this trend clearly observable [46-49].

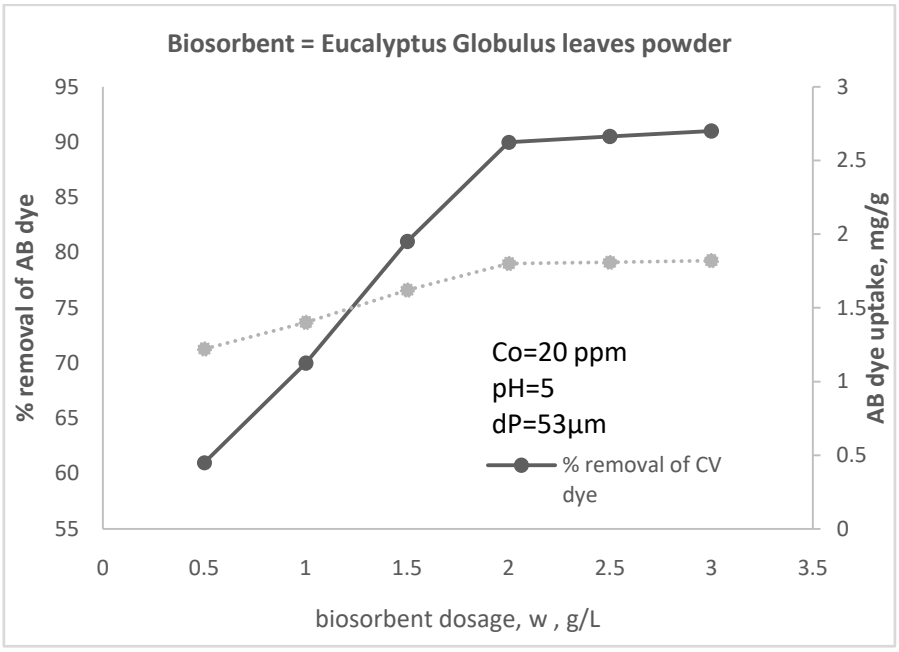

Fig. 3.5 Dependency of% biosorption of AB dye on biosorbent dosage

3.6 Effect of Temperature

Figure 3.6 illustrates the effect of temperature on the equilibrium uptake of AB dye by *Eucalyptus Globulus leaves powder*. The results indicate that the biosorption process is endothermic, as the dye uptake capacity increases with rising temperature. The experiment was conducted over a temperature range of 283 K to 323 K. This enhancement in biosorption at higher temperatures may be due to the formation of new active sites or improved penetration of dye molecules into the micropores of the biosorbent. Additionally, at elevated temperatures, the formation of multilayer adsorption on the surface of *Eucalyptus Globulus leaves powder* may occur, further contributing to increased dye uptake [50-53].

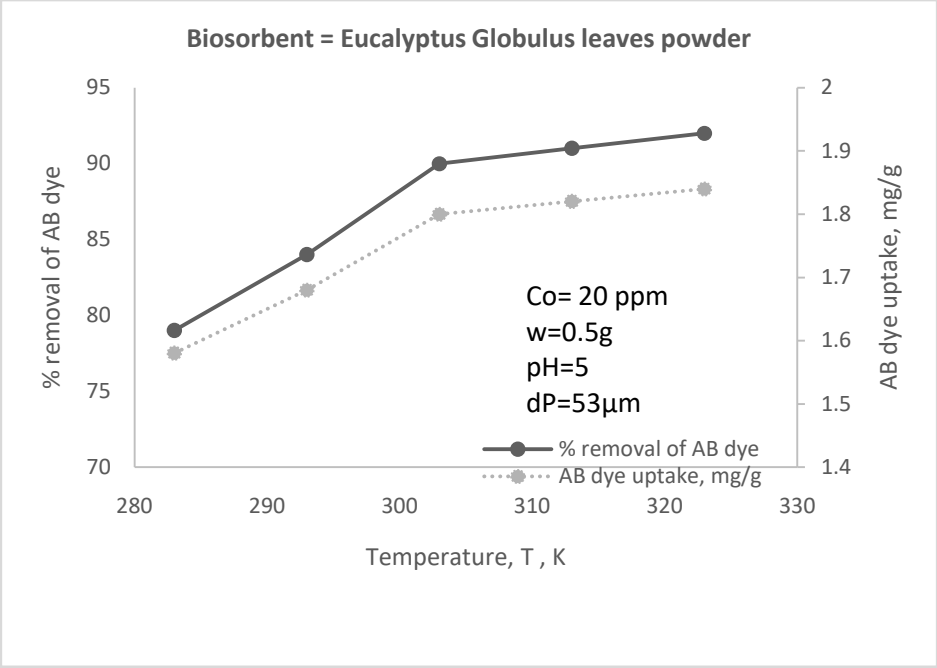

Fig. 3.6 Effect of temperature on% biosorption of AB dye

3.7 Isotherms

3.7.1 Langmuir isotherm

The Langmuir isotherm, represented in Figure 3.7, describes the biosorption behavior of AB dye onto *Eucalyptus Globulus leaves powder* and is expressed by the equation:

$$\frac{Ce}{qe} = 0.0567\ C_e + 6.4224 \qquad \text{.....(5.12)}$$

with a correlation coefficient (R^2) of 0.9961. This high R^2 value indicates a strong fit to the Langmuir model, suggesting a high degree of affinity and uniform binding of AB dye molecules onto the biosorbent surface [54-56]

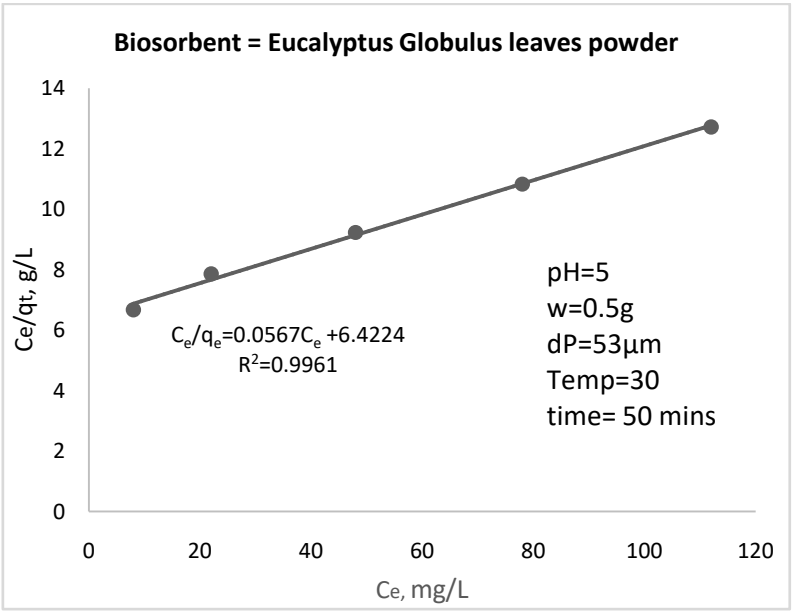

Fig. 3.7.1 Langmuir isotherm for % biosorption of AB dye

3.7.2 Freundlich Isotherm

Figure 3.7.2, which plots ln C_e against ln q_e, yields the following Freundlich isotherm equation:

$$\ln q_e = 0.7632 \ln C_e - 1.3636 \quad \ldots\ldots (5.13)$$

The correlation coefficient (R^2) of 0.9961 indicates a good fit to the model. The value of *n* (0.7632), which falls within the range 0 <*n*< 1, confirms that the biosorption process is favorable under the studied conditions [55-57]

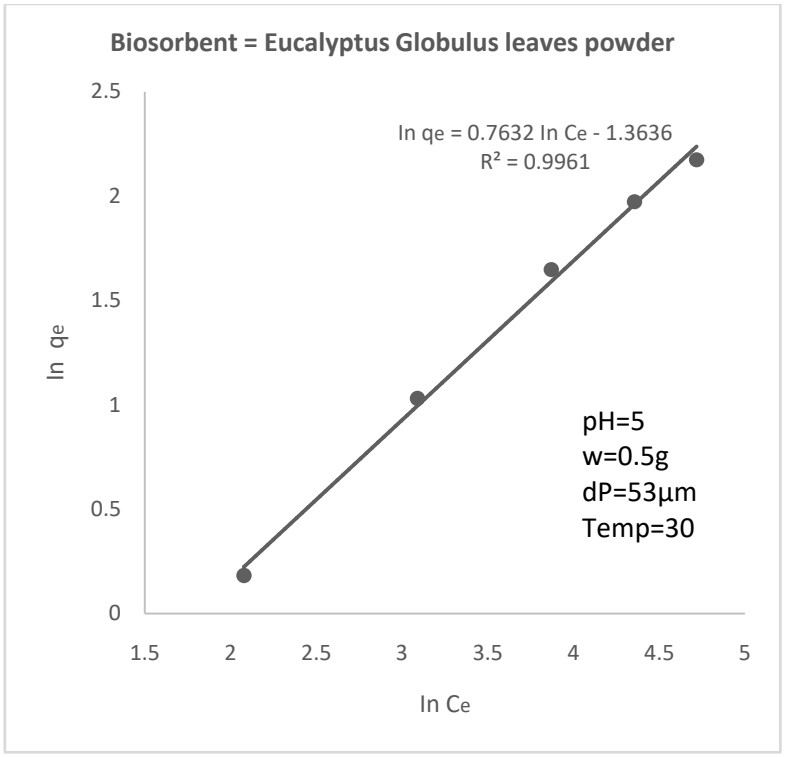

Fig. 3.7.2 Freundlich isotherm for % biosorption AB dye

3.7.3 Temkin isotherm

The experimental data were analyzed using the linear form of the Temkin isotherm, as shown in Figure 3.7.3 The resulting equation for the biosorption of AB dye is:

$$q_e = 0.3333 \ln C_e + 1.9436 \quad \ldots\ldots (3.1)$$

This linear relationship suggests that the heat of biosorption of AB dye onto *Eucalyptus Globulus leaves powder* decreases linearly with increasing coverage, which is consistent with the assumptions of the Temkin model.

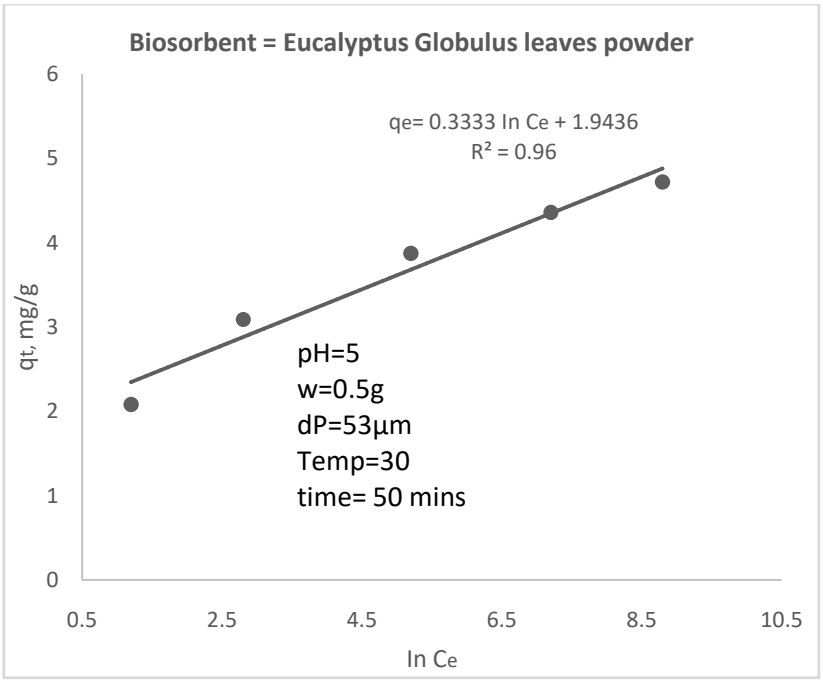

Fig. 3.7.3 Temkin isotherm for % biosorption of AB dye

The isotherm constants for the Langmuir, Freundlich, and Temkin models are summarized in Table 3.10. Among the three, the Langmuir isotherm shows the best fit to the equilibrium data with the highest correlation coefficient (R^2 = 0.9961), followed by the Freundlich (R^2 = 0.9961) and Temkin (R^2 = 0.96) isotherms, indicating that the biosorption process is best described by the Langmuir model [57-59].

Table – 3.1 Isotherm constants are obtained for various isotherm model as show

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
q_{m} = 17.6366 mg/g	K_f = 0.25573 mg/g	A_T = 340.8297 L/mg
R_L = 0.934	n = 0.7632	b_T =7558.1818
R^2 = 0.9961	R^2 = 0.9961	R^2 = 0.96

3.8 Kinetics

3.8.1 Lagergren first order rate constant

The experimental data were analyzed using both the Lagergren first-order rate equation and the pseudo-second-order rate equation. A plot of log ($q_e - q_t$) versus agitation time (t), based on the Lagergren model, is presented in Figure 3.8.1 Table 3.2 provides a summary of the rate constant values for both kinetic models. The Lagergren first-order kinetic equation is expressed as:

$$\log (q_e - q_t) = -0.0252t + 0.1258 \quad \text{..... (3.2)}$$

with a rate constant of **0.0580356min^{-1}**and a correlation coefficient (**R^2**) of **0.9858**.

These results indicate that both the first-order and second-order kinetic models adequately describe the biosorption interactions.

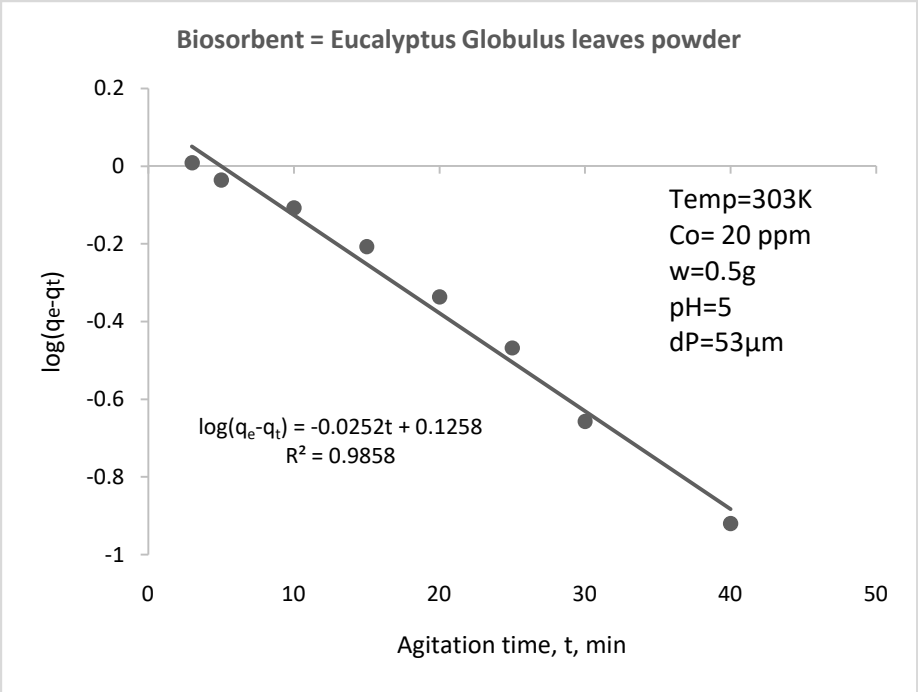

Fig. 3.8.1 first order kinetics for% biosorption of AB dye

3.8.2 Pseudo Second order rate equation

Figure 3.8.2 presents the pseudo-second-order kinetics plot of **t versus t/q_t** for the biosorption of AB dye. The corresponding rate constant values for both first- and second-order kinetic models are summarized in Table 3.2. It is observed that both models effectively describe the biosorption process. The pseudo-second-order kinetic equation is given as:

$$(t/q_t) = 0.5109\ t + 16.54 \quad \text{..... 5.16}$$

with a correlation coefficient **R^2 = 0.9595** [60-62]

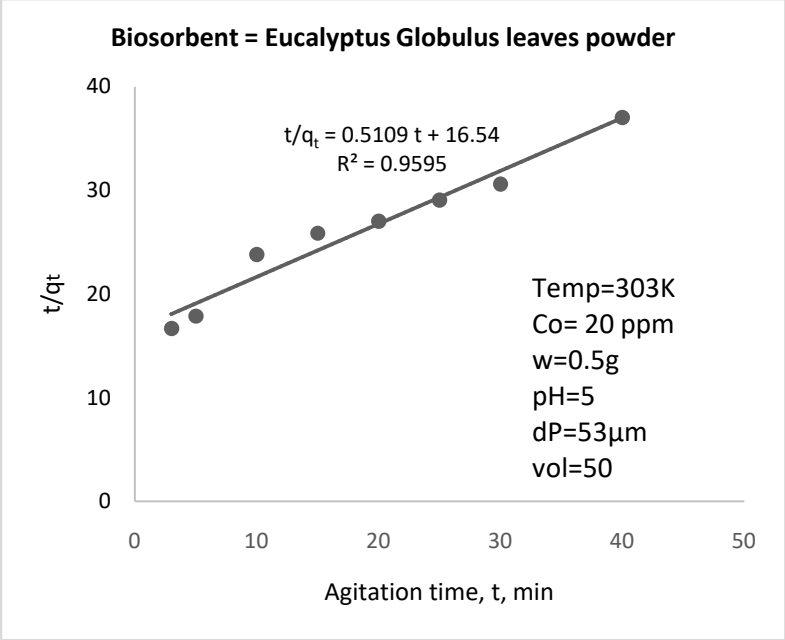

Fig. 3.11 second order kinetics for % biosorption of AB dye

Table – 3.2 Equations and rate constants

Order	Equation	Rate constant	R^2
Lagergren first order	$\log(q_e-q_t) = -0.0252t + 0.1258$	$0.0580356 min^{-1}$	0.9858
Pseudo second order	$(t/q_t) = 0.5109\ t + 16.54$	1.57E-02 g/ (mg-min)	0.9595

3.9 Thermodynamics

A set of thermodynamic parameters including the changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated to understand the nature of the biosorption process. The negative ΔG value of **–21,388.5804 J/mol** suggests that the biosorption of AB dye onto *Eucalyptus Globulus leaves powder* occurs spontaneously. Additionally, higher temperatures enhanced the biosorption efficiency, resulting in increased equilibrium biosorption capacity. The positive ΔH value of **22.1571 J/mol** confirms that the process is **endothermic**, while the positive ΔS value of **70.6625 J/mol K** indicates a strong affinity of *Eucalyptus Globulus leaves powder* for AB dye, reflecting increased randomness at the solid–solution interface during biosorption [61,62].

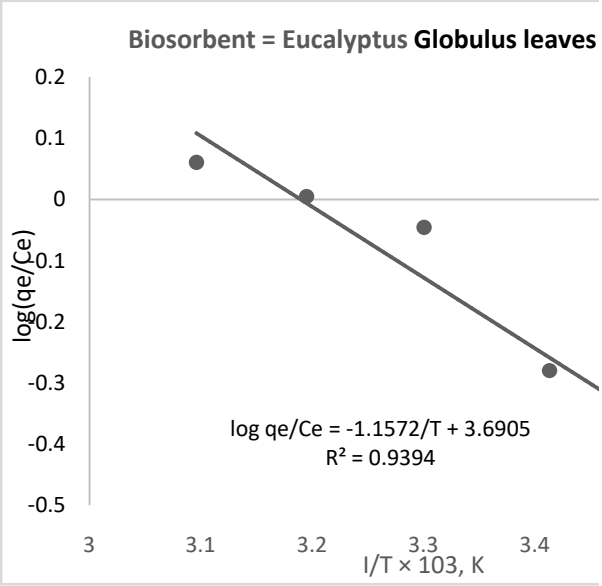

Fig 3.9 Vant off's plot for % biosorption of AB dye

4.0 Optimization using Response Surface Methodology (RSM)

4.1 Optimization using Central Composite Design

In the present study, the levels of four process input variables for% biosorption are shown in table-4.11

Table–4.11 Levels of different process variables in coded and un-coded form for % dye decolorization of Aniline blue dye using *Eucalyptus Globulus leaves* powder

Variable	Name	Range and levels				
		-2	-1	0	1	+2
X_1	pH of aqueous solution	3	4	5	6	7
X_2	Initial AB dye concentration, C_o, mg/L	10	15	20	25	30
X_3	Sorbent dosage, w, g/L	20	30	40	50	60
X_4	Temperature, K	283	293	303	313	323

To determine the optimal conditions for the biosorption of AB dye, it is essential to identify the parameters that most significantly influence the response. Table 4.11 presents the variations in the coded values of four key parameters—**pH (X_1), initial dye concentration (C_0, X_2), adsorbent dosage (w, X_3), and temperature (T, X_4)** along with the corresponding biosorption responses, based on experimental runs and predicted values from the Central Composite Design (CCD).

The regression model, derived from multiple regression analysis of the experimental data, expresses the percentage biosorption of AB dye as a function of these variables. The regression equation is as follows:

$$\% \text{ Biosorption} = Y = -1484.84 + 51.19 X_1 + 4.35 X_2 + 1.35 X_3 + 8.92 X_4 - 4.64 X_1^2 - 0.07 X_2^2 - 0.02 X_3^2 - 0.01 X_4^2 - 0.06 X_1X_2 - 0.01 X_1X_3 - 0.02 X_1X_4 - 0.000 X_2X_3 - 0.000 X_2X_4 + 0.000 X_3X_4 \quad \text{.....(5.17)}$$

Table – 4.12 Results from CCD for Aniline blue dye decolorization by *Eucalyptus Globulus leaves* powder

Run no.	X_1(pH)	X_2(C_o)	X_3(w)	X_4(T)	% dye decolorization of Aniline blue dye	
					Experimental	Predicted
1	4	15	30	298	74.88	74.90
2	4	15	30	308	76.60	76.59
3	4	15	50	298	75.56	75.56
4	4	15	50	308	77.26	77.26
5	4	25	30	298	76.76	76.73
6	4	25	30	308	78.38	78.41
7	4	25	50	298	77.38	77.41
8	4	25	50	308	79.12	79.10
9	6	15	30	298	77.10	77.08
10	6	15	30	308	78.76	78.76
11	6	15	50	298	79.74	79.74
12	6	15	50	308	81.42	81.41
13	6	25	30	298	77.88	77.91
14	6	25	30	308	79.62	79.58
15	6	25	50	298	80.62	80.59
16	6	25	50	308	82.24	82.25
17	3	20	40	303	74.18	74.17
18	7	20	40	303	79.48	79.51
19	5	10	40	303	76.52	76.52
20	5	30	40	303	79.18	79.19
21	5	20	20	303	77.14	77.15
22	5	20	60	303	80.48	80.49

23	5	20	40	293	78.14	78.13
24	5	20	40	313	81.48	81.49
25	5	20	40	303	92.00	92.00
26	5	20	40	303	92.00	92.00
27	5	20	40	303	92.00	92.00
28	5	20	40	303	92.00	92.00
29	5	20	40	303	92.00	92.00
30	5	20	40	303	92.00	92.00

The experimental setup for the Central Composite Design (CCD) included **2^4 factorial runs**, **6 central points**, and **8 axial points**, with agitation time maintained at **50 minutes** and biosorbent particle size fixed at **53 µm**. The observed response values under these coded experimental conditions were used to develop the regression model (Equation 5.17).

The results of this model were analyzed through **ANOVA (Analysis of Variance)**. Based on the **Fisher's F-test** and an extremely low **probability value (P_{model}> F = 0.000000)**, the ANOVA results (refer to Table 4.13) confirm that the model is **highly significant**, indicating that the differences among the treatments are statistically meaningful.

Table – 4.13 Analysis of variance (ANOVA) of Aniline blue dye decolorization for entire quadratic model

	SS	df	MS	F	p
(1)pH (L)	42.7734	1	42.7734	65917.9	0.000000
pH (Q)	394.2467	1	394.2467	607571.9	0.000000
(2) Concentration, mg/L(L)	10.6667	1	10.6667	16438.4	0.000000
Concentration, mg/L(Q)	342.9960	1	342.9960	528589.8	0.000000
(3) Dosage, g/L(L)	16.7334	1	16.7334	25787.8	0.000000
Dosage, g/L(Q)	298.0187	1	298.0187	459275.3	0.000000
(4) Temperature, K(L)	16.9344	1	16.9344	26097.5	0.000000
Temperature, K(Q)	254.5272	1	254.5272	392250.9	0.000000
1L by 2L	1.0000	1	1.0000	1541.1	0.000000
1L by 3L	3.9601	1	3.9601	6102.9	0.000000
1L by 4L	0.0004	1	0.0004	0.6	0.444599
2L by 3L	0.0004	1	0.0004	0.6	0.444599
2L by 4L	0.0001	1	0.0001	0.2	0.700161
3L by 4L	0.0000	1	0.0000	0.0	1.000000
Error	0.0097	15	0.0006		
Total SS	998.8515	29			

In the statistical analysis, **df** refers to the degrees of freedom, **SS** to the sum of squares, **F** to the F-value, and **P** to the probability value. The model shows a strong fit with an **R^2 value of 0.9896** and an **adjusted R^2 of 0.9896**, indicating excellent predictive accuracy.

According to Table 4.14, the **greater the 't' value** and the **smaller the 'P' value**, the more significant the corresponding coefficient is. Based on the analysis of 't' and 'P' values from Table 4.14, it is evident that the terms **X_1, X_2, X_3, X_4, X_1^2, X_3^2, X_4^2, X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_2X_4, and X_3X_4** have a high level of significance. These terms play key roles in explaining both the individual and interactive effects of the input variables on the biosorption of AB dye.

Table – 4.14 Estimated regression coefficients for the AB dye decolorization onto *Eucalyptus Globulus leaves* powder

Terms	Regression coefficient	Standard error of the coefficient	t-value	*P*-value
Constant	-11359.7	18.13641	-626.348	0.000000
X_1	38.6	0.39067	98.703	0.000000
X_2	-3.8	0.00486	-779.469	0.000000

X_3	6.1	0.07801	77.780	0.000000
X_4	-0.1	0.00019	-727.042	0.000000
X_1*X_1	2.5	0.03900	63.319	0.000000
X_2*X_2	-0.0	0.00005	-677.699	0.000000
X_3*X_3	74.0	0.11830	625.682	0.000000
X_4*X_4	-0.1	0.00019	-626.300	0.000000
X_1*X_2	-0.1	0.00127	-39.257	0.000000
X_1*X_3	0.0	0.00064	78.121	0.000000
X_1*X_4	-0.0	0.00127	-0.785	0.444598
X_2*X_3	0.0	0.00013	0.785	0.444598
X_2*X_4	-0.0	0.00025	-0.393	0.700161
X_3*X_4	-0.0	0.00013	-0.000	1.000000

Terms with **P ≥ 0.05** were considered **insignificant** and thus removed from the model. As a result, variable $\mathbf{X_2}$ was excluded, and the regression equation was simplified to the following reduced form:

% Biosorption = Y = −1484.84 + 51.19 X_1 + 4.35 X_2 + 1.35 X_3 + 8.92 X_4 − 4.64 X_1^2 − 0.07 X_2^2 − 0.02 X_3^2 − 0.01 X_4^2 − 0.06 X_1X_2 − 0.01 X_1X_3 − 0.02 X_1X_4 − 0.000 X_2X_3 - 0.000 X_2X_4+ 0.000 X_3X_4 (Equation 5.18)

The **regression coefficient (R^2) of 0.9994** indicates an exceptionally strong model fit, with only **0.006% of the total variation** left unexplained by the model [63-69].

An analysis of the **F-statistic** (as shown in the referenced table) confirms that the model is highly significant. This supports the conclusion that the regression equation effectively predicts the percentage biosorption of AB dye. In general, **P-values less than 0.05** signify that the terms are statistically significant at a **95% confidence level**.

Additionally, from Table 5.15, it is evident that **all squared terms** of the variables exhibit greater significance than their linear counterparts. Moreover, **all interaction terms** with **P < 0.05** are highly significant, indicating a strong influence on the biosorption capacity

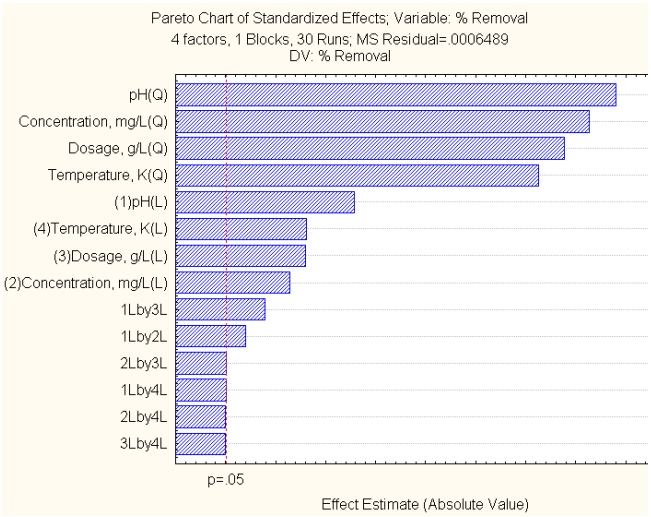

Fig. 4.11 Pareto Chart

The optimum set of conditions for achieving the maximum percentage biosorption of AB dye was found to be **pH = 5.1823**, **initial AB dye concentration = 20.4393 mg/L**, **biosorbent dosage = 41.4048 g/L**, and **temperature = 303.5884 K**. Under these optimal conditions, the extent of biosorption was **92.46%**. It is evident that the experimental values for percentage biosorption are in close proximity to those predicted by the **Central Composite Design (CCD)**. Experiments conducted in **triplicate** using the above-mentioned optimized parameters resulted in an average AB dye biosorption of **92.46%**, which is in good agreement with the predicted value.

4.1.2 Interpretation of residual graphs

Figure 4.1.2 displays the **normal probability plot of residuals**. The experimental data align well with the predicted values, indicating minimal error and validating the model's predictive capability.

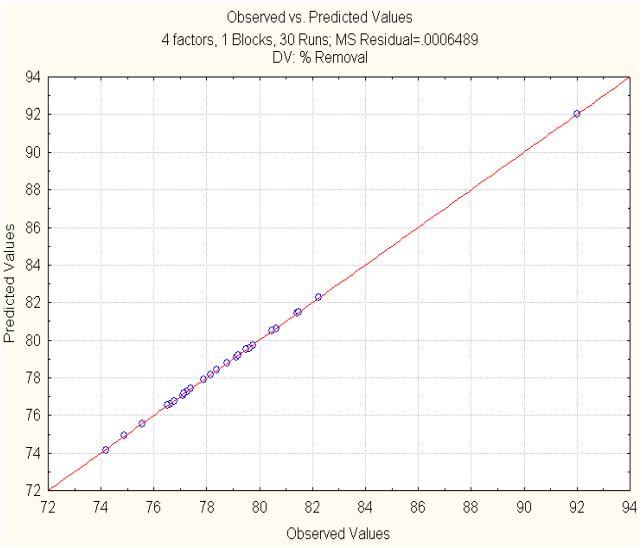

Fig. 4.1.2 Normal probability plot for % dye decolorization of Aniline blue dye

4.1.3 Interaction effects of biosorption variables

Figs. 4.1.3(a) to (f) present the **three-dimensional response surface plots**. The plots show that the **percentage biosorption** of the biosorbent reaches its **maximum at both low and high levels** of the variables. However, there exists a specific **intermediate region** where the biosorption efficiency is comparatively lower, indicating a **non-linear interaction** between the variables.

An **increasing or decreasing trend** in the percentage biosorption is **not clearly observed** across the variable range. The response appears to be influenced by complex interactions among the parameters.

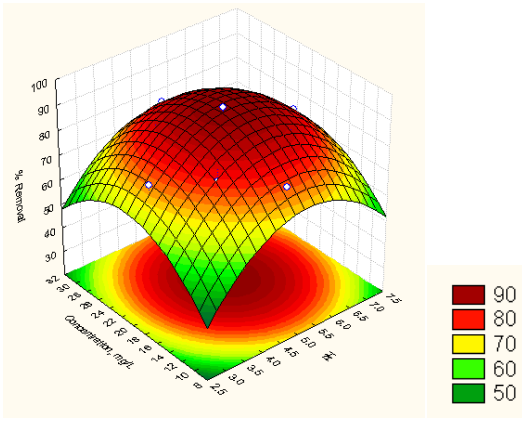

Fig. 4.1.3 (a). Surface contour plot effect of pH and concentration on the % AB dye decolorization

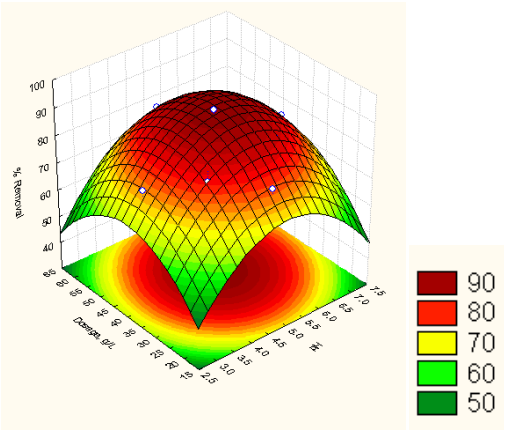

Fig. 4.1.3 (b). Surface contour plot effect of pH and dosage on the % AB dye decolorization

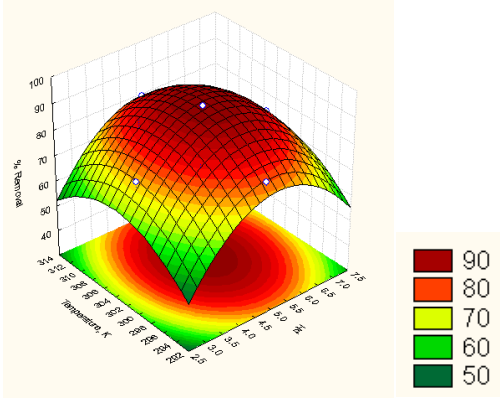

Fig. 4.1.3 (c). Surface contour plot effect of pH and temperature on the % AB dye decolorization

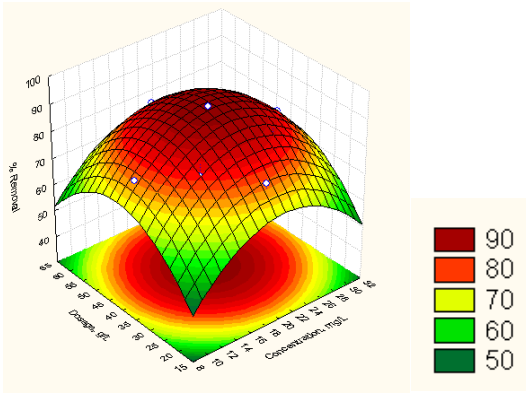

Fig. 4.1.3 (d). Surface contour plot effect of conc and dosage on the % AB dye decolorization

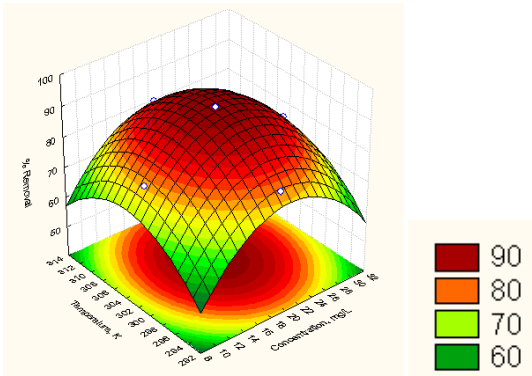

Fig. 4.1.3 (e). Surface contour plot effect of conc and temperature on the % AB dye decolorization

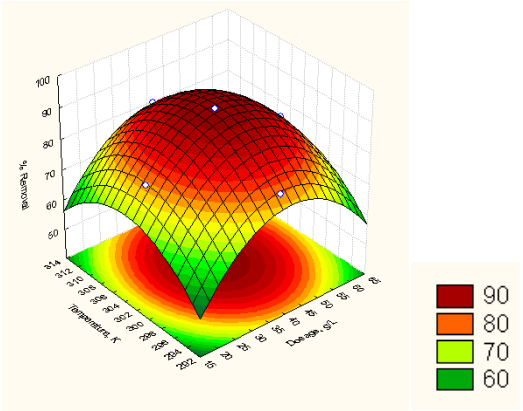

Fig. 4.1.3 (f). Surface contour plot effect of dosage and temperature on the % TYdye decolorization

Conclusion

1. The **equilibrium agitation time** for AB dye biosorption was found to be **50 minutes**.
2. The **optimum biosorbent dosage** required for effective biosorption is **53 g/L**.
3. The **maximum biosorption efficiency** was observed at **pH = 5**.
4. Based on the **predicted values from the RSM model**, the **maximum biosorption of AB dye (95.8056%)** is achieved when the process parameters are optimized as follows:
    - **pH** = 5.823

- **Biosorbent dosage (w)** = 41.4048 g/L
- **Initial dye concentration (Co)** = 20.4393 mg/L
- **Temperature (T)** = 303.5884 K

The investigation further confirms that the biosorption process is:

- **Endothermic**, as indicated by a positive enthalpy change (**ΔH = 22.1571 J/mol**)
- **Spontaneous**, due to the negative Gibbs free energy (**ΔG = -21388.5804 J/mol**)
- **Irreversible**, as shown by the positive entropy change (**ΔS = 70.6625J/mol·K**)

Acknowledgement

The author sincerely expresses his profound gratitude to **Andhra University** and the **Department of Chemical Engineering** for their generous support in providing the necessary chemicals, equipment, and laboratory facilities essential for the successful completion of this work.

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