



Treatment of Methylene Blue Dye using Natural Adsorbents

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Abstract: Methylene blue is a common dye utilized in various industries such as textiles, printing, and laboratory trying out. in terms of treating wastewater containing methylene blue dye, natural adsorbents can be effective and environmentally pleasant alternatives. Activated Carbon isn't always a "natural" in its processed shape, activated carbon can be derived from natural assets like coconut shells, wooden, or coal. It has a high surface place and porosity, making it effective for adsorbing a wide variety of pollution consisting of methylene blue dye. The maximum Langmuir value Q_e is 1.25 mg/l. The adsorbent is more observing the adsorbate in these factors of pH is 8.5, Temperature is 28.5°C, Concentration is 175 ppm, Dosage is 0.15 mg/l and Timing is 75 mins. The effectiveness of those natural adsorbents can range depending on factors consisting of the unique dye awareness, pH of the solution, contact time, and temperature. additionally, the regeneration and reusability of the adsorbents have to also be considered for sensible applications. normal, herbal adsorbents offer a promising approach for the remedy of methylene blue dye and other pollution in wastewater.

Keywords: Methylene Blue, Adsorption, Isotherm, Design expert (Software)

1. INTRODUCTION

In the textile industry, methylene blue is used as a dye for cotton, silk, and wool. Chemical shape of Methylene blue belongs to the thiazine elegance of dyes. Its chemical system is $C_{16}H_{18} ClN_3S$, and its molecular weight is 319.eighty-five g/mol. Structurally, it consists of 3 aromatic earrings: phenyl jewelry and one thiazine ring. Methylene blue is maximum commonly acknowledged for its deep blue shade in its oxidized form. however, it is able to seem colorless or mild blue whilst reduced. organic Staining of Methylene blue is frequently used as a organic stain in microscopy to focus on mobile structures and differentiate between cell kinds. The environmental impact of methylene blue may be harmful to aquatic lifestyles and the environment if no longer disposed of properly.

Efforts are made to limit its launch into water systems. Cassia fistula, typically called the golden bathe tree or Indian laburnum, is a flowering plant local to the Indian subcontinent and other parts of Southeast Asia. Its different clusters of shiny yellow flora make it a popular ornamental tree in tropical and subtropical regions international. The fruit of Cassia fistula is a long, cylindrical pod that usually measures about 30 to 60 centimeters in duration. It has a easy, difficult outer shell that turns from inexperienced to brown as it matures. The adsorption technique involves the binding of dye molecules onto the floor of the Cassia fistula adsorbent thru bodily or chemical interactions. The porous shape and surface chemistry of Cassia fistula contribute to its adsorption efficiency through supplying ample energetic web sites for dye molecules to stick to. using herbal adsorbents like Cassia fistula promotes environmental sustainability by using decreasing reliance on synthetic chemical compounds and minimizing waste generation.

2. Materials and Methods

2.1. Dye Removal Process

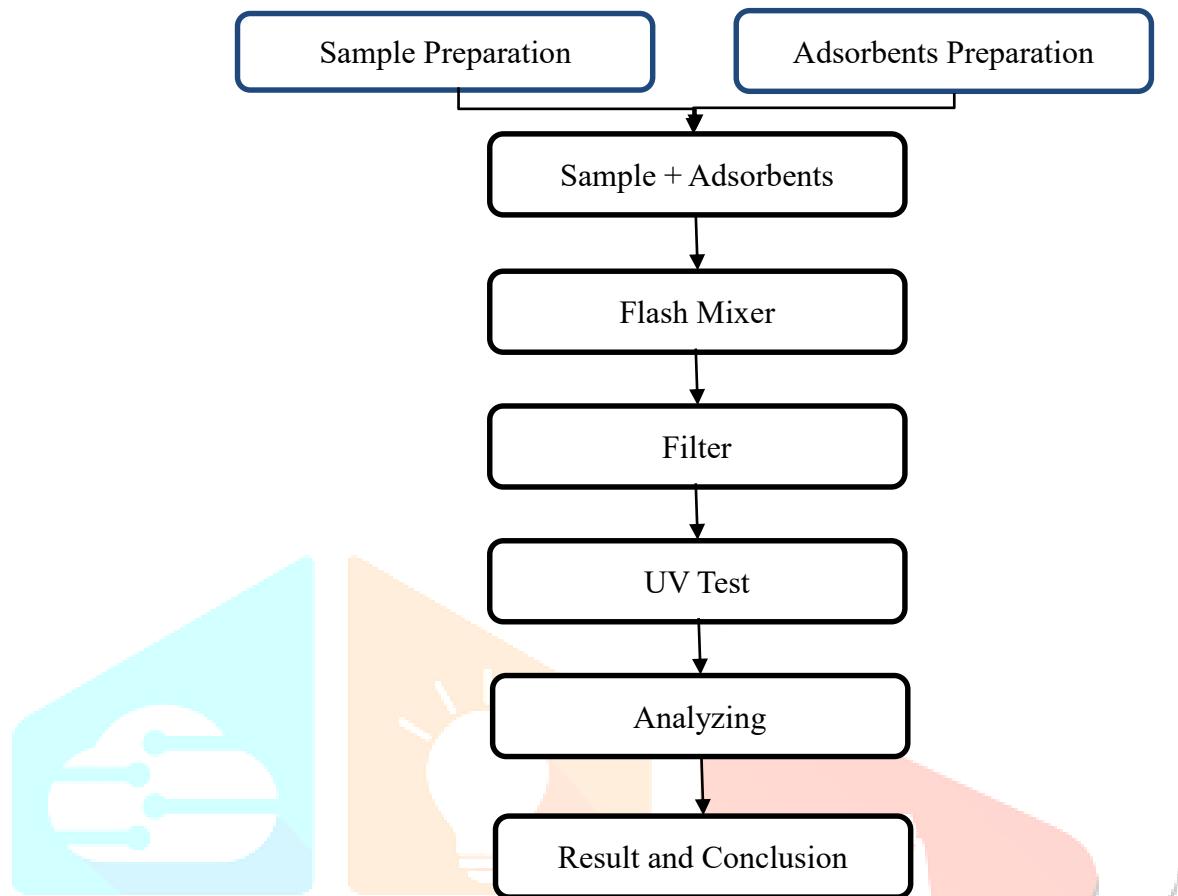


Figure 2.1: Dye Removal Process

2.2. Sample Preparation

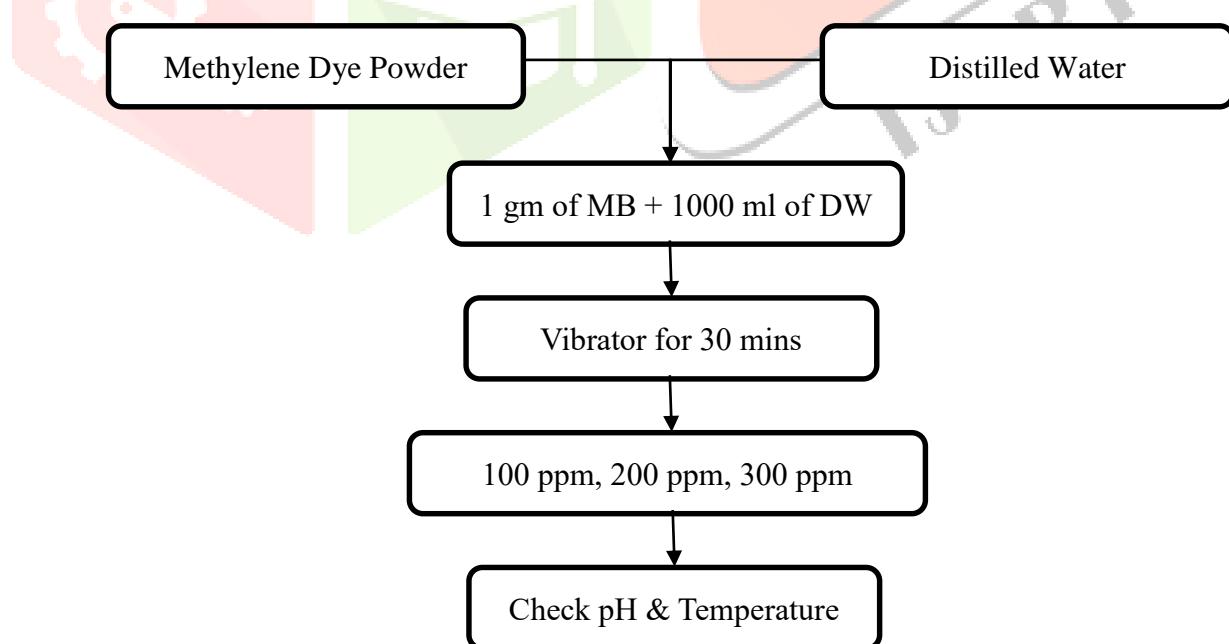


Figure 2.2: Sample Preparation

2.3. Adsorbent Preparation

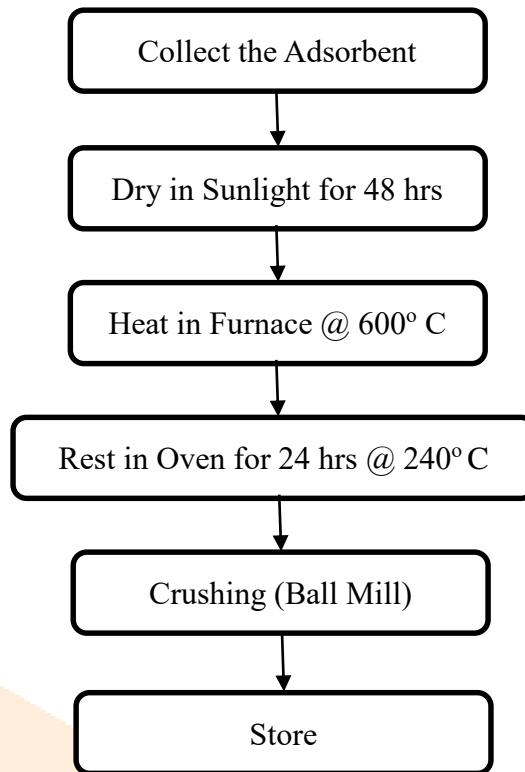


Figure 2.3: Adsorbents Preparation

2.4. Adsorbate Characterization

Methylene Blue (C₁₆H₁₈CIN₃S) is a cationic dye with molecular mass of 319.85 g/mol and maximum absorbance at $\lambda_{max} = 665$ nm. MB dye changed into used as major adsorbate without similarly purification (analytical grade, Solvachim, Morocco). The MB dye election turned into motivated with the aid of its extensive use, among others, in the fabric industry.

3. Design Expert Software Process

- i. Open the Design Expect Software 13
- ii. Select New Design
- iii. Click on Response Surface -> Randomized -> Box- Behnken / Central Composite
- iv. Fix the needed Factors
 - a. Numeric Factor - 6
 - b. Center Points per Block – 5 (Normally 40 points are allocated, If we tested more values means to add the center points block . Now here we added 5 because of we tested 45 samples)

	Name	Units	Low	High
A [Numeric]	pH		-1	1
B [Numeric]	Concentration	Ppm	-1	1
C [Numeric]	Dosage	Mg/l	-1	1
D [Numeric]	Temperature	°C	-1	1
E [Numeric]	Timing	mins	-1	1

Here to fix the low and high concentration values

- v. Click Next and Fill the Response (Number of times you get the result for above factors. Like we to do the 3 trials means, we have a 3 Responses for each factors)
- vi. Then click finish and fix the response values for analysis.
- vii. After enter the all needed data to select the Analysis and Start the Analysis.
- viii. After Analyzing we get the Fit Summary, Anova, R² Values
- ix. To select Coefficients Table to find the Correct fit of our Work
- x. Get the needed images after analyzing and place it in your research Work

The design expert software is used to analyzing on work and they give the suggestion to improve our work.

4. Result and Discussion

4.1. Adsorption Experiments

Table4.1: UV Values

S.No	Concentration	Dosage	Time	UV
	ppm	mg/l	min	
1	100	0.1	30	1.118
2	100	0.1	60	2.022
3	100	0.1	90	2.926
4	100	0.1	120	3.243
5	100	0.1	150	3.564
6	100	0.2	30	2.600
7	100	0.2	60	2.900
8	100	0.2	90	3.516
9	100	0.2	120	4.130
10	100	0.2	150	3.555
11	100	0.3	30	2.616
12	100	0.3	60	3.654
13	100	0.3	90	4.696
14	100	0.3	120	3.929
15	100	0.3	150	3.545
16	200	0.1	30	2.632
17	200	0.1	60	3.057
18	200	0.1	90	3.857
19	200	0.1	120	3.727
20	200	0.1	150	3.597
21	200	0.2	30	1.894
22	200	0.2	60	2.456
23	200	0.2	90	3.018
24	200	0.2	120	3.579
25	200	0.2	150	3.375

S.No	Concentration	Dosage	Time	UV
	ppm	mg/l	min	
26	200	0.3	30	3.022
27	200	0.3	60	3.660
28	200	0.3	90	4.297
29	200	0.3	120	3.725
30	200	0.3	150	3.149
31	300	0.1	30	4.149
32	300	0.1	60	3.842
33	300	0.1	90	4.099
34	300	0.1	120	3.866
35	300	0.1	150	3.633
36	300	0.2	30	4.153
37	300	0.2	60	4.027
38	300	0.2	90	3.897
39	300	0.2	120	3.767
40	300	0.2	150	3.534
41	300	0.3	30	4.515
42	300	0.3	60	4.208
43	300	0.3	90	3.901
44	300	0.3	120	3.668
45	300	0.3	150	3.439

4.1.1. Response of Test

Table 4.2.: Test Response

Response	Name	Units	Observations	Minimum	Maximum	Mean	Std. Dev.	Ratio
R1	Tree Waste		45.00	1.118	4.696	3.46	0.7073	4.20

4.1.2. Response Fit Summary

Table 4.3: Fit Summary

Source	Sequential p-value	Lack of Fit p-value	Adjusted R ²	Predicted R ²	
Linear	0.0063		0.2442	0.1024	
2FI	0.0007		0.6001	0.4703	Suggested
Quadratic	0.0125		0.7274	0.4305	Suggested
Cubic					Aliased

4.1.3. Fit Statistics

Table 4.4 Fit Statistics

Std. Dev.	0.3693	R ²	0.8513
Mean	3.46	Adjusted R ²	0.7274
C.V. %	10.67	Predicted R ²	0.4305
		Adeq Precision	12.0943

The Predicted R² of 0.4305 is not as close to the Adjusted R² of 0.7274 as one might normally expect; i.e. the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc. All empirical models should be tested by doing confirmation runs.

4.1.4. Summary Statistics

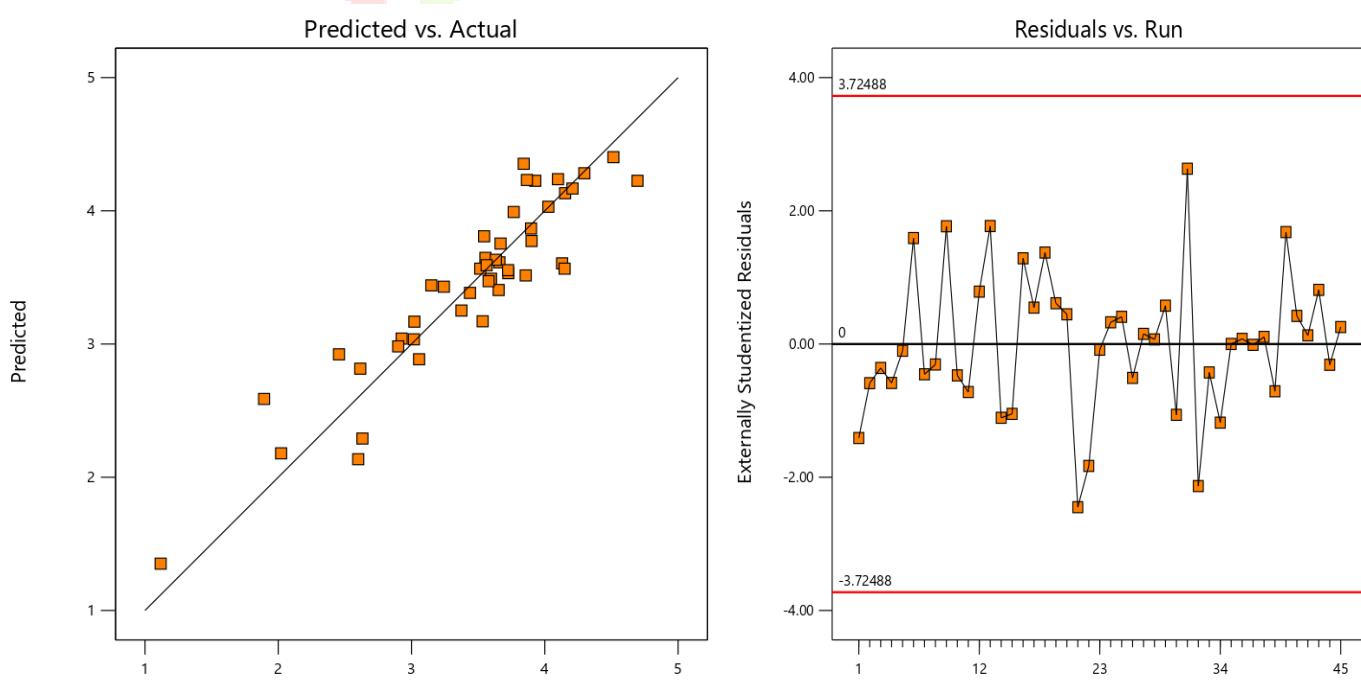


Table 4.5. Summary Statistics

Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	
Linear	0.6149	0.3301	0.2442	0.1024	19.76	
2FI	0.4473	0.7364	0.6001	0.4703	11.66	Suggested
Quadratic	0.3693	0.8513	0.7274	0.4305	12.54	Suggested
Cubic					*	Aliased

Table 4.6. Fitted Residuals and Cook's Distance

Run Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residuals	Externally Studentized Residuals	Cook's Distance	Influence on Fitted Value DFFITS	Standard Order
1	1.12	1.35	-0.2338	0.790	-1.382	-1.411	0.343	-2.738 ⁽¹⁾	6
2	2.02	2.18	-0.1577	0.485	-0.595	-0.587	0.016	-0.570	1
3	2.93	3.04	-0.1153	0.271	-0.366	-0.359	0.002	-0.219	16
4	3.24	3.43	-0.1876	0.263	-0.592	-0.583	0.006	-0.348	7
5	3.56	3.59	-0.0279	0.455	-0.102	-0.100	0.000	-0.091	44
6	2.60	2.14	0.4641	0.337	1.543	1.592	0.058	1.133	33
7	2.90	2.98	-0.0827	0.764	-0.461	-0.453	0.033	-0.816	19
8	3.52	3.57	-0.0500	0.813	-0.313	-0.307	0.020	-0.639	12
9	4.13	3.61	0.5244	0.298	1.695	1.769	0.058	1.154	30
10	3.56	3.65	-0.0922	0.728	-0.478	-0.471	0.029	-0.769	4
11	2.62	2.82	-0.1993	0.450	-0.728	-0.720	0.021	-0.652	13
12	3.65	3.41	0.2482	0.282	0.793	0.787	0.012	0.494	9
13	4.70	4.23	0.4705	0.437	1.698	1.772	0.106	1.560	35
14	3.93	4.23	-0.2968	0.467	-1.101	-1.106	0.051	-1.036	18
15	3.54	3.81	-0.2640	0.533	-1.046	-1.048	0.059	-1.119	42
16	2.63	2.29	0.3413	0.471	1.271	1.288	0.068	1.215	41
17	3.06	2.89	0.1709	0.307	0.556	0.548	0.007	0.365	25
18	3.86	3.52	0.3419	0.529	1.349	1.374	0.097	1.457	37
19	3.73	3.53	0.1945	0.281	0.621	0.613	0.007	0.383	5
20	3.60	3.49	0.1067	0.596	0.454	0.447	0.015	0.543	17
21	1.89	2.59	-0.6942	0.288	-2.228	-2.449	0.096	-1.559	27
22	2.46	2.92	-0.4670	0.475	-1.746	-1.829	0.131	-1.740	39
23	3.02	3.04	-0.0177	0.690	-0.086	-0.084	0.001	-0.126	2
24	3.58	3.47	0.1066	0.248	0.333	0.327	0.002	0.188	32
25	3.38	3.25	0.1235	0.357	0.417	0.410	0.005	0.305	21
26	3.02	3.17	-0.1464	0.408	-0.515	-0.507	0.009	-0.421	22
27	3.66	3.61	0.0465	0.351	0.156	0.153	0.001	0.113	23
28	4.30	4.28	0.0151	0.672	0.071	0.070	0.000	0.100	26
29	3.73	3.56	0.1698	0.382	0.585	0.577	0.010	0.453	40
30	3.15	3.44	-0.2916	0.444	-1.059	-1.062	0.043	-0.950	24
31	4.15	3.57	0.5830	0.551	2.357	2.632	0.325	2.918 ⁽¹⁾	45
32	3.84	4.35	-0.5115	0.516	-1.990	-2.133	0.201	-2.201 ⁽¹⁾	29
33	4.10	4.24	-0.1389	0.246	-0.433	-0.426	0.003	-0.243	31
34	3.87	4.23	-0.3658	0.284	-1.170	-1.180	0.026	-0.743	28
35	3.63	3.63	0.0003	0.651	0.001	0.001	0.000	0.002	34
36	4.15	4.13	0.0209	0.499	0.080	0.078	0.000	0.078	11
37	4.03	4.03	-0.0037	0.212	-0.011	-0.011	0.000	-0.006	8
38	3.90	3.87	0.0293	0.482	0.110	0.108	0.001	0.104	14
39	3.77	3.99	-0.2246	0.279	-0.716	-0.709	0.009	-0.441	3
40	3.53	3.17	0.3632	0.632	1.621	1.681	0.214	2.202 ⁽¹⁾	43

41	4.51	4.40	0.1122	0.500	0.430	0.422	0.009	0.423	15
42	4.21	4.17	0.0406	0.323	0.134	0.131	0.000	0.090	38
43	3.90	3.77	0.1271	0.824	0.820	0.814	0.150	1.761	36
44	3.67	3.75	-0.0867	0.450	-0.317	-0.311	0.004	-0.281	10
45	3.44	3.38	0.0548	0.676	0.261	0.255	0.007	0.369	20

4.1.5. Analysing Report

Current Transform: Tree Waste

Recommended Transform: None

Best Lambda	95 % CI Low	95% CI High
1.84	0.7400	3.17

Coefficient Table

Table 4.7: Coefficient P Values

	Tree Waste	p-values		Tree Waste	p-values		Tree Waste	p-values
Intercept	3.03838		AC	0.21813	0.1071	CE	-0.6179	0.0033
A	-0.09212	0.3752	AD	-0.3115	0.0825	DE	-0.478	0.0695
B	-0.14687	0.4149	AE	-0.0086	0.9567	A²	-0.0873	0.2137
C	0.67847	0.0002	BC	0.40256	0.0521	B²	0.14023	0.3807
D	0.10806	0.6901	BD	0.00981	0.9712	C²	0.52167	0.022
E	1.00769	< 0.0001	BE	0.14243	0.6047	D²	0.13725	0.6865
AB	-0.16536	0.2183	CD	-0.3893	0.035	E²	-0.7127	0.0104

4.1.6. Effect of Concentration between pH, Dosage, Temperature, Time

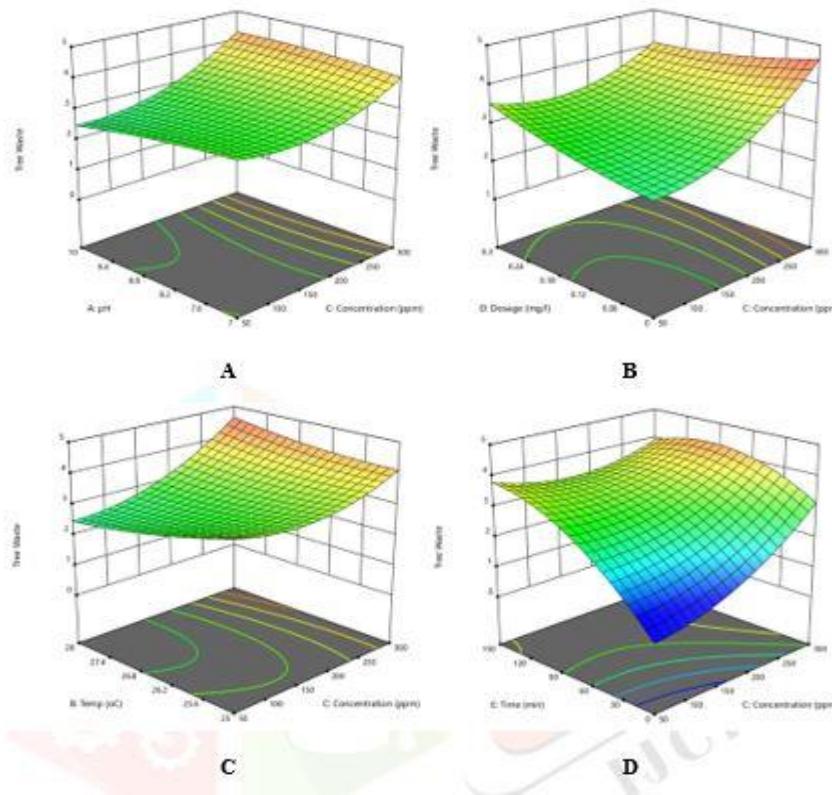
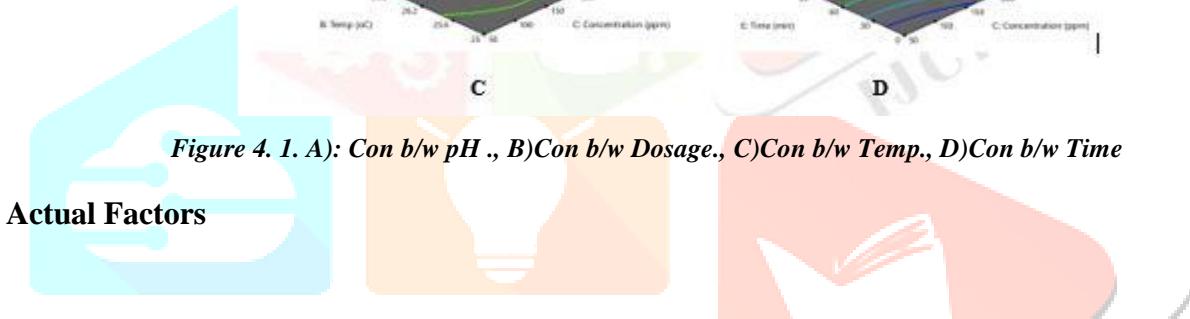


Figure 4.1. A): Con b/w pH ., B)Con b/w Dosage., C)Con b/w Temp., D)Con b/w Time

4.2. Actual Factors



Tree Waste
----- 95% CI Bands

Actual Factors

A = 8.5
B = 26.5
C = 175
D = 0.15
E = 75

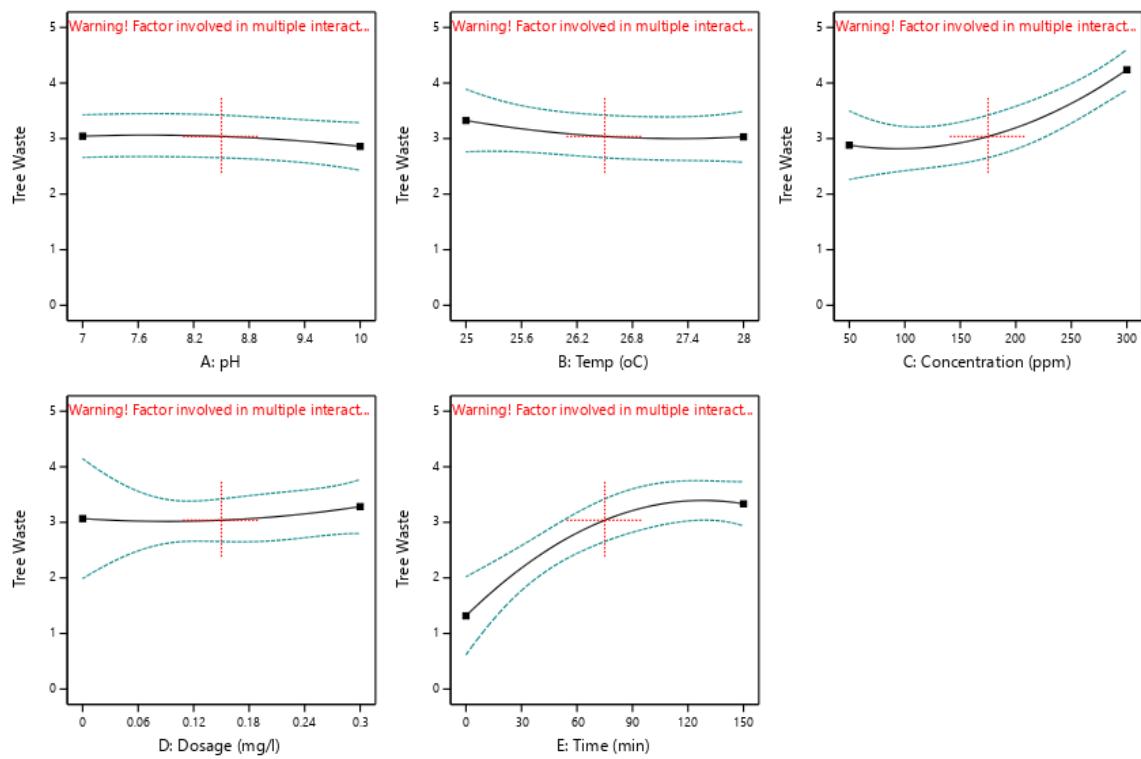


Figure 4.2 Actual Factor

The optimum factor for this adsorption process like pH is 8.5, Temperature is 28.5°C, Concentration is 175 ppm, Dosage is 0.15 mg/l and Timing is 75 mins

4.3. Adsorption Isotherms

Here we used Langmuir isotherm model for the adsorption phenomena. The expression of Langmuir's isotherm is

$$Qe = Qm \left(\frac{KL * Ce}{(1 + (KL * Ce))} \right)$$

Where,

- **Qe** is Adsorption Capacity at equilibrium (mg/g)
- **Qm** is Maximum adsorption capacity (mg/g)
- **KL** is Langmuir equilibrium constant (l/mg)
- **Ce** is Concentration of the solute at equilibrium (mg/l)

Table 4.8. Isotherm

ci	ce	1/ce	log ce	ln ce	qe(mg/g)	1/qe	log qe
100	92	0.011	1.964	4.522	2.020	0.495	0.305
200	156	0.006	2.193	5.050	3.020	0.331	0.480
300	255	0.004	2.407	5.541	3.770	0.265	0.576

KL=1/(SLOPE*Q MAX)

Qmax=1/intercept

The adsorption capacity of adsorbent is 1.25 mg/l . This is adsorbent value to observe the adsorbate.

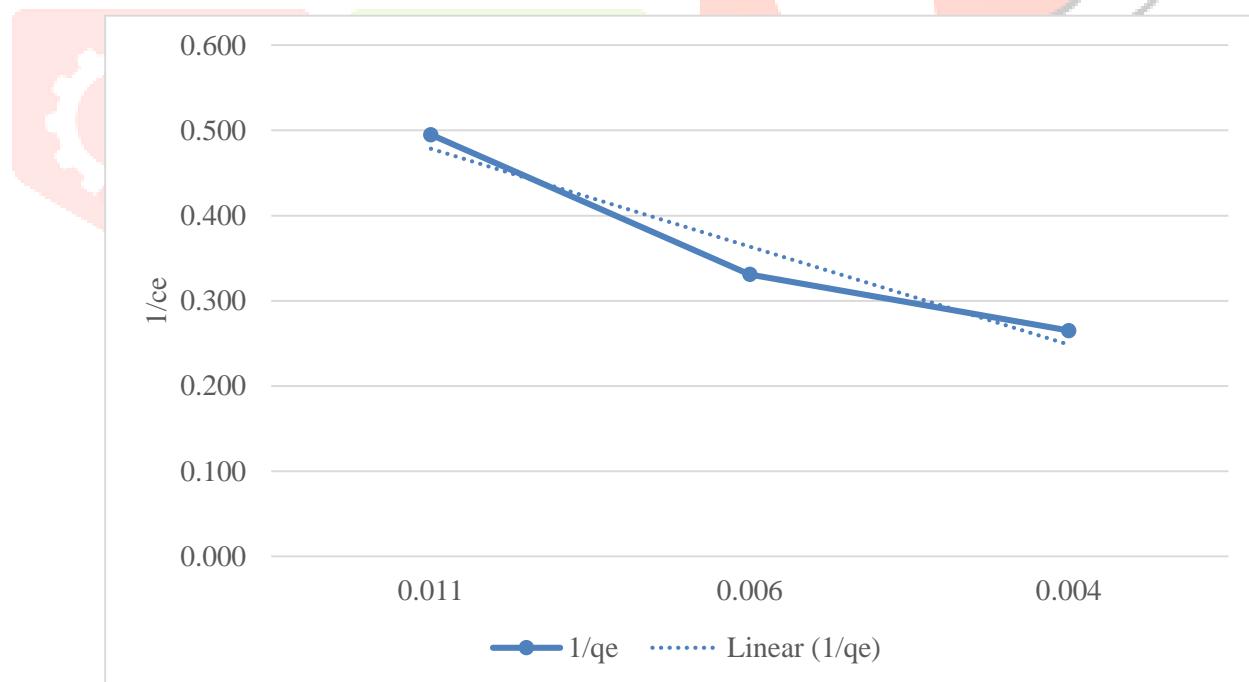


Figure 4.3 Langmuir Isotherm

5. Conclusion

Yes, those elements—pH, dosage, attention, time, and temperature—can indeed affect the adsorption process among an adsorbent and an adsorbate. those factors have interaction is crucial in optimizing adsorption tactics of dye effluent.

- ❖ pH: The pH of the solution can have an effect on the surface price of both the adsorbent and the adsorbate. certain adsorbents may have optimum adsorption capacities at precise pH ranges due to electrostatic interactions among the adsorbent surface and the charged species inside the solution
- ❖ Dosage: The amount of adsorbent added to the solution can significantly influence adsorption capacity. Increasing the dosage of adsorbent typically increases the amount of adsorbate removed from the solution until a point of saturation is reached.
- ❖ Concentration: The preliminary awareness of the adsorbate inside the answer impacts the charge and quantity of adsorption. higher preliminary concentrations frequently result in faster adsorption prices but also can attain saturation more quickly.
- ❖ Time: The period of touch among the adsorbent and the adsorbate influences the equilibrium adsorption capacity. usually, adsorption will increase with time till equilibrium is reached, and then similarly adsorption can be negligible.
- ❖ Temperature: Temperature affects adsorption kinetics and equilibrium. In some cases, higher temperatures can decorate adsorption by using growing the mobility of adsorbate molecules, while in others, lower temperatures might be extra favorable. moreover, temperature can affect the steadiness of the adsorbate-adsorbent interplay.

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