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Optimization of environmental parameters by Plackett-Burman design and response surface methodology for the adsorption of Malachite green onto *Gracilaria edulis*

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ABSTRACT

Gracilaria edulis, marine red seaweed was harvested from the coastal area of South Tamil Nadu, Rameswaram and was evaluated for the adsorption of Malachite Green. The algal biomass which is used as the adsorbent was pretreated for the activation of the binding sites on its surface. The environmental factors for the degradation process involve the pH (4–8), Biomass concentration (1 to 5 g/L), Dye concentration (10 to 20%), Time (120–180 min), Temperature (30–40 °C), and agitation-static were evaluated using Minitab 18 software. For the optimization process, the statistical techniques Plackett–Burman Design (PBD) and Response Surface Methodology (RSM) approaches were used. Plackett–Burman Design was performed for Malachite Green (MG) gave twelve trials and resulted in three significant parameters such as pH, temperature, and dye concentration. RSM was further used to determine the optimum parameters for the degradation. The maximum decolorization of Malachite Green was attained at pH = 4.5, dye concentration = 17, Temperature = 37 °C.

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1. Introduction

Environmental pollution is considered as a major problem in the environment. The problem mainly arises when the industries release the dye directly into the environment. Dye is used in paper, paint, tannery, cosmetic, wax, soap, mineral processing industry and textile industry. The discharge of dye without any treatment process causes serious health problems, strong odor, and hot [1]. Hence the dye effluent must be treated before released into the environment. The treatment of the dye from the industries can be done by various methods such as the physical method, chemical method and the biological method [2]. The biological method is found to be very efficient, low cost process and eco-friendly [3,4]. The biosorption process is carried out using the fungi, bacteria and algae. Adsorption technique is simple and effective way for the removal of dye from the wastewater. The biosorption study involves the solid phase (algae) known as biosorbent and a liquid

phase (water) known as adsorbate containing the suspended species to be adsorbed (dye).

In the present study the red algae *Gracilaria edulis* is used as the adsorbent for the biosorption of the Malachite Green dye. *Gracilaria edulis* is an alga which belongs to the kingdom Plantae and family *Gracilariaceae* [5]. Marine algae are used in only few cases for the adsorption of the dye. But the algae are abundantly available in the world's oceans. Thus, the study shows the degradation of the malachite green by use of the algae *Gracilaria edulis* is efficient.

Malachite Green is a cationic dye used in textile industry for silk, leather and paper. It is known by other names such as aniline green, diamond green, basic green, and Victoria Green B. This cationic dye is water soluble, belongs to triphenylmethane dye and appears as crystalline green powder. The cation has an intense green color which refers to the adsorption band 621 nm. The Malachite green dye is used as the antiseptic, antifungal, antihelminthic, antiparasitic and antibacterial. The Malachite green dye also considered as carcinogenic and when detected in the foodstuff, fishes, milk and human causes serious health problems [6]. The influence of temperature, time, pH, dye concentration, biomass dosage, and

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agitation-static were studied using the Plackett-Burman Design and Response Surface Methodology.

2. Materials and methods

2.1. Collection of algae

The sample red algae *Gracilaria edulis* was collected from Mandapam coast, Ramanathapuram district, TamilNadu, India. Once collected the algae was washed thoroughly with distilled water in order to remove the unwanted materials and remove the dirt. The washed algae were air dried for 24 h at 60 °C. The sample was powdered and then sieved to different particle size and is ready for the sorption process.

2.2. Preparation of dye

The Malachite green is a cationic basic dye which is used widely in the textile industries (Fig. 1). The Malachite green stock solution was prepared by dissolving 1 g of Malachite green in 1 L of distilled water [7]. The stock solution was diluted according to the required concentrations and the dilutes were used for the experiment. The pH of the solution was adjusted with 0.1 N hydrochloric acid or 0.1 N sodium hydroxide [8–11].

2.3. Pretreatment of the biomass

For the efficient adsorption of the dye from the effluent the algal biomass must be subjected to pretreatment. Physico-chemical modifications of biomass could lead to better sorption uptakes. The pretreatment process activates the algal surface binding sites [12–16].

The pretreatment is carried out by two methods

1. Physical methods
2. Chemical methods

2.4. Physical methods

Physical treatment of the biomass is done using the boiling water. Using the weighing balance, 30 g of biomass is weighed and added to 800 mL of 150 °C boiling water. It is stirred continuously for 15 min. Then it is filtered using Whatman filter paper and funnel to remove the water. It is then dried using the hot air oven at 60 °C for 24 h [17–21].

2.5. Chemical method

2.5.1. Pretreatment using calcium chloride

The 20 g of biomass is weighed and treated with 500 mL of 0.2 M calcium chloride. The solution should maintain pH of 5.

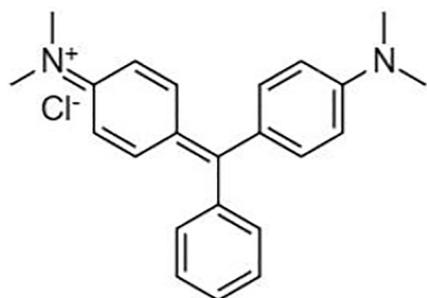


Fig. 1. Structure of Malachite Green.

The mixture is shaken in orbital shaker for 24 h at 25 °C overnight for complete crosslinking. The biomass is washed using distilled water to remove the traces of calcium chloride [22–26]. They are filtered and placed in the hot air oven for drying at 60 °C for 24 h [27–31].

2.5.2. Pretreatment using formaldehyde

The algal biomass was pretreated using 36% formaldehyde. Treat 20 g of dry *Gracilaria edulis* in 136 mL of 36% formaldehyde and 264 mL of 0.1 N HCl solutions. The mixture is shaken in orbital shaker for crosslinking. The biomass is washed using distilled water and again washed using 0.2 M sodium carbonate solution. It is dried over night at 60 °C and 110 °C for two hours.

2.6. Biosorption experiment

The experiment was performed in duplicate with the use of the algal biomass of *Gracilaria edulis* for the removal of the malachite green from the aqueous solution. The biosorption studies were conducted with the combination of the independent variables using statistical methods, Plackett-Burman Design and Response Surface Methodology. The experiment was carried out in a 250 mL conical flask with the required concentration of dye and biomass dosage at maintained conditions of the trials. It was centrifuged at 2000 rpm and the concentration of the dye solution was measured using UV-Vis spectrophotometer at 621 nm. The percentage decolorizations were determined using the below mentioned formula.

$$\text{Percentagedecolorization} = \frac{\text{InitialAbsorbance} - \text{FinalAbsorbance}}{\text{InitialAbsorbance}} \times 100 \quad (1)$$

2.7. Plackett-Burman design

Plackett Burman design is a very efficient method of screening to identify the significant factors among large number of factors that influences a process using a few experimental runs. Plackett-Burman Design is a statistical technique used to identify the significant parameters for the process of degradation of malachite green dye. pH, temperature, biomass concentration, dye concentration, time and agitation are the six parameters chosen for the experiment. The assigned six parameters gave twelve experimental designs. Plackett-Burman Design is used to identify the significant parameter for the degradation of dye. All the designs were carried out in duplicate and the percentage of biosorption is known as the response (Tables 1 and 2).

2.8. Statistical optimization using response surface methodology (RSM)

Based on the results of screening different parameters by Plackett-Burman Design, pH, Dye concentration and Temperature were found to be significant for the degradation of the dye. The

Table 1
Optimization study parameters from low to high level.

Parameters	Factor code	Low level	High level
pH	A	4	8
Temperature (°C)	B	30	40
Dye concentration (%)	C	10	20
Biomass dosage (g/L)	D	1	5
Static-Agitation	E	Static	Agitation
Time (min)	F	120	130

Table 2

Parameters for optimization according to Plackett-Burman Design.

Run order	pH	Temperature (°C)	Dye Concentration (%)	Biomass dosage (g/L)	Agitation	Time (min)
1	8	30	20	1	Static	120
2	8	40	10	5	static	120
3	4	40	20	1	Agitation	120
4	8	30	20	5	Static	180
5	8	40	10	5	Agitation	120
6	8	40	20	1	Agitation	180
7	4	40	20	5	static	180
8	4	30	20	5	Agitation	120
9	4	30	10	5	Agitation	180
10	8	30	10	1	Agitation	180
11	4	40	10	1	Static	180
12	4	30	10	1	Static	120

three parameters (variables) were optimized using the Response surface methodology. The experimental design included fifteen runs for the three variables (Tables 3 and 4).

3. Results and discussion

3.1. Plackett-Burman design

Plackett-Burman Design was performed in the present study for six parameters (pH, Temperature, Dye concentration, Biomass dosage, Time and Agitation). The influence of six parameters gave twelve runs using Plackett- Burman Design (Tables 5 and 6).

P-value is the probability value it denotes the significance of degradation. P-Value less than 0.05 is considered as the significant value. The temperature, pH, dye concentration and temperature are found to be the significant parameters.

The Pareto chart indicates the significant factors for degradation process. It shows the standardized effect of each parameter or the combination of parameters (Fig. 2).

$$\begin{aligned} \text{Experimental value}(Y) = & 0.2814 - 0.01150A - 0.002267B \\ & - 0.000386C + 0.00392D + 0.00867E \\ & + 0.000094F \end{aligned} \quad (2)$$

Y is the response (degradation) and the coefficient of each parameter indicates the effect of the parameters on the degradation of dye.

The R² value is the measure of variability in the observed response values can be explained by the experimental factors. The R-square value was found to be 95.06% for the degradation of dye. The adjusted R-square value is also very high 90.13% and indicates the degradation is significant.

3.2. Response surface methodology

Response surface methodology (RSM) is a collection of mathematical and statistical techniques through which we can determine the optimum concentration or conditions using Box-Behnken designs [16,17]. The effect of pH, dye concentration, and

Table 3

Optimization study parameters for RSM from low to high level.

Parameters	Factor code	Low level	High level
pH	A	4	8
Dye concentration (%)	B	10	20
Temperature (°C)	C	30	40

Table 4

Experimental design for Response Surface Methodology.

Run order	pH	Dye concentration (%)	Temperature (°C)
1	4	10	35
2	8	10	35
3	4	20	35
4	8	20	35
5	4	15	30
6	8	15	30
7	4	15	40
8	8	15	40
9	6	10	30
10	6	20	30
11	6	10	40
12	6	20	40
13	6	15	35
14	6	15	35
15	6	15	35

temperature were studied using response surface methodology by Box Behnken design (Tables 7 and 8).

From the table the model F value 26.69 and p value 0.001 was found significant. The model terms were found significant when the p value is less than 0.05.

$$\begin{aligned} \text{Experimental value}(Y) = & 71.3 + 5.43A + 1.433B + 7.594C \\ & - 0.2009A * A - 0.0708B * B - 0.1090C \\ & * C - 0.1352A * B - 0.0520A * C \\ & + 0.464B * C \end{aligned}$$

Coefficient of determination (R²) was found to be 95.96%. The R² values shows that they are in good agreement for the experimental and the predicted values. The predicted multiple correlation coefficients (predicted R²) were reported to be 94.48.

The contour plot for the interaction between the dye concentration and pH Fig. 3 shows that at initial pH 4 and at Dye concentration 16–19% the interaction was reported significant. The interaction between the temperature and pH in Fig. 2 also indicates at the level of pH 4 and Temperature 36–38 °C the biosorption of malachite green is significant. The plot in Fig. 3 indicates the interaction between the temperature and dye. It shows less significance when compared to the other parameter interactions. It also shows at Dye Concentration 14–20% and Temperature 34–38 °C the degradation is significant.

The optimum condition of response analyzed using response optimization for the biosorption of malachite green was obtained at pH = 4.5, Dye concentration = 17%, Temperature = 37 °C.

Table 5
Plackett-Burman Design matrixes for six variables and the observed response for adsorption of Malachite Green.

Run order	pH	Temperature (°C)	Dye Concentration (%)	Biomass dosage (g/L)	Agitation	Time (min)	Experimental value (%)	Predicted value (%)
1	8	30	20	1	Static	120	91.25	91.19
2	8	40	10	5	Static	120	88.32	88.29
3	4	40	20	1	Agitation	120	91.23	92.21
4	8	30	20	5	Static	180	88.55	88.29
5	8	40	10	5	Agitation	120	88.71	88.61
6	8	40	20	1	Agitation	180	79.08	80.01
7	4	40	20	5	Static	180	92.21	91.98
8	4	30	20	5	Agitation	120	90.54	90.52
9	4	30	10	5	Agitation	180	82.32	83.35
10	8	30	10	1	Agitation	180	88.04	88.02
11	4	40	10	1	Static	180	89.01	89.07
12	4	30	10	1	Static	120	87.07	87.88

Table 6
Analysis of variance (ANOVA) or degradation of malachite green generated my software Minitab.

Source	Degree of Freedom	Sum of Square	Mean Square	F- Value	P- Value
Model	6	0.0141	0.0023	16.03	0.004
pH	1	0.0063	0.0063	43.28	0.001
Temperature	1	0.0015	0.0025	10.51	0.023
Dye concentration	1	0.0044	0.0044	30.58	0.003
Biomass dosage	1	0.0007	0.0007	5.02	0.075
Agitation	1	0.0009	0.0009	6.15	0.056
Time	1	0.0001	0.000	0.66	0.455

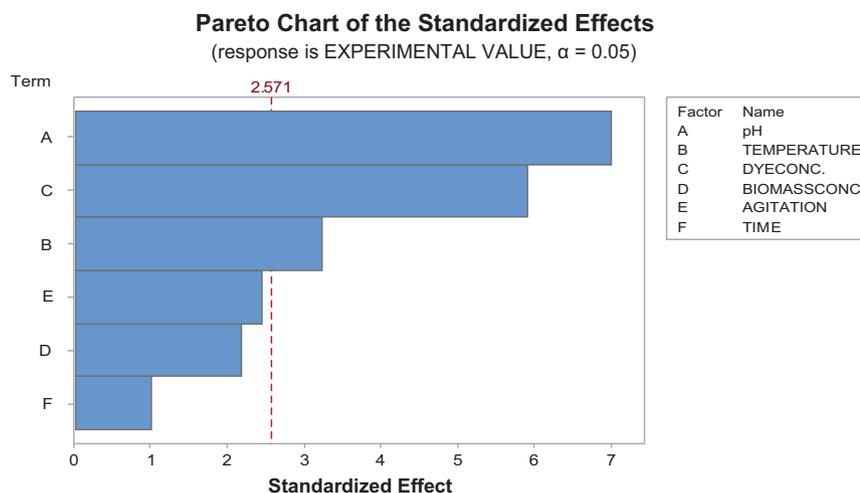


Fig. 2. Pareto chart indicating the significant parameters.

Table 7
Box Behnken Design and results for removal of Malachite Green dye.

Run order	pH	Dye concentration	Temperature (°C)	Experimental value (%)	Predicted value (%)
1	4	10	35	90.03	90.07
2	8	10	35	89.02	89.44
3	4	20	35	94.32	93.90
4	8	20	35	87.90	87.85
5	4	15	30	89.90	88.78
6	8	15	30	87.09	86.48
7	4	15	40	92.67	93.27
8	8	15	40	88.67	88.89
9	6	10	30	87.09	87.27
10	6	20	30	85.43	86.07
11	6	10	40	89.04	88.39
12	6	20	40	92.02	91.83
13	6	15	35	92.89	92.91
14	6	15	35	92.89	92.91
15	6	15	35	92.89	92.91

Table 8
Regression analysis (ANOVA) for response surface methodology of Malachite Green.

Source	Degree of Freedom	Sum of Square	Mean Square	F-Value	P-Value
Model	9	99.655	11.0728	26.69	0.001
A	1	22.278	22.2778	53.71	0.001
B	1	2.520	2.5200	6.08	0.057
C	1	23.736	23.7361	57.22	0.001
A*A	1	2.385	2.3853	5.75	0.062
B*B	1	11.551	11.5513	27.85	0.003
C*C	1	27.443	27.4429	66.16	0.000
A*B	1	7.317	7.3170	17.64	0.008
A*C	1	1.082	1.0816	2.61	0.016
B*C	1	5.382	5.3824	12.98	0.167

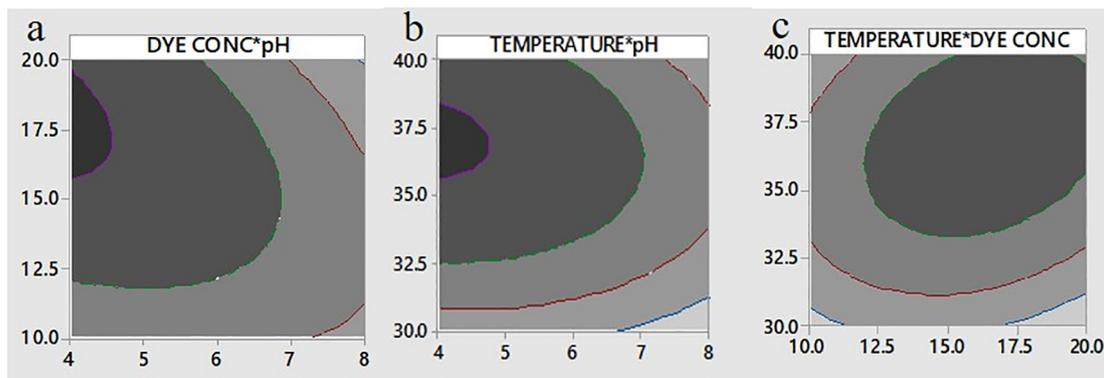


Fig. 3. Contour plot showing interactions between for dye conc.*pH; temp*pH; temp*dye conc.

4. Conclusion

The study demonstrates the use of statistical approach Plackett-Burman Design and response surface methodology for the biosorption of the malachite green dye using the red algae *Gracilaria edulis*. This is due to the vacant pores and charged functional groups on the surface of the adsorbent algae. Six parameters were studied and the significant parameter was found to be pH, dye concentration, and the temperature. Response Surface Methodology shows the optimum response of degradation was attained at pH = 4.5, Dye concentration = 17, Temperature = 37 °C. The red algal biomass has shown potential to adsorb the Malachite Green dye and future work plans to set up pilot scale followed by testing at industrial scale.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors contributions

Sharmila D and Thiruchelvi R have conceived and designed the experiment work. Sharmila D performed the experiment. Sharmila D and Thiruchelvi R worked together on manuscript writing. Venkataraghavan R helped in analyzing, compiling results, and suggestions in improving manuscript.

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