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Environmentally friendly processes

REMOVAL OF MALACHITE GREEN DYE USING ACTIVATED CARBON OBTAINED FROM *Prosopis juliflora*

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ABSTRACT

Activated carbon is the most efficient source in degradation of textile dyes. The source for activated carbon obtained from plants is the cheaper source and eco-friendly. Textile dye is one of the major pollutants that affect the environment adversely. *Prosopis juliflora* is the most abundant plant and is widely known for its water absorbing ability. In this study, activated carbon is prepared from the plant *Prosopis juliflora* and is activated using chemical agents. Malachite green is the dye used majorly in textile industry. Our research proves the feasibility of removal of malachite green dye using activated carbon prepared from *Prosopis juliflora.* Batch adsorption studies were done to study the effectiveness of the degradation. Using Response Surface Methodology, the optimum condition for removal of dye was calculated by influencing various parameters such as pH, temperature, dye concentration, activated carbon. The study proves that the low-cost adsorbent can effectively remove the malachite green dye.

Keywords: activated carbon, *Prosopis juliflora,* malachite green, Response Surface Methodology.

AIMS AND BACKGROUND

The emergence of water pollution is due to release of foreign materials that have the higher ability to deteriorate the water quality and affect the aquatic life. Textile effluents are one of the major influences of water pollution. Since textile industry are the current developing sector in the world, the discharge of toxic chemicals mainly dyes are at peak causing contamination. Till now, 80% of wastewater are not treated well. So, the research was mainly focused on the most efficient possible ways to treat wastewater[1]. Dyes are coloured chemical substances that are either chemically syn-

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thesised or naturally from plants and animals. They are widely used in food products, cosmetics, printing and also in research to identify the transparent structures under microscope. But, particular dyes are mainly used in paper, textile, plastics and leather industries. Malachite green is a cationic dye and used as triarylmethane dye in textile industry. They are also known as diamond green, Victoria green and aniline green. The dyes used in dyeing leather, paper, cotton, wool are also used as antiparasitic, antifungal, antibacterial agents in fishing farm industry. But they also have toxic effects on liver, lungs, kidney and also cause teratogenic effects in nervous system[2]. For the treatment of dyes, there is a wide range of methods available which have their own advantages and disadvantages. These methods were employed to reduce the toxicity of wastewater[3].

Adsorption method is the widely used technique in dye removal which is highly efficient, simple process and affordable. There are various adsorbents used in adsorption process like biosorbents, agricultural waste, natural materials, activated carbon, nanoparticles which are cost-effective and eco-friendly. Activated carbon is the most efficient adsorbent compared to other and have shown 99.8% removal efficiency but they are costly. So, biowaste-derived activated carbon has gained more attention in adsorption technique[4]. *Prosopis juliflora* (Seemai Karuvelam) is the plant available abundantly in Tamil Nadu known for drought resistant, source for fuel wood. Even though the plants have some medicinal value, they said to impact more on environment. They are considered as the worst invaders and the government has been planned to uproot the trees in the period of next ten years. *Prosopis juliflora* is used as a precursor of activated carbon as it is abundant and is available at low cost. Since the plant did not have much commercial value, it is employed in the preparation of bio-waste derived activated carbon and used in the degradation of textile dyes[5].

EXPERIMENTAL

Collection of Prosopis juliflora. The major raw material used in this research work was *Prosopis juliflora*, a small tree in the family Fabaceae, a kind of mesquite that was obtained from different locations in Pallavaram, Tamil Nadu. Initially the plant was washed and shade dried for 5 days. Then the plant was powdered and further taken for chemical activation.

Preparation of adsorbent. The plant was treated with sulphuric acid for activation process. It was impregnated with 1:1 ratio and left it for 24 h and then oven dried at 100°C for 3 days. It was then added to the calcination. To get rid of the surplus sulphuric acid, the carbonaceous substance was rinsed numerous times with distilled water. The resulted activated carbon was crushed and blended using mortar and pestle. Then it was stored for further degradation[6].

Preparation of dye. The Malachite green is a cationic basic dye which is widely used in the textile industries. The solutions of the Malachite green were prepared by dissolving various concentrations such as 20, 40, 60, 80, and 100 mg of Malachite green in 1 l of distilled water. The pH of the solutions was adjusted with 0.1 N HCl or 0.1 N NaOH.

ANALYTICAL STUDIES

The presence of various functional groups in the adsorbent material was studied using Fourier Transform Infrared (FTIR). The FT-IR spectra of the Malachite green dye before and after adsorption were carried out as a qualitative analysis to gain better insights into the surface functional groups available on the surface of the investigated adsorbent because the chemical structure of an adsorbent is of vital importance in understanding its adsorption nature.

RESPONSE SURFACE METHODOLOGY

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques through which we can determine the optimum concentrations or conditions using Box-Behnken designs. RSM is a second order polynomial equation which works on the principle of relationships between diverse explanatory variables and response variables. The measure of performance of the process is called response and the variables that are used in the process are called as independent variables. Experimental domain depicts the maximum and minimum limits of independent variables. Experimental design is the system created with several independent variables using matrix[7]. Box Behnken and central composite design are some of the experimental designs. Dependent variables are output variables produced by independent variables. Residual is the differences resulted between calculated and experimental value of the process under determined condition. Factors are also known as independent variables used in the process which indicate pH, temperature, dye concentration, agitation time.

The system was explained by the second order polynomial equation:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3,$$

where Y is the response measured (dye degradation %) and X_1, X_2, X_3 – the parameters. The optimum value is obtained by the regression equation, by analysing the points[8,9].

In the present work four significant parameters for Malachite green (pH, temperature, activated carbon concentration and dye concentration) were chosen according to Central Composite Design. The four parameters for Malachite green are: pH 4–8, temperature: 25–65°C, dye concentration: 20–100 mg, activated carbon concentration: 5–10 g (Table 1).

Response surface methodology (Central Composite Design) was developed for four parameters over 30 trials using the Minitab 21 commercial software (Table 2).

Table 1. Level of parameters tested for Malachite green in Central Composite Design

S. No	Parameters	Range
1	pH	4–8
2	Dye concentration	20–100 mg
3	Activated carbon concentration	5–10 g
4	Temperature	25–65°C

Table 2. Trials given by Central Composite Design for Malachite green dye

S.No	Run order	pH	Temperature (°C)	Dye concentration (mg)	Activated carbon concentration (g)
1	1	4	65	20	5.0
2	2	8	25	20	5.0
3	3	6	45	60	7.5
4	4	4	65	100	10.0
5	5	4	25	20	10.0
6	6	8	65	100	5.0
7	7	8	65	20	10.0
8	8	4	25	100	5.0
9	9	8	25	100	10.0
10	10	6	45	60	7.5
11	11	6	45	140	7.5
12	12	6	45	60	7.5
13	13	6	45	60	2.5
14	14	2	45	60	7.5
15	15	6	25	60	7.5
16	16	10	45	60	7.5
17	17	6	45	60	12.5
18	18	6	45	60	7.5
19	19	6	85	60	7.5
20	20	6	45	20	7.5
21	21	4	25	20	5.0
22	22	8	25	20	10.0
23	23	4	65	20	10.0
24	24	4	65	100	5.0
25	25	8	65	20	5.0
26	26	6	45	60	7.5
27	27	8	25	100	5.0
28	28	6	45	60	7.5
29	29	4	25	100	10.0
30	30	8	65	100	10.0

RESULTS AND DISCUSSION

The present study shows that the activated carbon obtained from *Prosopis juliflora* has the capacity to remove the Malachite green dye.

FTIR CHARACTERISATION

Fourier-transform infrared spectroscopy (FTIR) is a technique that works by analysing the infrared spectral compounds. The FTIR analysis was made to identify the functional group of the compounds. It was done to identify whether nitrogen, carbon, oxygen, hydrogen, sulphur group are present in the activated carbon sample. The identification of functional group is to check which functional group play important role in dye degradation[6].

Characterisation of activated carbon using FTIR. The qualitative analysis of activated carbon was carried out by FTIR spectrum. The FTIR spectrum of activated carbon obtained from *Prosopis juliflora* is shown in Fig. 1. The spectral range is measured between 400–4000 cm^{-1} (Table 3) and the figure illustrates that the bands at 3851.95 and 3403.01 cm^{-1} are due to O–H bending and OH stretching which implies the presence of alcohol group, respectively. The band observed at 2920.81 cm^{-1} is attributed to the presence of aldehyde group, C–H stretching. The band at 1700.40 cm^{-1} is an indication of carboxylic group, C=O stretching. The band at 1619.57 cm^{-1} is due to the unsaturated ketone C=C stretching. The bands at 1192.73 and 1121.89 cm^{-1} are due to C–O stretching. Finally, the band at 752.51 cm^{-1} is due to C–H bending while the bands at 656.77 and 603.70 cm^{-1} – to C–H stretching.

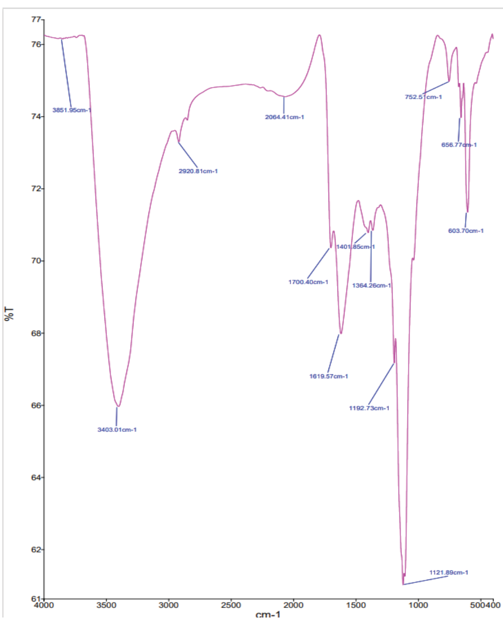

Fig. 1. FTIR analysis of activated carbon

Table 3. FTIR analysis of activated carbon

No of peaks	Wave number (cm^{-1})	Functional group
1	3851.95	O–H bending
2	3403.01	O–H stretching
3	2920.81	C–H stretching
4	2064.41	C=C stretching
5	1700.40	C=O stretching
6	1619.57	C=C stretching
7	1401.85	O–H bending
8	1364.26	C–H bending
9	1192.73	C–O stretching
10	1121.89	C–O stretching
11	752.51	C–H bending
12	656.77	C–H stretching
13	603.70	C–H stretching

FTIR characterisation of Malachite green dye before and after adsorption. The FTIR spectra of Malachite green dye before (Fig. 2 and Table 4) and after adsorption (Fig. 3 and Table 5) were analysed. They showed a shift in the bands. The bands at 3337.66, 2104.37 and 1635.42 cm^{-1} were shifted to 3338.00, 2105.24 and 1635.33 cm^{-1}, respectively. The shift in bands showed that functional group may be involved in adsorption process. The bands at 3337.66 and 3338.00 cm^{-1} are due to O–H stretching indicating the presence of alcohol group. The bands at 2104.37 and 2105.24 cm^{-1} are due to the presence of C=C stretching. The bands at 1635.42 and 1635.33 cm^{-1} are indication of aromatic compounds due to C=C stretching.

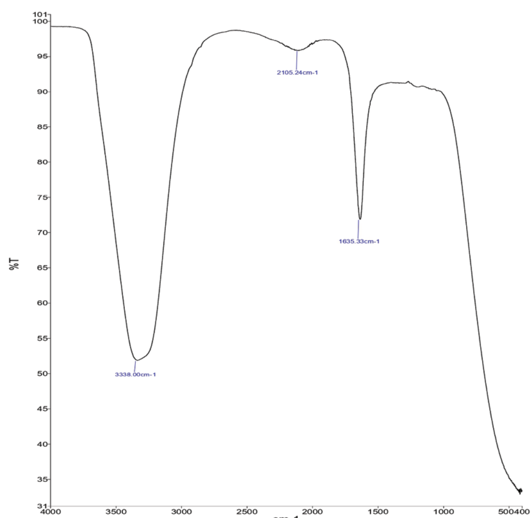

Fig. 2. FTIR analysis of Malachite green before adsorption

Table 4. FTIR analysis of Malachite green before adsorption

No of peaks	Wave number (cm^{-1})	Functional group
1	3338.00	O–H stretching
2	2105.24	C=C stretching
3	1635.33	C=C stretching

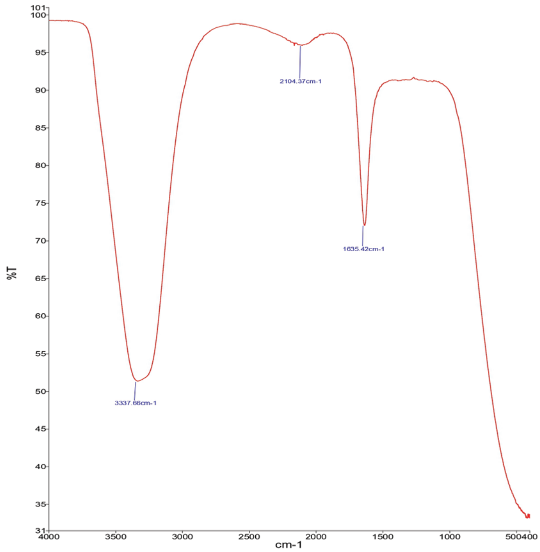

Fig. 3. FTIR analysis of Malachite green after adsorption

Table 5. FTIR analysis of Malachite green after adsorption

No of peaks	Wave number (cm^{-1})	Functional group
1	3337.66	O–H stretching
2	2104.37	C=C stretching
3	1635.42	C=C stretching

OPTIMISATION STUDIES ON RESPONSE SURFACE METHODOLOGY (RSM) FOR MALACHITE GREEN

The efficiency of Malachite green dye degradation is investigated using Central Composite design and the result was obtained by using the experimental design to identify the optimal condition among the significant factors such as pH, temperature, dye concentration and activated carbon concentration (Table 6).

Table 6. Central Composite Design for parameters of Malachite green dye degradation

S.No	Run order	pH	Temperature (°C)	Dye concentration (mg)	Activated carbon concentration (g)	Experimental value (%Removal)	Predicted value (%)
1	2	3	4	5	6	7	8
1	1	4	65	20	5.0	78.45	77.4144
2	2	8	25	20	5.0	65.76	67.4294
3	3	6	45	60	7.5	96.45	97.5207
4	4	4	65	100	10.0	84.34	82.1078
5	5	4	25	20	10.0	78.67	76.8727
6	6	8	65	100	5.0	79.56	80.7944
7	7	8	65	20	10.0	82.78	81.3328
8	8	4	25	100	5.0	69.43	70.3144
9	9	8	25	100	10.0	76.74	77.2127
10	10	6	45	60	7.5	96.34	97.5207
11	11	6	45	140	7.5	72.43	75.3268
12	12	6	45	60	7.5	96.45	94.4727
13	13	6	45	60	2.5	67.45	68.1285
14	14	2	45	60	7.5	65.78	69.7868
15	15	6	25	60	7.5	68.79	70.2868
16	16	10	45	60	7.5	72.78	69.8168
17	17	6	45	60	12.5	78.55	78.9152
18	18	6	45	60	7.5	96.67	94.4727
19	19	6	85	60	7.5	85.65	85.1968
20	20	6	45	20	7.5	73.49	71.6368
21	21	4	25	20	5.0	64.21	62.4254
22	22	8	25	20	10.0	73.43	75.6987
23	23	4	65	20	10.0	83.43	85.8938
24	24	4	65	100	5.0	82.34	79.5904
25	25	8	65	20	5.0	76.49	78.8154
26	26	6	45	60	7.5	96.45	97.4667
27	27	8	25	100	5.0	77.85	74.9054
28	28	6	45	60	7.5	96.56	97.4667
29	29	4	25	100	10.0	81.39	78.5838
30	30	8	65	100	10.0	75.83	77.1337

Table 7. ANOVA for Malachite Green: Central Composite Design

Source	DF	Adj. SS	Adj. MS	*F*-value	*P*-value
Model	16	3162.19	197.64	53.92	0.000
Linear	4	269.17	67.29	18.36	0.000
pH	1	104.13	104.13	28.41	0.000
Temperature (°C)	1	29.73	29.73	8.11	0.014
Dye concentration (mg)	1	25.28	25.28	6.90	0.021
Charcoal concentration (g)	1	110.04	110.04	30.02	0.000
pH × pH	1	426.08	426.08	116.24	0.000
Temperature × temperature	1	1282.83	1282.83	349.97	0.000
Dye concentration × dye concentration	1	426.08	426.08	116.46	0.000
Charcoal concentration × charcoal concentration	1	1487.35	1487.35	405.77	0.000
pH × temperature	1	0.71	0.71	0.19	0.667
pH × dye concentration	1	4.11	4.11	1.12	0.309
pH × charcoal concentration	1	28.76	28.76	7.85	0.015
Temperature × dye concentration	1	10.26	10.26	2.80	0.118
Temperature × charcoal concentration	1	3.49	3.49	0.95	0.347
Dye concentration × charcoal concentration	1	1.94	1.94	0.53	0.480

Adj. SS – Adjusted sum of squares; Adj. MS – Adjusted mean square.

The analysis of variance (ANOVA) for the degradation of Malachite green dye by *Prosopis juliflora* derived activated carbon is given in Table 7. *P* value less than 0.05 indicates that the models are significant. *P* value more than 0.05 indicates that the models are insignificant[10,11].

Based on the results, the relationship between the removal percentage of dye and significant parameters are expressed by the second order polynomial equation:

$$\text{Experimental value } (Y) = -98.4 + 21.82\,A + 1.583\,B + 0.615\,C + 17.70\,D - 1.542\,A\times A - 0.01046\,B\times B - 0.003280\,C\times C - 0.8380\,D\times D - 0.0218\,A\times B - 0.00095\,A\times C - 0.304\,A\times D - 0.001752\,B\times C - 0.0293\,B\times D - 0.01518\,C\times D,$$

where A is pH, B – the temperature, C – the dye concentration, and D – charcoal concentration.

From the equation above, *Y* is the response and the coefficient of each parameter indicates the effect of parameter on dye removal.

The observed response values' variability can be understood by experimental factors according to the R^2 value (Table 8). For the elimination of dye employing activated carbon, the R^2 level is 96.17%, and the corrected R^2 value is 91.45%.

Table 8. Model summary

	R^2	R^2 (adj.)	R^2 (pred.)
2.97614	96.17%	91.45%	71.53%

The contour plots are graphical representations in three dimensions. The plots show the interaction between the given parameters and the optimum condition for degradation. The contour plot of the second order polynomial equation is done by the interaction of two variables within the experimental ranges[12].

Figure 4 shows the contour plot of interaction between various process parameters in dye removal. The interaction at pH 6 to 8 and temperature 40–45°C also showed significant removal of dye. At pH 6 and at dye concentration 60 mg, the interaction was reported insignificant. Also, the interaction of activated carbon concentration of 7.5–10 g and pH 6, increased activated carbon concentration of 7.5–10 g and dye concentration of 20–60 mg all showed a significant degradation of Malachite green. Dye concentration of 20–60 mg and increase in temperature of 50–55°C, activated carbon concentration of 5 g and temperature 60°C showed less significant degradation. Increase in activated carbon concentration, pH 6–8, temperature of 40–45°C showed an increase in degradation efficiency.

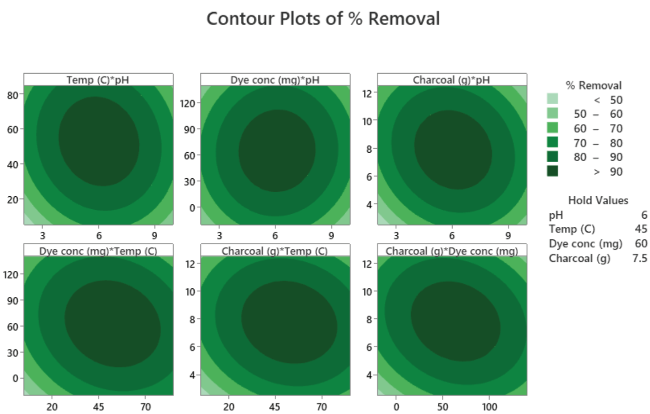

Fig. 4. Contour plot for Malachite green dye removal

The surface plot in Fig. 5 indicates the interaction between the parameters of degradation process. The curved surface of the plot demonstrates the significant interaction between two parameters. From the figure it is inferred that the increase of pH at level of 6–8 shows significant increase in dye removal after that there is decline in degradation efficiency. The optimum pH for degradation is between 6. The percentage removal also increased with increase in temperature between 45 and 55°C. The activated carbon concentration in the range of 7.5 to 10 and dye concentration at 60 mg/l also showed significant dye removal. The breakdown efficiency is low when only a little amount of activated carbon is supplied because the active site just on surface was heavily dye-bonded.

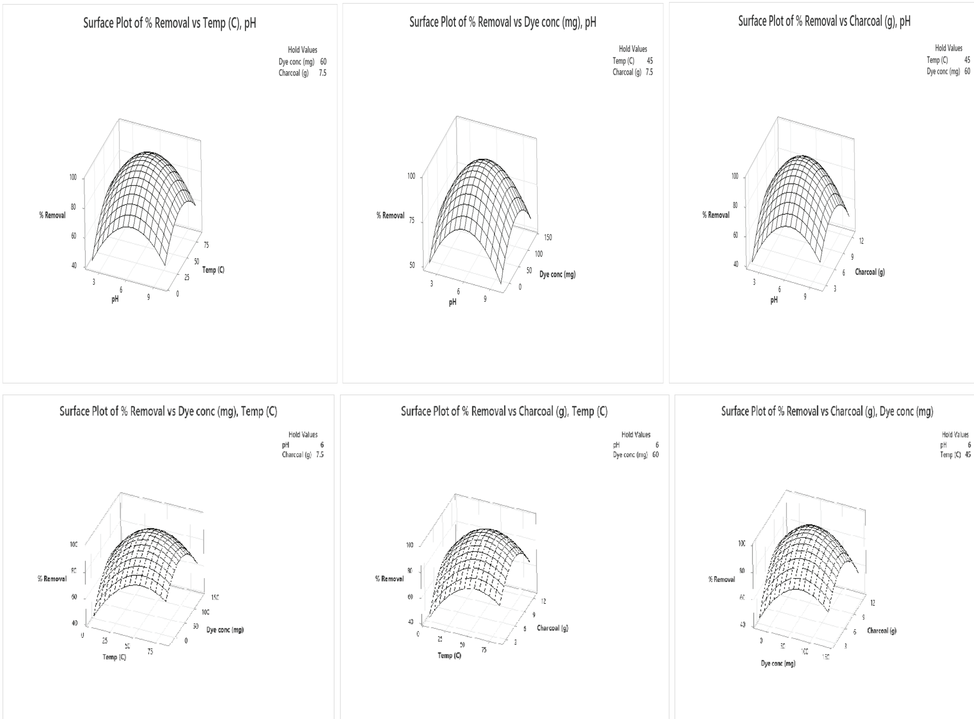

Fig. 5. Interactive effect of various parameters on dye removal

From Response Surface Methodology, we can confirm the significant value for degradation of Malachite green dye using *Prosopis juliflora* derived activated carbon at pH 6, temperature 45°C, dye concentration – 60 mg, activated carbon concentration – 7.5 g. The optimal predicted value (Y) is 97.53 (Fig. 6).

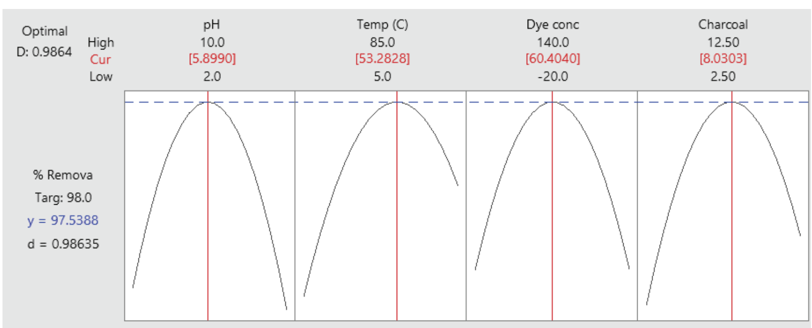

Fig. 6. Optimal prediction for Malachite green dye degradation

CONCLUSIONS

The study showed that the use of activated carbon obtained from *Prosopis juliflora* showed higher efficiency of 96.5% degradation of Malachite green dye. The significant value for Malachite green dye degradation is at pH 6, temperature 45°C, dye concentration of 60 mg, activated carbon concentration of 7.5 g. The results reveal that the activated carbon obtained from *Prosopis juliflora* can be considered as the potential adsorbent of dyes. Thus, the plant-derived activated carbon provides cheaper and eco-friendly degradation of textile dyes.

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