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Process Optimization of Removal of Methylene Blue using Waste-derived Adsorbent

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Abstract:

Waste tea leaves were used as a source of Activated Carbon (AC) which was chemical activated using Sodium Hydroxide (NaOH). SEM and XRD was carried out for the characterization of AC. L16 Taguchi method was implemented to determine the optimum parameters values required for removal of methylene blue (MB).The optimum conditions obtained from Taguchi for a 97.30% removal MB on AC from spent tea leaves is Adsorbent Dosage of 650mg/L, Initial dye conc. 2.71ppm, time 30 min. and temperature at 30°C.

Keywords **—Activated Carbon, Taguchi, ANOVA, parameters, methylene blue, waste tea leaves**

I. INTRODUCTION

The dawn of industrialization has various negative impacts on the environment. Industries like leather, food, textile,and paper have a broad application of dyes. Around 2% of the total 700000 tons of dye is discharged into the environment. The dye contains aromatic structure which makes them toxic and also carcinogenic and hence creates a threat to both humans and animals. Thus the dye-containing effluent from these industries must be refined before their release in the ecosystem. Natural dyes are less stable and flexible than synthetic dyes. Depending on the charge and their nature, dyes are divided into non-ionic, anionic and cationic dyes [1]. In textile industry methylene blue (MB) is very frequently used for dyeingwool, silk,and cotton. Contact with methylene blue causes irritation and a burning sensation to the eye which might lead to permanent damage to both the animal and human eyes. Inhalation of this dye causes breathing problems along with small periods of rapid and shortbreathing. Ingestion of MB produces a burning sensation and may cause nausea, vomiting, profuse sweating,mental confusion,and gastrointestinal related problems [2].There are many dye wastewater treatment methods available including coagulation, reverse osmosis,photo-degradation, chemical oxidation, membrane filtration methods, ozonation, and biosorption. However, the above-mentioned methods are generally ineffective in dye wastewater treatment or have high operating costs [1, 3]. Due to this reason adsorption is chosen as the suitable method for dye removal. Both synthetic and natural adsorbents have been used for this process. However, Activated Carbon has attracted much attention for the removal of dyes from wastewater because it is easy to separate and can withstand high temperature and a wide range of pH.Due to its high porosity, it has large adsorption capacity and thus it is used for dye adsorption in various industrial processes. To overcome these disadvantages, more and more attention has been paid to the modification of activated carbons and synthesis of high-performance adsorbents to treat dye wastewater. A popular method is using metal oxides to modify activated carbon. Modifying activated carbon with metal oxides may provide a structure with enhanced porosity, which can be varied in terms of pore structure and surface,functional groups. Therefore, its adsorption properties are altered. According to literature reports, metal oxides such as aluminum oxide, iron oxide, zinc oxide, manganese oxide, copper oxide and vanadium oxide have been used to impregnate activated carbon to enhance its adsorption capability or improve its catalytic oxidation capability for dye wastewater [4].

The source of Activated Carbon plays a significant role in its quality. Biomass like agricultural waste, wood, leaves, baggage, various seeds etc. has been used as the source of Activated Carbon. Tea is the oldest and the most widely consumed and the lowest cost beverage in the world after water. It is considered to be one of the major components of world beverage market which provides more than 2,000 different types of tea for consumption. Currently, India produces 23% of total world production and consumes about 21% of total world consumption of tea. This shows that nearly 80% of the tea produced is consumed within the country. Spent tea leaves can be used as a source of Activated Carbon. According to various reports it has been seen that the total carbon content of spent tea leaves is approximately 30%. This carbon content can be chemically or physically activated to Activated Carbon [5]. This is a low-cost adsorbent produced from a waste material which can be used to adsorb various dyes.

To increase the quality of activated carbon and obtain the optimum parameter conditions Taguchi Methodology has been implemented. The Full Factorial Design requires a large number of experiments to be carried. It becomes laborious and complex if the number of factors increases. To overcome this problem Taguchi suggested a specially designed method called the use of the orthogonal array to study the entire parameter space with a lesser number of experiments to be conducted. In this paper, Taguchi methodology has been implemented for determining the optimum adsorption parameters for the removal of methylene blue using activated carbon from spent tea leaves.

II. MEASUREMENTS AND METHODS

A. *Measurements*

For determination of the removal percentage of MB solution,the UV-Visible spectrophotometer was used (PerkinElmer UV/VIS Lambda 365). For the surface topographical characterization of Scanning Electron Microscope (FEI INSPECT F50 FESEM) was used Tungsten filament was used with an emission current of 100mA° and the accelerator voltage was 10kV. From Fig. 4we can see the surface topographical difference at different magnifications (100 µm and 5µm). X-Ray Diffractometer (Rigaku Ultima III) was used to determine the peaks of obtained Activated carbon.

B. *Preparation of Activated Carbon*

Spent tea leaves were collected from the local shops and stalls. These spent tea leaves were repeatedly washed to get rid of the dirt and loose soil particles. Then they were dried for 48hrs at 80°C in a hot air oven. The spent tea leaves were carbonized at 450°C for 2hrs. The carbonized tea was sieved with a 250µm mesh and fine particles were obtained which were subjected to further chemical treatment. 5% Sodium Hydroxide (NaOH) solution was added to the carbonized tea leaves in a ratio of 1.5:1 (NaOH: Carbonized tea). The entire mixture was kept overnight at a constant RPM of 300 and at room temperature. It was then neutralized using 0.1M HCl solution and dried for 24hrs. This chemically activated teas leaves were further subjected to carbonization at 350°C for 2hrs. The prepared activated carbon (AC) was stored in dry place for further use

C. *Experimental procedure*

All the experiments were carried out in batch mode and the adsorbents were added in a 250ml of Erlenmeyer flask with 200ml of MB solution with different initial concentrations. The setup was placed on a magnetic stirrer and the RPM was maintained at 300 for all the experiments. The temperature was controlled according to the requirement. After a certain fixed time, the solution was filtered and the final MB solution concentration was measured using UV-Visible Spectrophotometer at a wavelength of 663.5nm. All the experiments were conducted at 8pH which gave the best removal results which were maintained by adding 0.1M HCl and 0.1M NaOH solution. The percentage removal of dye was calculated using the following equation:

$$Removal\ \% = \frac{C_i - C_f}{C_i} * 100$$

Where C_i= Initial MB solution concentration

C_f= Final MB solution concentration

D. *Design of Experiments*

From variousliterature, it was found that the most influential parameters for the removal of dye by activated carbon are Adsorbent Dosage, initial dye concentration, time and temperature. In this paper chemical activation of spent tea leaves was chosen. Taguchi method was used to analyze the different effects that the parameter has on the removal of MB from the solution. L16 experiments were conducted at different levels of the four parameters. From Table 1 we can see that the Adsorbent dosage (50 – 650 mg/L), initial dye concentration (2.26 – 5.65 ppm), time (10 – 40min) and temperature (30°C – 90°C) were chosen. Total sixteen runs were carried out at different Adsorbent Dosage, initial dye concentration, time and temperature. The removal % of MB solution was calculated for each of the runs.Thus removal percentage for each of the experiments was conducted and the results obtained wereanalyzed using Taguchi method. The delta ranking system also determined the maximum and minimum influence that the parameters have on the result.

TABLE 1: DIFFERENT PARAMETERS WITH THE LEVELS

Levels	Adsorbent mg/l	Dye Conc. ppm	Time min	Temp. °C
1	50	1.3	10	30
2	250	1.9	20	50
3	450	2.5	30	70
4	650	3.1	40	90

Each of these parameters has four levels. The levels are evenly spaced as shown in Table 1. The orthogonal array obtained using MINITAB17 software, has a set of 16 experiments as shown in Table 2. Each set has a different level of parameters. To reduce the noise affect the entire set of experiments were carried out twice.

TABLE 2: DESIGN OF EXPERIMENTS USING L16 TAGUCHI METHOD

Run Number	Adsorbent mg/L	Dye Conc. Ppm	Time min	Temp. °C
1	50	1.3	10	30
2	50	1.9	20	50
3	50	2.5	30	70
4	50	3.1	40	90
5	250	1.3	20	70
6	250	1.9	10	90
7	250	2.5	40	30
8	250	3.1	30	50
9	450	1.3	30	90
10	450	1.9	40	70
11	450	2.5	10	50
12	450	3.1	20	30
13	650	1.3	40	50
14	650	1.9	30	30
15	650	2.5	20	90
16	650	3.1	10	70

III. RESULTS AND DISCUSSION

A. *Characterization of Activated Carbon*

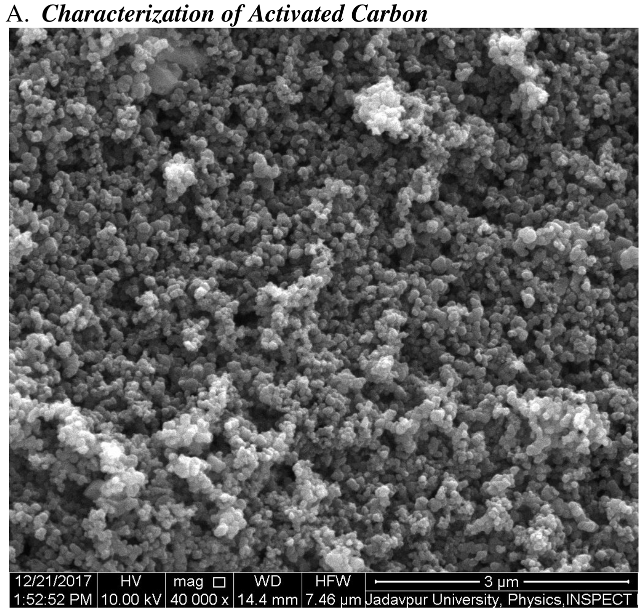

Figure 1: SEM image of AC at 3μm Magnification

From Fig. 1 we can visualise the topographical morphology of the AC. The pores are distinctly visible at a magnification of 3μm. The raw AC from waste tea leaves showed acceptable removal % of MB dye which is clearly evident from the SEM image.

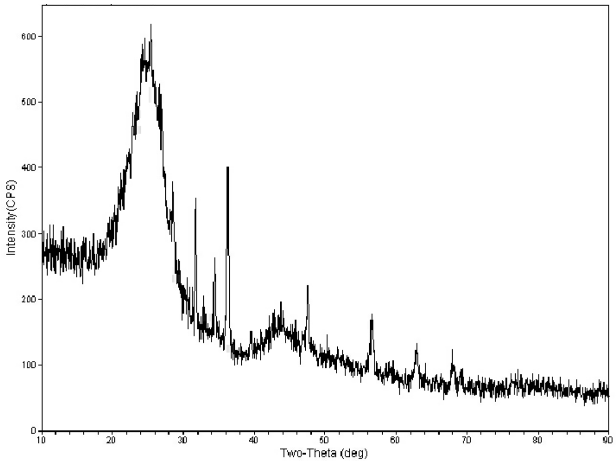

Figure 2: XRD Graph of the prepared AC

From Fig. 2 we can see that he prepared activated carbon exhibits a very broad band of diffraction peaks along with the absence of sharp peaks which indicated that it is predominantly an amorphous structure. There are two broad diffraction peaks around 2θ = 24.6° and 43.1° in spectrum, corresponding to the diffraction of (0 0 2) and (1 0 0), respectively.

B. ***Effect of parameters on the removal of MB***

1) Adsorbent Dosage

The adsorbent dosage varied from 50 – 650 mg/L. From Figure 3.it is evident that there was a steady increase in the removal % of MB as the amount of adsorbent dosage increased. This is due to the fact that with the increase in dosage the number of free pores and surface area increased greatly and thus adsorption increased resulting in higher removal efficiency. However, the removal % remained almost constant from 525mg/L around 96%. This is probably due to the conglomeration of adsorbent particles which results in no further increase in surface area of the AC [6]. Thus the removal % becomes almost constant.

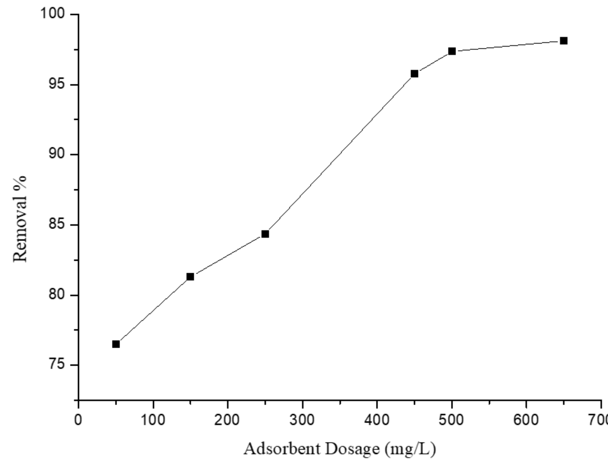

Figure 3: Effect of Adsorbent Dosage on MB Removal
Initial Dye Conc.: 3.2ppm, Time: 20mins, Temperature: 30°C

2) Initial Dye Concentration

An initial concentration range of 1.5ppm – 6.5ppm was taken where absorption onto AC was carried out. The removal % has a steady decrease trend as the concentration of the dye increases.At low concentrations, there will be unoccupied active sites on the adsorbent surface.From Figure 4 we can see that initially, the removal percentage was around 97% due to the presence of abundant free pores but as the concentration increased the pores became blocked and the removal % decreased. The highest removal % was 97% at 1.5ppm and least was 77% at a 6.5ppmconcentration of MB solution.

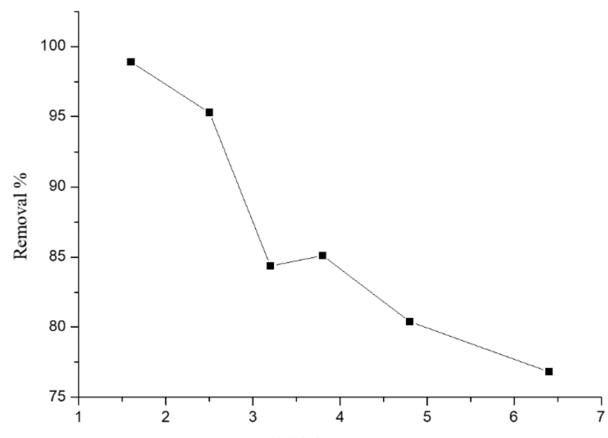

Figure 4: Effect of Initial Dye Concentration on MB Removal
Adsorbent Dosage: 250mg/L, Time: 20mins, Temperature: 30°C

3) Time

A 50-minute time range was taken where the removal % of MB solution onto AC was studied. From the Figure 5.it is evident that there is a continuous increase in the removal % with time. The change in the rate of adsorption might be due to the fact that initially all the adsorbent sites are vacant and a solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in a number of vacant sites of adsorbent and dye concentrations. The decreased adsorption rate, particularly, toward the end of experiments, indicates the possible monolayer formation of MB on the adsorbent surface. This may be attributed to the lack of available active sites required for further uptake after attaining the equilibrium [7].

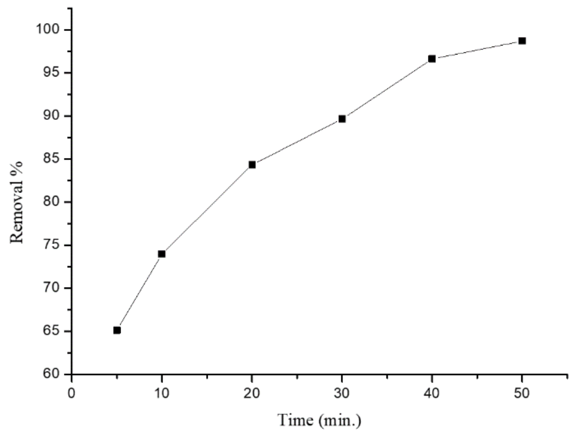

Figure 5: Effect of Time on MB Removal
Adsorbent Dosage: 250mg/L, Initial Dye Conc.: 3.2ppm, Temperature: 30°C

4) Temperature

With the rise in temperature, there has been a continuous decrease in the removal % of the dye. Increase in temperature results in random motion of fluid particles. The intermolecular distance increases and there is a constant rapid motion of the molecules [8]. Due to this, as the temperature rises the MB molecules start to vibrate rapidly and theirprobability of getting absorbed into the AC pore reduces. From the Figure 6 it is evident that at a low temperature of 30°C the molecular motion was very low and the removal % was 84% but at higher temperatures around 80-100°C, the removal % dropped to 65%.

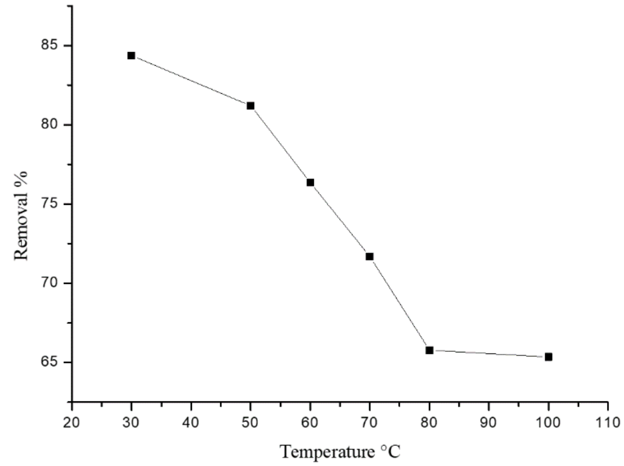

Figure 6: Effect of Temperature on MB Removal
Adsorbent Dosage: 250mg/L, Initial Dye Conc.: 3.2ppm, Time: 20mins.

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C. ***Taguchi table response***

Experiments were carried out according to the table. The removal percentage of each of the given set of runs was calculated by adsorption of MB dye onto the AC produced from spent tea leaves. The S/N Ratio of each of the experiments was calculated using removal percentage as the target response. Hence the "Larger is better" is taken for the S/N ratio which is determined by the following formula:

$$\frac{S}{N} = -10 * Log\left(\sum \frac{1/Y^2}{n}\right)$$

Where Y is the response and n is the number of repetitions of the experiments and 'n' represents a total number of replications of each test run [9].All the values obtained are positive. The S/N values of each of the experiments are given in Table 3.

TABLE 3: RESULTS OBTAINED FROM TAGUCHI DESIGN EXPERIMENTS

Run Number	Removal %	S/N Ratio
1	85.35	38.6241
2	79.91	38.0520
3	83.41	38.4244
4	37.02	31.3687
5	88.7	38.9585
6	96.1	39.6545
7	91.46	39.2246
8	93.43	39.4097

9	90.05	39.0897
10	96.7	39.7085
11	94.67	39.5242
12	96.6	39.6995
13	95.9	39.6364
14	97.83	39.8094
15	96.32	39.6743
16	88.5	38.9389

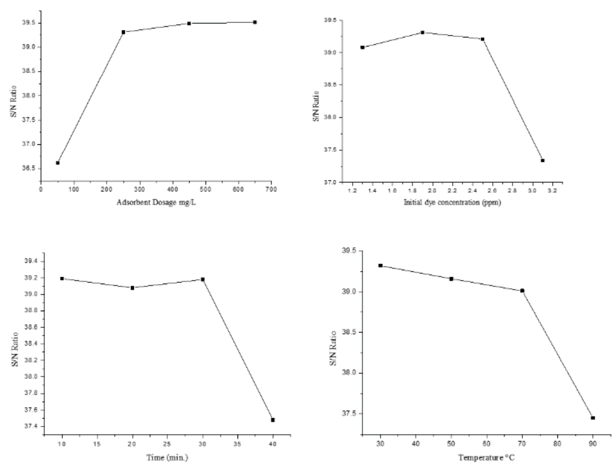

Figure 7: Effect of S/N Ratio of different parameters

Figure 7 shows how the S/N ratio increased in the beginning with the increase in adsorbent dosage but about 300mg/L of AC Dosage, the S/N ratio almost became constant. With temperature, time and initial dye concentration the S/N ratio witnessed a decreasing trend.

TABLE 4: DELTA RANKING OF THE CHOSEN PARAMETERS

Level	Adsorbent mg/L	Initial Dye Conc. Ppm	Time min	Temp. °C
1	36.62	39.08	39.19	39.32
2	39.31	39.31	39.08	39.16
3	39.49	39.21	39.18	39.01
4	39.51	37.34	37.48	37.45
Delta	2.90	1.97	1.70	1.87
Rank	1	2	4	3

The S/N ratios for each of the parameters determine the delta ranking of the parameters. From the delta ranking Table 4, we can evaluate the priority of the parameters for its effect on the removal % of the MB dye on the AC from spent tea leaves. Priorities of the parameters are as follows: Adsorbent Dosage> Dye Concentration> Temperature> Time.

The dosage of the spent tea leaves AC has the most influence on the removal % and time has the least influence on it. The aim of this experiment is to reach the highest signal to noise (S/N) ratio. S/N shows the best database on the basis of minimum deviation and will help us to determine the effect of each factor. To indicate the most effective parameter for adsorption of MB dye on AC from spent tea leaves, analysis of variance (ANOVA) was performed. The results of ANOVA for dyes are given in Table 5. The degree of freedom (DOF) for each factor was 3 with total DOF of 15.

TABLE 5: ANALYSIS OF VARIANCE (ANOVA) OBTAINED

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Adsorbent Dosage (mg/L)	3	1511.6	503.9	3.18	0.184
Initial dye conc. (ppm)	3	497.0	165.7	1.04	0.486
Time (min.)	3	337.6	112.5	0.71	0.608
Temp. °C	3	390.8	130.3	0.82	0.562
Error	3	475.6	158.5	-	-
Total	15	3212.6	-	-	-

According to Fischer's F-statistics, the obtained regression model is considered to be significant if the p probability value is low [10]. A t-test was implemented to confirm the significance of the obtained regression coefficients of each of the parameters and the interaction between the different parameters was determined by p values. If the probability p-value is less than 0.05 then the factors affecting the removal of MB is considered to be significant [11. 12]. Thus we can evaluate that the chosen parameters do not play many roles in the removal of MB, however, Adsorbent Dosage has a relatively better effect than the other parameters.

D. *Optimization of Parameters*

The optimum experimental conditions are given in Table 6 and show that the optimum condition based on Mean effect and S/N ratio is the same. Taguchi has the ability to predict the removal percent of dyes in optimum condition[13, 14]. The amounts predicted by Taguchi design method were 97.30% removal for MB, which was very close to those achieved experimentally in the same condition with the closeness of 92.86%.

TABLE 6: OPTIMIZED PARAMETERS OBTAINED IN THIS WORK

Adsorbent Dosage (mg/L)	650
Initial dye conc. (ppm)	1.9
Time (min.)	30
Temperature °C	30

IV. CONCLUSION

In this study, Taguchi design of experiment was done to find the best condition for removal of MB solution using AC from spent tea leaves. It was found that Taguchi design was a suitable method for optimizing parameters. This method provided a minimal number of trials with high precision and accuracy and has the merits of reducing cost and time of experimental investigation and consequently reduces chemical consumption for the optimization process. According to Delta Ranking, the most important and affecting factor on adsorption of MB was Adsorbent dosage and the least important factor in adsorption was a time of contact. The optimum conditions obtained from Taguchi for a 97.30% removal MB on AC from spent tea leaves is Adsorbent Dosage of 650mg/L, Initial dye conc. 2.71ppm, time 30 min. and temperature at 30°C.

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