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Dye Removal from Aqueous Solutions Using Natural and Biochar Butt: Full Factorial Design Approach

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Abstract: High concentrations of dye-containing wastewater are generated from industries that produce intense dyes, such as textiles. These wastewaters cause serious environmental and human health problems when they are discharged into natural environments without adequate treatment. Adsorption is a frequently used, effective, and easy method to prevent this situation. However, commercial activated carbon, which is used as an adsorbent material, is often needed to be regenerated, and, this creates economic problems. This study investigated the usability of cigarette butts as an inexpensive alternative to commercial activated carbon. Cigarette butts in natural and biochar forms were used to remove malachite green dyestuff. 2^3 full factorial modeling was used to model the adsorption efficiency. Because of this modeling, the parameters that have the main effect on adsorption have been revealed. In the experiments, 3 factors were examined at 2 levels. These are, adsorbent amount (0.005 g/30 mL and 0.1 g/30 mL), initial dye concentration (50 mg/L and 500 mg/L), and adsorbent type (natural and biochar butts). The dyestuff removal efficiency was obtained in the study, up to 96%. According to the results of the model graphics, the factor that has the most effect on adsorption is the adsorbent type. The biochar form gave very high efficiency results compared to the natural form. It was seen that the adsorbent dose was the factor with the lowest effect on the adsorption efficiency.

Keywords: Adsorption, biochar, butt, dye, full factorial design.

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INTRODUCTION

Dyes are widely used in various industries, such as textiles, paper, plastics, cosmetics, ceramics, and leather, for coloring their final products. To remove dyes from aqueous solutions, many chemical or biological treatments have been used either individually or together (1-2). There are several methods for dye removal, such as adsorption, oxidation-ozonation, coagulation, coagulation-flocculation, and biological methods. Among these removal methods, adsorption is an attractive alternative method. Many adsorbents have been tested on the possibility to lower concentrations from aqueous solutions, such as active carbon, peat, olive oil waste, chitin, red mud, calcite, clay, natural zeolites, bentonite, sepiolite, perlite, iron oxide coated sand, burnside, and others (3).

Malachite green is a toxic chemical often used to dye materials such as fabric, leather, and paper. Although it causes many health problems, it is widely used today due to its cheapness and ease of use. Malachite green is found in many industrial wastewater-containing dyes. Due to its harmful effects on nature and human health, its treatment is mandatory. Therefore, malachite green was chosen as the dyestuff in this study.

Industrial and technological progress required massive consumption of natural energy resources in recent years. For this reason, energy resources have started to decrease rapidly. Biomass is much more than firewood or just another fuel source. Electrical or stationary energy can be provided by hydro, solar, thermal, geothermal, wind, wave, and even nuclear power in a post-fossil fuel and C-constrained economy (4-5). Biomass can produce primary gas, liquids, solids, or the C-based chemicals we currently obtain from fossil supplies. It is worth noting that during its growth phase, biomass contributes significantly to providing ecosystem services, other organisms' biodiversity, and recreational values. The energy stored in biomass can be used to produce renewable electricity, thermal energy, or transportation fuels (6).

Previous studies have reported the application of hydrochar as adsorbents for the removal of metals (7), dyes (8), drugs (9) and herbicides (10) from aqueous solutions. However, restrictions on applying hydrocarbons for adsorption processes cause low adsorption capacity, generally due to low porosity and specific area. For more efficient use of these materials, hydrochars should be subjected to an activation process to increase their adsorption capacity (11). The activating agent plays a vital role in forming the pore structure and determining the physicochemical properties of the resulting hydrocarbons. Typical activation approaches can be divided into physical and chemical activation. It has many advantages such as chemical activation, low operating temperature, short activation time, well-developed pore structure and high efficiency (12).

In this study, butts with high waste capacity were selected as biomass. Disposed of cigarette filters, in the form of cigarette butts, are a major waste disposal and environmental pollution hazard, mainly because they contain biodegradable cellulose acetate; Worldwide, 5.8 trillion cigarettes are smoked annually and 4 million 800 thousand tons of cigarette butts are produced (13). In addition to causing litter, cigarette butts contain pollutants such as toxic heavy metals that may leak into waterways, potentially damaging humans and wildlife. To convert hazardous wastes into high-value products, this study investigates the evaluation of smoked cigarette filters/butts disposed of (14). In addition, the large amount and waste state of butts make it a more economical adsorbent option. Adsorption studies with butts are also very limited in the literature. For all these reasons, butts were chosen as an adsorbent in this study.

This study investigated the efficiency of large cigarette butts in the form of waste in removing malachite green with activated hydrochar forms. The conditions under which the removal efficiency depends on the selected adsorption conditions were examined by applying to the full factorial model.

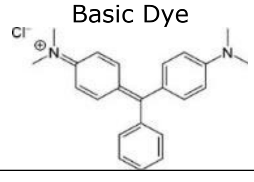
MATERIAL AND METHOD

Materials

The remaining cigarette butts after consumption were used as adsorbents. Cigarette butts collected by our means were separated from the paper and prepared for experiments with only filter parts remaining.

Basic dye form of Malachite Green ($C_{23}H_{26}ClN_2$) was selected for adsorption studies. The stock solution of 1000 mg/L was prepared by dissolving accurately weighed amounts of malachite green in 1000 mL distilled water. Table 1 shows some properties of the dye. All experiments were performed in duplicate and the average values were used for data analysis.

Table 1: Some properties of malachite green dye.

Basic Dyes Properties	Malachite green
C.I. No	42000
CAS No	5596-64-2
Chemical Formula	$C_{23}H_{26}C1N_2$
Molecular Weight (g/mol)	364.92
Melting Point (°C)	164
C.I. Name	Basic Dye
Molecular Structure	

Method

Hydrocar production

Butts separated from paper to be converted into hydrocarbons: The experiment was carried out by mixing 1:8 (solid: liquid) with pure water in a 250-mL fully enclosed steel reactor.

80 mL of purified water was placed in the reactor with 10 g of butts. After completely closing the

reactor, it was left in the ash oven at 250°C for 5 hours. At the end of the time, the reactor was removed from the furnace and cooled with cold water. The slurry sample was taken into the washing paper and dried in the oven at 50-60 °C for 24 hours. The result was a black powder of hydrochar.

Chemical activation phase
The dry hydrocarbon tobacco was activated by mixing in a pyrolysis mechanism at 600 °C with 1:4 KOH and washing with acid; KOH in dry pellets was pulverized using a pestle, mixed with 10 g of hydrochars and 40 g of powdered KOH. The mixture was pyrolyzed at 600 °C, 5 °C/min, one hour residence time, and 100 mL/min nitrogen gas flow rate. The product obtained after pyrolysis was placed in vacuum filtration apparatus and washed with 2 M hydrochloric acid (HCl) dropwise. After the reaction with acid, it was washed several times with purified water to neutralize. After washing, it was dried in the oven at 50-60 °C for 24 hours. As a result of all these processes, approximately 2-3 g of product is obtained.

Adsorption study and full factorial modeling
In this study, a Full Factorial Design of the Experiment was designed to investigate the effect of adsorbent amount, initial dye concentration and adsorbent type on the removal of malachite green dye ions with natural and biochar butts. The samples were mixed at predetermined periods at a temperature of 23 °C in a shaker at 150 rpm until equilibrium was reached. The concentrations of the dyes were determined using a UV/Vis Spectrophotometer.

The removal efficiency (E) of natural and biochar butt on malachite green dye was calculated according to the following formula (Eq. 1):

$$E(\%) = (C_0-C_e)/C_0 \times 100 \quad (1)$$

Where C_0 is the initial concentration of the dye solution and C_e is the final concentration of the dye solution.

Full Factorial Design of Experiments examines every possible combination of factors at the levels tested (15-16). The general notation for a full factorial design run at b levels is bk Runs, where k is the number of factors (17).

This study aims to maximize the removal of malachite green dye ions (response variable). In this respect, experimental factors, which are adsorbent amount, initial dye concentration, and adsorbent type, were selected as possible candidates affecting the removal percentage. By considering the earlier studies, two levels for each factor were determined. The 2^3 factorial design with high and low levels of factors are given in Table 2 (b=2 and k=3).

Table 2: The levels of experimental factors.

Factor	Low Level (-1)	High Level (+1)
Adsorbent Amount (g/30 mL) (A)	0.005	0.1
Dye Concentration (mg/L) (B)	50	500
Adsorbent type (C)	Natural butt	Biochar butt

The results of each run with duplicate tests are shown in Table 3. Interaction is a variation among the differences between means for varying levels of one factor over different levels of the other factor.

Table 3: Experimental design matrix of malachite green dye removal efficiency.

Run No.	Factor			Efficiency (%)		
				Replicate		
	A	B	C	I	II	Average
1	-1	-1	-1	22.88	21.59	22.24
2	+1	-1	-1	30.83	29.72	30.28
3	-1	+1	-1	5.26	4.82	5.04
4	+1	+1	-1	8.42	11.07	9.75
5	-1	-1	+1	92.03	87.69	89.86
6	+1	-1	+1	98.30	94.60	96.45
7	-1	+1	+1	70.04	65.69	67.87
8	+1	+1	+1	73.52	75.15	74.34

Using plus and minus signs to represent high and low levels of a factor, main effects given in Table 4 were calculated by using the following general equation (18-19).

Table 4: Estimated Effects and Coefficients for malachite green dye removal efficiency.

Term	Effect	Coeff.	SE Coeff.	T	P
Constant		49.477	0.501	98.82	0.00
Adsorbent Amount	6.451	3.226	0.501	6.44	0.00
Initial Concentration	-20.45	-10.23	0.501	-20.4	0.00
Adsorbent Type	65.303	32.651	0.501	65.21	0.00
Adsorbent Amount Initial Concentration*	-0.864	-0.432	0.501	-0.86	0.41
Adsorbent Amount Adsorbent Type*	0.079	0.040	0.501	0.08	0.93
Initial Concentration Adsorbent Type*	-1.596	-0.798	0.501	-1.59	0.15
Adsorbent Amount Initial Concentration* Adsorbent Type*	0.805	0.402	0.501	0.80	0.44

S=2.00276, R-Sq=99.83%, R-Sq(pred)=99.32%, R-Sq(adj)=99.68%

RESULTS AND DISCUSSION

The residuals also appraised the sufficiency of the models. The observed residuals are plotted against the expected values, given by a normal distribution in Figure 1. Trends seen in Figure 1 reveal reasonably well-behaved residuals. In these graphics, the residuals seem to be randomly scattered.

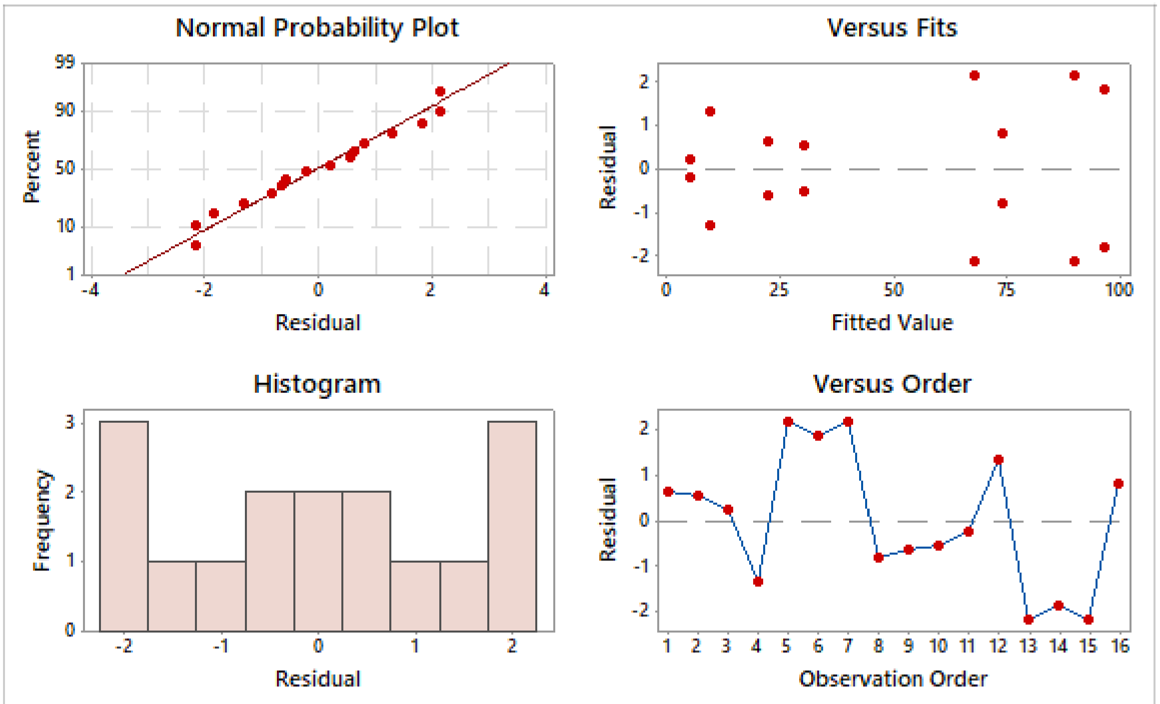


Figure 1: Residual plots for methyl red dye removal efficiency.

The Cube Plot in Figure 2 shows the predicted removal efficiency at combinations of the low and high levels for experimental factors. In the study, the highest expected value for the response variable is obtained at methyl red initial concentration at a high level, adsorbent amount at low level and adsorbent type at biochar butt.

The R-square of the model (99.83%) was higher than the predicted value (99.32) % and fit well the model's results. These results argued good agreements between the predicted and experimental values of malachite green dye removal efficiency (Table 3).

The most critical parameters affecting the efficiency of an adsorption process are adsorbent type, initial concentration and adsorbent amount. To determine the effects of these parameters, experiments were performed at different combinations of the physical parameters using statistically designed experiments.

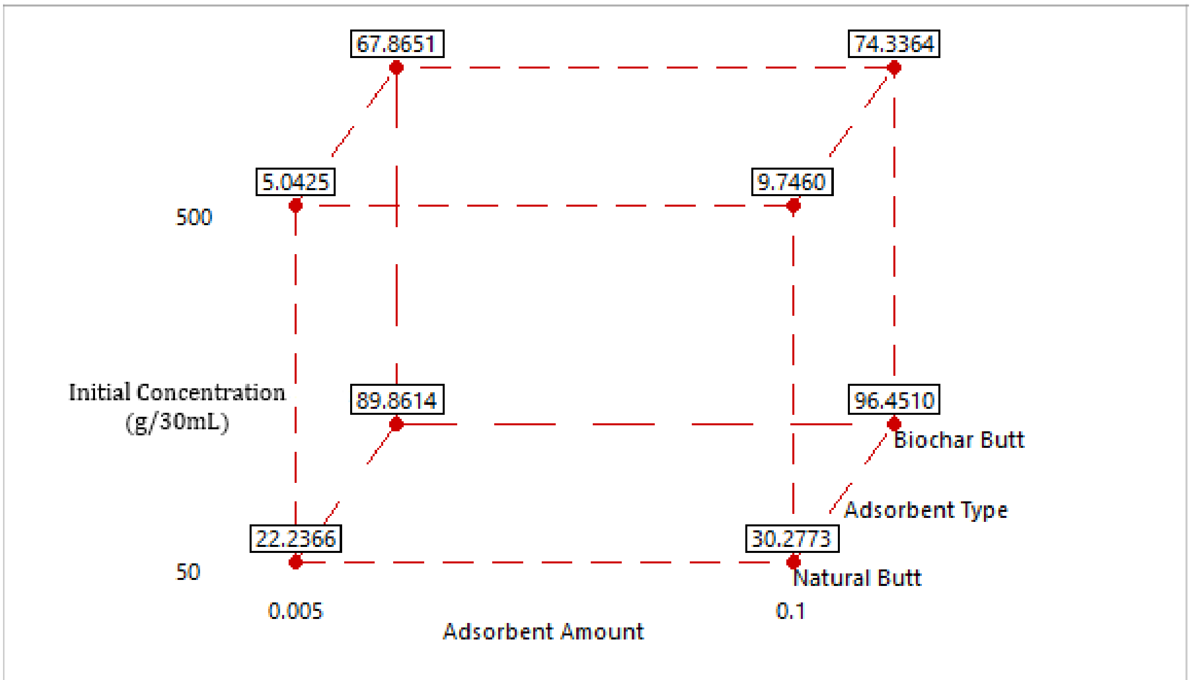


Figure 2: Cube plot malachite green dye removal efficiency.

A normal probability plot of the standardized effects, the aim of which is to determine the statistical significance of both the main and interaction effects, is given in Figure 3. The insignificant effects will fall along a line; however, the significant effects will stray farther from the line. According to Figure 3 and Figure 4, the main effects C, B and A are statistically significant. Since C and A lie on the right-hand side of the line, their contributions positively affect the model. The reverse is valid for the rest of the significant results, which lie on the left-hand side. The adsorbent type appears to have the largest effect because it lies furthest from the line.

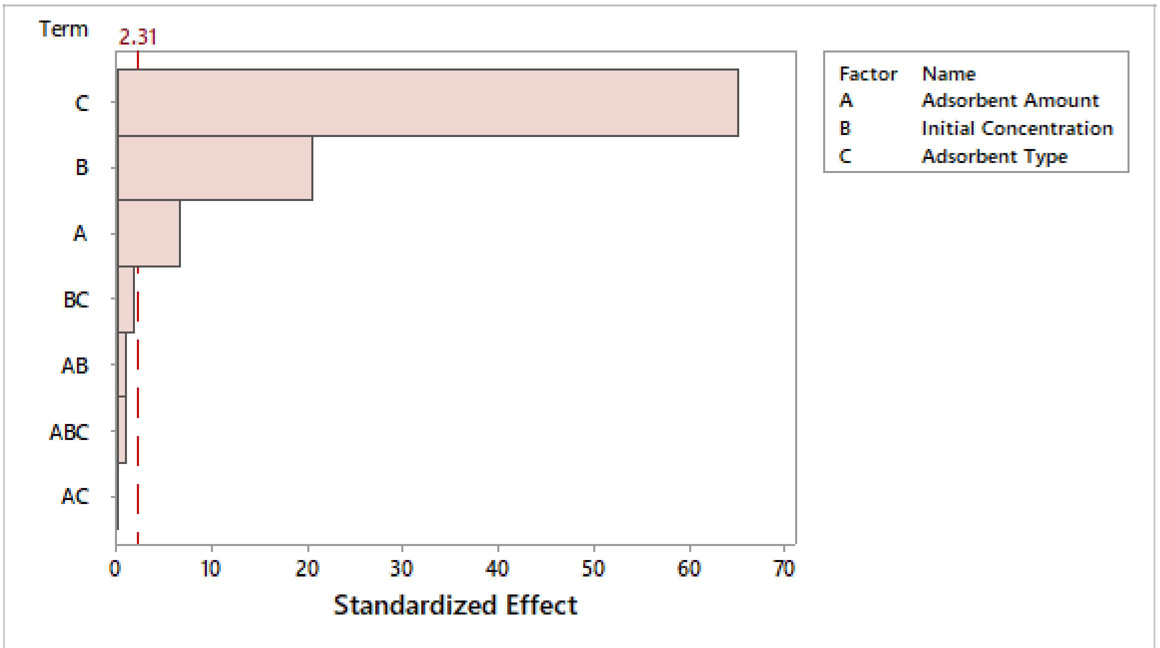


Figure 3: Pareto chart of the standardized effects for malachite green removal.

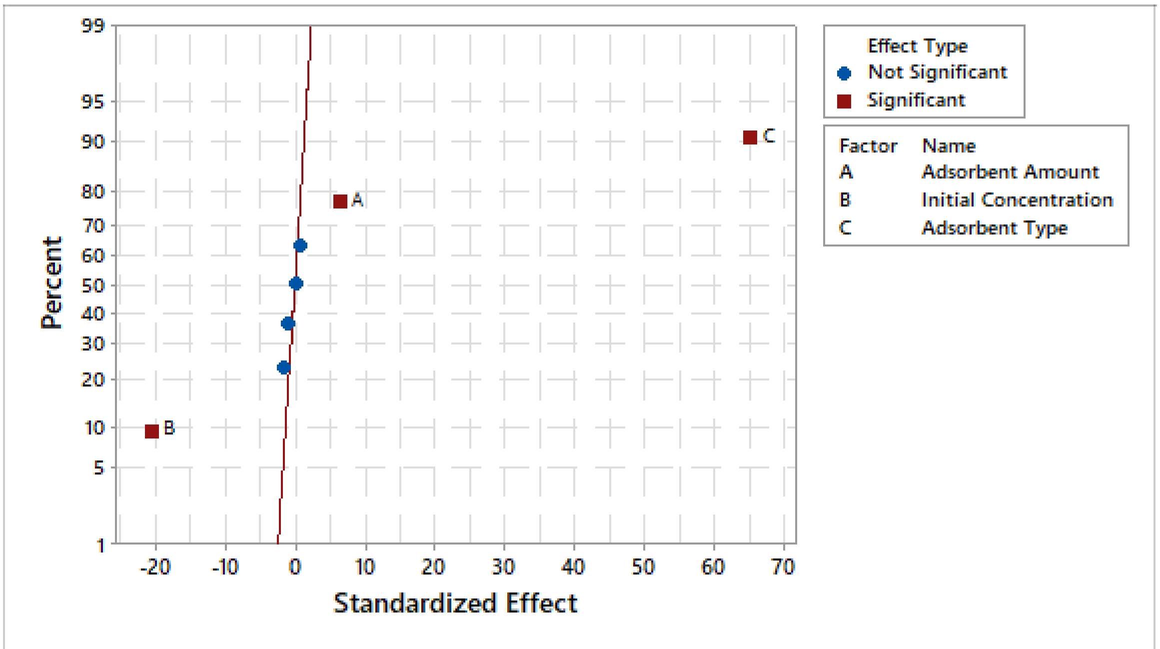


Figure 4: Normal plot of the standardized effects for malachite green removal.

Figure 5 shows the main effects plot, offering the effect of each variable on the response factor. The main effect is significant if the mean for one level of the factor is sufficiently different from the mean for another level of the factor.

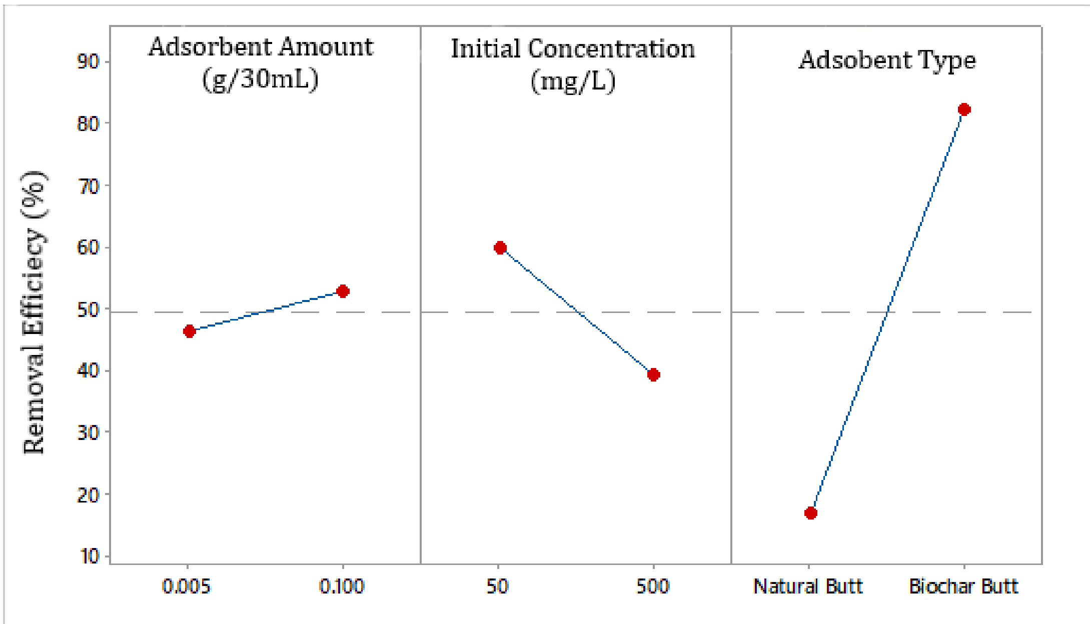


Figure 5: Main Effects plot for malachite green removal efficiency from aqueous solutions.

That is, lines with steeper slopes (up or down) have a more significant impact on the output means than lines with little or no slope (horizontal). This type of figuration shows the contribution to the response factor of changing one of the influential variables. When the effect of a factor is negative, removal efficiency decreases as the factor changes from low to high levels. In contrast, if the effect is positive, removal efficiency increases for a high level of the same factor. If the magnitude of the main effect is small, the slope would be close to zero.

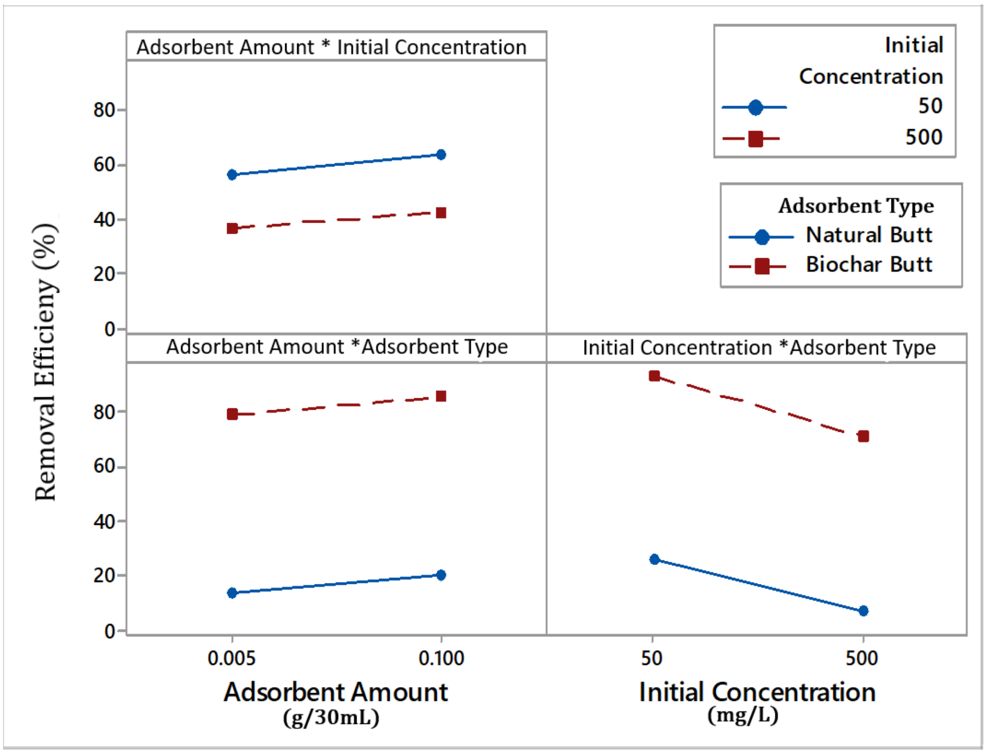


Figure 6: Interaction plot for malachite green removal efficiency from aqueous solutions.

The plot shows the possible interaction between the mean responses of the factors under assessment. An interaction plot circumstances the impact that the act of changing the settings of one factor has on another factor. Graphically, two parallel lines of factors indicate no interaction between them; however, non-parallel lines suggest that the two factors interact together. The interaction plot in Figure 6 confirms that there is no interaction between the factors.

In order to see the effects of interactions between experimental factors, a multi-vari chart was generated (Figure 7). This chart shows that the effect of adsorbent type is clearly observed for the biochar butt is more efficient than the natural butt.

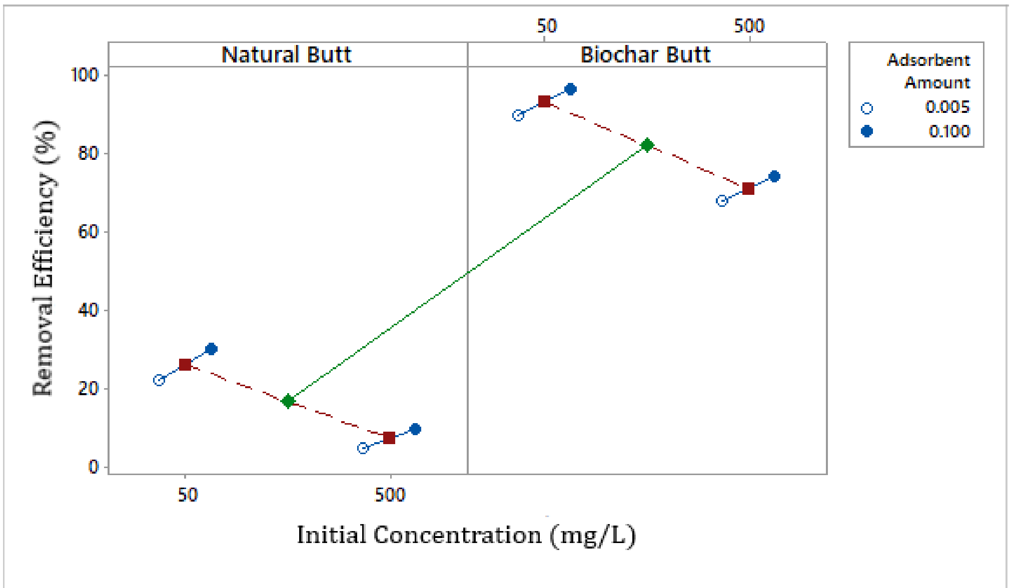


Figure 7: Multi-Vari Chart for malachite green removal efficiency from aqueous solutions.

CONCLUSION

The scope of this study was to investigate the effectiveness of the natural and biochar butts in removing malachite green dye ions from aqueous solutions. For this purpose, a 2^3 full factorial design was employed to evaluate the importance and interactions of adsorbent amount, initial dye concentration and adsorbent type. Full factorial design model used some experimental data to predict the response of the experiments at new similar conditions for the problem of malachite green dye by natural and biochar butts. The factorial design results show that "adsorbent type (factor C)" had the most potent effect on the removal efficiency of malachite green dye. The negative coefficient means that increasing initial concentration (factor B) decreases removal efficiency.

On the other hand, the positive sign of adsorbent type (factor C) and adsorbent amount (factor A) means that there is a direct relation between these factors and the response. The results of this study clearly show that adsorbent type, initial dye concentration, and adsorbent amount were significant for the removal efficiency of malachite green dye. The proposed modeling method also decreases the number of experiments to remove the adsorption efficiency for removing malachite green dye ions. This decreases the cost of the experimental studies.

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