ISSN (e): 2250 – 3005 || Volume, 08 || Issue, 9|| Sepetember – 2018 ||
International Journal of Computational Engineering Research (IJCER)

Application Of Central Composite Design In The Adsorption Of Malachite Green Dye By Using Carbonized Eucalyptus

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ABSTRACT::*The adsorption of Malachite Green (MG) dye was performed in this study on carbonized Eucalyptus wood. The batch experiments were performed to optimize the parameters for the maximum adsorption of the MG dye and the parameters included were - amount of adsorbent, initial dye concentration, contact time and pH of the dye solution. The response surface methodology was applied to design the experiments, model the process and optimize the variables. Central composite design was successfully employed for experimental design and analysis. The maximum adsorption of 97.95% was obtained at 49.75 mg/l initial dye concentration, 1.37 g/L adsorbent, pH 9.96 and contact time of 116.6 minutes. The optimum values of these parameters were calculated and the experimental values were found in good agreement with the model predicted. Thus, this study indicates carbonized Eucalyptus wood as effective adsorbent for the removal of malachite green dye from aqueous solutions.*

KEYWORDS: *Adsorption, Carbonized Eucalyptus, Dye removal, Malachite Green, Wastewater Treatment*

Date of Submission: 17-10-2018 Date of acceptance: 03-11-2018

I. INTRODUCTION

Effluents discharged from textile and dyestuff industries to neighboring water bodies and wastewater treatment systems are currently causing significant health concerns. Thus, removing off these coloured dyes from waste water is really necessary for the environmental aspects. Malachite green is an organic compound that is used as a dyestuff and controversially as an antimicrobial in aquaculture. Malachite green is traditionally used as a dye for materials such as silk, leather, and paper. Although called malachite green, this dye is not prepared from the mineral malachite - the name just comes from the similarity of color. Malachite green (MG) is water soluble cationic dye that appears as green crystalline powder and belongs to triphenylmethane category [1]. Malachite green is classified a Class II Health Hazard and it has properties that make it difficult to remove from aqueous solutions and also toxic to major microorganisms[2]. Due to its low manufacturing cost, malachite green is still used with less restrictive laws for non aquaculture purposes.

Possible methods of dye removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation, electro-dialysis, cloud point extraction etc. [3,4]. Among the different physical, chemical and biological treatment methods of dye removal from aqueous solutions, Adsorption is an attractive and effective method for dye removal from wastewater, especially if the adsorbent is cheap and widely available [5,6,7,8,9]. Adsorption is a surface phenomenon in which the multi-component mixture gets attached to the solid surface by physical or chemical bond [10]. Many low-cost adsorbents have been investigated on fly ash for dye adsorption[11]. Its adsorption capacity depends on the properties of adsorbent such as porous structure, chemical structure and surface area. The activated carbon is a largely used adsorbent because of the fact that it has a high adsorption capacity of organic materials [12,13]. Previously several researchers had proved several low cost materials such as, wheat bran [14] , tamarind fruit shell [15], marine alga Caulerpa racemosa var. cylindracea [16], hen feathers [17] (Mittal, 2006), pithophora species fresh water algae [18] (Kumar et al., 2006) etc.

In this work, our target is to study the dye Malachite green adsorption on Charcoal prepared from Eucalyptus. Various experimental parameters analyzed in this study include amount of adsorbent, initial concentration of dye, contact time and pH of solution. The five level central composite design was used to determine the optimization values of the operating variables.

II. MATERIALS AND METHODS

2.1 Materials

Eucalyptus wood was obtained from the roadside in front of Shaheed Bhagat Singh State Technical Campus, Ferozepur (India). The dye, Malachite Green (MG), was purchased from S D Fine Chemicals, India. The Eucalyptus wood was first cleaned with distilled water to remove the soil, sand and any other undesirable material and then, kept in sunlight for seven days. It was cut into small pieces, dried at 50°C in an air oven for 24 h. and further reduced to small size particles through grinding. The raw material was then carbonized at 350-400 °C under nitrogen atmosphere in high temperature furnace for 4 hours till the fumes disappeared. The produced char was grinded, sieved and stored in an air tight container and labeled as Eucalyptus wood Charcoal (EWC).

2.2 Experimental Set-up and analysis of dye

The experiments were conducted in 250 mL Erlenmeyer flasks with the working volume of 100 mL of aqueous solution. The pH of the solution was adjusted to the desired value by adding 0.1 M NaOH or HCl. The required amount of adsorbent dose was added in the flasks. The flasks were shaken for the specified time period in shaker at 120 rpm. The flasks were withdrawn from the shaker after the desired time of operation. The supernatant and the spent adsorbent were separated by using the centrifugation at 5000 rpm for 15 minutes and operation (R24 REMI Centrifuge, Mumbai, India). The residual dye concentration in the supernatant was analyzed by measuring the solution absorbance at $\lambda = 588$ nm using a UV–visible spectrophotometer (Model - EI-2375, Electronics India). All experiments were carried out in triplicate and the average values are presented.
The percentage removal of dye was calculated as:

$$\%\ \text{Dye removal} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where, C_o and C_e (mg/L) are initial concentration and equilibrium concentration respectively.

III. RESULTS AND DISCUSSION

Various parameters such as initial dye concentration, adsorbent dose, contact time and pH were optimized by using central composite design (CCD). The acidic and basic treatment of the adsorbent was also studied. CCD reduced the experimental work to 30 trials.

3.1 Acidic vs. basic treatment of adsorbent

Two samples of 100 ml with initial dye concentration of 30 mg/l with pH 6 were taken in 250 ml conical flasks. Then 3 g/l acidic and basic adsorbents were added individually in both the flasks. Both samples were kept on the shaker for 60 minutes and then filtered. Both the samples were analyzed under UV spectrophotometer and it was concluded that the adsorbent activated with 0.1 N HCl showed good results as compared to the adsorbent activated with 0.1 N NaOH (Fig. 1). All further experiments were conducted using acid activated adsorbent.

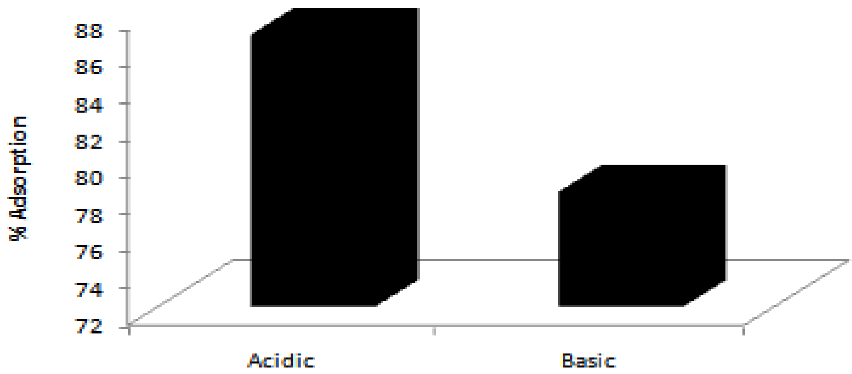

Fig. 1 Acidic vs. basic treatment of EWC adsorbent

3.2 Effect of contact time

The impact of contact time by changing pH, adsorbent dose and initial dye concentration on adsorption of Malachite green dye is represented by **Fig. 2 (a), (b) & (c)** respectively. It is clearly depicted in the figure that the rate of adsorption increases with increase in time. But at later stages, the rate of adsorption decreases. The concentration of dye does not change significantly after 120 minutes. This gives the equilibrium time for adsorption as 120 minutes. It is primarily because of the saturation of the active sites which do not permit furthermore adsorption to occur. This can be explained by the fact that initially, the number of surface sites is very large which allows adsorption to take place very easily. But as the time passes, the active sites get saturated thus slowing down the rate of adsorption.

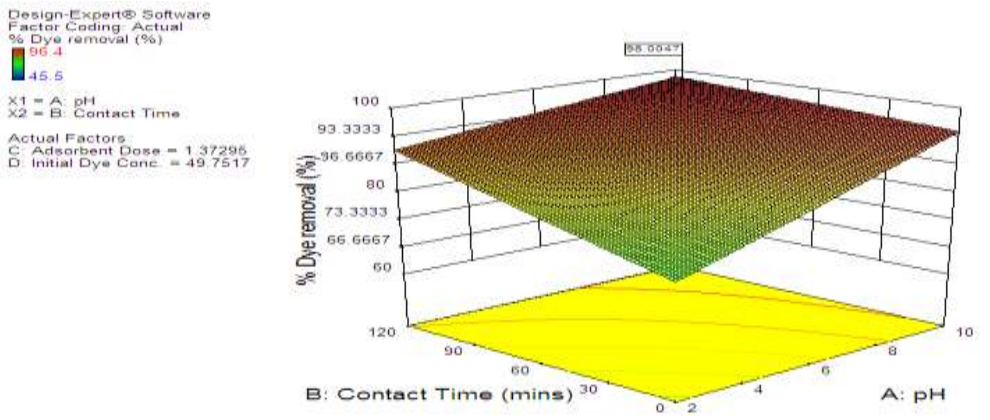

Fig 2(a) Effect of contact time with change in pH at Adsorbent dosage 1.37 g/l and initial dye concentration of 49.7 mg/l

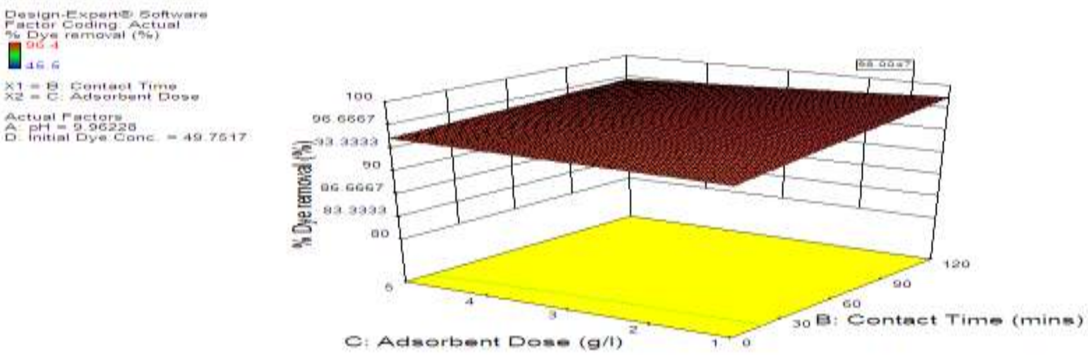

Fig 2(b) Effect of contact time with change in adsorbent dose at pH 9.96 and initial dye concentration of 49.75 mg/l

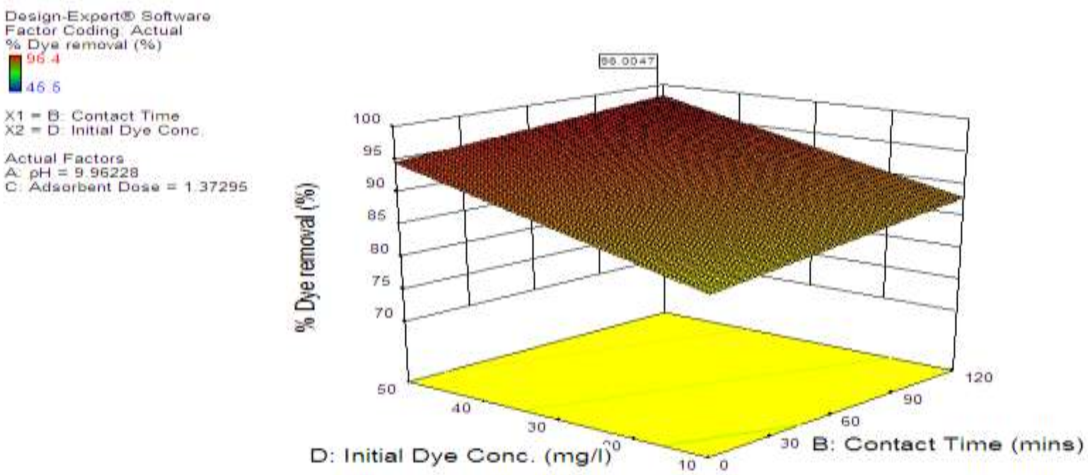

Fig 2(c) Effect of contact time with change in initial dye concentration at pH 9.96 and adsorbent dose of 1.37 g/l

3.3 Effect of pH

Since pH of the solution influence the surface charge of the adsorbent and also the ionization of adsorbate and hence it is a very important parameter to examine the adsorption process. The initial pH of the dye solution has a very strong impact on the adsorbent's surface properties as well as the degree of ionization of dye molecules. Thus it becomes important to study the effect of pH on adsorption process. **Fig 3(a), 3(b) and 3(c)** respectively shows the effect of initial pH on the amount of dye solution adsorbed by EWC adsorbent. In the experiment, 100ml dye solutions and varying adsorbent dose and contact time in the pH range 2-10 have been studied. The pH of the solutions was adjusted by using 0.1 N hydrochloric acid (HCl) and 0.1 N sodium hydroxide (NaOH) solution. It is evident from the graph that the removal efficiency of dye is reasonably high in the pH range 4-10 and declined at lower pH. The optimum pH was found to be 9.96.

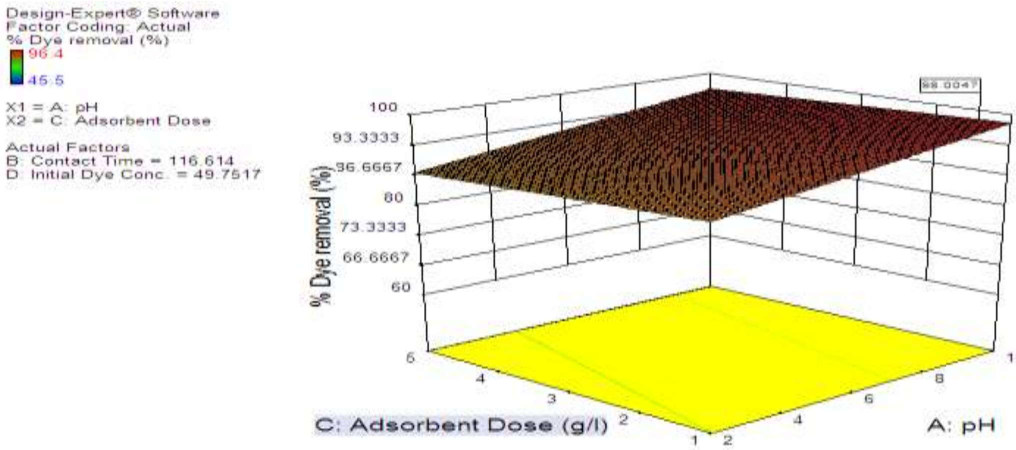

Fig 3(a) Effect of pH with change in adsorbent dose at contact time 116.614 minutes & initial dye conc. of 49.75 mg/l

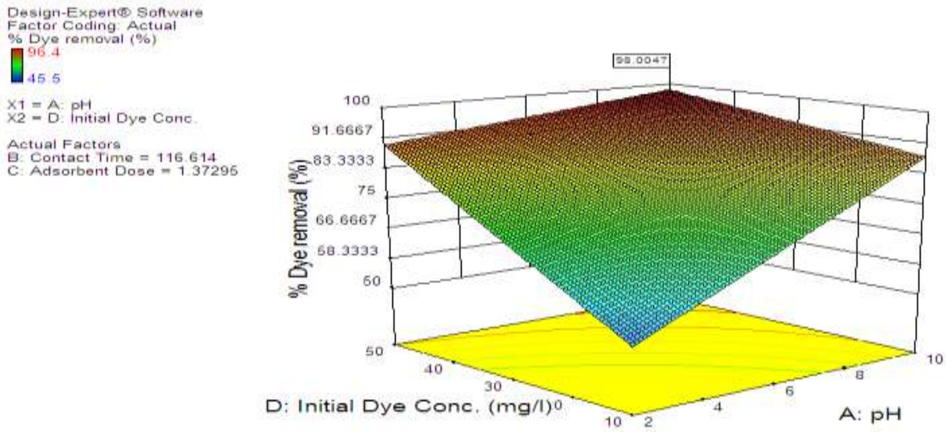

Fig 3(b) Effect of pH with change in initial dye conc. at contact time 116.6 minutes & adsorbent dose of 1.37 g/l

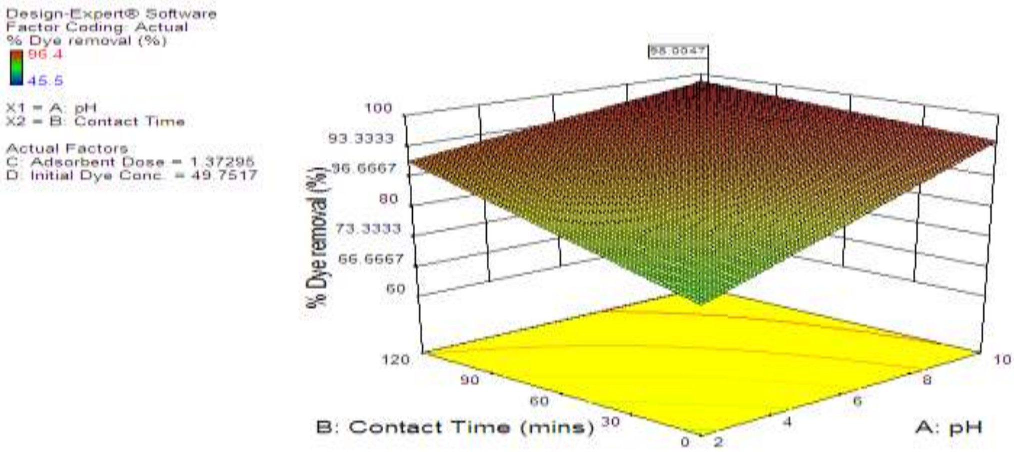

Fig 3(c) Effect of pH with change in contact time at adsorbent dose of 1.37 g/l & initial dye concentration of 49.75 mg/l

3.4 Effect of adsorbent dosage

The effects of adsorbent i.e. EWC dosage on the percentage removal of dye at initial concentration of approx 50 mg/l at room temperature was studied for different dosage of 0.1g, 0.3g and 0.5g in 100 ml solution. **Fig 4(a), 4(b) and 4(c)** respectively shows that the percentage removal of dye increases with increase in the adsorbent dosage upto a point but after that there is no significant increase in the removal. The optimum adsorbent dose was found to be 1.37 g/l. This can be explained by the fact that on increasing adsorbent dosage, the surface area of the adsorption sites increases. But there is no significant increase in adsorption capacity further even after adding more adsorbent.

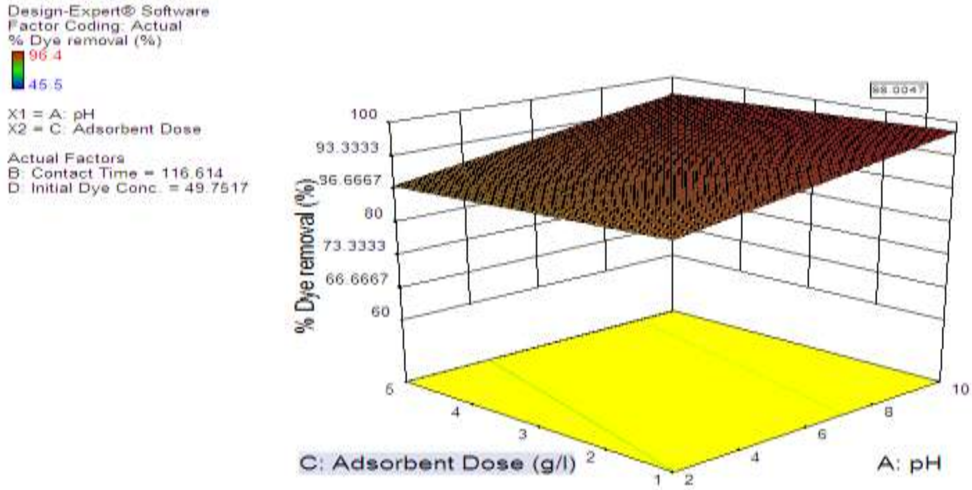

Fig 5(a) Effect of adsorbent dosage with change in pH at contact time 116.614 minutes and initial dye conc. of 49.75 mg/l

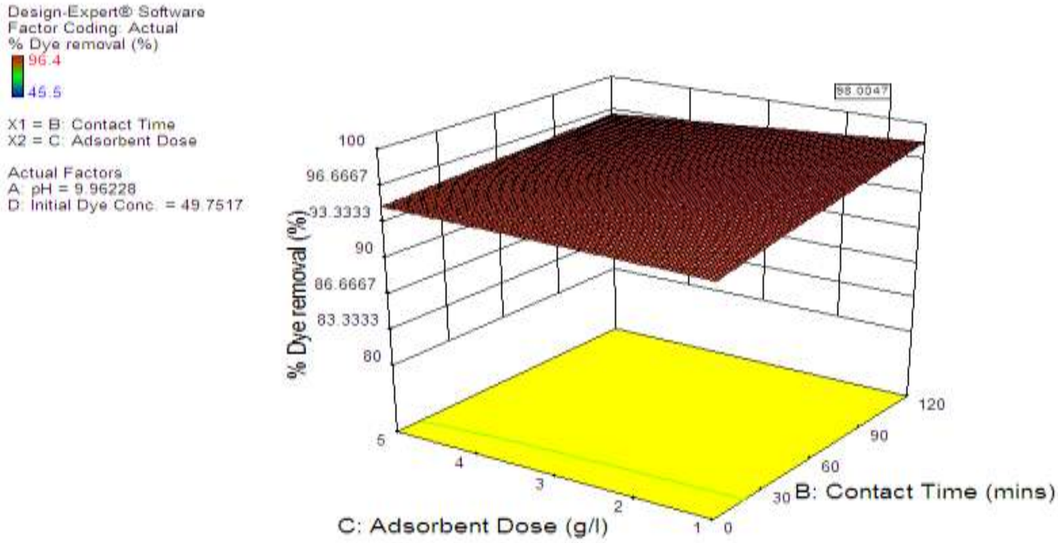

Fig 5(b) Effect of adsorbent dosage with change in contact time at pH 9.96 and initial dye conc. of 49.75 mg/l

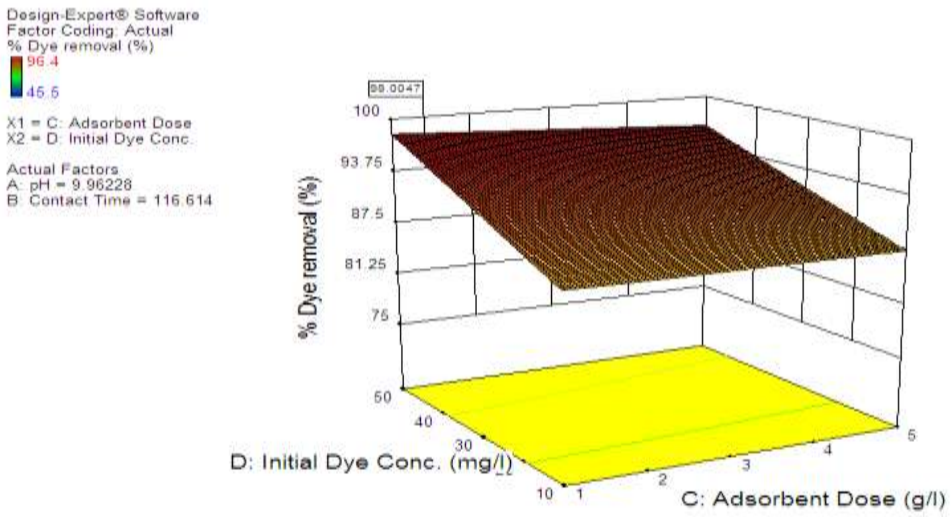

Fig 5 (c) Effect of adsorbent dosage with change in initial dye conc. at contact time 116.6 minutes & pH 9.96

3.5 Effect of initial dye concentration

The dye concentration has an apparent influence on its removal from aqueous phase. The effect of malachite green dye concentration on the efficiency of adsorption was also investigated in the initial concentration range of 10-50 mg/l as shown in **Figure 6(a), 6(b) and 6(c)** respectively. The adsorption capacity increases with increase in initial dye concentration because high concentration of dye results in high driving force for mass transfer. The active sites of adsorbent get surrounded by higher number of dye molecules due to the high concentration of dye which leads to more efficient adsorption. The optimum initial dye concentration was found to be 49.75 mg/l.

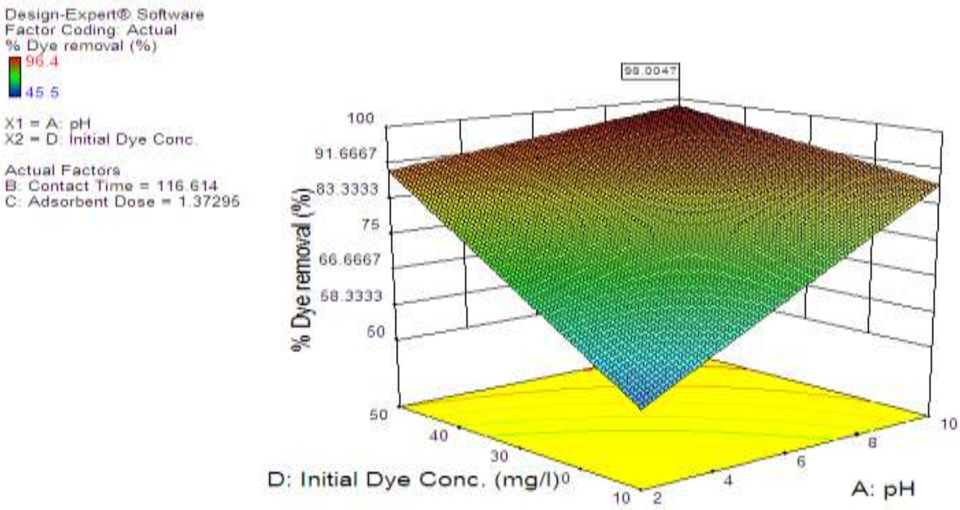

Fig 6(a) Effect of initial dye conc with change in pH at contact time 116.614 minutes & adsorbent dose of 1.37 g/l

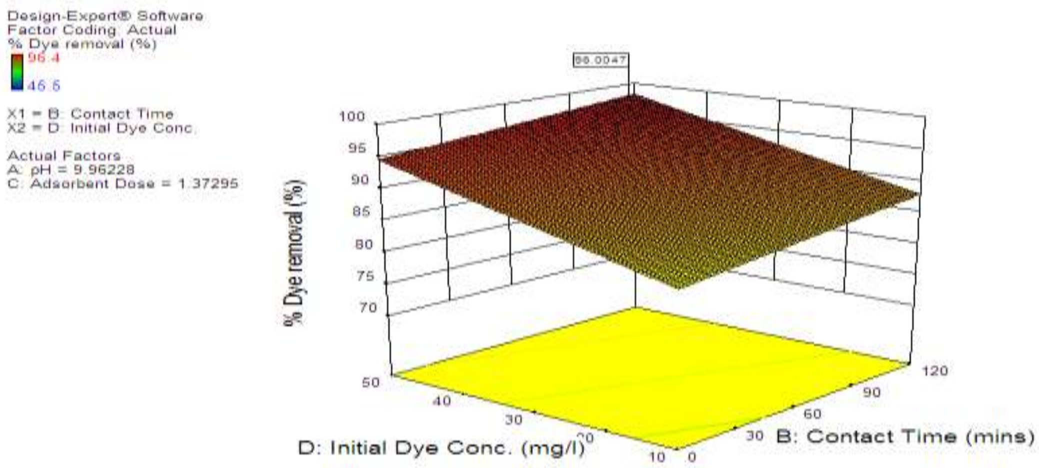

Fig 6(b) Effect of initial dye conc with change in contact time at initial pH 9.96 & adsorbent dose of 1.37g/l

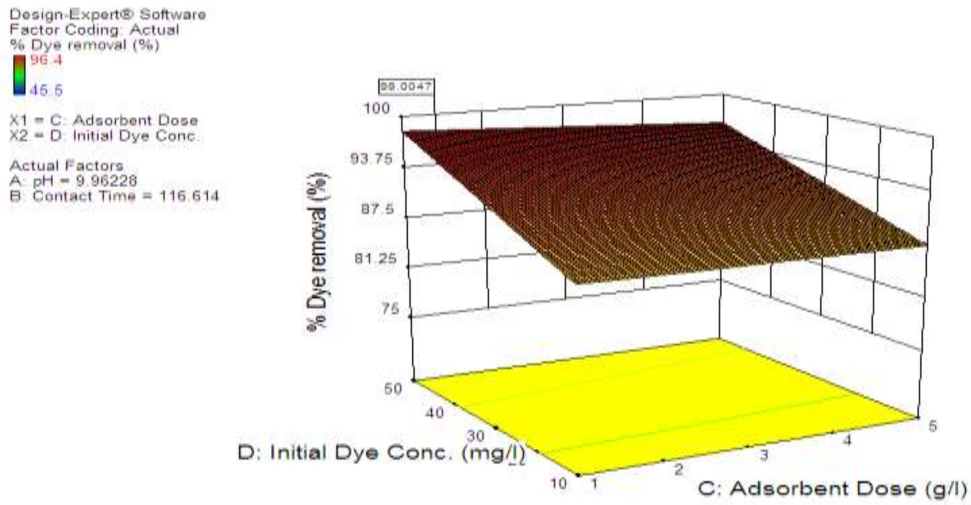

Fig 6(c) Effect of initial dye concentration with change in adsorbent dose at contact time 116.614 minutes and pH 9.96

3.6 Cubical Representation

Cubical representation for effect of contact time, pH and adsorbent dose keeping initial dye concentration of 49.8 mg/l is shown in Fig 7.

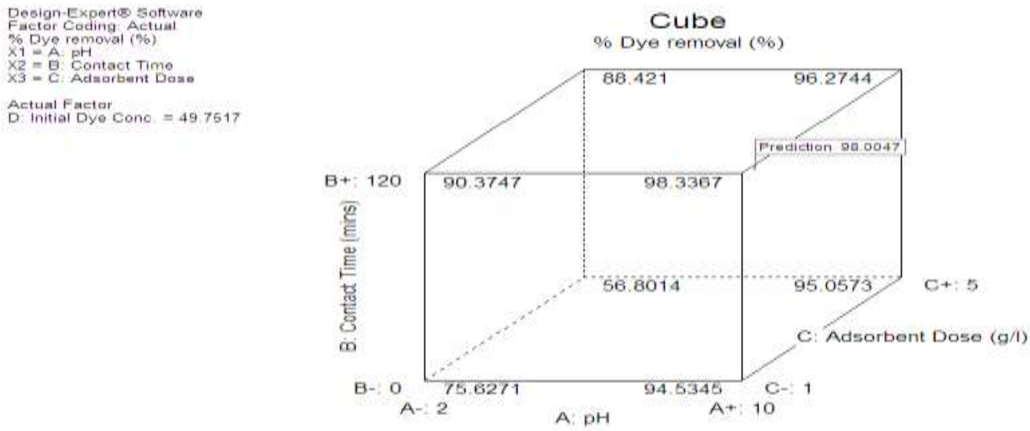

Fig 7 Effect of contact time, pH, and adsorbent dose at initial dye concentration of 49.8 mg/l.

3.7 Model validation

The responses for the adsorption of malachite green dye from aqueous solution by using EWC as an adsorbent were measured based on the conditions of various parameters as shown in Table 1. The regression equations were obtained by fitting the experimental data using linear, interactive and cubical models and the predicted values were obtained from them. The percentage error between the actual and predicted values of dye removal were found to be less than 5% for each experiment conducted as shown in Table 1 which depicts the validation of the model. Similar correlation can be concluded from the **Fig 8** which gives the graphical representation of the actual vs. predicted values for dye removal.

Table 1 Central composite design used and responses of adsorption

S.No	Factor 1	Factor 2	Factor 3	Factor 4	% Dye removal		error %
	A:pH	B:Contact Time	C:Adsorbent Dose	D:Initial Dye Conc.			
		mins	g/l	mg/l	Actual	Predicted	
1	10	120	5	10	87.2	87.74	-0.62
2	6	60	3	30	83.8	80.32	4.15
3	2	60	3	30	78.2	69.77	10.78
4	2	120	1	50	87.8	90.63	-3.22
5	6	60	5	30	76.5	81.20	-6.14
6	10	0	1	50	92.1	94.57	-2.68
7	2	0	1	10	54.2	56.84	-4.88
8	6	60	3	30	83.9	80.32	4.26
9	10	120	1	10	86.9	88.20	-1.49
10	10	60	3	30	92.6	90.87	1.86
11	2	120	5	10	79.3	80.67	-1.73
12	2	0	5	50	54.2	56.74	-4.69
13	10	0	5	50	93.4	94.97	-1.68
14	6	60	3	30	84	80.32	4.38
15	6	60	3	30	83.8	80.32	4.15
16	6	60	3	30	83.6	80.32	3.92
17	6	60	1	30	80.9	79.45	1.79
18	10	0	1	10	81.8	83.59	-2.19
19	10	0	5	10	82.3	83.30	-1.21
20	2	120	5	50	86.4	88.45	-2.37
21	10	120	1	50	96.4	98.38	-2.06
22	6	60	3	10	72.2	73.68	-2.05
23	6	60	3	30	83.7	80.32	4.03
24	6	60	3	50	91.1	86.97	4.54
25	10	120	5	50	95.1	96.24	-1.20
26	2	0	1	50	72.4	75.74	-4.61

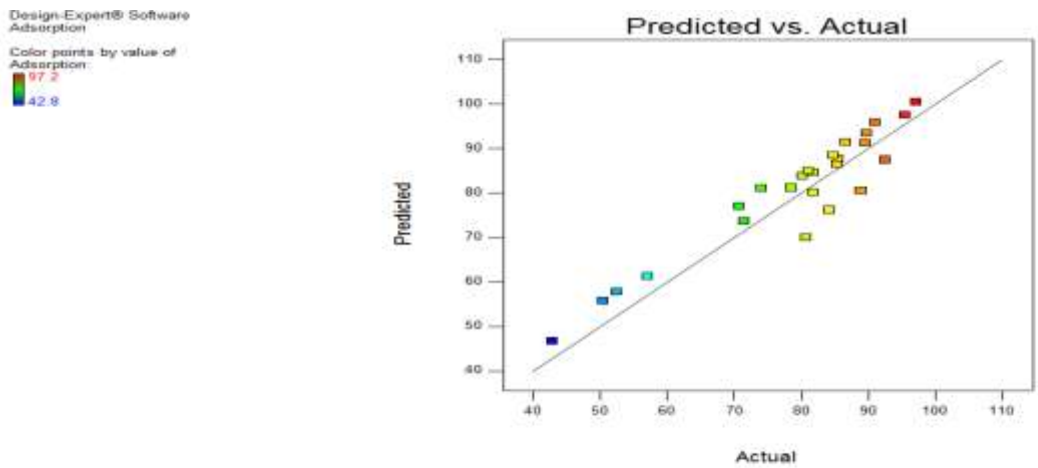

Fig 8 Comparison of actual result with predicted for dye removal

IV. CONCLUSION

The present study shows that malachite green dye could be adsorbed from the aqueous solutions in eco-friendly conditions using carbonized eucalyptus adsorbent. The results obtained from the present investigation revealed the ability of eucalyptus charcoal for removing malachite green dye. The effects of various parameters such as contact time, pH, adsorbent dose and initial dye concentration were studied. Central composite design was used for optimizing the reaction conditions. The optimum parameters were determined as pH to be 9.96, contact time to be 116.6 minutes, adsorbent dose to be 1.37 g/l and initial dye concentration to be 49.7 mg/l. Under these conditions, the removal of dye was observed to be 97.95%. Central composite design proved to be a successful model for studying the responses of deoiled eucalyptus stem as an adsorbent for malachite green dye removal.

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Rajiv Arora, "Application Of Central Composite Design In The Adsorption Of Malachite Green Dye By Using Carbonized Eucalyptus "International Journal of Computational Engineering Research (IJCER), vol. 08, no. 09, 2018, pp 16-24