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RESEARCH PAPER

Optimisation of Crystal Violet and Methylene Blue Dye Removal from Aqueous Solution onto Water Hyacinth using RSM

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ABSTRACT

In this study, the adsorptive removal of two dyes (crystal violet (CV) and methylene blue (MB)) with HNO_3 pre-treated water hyacinth powder (WHP) adsorbent was analysed. The experiments were designed using response surface methodology (RSM) with variable input parameter pH (2-12), adsorbent dose (0.5-3 g/L), initial dyes concentration (25-200 mg/L) and time (10-180 min). The optimization condition for dye removal were (pH = 7.22, adsorbent dose = 3.0 g/L, initial dye concentration = 195.28 mg/L and time of contact = 99.29 min) for CV with removal of 98.20% and (pH = 9.82, adsorbent dose = 2.96 g/L, initial dye concentration = 199.36 mg/L and contact time = 111.74 min) for MB with removal of 97.843%. The above findings observed that pre-treated water hyacinth powder can be utilised as a cost-effective and efficient adsorbent for dye effluent wastewater treatment.

KEYWORDS: Adsorption; Central composite design; Dye; Water hyacinth.

INTRODUCTION

Dyes are used for various industrial processes like textile, plastics, leather, food, and cosmetics. The increasing consumption of dye leads to an increase in the quantity of effluents generation. Hence, the problem associated with it like interference with the photosynthesis of aquatic life beneath the water surface. It is estimated that about 2% of the dye is directly discharged into effluents from manufacturing plants, and around 10% are lost through the textile dying process (Mittal et al., 2010). Due to its complex nature, it is non-biodegradability and toxic to human, plant, and animals. Dyes are classified as cationic, anionic and non-ionic (Vakili et al., 2016). Cationic dyes are the most threatening due to their toxic nature and can interact with the cell membranes (negatively charged), enter the cell and concentrate in the cytoplasm (Bayramoglu et al., 2009). Treatment of textile waste effluent is one of the major problems to be solved by the researchers. Their non-biodegradable nature and ability to be persistent makes most of the available method not effective. Among numerous dye removal methods, adsorption is mostly preferable compared to the other methods for dye removal from aqueous solution due to its economy, simplicity, and ease in design and operation and are insensitive to the toxicity (Akar et al., 2009; Chiou and Li, 2003; Mohan et al., 2008).

Many methods like adsorption (Gupta and Suhas, 2009), membrane separation (Lin et al., 2016), progradation (Gosetti et al., 2004), biochemical degradation (Kumar et al., 2006), ultrasonic-assisted adsorption (Bagheri et al., 2017), ozonation (Ahmad and Alrozi, 2011) have been used for colour wastewater treatment. Still, most of them are costly and not feasible for application in the developing countries due to cost constrain and its application. There is a

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need for exploring the new and cost-effective material for dye removal from an aqueous solution. Adsorption is a feasible and most used dye removal method due to its efficiency, economic, and ease of operation. Previous researchers have used various waste and agricultural residue such as oil palm empty fruit bunch (Tan et al., 2009), orange peel (Khaled et al., 2009), coconut shell and rice straw (Wang et al., 2007), corn cob (Medhat et al., 2021), Moringa oleifera leaf (Do et al., 2020) as an adsorbent for the removal of dyestuff from coloured wastewater.

Water hyacinth (WH) is an invasive aquatic weed with a high production rate and is abundantly available in nature. This makes it one of the most versatile biomasses for various processes like adsorption. Water hyacinth disposal is a significant issue, and landfilling is not an effective way of disposal. This will solve the problem of huge WH biomass handling and solve the problem of dye contaminated wastewater. Saltabaş et al. (2012) and Prasad and Yadav, (2020) have conducted kinetics and adsorption isotherm experiment for methylene blue removal, but no work is reported to optimise dye removal using RSM.

Response surface methodology (RSM), a mathematical and statistical tool useful in analysing the effect of several independent variables on the particular system under consideration to predict the target response (Myers et al., 2009). It helps in the interaction between the various operating parameter by developing a mathematical model that describes the overall process. Central composite design (CCD) is the most common and efficient RSM used in the analysis. It reduces the number of experiments to be carried out and gives high accuracy results. Several studies have successfully used the CCD design like removal of MB from water by nano zero-valent iron (Khosravi and Arabi, 2016), sorption of MB onto *Lemna major* (Sadhukhan et al., 2016), removal of copper (II) and lead (II) by defatted papaya seed (Garba et al., 2015) and extraction of sunflower oil (Rai et al., 2016).

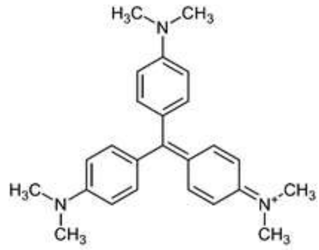
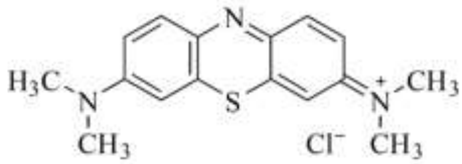
In this study, CCD has been used to optimise the crystal violet (CV) and methylene blue (MB) synthetic wastewater using an adsorption process from HNO_3 pre-treated water hyacinth powder (WHP).

MATERIALS AND METHODS

To prepare the adsorbent, WH was collected from the Tapi river, Near Jahangirpura, Surat, Gujarat, India. It was washed many times with tap water to remove adhering particles and dried in open followed by oven drying at 80□C for 24 hours (till constant weight) followed by grounding and sieving to a particle size of 216 µm. For activation, WHP was kept in 2N HNO_3 for 24 hours with a mixing ratio was 1g of dried WHP with 10 ml 2M NHO_3 (El-Khaiary, 2007). The material passing 216 µm sieve was used for further analysis.

Analytical grade chemicals were used in this study without any purification. The adsorbate was CV and MB dye. The dye name, structure, molecular weight and molecular formula are represented in Table 1. Stock solution (500 mg/L) consists of adding the known amount of dye in deionised water. To get the required concentration for the experiments, the stock solution was further diluted to get the known concentration.

Table 1. Characteristics of CV and MB dyes.

Name of dye	Molecular weight	Structure	Molecular formula
Crystal violet	407.979 g/mol	 Crystal Violet (CV)	$C_{25}H_{30}ClN_3$
Methylene blue	319.85 g/mol		$C_{16}H_{18}ClN_3S$

An adsorption experiment was conducted in a batch system where the removal of CV and MB dye was performed in an Erlenmeyer flask (250 mL) with 100 mL dye solution. The flask was shaken in an orbital shaker at 200 rpm for a specified amount of time. Batch experiments were conducted by varying experimental variables such as pH (2-12), WHP dose (0.5-3 g/L), initial dye concentration (25-200 mg/L) and contact time (10-180 min). The solution pH was adjusted to get the desired value using 0.1M (HCl/NaOH). After mixing for a stipulated time, the supernatant was collected and centrifuged at 5000 rpm for 5 min (Samarbaf et al., 2019). The concentration of CV and MB was measured using UV-VIS Spectrophotometer (Systronics Spectrophotometer 169) at a maximum wavelength of 542 and 665 nm, respectively. The percentage of colour removal efficiency was calculated as:

$$Colour\ removal\ (\%) = (Co - Ce)/Co\ x\ 100 \quad (1)$$

where $Co\ and\ Ce$ are initial and final concentration (MB and CV dye) after the adsorption process in mg/L. Hence, a pre-treated adsorbent was used further, as can be seen in Table 2.

Table 2. Comparison of removal efficiency of dyes using WHP adsorbent with and without pre-treatment.

Sr. no	Treatment	Maximum removal efficiency (%)	
		MB	CV
1	HNO_3 pre-treatment	92.74	98.52
2	Without pre-treatment	82.72	84.26

Experiments were designed using CCD, a subset of RSM for colour removal by WH A total of 30 experiments were calculated, including 16 factorial points, 8 axial points, and 6 replicates at the centre point. RSM is an experimental strategy to find the optimum condition required in a multivariable system, and it is used for developing, improving and optimising the process parameter (Khosravi and Arabi, 2016). It reduces the number of experiments to perform for the interactive effect of multiple input variables. In this study, experiments were designed using CCD, a subset of RSM for colour removal by WHP using four independent variables pH (2-12), WHP dose (0.5-3 g/L), initial dye concentration (25-200 mg/L) and contact time (10-180 min). The number of experiments (*N*) to perform was calculated using the following equation:

$$N = 2^k + 2k + Co \quad (2)$$

Where k = number of input variable and Co = number of central points. The independent variables with range and levels used in the experiment are shown in Table 3. The following polynomial equation was used to evaluate and fit into the second-order polynomial equation:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{i \neq j=1}^{k} \beta_{ij} X_i X_j + \epsilon \quad (3)$$

where, y = the predicted response; xi and xj = the input variables, β_0, βi, βij, *and* βij, = regression constants for intercept, linear, quadratic and interaction coefficients respectively, k = number of variables studied and ϵ = random error.

Table 3. Optimum conditions for CV and MB dyes removal using WHP.

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A: pH	is in range	2	12	1	1	3
B: WHP Dose	is in range	0.5	3	1	1	3
C: Initial Dye Concentration	is in range	25	200	1	1	3
D: Time	is in range	10	180	1	1	3
Colour Removal	maximize	80	100	1	1	3

The sample prepared was characterised to get its true nature in the adsorption process using scanning electron microscope (SEM) (SU7000, Hitachi) and Fourier transform infrared (FT-IR) (FTIR-8400S, Shimadzu) with a range of 4000-400 cm^{-1}.

RESULTS AND DISCUSSION

The morphological study of adsorbent was done using SEM (Huang et al., 2011), and the functional group present on the WH was studied using FTIR. FTIR results help understand the functional group, and SEM helped understand the adsorbent's surface morphology (Lalhruaitluanga et al., 2011). SEM of water hyacinth powder showed porous structure, which increases the adsorbent surface area for dye removal, as shown in Figure 1.

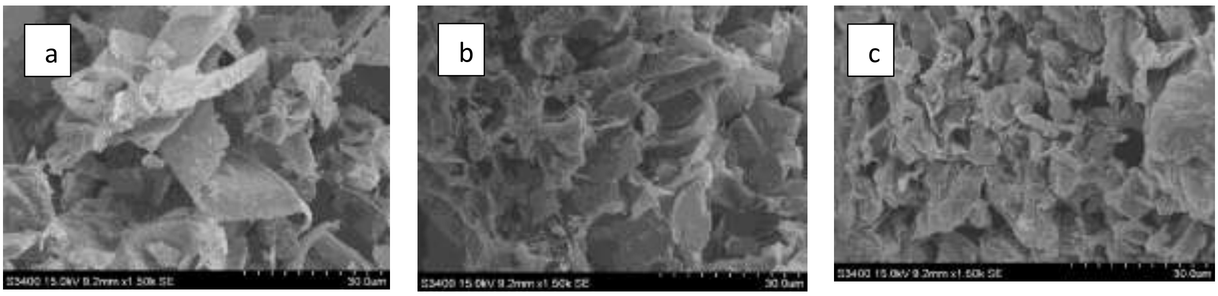


Figure 1. Scanning electron microscope of (a) pre-treated WHP with HNO_3 (b) After adsorption of CV (c) After Adsorption of MB.

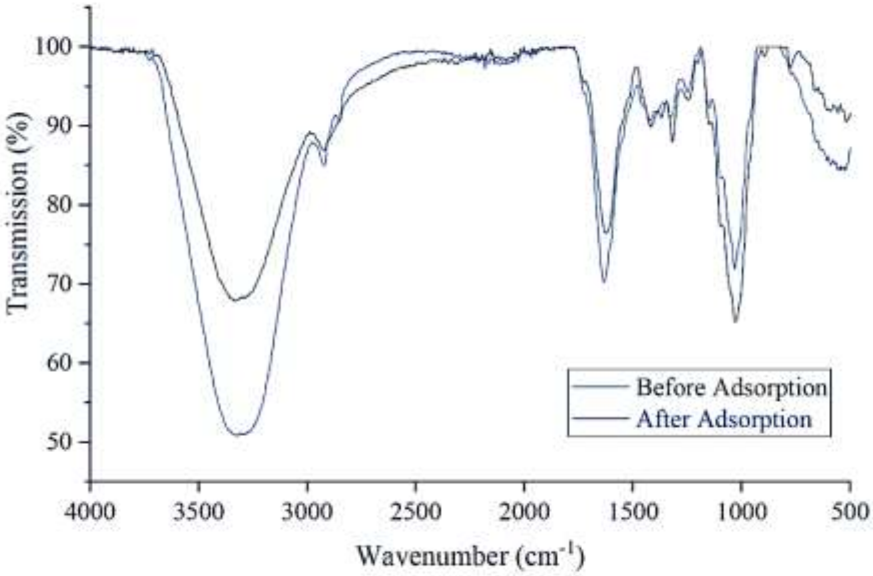


Figure 2. FTIR spectra of WHP before and after adsorption of MB.

FTIR analysis shows a peak at regular interval shows the complex nature of water hyacinth. From Figure 2 it can be seen that the functional group O-H stretching at 3322 cm^{-1} – 2914 cm^{-1}, 1619 cm^{-1} was assigned to C=C conjugated with the carbonyl, peak at 1492 cm^{-1} is due to $–NO_2$ wagging, and 1181 cm^{-1} are due to C–H symmetry for MB dye. A similar shift in the band was observed for CV (Figure not shown). The change in the peaks suggests the dye molecule's interaction with the adsorbent's functional group (Zhou et al., 2007).

Table 4. Experimental and predicted values of CV and MB dye with designed experimentation.

Run	A: pH	B: WHP Dose (mg/L)	C: Initial dye concentration (mg/L)	D: Time	Removal Efficiency (%)			
					CV		MB	
					Experimental	Predicted	Experimental	Predicted
1	2	1.75	112.5	95	77.51	77.78	82.03	80.69
2	2	0.5	200	180	56.75	57.05	66.55	67.25
3	2	3	200	180	87.12	87.31	62.88	62.13
4	2	3	200	10	80.13	80.38	57.06	57.67
5	7	1.75	112.5	10	79.83	80.38	59.50	66.29
6	7	0.5	112.5	95	87.46	88.43	42.90	42.50
7	7	1.75	112.5	95	90.59	88.57	88.31	89.98
8	7	1.75	112.5	95	84.37	88.57	92.74	94.97
9	7	1.75	112.5	180	83.32	84.15	82.22	80.69
10	2	3	25	180	49.54	48.79	81.06	74.12
11	12	3	200	10	87.81	87.57	36.02	35.83
12	2	3	25	10	48.38	48.67	66.76	66.39
13	12	0.5	200	180	88.73	88.24	47.49	45.63
14	7	1.75	112.5	95	86.91	88.57	82.31	80.69
15	7	1.75	25	95	61.40	62.65	62.95	63.30
16	12	0.5	200	10	80.22	80.81	73.82	75.81
17	7	3	112.5	95	86.91	87.32	78.17	79.32

Run	A: pH	B: WHP Dose (mg/L)	C: Initial dye concentration (mg/L)	D: Time	Removal Efficiency (%)			
					CV		MB	
					Experimental	Predicted	Experimental	Predicted
18	7	1.75	112.5	95	98.32	88.57	28.30	38.90
19	2	0.5	25	180	57.73	57.78	91.97	94.49
20	7	1.75	200	95	89.42	89.55	80.37	82.01
21	12	1.75	112.5	95	84.46	85.57	88.62	90.35
22	2	0.5	200	10	40.07	39.47	5.66	2.86
23	12	3	25	180	22.62	23.04	84.02	80.89
24	2	0.5	25	10	47.03	47.01	12.61	12.50
25	12	3	25	10	33.51	33.06	82.86	80.69
26	12	0.5	25	180	66.59	66.17	82.86	80.69
27	12	3	200	180	84.50	84.36	82.86	80.69
28	7	1.75	112.5	95	87.59	88.57	72.77	69.88
29	12	0.5	25	10	65.92	65.54	85.37	85.80
30	7	1.75	112.5	95	87.78	88.57	48.13	46.14

The result obtained experimentally and predicted response obtained in CV and MB removal with four factors are presented in Table 4. The relation between the independent variable and response of second-order polynomial equation for removal of CV and MB dye cab be described as follows:

$$Colour\ Removal\ (MB) = +80.69 + 17.61A + 7.30\,B - 7.58\,C + 7.09\,D - 0.0741\,AB + 8.43\,AC - 1.30\,AD + 9.16\,BC + 0.0394\,BD - 3.52CD - 24.18A^2 - 7.10B^2 + 6.21C^2 + 2.20D^2 \quad (4)$$

$$Colour\ Removal\ (CV) = +88.57 + 3.89A - 0.5557\,B + 13.45\,C + 1.89\,D - 8.54\,AB + 5.70\,AC - 2.53\,AD + 9.81\,BC - 2.66\,BD + 1.70\,CD - 6.90\,A^2 + 0.6941\,B^2 - 12.47\,C^2 - 6.31\,D^2 \quad (5)$$

The coefficient with one factor, two factors, and second-order term represents the effect of the particular factor, the interaction between the two factors and quadratic effect, respectively, on the colour removal. The ANOVA results for equation 4 and 5 are shown in Table 5. The value of *P* less than 0.05 was chosen as criteria, and the result shows that it is statically significant of a variable of an effect at a 95% confidence level. The result indicates that the regression model has a high value of determination (R^2 = 0.988 and R^2 = 0.9815) for CV and MB. This indicates that the variability of the 98.8% and 98.15% of the total variation for removal of CV and MV in the model is due to the experimental variables (Garba and Rahim, 2014). The adequate model should have R^2 value not less than 0.75 (Le Man et al., 2010). Thus, the model is feasible for the range of experimental variables. Rai et al. (2016) reported that if R^2 Adj. and pred. lies within the range of 20% then the model is in good agreement. Model terms are significant when the value of *F* is large and $P < 0.05$. The ANOVA regression model also indicates that the model is highly significant with the calculated F value (10.96 and 56.74 for CV and MB, respectively) low probability value, as shown in Table 6. All linear terms are significant, and from interaction AB, AD, and BC and quadratic term D^2 are not significant for MB i.e., these terms of MB have no compelling effect on the removal efficiency. For CV, all the terms were significant. From the above statistical result, models were suitable for predicting both CV and MB removal in the range of this study.

Table 5. ANOVA result for CV and MB dye removal result obtained from RSM.

Source	Degree of freedom	CV			MB		
		Sum of square	F-value	P-value	Sum of square	F-value	P-value
Model	14	11188.41	10.96	< 0.0001 significant	15258.70	56.74	< 0.0001 significant
Residual	15	128.72			288.12		
Lack of fit	10	10.40			287.41		
Pure error	5	118.33			0.7156		

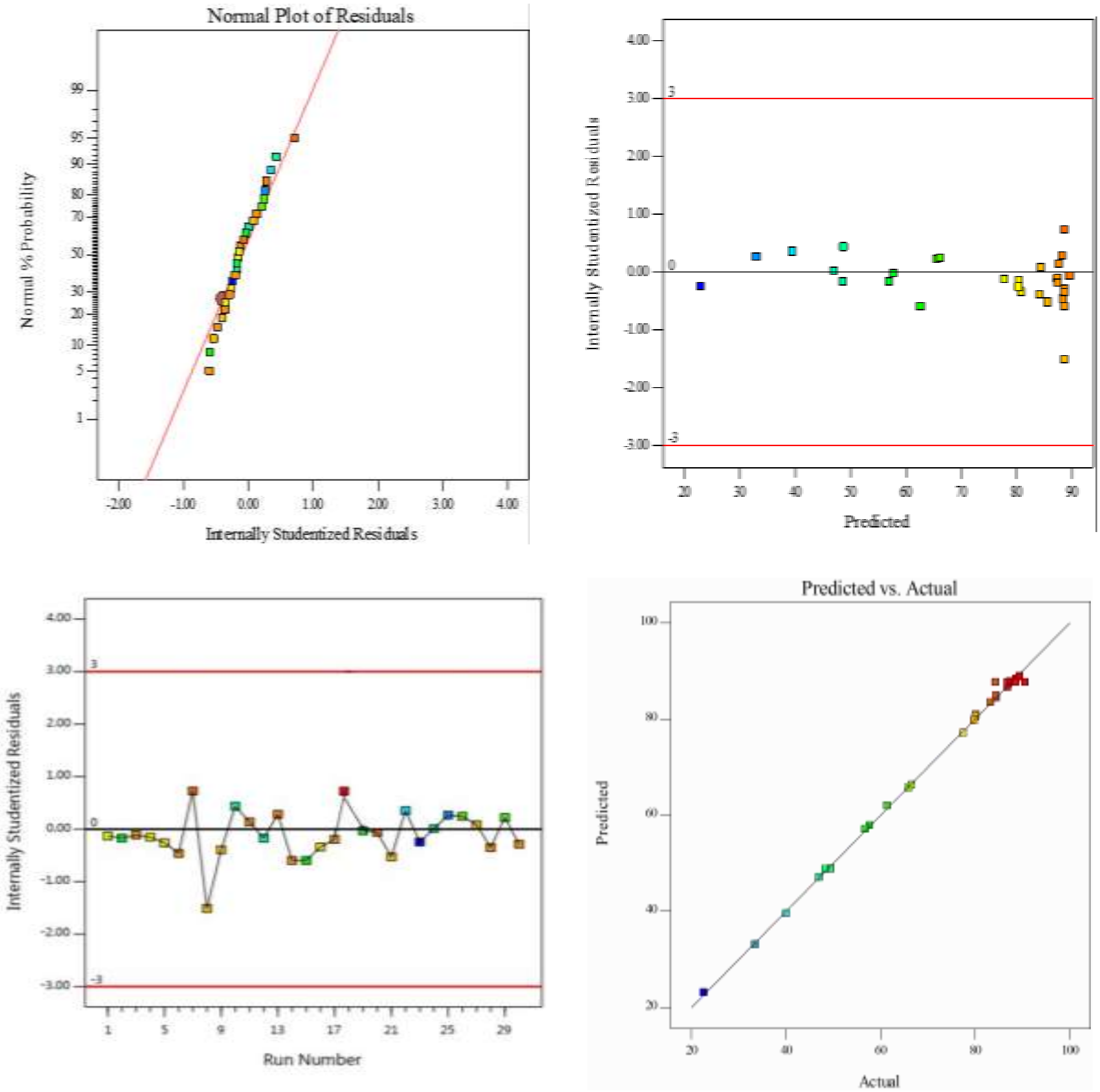
CV: $R^2 = 0.988$; Adjusted $R^2 = 0.978$; Predicted $R^2 = 0.9833$; A P = 32.1087
MB: $R^2 = 0.9815$; Adjusted $R^2 = 0.9642$; Predicted $R^2 = 0.9222$; A P = 29.72

Table 6. Analysis of variance (ANOVA) for response surface quadratic model on adsorption of CV and MB.

Source	Sum of Squares		df		Mean Square		F-value		p-value	
	CV	MB	CV	MB	CV	MB	CV	MB	CV	MB
Model	15391.09	15258.70	14	14	1099.36	1089.91	9171.00	56.74	< 0.0001	< 0.0001
A	3189.42	5581.10	1	1	3189.42	5581.10	26606.49	290.56	< 0.0001	< 0.0001
B	171.34	958.61	1	1	171.34	958.61	1429.34	49.91	< 0.0001	< 0.0001
C	5116.74	1035.35	1	1	5116.74	1035.35	42684.38	53.90	< 0.0001	< 0.0001
D	3.18	904.36	1	1	3.18	904.36	26.53	47.08	0.0001	< 0.0001
AB	1475.40	0.0879	1	1	1475.40	0.0879	12307.98	0.0046	< 0.0001	0.9470
AC	68.42	1136.30	1	1	68.42	1136.30	570.75	59.16	< 0.0001	< 0.0001
AD	81.71	26.88	1	1	81.71	26.88	681.65	1.40	< 0.0001	0.2552
BC	936.42	1341.46	1	1	936.42	1341.46	7811.72	69.84	< 0.0001	< 0.0001
BD	9.93	0.0248	1	1	9.93	0.0248	82.83	0.0013	< 0.0001	0.9718
CD	246.88	198.64	1	1	246.88	198.64	2059.52	10.34	< 0.0001	0.0058
A^2	325.48	1514.81	1	1	325.48	1514.81	2715.15	78.86	< 0.0001	< 0.0001
B^2	42.52	130.60	1	1	42.52	130.60	354.71	6.80	< 0.0001	0.0198
C^2	114.98	99.94	1	1	114.98	99.94	959.15	5.20	< 0.0001	0.0376
D^2	56.37	12.57	1	1	56.37	12.57	470.28	0.6544	< 0.0001	0.4312
Residual	1.80	288.12	15	15	0.1199	19.21				

df = degree of freedom

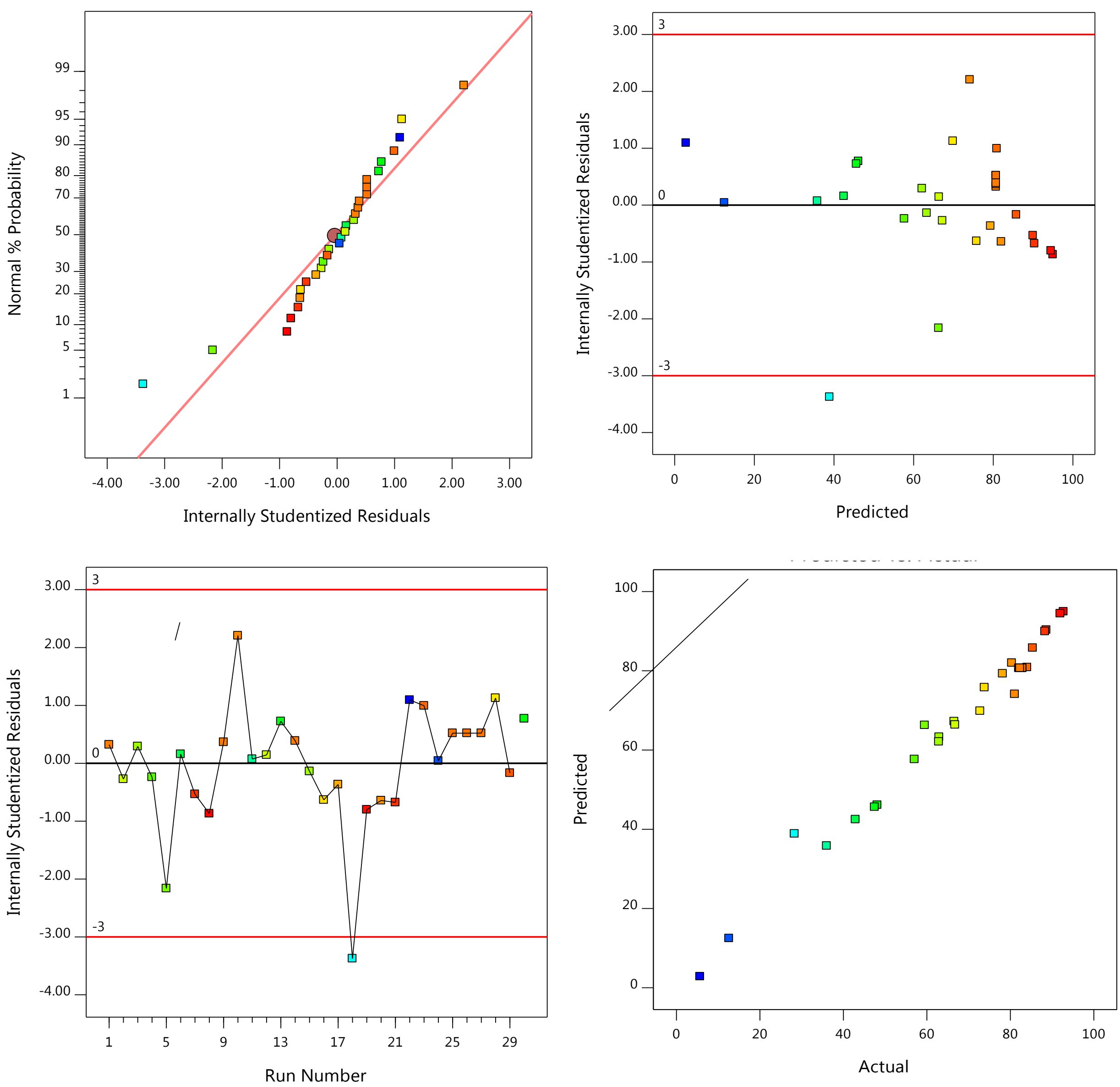
The significance of the model was also evaluated through the residuals. The predicted and experimental values show a good correlation implying that the developed model successfully apprehended the relation between the adsorption process and its interaction between the process variables for dye removal, as shown in Figure 3 and 4 the experimental values are obtained from experimentation and the predicted values are obtained from the regression models of equation 4 and 5. Thus the developed model (for CV and MB) can relate the responses and the significant variables.



y = 0.9886x + 0.8275

R^2 = 0.9886

Figure 3. Statistical analysis and residual plots for CV removal.



y = 0.9815x + 1.2412
$R^2 = 0.9815$

Figure 4. Statistical analysis and residual plots for MB removal.

Adequate Precision is the measure of the signal to the noise ratio. The desirable limit is greater than 4. In this analysis, a ratio of 298.31 and 29.72 for CV and MB removal was obtained, indicating that the model can navigate the designed space.

The surface and contour plots for the combined effect of adsorbent dose and solution pH play a vital role in the percentage removal efficiency of colour onto the adsorbent's surface. As illustrated in Figure 5, the contour and surface plots of the solution pH and WHP dose effect on the removal efficiency at the initial dye concentration of 112.5 mg/L and 90 min contact time. The pH affects the adsorption process by altering the adsorbent surface charge. It shows the relation between the H^+ ions and adsorbate ions onto the adsorbent surface's active site (Chowdhury and Saha, 2010). The adsorbent dose has a direct relationship with CV and MB dye removal. With an increase in adsorbent dose from 0.5 to 1.75 and pH from 2 to 7 the removal increases to 98.32% for CV dye at initial dye concentration 112.5 mg/L and time of contact 95 min. The removal was increased until pH 7, and after that, it does not increase. The maximum adsorption of CV occurred in the pH range of 6-7. For MB, the removal rises to 92.74% for an initial dye concentration of 200 mg/L, pH 12, WHP dose 3 mg/L and time of contact 180 min. It is a basic dye that imparts positive ions when dissolved in water. When the aqueous solution's pH is increased, the surface becomes negatively charged, resulting in increased removal efficiency due to an increase in an electrostatic attraction between the positive dye and negatively charged adsorbent (Pathania et al., 2017). For both CV and MB, as the adsorbent dose increases, the surface area increases, hence removing efficiency increases.

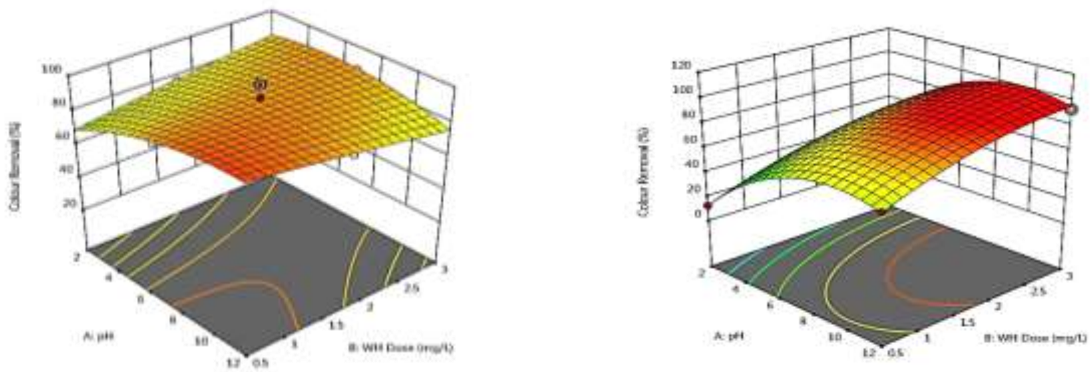


Figure 5. Surface plots of CV and MB removal through WHP as a function of pH and adsorbent dosage.

The combined effect of pH of the solution and contact time with initial dye concentration 112.5 mg/L, 200 mg/l and the adsorbent dose of 1.75 g/L, 3g/L is shown in Figure 6 for CV and MB, respectively. The contact time is vital for the removal efficiency of the batch process system. As the dose increases, the removal efficiency increases with contact time variation of 95 min and 180 min for CV and MB removal, respectively, and after that reduces within the experimental range. The adsorption pH dependence can be explained in terms of the pH of the solution and pH_{ZPC} of the adsorbent. At $pH < pH_{ZPC}$, a relatively low number of the negatively charged site is present, not favouring the adsorption. As the negatively charged site increases, adsorption is favourable with a maximum adsorption at pH of 7-8 and 11-12 for CV and MB dyes. It is attributed to the presence of functional groups onto the surface of WHP.

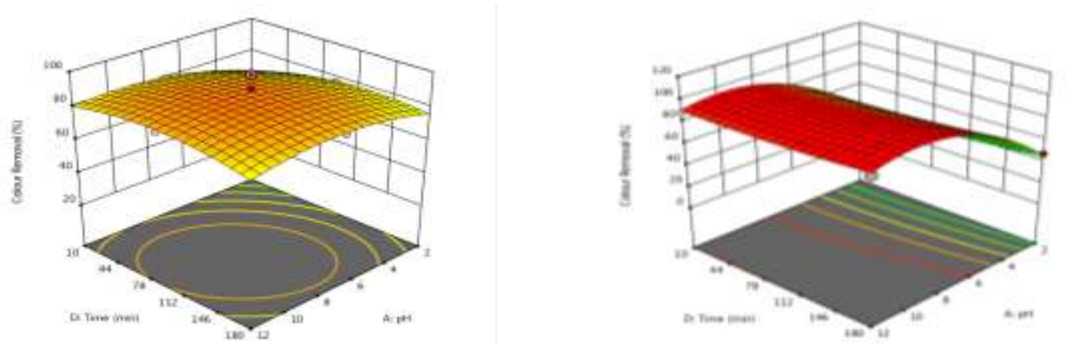


Figure 6. Surface plots of CV and MB removal through WHP as a function of pH and contact time.

The combined effect of pH and initial dye concentration at 1.75 mg/L adsorbent dose and 95 min contact time for CV and 3 mg/L adsorbent dose and 180 min contact time for MB is shown in Figure 7. At a lower dose, the removal efficiency reduces with an increase in concentration and removal efficiency increases with an increase in dose. As the initial dye concentration and dose increases, the adsorption increases due to increased adsorption sites and surface area. After that, adsorption reduces due to the saturation of available adsorption sites. This may be because at a lower dose, increasing dye concentration after saturation, the number of available binding sites is limited and leads to a decline in removal efficiency. As dose increases, an increase in the active binding sites results in increased removal efficiency with an increase in dye concentration. A similar pattern was observed for both dyes.

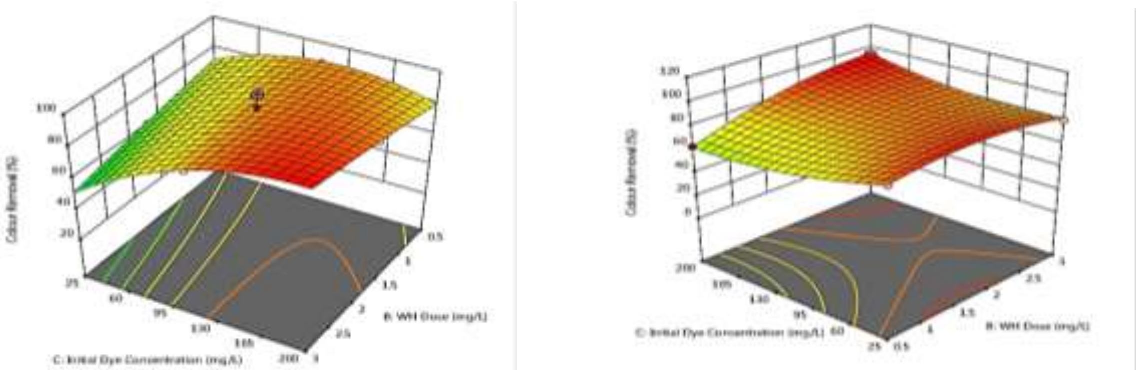


Figure 7. Surface plots of CV and MB removal through WHP as a function of dose and initial dye concentration.

As the dose increases, with time, the removal also increases initially and after that decreases for both dyes CV and MB, as shown in Figure 8. It can be attributed to increasing dose increases the adsorption site resulting in increased adsorption rate resulting in higher efficiency initially, and it reduces with time (Prasad et al., 2021). For CV adsorbent dose of 1.75 mg/L and contact time 95 min, maximum removal of 98.32% and for MB adsorbent dose of 3 g/L and contact time 180 min removal of 92.74% was obtained.

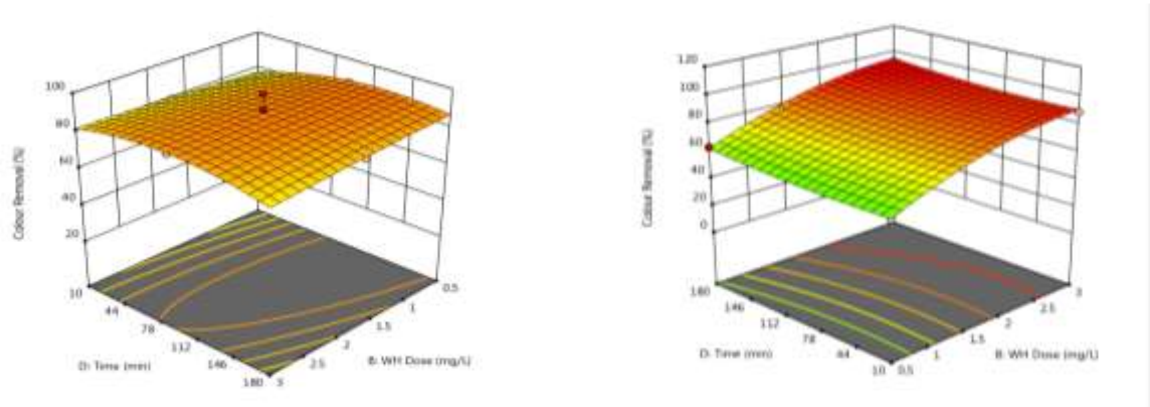


Figure 8. Interactive influence of contact time and adsorbent dose on the dye removal from color wastewater

The effect of initial dye concentration and contact time for removing CV and MB at PH of 7 and 12 for CV and MB and the adsorbent dose of 1.75 and 3 mg/L is shown in Figure 9. The removal efficiency increased initially then decreases with an increase in the dye concentration. This is due to the shortage of available surface area with an increase in dye concentration. Similar results were reported by Bulut and Aydin (2016) for MB removal using wheat shells.

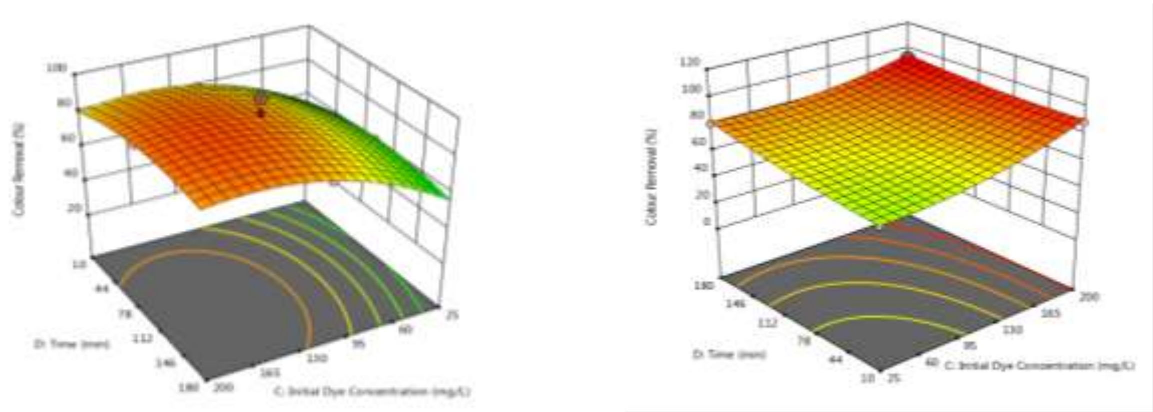


Figure 9. Surface plots of CV and MB removal through WHP as a function of initial dye concentration and contact time.

The optimisation of CV and MB removal was done to determine the optimal condition required to remove CV and MB showing maximum response towards colour removal. The desirability criteria were set from 0.0-1.0 to determine the optimum condition required for maximum response. The value closer to 1.0 gives an optimised condition with the maximum response (Vaez et al., 2012).

The goal was set "in range" for each variable parameter with the lower and upper limit as per the design. The goal for colour removal response was set as "maximise" and the equal importance of '3' was given to all four parameters and responses as shown in Table 3. The optimum condition obtained was pH = 7.219, WHP dose =3.0 g/L, initial dye concentration = 195.308 mg/L and time = 99.92 min with colour removal = 98.203% for CV. pH = 8.66, WHP dose = 2.14 g/L, initial dye concentration = 49.86 mg/L and time = 169.36 min with colour removal of = 99.73% for MB. To validate the optimal condition for maximising the result, experiments were carried out in duplicate under these conditions, and 97.89 % and 98.23 % removal efficiency was achieved for CV and MB, respectively.

SEM image showed a porous structure on the water hyacinth surface after adsorption of dye got occupied, indicating the adsorption process. For CV, pH affects the adsorption process of ionic adsorbates and influences the dye structure, thereby interacting with the water hyacinth (Hou et al., 2011). The increase in removal capacity can be due to a reduction in H^+ ions competing with cationic dye at a low pH value for the appropriate site on the water hyacinth surface (Chowdhury and Saha, 2010) reduces with an increase in pH. The result shows that a substantial amount of dye could be removed using adsorbent at neutral pH (7.219 for CV and 8.66 for MB). Similar results have been reported for CV by Sarma et al. (2016); Khan et al. (2015) and Basaleh et al. (2019) for MB. The adsorbent dose played a significant role in percentage colour removal. The experimental result showed that both dyes were favourably adsorbent on the adsorbent due to the hydroxyl group's presence on the adsorbent, which was confirmed from the FTIR results. Beyond a dose of 3 g and 2.14 g for CV and MB, no further increase in the removal was observed, which may be due to the unavailability of adsorbent sites (Tharaneedhar et al., 2017). Similar results were observed by Basaleh et al. (2019) for MB removal using polyamide-vermiculite nanocomposites. The effect of contact time and dye concentration results was similar to the results (Chowdhury et al., 2013; Fernandes et al., 2007; Kushwaha et al., 2014).

The effect of the initial operating parameter and their interactions were assessed, and from ANOVA results, it was observed that for CV all influential parameter and their interaction contributed to the removal efficiency as $p < 0.0001$. The p-value less than 0.05 indicated significance of the model. For MB, the interaction between AB, AD, DB, B^2, C^2, and D^2 had the least effect on the removal efficiency with p >0.0001. If the p-value greater than 0.10, the model terms are insignificant (Kumari and Gupta, 2019). The model was significant with R^2 = 0.988 and 0.9815 for CV and MB. The experimental result obtained by optimisation value confirms the success of this model for dye removal.

CONCLUSIONS

This study was aimed to optimise the CV and MB dye removal from variable input parameter of pH, WHP dose, initial dye concentration and time. The effect of different parameters and their interaction were studied for increasing the removal efficiency of both dyes. The removal efficiency was determined using the second-order polynomial equation. The optimal condition for removal was obtained as pH of 7 and 12, initial dye concentration 112.5 mg/L 200 mg/L, WHP dose75 mg/L, 3mg/L and contact time of 95 min., and 180 min. for removal of CV and MB respectively onto WHP. The result showed that the WHP pre-treated with nitric acid proved better dye removal efficiency with maximum removal of 98.23% and 92.74% with a coefficient of correlation (R^2) of 0.988 and 0.981 for CV and MB, respectively. The removal of CV was significantly higher than MB for all the experimental sets. Finally, the reported result shows the suitability of response surface methodology for optimising dye removal in the operating conditions for maximising the removal efficiency onto the WHP.

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CONFLICT OF INTEREST
The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING
No life science threat was practiced in this research.

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