Process optimisation of methylene blue sequestration onto physical and chemical treated coffee husk based adsorbent

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Abstract

Coffee husk (CH) was physically and chemically treated with autoclaving (SCH) and NaOH (NCH) to develop low-cost adsorbent for the removal of methylene blue (MB) from synthetic wastewater, and their adsorption efficiencies were evaluated in batch mode. The prepared adsorbent was characterised by SEM, FTIR and point of zero charge. The central composite rotatable design (CCRD) was employed to optimise the adsorption process parameters such as pH, adsorbent dosage and initial MB concentration. The second-order quadratic model fitted best with the experimental adsorption data, and ANOVA results showed that the developed model was significant. The linear terms in the model significantly influence the adsorption capacity of SCH and NCH, but interaction terms were not significant. At optimised conditions, the developed adsorbents can remove > 90% of MB from the aqueous solution. Freundlich model showed a better fit with the adsorption isotherm data with R^2 greater than 0.95. Kinetics of MB adsorption onto SCH and NCH followed the pseudo-second-order model. The maximum monolayer adsorption capacity was found to be 129 and 200 mg/g for SCH and NCH, respectively. The present study showed that pretreated coffee husk waste can be used as an alternative for expensive adsorbents for the removal of dyes from wastewater.

Keywords Coffee husk · Pretreatment · Methylene blue · Adsorption · Optimisation

1 Introduction

Dyes are mostly organic molecules that can attach themselves to fabrics or surfaces to impart colour. Synthetic dyes are largely used in many sectors of advanced technology, such as in the textile, paper, plastics, food processing, leather tanning, printing, rubber and cosmetics industries [1, 2]. Annually around 7×10^5 tons of commercial synthetic dyes is produced worldwide and the textile industry alone consumes more than 10,000 tons of dyes. Approximately 10–15% of the total dyestuff is utilised

or released into the natural environment aesthetically unfavourable, and these recalcitrant and coloured dye molecules are not so easy to degrade biologically and are resistant to degrade on exposure to water, to light and also to various chemicals [3, 4]. Due to the toxic, carcinogenic, mutagenic and allergic nature of dyes, the direct discharge of untreated dye effluent can cause hazardous effects on living systems [5]. Several physicochemical and biological methods such as ozonation, chemical coagulation, chemical and electrochemical oxidation, photocatalysis, adsorption, and aerobic and anaerobic digestion are widely used

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for removal of dyes from wastewater [3, 6, 7]. Among these methods, adsorption has emerged as an effective and economical alternative due to its ease of operation, simplicity of design, insensitivity to toxic substances and complete amputation of pollutants rather than getting degraded to hazardous intermediates [8, 9]. The high cost and difficulty in regeneration are still concerned with the use of activated carbon, and it has motivated the research community to develop efficient and cost-effective alternative adsorbents for removal of dyes [5].

In recent days, agricultural industry by-products have attracted the research community in the field of the adsorption separation process for the removal of pollutants from the wastewater and key focus is because of the widespread availability of agricultural and allied industry residues. These adsorbents are biodegradable in nature and make it eco-friendly and also reduce the secondary pollution caused due to the disposal of adsorbent [10, 11]. Agricultural by-products are renewable in nature and available in bulk amount, and they are less expensive compared to other commercial adsorbents [12]. Agricultural waste such as coir pith, orange peel, banana peel, rice husk, straw, date pit, oil palm trunk fibre, durian peel, almond shell, pomelo peel, broad bean peel, peanut hull, *Citrullus lanatus* rind and coffee waste is widely studied in adsorption of dyes in their native and modified forms [10, 13–15]. These waste materials contain biopolymers and act as attractive alternative adsorbents due to their physicochemical characteristics, chemical stability and high reactivity towards water-soluble pollutants. These biopolymers also possess various functional groups such as alcohols, aldehydes, ketones, carboxylic, phenolic and ether that help in the removal of a wide range of pollutants [16].

Besides these advantages, agro-waste also possesses some disadvantages such as releasing soluble organic components present in biomass such as lignin, tannin, pectin and cellulose into the effluent stream and increases the biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) and depletes oxygen content in the aquatic environment [17]. And also direct utilisation of biomass as adsorbent is many a time uneconomical due to low adsorption capacity and efficiency. These problems can be overcome by modifying or pretreating the biomass before employing in adsorption studies [18]. Physical and chemical treatments are generally used to improve the adsorption capacity by modifying the surface characteristics [19]. Physical pretreatment methods involve heating, autoclaving, freeze-drying and boiling [20]. Chemical treatment majorly uses chemicals that includes solutions of alkali (Na_2CO_3 , NaOH , $\text{Ca}(\text{OH})_2$), mineral acid solutions (HCl , HNO_3 , H_2SO_4 , tartaric acid, citric acid and formic acid), organic compounds

(formaldehyde, CH_3OH , and epichlorohydrin) and oxidising agents (H_2O_2 , K_2MnO_4 and propylene oxide) [21, 22].

The physical modification of biomass removes impurities, organic and mineral contents from the surface of agro-waste [23–25]. Autoclaving is one of the physical treatment techniques used by many researchers to improve the adsorption properties of various biological materials such as fungi, algae and agricultural waste. Cells in the biomass subjected to autoclaving undergo rupture and denaturation and increase the surface area and porosity of the biomass and expose the hidden or embedded functional sites to the pollutants [26–28]. Among various chemical treatments, alkali pretreatment is widely used for surface modifications of agricultural waste to improve the adsorption efficiency and capacity. Alkali such as NaOH breaks down the covalent bond between components of lignocellulose by hemicellulose hydrolysis and lignin depolymerisation. This influences significantly on the molecular, supramolecular and morphological properties of cellulose matrix [29, 30]. It will also influence the changes in crystallinity, pore architecture, accessibility, stiffness, unit cell structure and orientation of fibrils cellulosic fibres. NaOH treatment also eliminates the impurities such as natural fats, waxes and other low molecular weight compounds from the biomass and reveals the active functional groups which are easily accessible for pollutant adsorption [31, 32]. NaOH also improves the mechanical and chemical properties such as reactivity, durability and ion exchange capacity of natural material [33].

This study aimed at comparison of physical (autoclaving) and chemical treatment (NaOH) of coffee husk on adsorption efficiency of methylene blue. The influence of process parameters such as pH, adsorbent dose, initial dye concentration on MB adsorption capacity of SCH and NCH were optimised using response surface methodology.

2 Materials and methods

2.1 Materials

Coffee husk biomass was collected from coffee curing works located in Hassan, India. Analytical-grade sodium hydroxide, hydrochloric acid, sodium chloride, methylene blue (molecular formula - $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, molecular weight – 319.85 g/mol and λ_{max} – 664 nm) were procured from S D Fine-Chem Limited, India. Double distilled water was used throughout the studies.

2.2 Preparation of adsorbent

The coffee husk biomass was manually cleaned to remove foreign material and dried at 40 °C for 24 h to remove

moisture. The dried biomass was ground in domestic blender to obtain approximately uniform-sized particles of < 400 µm. Physically treated biomass was prepared by an autoclaving mixture of coffee husk and double distilled water in the ratio of 1:10 for 1 h at 121 °C and 15 Psi pressure. Chemically treated biomass was prepared by treating coffee husk with 2% NaOH (coffee husk: 2% NaOH = 1:10 ratio) at 30 °C for 2 h. Both the adsorbents were washed repeatedly with double distilled water till the washed solutions turn colourless. The washed adsorbent was dried at 80 °C and ground to obtain uniform-sized particles. The autoclaved and NaOH-treated coffee husk biomass was named as SCH and NCH, respectively.

2.3 Instrumentation

The Shimadzu UV-1800 double-beam UV-visible spectrophotometer was employed to determine the concentrations of methylene blue in the aqueous phase. SYSTRON-ICS pH meter (µC pH System 361) was used to measure pH. Tescan-Mira-3 LMH field emission scanning electron microscope (FESEM) was used to study the morphological characteristics of SCH and NCH. The functional groups present before and after adsorption on adsorbents are examined using Thermo NicoletAvatar-370 Fourier transform infrared spectrometer (FTIR) in the range of 4000–400 cm⁻¹. The point of zero charge of the adsorbent was determined by solid addition method described elsewhere [34].

2.4 Design of experiments

Conventional one factor/variable at a time (OFAT/OVAT) optimisation approach that involves studying the effect of one factor keeping other factors constant is time-consuming and also not economical. OFAT methods of identifying optimum conditions require a larger number of experiments, and it ignores the interaction effect of parameters involved in the adsorption of dyes [35]. To overcome these problems, many researches are employing response surface methodology (RSM) to optimise the adsorption process. RSM is a combined statistical and mathematical method that uses the polynomial equation to study the relationship between the numerous independent parameters and also one or more responses [36]. Compared to conventional optimisation technique, RSM reduces the time and cost involved [37]. The most popular design strategy, central composite rotatable designs (CCRD), was employed in the present study to optimise the process parameters such as adsorbent dosage, initial dye concentration, pH and their interaction in adsorption of methylene blue onto physically (SCH) and chemically treated (NCH) coffee husk. The other parameters such as time, temperature and agitation speed were kept constant. The

dye removal efficiency (%) was considered as the response variable which is dependent on the selected independent variables and used to develop an empirical model.

The design of experiments for the adsorption study was constructed through Design-Expert V10 statistical software package to investigate the effect of different parameters and determine the best mathematical model. The range of parameters is chosen based on the preliminary studies done in the laboratory. CCRD comprises of three operations, viz. 2ⁿ factorial runs, 2n axial runs and n_C centre runs [38]. A total number of runs can be calculated from Eq. 1:

$$N = 2^n + 2n + n_c \quad (1)$$

where N represents the total number of experimental runs, n indicates the number of independent variables and n_C indicates the centre points. Based on this equation, CCRD matrix is obtained from the Design-Expert; a total of 17 experiments consist of eight factorial, six axial and three centres or replicate points for three independent variables. The coded values of independent variables as -1 and +1 represent eight factorial points at their lower and higher levels, respectively [39]. The six axial or outer points located at -1.68 (-α) and +1.68 (α) and 0 represent the centre points used to examine the error in experimentation and to confirm the reproducibility of obtained data. The value of α characterise the distance of an axial point from the centre which makes the design rotatable and value of 1.68 is obtained from Eq. 2:

$$\alpha = [2^n]^{1/4} \quad (2)$$

where 2n indicates the factorial runs [40]. The codes, range and level for three independent variables for SCH and NCH adsorbent are presented in Table 1, and CCRD design matrix for SCH and NCH adsorbent is given in Tables 2 and 3.

2.5 Batch adsorption studies

The adsorption of methylene blue onto SCH and NCH adsorbent was studied in batch mode. Adsorption experiments were carried out using a known concentration of 50 ml methylene blue solution in a 250-ml conical flask and agitated mechanically at 150 rpm in an incubating shaker at a constant temperature (30 °C). Based on the CCRD design matrix provided in Tables 2 and 3, the adsorption experiments were conducted, and after required incubation time, the solution was centrifuged at 10,000 rpm. The residual dye concentration in the supernatant was measured at 664 nm using

Table 1 Independent variables and their levels in the CCRD for MB adsorption onto SCH and NCH

Variables	SCH					NCH				
	Range and level					Range and level				
	−α (−1.68)	1	0	1	α (1.68)	−α (−1.68)	1	0	1	α (1.68)
pH	2	3.62	6	8.38	10	2	3.62	6	8.38	10
Initial dye concentration, mg/L	20	36.22	60	83.78	100	25	50.34	87.50	124.66	150
Adsorbent dosage, g/L	0.2	0.36	0.60	0.84	1.0	0.1	0.18	0.30	0.42	0.5

Table 2 CCRD matrix and experimental and predicted dye removal efficiencies of SCH

Run	Factor 1 A: pH	Factor 2 B: Initial dye concentration, mg/L	Factor 3 C: SCH dosage, g/L	Dye removal efficiency (%)		
				Experimental	Predicted	Relative error (%)
1	10.00	60.00	0.60	87.25	83.39	4.42
2	6.00	60.00	1.00	75.66	74.06	2.12
3	8.38	83.78	0.36	48.21	49.27	2.20
4	3.62	83.78	0.36	22.03	18.17	17.54
5	6.00	60.00	0.60	71.75	69.91	2.55
6	6.00	100.00	0.60	45.23	48.35	6.90
7	3.62	83.78	0.84	43.64	42.81	1.92
8	2.00	60.00	0.60	18.64	20.85	11.85
9	6.00	60.00	0.60	65.58	69.91	6.61
10	8.38	83.78	0.84	76.38	75.71	0.87
11	3.62	36.22	0.84	55.91	56.01	0.19
12	8.38	36.22	0.84	94.25	99.28	5.34
13	6.00	60.00	0.60	72.13	69.91	3.08
14	6.00	60.00	0.20	37.29	37.24	0.12
15	3.62	36.22	0.36	36.85	38.67	4.95
16	8.38	36.22	0.36	78.14	80.14	2.56
17	6.00	20.00	0.60	90.18	85.41	5.29

UV-VIS spectrophotometer. The dye removal efficiency and adsorption capacity were calculated using Eqs. 3–5 [1, 41].

$$\text{DRE} = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (4)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (5)$$

where C_0 , C_t or C_e are the initial and final concentration (mg/L) of MB dye in the solution. q_t and q_e are the adsorption capacities at time t or equilibrium time.

3 Results and discussion

3.1 Characterisation of adsorbent

3.1.1 SEM analysis

Morphological structures of raw (RCH), autoclaved (SCH) and sodium hydroxide-treated (NCH) coffee husk are illustrated in Fig. 1. These SEM micrographs provide useful information on the effect of pretreatment on the surface morphology of coffee husk. According to Fig. 1a, the surface of raw coffee husk is smooth and compact. Raw biomass has a comparatively less irregular structure including the pores. This nature of the surface might be due to adhesion of impurities and made the pores on the biomass smaller and blocked. However, from Fig. 1b it is

Table 3 CCRD matrix and experimental and predicted dye removal efficiencies of NCH

Run	Factor 1 A: pH	Factor 2 B: Initial dye concentration, mg/L	Factor 3 C: NCH dose, g/L	Dye removal efficiency (%)		
				Experimental	Predicted	Relative error (%)
1	6	87.5	0.3	78.5	72.74	7.34
2	6	25	0.3	79.03	68.8	12.91
3	3.62	50.34	0.42	48.31	50.57	4.68
4	8.38	124.66	0.42	74.13	70.22	5.27
5	6	87.5	0.3	69.97	72.74	3.96
6	3.62	124.66	0.18	17.08	15.33	10.27
7	3.62	50.34	0.18	13.22	23.1	74.79
8	3.62	124.66	0.42	29	32.84	13.27
9	6	150	0.3	37.08	38.82	4.72
10	10	87.5	0.3	74.68	71.81	3.84
11	8.38	124.66	0.18	44	47.72	8.45
12	6	87.5	0.5	87.18	84.16	3.47
13	6	87.5	0.1	47.58	42.15	11.42
14	2	87.5	0.3	10.16	4.57	54.98
15	8.38	50.34	0.18	63.55	65.68	3.35
16	6	87.5	0.3	71.14	72.74	2.26
17	8.38	50.34	0.42	90.39	98.12	8.55

evident that there is no obvious distinction between the morphology of RCH and SCH. Compared to RCH and SCH, the NCH (Fig. 1c) surface was highly rough and changed to porous structure with cavities, ridges and varied heterogeneous pores. This attribute is due to the removal of impurities present and disintegration of polymers present in the coffee husk biomass. The NaOH treatment induces the cracking in the biomass and increases the roughness. The removal of water-soluble compounds also contributes to an increase in surface roughness and porosity. This heterogeneous nature of adsorbent provides more surface area with high chances of dyes trapped and adsorbed on the surface [30, 33, 42].

3.1.2 FTIR analysis

The FTIR spectra of raw coffee husk biomass are presented in Fig. 2. The peaks close to 3410 cm^{-1} and 1052 cm^{-1} represent the stretching vibrations of -O-H and C-O-C present in cellulose and lignin in the coffee husk. The well-defined peaks at 2928 and 1376 cm^{-1} are the characteristic peaks for C-H bond stretching and bending vibrations, respectively. The peaks located at 1746 and 1628 cm^{-1} are attributed to stretching vibrations of aldehydes and ketones, and peak at 1429 cm^{-1} can be assigned to carboxyl group C-O bond stretching vibration. Peaks at 1248 and 1437 cm^{-1} correspond to C-N stretching vibration of the amine group and O-H bending vibration of the carboxylic group, respectively [43–48].

FTIR spectra of SCH are illustrated in Fig. 3. Most of the peaks present in the raw CH spectra are also present in the SCH spectra, but with the reduced intensities. It shows that treatment has removed the leachables from the biomass and exposed the buried residues present in the biomass due to autoclaving of biomass. Various functional groups present on the SCH biomass have facilitated the adsorption of MB. The MB-adsorbed SCH FTIR spectra given in Fig. 3 show a distinct peak at 1330 and 1384 cm^{-1} which indicates the presence of -C-N bonds of aromatic amines attributed to adsorption of MB on SCH. Also, the increase in peak intensity at 1597 cm^{-1} after adsorption indicates an increase in the number of -C=C bonds due to cyclic alkene probably due to adsorption of MB [49, 50].

FTIR spectra of sodium hydroxide-treated coffee husk biomass are given in Fig. 4, and there is a significant change in the spectra of raw and NaOH-treated coffee husk biomass. The disappearance of peak at 1746 cm^{-1} attributes uronic ester groups and indicates the substantial reduction in lignin and hemicellulose content in the coffee husk biomass [51, 52]. Some of the new peaks in the spectra of NCH clarify the modification of raw coffee husk. From Fig. 4, peak 1328 cm^{-1} indicates the -C-N bonds of the methylene blue aromatic amine and clarifies the adsorption.

Fig. 1 SEM micrographs of **a** raw coffee husk, **b** SCH, **c** NCH

Fig. 2 FTIR spectrum of raw coffee husk

Fig. 3 FTIR spectra of SCH and MB-adsorbed SCH

Fig. 4 FTIR spectra of NCH and MB-adsorbed NCH

3.2 Optimisation of process parameters

3.2.1 Development of the regression model

In the CCRD, three independent parameters, viz. pH, initial MB concentration and adsorbent dosage, were prescribed into five levels and were selected for each of the experiments. The experimental design suggested by Design-Expert V10 software along with actual and predicted dye removal efficiency for SCH and NCH adsorbent is presented in Tables 2 and 3. Analysis tools available in the Design-Expert were employed to analyse the experimental data and fitted to the polynomial models which explains the effect of linear, two-factor interaction and quadratic over the responses. The best model is selected according to the significant model p value, insignificant lack of fit value and maximum values of adjusted and predicted R^2 values [53, 54]. The model fit summary given in Tables S1 and S2 shows the results of statistical analysis of the selected models at the confidence level of 95% (p -value < 0.05). Among all the models fitted, the quadratic model is of good choice since the lack of fit value was insignificant with higher values of adjusted and predicted R^2 values for both the adsorbents. Another important parameter that supports the selection and validation of

the best model is predicted residual error sum of squares (PRESS), and it is a measure between the actual and predicted values of the response. PRESS can be calculated

from the mean square of the differences between actual and predicted responses, and the best model has the lowest values of PRESS values [55, 56]. In the present study,

Table 4 Regression statistics of quadratic model

SCH				NCH			
Std. Dev.	4.34	R-Squared	0.9851	Std. Dev.	7.79	R-Squared	0.9496
Mean	59.95	Adj R-Squared	0.9659	Mean	57.52	Adj R-Squared	0.9042
C.V. %	7.23	Pred R-Squared	0.9011	C.V. %	13.54	Pred R-Squared	0.7120
Press	873.36	Adeq Precision	24.3872	Press	3462.83	Adeq Precision	16.9890
-2 Log Likelihood	83.04	BIC	111.3744	-2 Log Likelihood	125.00	BIC	154.9525
AICc	139.71			AICc	169.44		

Table 5 Analysis of variance of the response surface quadratic model for the prediction of dye removal efficiency of SCH

Source	Sum of squares	Df	Mean square	F value	P-value (Prob > F)	Significance
Model	8698.69	9	966.52	51.39	<0.0001	Significant
A-pH	4721.32	1	4721.32	251.03	<0.0001	
B-Initial dye concentration	1658.13	1	1658.13	88.16	<0.0001	
C-SCH dose	1636.21	1	1636.21	87.00	<0.0001	
AB	53.71	1	53.71	2.86	0.1349	
AC	1.63	1	1.63	0.09	0.7771	
BC	26.67	1	26.67	1.42	0.2725	
A ²	446.03	1	446.03	23.72	0.0018	
B ²	12.99	1	12.99	0.69	0.4333	
C ²	286.67	1	286.67	15.24	0.0059	
Residual	131.65	7	18.81			Not significant
Lack of fit	104.63	5	20.93	1.55	0.4370	
Pure error	27.03	2	13.51			
Cor total	8830.35	16				

Table 6 Analysis of variance of the response surface quadratic model for the prediction of dye removal efficiency of NCH

Source	Sum of squares	Df	Mean square	F value	P-value Prob > F	Significance
Model	11,415.90	9	1268.43	20.92	<0.0001	Significant
A-pH	5456.39	1	5456.39	89.97	<0.0001	
B-Initial dye concentration	1086.57	1	1086.57	17.92	0.0017	
C-NCH dose	2130.58	1	2130.58	35.13	0.0001	
AB	51.82	1	51.82	0.85	0.3770	
AC	12.42	1	12.42	0.20	0.6606	
BC	49.45	1	49.45	0.82	0.3878	
A ²	2150.81	1	2150.81	35.47	0.0001	
B ²	644.66	1	644.66	10.63	0.0086	
C ²	165.61	1	165.61	2.73	0.1294	
Residual	606.44	10	60.64			Not significant
Lack of fit	399.74	5	79.95	1.93	0.2433	
Pure error	206.71	5	41.34			
Cor Total	12,022.34	19				

compared to the other three models, the quadratic model has the lower values of PRESS for both the adsorbents. The detailed regression statistics are provided in Table 4.

3.2.2 Statistical analysis (ANOVA)

The results of ANOVA for a selected quadratic model with estimated coefficients are summarised in Tables 5 and 6 for SCH and NCH, respectively. The ANOVA results show that the developed models are highly significant with $p < 0.0001$ for the adsorbents. Larger model F-value for SCH and NCH further confirms the significance of the model, and there is only a 0.01% chance that an F-value this large could occur due to noise. The model terms are significant if the values of prob > F less than 0.05 and values more than 0.1 indicate model terms are not significant. In the case of SCH adsorbent, the model terms A, B, C, A^2, C^2 are significant model terms, but for NCH adsorbent A, B, C, A^2 and B^2 terms are significant model terms. The values of prob > F greater than 0.1 indicate the model terms do not significantly influence the process of methylene blue dye adsorption efficiency. The lack of fit F-value of 1.55 and 1.93 for SCH and NCH, respectively, specifies that the lack of fit F-value is not significantly relative to the pure error. And also $p > F$ value greater than 0.05 also justifies the lack of fit of the model is not significant and one has to select the model with insignificant lack of fit. For both adsorbents, the difference 0.2 indicates that predicted R^2 is in reasonable agreement with the adjusted R^2 . For a good model, the signal-to-noise ratio measured from adequate precision greater than 4 is desirable. The large value of 24.39 and 16.99, respectively, for SCH and NCH indicates the adequate signal and can be used to navigate the design space. The final model obtained based on the ANOVA in terms of actual variables representing the dye removal efficiency (DRE) of SCH and NCH is given in Eq. 6 and 7, respectively:

$$\text{DRE}_{\text{SCH}} = -57.76 + 23.43A - 0.15B + 128.84C - 0.05AB + 0.80AC + 0.32BC - 1.11A^2 - 1.90 \times 10^{-3}B^2 - 89.14C^2 \quad (6)$$

$$\text{DRE}_{\text{NCH}} = -146.54 + 35.52A - 0.95B + 271.65C - 0.03AB + 4.40AC - 0.56BC - 2.16A^2 - 4.84 \times 10^{-3}B^2 - 239.71C^2 \quad (7)$$

These equations in terms of actual factors can be used to predict the dye removal efficiency of the adsorbent for given values of the independent variable. In the above equation, positive sign of constants indicates the synergistic effect of variables improving the adsorption capacity by favouring the adsorption process. The negative value shows that the variables have an antagonistic effect on the

adsorption capacity and unfavourable to the adsorption process [57, 58].

Figure S1 shows the plot of residuals' normal probability (%) and the internally studentised residuals. It is observed that the residual distribution is very normal without significant outliers with averaging all the points on the straight line. This attribute indicates that there are no necessary of response transformation and no apparent problem with normality [59, 60]. The relationship between the experimental and predicted dye removal efficiencies is shown in Figure S2 and indicates that all the model points fall on a straight line showing predicted values were best fitted with actual values. Hence, the developed response surface model developed in this study can be satisfactorily used in the optimisation of the process for adsorption of MB onto SCH and NCH adsorbent.

3.3 Response surface analysis

3.3.1 Main effects of parameters on adsorption efficiency

The perturbation plots assist in comparing the effects of the selected parameters at a specific point in the design space [61, 62]. The response can be plotted by changing only one parameter over the range while keeping all the other parameters constant. The Design-Expert software used in this study sets the midpoint (coded 0) as the reference point for all the factors. Figure S3 shows the perturbation plot employed to investigate the effect of independent variables simultaneously on MB removal efficiency of SCH and NCH adsorbent. In the present study, the variables such as pH, initial dye concentration and adsorbent dosage are considered for obtaining maximum dye removal efficiency. A sharp curvature of all the parameters indicates that the dye removal efficiency is very sensitive to these factors. The plateau-like curve of initial dye concentration for SCH indicates insensitivity of the dye removal efficiency in working concentration levels.

The initial pH of dye solution is a vital parameter in the adsorption studies, which significantly affects the removal capacity of the adsorbent, and it is a necessity to find the optimum pH of the adsorption processes. In water treatment, the pH of the solution varies the degree of ionisation of the dye molecules and also the surface properties of the adsorbent. Figures S4(a) and S5(a) show the effect of pH on MB adsorption capacity onto SCH and NCH, respectively, at midpoints of initial dye concentration and adsorbent dosage. From these results, it shows that the dye removal efficiency of methylene blue significantly increased as there is an increase in pH for both SCH and NCH. But for NCH after pH 8, the dye removal efficiency was slightly increased. This attribute can be explained from the point of zero charge value of SCH and NCH adsorbent, and the pH_{pzc}

value was found to be 4.35 and 6.95 for SCH and NCH, respectively (Fig. 5). For cationic dyes, the maximum dye removal efficiency has occurred at pH greater than pH_{pzc} and anionic dyes show better efficiency at $pH < pH_{pzc}$. This is because, at pH values less than pH_{pzc} , the H^+ ion concentration in the solution increases, and the adsorbent surface acquires positive charge by H^+ ion adsorption on the surface from the solution. In other words, surface adsorbent gets protonated in acidic medium and develop strong electrostatic forces of attraction between the anionic dye and adsorbent surface. The pH value above the point of zero charge, OH^- ions increases and the adsorbent surface will be negatively charged. This developed the attractive force between the positively charged cationic dye such as MB and negatively charged SCH and NCH adsorbent [63, 64].

The effect of initial MB concentration at midpoints of pH and adsorbent dosage on SCH and NCH is presented in Figures S4(b) and S5(b), respectively. From this, it is revealed that dye removal efficiency decreases with the

increase in initial MB concentration. This is ascribed due to the availability of many unoccupied adsorption sites at lower concentration that facilitates the greater adsorption efficiency. At higher concentration, these necessary active sites will be lacking and competition may exist between dye molecules which reduces the dye removal efficiency [65, 66]. From Figures S4(c) and S5(c), it is evident that adsorbent dosage has a significant effect on the MB removal efficiency onto SCH and NCH. The increase in dye removal efficiency is due to a proportional increase in the number of available adsorption sites with an increase in adsorbent dosage [34].

3.3.2 Interaction Effect of parameters on adsorption efficiency

The influence of selected process parameters on the MB dye removal efficiency of SCH and NCH is studied using surface and counterplots given in Fig. 6 and 7. The interactive effect of pH and initial dye concentration presented in Figs. 6a and 7a shows that increase in pH increased the removal efficiency for both the adsorbents, but after pH 8, the removal efficiency decreased slightly for NCH adsorbent. The increased in initial dye concentration significantly decreased the dye removal efficiency at constant adsorbent dosage. It indicates the unavailability of adsorption sites at higher dye concentration. The interaction of pH and adsorbent dosage shown in Figs. 6b and 7b indicates the pH and adsorbent dosage has a synergetic effect on dye removal efficiency. Besides, the interactive effect of initial dye concentration and the adsorbent dosage is given in Figs. 6c and 7c suggesting that MB initial concentration has an antagonistic effect on dye removal efficiency.

3.3.3 Numerical optimisation and validation of the model

The optimum condition of the selected process parameters to obtain maximum dye removal efficiency was determined based on the desirability function. Numerical optimisation available in Design-Expert was employed in identifying the specific points that maximise the value of desirability function. According to the calculations, chosen optimum condition at the desirability value of 1 is given in Table 7. The reliability of predicted response at optimum conditions is validated by conducting experiments in duplicates, and the data are presented in Table 7. The experimental dye removal efficiencies are closer to the predicted dye removal efficiencies and confirm the validity of the proposed quadratic model to optimise the pH, initial dye concentration and adsorbent dosage on the adsorption of MB onto SCH and NCH.

Fig. 5 Point of Zero Charge **a** SCH and **b** NCH

Fig. 6 Response surface plots for SCH adsorbent

Table 7 Optimum experimental conditions for methylene blue removal using SCH and NCH adsorbent

Adsorbent	Predicted optimum values			Desirability	DRE _{Predicted}	DRE _{experimental}	Residual error (%)
	pH	Initial dye concentration, mg/L	Adsorbent dosage, g/L				
SCH	7.637	37.786	0.740	1	94.629	93.528	1.16
NCH	7.914	84.495	0.406	1	91.298	92.482	1.30

Fig. 8 PSO plot for adsorption of MB onto SCH and NCH

3.3.4 Adsorption kinetics

Kinetics analysis of the adsorption process explains the rate of uptake of adsorbent and also aids to determine the residence time of the adsorption. It is one of the important characteristics in defining the efficiency of adsorption [5]. The effect of time on adsorption of MB on SCH and NCH was carried out at experimental conditions: 25 mg/L,

0.3 mg/L of SCH and NCH dosage, pH 8, 50 ml of volume, 30 °C, and the time is varied between 0 and 120 min. To understand the kinetics mechanism, two well-known kinetic models were employed such as pseudo-first-order (PSO) and pseudo-second-order (PSO) model. A detailed description of these models is presented in Table S3 [2, 7, 34]. The PSO kinetic fitting curves and the results obtained from the nonlinear regression analysis are presented in Fig. 8 and Table 8, respectively. The data presented in Table 8 suggest that PSO model better explains the kinetic data with high values R^2 and low values of RSS and ARE. This is possibly attributed due to the formation of a chemical bond or electrostatic attraction between adsorbate and adsorptive sites present on the SCH and NCH, and maybe chemisorption is the rate-controlling step. Also, the adsorption rate is proportional to the square of a number of unoccupied adsorption sites [67, 68].

3.3.5 Adsorption isotherm

To estimate the maximum adsorption capacity and to optimise the design of adsorption systems, widely used isotherm models, Langmuir, Freundlich, Temkin and D-R isotherm model, were employed. The details of these models are given in Table S4 [4, 69]. The effect of initial dye concentration MB on adsorption capacity of SCH and NCH was studied under experimental conditions: 50 ml dye solution, pH 8, temperature 30 °C and adsorbent dosage of 0.3 g/L and 0.2 g/L for SCH and NCH, respectively.

Table 8 Kinetics constants and statistical parameters for MB adsorption onto SCH and NCH adsorbent

Adsorbent	Model	Model parameters		Statistical parameters		
				R^2	RSS	ARE
SCH	PFO	k_1	q_e	0.9790	36.0025	7.6827
		0.0532	35.4344			
	PSO	k_2	q_e	0.9949	7.7663	3.3095
		0.0016	40.7976			
NCH	PFO	k_1	q_e	0.9820	27.7171	4.9076
		0.0829	37.4395			
	PSO	k_2	q_e	0.9969	4.6567	2.1680
		0.0027	41.9192			

Table 9 Adsorption isotherm constants and statistical parameters for adsorption of MB onto SCH and NCH

Adsorbent	Model	Model parameters		Statistical parameters		
				R ²	RSS	ARE
SCH	Langmuir	K _L	q _{max}	0.9290	443.60	12.29
		0.0791	129.43			
	Freundlich	K _f	n	0.9600	182.60	5.91
		27.493	3.01			
SCH	Temkin	K _T	b _T	0.9562	198.16	6.1
		0.042	36.44			
	D-R	Q _{DR}	K _{DR}	0.9412	202.12	9.2
		112.18	2.35 × 10 ⁻³			
NCH	Langmuir	K _L	q _{max}	0.9213	1497.48	13.55
		0.1271	199.73			
	Freundlich	K _f	n	0.9871	163.58	3.23
		52.899	3.31			
NCH	Temkin	K _T	b _T	0.9789	283.211	4.63
		1.807	38.071			
	D-R	Q _{DR}	K _{DR}	0.7757	1555	16.12
		159.55	8.57 × 10 ⁻⁴

Fig. 9 Freundlich adsorption isotherm plot for adsorption of MB onto SCH and NCH

The initial concentration of methylene blue was varied between 25 and 150 mg/L.

The results obtained from nonlinear regression analysis of selected isotherm models and isotherm fitting curve for Freundlich model are presented in Table 9 and Fig. 9, respectively. From these results, it was observed that the Freundlich model is fitted best with experimental data with higher values of R² and lower values of RSS and ARE compared to other selected models. This indicates that adsorption of MB on SCH and NCH is multilayer and

Table 10 Comparison of adsorption capacities of various NaOH-treated biomass-based adsorbents for removal of methylene blue

Sl. No.	Biomass	q _{max} (mg/g)	References
1	Foumanat tea waste	461.00	[33]
2	Rice husk	342.43	[31]
3	Cocoa pod husk	263.90	[71]
4	Rejected tea	242.11	[72]
5	Pinecone powder	142.25	[73]
6	Sawdust	109.80	[74]
7	Brazilian ironwood fruits	125.20	[75]
8	Orange tree sawdust	78.70	[76]
9	Coffee husk (NaOH treated)	199.73	Present study
10	Coffee husk (autoclaved)	129.43	Present study

is appropriate to heterogeneous surfaces with different adsorption energies having adsorption sites. The values of n in the range between 1 and 10 indicate the adsorption of MB onto SCH and NCH is favourable [70]. According to the Langmuir model, the maximum monolayer adsorption capacity was found to be 129.43 and 199.73 mg/g for SCH and NCH, respectively. The adsorption capacity of NCH is higher than SCH, and the higher adsorption capacity of NCH is due to the reduced particle size and rough surfaces developed after NaOH treatment. The maximum adsorption capacities (q_{max}, mg/g) MB onto various NaOH-treated biomass are presented in Table 10. This is evident that the NCH has potential in the removal of cationic dyes from the wastewater.

4 Conclusion

In this study, the eco-friendly and low-cost adsorbent developed based on coffee husk agricultural waste through a physical and chemical treatment was employed for methylene blue removal from synthetic wastewater. Besides reducing the coffee husk waste, the outcomes also provide additional benefits to dye effluent treatment from wastewater. The influence of adsorption process parameters, viz. solution pH, adsorbent dosage and initial dye concentration, was investigated by response surface methodology (RSM). For SCH adsorbent, the optimum conditions obtained were at pH of 7.637, initial dye concentration of 37.78 mg/L and adsorbent dosage of 0.740 g/L, which yielded MB removal percentage of 93.52. In the case of NCH adsorbent, the optimum conditions were found to be pH of 7.914, initial dye concentration of 84.495 and adsorbent dosage of 0.406, which yielded MB removal of 92.48%. It was found that the equilibrium data regressed very well with Freundlich isotherm model, which demonstrated multilayer adsorption of MB onto SCH and NCH. The kinetics of MB adsorption onto SCH and NCH has followed the pseudo-second-order kinetic model. Characterisation of adsorbent using SEM and FTIR revealed that there are significant changes in physicochemical properties of raw and treated coffee husk biomass which plays an important role in the adsorption of MB onto SCH and NCH. The overall adsorption results revealed that the NCH is a feasible and low-cost adsorbent for the removal of MB dye aqueous solutions.

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Compliance with ethical standards

Conflict of interest The author(s) declared no conflict of interest.

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