Methylene Blue Adsorption onto Cockle Shells-Treated Banana Pith: Optimization, Isotherm, Kinetic, and Thermodynamic Studies

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Abstract: *Two low-cost wastes, banana pith (BP) and cockle shells (CS) were explored towards methylene blue (MB) removal. The performance of cockle shells-treated banana pith (CS-BP) in MB removal was compared with untreated BP and commercially $Ca(OH)_2$-treated BP ($Ca(OH)_2$-BP). The adsorption efficacy was following the order of BP < CS-BP < $Ca(OH)_2$-BP, indicating the positive role of alkaline treatment towards MB removal and great potential of CS as a low-cost activation material. The optimization of MB removal onto CS-BP was executed by response surface methodology (RSM) with three independent variables (adsorbent dosage (X_1), initial pH (X_2) and initial MB concentration (X_3)), and the optimal condition was achieved at X_1 = 1.17 g/L, X_2 = pH 7 and X_3 = 214 mg/L, with 87.32% of predicted MB removal. The experimental data well-fitted the pseudo-second-order kinetic (R^2 > 0.99) and the Langmuir isotherm (R^2 = 0.999) models, demonstrating the chemisorption and naturally homogeneous process. Thermodynamics study discovered that the MB removal by CS-BP is endothermic, feasible, spontaneous and randomness growth at a solid-solute interface. It is affirmed that CS could be employed as a low-cost activation material and CS-BP as a low-cost adsorbent.*

Keywords: *cockleshells; banana pith; methylene blue; low-cost adsorbent; alkaline treatment*

■ INTRODUCTION

Numerous industries are using dyes in coloring their final product and consequently caused severe problems in the form of colored wastewaters that require pre-treatment before being disposed to the environment [1]. Majority of the commercial dyes used is poisonous to aquatic life owing to the existence of chlorides and metals. As a result, the treatment of dye-containing effluent is a crucial task and the scientific interest in decolorization of dye effluents has been increasing in the last few decades. The removal of dyes has been studied using several techniques including biological, physical and chemical methods, however, the biological method has not been very successful, owing to the essential non-biodegradable nature of most of the dyes [2]. In addition, the high difficulty to treat dye-containing effluent can be

claimed on the aerobic digestion resistant, recalcitrant organic molecules present and stability towards photo degradation, biodegradation and oxidizing agents [3].

Adsorption method appeared as the best technique among various dye removal techniques due to its good performance in the removal of different types of coloring materials [2,4-5]. Regarding the adsorbent material, activated carbon has been commercially used for adsorption process owing to its excellent adsorption ability [6-7]. Regrettably, its relatively high cost limits its widespread usage in wastewater treatment. For the sake of reducing the cost of treatment, alternative adsorbents, particularly from agricultural wastes, have been investigated and reported, on account of the arose disposal problem as well as the no economic value of agricultural wastes [2].

Banana pith (BP) is one of the agricultural wastes which is available abundantly all the year round, yet being disposed of without being utilized properly and effectively. Therefore, the attempt to utilize BP as an economical adsorbent not only can minimize environmental pollution but can also increase its economic value. However, the challenge arose when the untreated agricultural waste adsorbents possess drawbacks as reported in the literature, for instance, low performance in adsorption process [8].

Therein, researchers have studied the agricultural wastes activation, and alkaline treatment can be considered as one of the broadly adopted methods. It has been reported that alkaline treatment substantially influences the morphology of the adsorbent by producing a porous surface of adsorbent which is favorable for adsorption process [9]. However, in order to reduce the cost, it is desirable to study the utilization of wastes as alternative low-cost materials to substitute the commercial chemical materials for alkaline treatment. Cockle shells (CS) is an abundant and non-edible waste that is widely found in many coastal areas. Owing to the high composition of calcium carbonate ($CaCO_3$) in CS, CS has great potential as an economical activation material for alkaline treatment of BP.

In this study, we attempt to use BP as a low-cost adsorbent and its adsorption competency was improved by employing the cockle shell (CS) as the low-cost activation material. Adsorption conditions of Methylene Blue (MB) removal onto cockle shells-treated banana pith (CS-BP) was optimized using Response Surface Methodology (RSM), while the physicochemical properties of fresh and spent adsorbent were analyzed using several characterization analyzers.

■ EXPERIMENTAL SECTION

Materials

The banana piths (BPs) were collected from the banana farm, Pahang, Malaysia. The commercial calcium hydroxide ($Ca(OH)_2$) was purchased from Merck and used in the alkaline treatment of the adsorbent.

Instrumentation

Instruments used in this study included oven, furnace (Memmert UFB-500, Germany), stirring hotplate with digital display (Corning PC-420D), XRF (Bruker S8 TIGER ECO), FTIR (Nicolet iS5, Thermo Scientific), SEM (LYRA3 XM, Tescan) and BET (Quantachrome Autosorb-1 analyzer).

Procedure

Preparation of adsorbent

The BPs were cut into pieces in 1–2 cm length and soaked in water for adhering impurities elimination. The samples were oven-dried (80 °C, 12 h) before grounded and sieved (300–500 μm). Meanwhile, the cockle shells (CS, collected from the beach, Pahang, Malaysia) were cleaned with water, dried (80 °C, 12 h), grounded to the specific size (355–600 μm), and finally followed with calcination process (850 °C, 3 h). During the calcination process, calcium carbonate ($CaCO_3$) consist of CS changed to calcium oxide (CaO) via the decomposition process ($CaCO_3 \rightarrow CaO + CO_2$).

The BP pre-treatment with commercial $Ca(OH)_2$ was performed in accordance with the method described in the literature [2]. In brief, $Ca(OH)_2$ powder (8.6 g) was dissolved into deionized water (1 L), followed by the addition of powdered BP (10 g). The mixture was agitated (room temperature, 4 h), filtered and oven-dried (80 °C, 12 h) to produce $Ca(OH)_2$-BP. An identical technique was executed for preparing the CS-BP by using CS as

alkaline material. The CaO consist of calcined CS converted into $Ca(OH)_2$ once it contacts with H_2O.

Characterization of adsorbent

XRF was used to analyze the chemical composition of CS sample, meanwhile, the Fourier-transform infrared spectrometer (FTIR), surface area analyzer and scanning electron microscopy (SEM) were used to analyze the physicochemical properties of fresh adsorbents (BP, CS-BP) and spent adsorbent (MB-CS-BP). In brief, FTIR analysis was used for the study of adsorbents' chemical properties and functional groups involved in the adsorption process, while the morphological characteristics and surface features were studied using SEM. The textural properties (BET surface area (S_{BET}) and pore volume (V_p)) of adsorbents were quantified using BET analyzer at -196 °C.

Adsorption experiments

A total number of 16 adsorption experiments with 2 replicates at the center point were executed by alternating the process parameters corresponding to the experimental design generated by RSM for adsorption study. Prior to the adsorption experiments, the stock solution was prepared by dissolution of the finite quantity of measured MB ($C_{16}H_{18}N_3SCl$, C.I.52015, 99%, Merck) in deionized water, before being adjusted to desired concentrations (50–500 mg/L) and pH (pH 2–10). Adsorption experiments started with the addition of the requisite dosage of CS-BP (0.25–2.5 g/L) into MB solution (200 mL) under constant stirring (ambient temperature, 2 h). The samples were taken out at proper time intervals, followed by centrifugation (20 min). UV/Vis spectrophotometer (LAMBDA 850, PerkinElmer) was used to identify the remaining MB concentration with maximum wavelength (λ_{max}) of 664 nm. The experiments were conducted triplicates for accuracy. The amount of MB adsorbed at equilibrium, q_t (mg/g) and percentage of MB removal were calculated using Eq. (1) and (2), respectively.

$$q_t = \left(\frac{C_0 - C_t}{W}\right) \times V \quad (1)$$

$$\text{Removal } (\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (2)$$

where C_0 and C_t are the liquid phase concentration of the MB at time zero and at any time t (mg/L), W is the adsorbent mass (g) and V is the volume of the MB solution (L).

Experiment design and optimization

The process parameters influencing the adsorption process were analyzed using face-centered central design (FCCCD) method generated from RSM (Statsoft Statistica 8.0 software). Three independent variables (adsorbent dosage, initial pH, and initial concentration) were selected, and their relationship with response (MB removal) was appraised by the equation model. The significant of the equation model was assessed using analysis of variance (ANOVA, 5% level of significance) in accordance with the method described in the literature [10].

Adsorption kinetics

Pseudo-first-order and pseudo-second-order models were executed to govern the mechanism of the MB adsorption onto CS-BP. The linearized forms of the models are expressed as following equations [11]:

Pseudo-first-order:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Pseudo-second-order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium (mg/g) and at any time t (mg/g), and k_1 and k_2 are the adsorptions constant of pseudo-first-order and pseudo-second-order model.

Adsorption isotherm

Langmuir [12], Freundlich [13], Temkin [14], and Dubinin-Radushkevich [15] models were executed to analyze the type of MB distribution, as well as the interaction between CS-BP surface and MB molecules. The linearized forms of the models are expressed as following equations:

Langmuir:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (5)$$

Freundlich:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (6)$$

Temkin:

$$q_e = B\ln A + B\ln C_e \quad (7)$$

Dubinin-Radushkevich:

$$\ln q_e = \ln q_m - K_{DR}\varepsilon^2 \quad (8)$$

where C_e and q_e are the MB concentration (mg/L) and MB adsorption capacity (mg/g) at equilibrium, while q_m is the maximum adsorption capacity (mg/g). K_L and K_f are the equilibrium constant for Langmuir (L/mg) and Freundlich ((mg/g)(L/mg)$^{1/n}$). n is an empirical constant for the Freundlich equation. For Eq. (8), A is the Temkin equilibrium binding constant (L/g), while B is the Temkin constant. For equation (9), K_{DR} is the Dubinin-Radushkevich constant (mol^2/kJ^2) and ε is the Polanyi potential (J/mol). ε can be determined from ε = RT ln (1+1/C_e), where R is the ideal gas constant (8.314 J/mol·K) and T is absolute temperature (K). The fundamental characteristic of the Langmuir isotherm can be analyzed using the dimensionless constant separation factor, R_L (R_L = 1/(1+K_LC_0)) [16]. The value of R_L parameter can be either R_L = 0, 0 < R_L < 1, R_L = 1, or R_L > 1, indicating to irreversible, favorable, linear, or unfavorable, respectively [16].

Adsorption thermodynamic

The Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were evaluated to investigate the thermodynamic nature of MB adsorption over CS-BP and the equations used as follows [2]:

$$\Delta G° = -RT\ln K_D \quad (9)$$

$$\ln K_D = \frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (10)$$

where R is the ideal gas constant (8.314 J/mol·K), T is the absolute temperature (K) and K_D is the Langmuir isotherm constant (L/mg).

■ RESULTS AND DISCUSSION

Effect of Alkaline Treatment

Fig. 1 depicts the influence of banana pith (BP) pre-treatment on the methylene blue (MB) removal, in which the error bars representing the standard errors by the mean of three replicates of the experiments carried out in this study. The performance of untreated BP on the adsorption of MB was compared with treated BP ($Ca(OH)_2$-BP and CS-BP). The $Ca(OH)_2$-BP (80.6%) and CS-BP (74.1%) show higher adsorption uptake as compared to the untreated BP (66.5%), indicating the positive role of alkaline treatment towards MB removal and great potential of CS as a low-cost activation material. The positive role of alkaline treatment might be due to an increase in the electronegativity and the surface areas of adsorbents after the alkaline treatment. The great potential of CS as an activation material in accordance with XRF analysis in which the calcined CS contains 98.2% of CaO, which can be considered as a promising economical replacement over commercial $Ca(OH)_2$. The positive role of adsorbent activation towards dye removal was also reported in the literature [17]. Jain and Gogate [9] found that the activation of *Prunus dulcis* leaves by NaOH increased the adsorption capacity of *Prunus dulcis* leaves towards Acid Blue 113 removal from 10.87 to 25.51 mg/g due to the presence of surface porous after NaOH activation which is favorable for adsorption process.

Characterization of Untreated BP and Treated-BP

The details on the functional groups involved during the pre-treatment process and the binding mechanism

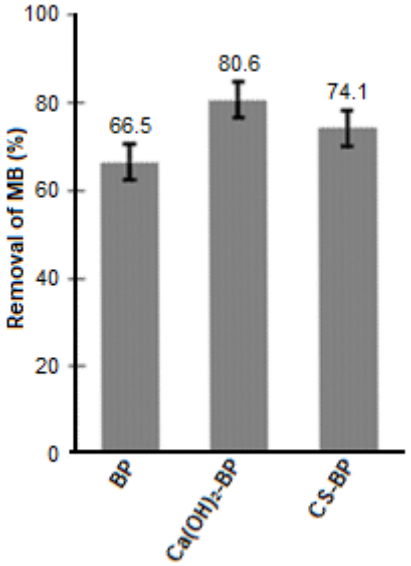

Fig 1. Influence of the alkaline treatment on the MB removal (m = 0.5 g/L, pH 6, C_0 = 100 mg/L, T = 30 °C, contact time = 120 min)

between treated BP and MB molecules were determined using FTIR analysis as shown in Fig. 2. Several major absorbance bands at 3283, 2917, 1591, 1316, 1031, 460 and 438 cm^{-1} were observed for BP. In accordance with the literature, the broad absorption peak at 3283 cm^{-1} corresponded to the O-H stretching in cellulose, while the peak observed at 2917 cm^{-1} assigned to the C–H asymmetric stretching of CH_2 groups [10,18]. The peaks at 1591 and 1316 cm^{-1} attributed to the C=C and C=O stretching, while 1031, 460 and 438 cm^{-1} attributed to the C-H deformation. New bands were discerned at 1386, 871 and 711 cm^{-1} after the BP treatment with CS indicating the presence of inorganic carbonate, demonstrating the success of alkaline treatment process. After the MB adsorption onto CS-BP, the intensities of the bands were slightly decreased and the existence of organic sulfur was observed at the band of 1419 cm^{-1} [18]. The decreased in the intensity at 871 and 711 cm^{-1} bands and the presence of a new band at 1419 cm^{-1} provide strong evidence of the interactions between dye molecules with the inorganic carbonate of CS-BP in accordance with the literature [19].

The topology of BP, CS-BP, and MB-CS-BP was identify using SEM analysis and the result is shown in Fig. 3. Before the treatment with CS, the crushed particles with clustered arrangement can be seen on the surface of BP (Fig. 3(a)). Rough BP surface was observed after the CS pre-treatment (Fig. 3(b)) which signifies the high possibility of MB to be adsorbed. The smooth surface of CS-BP-MB (Fig. 3(c)) confirming the coverage of CS-BP surface with MB molecules via the adsorption process.

The textural properties (S_{BET} and V_p) of BP, CS-BP and MB-CS-BP were S_{BET} = 12.31, 16.06 and 11.51 m^2/g, respectively, and V_p = 0.019, 0.023 and 0.011 cm^3/g, respectively. The findings revealed that the activation of BP using CS increase the number of pores and thus increase the S_{BET} and V_p. This advantage increases the possibility of MB molecules to be trapped onto the surface and pores of CS-BP, which was evidenced by the decrease of S_{BET} and V_p for MB-CS-BP. The changes in the surface features of adsorbent by alkaline activation were also reported by Jain and Gogate (2017) for NaOH treated *Prunus dulcis* leaves [9]. They stated that the increment in S_{BET} and V_p of the adsorbent which is favorable for adsorption process indeed resulted from the pores evolved upon NaOH activation.

Statistical Analysis of MB Removal by CS-BP

The influences of the independent variables on the response had been investigated by the batch study of 16 experiments using RSM and the results were presented in Table 1.

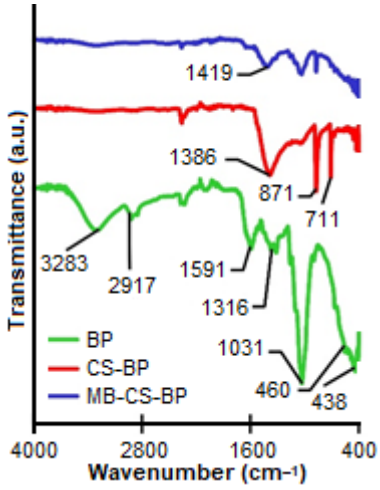

Fig 2. FTIR spectra of BP, CS-BP, and MB-CS-BP

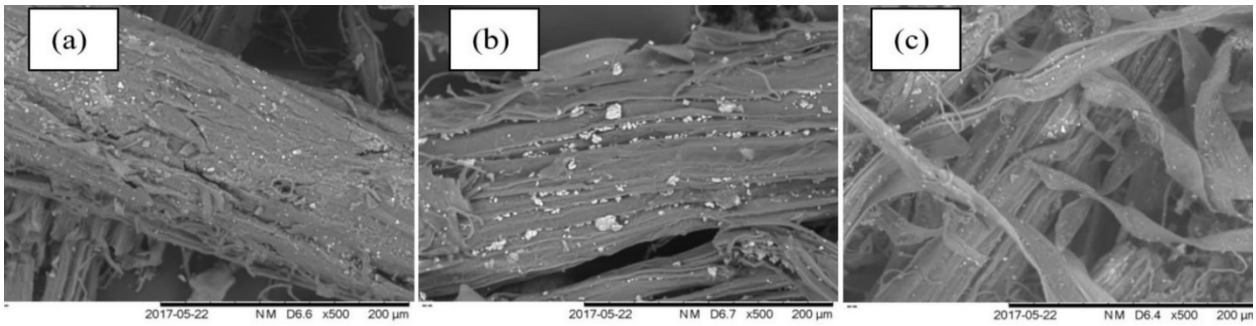

Fig 3. SEM images of (a) BP, (b) CS-BP, (c) MB-CS-BP

The quadratic model for MB removal by CS-BP is presented in Eq. (11):

$$Y = 65.9826 + 6.6710X_1 + 4.3866X_2 + 0.0253X_3 - 1.5075X_1^2 - 0.2736X_2^2 - 0.00004X_3^2 - 0.4139X_1X_2 - 0.0017X_1X_3 - 0.0011X_2X_3 \quad (11)$$

The validity of the statistical model was analyzed by plotting the graph of predicted values versus the experimental values (not shown). The linear coefficient of the graph is 0.9786 implying the reasonable of predicted values in conformity with the experimental values. The statistical significance of the model was accessed using ANOVA and the result was tabulated in Table 2. The result discovered the significance of the model as expressed by the larger F-value (30.671) in comparison with the tabulated F-value (4.10).

Fig. 4 shows the Pareto chart of MB removal onto CS-BP. The critical parameter for the regression model represents the smaller magnitude of the p-value and larger magnitude of the t-value. As shown in Fig. 4, all linear, quadratic and interaction terms are statistically significant ($p < 0.05$) excluding linear term of adsorbent

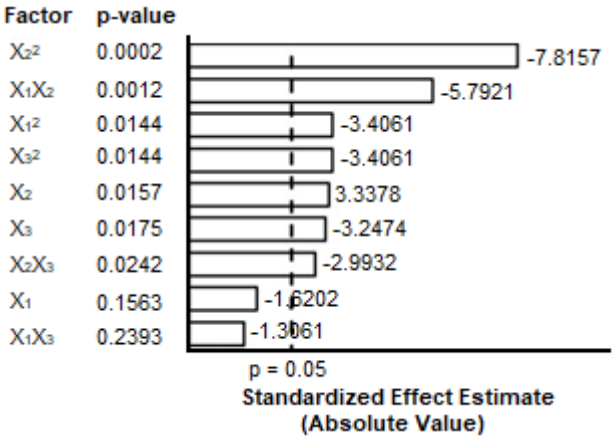

Fig 4. Pareto chart of MB removal by CS-BP

Table 1. The design of experiments and experimental response for MB removal by CS-BP

Run	Independent variables						Response
	Adsorbent dosage, X_1 (g/L)		Initial pH, X_2		Initial Concentration, X_3 (mg/L)		MB removal, Y (%)
	Coded	Uncoded	Coded	Uncoded	Coded	Uncoded	
1	-1	0.25	-1	2	-1	50	75.89
2	-1	0.25	-1	2	1	500	76.50
3	-1	0.25	1	10	-1	50	83.10
4	-1	0.25	1	10	1	500	81.00
5	1	2.50	-1	2	-1	50	79.47
6	1	2.50	-1	2	1	500	79.54
7	1	2.50	1	10	-1	50	80.37
8	1	2.50	1	10	1	500	75.45
9	-1	0.25	0	6	0	275	86.50
10	1	2.50	0	6	0	275	83.50
11	0	1.375	-1	2	0	275	81.99
12	0	1.375	1	10	0	275	83.07
13	0	1.375	0	6	-1	50	86.50
14	0	1.375	0	6	1	500	83.50
15 (C)	0	1.375	0	6	0	275	87.28
16 (C)	0	1.375	0	6	0	275	87.50

Table 2. ANOVA results for MB removal by CS-BP

Sources	Sum of Square (SS)	Degree of Freedom (df)	Mean Square (MS)	F-value
Regression (SSR)	227.10	9	25.233	30.671
Residual	4.9362	6	0.8227	
Total (SST)	232.03	15		

dosage (X_1) and an interaction term of adsorbent dosage and initial concentration (X_1X_3). The quadratic term of initial pH (X_2^2) was the utmost crucial variables for the adsorption of MB onto CS-BP.

Meanwhile, the least crucial factor on the MB adsorption was indicated by the X_1X_3. The crucial of the initial pH probably due to the properties of MB, which exists in the form of positively charged ions in aqueous solution. Thus, the changes in the charge of the initial MB solution will influence the adsorption performance.

Fig. 5 displays the 3D plots showing the influences of independent variables towards the removal of MB. As displayed in Fig. 5(a), the percentage of MB removal inclined parallel with the increment in adsorbent dosage and initial pH. At the adsorbent dosage of 0.8–1.5 g/L and an initial pH of 5.5–7.5, the maximum dye removal of > 86% was accomplished before slightly decreased at higher values. As the adsorbent dosage was increased, the quantity of the binding sites accessible for adsorption was increased as well due to the rise in the adsorbent's dosage.

Meanwhile, the enhancement of the MB removal at higher pH can be claimed on the electrostatically adsorbed of the positively charged of MB cations onto the negatively charged surface of CS-BP [20]. The influence of pH on the adsorption performance can be depicted on the basis of zero-point change (pH_{zpc}) of the CS-BP, which was confirmed at ~pH 7.45. The influence of pH on the removal percentage in agreement with the report declared for the MB removal onto cashew nutshell [21] and breadnut peel [22], in which the MB withdrawal percentage increased with increment in initial pH.

Fig. 5(b) displays the 3D plot for the influences of adsorbent dosage (X_1) and the initial concentration (X_3) on the MB removal percentage. The percentage of MB removal increase with the increase of the adsorbent dosage. In contrast, the MB removal was declined with the increment of the MB initial concentration. The reduced in the percentage of MB removal at higher concentration probably be due to the inadequate quantity of active adsorbent sites to accommodate the high concentration of dye ions [23]. The highest dye removal (> 86%) was accomplished at 0.9–1.6 g/L adsorbent dosage and 150-300 mg/L initial concentration.

The influences of initial pH (X_2) and initial concentration (X_3) on the MB removal are illustrated in Fig. 5(c). The plot shows that increasing pH and reducing initial MB concentration will subsequently increase the percentage of MB removal. This result related to the changes in the charge of the adsorbent surface and the ratio of dyes to the available surface site [24]. It was discovered that > 86% of MB withdrawal was acquired in the range of 5.5–7.5 initial pH and 150–300 mg/L initial concentration. An identical trend was claimed for the MB adsorption onto chitosan/zeolite composite [25], in which the MB withdrawal percentage increased with the growth of initial pH but a decline in the initial dye concentration.

The optimization study revealed that the optimal MB removal onto CS-BP was at 1.17 g/L adsorbent dosage, initial pH of 7 and 214 mg/L initial concentration with predicted percentage MB removal of 87.32%. An additional experiment was carried out at the optimal condition as validation purpose and the result showed 80.07% of MB removal was achieved.

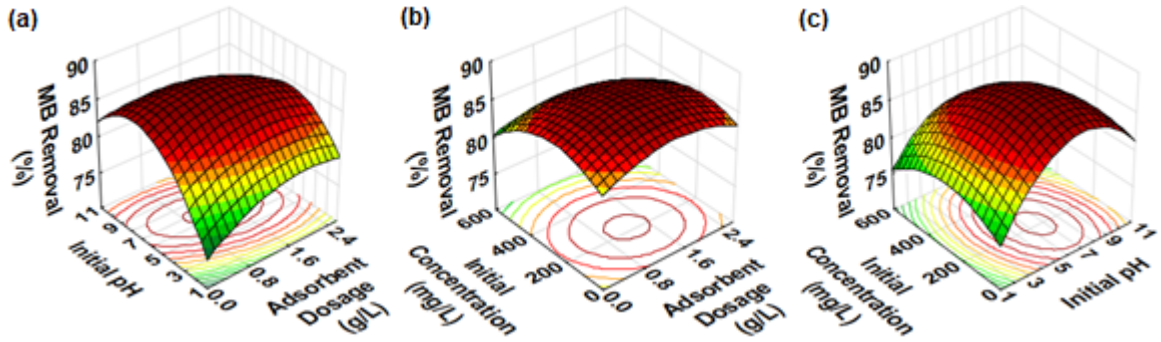

Fig 5. Response surface plots showing influences of (a) adsorbent dosage – initial pH interaction, (b) adsorbent dosage – initial concentration interaction, and (c) initial pH – initial concentration interaction, towards MB removal by CS-BP

Table 3. Kinetic parameters for adsorption of MB by CS-BP

Kinetic Model	Parameters	50 mg/L	100 mg/L	200 mg/L	300 mg/L	500 mg/L
Experimental	$q_{e,exp}$ (mg/g)	42.18	57.54	76.16	80.65	83.76
Pseudo-first order	q_e (mg/g)	2.575	4.462	4.467	4.558	4.788
	k_1 (min^{-1})	0.136	0.026	0.022	0.020	0.022
	R^2	0.962	0.966	0.971	0.981	0.932
Pseudo-second order	q_e (mg/g)	42.017	59.172	76.923	81.301	84.033
	k_2 (min^{-1})	0.008	0.003	0.003	0.002	0.002
	R^2	0.997	0.993	0.995	0.994	0.992

Adsorption Kinetic

The kinetic study was carried out at m_{CS-BP} = 1.17 g/L, pH 7, T = 30 °C and C_0 = 50–500 mg/L. As tabulated in Table 3, pseudo-second-order model was shown as the best model with higher R^2 (> 0.992) and closer q_e values to experimental data ($q_{e,exp}$) in comparison with the pseudo-first-order model. The findings depicted that the MB adsorption by CS-BP was controlled by the chemisorption process and the number of the available active sites directly affect the rate of reaction. The comparable adsorption kinetic finding was reported for MB adsorption by oil palm ash zeolite/chitosan [26], weeds [27] and *Ficus carica* bast [18].

Adsorption Isotherm

The isotherm study was executed at m_{CS-BP} = 1.17 g/L, pH 7, T = 30 °C and C_0 = 50–500 mg/L. As tabulated in Table 4, the Langmuir isotherm model was shown as the best model with the highest R^2 (0.999) amongst the four isotherms employed. The good fitting with the Langmuir isotherm model depicted that the MB adsorption onto CS-BP is monolayer adsorption and takes place on a surface that is homogeneous in nature [28]. Corresponding to Table 4, the K_L value was 0.102 which expresses that the MB molecules are favorably adsorbed on CS-BP with maximum adsorption capacity, q_m of 85.47 mg/g. An indistinguishable tendency was proclaimed for MB adsorption onto biomass fly ash geopolymer monoliths [29]. The value of q_m was compared to several untreated and modified biosorbents were tabulated in Table 5. As observed, CS-BP has superior adsorption volume than the others, denoting the

Table 4. Isotherm parameters for MB removal onto CS-BP

Isotherm Model	Parameters	Value
Langmuir	R^2	0.999
	q_m (mg/g)	85.47
	K_L (L/mg)	0.102
	R_L	0.089
Freundlich	R^2	0.959
	n	8.953
	K_f (mg/g)(L/mg)$^{1/n}$	5.124
Temkin	R^2	0.930
	B (J/mol)	15.44
	A (L/g)	15.65
Dubinin-Radushkevich	R^2	0.974
	q_m (mg/g)	6.756
	K_{ad} (10^4)	1

Table 5. Comparison of maximum adsorption capacity of MB onto various untreated and modified low-cost adsorbents

Adsorbent	Adsorption capacity (mg/g)	Ref
Cockle shells-treated banana pith	85.47	This study
Banana empty fruit bunch AC-H_3PO_4	76.13	[30]
Banana empty fruit bunch AC-KOH	71.06	[30]
Salix babylonica (Weeping willow) leaves	60.97	[31]
Banana leaves AC	48.01	[32]
Haloxylon recurvum stems	22.93	[33]
Brazil nut shells	7.81	[34]

Table 6. Thermodynamic parameter for MB removal onto CS-BP

ΔH°	ΔS°	ΔG° (kJ/mol)		
(kJ/mol)	(J/mol·K)	30 °C	35 °C	40 °C
13.7455	57.0041	-3.5281	-3.8087	-4.0983

capability of CS-BP as an alternate low-cost adsorbent for MB removal.

Thermodynamic Study

The thermodynamic study was investigated at optimal condition (m_{CS-BP} = 1.17 g/L, pH 7, C_0 = 214 mg/L, and time of contact = 120 min) within 30–40 °C temperature range and the findings are listed in Table 6. The positive values of ΔH° (+ 13.7455 kJ/mol) and ΔS° (+ 57.0041 J/mol) indicated the endothermic process and randomness increment at a solid-solute interface with certain structural alternations in adsorbent and adsorbate [35]. The decreasing ΔG° values with increasing temperature indicates that the removal of MB onto CS-BP is feasible, spontaneous and increase in the degree of spontaneity at a higher temperature.

■ CONCLUSION

A new low-cost adsorbent (cockle shells-treated banana pith (CS-BP)) was successfully developed owing to its effectiveness in MB removal. Besides providing additional advantageous over industrial wastewater treatment, the solid wastes disposal of CS and BP can also be minimized. Investigation of MB removal by RSM under three independent parameters (adsorbent dosage (X_1), initial pH (X_2) and initial dye concentration (X_3)) was executed. Optimum condition (X_1 = 1.17 g/L, X_2 = pH 7, X_3 = 214 mg/L) yielded predicted MB removal of 87.32% (according to RSM). Based on the Pareto chart, the most paramount factor for MB removal by CS-BP was the X_2^2. The experimental data was well-fitted with pseudo-second-order kinetic and Langmuir isotherm models, demonstrated a chemisorption process with monolayer and homogeneous process. Thermodynamic investigations revealed that the MB adsorption onto CS-BP is an endothermic, randomness growth at the solid-solute interface, feasible, spontaneous and increase in the degree of spontaneity at a higher temperature.

The higher surface area, the presence of new bands which implies the existence of inorganic carbonate and rough surface of CS-BP as shown by BET, FTIR and SEM results, demonstrating the success of the alkaline treatment process. These combinations are the main contributors to the good MB adsorption by CS-BP.

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