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Equilibrium, kinetics, and optimization studies of methylene blue removal from aqueous solution using corn stalk wastes

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ABSTRACT

Methylene blue (MB) removal from aqueous solution has been investigated using corn stalk wastes as an available and low-cost adsorbent. The adsorbent was characterized using scanning electron microscopy, Brunauer–Emmett–Teller, and Fourier-transform infrared spectroscopy. The effects of independent variables and their interaction have been optimized using central composite design (CCD) through response surface methodology. The statistical analysis of data through analysis of variance showed that the experimental data of CCD are fitted with a second-order polynomial regression. The maximum MB removal efficiency of 98% was observed at an initial concentration of 10 mg dye/L, adsorbent dosage of 1.4 g/L, contact time of 50 min and pH 11. Kinetics and isotherm studies indicated that the experimental data can be well presented and described by the pseudo-second-order and Langmuir models, respectively. The produced activated carbon from corn stalk wastes as a cheap and available adsorbent can be considered as an appropriate method for dye removal from aqueous environment.

Keywords: Treatment; Adsorption; Activated carbon; Corn stalk; Dye; Kinetics

1. Introduction

In recent decades, dye production and consumption have increased significantly as a result of increasing population growth, and industrial activities [1]. Therefore, it known as the most abundant contaminant for water sources. Among organic dyes, methylene blue (MB), a cationic dye, because of wide usage in different activities such as printing, pesticide, textile, chemical indicators, dyeing, cosmetics, coating for paper stock, and pharmaceutical products can easily be found in wastewater [2,3]. This important aromatic compound, $C_{16}H_{18}N_3SCL·2H_2O$, (Fig. 1) can cause different harmful effects in humans, such as nausea, vomiting, diarrhea, cyanosis [3,4]. Therefore, removing this hazardous dye form wastewater before discharging into the aquatic environment has expanded wide consideration because of its harmful effects on the environment and human health [2,5].

Many techniques have suggested through previous studies for removing MB from water and wastewater such as biological treatment, adsorption, solvent extraction, chemical coagulation, photocatalytic degradation, oxidation, membrane filtration, and electrochemical degradation. Nowadays, adsorption process as an effective technology has been widly appiled in dyes removal because of low energy consumption, ease of operation, simplicity of design, easy availability, low cost and possibility of regeneration [6].

The utilization of commercial activated carbon, in spite of its effectiveness, is limited due to high cost and hard to

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be regenerated [7]. Previous research works introduced different activated carbons prepared from agricultural wastes as plentiful, economy, and eco-friendly adsorbents for replacement of the commercial activated carbons [7].

Recently, different agricultural wastes as precursors for generating activated carbon, for example, rice straw [8], sawdust [9], apricot stone [10], peanut shells [11], coconut shell [12], nutshells [13], vine waste [14] and algae [15] have been used for removing MB from water and wastewater. The efficiency of activated carbon to adsorb pollutants from aqueous solutions is influenced by its physicochemical characteristics, which they depend on the precursor composition of raw material [16]. Therefore, various methods have been used to prepare activated carbon, which among them integrated techniques, including acidification and thermal activation play key role to enhance the quality of the activated carbon (AC) [17].

The generated AC from corn stalk wastes (CSW) as a promising natural precursor, which exists richly in Iran has atracted the attantion of researchers in provious studies [18]. The corn stalk as a lignocellulosic material consist of three major chemical components including lignin, hemicellulose, and cellulose, which the annual production of corn stalk around the world has been reported about 520 × 10^9 kg [19–21].

In this study, corn stalk has been used to prepare AC by integrated method, chemical-thermal technique that using phosphoric acid as chemical activator. The impact of operating variables namely adsorbent dosage, MB initial concentrations, contact time and pH on the adsorption process were investigated and optimized by central composite design (CCD) through response surface methodology (RSM). The adsorption isotherm and kinetic parameters were also calculated and discussed.

2. Materials and methods

2.1. Chemicals and stock solution

The MB was purchased from Sigma-Aldrich and it was used to prepare stock solutions. Other chemicals such as sodium hydroxide (NaOH), hydrochloric acid (HCl), and phosphoric acid (H_3PO_4) were obtained from Merck Company, Germany; these chemicals were taking into work without any further purification. The initial MB concentrations have been achieved by diluting the stock solution, 1 g of MB in 1 L of water, to prepare desire concentrations in each run.

2.2. Activated carbon preparation

The corn stalks as an abundant and available waste were collected from a corn farm in Kermanshah City, Iran.

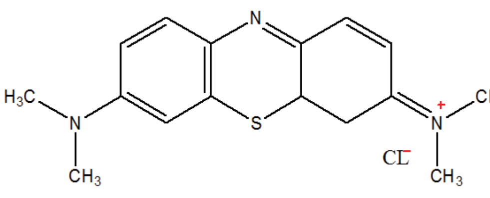

Fig. 1. Chemical structure of methylene blue.

The collected corn stalk wastes have been cut in the size of 3–5 cm. In order to eliminate dust and impurities, the corn stalks were washed several times with distilled water and then were placed in an oven for drying at 60°C for 3 h to obtain the constant mass. The raw materials were impregnated overnight with H_3PO_4 solution (1:10 W/V) at 25°C ± 2°C. The thermal activation was performed in a furnace at 500°C for 60 min. The prepared activated carbon was cooled at room temperature, and then washed with distilled water until the pH of the solution reached ~7. Finally, activated carbon was dried using an oven at 105°C, and stored in a vacuum desiccator until it was characterized for physical and chemical properties or applied in adsorption process.

2.3. Adsorbent characterization

The morphological characteristics of the corn stalk wastes activated carbon (CSW-AC) have been done using scanning electron microscopy (MIRA III, TESCAN, Czech Republic). The pore volume and specific surface area of the CSW-AC were carried out using Brunauer–Emmett–Teller (BET) surface area analyzer (BELSORP MINI II, BEL, Japan) through the adsorption/desorption isotherms of N_2 conducted at 77 K. The Fourier-transform infrared (FTIR) spectra of the adsorbent was tested using spectrophotometer.

2.4. Experimental design and performance

CCD as the most widely applied type of surface response method (RSM) was applied for modeling, optimizing, and determining the effects of the independent variables and the simultaneous interactions of variables namely MB concentration, pH, AC dosage and contact time on the MB removal efficiency using Design-Expert 8.0.1 software. The four selected independent variables have been arranged at five levels (pH: 3, 5, 7, 9 and 11; MB concentration: 10, 40, 70, 100 and 30 mg/L; adsorbent dose: 0.2, 0.5, 0.8, 1.1 and 1.4 g/L; and contact time: 10, 20, 30, 40, and 50 min) for 26 experiments. The results of dye removal efficiency have been reported in Table 1.

Statistical data analysis has been carried out using the analysis of variance (ANOVA), which the function of the response characterized by quadratic polynomial equation [Eq. (1)] [22,23].

$$Y = \beta_0 + \sum_{i=1}^{n}\beta_i X_i + \sum_{i=1}^{n}\beta_{ij} X_i^2 + \sum_{i=1}^{n}\sum_{i=1}^{n-1}\beta_{ij} X_i X_j \quad (1)$$

where Y is the predicted response, β_0 the constant coefficient, β_i the linear coefficients, β_{ij} the interaction coefficients and ii the quadratic coefficient.

The adsorption experiments were performed by the CSW-AC with 100 mL of MB solution at room temperature (25°C ± 2°C) using a shaker (OS4LD, FSA, IRAN) at a constant mixing of 180 rpm under different process conditions. After adsorption experiments, the adsorbent was immediately separated through a centrifuge (CE-148, Shimifann, IRAN) at 4,000 rpm for 3 min. Then, the concentration of the remaining MB dye was analyzed with a UV spectrophotometer (Jenway 6305, Germany) at a wavelength of 665 nm.

Table 1
Experimental design and results of the central composite design

RUN	Operating parameters				Observed	
	pH	C (mg/L)	PAC (g/L)	Time (min)	Removal efficiency (%)	Adsorption capacity (mg/g)
1	3	10	0.2	10	53.54	2.68
2	3	10	1.4	10	96.02	0.69
3	3	10	0.2	50	85.21	4.26
4	3	10	1.4	50	98.14	0.70
5	11	10	0.2	10	60.16	3.01
6	11	10	1.4	10	98.04	0.70
7	11	10	0.2	50	84.69	4.23
8	11	10	1.4	50	98.39	0.70
9	3	130	0.2	10	18.27	11.87
10	3	130	1.4	10	49.54	4.60
11	3	130	0.2	50	23.32	15.16
12	3	130	1.4	50	83.74	7.78
13	11	130	0.2	10	29.33	19.06
14	11	130	1.4	10	62.58	5.81
15	11	130	0.2	50	30.35	19.73
16	11	130	1.4	50	87.01	8.08
17	7	70	0.8	30	79.07	6.92
18	7	70	0.8	30	79.26	6.94
19	7	70	0.5	30	54.66	7.65
20	7	70	1.1	30	92.92	5.91
21	7	70	0.8	20	67.91	5.94
22	7	70	0.8	40	81.92	7.17
23	7	40	0.8	30	97.38	4.87
24	7	100	0.8	30	62.33	7.79
25	9	70	0.8	30	82.38	7.21
26	5	70	0.8	30	73.02	6.39

After determining the MB dye concentration, estimation of the adsorption capacity (q_e, mg/g) was done by Eq. (2) and the removal percentage (%) was determined by Eq. (3) [24]:

$$\text{Adsorption capacity}\left(q_e, \frac{\text{mg}}{\text{g}}\right) = \frac{\left(C_0 - C_e\right)}{M} \times V \quad (2)$$

$$\text{Removal efficiency of MB}\left(\%\right) = \frac{\left(C_0 - C_t\right)}{C_0} \times 100 \quad (3)$$

where C_0 is the initial concentration of MB (mg/L) and C_e is the final concentration of MB after reaction time of t based on mg/L, q_e point out the amount of MB adsorbed per unit mass of the AC (mg/g); V is the volume of solution (L), and M is the mass of the CSW-AC (g).

3. Results and discussion

3.1. Characterization of CSW-AC

The physical features of the CSW-AC, examined by scanning electron microscopy (SEM) are shown in Fig. 2a. From Fig. 2a it is clear that there is honeycomb porous structure with high surface area for produced CSW-AC, which extensively can improve the MB removal. The results of BET method (Fig. 2b) indicated that the estimations of the surface area for CSW-AC was 512.530 m^2/g.

The surface chemistry of CSW-AC has been studied using FTIR analysis between 3,900–600 cm^{-1}. The FTIR is an important tool to recognize some significant functional groups that are able to adsorb contaminants [25]. Fig. 3 represents the FTIR spectrum of the adsorbent before and after adsorption process. The bands between 1,500–1,800 cm^{-1} correspond the functional groups such as –C=O and CH_2 stretching, which are the most effective functional groups in comparison with others, located between 900–1,500 cm^{-1} such as C=C, CH_3, C–C, and C–H bands on the surface of prepared activated carbon [5,21].

3.2. Statistical analysis and modeling

The ANOVA was applied to indicate the interactive effects of independent variables on the MB removal process, and modeling the response, dye removal, based on p-values and F-test [3]. The designed experiments and the results of adsorption process by CCD have been

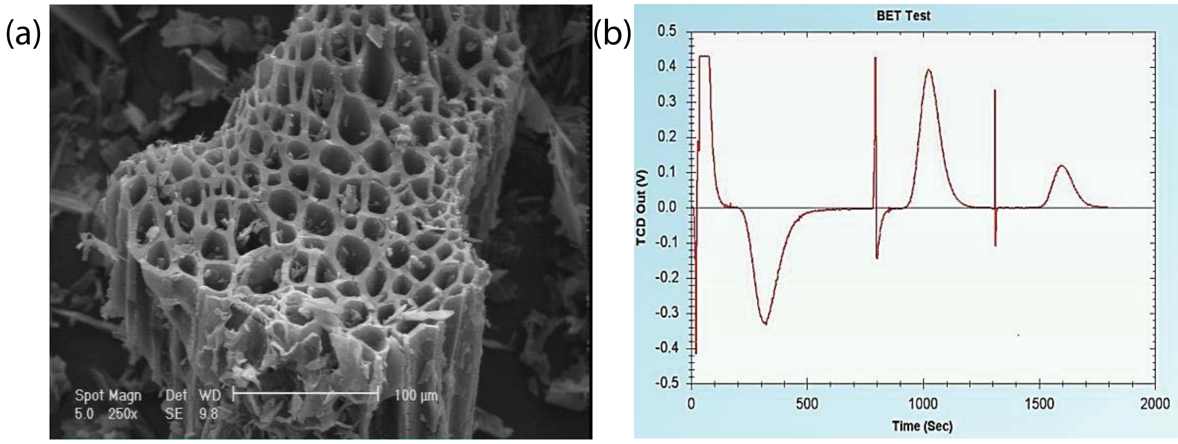

Fig. 2. SEM image (a) and BET test (b) for CSW-AC.

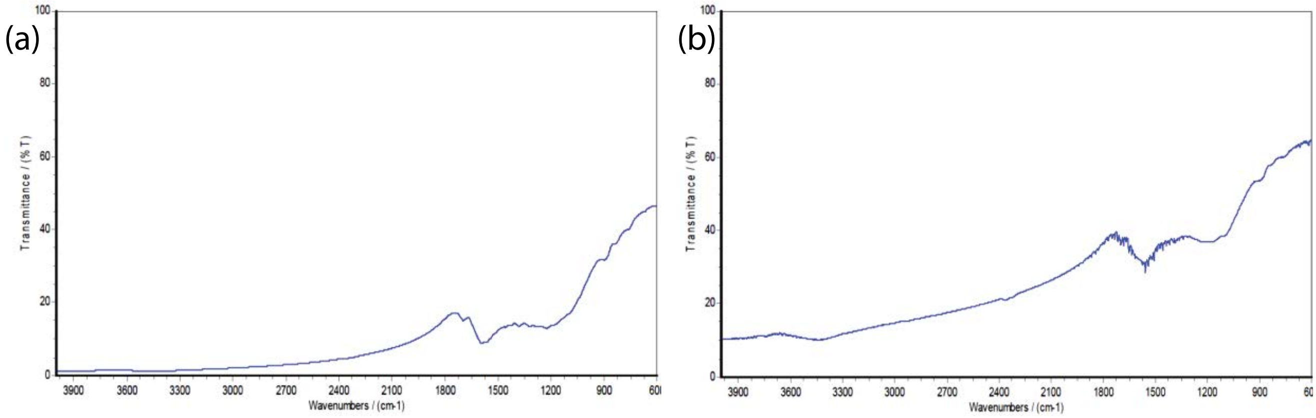

Fig. 3. FTIR spectrum of CSW-AC before and after MB adsorption.

represented in the Table 1 using CSW-AC. A mathematical model [Eq. (4)], quadratic model, has been developed to correlate the MB removal to the adsorption process in order to analyze the effect of variables interactions [7]. Table 2 represents the ANOVA results of quadratic model for dye removal. The statistical regression coefficients less than 5% indicate the significance of all factors for MB removal. The results showed that *p*-values > *F*-values for the percentage removal of MB is lower than 0.05 that indicate a quadratic model was significant. R^2 was found to be 92.63, which implies on the great correlation between predicted and observed removal efficiency. The lack of fit according to Table 3 shows the experimental error (pure error) and residuals. "*F*-value of Lack-of-fit" implies the model correlation between the main variables and response for MB removal, which it is not significant, compared to the pure error and the related *p*-value. The high value of the Adj. *R*-squared and R^2 were estimated 0.9099 and 0.9263 for MB removal, respectively. The results approve the statistical model fitted the adsorption data well and the model can predict MB removal in different conditions. The adequate precision has been used to determine signal to noise ratio, which the value more than 4 indicating the adequateness of model signal [4]. The achieved value of adequate precision in this study was 30.605 for MB, which shows an adequate signal. The results for removing MB by adsorption using the AC indicated that the quadratic model is the best fitness according to Eq. (4).

$$\begin{aligned}\text{MB removal}\left(\%\right) = {} & +77.68 - 18.63A + 18.64B \\ & + 2.87C + 7.89D + 4.67AB \\ & + 1.64AC + 0.39AD - 0.36BC \\ & - 0.081BD - 1.43CD + 10.27A^2 \\ & - 13.99B^2 + 1.65C^2 - 9.49D^2 \end{aligned} \tag{4}$$

The applicability of the quadratic model has been investigated by comparing data achieved through adsorption process for removing MB with the predicted values (Fig. 4a and b). Fig. 4a indicates the high correlation between the observed and predicted values for MB removal. Fig. 4b shows a straight line, which consist of the residuals at different normal % probability.

3.3. Effect of operational parameters

3.3.1. Effects of AC dosage and pH

The effects of the solution pH and AC dosage on the removal of MB, have been investigated by changing the

Table 2
ANOVA results for process responses

Model	Sum of squares	d.f.	Mean square	F-ratio	p-value
	41,527.08	14	2,966.22	56.57	<0.0001
A	17,185.90	1	17,185.90	327.79	<0.0001
B	17,202.11	1	17,202.11	328.10	<0.0001
C	407.12	1	407.12	7.77	0.0070
D	3,084.32	1	3,084.32	58.83	<0.0001
AB	1,047.39	1	1,047.39	19.98	<0.0001
AC	128.31	1	128.31	2.45	0.1227
AD	7.11	1	7.11	0.14	0.7138
BC	6.18	1	6.18	0.12	0.7325
BD	0.32	1	0.32	6.044E-003	0.9383
CD	97.81	1	97.81	1.87	0.1768
A^2	52.66	1	52.66	1.00	0.3201
B^2	97.64	1	97.64	1.86	0.1772
C^2	1.36	1	1.36	0.026	0.8724
D^2	44.92	1	44.92	0.86	0.3582
Residual	3,303.10	63	52.43		
Lack of fit	3,302.98	10	330.30	1.440E+005	<0.0001
Pure error	0.12	53	2.293E-003		
Total	44,830.18	77			
R^2: 92.63; Adj. R-Squared: 90.99; Adeq. precision: 30.605.					

Table 3
Comparison of adsorption capacities of various adsorbents for MB

Precursor	Adsorption capacity (mg/g)	Reference
Clay—biochar	11.94	[30]
Potato peels	33.55	[31]
Coir pith carbon	5.87	[32]
Silkworm exuviae	25.53	[33]
Rice husk activated carbon	9.83	[34]
Tamarind fruit shell	1.72	[35]
Banana peel	20.8	[36]
Orange peel	18.6	[36]
Neem leaf powder	8.76	[37]
Corn stalk wastes	16.16	This study

initial pH (3–11) using different AC dosage (0.2, 0.5, 0.8, 1.1 and 1.4 g/L). The results indicated the significant effect of pH on the adsorption process in the removal of dye (Fig. 5). The pH is another main parameter, which affects the molecule structure of dye and the surface charge of AC [26]. As shown in Fig. 5, the efficiency of MB adsorption increases by increasing pH from 7 to 11 and at low pH range of 3 to 5 almost the efficacy of dye removal was constant. However, the adsorption of MB increased from 73.02% to 82.3% with increasing the pH value from 5 to 9 but the highest dye removal efficiency (87.01%) was obtained at pH 11. At lower pH, the surface charge of AC was positive due to the adsorption of H^+. On the other hand, the MB is a cationic dye so generated positive ions in the solutions. Thus at lower pH, due to electrostatic repulsion between the MB ions and the positively charged surface of AC efficiency was less. At higher pH, the surface charge of the AC was negative, which cause an electrostatic attraction between the negatively charged of AC and cationic dye molecule, which cause an increase in the efficiency of the adsorption process.

The results confirmed that with increasing adsorbent dosage from 0.2 to 0.8 g/L, the percentage removal of MB was negligible. Further increase of AC to 1.1 g/L showed significant increase in the removal of MB (92%). However, the removal of MB was boosted by an increase in adsorbent dosage because of increasing available adsorbent surface area, but the adsorption capacity decreased from 7.65 to 5.91 mg/g. At the higher dosage of AC (1.4 g/L), the efficiency of system slightly decreased. The decrease in adsorption capacity with additional dose of adsorbent is basically due to adsorption sites remaining unsaturated in the adsorption reaction [6]. Similar results have been reported in the literature [27,28].

3.3.2. Effects of MB concentration and contact time

The surface response plots on the interaction with reaction time are depicted in Fig. 6. Fig. 6 displays the effects of the MB concentration (within 10–130 mg/L) and reaction time (within 10–50 min) on the adsorption process of MB. As noticed in the attained results, the efficiency of process was enhanced by increasing the reaction time and decreased with increasing MB concentration. The effect of initial MB concentration on the process was significant,

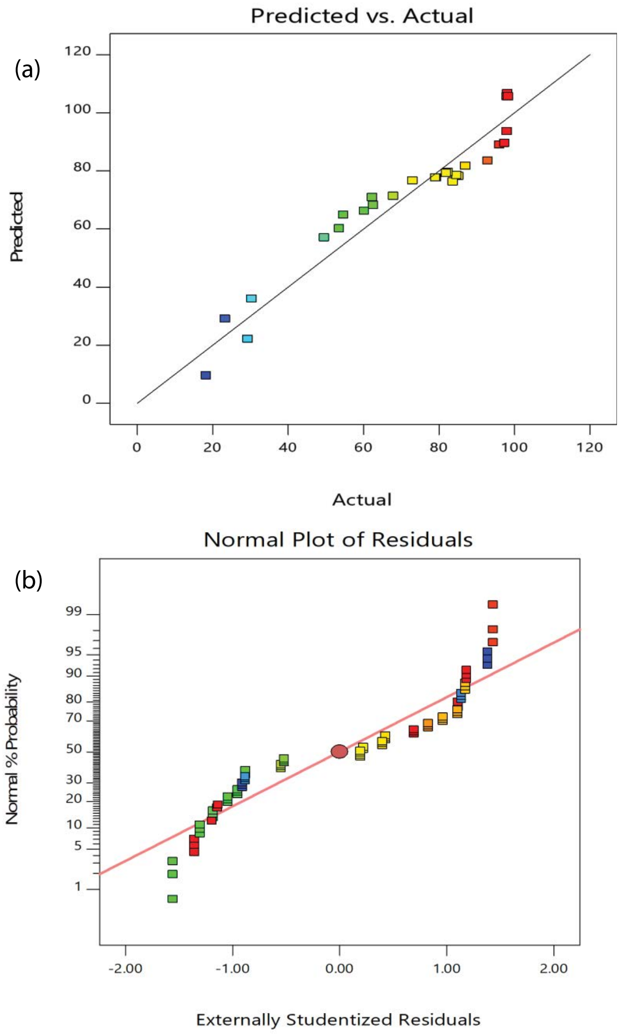

Fig. 4. Experimental data vs. predicted data by the statistical model (a) and normal probability of residuals (b).

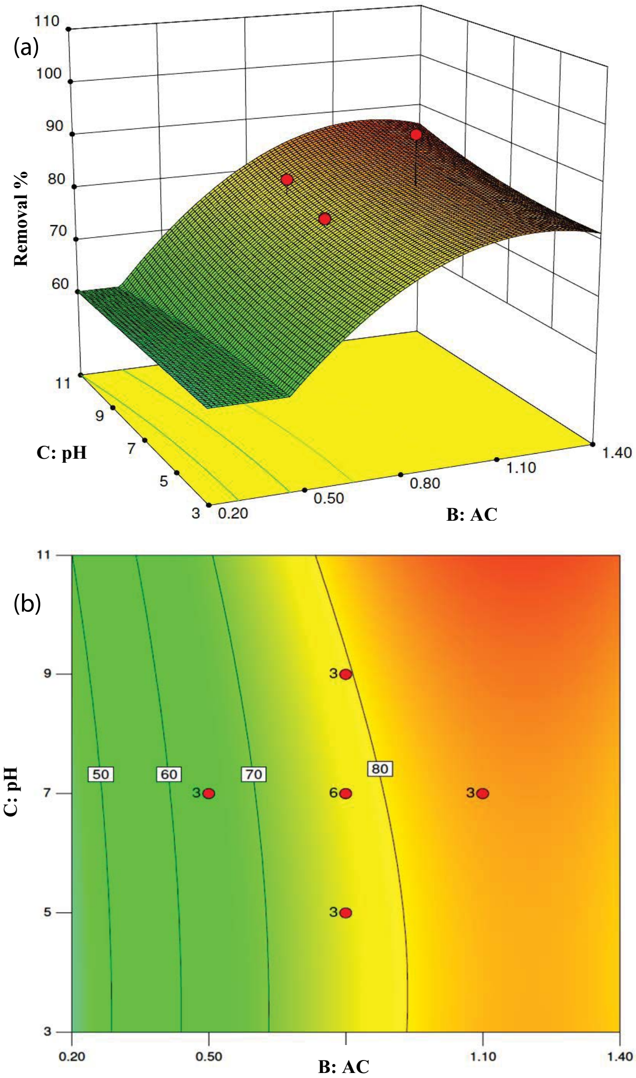

Fig. 5. Response surface plots (a) and response contour plot (b) of pH and AC dosage in the removal of MB (MB = 70 mg/L and contact time = 30 min).

while the result indicated the mild effect of the reaction time on the MB adsorption. Dutta et al. [29] also observed same results in their study; the removal of MB using adsorbent prepared from citrus fruit peel. Their results showed that the increase of MB concentration was cause of decrease in the efficiency of system. The result showed that at the constant time by increasing MB concentration efficiency of system significantly decreased from 98.39% to 87.01% (Table 2). The MB removal slowly increased with an increase in adsorption time at the beginning of process. This condition is due to the presence of a limited number of active sites on the adsorbent surface that can be saturated in the presence of an optimal concentration of dye [27]. The results same as previous studies indicated that the content time had obvious effect on the process, which with more contact time, the transferring mass carried out more from solid to liquid phase until equilibrium condition [29]. Almasi et al. reported same results. They investigated the effect of content time on the removal of Reactive Red 2 using activated carbon prepared from walnut shell. The results indicated that the efficiency of adsorption relatively depend on the contact time. Nevertheless, over time, the ability of adsorbent decreased due to development of first MB layer on the surface of adsorbent [24].

3.4. Process optimization and comparison

With multiple responses, need to be found "sweet spots," regions where requirements simultaneously meet the critical properties. The graphical optimization results present the zone of possible response values in the factor space that allows choosing the optimum operating conditions [26]. Fig. 7 shows the graphical optimization, which indicated the region of possible response values (yellow section) in the factors space. The optimum region was identified based on an MB removal of 90%. In order to verify the accuracy of the model, a point within the optimal area was selected to

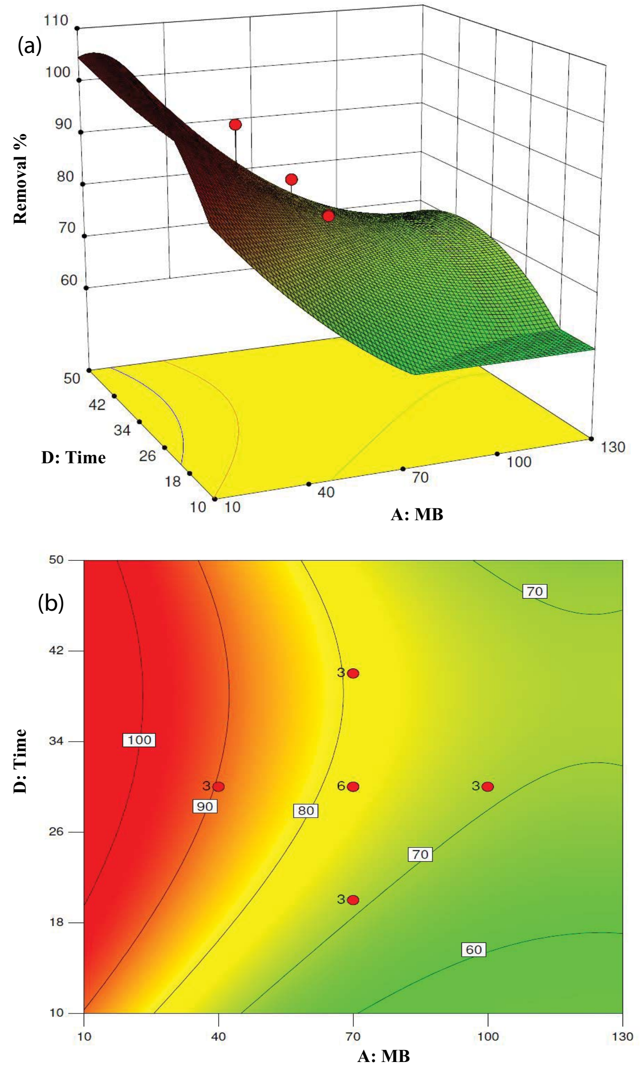

Fig. 6. Response surface plots (a) and response contour plot (b) of MB concentration and contact time in the removal of MB (pH = 7 and AC dosage = 0.8 g/L).

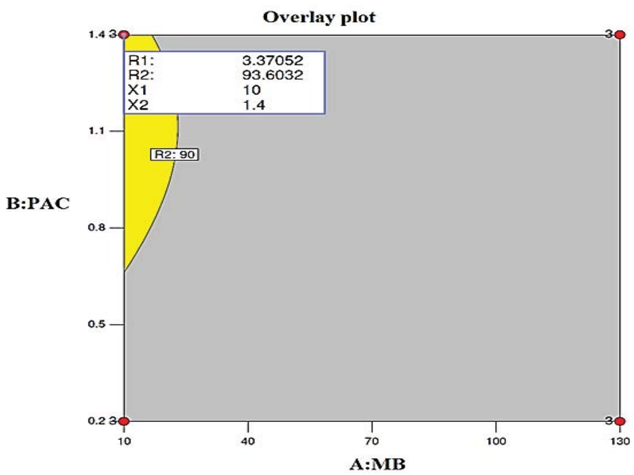

Fig. 7. Overlay plot for the optimum region.

perform in the validation experiment and the actual result was compared with the predicted. The point is chosen within the optimum region (MB concentration = 1.2 mg/L, AC dosage = 100 mg/L and 93.6% removal). The obtained experimental result confirmed that the model was able to make a reasonably accurate prediction for the optimum conditions and the experimental value was determined to be quite close to the model prediction.

The adsorption capacity of prepared AC has been compared with different adsorbents that previously applied in the removal of MB from aqueous solutions (Table 3). The result indicated that the adsorption capacity of MB on the CSW-AC is higher than of many other previously reported adsorbents.

3.5. Adsorption kinetics

Kinetic study is an important aspect in the design of adsorption system because it determines the mechanism and rate of the process, which influenced by many factors associated to the condition of the adsorbent and the physicochemical state in which adsorption process occurs. In this study, pseudo-first-order and pseudo-second-order as conventional kinetics models have been used to study the mechanism of process in the removal of MB. Eqs. (5) and (6) describe the above-mentioned models [38,39].

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{K_1}{2.303}t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad (6)$$

where q_e, and q_t (mg/g) are the amounts of adsorbed dye per unit of adsorbent at equilibrium time (min) and at time t (min), respectively. K_1 (min^{-1}) is the pseudo-first-order rate constant and K_2 (g/mg min) is the pseudo-second-order rate constant.

The plots of kinetic models and the kinetic parameters for different concentrations of MB are represented in Fig. 8a, b and Table 4, respectively. The applicability of models have been examined through two important parameters namely correlation coefficient (R^2) and agreement between the calculated and experimental values of q_e. The high value of R^2 (0.927–0.998) and high agreement between the calculated q_e and the theoretical q_e significantly describe the MB adsorption by the pseudo-second-order kinetic model. Therefore, this evaluation demonstrates that the chemical adsorption is the limited and controlled step in the adsorption process. Similar results were reported for the adsorption kinetics of MB on the activated carbon obtained from waste potato peels [29]. Therefore, this assessment indicates that adsorption sites have more influence on the adsorption rather than the concentration of the dye in the solution [30,31].

3.6. Adsorption isotherms

Previous studies have applied different isotherm models to report the distribution state of contaminant molecules

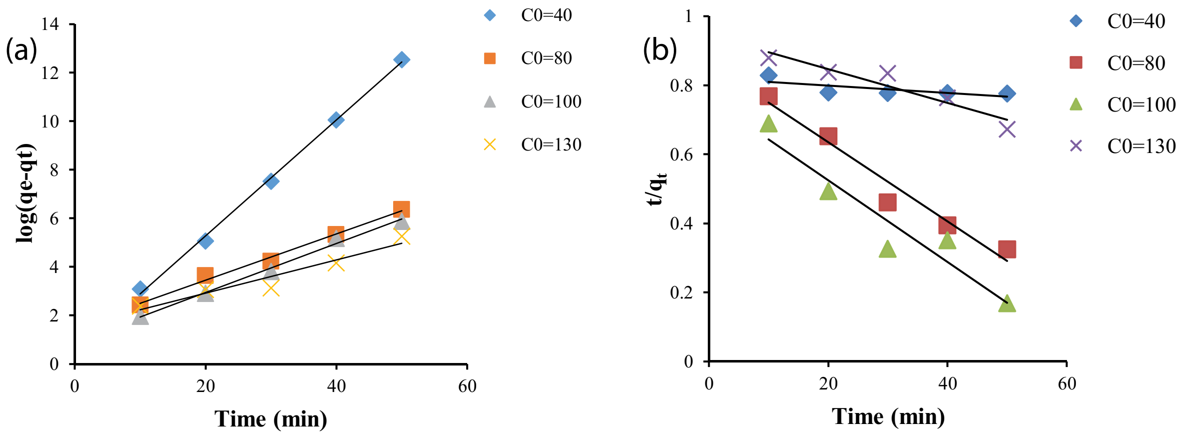

Fig. 8. Pseudo-second-order (a) and pseudo-first-order kinetics for the adsorption (b) of MB onto the AC.

Table 4
Kinetic parameters for the adsorption of MB onto the AC

C_o (mg/L)	$q_{e,\exp}$ (mg/g)	Pseudo-first-order		Pseudo-second-order	
		K_1 (min^{-1})	R^2	K_2 (min^{-1})	R^2
40	4.19	0.0025	0.545	0.114	0.998
80	10.49	0.026	0.96	0.006	0.992
100	9.91	0.027	0.91	0.011	0.993
130	14.62	0.011	0.9	0.003	0.927

between the liquid phase and the solid phase [40–42]. The focus of isotherm study is on the determine the relationship between the equilibrium adsorption capacity and the equilibrium concentration of pollutants under certain conditions to determine capacity, mechanism and behavior of adsorption [27]. The Langmuir and Freundlich models have been used to describe the MB adsorption behavior, which first one assumes the surface adsorption on the adsorbent with homogeneous sites through a monolayer sorption and second one developed based on multi-layer adsorption on heterogeneous surfaces energies [43]. Eqs. (7) and (8) as linear form of aforementioned models have been used to study the mechanism of MB adsorption using AC [44,45].

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{7}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{8}$$

where q_m is the adsorption capacity (mg/g), C_e (mg/L) is the equilibrium concentration of MB, K_F (mg/g) is the Freundlich constant, b (mg/L) is the Langmuir adsorption constant, q_m (mg/g) is the Langmuir maximum adsorption capacity.

The isotherm plots and the equilibrium parameters are shown in Fig. 9 and Table 5. Based on the values of R^2, the Langmuir model with R^2 of 0.98 was more appropriate for the experimental equilibrium adsorption data than the Freundlich model with R^2 of 0.8816, which confirm the monolayers sorption of dye on the CSW-AC (Fig. 9).

4. Conclusion

In this study, CSW-AC was tested and evaluated as a low-cost adsorbent in the removal of MB from aqueous solutions. The CCD was used to investigate the effect of main variables namely solution initial pH, adsorbent dosage, contact time, and initial MB concentration, which have

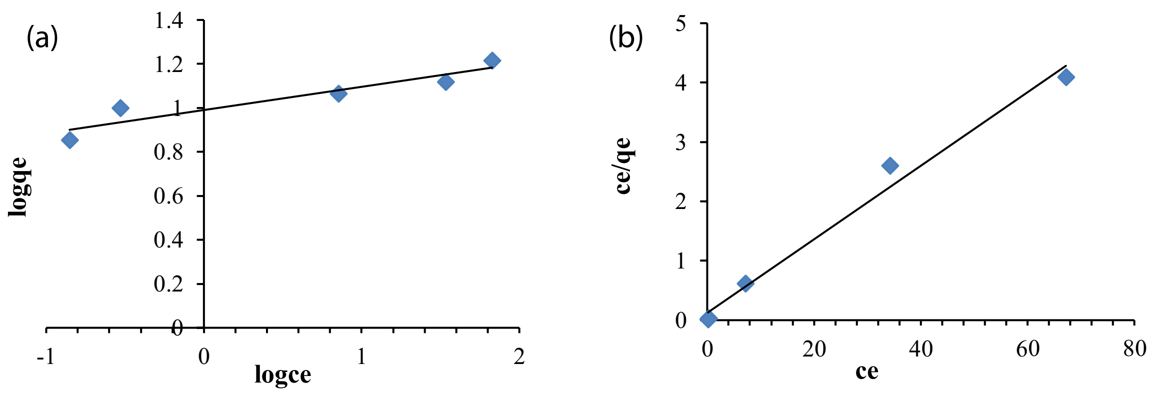

Fig. 9. Adsorption isotherm of MB onto AC, (a) Freundlich adsorption isotherm and (b) Langmuir adsorption isotherm.

Table 5
Langmuir and Freundlich isotherm parameters for MB adsorption

Langmuir isotherm models				Freundlich isotherm models		
R_L	q_m (mg/g)	b (L/mg)	R^2	R^2	n	K_F (mg/g)(L/mg)$^{(1/n)}$
0.019	16.16	0.506	0.9853	0.8816	9.47	9.78

great impact on the adsorption process. Maximum 98% removal of MB has been achieved when 10 mg/L MB has been contacted with 1.4 g adsorbent at ~25°C temperature. Thus, high removal of dye indicates the high capacity of CSW-AC. Removal of MB has also been optimized using RSM. The effects of main variables, and their interaction based on the developed model showed that the initial concentration of MB had the maximum effect on the process. Both the kinetic and isotherm models are investigated to describe the MB adsorption data, showing a higher suitable to the pseudo-second-order reaction and Langmuir adsorption isotherm models, respectively. It was observed that produced AC from corn stalk wastes as a cheap and available adsorbent can be considered as an appropriate method for dye removal from aqueous environment.

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