Utilization of watermelon (Citrullus lanatus) rinds as a natural low-cost biosorbent for adsorption of methylene blue: kinetic, equilibrium and thermodynamic studies

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ABSTRACT
This work presents the viability of biomass waste watermelon (Citrullus lanatus) rinds (WMR) as low-cost adsorbent for the removal of methylene blue (MB) from aqueous solution. The physicochemical properties of WMR were characterized using instrumental analyses such as CHNS-O analyzer, Brunauer-Emmett-Teller (BET), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and point of zero charge (pHpzc) analysis. The kinetic data revealed that the present system obeyed pseudo-second-order kinetic model. The equilibrium data were found to better fit with the Langmuir isotherm model than the Freundlich model. The adsorption capacity of WMR for MB was 188.68 mg/g at 303 K. The thermodynamic adsorption parameters, namely standard enthalpy ($\Delta H^\circ$), standard entropy ($\Delta S^\circ$) and standard free energy ($\Delta G^\circ$) showed that the adsorption of MB onto WMR was spontaneous and exothermic under the experimented conditions. These results indicate that the WMR can be feasibly employed for the eradication of MB from aqueous solution.

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1. Introduction

The release of effluents containing dyes by various industries is a serious environmental issue due to their detrimental impacts upon aquatic organisms and human beings. These discharged dyes are considered source of non-aesthetic pollution and eutrophication, toxic and potentially carcinogenic due to their complex aromatic structures and synthetic nature [1]. Methylene blue (MB) represents one of the most widely used basic dye for dyeing cotton, wool and silk. MB has been known to cause several adverse health effects, such as dysfunction of brain, liver, kidney, reproductive and central nervous system [2]. Effective elimination of MB from industrial effluents has therefore received increasing attention.

Many wastewater treatment methods including adsorption [3–7], electrochemical treatment [8], membrane filtration [9], Fenton chemical oxidation [10] and photocatalysis [11–16] have been studied for the removal of MB. Of all these techniques, adsorption is extensively preferred due to its effectiveness, simplicity, flexibility and ease of operation without generating hazardous secondary products [4,5]. Moreover, there are many types of adsorbents available for MB removal. Activated carbon is the most commonly applied adsorbent for removal of a vast variety of dyes, including MB, but is deemed too expensive and difficult for regeneration [17]. Therefore, there have been demands for alternative low-cost adsorbents in order to make the adsorption process a viable wastewater treatment technology [18,19]. In recent years, adsorption process by means of biomass wastes has been regarded as the most affordable and feasible option for removal of dyes. Hence, the past few years have seen the successful applications of fruit peels such as orange peel [20,21], mango peel [6], pomelo peel [22], grapefruit peel [23], lemon peel [24], banana peel [21, 25,26], jackfruit peel [27], durian peel [28] and passion fruit peel [29,30] for removing dyes from aqueous solution via adsorption process.

Watermelon (Citrullus lanatus) being a very famous short-term non-seasonal fruit in Malaysia has been categorized under major fruits by the Ministry of Agriculture and Agro-based Industry, with an average production of 154,416 tones [31]. The refreshing and diuretic properties of its red flesh present inside, together with its pleasant taste, make it a popular choice for producing juices and salads. However, the outer watermelon rind (WMR) is regarded as waste which possesses no commercial value. The WMR consists proteins [32],
carotenoids, cellulose [33], citrulline [34] and pectins [35] which are abundant with functional groups such as hydroxyl, carboxyl and amine that can easily attract cationic compounds. The present work aims to investigate the use of untreated WMR as a low-cost adsorbent for the removal of MB from aqueous solution through batch mode adsorption studies at varying experimental conditions. The physicochemical properties of WMR before and after MB adsorption were evaluated in order to understand the adsorption behaviour of MB onto WMR.

2. Materials and methods

2.1. Adsorbate (MB)

MB (C₁₆H₁₈Cl₃S.xH₂O, molecular weight: 319.86 g/mol) attained from R&M Chemicals was applied as an adsorbate. All MB solutions were diluted with 18 MΩ cm ultra-pure water.

2.2. Preparation of WMR as adsorbent

The WMR was obtained from a local fresh juice shop in Penang, Malaysia. WMR was firstly washed with water and then dried at 105°C in the oven for 24 h to remove the moisture contents. The dried WMR was subsequently ground and sieved to the size of 1–2 mm. The ultimate elemental analysis of WMR was executed using a CHNS-O analyzer (Perkin-Elmer, Series II, 2400). The surface morphology of WMR before and after adsorption of MB was observed using a scanning electron microscope (SEM; FESEM CARL ZEISS, SUPKA 40 VP). The functional groups of WMR before and after MB were studied via Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer, Spectrum RX I) in transmission mode with a spectral range from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹. All samples were prepared with spectroscopic grade KBR which comprises ∼80% (w/w) of the total sample and were evaluated in the form of finely ground powders. The pH at the point-of-zero charge (pHₚζc) was estimated by the solid addition method using a pH meter (Metrohm, Model 827 PH Lab, Switzerland), as described by Lopez-Ramon et al. [36].

2.3. Batch mode adsorption experiments

The batch mode adsorption experiments of 100 mL MB onto WMR were carried out in 250 mL capped Erlenmeyer flasks and were agitated in an isothermal water bath shaker (Memmert waterbath, model WNB7–45, Germany) at fixed shaking speed of 120 stroke min⁻¹ and 303 K until equilibrium was achieved. Batch mode adsorption experiments were performed by varying the adsorbent dosage (0.02–0.20 g), solution pH (3–10), initial MB concentration (50–400 mg/L), and contact time (0–180 min) to determine the optimum uptake conditions for MB adsorption. For the quantification of the adsorbed MB, the supernatant of the WMR-MB mixture was collected with a 0.20 μm Nylon syringe filter and the concentrations of MB were monitored at different time interval using a HACH DR 2800 Direct Reading Spectrophotometer at the maximum wavelength (λₘₐₓ) of absorption at 661 nm. In the thermodynamic study, similar procedures were applied at 313 and 323 K, with the other parameters held constant. Blanks tests were carried out to account for the colour leached by the adsorbent and adsorbed by the glass containers, in which blank runs with only the adsorbents in 100 mL of ultra-pure water and 100 mL of MB solution without any adsorbent were conducted concurrently at similar conditions. The adsorption capacity at equilibrium, qₑ (mg g⁻¹) and the percentage of colour removal, Rₑ (%) of MB were calculated using Equations (1) and (2):

\[ qₑ = \frac{Cₒ − Cₑ}{W} \]  \hspace{1cm} (1)

\[ Rₑ (%) = \frac{Cₒ − Cₑ}{Cₒ} \times 100 \]  \hspace{1cm} (2)

Co is the initial MB concentration (mg/L); Ce is the MB concentration at equilibrium (mg/L); V is the volume of MB solution (L) and W is the dry mass of adsorbent WMR (mg). Adsorption experiments were conducted in triplicate under identical conditions and the results are reported as an average value.

3. Results and discussion

3.1. Characterization of WMR

The outcome of the ultimate elemental analysis of WMR indicates that oxygen (51.50 wt.%) and carbon (41.50 wt.%) are the major constituents of WMR along with the quantifiable amount of hydrogen (6.12 wt.%) and nitrogen (0.88 wt.%). The pattern of adsorption onto biomass materials is highly associated with the availability of the active functional groups and bonds of the WMR surface. For the elucidation of these active sites, FTIR spectroscopy was performed upon the WMR before and after MB adsorption. Several IR bands appearing in the FTIR spectrum of WMR before adsorption (Figure 1(a)) that signify various functional groups, in accordance with their respective wavenumber (cm⁻¹) position, are as reported in the literature [37]. The broad and intense band at 3375 cm⁻¹ is attributed by the –OH stretching vibrations of cellulose, pectin and lignin while the band at 2922 cm⁻¹ corresponds to the –CH stretching vibrations of the methyl group. The band at 1735 cm⁻¹ indicates the C = O stretching of carboxylic acid or esters. The asymmetric and symmetric vibrations of –COO of the ionic carboxylic groups within WMR are represented by the band at 1630 and 1433 cm⁻¹, respectively. The band at 1380 cm⁻¹ can be ascribed to the symmetric stretching of –COO of
pectin. The IR bands between the 1300 and 1000 cm$^{-1}$ region are assigned to the C–O and C–O–C stretching vibrations in carboxylic acids, alcohols, phenols or ester groups. Thus, the IR spectral of WMR before MB adsorption strongly shows that the external surface of WMR is rich in carboxylic and hydroxyl groups, which can be deprotonated to bind the positively charged MB. As depicted by the IR spectral of WMR after MB adsorption (Figure 1(b)), some of the bands shifted and became more pronounced in which the attenuated bands at about 1620 cm$^{-1}$ (–N–H bending) and 1240 cm$^{-1}$ (C–N vibration) suggest the interaction of MB molecules with...
the functional groups of WMR. The reductions in the band intensities upon adsorption were also observed by Kallel et al. [38] for the adsorption of MB onto garlic straw. The pH_pzc of WMR was determined to find out the pH at which the electrical charge of the surface of WMR was zero. Figure 2 shows that the pH_pzc of WMR was at pH 4.3 which reflected the acidity of WMR, in agreement with the aforementioned IR results (Figure 1) that carboxylic acids are present in abundance within WMR. Adsorption of anions is favoured at solution pH below the pH_pzc value as the surface of WMR is positively charged due to protonation whereas at solution pH above the pH_pzc value, the surface of WMR becomes negatively charged and thus, adsorption of cations is preferred. In this regard, it is predicted that the adsorption of the cationic MB by WMR will be appropriate at solution pHs above 4.3 because of electrostatic interactions. The surface morphology of WMR before and after MB adsorption was observed based on the SEM images presented in Figure 3. According to Figure 3(a), the WMR before MB adsorption possesses uneven and irregular surface with considerable layers of rough heterogeneous pores which offers high possibility for dye molecules to be adsorbed [39]. Thus, the SEM image of WMR after MB adsorption in Figure 3(b) reveals smoother surface features with apparent reduced pore structures, indicating the uptake and entrapment of MB molecules by the accessible pore vicinities of the WMR surface. Figure 3(b) proves the engagement of MB onto WMR and this may be related to the presence of carboxylic and hydroxyl groups within WMR, as evidenced by the IR spectral (Figure 1) discussed earlier on, which act as active sites for the adsorption of MB molecules.

3.2. Batch mode adsorption of MB

3.2.1. Effect of adsorbent dosage

The effect of the adsorbent dosage on the removal of MB by WMR was studied using varying amount of WMR, ranging from 0.02 to 0.20 g at fixed MB volume of 100 mL and initial dye solution, C_0, of 100 mg/L. During this experiment, other operational parameters were held constant at 303 K, shaking speed of 120 stroke/min, contact time of 180 min and an unadjusted pH value of 5.6 for the initial MB solution. The outcome of this experiment showed that the removal MB increased proportionally with the WMR dosage until 0.06 g and further addition rendered no significant impact on the MB removal percentage. The increase in the MB removal with the increasing mass of WMR was attributed to the greater number of adsorption sites on the adsorbent surface which allowed more bindings of MB molecules with WMR [27]. However, further addition of WMR dosage beyond 0.06 g did not see any improvement in the adsorption percentage of MB. This observation could be caused by the aggregations of WMR particles at higher dosages which led to decrease in the effective surface area of WMR for MB uptake. Therefore, 0.06 g of WMR was selected for the following experiments.

3.2.2. Effect of pH

The pH value of the solution, which influences the surface charge of the adsorbent and the speciation magnitude of dye, plays a vital role in governing the adsorption process. Figure 4 shows the effect of pH on the adsorption of MB onto WMR. As observed, the adsorption of MB onto WMR increased gradually with the increasing solution pH up to pH 5.0 after which further increase in pH values exhibited no significant changes. Lower value of adsorption capacity at acidic pH may be either due to excess concentration of H+ ions competing with the MB dye cations for adsorption sites. Moreover, at solution pH < pH_pzc = 4.3, the surface of WMR was essentially positively charged and thus, repulsion between the MB cations and the WMR may have occurred and decreased the MB adsorption capacity. On the other hand, as the pH of the process increased, the surface of WMR was likely to adopt negative surface charges and became increasingly favourable for MB adsorption due to electrostatic
forces of attraction. The observation that the adsorption of MB remained almost constant from pH 5.0 onwards may be due to the complete deprotonation of the active group, i.e., COOH $\rightarrow$ COO$^-$ of WMR surface when the solution pH surpassed 5 \[40\]. Thus, the optimum pH for the removal of MB by WMR was at pH 5.0–6.0. Since the unadjusted pH of the initial MB solution (5.6) lies within the optimal pH range and in order to lessen chemical and time consumptions, further experiments on the adsorption of MB by WMR were conducted at pH 5.6.

3.2.3. Effect of initial dye concentration and contact time

The study on the effect of initial concentration and contact time on MB adsorption onto WMR shows that the adsorption process at the initial stage was fast with respect to the contact time and gradually became slower as equilibrium state was approached. At the initial stage of the adsorption process, there were more vacant active surface sites of WMR which were available for the uptake of MB molecules and as the time lapsed, the availability of the sites became limited which led to the slowing down of the process. The increase in the initial concentration of MB, however, increased the adsorption capacity of WMR. The amount of MB adsorbed by WMR at equilibrium increased significantly from 77 to 196 mg/g as the initial concentration of MB was increased from 50 to 400 mg/L. This effect can be ascribed to the enhanced driving force of the mass transport of MB molecules towards the active pores within the inner depth of WMR at higher initial dye concentration. At low initial MB concentration, even though the driving force was slower, the uptake of the limited amount of the dye by WMR led to faster establishment of the equilibrium state. However, at higher concentration of MB, the attainment of equilibrium state required longer time to achieve since higher driving force allowed the MB molecules to penetrate deeper into the porous interior of the adsorbent \[28\]. This explanation corroborates with the outcome of this experiment, whereby 50 mg/L of MB took 30 min to reach the adsorption equilibrium state while MB with concentration of 400 mg/L required 150 min. Hence, it is shown that initial dye concentration plays an important role in the adsorption capacity of MB by WMR. Similar findings have been reported for MB adsorption onto other biomass wastes \[25,41\].

3.3. Adsorption isotherm studies

The adsorption equilibrium data of MB onto WMR was assessed using the two commonly used isotherm models to describe the interaction between the adsorbent and the adsorbate with the quality of the fit evaluated using the coefficient of determination, $R^2$ values. The Langmuir isotherm model assumes that the adsorption is localized on a monolayer and all adsorption sites at the adsorbent are structurally homogeneous, with no interaction between molecules adsorbed on adjacent sites \[42\]. The adsorbent possesses the finite adsorption capacity in which no further adsorption can occur once a molecule occupied a site and reached an equilibrium saturation point \[43\]. The linear mathematical expression of Langmuir isotherm is represented by Equation (3):

$$\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{1}{q_m}C_e$$
where $C_e$ is the equilibrium concentration (mg/L) and $q_e$ is the amount of adsorbed species per specified amount of adsorbent (mg/g) while $K_L$ (L/mg) and $q_m$ (mg/g) are the Langmuir constants associated to the adsorption affinity and capacity, respectively. Thus, a plot of $C_e/q_e$ vs. $C_e$ should yield a straight line with a slope $(1/q_m)$ and intercept $(1/q_mK_L)$ as shown in Figure 5(a). On the contrary, the Freundlich adsorption isotherm is based on the assumption that the adsorption occurs on heterogeneous surfaces of non-identical sites with different energy of adsorption. This empirical isotherm model is often employed to describe multilayer adsorption with interaction between the adsorbed molecules and is not limited to monolayer formation of adsorbate molecules on the adsorbent [44]. The well-known linear mathematical form of Freundlich isotherm is shown by Equation (4):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$  

(4)

where $K_F$ [mg/g (L/mg)$^{1/2}$] and $1/n$ are the Freundlich isotherm constants related to the adsorption capacity and intensity, respectively. The $K_F$ and $n$ values can be derived from the intercept and slope of the $\ln q_e$ vs. $\ln C_e$ plot given in Figure 5(b). The Langmuir isotherm model showed better fit for the MB adsorption equilibrium data, as evidenced by the greater $R^2$ value (0.983) as compared to that of the Freundlich model (0.672).
Table 1. Comparison of adsorption capacities for MB by different untreated fruit peels adsorbents.

| Fruit peels adsorbents | Adsorbent dosage (g) | Adsorption capacity, \( q_m \) | References |
|------------------------|----------------------|-----------------------------|------------|
| Orange peel            | 0.10 g/100 mL        | 218 mg/g                    | [20]       |
| Orange peel            | 0.10 g/100 mL        | 18.60 mg/g                  | [21]       |
| Pomelo peel            | 0.40 g/100 mL        | 133 mg/g                    | [22]       |
| Banana peel            | 0.10 g/100 mL        | 20.80 mg/g                  | [21]       |
| Banana peel            | 1 g/1000 mL          | 18.65 mg/g                  | [25]       |
| Banana peel            | 0.10 g/100 mL        | 111.11 mg/g                 | [26]       |
| Jackfruit peel         | 0.60 g/200 mL        | 285.71 mg/g                 | [27]       |
| Yellow passion fruit   | 1 g/50 mL            | 0.0066 mmol/g               | [29]       |
| Yellow passion fruit   | 1 g/100 mL           | 44.7 mg/g                   | [30]       |
| WMR                    | 0.12 g/100 mL        | 188.68 mg/g                 | This work  |

The dimensionless separation factor, \( R_L \), associated to Langmuir isotherm can be obtained to evaluate the feasibility of the adsorption on the adsorbent [45] by using Equation (5):

\[
R_L = \frac{1}{1 + K_L C_0} 
\]

where \( C_0 \) refers to the initial concentration of the adsorbate. The value of \( R_L \) indicates the adsorption process to be either irreversible (\( R_L = 0 \)), favourable (\( 0 < R_L < 1 \)), linear (\( R_L = 1 \)) or unfavourable (\( R_L > 1 \)). The obtained \( R_L \) values at different MB concentrations are in the range of 0–1 for all initial concentrations, indicating that the adsorption of MB onto WMR is a favourable process. The \( R_L \) values gradually decrease as the concentrations were increased, showing that higher initial concentration of MB may improve the adsorption process [46].

Based on the Freundlich isotherm model, the slope, \( 1/n \) ranging between 0 and 1, is a measure of surface heterogeneity, whereby the surface is more heterogeneous as the \( 1/n \) value approaches zero. A value of \( 1/n < 1 \) indicates a normal Langmuir isotherm while \( 1/n > 1 \) is reflective of cooperative adsorption [47]. Moreover, the value of exponent \( n > 1 \) is an implication of a favourable adsorption process. In this case, the obtained \( 1/n \) value for WMR is below unity, indicating that the favourable MB adsorption process conformed a normal Langmuir isotherm characteristic. These results affirmed that the surface binding sites of WMR are homogeneous in nature whereby each MB is attached with similar adsorption energy. The results show that the formation of a surface monolayer of MB molecules for WMR, in which the monolayer adsorption capacity, \( q_m \), for WMR towards MB was compared against that of the other types of fruit peels in Table 1. As listed in Table 1, WMR exhibits higher MB adsorption capacity when compared with some of the untreated fruit peels. Only the jackfruit and orange peels tested by Boumediene et al. [20] and Hameed [27], respectively, show greater MB adsorption capacity than WMR. This proves the viability of WMR as one of the most superior adsorbents for removal of MB from aqueous solution.

3.4. Adsorption kinetic studies

The adsorption kinetic of MB onto WMR data were analysed using the pseudo-first-order (PFO) and pseudosecond-order (PSO) model to determine the adsorption rate and to explain the adsorbate–adsorbent interactions that occurred. The conformity between the experimental data and the model predicted values was presented by the coefficient of determination, \( R^2 \) values. The PFO is constructed based on the prediction that the change of adsorbate uptake rate with time is proportional to the difference in concentration at equilibrium and the amount of adsorbed adsorbate with time [48] and is expressed as Equation (6):

\[
\ln (q_e - q_t) = \ln (q_e) - k_1 t
\]

where \( q_e \) (mg/g) and \( q_t \) (mg/g) are the amount of adsorbate adsorbed onto adsorbent at equilibrium and time \( t \), respectively, while \( k_1 \) is the PFO rate constant. The \( k_1 \) values can be determined from the slope of the plot of \( \ln(q_e - q_t) \) vs. \( t \) shown in Figure 6(a). Meanwhile, the PSO is based on the assumption that the rate-limiting step of the adsorption process may be chemisorption involving sharing or exchange of electrons between adsorbent and adsorbate [49]. The linear form of the PSO model is described by Equation (7):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( k_2 \) (g/min mg) is the PSO rate constant. The \( k_2 \) and theoretical \( q_{e,cal} \) values can be calculated from the intercept and slope of the \( t/q_t \) vs. \( t \) plot depicted in Figure 6(b). The kinetic data for the adsorption of MB onto WMR were calculated from the related plots and are tabulated in Table 2. The presented data shows that the MB adsorption kinetic data was better fitted by the PSO model with \( R^2 \) values of ≥ 0.997 for all tested concentrations. This result infers that the rate of MB adsorption onto WMR seemed to be governed by chemical process that involved sharing of electrons or by covalent forces through exchanging of electrons between adsorbent and adsorbate. Similar finding was obtained for the adsorption of MB onto orange peel [20] and jackfruit peel [27].

3.5. Adsorption thermodynamics studies

The thermodynamic parameters of adsorption of MB onto WMR were derived from the experimental data obtained at 303, 313 and 323 K to deduce the nature and thermodynamic feasibility of the adsorption process. The standard free energy change (\( \Delta G^\circ \)), enthalpy change (\( \Delta H^\circ \)) and entropy change (\( \Delta S^\circ \)) related to the adsorption processes are calculated using
Equations (8)–(10):

\[ k_d = \frac{q_e}{C_e} \]  
\[ \Delta G^\circ = -RT \ln k_d \]  
\[ \ln k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \]

where \( k_d \) is the distribution coefficient, \( q_e \) is the concentration of MB adsorbed onto WMR at equilibrium (mg/L), \( C_e \) is the equilibrium of MB in the liquid phase (mg/L), \( R \) is the universal gas constant (8.314 J/mol K),

Table 2. Comparison of the PFO and PSO models for the adsorption of MB on WMR.

| Concentration (mg/L) | 50    | 100   | 200   | 300   | 400   |
|----------------------|-------|-------|-------|-------|-------|
| **PFO**              |       |       |       |       |       |
| \( q_{e,exp} \)      | 77.222| 146.233| 163.623| 166.667| 196.347|
| \( q_{e,cal.} \)     | 9.982 | 80.294| 82.179| 70.654| 145.82 |
| \( k_1 \)            | 0.0516| 0.0326| 0.0141| 0.0129| 0.0237 |
| **PSO**              |       |       |       |       |       |
| \( q_{e,cal.} \)     | 77.519| 153.846| 166.667| 166.667| 204.082|
| \( k_2 \)            | 0.0213| 0.0007| 0.0007| 0.0008| 0.0004 |
| \( R^2 \)            | 1.000 | 0.998 | 1.000 | 0.998 | 0.997  |

Figure 6. Kinetic profiles for the adsorption of MB onto WMR: (a) PFO (b) PSO.
and $T$ is the absolute temperature (K). The values of $\Delta H^\circ$ and $\Delta S^\circ$ were calculated from the slope and intercept of Van’t Hoff plot ($\ln k_d$ vs. $1/T$) given in Figure 7 and the values of the parameters are listed in Table 3. As the adsorption temperature increased, the values of $k_d$ decreased, indicating that the MB adsorption capacity of WMR decreased with the rise of temperature and this suggested that the adsorption process was exothermic in nature. The observation can be attributed to the weakening of bonds between the adsorbate molecules and active sites of adsorbents at high temperatures [50]. The negative $\Delta G^\circ$ values advocated that the adsorption process was spontaneous and more favourable at low temperature. Negative value of $\Delta H^\circ$ ($-6.267$ kJ/mol) confirmed the exothermic nature of the adsorption process and the negative $\Delta S^\circ$ ($-1.503$ J/mol K) value revealed the decrease in the randomness at solid-solution interface. There is an unequal release of energy during the adsorption process and the magnitude of $\Delta H^\circ$ value offers information about the forces that governed the adsorption process. The energy ($\Delta H^\circ$) related to physical forces: van der Waals (4–10 kJ/mol), hydrophobic interaction (5 kJ/mol), hydrogen bonding (2–40 kJ/mol), coordination exchange (40 kJ/mol), dipole bond forces (2–29 kJ/mol) and electrostatic interaction (20–80 kJ/mol) while for chemical forces ($>60$ kJ/mol) [51]. In this work, the $\Delta H^\circ$ value was found 6.267 kJ/mol, confirming that physical forces were involved in the adsorption of MB onto WMR.

**Table 3.** Thermodynamic parameters values for the adsorption of MB onto WMR.

| Temperature (K) | $k_d$ | $\Delta G^\circ$ (kJ/mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (J/mol K) |
|----------------|-------|---------------------------|---------------------------|---------------------------|
| 303            | 10.18 | -5.811                    | -6.267                    | -1.503                    |
| 313            | 9.01  | -5.796                    |                           |                           |
| 323            | 8.74  | -5.781                    |                           |                           |

**Conclusion**

The biomass waste WMR exhibited great potential as low-cost adsorbent for effective removal of MB from aqueous solution. Physicochemical characterizations revealed that the carboxyl and hydroxyl groups of WMR play important role in the adsorption of MB. The optimum WMR dosage was 0.06 g and superior MB adsorption capacity was obtained in solution pH 5 onwards. The adsorption increased with increasing MB concentration. The adsorption equilibrium data obeyed the Langmuir isotherm model and the monolayer adsorption capacity, $q_m$, was found to be 188.68 mg/g. Meanwhile, the PSO model was determined to be better fit for the kinetic data as compared to the PFO model. The thermodynamic parameters values showed that the MB adsorption by WMR was a spontaneous and exothermic process. The WMR showed greater adsorption capacity towards MB than other fruit peels and can be easily prepared without any chemical treatment. For future studies, the usability of WMR for pollutants removal from real wastewater will be tested and as comparison, a fixed bed column will be employed to investigate the effect of reactor design.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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