Adsorptive removal of methylene blue by chemically treated cellulosic waste banana (*Musa sapientum*) peels

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**ABSTRACT**

Acid-treated banana peel (ATBP) was developed by H\textsubscript{2}SO\textsubscript{4} activation to be a potential adsorbent for methylene blue (MB) from aqueous solution. Batch mode adsorption studies were conducted by varying adsorbent dosage (0.02–0.30 g), solution pH (3–12), initial MB concentrations (10–300 mg/L) and contact time (0–1440 min). The adsorption data of MB by ATBP were in agreement with Langmuir isotherm, with maximum adsorption capacities of 250 mg/g at 303 K. The pseudo-first-order kinetic model best described the kinetic data. The adsorption of MB onto ATBP surface was endothermic in nature and spontaneous under the experimented conditions. Results supported the potential use of the ATBP as an effective adsorbent for the treatment of cationic dyes such as MB from aqueous solution.

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**1. Introduction**

Over the years, the quality of water is reducing due to the anthropogenic activities, population growth, unplanned urbanization, unskilled utilization of natural water resources and rapid industrialization. Textile, rubber, paper, plastics, leather and food industries use dyes to colour their products while remaining unspent dyes are settled into natural water bodies. The discharge of dye-contained wastewaters into ecosystem is a dramatic source of aesthetic pollution, eutrophication and perturbation in aquatic life as most of dyes are highly visible, stable and unaffected to chemical, photochemical as well as biological degradation [1–3].

Methylene blue (MB) is a thiazine/cationic dye, which is most commonly used for colouring among all other dyes of its category. It is selected to represent a group of dyes, which are commonly large in molecular size and difficult to be degraded in natural environment. It is generally used for dyeing cotton, wool, silk, textiles and leather, printing calico and biological staining methods [4]. Owing to its high water solubility, wastewater containing MB is hazardous to environment and human health. It causes a noticeable coloration and classified as toxic colorants at concentration as low as 1 mg/L [5]. Due to this fact, the discharged of MB into water bodies contribute major aesthetic and ecological problems. The presence of MB in water hindered the transmission of sunlight thus reducing the photosynthesis activities of aquatic flora and oxygenation of water reservoirs. While from the human health angle, MB results in harmful effects such as eye irritation, gastrointestinal irritation and nausea upon ingestion, including vomiting and diarrhoea [6]. Removal of MB from wastewater is a main environmental challenge and there is a continuous need to have an effective procedure that can efficiently remove it economically.

A wide range of chemical and physical treatment technologies are available for dyes removal with different degree of accomplishment to minimize water contamination. These technologies include bioremediation [7], electrochemical degradation [8], cation exchange membranes [9], Fenton chemical oxidation [10] and photocatalysis [11,12]. However, the shortcomings of most of these methods are high operational and maintenance costs, generation of toxic sludge and complex procedure involved in the treatment [13]. In contrary, adsorption has been massively proved to be a well-established and most widely used technique among other water purification processes. This technique is the procedure of choice and gives the best results as it can be used to eliminate suspended solids, odours, organic matter and oil from aqueous solutions. Adsorption-based treatment with suitable adsorbent materials shows high performance and selectivity, flexibility and simplicity of design, convenience of operation without producing harmful by-products as well as economically cost effective [14]. An excellent adsorbents for adsorption process of dye molecules should meet several conditions, such as; low cost, readily available, large capacity and rate of adsorption, high selectivity for different concentrations and efficient for removal of a wide variety of target dyes [15].
Activated carbon (AC) is a carbonaceous materials [16], with high porosity [17–21], high physicochemical stability [22], high adsorptive capacity [23], high mechanical strength [24,25], high degree of surface reactivity [26,27], with immense surface area [28,29] which can be differentiated from elemental carbon by the oxidation of the carbon atoms that found at the outer and inner surfaces [30]. Therefore, AC has been broadly exploited in versatile applications such as gas separation, solvents recovery, gas storage, super capacitors electrodes, catalyst support, adsorbent for organic and inorganic pollutants from drinking water, and so on [31]. However, a high cost of commercialized AC production limits its application in various technologies. Recognizing this economic obstacle, researchers have been made extensive efforts in low-cost alternatives to AC from a range of carbonaceous precursors, such as ligno-cellulosic materials [32], biopolymer [33], coal [34], char [35], and fruit peels [36]. The textural properties and adsorption capacities of AC are mainly depend on the nature of the precursor, activation method, type of activation agent and preparation mode [37].

Chemical surface modification methods are widely used to prepare hydrophilic carbonaceous materials and biochar. Hydrophilicity of the carbonaceous materials is associated essentially with the presence of oxygen containing groups on the surface such as carboxylic, phenolic and lactonic groups. Sulphuric acid (H$_2$SO$_4$) as a super oxidizing agent was frequently used in liquid phase oxidation process for enhancing the oxygen content on the treated surface [38]. Researches had been demonstrated that the amount of oxygen containing surface functional groups, specific surface area and pore structure highly depend on the concentration of activation agents. While oxygen content of carbonaceous materials usually increases with the increase of activation agent concentration, the surface area and pore volume values decrease adversely [39]. Nowadays, interests are growing in the utilizing of agricultural waste and food residues as low-cost and steady sources for the developing rich carbonaceous materials with multifunctional functional groups that can be potentially applied for removal of water pollutants.

In Malaysia, banana (Musa sapientum) is massively cultivated and remains the second most important fruit crop after durian [40]. As the processing industries of bananas is growing, huge quantities of banana peel (BP) are generated. It is thus significant and even essential to find applications for this waste. The texture of BP is porous and formed by cellulose, hemicellulose, pectins, lignin, starch and proteins, peculiarities that have motivated several applications [41]. The use of BP as a precursor for producing biochar will provide solution to environmental problems caused by this waste as well as produce a value-added product from a low-cost material. In fact, treatment of BP with H$_2$SO$_4$ can produce hydrophilic carbonaceous with high oxygen content and rich with (-SO$_2$H) groups. This acid-treated banana peel (ATBP) with unique surface characteristic and multifunctional groups would be acted as a superior low-cost adsorbent for capturing cationic dyes from aqueous solutions. In this regard, MB was chosen a typical cationic dye to figure out the adsorptive properties of the ATBP. Sulphuric acid (H$_2$SO$_4$) is frequently used as a low cost activation agents for the preparation of carbonaceous adsorbents from ligno-cellulosic materials such as coconut leaf [32], mango peel [36], euphorbia rigid [42], bagasse [43], almond husk [44], parthenium hysterophorus [45], sunflower oil cake [46], pine-fruit shell [47], Delonix regia pods [28], wild carrot [48], Ficus carica [49] potato peel and neem bark [50].

## 2. Materials and methods

### 2.1. Adsorbate (MB)

The cationic dye, methylene blue (MB) was used as an adsorbate in this work. MB was purchased from R&M Chemicals, Malaysia with chemical formula (C$_{16}$H$_{18}$ClN$_3$S.$\times$H$_2$O) and molecular weight (319.86 g/mol). Ultra-pure water was used to prepare all solutions.

### 2.2. Preparation and characterization of ATBP

The banana peel (BP) was obtained from a local fruit stall in Penang, Malaysia. The BP was first washed with water to remove dirt and subsequently dried at 105°C for 24 h to remove the moisture contents. The dried BP was ground and sieved to the size of 250–500 $\mu$m before impregnate with concentrated H$_2$SO$_4$ (95–98%). The mixing ratio was fixed at 1 g of dried BP powder with 1 mL of concentrated H$_2$SO$_4$ according to the method reported by Garg et al. [51]. The acid-treated form of banana peel (ATBP) was washed with hot distilled water until the filtrate water was clear reached a neutral pH value. The elemental analysis was carried out using a CHNS-O analyser (Flash 2000, Organic Elemental Analyser, Thermoscientific). The oxygen contents were calculated by difference. X-ray diffraction analysis (XRD) was performed by X-ray diffraction (XRD) in reflection mode (Cu Kα radiation) on a PANalytical, X’Pert Pro X-ray diffractometer. Scans were recorded with a scanning rate of 0.59°/s. The diffraction angle (2θ) was varied from 10° to 90°. Textural characterization of TBP was carried out by N$_2$ adsorption using Micromeritics ASAP 2060, USA. FT-IR spectral analysis of TBP was performed on a Perkin Elmer, Spectrum One in the 4000–500 cm$^{-1}$ wavenumber range. The surface physical morphology was examined by using scanning electron microscopy (SEM; SEM-EDX, FESEM CARL ZEISS, SUPKA 40 VP). The pH at the point-of-zero charge (pH$_{pzc}$) was estimated using a pH metre (Metrohm, Model 827 pH Lab, Switzerland), as described elsewhere [52].
Table 1. Characterization in contents of ATBP.

| Properties/characteristics | Values      |
|---------------------------|-------------|
| Proximate analysis        |             |
| Bulk density (g/mL)       | 0.91        |
| Ash content (wt %)        | 4.97        |
| Moisture content (wt %)   | 3.50        |
| Elemental analysis (wt. %)|             |
| Carbon, C                 | 55.54       |
| Hydrogen, H               | 4.24        |
| Nitrogen, N               | 2.08        |
| Sulphur, S                | 0.19        |
| Oxygen, O (by difference) | 37.95       |
| EDX (wt. %)               |             |
| Carbon, C                 | 72.16       |
| Oxygen, O                 | 26.31       |
| Sulphur, S                | 1.53        |
| Typical properties        |             |
| Total pore volume (cm³/g) | 2.88 × 10⁻³ |
| Mean pore width (nm)      | 36.88       |
| BET surface area (m²/g)   | 1.73        |

2.3. Batch adsorption experiments

The batch adsorption experiments of MB adsorption onto ATBP surface were performed in a set of 250 mL Erlenmeyer flasks containing 100 mL of MB solution. The flasks were capped and agitated in an isothermal water bath shaker (Memmert, water bath, model WNB7-45, Germany) at fixed shaking speed of 110 stroke/min and 303 K until equilibrium was achieved. Batch adsorption experiments were carried out by varying several experimental variables such as adsorbent dosage (0.02 to 0.3 g), pH (3 to 12), initial dye concentration (10 to 300 mg/L) and contact time (0 to 1440 min) to determine the best uptake conditions for adsorption. The pH of MB solution was adjusted by adding either 0.10 mol/L HCl or NaOH. After mixing of the ATBP-MB system, the supernatant was collected with a 0.20 μm Nylon syringe filter and the concentrations of MB were monitored at a different time interval using a HACH DR 2800 Direct Reading Spectrophotometer at the maximum wavelength (λmax) of absorption at 661 nm. As for the thermodynamic studies, the same procedures were repeated and applied at 313, 323 and 333 K with the other parameters keep constant. The blank test was carried out in order to account for colour leached by the adsorbent and adsorbed by the glass containers, blank runs with only the adsorbent in 100 mL of doubly distilled water and 100 mL of dye solution without any adsorbent were conducted simultaneously at similar conditions. The adsorption capacity at equilibrium, qe (mg/g) and the percent of colour removal, CR (%) of MB were calculated using Equations (1) and (2).

\[ q_e = \frac{(C_0 - C_e)V}{W}, \]  
\[ CR\% = \frac{(C_0 - C_e)}{C_0} \times 100, \]

where \( C_0 \) and \( C_e \) (mg/L) are the initial and equilibrium concentrations of MB, respectively, \( V \) (L) is the volume of the solution and \( W \) (g) is the mass of dry adsorbent used.

3. Results and discussion

3.1. Characterization of ATBP

3.1.1. Physical properties

The results of physical characterization of ATBP are recorded in Table 1. The ultimate results indicate that ATBP has a moderately high carbon (55.54%) and oxygen content (37.95%) with low surface area (1.73 m²/g). The low surface area of ATBP can be attributed to the high concentration of activation agent H₂SO₄, which basically responsible for increasing the oxygen content on ATBP surface and decreasing adversely the surface area and pore volume [39]. From Table 1, the detected amount of sulphur (S) can be attributed to the role of H₂SO₄ which was basically responsible for creating sulphonic acid groups (–SO₃) onto ATBP surface. The presence of sulphonic acid groups (–SO₃) on the surface of ATBP will definitely turn the surface characteristic of ATBP to become more negatively charged and adsorption of cationic dye such as MB will be very much preferable. The BET isotherm of ATBP is plotted an illustrated in Figure 1.

3.1.2. XRD analysis of ATBP

The XRD pattern of the ATBP is shown in Figure 2. XRD pattern is indexed based on a standard diffraction reference pattern (PCPDF No: 898487). Appearance of a broad diffraction background and the absence of a sharp peak reveal a predominantly amorphous structure [53]. Overall, there were two XRD peaks at 2θ = 24° (002) and 2θ = 42° (101) in the spectrum. These signatures relate to crystalline carbon with expanded lattice parameters (carbon with impurities).

3.1.3. FTIR spectral analysis

FTIR spectroscopy provides structural and compositional information on the active functional groups
presented in the ATBP. FTIR spectrum of ATBP before adsorption (Figure 3(a)) showed various functional groups, in agreement with their respective wavenumber (cm$^{-1}$) position as documented in literature. The weak band observed $\sim$ 3500 cm$^{-1}$ is assigned to the overlapping of the stretching vibrations of the hydroxyl (O–H) and amine (N–H) groups [54]. The band at $\sim$ 1700 cm$^{-1}$ associated to C=O stretching of ketones, aldehydes, lactones or carboxyl groups. The absorptions peaks between 1300 and 1000 cm$^{-1}$ are observed for oxidized carbon materials and are assigned to C–O and/or C–O–C stretching in acids, alcohols, phenols, ethers and/or esters groups and sulphonic acid groups (–SO$_3$) [32,53,54]. The availability of sulphonic acid groups (–SO$_3$) in the FTIR spectrum is in line with previously discussed results of elemental analysis and EDX analysis. In this respect, the FTIR spectrum of ATBP before adsorption indicates that the external surface of ATBP is rich in SO$_3$H group in addition to various functional groups, containing oxygen of carboxylic and carbonyl species. These active groups on ATBP surface are responsible for enhancing the adsorption of cationic species such as MB due to the electrostatic interaction. After MB adsorption (Figure 3(b)), the band shifted and became more pronounced in which the attenuated bands at $\sim$ 850 cm$^{-1}$ (–CH$_2$ vibration) suggest the interaction of MB molecules with the functional groups of ATBP.

### 3.1.4. SEM analysis

SEM images were recorded to visualize the surface physical morphology of ATBP. The SEM results of ATBP before and after adsorption are shown in Figure 4(a,b), respectively. As can be seen in Figure 4(a), the external surface of ATBP appears to be highly porous and heterogeneous. Pores with different size and irregular shape are also clearly visible. Those pores are pitted and fragmented due to evaporation of the H$_2$SO$_4$ during carbonization, leaving the space being previously occupied by the activation agent. Therefore, the resulting pore structure is suitable for the adsorption of MB within the pore structure of ATBP. After MB adsorption, the ATBP surface is transformed to be more compact, smoother and less open pores are seen due to filling of MB molecules on the ATBP surface.

### 3.1.5. Point-of-Zero charge (pH$_{PZC}$)

The point-of-zero charge (pH$_{PZC}$) test estimates the pH at which the net charge of the surface is zero. Figure 5 shows the pH$_{PZC}$ result of the experiment performed with the ATBP, where the pH ranged from 3 to 12. The pH$_{PZC}$ of the ATBP was 6.8. In general, MB adsorption is favoured at pH $>$ pH$_{PZC}$ due to presence of functional groups such as OH,COO- groups while anionic dye adsorption is favoured at pH $<$ pH$_{PZC}$ where the surface becomes positively charged. In this respect, Jawad
et al., reported that the pH\textsubscript{pzc} values of the coconut leaf and mango peel treated with H\textsubscript{2}SO\textsubscript{4} were 3.20 [32] and 4.60 [36] respectively.

3.2. MB adsorption

3.2.1. Effect of the adsorbent dosage

Adsorbent dosage shows a profound effect on the adsorption process, due to the reason that it predicts the cost of pollutant to be treated. The effect of adsorbent dosage on the removal of the MB from aqueous solution was determined using variable quantities of ATBP adsorbent ranging from 0.02 to 0.30 g at fixed volumes (100 mL) and initial dye solution, Co was 100 mg/L. For these experiments, other operation parameters were held constant at 303 K, shaking speed of 110 stroke/min, contact time of 1440 min and an unadjusted pH at 5.60 for the initial MB solution. The result for adsorptive removal of MB with respect to adsorbent dosage is displayed in Figure 6. It is apparent that the percentage removal of MB increases rapidly with increase in the dosage of ATBP due to the greater availability of the exchangeable sites or surface area [55,56]. In present work, the highest level of MB removal was achieved using 0.08 g/100 mL ATBP dose and thereafter, further increase in adsorbent dosage did not exert an appreciable increase in the MB removal percentage. Due to conglomeration of adsorbent particles, there is no increase in effective surface area of ATBP. Therefore, in the further experiments the adsorbent dosage was fixed at 0.08 g.

3.2.2. Effect of pH

The pH of the solution influences the speciation of the dyes, along with the surface charge of the adsorbent. Figure 7 shows the effect of variable pH from 3 to 12 on the adsorption capacity with MB. At lower pH, the surface charge may be positively charged, thus making (H\textsuperscript{+}) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed [57]. At higher pH values, the surface of ATBP adopts a negative surface charge, which contributes to enhanced uptake of positively charged dye species via attractive electrostatic attraction, in accordance with an increase in the rate of adsorption [58]. To continue this work, the effective pH for ATBP was fixed at 10, and used in further adsorption studies herein.
3.2.3. Effect of initial dye concentration and contact time

Figure 8 shows the graph plotted between the amounts of MB adsorbed ($q_t$) versus time at different initial MB concentrations. The time variation plot indicates that the removal of MB is rapid in initial stages but when it approaches equilibrium, it slows down progressively [59]. This may be due to the availability of vacant surface sites during the preliminary stage of adsorption, and after a certain time period the vacant sites get occupied by MB molecules which lead to create a repulsive force between the ATBP on the MB surface and in bulk phase. The amount of MB adsorbed by the ATBP adsorbent at equilibrium enhance rapidly from 16.63 to 259.70 mg/g as the initial dye concentration increased from 10 to 300 mg/L. In batch adsorption, the removal rate of the adsorbate from aqueous solutions is controlled mostly by the transport of dye molecules from the surrounding sites to the interior sites of the adsorbent particles [60]. Hence it can be stated that, the increase of adsorption capacity is mainly determined by the fact that the high initial MB concentration not only provides a large driving force to overcome all mass transfer resistances between the aqueous and solid phases [57], but also determines a higher probability of collision between MB ions and ATBP surface. Additional time was needed to reach equilibrium for higher MB concentration because there was a tendency for MB molecules to penetrate deeper within the interior surface of the ATBP and be adsorbed at active pore sites. This indicates that the initial dye concentration plays a significant role in the adsorption capacity of MB onto ATBP sorbent.

3.3. Adsorption isotherm

The application of adsorption isotherm is very useful to describe the interaction between the adsorbate and the adsorbent of any system [52]. The parameters obtained from the different models provide important information on the sorption mechanisms, surface properties and affinities of the adsorbent. In this work, the adsorption isotherm results for ATBP were fitted using most accepted surface adsorption models for single solute systems, which are Langmuir, Freundlich and Temkin model. Langmuir model proposed that adsorption occurs at specific homogenous sites within the adsorbent [61]. It explains monolayer adsorption which lies on the fact that no further adsorption takes place once the active sites are covered with dye molecules. The saturated monolayer isotherm is presented by the following expressions:

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}k_L} + \frac{1}{q_{\text{max}}}C_e, (3)$$

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), $k_L$ is the Langmuir affinity constant and $q_{\text{max}}$ is the amount of adsorbate required to form an adsorbed monolayer. Hence, a plot of $C_e/q_e$ versus $C_e$ should be a straight line with a slope ($1/q_{\text{max}}$) and an intercept ($1/q_{\text{max}}k_L$) as shown in Figure 9(a).

On the other hand, the Freundlich model [62] describes the multilayer adsorption process on heterogeneous adsorption sites, as described by a form of the Langmuir equation that varies as a function of the surface coverage. Freundlich model is presented as Equation (4):

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e,$$  \hspace{1cm} (4)

where $C_e$ is the equilibrium concentration of the adsorbate (mg/L), $q_e$ is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g). The affinity constant $k_F$ (mg/g (l/mg)$^{1/n}$), relates to the adsorption capacity of the adsorbent and $n$ is the constant where indicates the relative favourability of the adsorption process. Thus, a plot of $\ln q_e$ versus $\ln C_e$ should be a straight line with a slope $1/n$ and an intercept of $\ln k_F$ (Figure 9(b)).
Temkin model [63] assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent/adsorbate interactions, and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. Temkin isotherm can be expressed in its linear form is presented as Equation (5):

$$q_e = B \ln k_T + B \ln C_e.$$  

A plot of $q_e$ versus $\ln C_e$ yielded a linear line enables to determine the isotherm constants $k_T$ and $B$ (Figure 9(c)). $k_T$ is the Temkin equilibrium binding constant (L/mg) that corresponds to the maximum binding energy, and constant $B$ is related to adsorption heat. The adsorption heat of all the molecules in the layer is expected to decrease linearly with coverage because of adsorbate/adsorbate interactions. The isotherms related parameters were calculated, and the results are shown in Table 2. Based on calculated data, Langmuir model yielded the best fit with the highest correlation coefficients, $R^2$ value (0.990) compared with the Freundlich (0.990) and Temkin (0.922) models. This implied the homogeneous and the monolayer coverage of MB has taken place on the ATBP surface. The ATBP surface is made up of small adsorption patches, which are energetically equivalent to each other in terms of adsorption phenomenon. The monolayer adsorption capacity ($q_{max}$) for ATBP with MB was compared with other types of H$_2$SO$_4$-treated lignocellulosic materials as recorded in Table 3. ATBP shows a relatively high adsorption capacity for MB, where $q_{max}$ was 250 mg/g, exceeding values reported for other biomass treated with H$_2$SO$_4$ activation for the uptake of MB.

### 3.4. Adsorption kinetics

The Pseudo-First-Order model (PFO) and Pseudo-Second-Order model (PSO) were used to investigate the adsorption kinetics of MB dye on ATBP surface. The PFO was originally proposed by Lagergren [64] and its
Table 3. Comparative of adsorption capacities for MB onto different biomass materials treated with H$_2$SO$_4$.

| H$_2$SO$_4$-treated biomass | Adsorbent dosage, g | pH | Temp. (K) | $q_{\text{max}}$ (mg/g) | References |
|---------------------------|---------------------|----|----------|------------------------|------------|
| Banana peel               | 0.08 g/100 mL       | 11 | 303      | 250                    | This study |
| Pine-fruit shell          | 0.3 g/100 mL        | 8.5| 298      | 529                    | [47]       |
| Mango peels               | 0.14 g/100 mL       | 5–6| 303      | 277.8                  | [36]       |
| Coconut leaf              | 0.15 g/100 mL       | 6  | 303–322  | 162.9–149.3            | [32]       |
| Euphorbia rigida          | 0.2 g/100 mL        | 6  | 293–313  | 114                    | [42]       |
| Bagasse                   | 0.4 g/100 mL        | 9  | 300–333  | 49.8–56.5              | [43]       |
| Ficus carica              | 0.5 g/100 mL        | 8  | 298–323  | 47.62                  | [49]       |
| Parthenium hysterophorus  | 0.4 g/100 mL        | 7  | 298      | 39.7                   | [45]       |
| Delonix regia pods        | 0.2 g/100 mL        | 7  | 298      | 23.3                   | [28]       |
| Wild carrot               | 0.05 g/100 mL       | 6  | 298      | 21                     | [48]       |
| Sunflower oil cake        | 0.2 g/100 mL        | 6  | 288–318  | 16.43                  | [46]       |

Figure 10. Kinetic profiles for the adsorption of MB onto ATBP: (a) Pseudo-First-Order (b) Pseudo-Second-Order.

The linearized form is given by Equation (6):

$$\ln (q_e - q_t) = \ln q_e - k_1 t,$$

where $q_e$ is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), $q_t$ is the amount of solute adsorbed at any time (mg/g), and $k_1$ is the adsorption constant. This expression is the most popular form of PFO model. $k_1$ values at different initial MB concentrations were calculated from the plots of $\ln (q_e - q_t)$ versus $t$ (Figure 10(a)) and the values are given in Table 4. The linear form of the PSO model is given by Equation (7) [65]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$

where the PSO rate constant ($k_2$; g/mg min) and $q_{e,\text{cal}}$ were calculated from the intercept and slope of $t/q_t$ versus $t$, shown in Figure 10(b). In Table 4, the observed $R^2$ values are nearly unity ($R^2 \geq 0.99$) for the PSO kinetic model, where the values of $q_{e,\text{cal}}$ are in good agreement with $q_{e,\text{exp}}$. This suggests that the adsorption systems studied belong to the PSO kinetic model. Considering to batch adsorption of MB, the adsorption mechanism is assumed to involve several steps and is defined as follows: dye movement from the bulk of the MB solution to the external surface of the ATBP (liquid phase mass transfer step); diffusion of MB molecules through the boundary layer around the ATBP (external diffusion step); adsorption of dye molecules to the active sites on the surface of ATBP (adsorption step); intraparticle diffusion of dye molecules through the pores of ATBP (internal mass transfer step). It is well known that

Table 4. PFO and PSO kinetic parameters and their corresponding values at different initial dye concentrations by ATBP.

| Parameter | Concentration, $C_0$ (mg/L) |
|-----------|-----------------------------|
| $q_{e,\text{exp}}$ (mg/g) | 10  | 30  | 50  | 80  | 100 | 150 | 200 | 250 | 300 |
| PFO       | 16.63 | 42.39 | 61.41 | 100.09 | 122.45 | 194.20 | 207.19 | 234.02 | 259.70 |
| $q_{e,\text{cal}}$ (mg/g) | 0.14 | 0.16 | 6.41 | 29.71 | 116.34 | 155.26 | 192.48 | 208.62 | 205.66 |
| $k_1 \times 10^3$ | 28.40 | 40.20 | 5.90 | 7.80 | 6.70 | 3.10 | 3.20 | 2.80 | 3.30 |
| $R^2$     | 1.000 | 1.000 | 1.000 | 1.000 | 0.987 | 0.939 | 0.940 | 0.948 | 0.978 |
| PSO       | 16.64 | 42.37 | 61.35 | 101.01 | 126.58 | 200.00 | 208.33 | 232.56 | 263.16 |
| $k_2 \times 10^{-5}$ | 4.63 $\times 10^{-1}$ | 4.64 $\times 10^{-1}$ | 7.63 $\times 10^{-3}$ | 1.67 $\times 10^{-3}$ | 1.28 $\times 10^{-4}$ | 4.88 $\times 10^{-5}$ | 4.43 $\times 10^{-5}$ | 3.80 $\times 10^{-5}$ | 5.05 $\times 10^{-5}$ |
| $R^2$     | 1.000 | 1.000 | 1.000 | 1.000 | 0.987 | 0.939 | 0.940 | 0.948 | 0.978 |
the dominant process in wastewater adsorption applications is mass transfer step because the adsorption of dye to active sites occurs quickly [66]. In fact, liquid phase oxidation of ATBP with H2SO4 will produce more negatively charged surfaces of ATBP and this favour to uptake of more cationic groups due to decreased electrostatic repulsion between MB and the surface of ATBP. Furthermore, high content of oxygen on the ATBP surface was observed due to the wet oxidation process with H2SO4 as shown in Table 1. This oxygen extracts electrons from the π band of the carbon, reducing the interactions between the MB molecules and carbon. This is due to the weakening of dispersion forces between the π electron system of the aromatic ring of MB and the π band of the graphitic planes of the carbon, which are basically responsible for the adsorption [66].

3.5. Adsorption thermodynamics

Thermodynamic parameters provide further information about inherent energetic changes associated with adsorption process. The set of thermodynamic parameters of MB onto ATBP were determined by carrying out the adsorption experiments at 313, 323 and 333 K. Thermodynamic constants such as, standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated using the following equation [67]:

\[ k_d = \frac{q_e}{C_e}, \]

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]

\[ \ln k_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}, \]

where \( k_d \) is the distribution coefficient, \( q_e \) is the concentration of MB adsorbed on ATBP at equilibrium (mg/L), \( C_e \) is the equilibrium concentration of MB in the liquid phase (mg/L), \( R \) is the universal gas constant (8.314J/mol.K) and \( T \) is the absolute temperature (K). The values of \( \Delta H^o \) and \( \Delta S^o \) were calculated from the slope and intercept of van’t Hoff plots of ln(kd) versus 1/T respectively (Figure 11). The thermodynamic parameters are listed in Table 5. In general, the negative values for \( \Delta G^o \) at all the studied temperature indicate the feasibility and spontaneity of the adsorption process. The adsorption reaction is spontaneous process at high temperature, and not requires any energy from an external source to uptake dye molecules onto ATBP surface [68]. A positive value of \( \Delta S^o \) implies an increased disorder at the solid/liquid interface during the adsorption process causing the MB molecules to escape from ATBP surface to the liquid phase.

![Figure 11. Plot of ln k_d vs. 1/T for calculation of thermodynamic parameters for the adsorption of MB onto ATBP.](image)

| Temperature (K) | k_d | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (J/molK) |
|----------------|-----|-------------|-------------|--------------|
| 303            | 478.88 | −14.95      | 34.45       | 163.05       |
| 313            | 482.84 | −16.58      | 30.21       | 159.05       |
| 323            | 617.94 | −18.21      | 33.21       | 162.05       |
| 333            | 1773.75 | −19.85     | 35.75       | 157.05       |

4. Conclusion

The research work clearly shows that acid-treated banana peel (ATBP) by H2SO4 activation provides a low-cost adsorbent for the removal of MB dye from aqueous solutions. The adsorption experiments indicated that the pseudo-second-order model provided the best description of the kinetic uptake properties, while adsorption results at equilibrium are described by the Langmuir model where the maximum adsorption capacity (qmax) is 250 mg/g. The thermodynamic parameters indicate that the adsorption process is an endothermic in nature and a spontaneous adsorption process. The results indicated that ATBP is an efficient adsorbent for MB adsorption.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Mubarak NSA, Jawad AH, Nawawi WI. Equilibrium, kinetic and thermodynamic studies of reactive Red 120 dye
adsorption by chitosan beads from aqueous solution. Energ Ecol Environ. 2017;2:85–93.

[2] Jawad AH, Ishak MAM, Farhan AM, et al. Response surface methodology approach for optimization of color removal and COD reduction of methylene blue using microwave-induced NaOH activated carbon from biomass waste. Desalin Water Treat. 2017;62:208–220.

[3] Jawad AH, Mubarak NSA, Nawawi WI. Optimization of sorption parameters for color removal of textile Dye by cross-linked chitosan beads using Box-behnken design. MATEC Web Conf. 2016;47:05009.

[4] Jawad AH, Rashid RA, Mahmud RMA, et al. Adsorption of methylene blue onto coconut (Cocos nucifera) leaf: optimization, isotherm and kinetic studies. Desalin Water Treat. 2016;57:8839–8853.

[5] Jawad AH, Sabar S, Ishak MAM, et al. Microwave-assisted preparation of mesoporous activated carbon from coconut (Cocos Nucifera) leaf by \( \text{H}_2\text{PO}_4 \) activation for methylene blue adsorption. Chem Eng Commun. 2017;204(10):1143–1156.

[6] Jawad AH, Rashid RA, Imsmail K, et al. High surface area mesoporous activated carbon developed from coconut leaf by chemical activation with \( \text{H}_2\text{PO}_4 \) for adsorption of methylene blue. Desalin Water Treat. 2017;74:326–335.

[7] Khataee AR, Movafeghi A, Torbati S, et al. Phytomedia- tion potential of duckweed (\textit{Lemna minor L}) in degradation of CI. Acid Blue 92: artificial neural network modeling. Ecotoxicol Environ Saf. 2012;80:231–298.

[8] Fan L, Zhou Y, Yang W, et al. Electrochemical degradation of aqueous solution of Amaranth azo dye on ACF under potentiostatic model. Dyes Pigments. 2008;76:440–446.

[9] Wu JS, Liu CH, Chu KH, et al. Removal of cationic dye methyl violet 28 from water by cation exchange membranes. J Membr Sci. 2008;309:239–245.

[10] Woo YS, Rafatullah M, Al-Karkhi AFM, et al. Removal of pollutants with activated carbon produced from \( \text{K}_2\text{CO}_3 \) activation of lignin from reed black liquors. Chem Biochem Eng Q. 2006;20:429–435.

[11] Yacob AR, Majid ZA, Dasril RSD, et al. Comparison of various sources of high surface area carbon prepared by different types of activation. Malays J Anal Sci. 2008;12:264–271.

[12] Zhu Z, Li A, Xia M, et al. Preparation and characterization of polymer based spherical activated carbons. Chin J Polym Sci. 2008;26:645–651.

[13] Hu Z, Srinivasan MP. Mesoporous high-surface-area activated carbon. Micro Meso Mater. 2001;43:267–275.

[14] Guo S, Peng J, Li W, et al. Effects of \( \text{CO}_2 \) activation on porous structures of coconut shell-based activated carbons. Appl Surf Sci. 2009;255:8443–8449.

[15] Sahu JN, Acharya J, Meikap BC. Optimization of production conditions for activated carbons from tamarind wood by zinc chloride using response surface methodology. Bioresour Technol. 2010;101:1974–1982.

[16] Dias JM, Alvim-Ferrazza MCM, Almeida MF, et al. Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. J Environ Manag. 2007;85:833–846.

[17] Khah AM, Ansari R. Activated charcoal: preparation, characterization and applications: a review article. Int J Chem Technol Res. 2009;1:859–864.

[18] Ho YS, Malaryvzhi R, Sulochana N. Equilibrium isotherm studies of methylene blue adsorption onto activated carbon prepared from \textit{Delonix regia} pods. J Environ Prot Sci. 2009;3:1–6.

[19] Idris S, Jyaka YA, Dauda BEN, et al. Kinetic study of utilizing groundnut shell as an adsorbent in removing chromium and nickel from Dye effluent. Chem Sci J. 2012;2:12–24.

[20] Al-Qodah Z, Shawabkah R. Production and characterization of granular activated carbon from activated sludge. Braz J Chem Eng. 2009;26:127–136.

[21] Xu J, Chen L, Qu H, et al. Preparation and characterization of activated carbon from reedy grass leaves by chemical activation with \( \text{H}_2\text{PO}_4 \). Appl Surf Sci. 2014;320:674–680.

[22] Jawad AH, Rashid RA, Ishak MAM, et al. Adsorption of methylene blue onto activated carbon developed from biomass waste by \( \text{K}_2\text{CO}_3 \) activation. J Taiwan Inst Chem Eng. 2016;47:233–246.

[23] Al-Qodah Z, Shawabkah R. Production and characterization of granular activated carbon from activated sludge. Braz J Chem Eng. 2009;26:127–136.

[24] Xue Y, Zhang JP, Yang G, et al. Removal of pollutants with activated carbon produced from \( \text{K}_2\text{CO}_3 \) activation of lignin from reed black liquors. Chem Biochem Eng Q. 2006;20:429–435.

[25] Yacob AR, Majid ZA, Dasril RSD, et al. Comparison of various sources of high surface area carbon prepared by different types of activation. Malays J Anal Sci. 2008;12:264–271.

[26] Zhu Z, Li A, Xia M, et al. Preparation and characterization of polymer based spherical activated carbons. Chin J Polym Sci. 2008;26:645–651.

[27] Hu Z, Srinivasan MP. Mesoporous high-surface-area activated carbon. Micro Meso Mater. 2001;43:267–275.

[28] Guo S, Peng J, Li W, et al. Effects of \( \text{CO}_2 \) activation on porous structures of coconut shell-based activated carbons. Appl Surf Sci. 2009;255:8443–8449.

[29] Sahu JN, Acharya J, Meikap BC. Optimization of production conditions for activated carbons from tamarind wood by zinc chloride using response surface methodology. Bioresour Technol. 2010;101:1974–1982.

[30] Dias JM, Alvim-Ferrazza MCM, Almeida MF, et al. Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. J Environ Manag. 2007;85:833–846.

[31] Khah AM, Ansari R. Activated charcoal: preparation, characterization and applications: a review article. Int J Chem Technol Res. 2009;1:859–864.

[32] Ho YS, Malaryvzhi R, Sulochana N. Equilibrium isotherm studies of methylene blue adsorption onto activated carbon prepared from \textit{Delonix regia} pods. J Environ Prot Sci. 2009;3:1–6.

[33] Idris S, Jyaka YA, Dauda BEN, et al. Kinetic study of utilizing groundnut shell as an adsorbent in removing chromium and nickel from Dye effluent. Chem Sci J. 2012;2:12–24.

[34] Al-Qodah Z, Shawabkah R. Production and characterization of granular activated carbon from activated sludge. Braz J Chem Eng. 2009;26:127–136.

[35] Xue Y, Zhang JP, Yang G, et al. Removal of pollutants with activated carbon produced from \( \text{K}_2\text{CO}_3 \) activation. J Taiwan Inst Chem Eng. 2016;47:233–246.

[36] Al-Qodah Z, Shawabkah R. Production and characterization of granular activated carbon from activated sludge. Braz J Chem Eng. 2009;26:127–136.

[37] Xue Y, Zhang JP, Yang G, et al. Removal of pollutants with activated carbon produced from \( \text{K}_2\text{CO}_3 \) activation. J Taiwan Inst Chem Eng. 2016;47:233–246.
equilibrium and thermodynamic. Desalin Water Treat. 2017;59:210–219.

[37] Liu QS, Zheng T, Li N, et al. Modification of bamboo-based activated carbon using microwave radiation and its effects on the adsorption of methylene blue. Appl Surf Sci. 2016;256:3309–3315.

[38] Gokce Y, Aktas Z. Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol. Appl Surf Sci. 2014;313:352–359.

[39] Valdes H, Sanchez-Polo M, Rivera-Utrilla J, et al. Effect of ozone treatment on surface properties of activated carbon. Langmuir. 2002;18:2111–2116.

[40] Salman JM, Njoku VO, Hameed BH. Adsorption of pesticides from aqueous solution onto banana stalk activated carbon. Chem Eng J. 2011;174:41–48.

[41] Happi Emaga H, Herinavalona Andrianaivo R, Wathelet B, et al. Effects of the stage of maturation and varieties on the chemical composition of banana and plantain peels. Food Chem. 2007;103:590–600.

[42] Gerçel Ö, Özcan A, Özcan AS, et al. Preparation of activated carbon from a renewable bio-plant of euphorbia rigida by H2SO4 activation and its adsorption behavior in aqueous solutions. Appl Surf Sci. 2007;253:4843–4852.

[43] Low LW, Teng TT, Ahmad A, et al. A novel pretreatment method of lignocellulosic material as adsorbent and kinetic study of dye waste adsorption. Water Air Soil Pollut. 2011;218:293–306.

[44] Hasar H. Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk. J Hazard Mater. 2003;97:49–57.

[45] Lata H, Garg VK, Gupta RK. Removal of a basic dye from aqueous solution by adsorption using parthenium hysterophorus: An agricultural waste. Dyes Pigm. 2007;7:653–658.

[46] Karagöz S, Tay T, Ucar S, et al. Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption. Bioresour Technol. 2008;99:6214–6222.

[47] Royer B, Cardoso NF, Lima EC, et al. Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions—kinetic and equilibrium study. J Hazard Mater. 2009;164:1213–1222.

[48] Mahadeva Swamy M, Nagabhushana BM, Hari Krishna R, et al. Fast adsorptive removal of methylene blue dye from aqueous solution onto a wild carrot flower activated carbon: isotherms and kinetics studies. Desalin Water Treat. 2017;71:399–405.

[49] Pathania D, Sharma S, Singh P. Removal of methylene blue by adsorption onto activated carbon developed from ficus carica bast, Arab. J Chem. 2017;10:51445–51451.

[50] Sharma N, Tiwari DP, Singh SK. The efficiency appraisal for removal of malachite green by potato peel and neem bark: isotherm and kinetic studies. Int J Chem Environ Eng. 2014;5:83–88.

[51] Garg VK, Kumar R, Gupta R. Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of Prosopis cineraria. Dyes Pigments. 2004;62:1–10.

[52] Lopez-Ramon MV, Stoeckli F, Moreno-Castilla C, et al. On the characterization of acidic and basic surface sites on carbons by various techniques. Carbon N Y. 1999;37:1215–1221.

[53] Barpanda P, Fanchini G, Amatucci GG. Structure, surface morphology and electrochemical properties of brominated activated carbons. Carbon N Y. 2011;49(2011):2538–2548.

[54] Jawad AH, Nawi MA. Characterizations of the photocatalytically-oxidized crosslinked chitosan-glutaraldehyde and its application as a sub-layer in the TiO2/CS-GLA bilayer photocatalyst system. J Polym Environ. 2012;20:817–829.

[55] Jawad AH, Kadhum AM, Ngoh YS. Applicability of dragon fruit (Hylocereus polyrhizus) peels as low-cost biosorbent for adsorption of methylene blue from aqueous solution: kinetics, equilibrium and thermodynamics studies. Desalin Water Treat. 2018;109:231–240.

[56] Rashid RA, Jawad AH, Ishak MAM, et al. FeCl3-activated carbon developed from coconut leaves: characterization and application for methylene blue removal. Sains Malaysiana. 2018;47(3):603–610.

[57] Jawad AH, Ngoh YS, Radzun KA. Utilization of watermelon (Citrullus lanatus) rinds as a natural low-cost biosorbent for adsorption of methylene blue: kinetic, equilibrium and thermodynamic studies. J Taibah Univ Sci. 2018;12(4):371–381.

[58] Chakraborty S, Chowdhury S, Saha PD. Adsorption of crystal violet from aqueous solution onto NaOH-modified rice husk. Carbohydr Polym. 2011;86:1533–1541.

[59] Jawad AH, Mehdi ZS, Ishak MAM, et al. Large surface area activated carbon from low-rank coal via microwave-assisted KOH activation for methylene blue adsorption. Desalin Water Treat. 2018;110:239–249.

[60] Jawad AH, Waheeb AS, Rashid RA, et al. Equilibrium isotherms, kinetics, and thermodynamics studies of methylene blue adsorption on pomegranate (Punica granatum) peels as a natural low-cost biosorbent. Desalin Water Treat. 2018;105:322–331.

[61] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc. 1918;40:1361–1403.

[62] Freundlich H. Ueber die adsorption in Loesungen (Adsorption in solution). Z Phys Chem. 1906;57:385–470.

[63] Temkin MJ, Pyzhev V. Recent modifications to Langmuir isotherms. Acta Physiochim USSR. 1940;1541.

[64] Lagergren S. Zur theorie der sogenannten adsorption geloster stoffe. K. Sven. Vetenskapsakad. Handl. 1898;24:1–39.

[65] Ho YS, McKay G. Sorption of dye from aqueous solution by beat. Chem Eng J. 1998;70:115–124.

[66] Valdes H, Sanchez-Polo M, Rivera-Utrilla J, et al. Effect of ozone treatment on surface properties of activated carbon. Langmuir. 2002;18:2111–2116.

[67] Karaçetin G, Sivrikaya S, Imamoglu M. Adsorption of methylene blue from aqueous solutions by activated carbon prepared from hazelnut husk using zinc chloride. J Anal Appl Pyrolysis. 2014;110:270–276.

[68] Rashid RA, Jawad AH, Ishak MAM, et al. KOH-activated carbon developed from biomass waste: adsorption equilibrium, kinetic and thermodynamic studies for methylene blue uptake. Desalin Water Treat. 2016;57:27226–27236.

[69] Singh KP, Shikha G, Arun KS, et al. Optimizing adsorption of crystal violet dye from water by magnetic nanocomposite using response surface modeling approach. J Hazard Mater. 2011;186:1462–1473.