1. Introduction

Textile dyes are frequently utilized in unlimited industrial applications such as textile, printing, paint, food, and cosmetics as a colouring agent [1]. The discharge of dye contaminated water is one of the most important environmental problems due to its risks on aquatic life and human health [2]. Methylene blue (MB) dye is widely used in the textile industry for dyeing cotton, wood, and leather, in addition to the pharmaceutical industries [3]. MB dye causes harmful effects on human health such as nausea, vomiting, heart rate increasing and eye/skin irritation [4,5]. Several methods were applied to remove textile dyes prior to discharge into water such as adsorption [6], photocatalysis [7], oxidation [8], and coagulation [9]. Adsorption is a prime wastewater treatment method for dye removal due to its simplicity of design, non-generation of toxic materials, low cost and high efficiency [10,11]. Activated carbon is the most common adsorbent utilized for the treatment of a wide range of water pollutants [12]. However, activated carbon requires a high cost for preparation and regeneration. Therefore, the researchers shifted towards natural biopolymers, biomass, and waste materials as an economical alternative and environment-friendly adsorbents [13–16].

In recent years, various types of biomass, such as coconut husk [17], loofah sponge [18], algae [19], and soy waste [20], were utilized for dyes and metal ion removal from aqueous environment. Generally, various biomass and agricultural wastes are preferred for preparing carbonaceous adsorbents due to its multiple advantages such as renewability, low-cost precursor, and environment friendliness [21]. Biomass materials and agricultural wastes were widely utilized as low-cost biosorbents for the removal of cationic dyes dye such as Citrus limetta peel waste [22], Cucumis sativus peel waste [23], Punica granatum peel [24], sulphuric acid-treated orange peel [25], fallen leaves [26], Tectona grandis sawdust [27], and Luffa aegyptiaca peel [28]. The adsorption capacity and surface property of the adsorbent prepared from biomass depend on the type of chemical activator, and the source of the precursor, in addition to the activation process [29].

Chemical activation of biomass is one of the most significant methods frequently applied for developing oxygenated and hydrophilic carbonaceous adsorbents that contain different types of functional groups such as carboxyl (-COOH) and hydroxyl (-OH) groups. Sulphuric acid (H₂SO₄) is one of the super-oxidizing agents that are frequently utilized as a chemical activator for enhancing the surface functionality of biomass materials with oxygenated-acidic functional groups [30]. Previous studies indicate that the concentration of the chemical activators is responsible for enhancing the oxygenated-functional group content on the surface of treated biomass [31,32]. Therefore, H₂SO₄ acid was

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selected to be an oxidizing activator in this research due to its many desirable properties such as super oxidation power, cost-effectiveness, relatively low activation temperature, and the ability to tune the amorphous domains of cellulosic materials into aromatize form of carbon framework [33,34].

Therefore, the main aim of this study is to develop acid-functionalized biosorbent from renewable bio mass waste, namely coconut shell (CS) by the chemical treatment method with sulphuric acid (H_2SO_4) to obtain sulphuric acid-treated coconut shell (SATCS) as a low-cost biosorbent. The effectiveness of the developed SATCS was tested for the removal of MB dye from the aqueous environment under optimum adsorption operational parameters such as adsorbent dosage, solution pH, contact time and MB dye concentration. Moreover, the adsorption mechanism of MB on the surface of SATCS was discussed.

2. Experimental procedure

2.1. Materials

Methylene blue (MB) dye (MW: 319.86 g/mol, assay: ~ 99%, \( \lambda_{\text{max}} = 661 \) nm) and sulphuric acid (H_2SO_4, 95–98%) were purchased from R&M Chemicals. The other reagents utilized throughout this study were of analytical grade. All experiments of this research were performed using ultrapure water.

2.2. Preparation of sulphuric acid-treated coconut shell (SATCS)

Coconut shell (CS) was collected from a local market in Shah Alam, Selangor, Malaysia. CS was fully rinsed by using tap water, then by distilled water to eliminate soluble impurities, and then crushed and sieved to a certain mesh size of \( \leq 1 \) mm. The impregnating process with concentrated sulphuric acid (H_2SO_4, 95–98%) was carried out following the published activation procedure by Garg et al. [35], with a mixing ratio of 1 g coconut shell powder and 1 mL of sulphuric acid. The obtained sulphuric acid-treated coconut shell (SATCS) was washed many times in boiled and distilled water in order to reach a neutral pH value. After that, SATCS powder is left for 24 h for the drying process inside an oven at 100°C. The final dried powder form of SATCS was sieved to the desired mesh size of \( \leq 0.25 \) mm for further applications.

2.3. Characterization of SATCS

The characterization of SATCS was performed by various analytical methods and techniques. The point of zero charge (pH_{zpc}) for SATCS was determined based on the reported method [36]. The porosity and pore volume of the SATCS was investigated by Micromeritics ASAP 2060 analyser at 77 K. Scanning electron microscope (SEM) (Hitachi, TM3030Plus, Tabletop Microscope) was utilized to determine the morphological characteristics of SATCS before and after the adsorption of MB molecules. The X-Ray diffraction (XRD, X’Pert PRO, PANalytical) was used to determine the crystallinity of SATCS. Fourier Transform Infrared (FTIR) spectroscopy was performed by using Perkin-Elmer, Spectrum RX I to identify the available functional group on the surface of SATCS before and after adsorption. The CHNS analysis (Flash 2000, Organic Elemental Analyser) was performed to determine the elemental composition of SATCS.

2.4. Batch adsorption experiments

The adsorption experiments of MB dye on SATCS were investigated in a batch mode. The experiments were carried out in a series of Erlenmeyer flask (250 mL) containing MB dye solution (100 mL) with different initial MB dye concentrations (25–200 mg/L). The different dosages of SATCS (0.02–0.2 g) were added to the 100 mL of MB dye solution with different levels of pH (3–10), and agitated at a fixed shaking speed of 110 strokes/min at 303 K by using a water bath (WNB7-45, Memmert, Germany). After the adsorption process, the adsorbents was separated from aqueous solutions using a syringe filter (0.20 \( \mu \)m), and the MB dye uptake was calculated by UV-Vis spectroscopy (HACH DR 2800) at 661 nm. Equilibrium isotherms were performed at optimum conditions (temperature = 303 K, adsorbent dosage = 0.1 g/100 mL, and pH = 8) by using initial MB concentrations from 25 to 200 mg/L. The MB dye removal (DR%) and adsorbed amount of MB dye at equilibrium, \( q_e \) (mg/g) were determined by the following Equations (1) and (2), respectively.

\[
DR\% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)
\]

\[
q_e = \left( \frac{C_0 - C_e}{W} \right) \times V \quad (2)
\]

where \( C_0 \) (mg/L) is the MB initial concentration while \( C_e \) (mg/L) is the equilibrium concentration of MB. \( V \) (L) is the volume of MB solution, and \( W \) (g) is the weight of SATCS.

3. Results and discussion

3.1. Characterization

3.1.1. Physicochemical properties of SATCS

The textural properties and elemental analysis of SATCS are recorded in Table 1. It is observed that the SATCS has a relatively high content of C (51.90%) with a high content of O (44.63%), while the contents of H (2.97%) and N (0.37%) are relatively low. This observation can be attributed to the releasing of volatile compounds during carbonization to eliminate non-carbon species and
Table 1. The physicochemical properties of the SATCS.

| Analysis                          | Values |
|----------------------------------|--------|
| Elemental analysis (wt. %)       |        |
| C                                | 51.9   |
| H                                | 2.97   |
| N                                | 0.37   |
| S                                | 0.13   |
| O (by difference)                | 44.6   |
| Surface property                 |        |
| Volume in pores (cm³/g)          | 0.00018|
| Total volume in pores (cm³/g)    | 0.00203|
| Total area in pores (m²/g)       | 0.08   |
| BET surface area (m²/g)          | 1.14   |
| Langmuir surface area (m²/g)     | 1.65   |

3.1.2. XRD analysis
The crystallinity and amorphous nature of SATCS is investigated by the XRD analysis. Figure 1 presents the XRD pattern of the SATCS. As can be seen, two broad diffraction peaks display at \(2\theta = 24^\circ\) (002) and \(2\theta = 42^\circ\) (100), indicating the SATCS an amorphous structure and composed of crystallographic planes of carbonaceous materials [37,38].

3.1.3. FTIR analysis
The surface functional groups of SATCS are identified by the FTIR spectral analysis. Figure 2(a) displays the FTIR spectrum of SATCS before MB dye adsorption. It is observed from Figure 2(a) that characteristic peaks show at 3400 and 1700 cm\(^{-1}\) corresponding to the (\(\nu\)-O–H groups) and (\(\nu\)-C = O of RCOOH or RCOOR), while peaks at 1610 and 1560 cm\(^{-1}\) attributed to the asymmetric and symmetric of \(\nu\)-COO [39], respectively. The bands at \(\sim 1610\) and \(1200\) cm\(^{-1}\) indicate the (\(\nu\)-C = C of aromatic rings) [40] and (\(\nu\)-C–O–C and/or \(\nu\)-C–O of Ar-OH, ROH, and H\(_2\)SO\(_4\) acid) [14], respectively.

3.1.4. pH\(_{\text{pzc}}\) analysis
pH\(_{\text{pzc}}\) analysis was performed to determine the surface charge of the SATCS. The value of pH\(_{\text{pzc}}\) for the SATCS was found to be 3.0, as presented in Figure 3. This result indicates the acidic characteristic of the SATCS surface which might be attributed to the existence of some acidic functional groups such as COO\(^-\) and SO\(_3\)\(^-\) on the SATCS surface. Generally, the surface of the SATCS can be obtained a negative charge at pH value above the pH\(_{\text{pzc}}\), and as a result, the adsorption of cationic species such as MB dye would be preferable. A similar observation was noticed by other researchers for the pH\(_{\text{pzc}}\) values after various biomass materials treated with H\(_2\)SO\(_4\) such as coconut leaf (pH\(_{\text{pzc}}\) = 3.2) [14] and mango peel (pH\(_{\text{pzc}}\) = 4.6) [41].

3.1.5. SEM analysis
The surface morphology of SATCS before and after MB dye adsorption is observed by the SEM analysis. Figure 4(a,b) displays the SEM images of the SATCS.

enrich carbon. The high oxygen content and detectable amount of sulphur can be attributed to the role of sulphuric acid as a chemical activator. However, the low surface area (1.137 m\(^2\)/g) of SATCS can be attributed to a high concentration of H\(_2\)SO\(_4\) acid which is responsible for reducing the pore volume on the surface of SATCS [32].

The FTIR spectrum of SATCS after MB dye adsorption is shown in Figure 2(b). It was observed from Figure 2(b), some bands are shifted to higher wavenumbers, indicating the interactions between adsorption functional groups of SATCS and MB dye molecules that are loaded on the surface of the SATCS.

The pH\(_{\text{pzc}}\) of SATCS.

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Figure 4. SEM images of (a) SATCS, and (b) SATCS after MB dye adsorption with a magnification of ×700.

before and after MB dye adsorption, respectively. From Figure 4(a), it is observed that the surface of the SATCS appears as a rough, porous surface with visible cracks and irregular shape pores. The generated pores on the surface of the SATCS could be ascribed to the evaporative loss of the chemical activator during the activation process. The presence of these pores within the structure of the SATCS exhibits an essential role in the adsorption process of MB dye molecules. The surface of the SATCS after the adsorption of MB dye (Figure 4(b)) turned to be less porous with the evanescence of crevices on the SATCS surface, indicating successful loading of MB dye molecules on the SATCS surface.

3.2. Adsorption study

3.2.1. Effect of SATCS dosage
The influence of SATCS dosage on the removal of MB dye by the SATCS was tested by varying the adsorbent dosage from 0.02 to 0.2 g with fixed volume and initial concentration of MB dye, solution pH, temperature, contact time, and shaking speed at 100 mL and 200 mg/L, 5.6, 303 K, 480 min, and 110 strokes/min, respectively. As shown in Figure 5, the removal of MB dye increased from 9.3% to 83% with increasing adsorbent dosage from 0.02 g/100 mL to 0.1 g/100 mL. The highest MB dye removal (83%) was obtained at 0.1 g/100 mL, which can be assigned to higher surface area and/or the adsorption active sites that are available for the adsorption of MB molecules. Further increase in adsorbent dosage above 0.1 g did not show any further improvement in MB removal. Therefore, 0.1 g/100 mL was chosen to be an optimum adsorbent dosage for further investigations.

3.2.2. Effect of solution pH
The effect of initial solution pH on the adsorption capacity of MB dye onto the SATCS was performed at different pH levels (pH 3–10) with fixing others adsorption parameters (adsorbent dosage 0.1 g/100 mL, concentration 200 mg/L, and temperature 303 K). It is observed from Figure 6, with the increase in solution pH from 3 to 8 the adsorption capacity, \( q_t \) (mg/g) rises from 76.3 mg/g to 82.3 mg/g. The highest adsorption capacity of the MB was recorded at solution pH 8, and a gradual decrease in adsorption capacity could be noticed at acidic medium. The pHpzc value of the SATCS was found to be 3, as shown in Figure 3, indicating the surface of the SATCS is positively charged. On the other hand, the surface of the SATCS can be converted to negative charge at basic pH environment, and therefore a strong electrostatic attraction can occur between the negatively charged functional group on the SATCS surface and positively charged group of MB and [42]. Therefore, solution pH 8 is determined to be the best solution pH for further applications.

3.2.3. Effect of initial MB concentration and contact time
The influence of initial MB dye concentration and contact time on adsorption equilibrium was investigated. The adsorption capacity, \( q_t \) (mg/g) against time at several initial MB dye concentrations of 25, 50, 75, 100 and 200 mg/L is investigated and depicted in Figure 7, while

Figure 5. Influence of SATCS dosage on MB dye removal (V: 100 mL; [MB] = 200 mgL\(^{-1}\); solution pH: 5.6, \( T = 303 \) K).
Figure 6. Influence of pH on MB dye uptake using SATCS (V: 100 mL; [MB] = 200 mg/L; SATCS dosage: 0.1 g/100 mL, T = 303 K).

Figure 7. Influence of initial MB dye concentration and contact time on adsorption of MB by SATCS (V = 100 mL, T = 303 K, solution pH = 8, SATCS dosage = 0.1 g/100 mL).

Figure 8. Non-linear plots of PFO and PSO models for MB adsorption on the SATCS surface (V = 100 mL, SATCS dose = 0.1 g, solution pH 8, shaking speed = 110 strokes/min, and 303 K).

Table 2. Kinetic parameters for the adsorption of MB by SATCS at 303 K.

| Co (mg/L) | 25   | 50   | 75   | 100  | 200  |
|-----------|------|------|------|------|------|
| q<sub>e</sub>,exp (mg/g) | 22.2 | 30.4 | 38.3 | 43.5 | 78.8 |
| q<sub>e</sub>,cal (mg/g) | 24.7 | 29.9 | 35.6 | 41.1 | 70.5 |
| k<sub>1</sub> (1/min) × 10<sup>-2</sup> | 7.82 | 7.77 | 12.2 | 12.1 | 9.71 |
| R<sup>2</sup> | 0.98 | 0.97 | 0.97 | 0.97 | 0.90 |
| ARE | 53.8 | 48.4 | 85.5 | 92.2 | 105.2 |
| q<sub>e</sub>,cal (mg/g) | 22.1 | 31.4 | 39.3 | 45.2 | 78.2 |
| k<sub>2</sub> (g/mgmin) × 10<sup>-3</sup> | 4.11 | 3.00 | 4.20 | 3.70 | 1.70 |
| R<sup>2</sup> | 0.98 | 0.98 | 0.99 | 0.99 | 0.97 |
| ARE | 18.5 | 22.1 | 26.4 | 12.2 | 9.6 |

3.3. Adsorption kinetic

The non-linear pseudo-first-order (PFO) and non-linear pseudo-second-order (PSO) kinetic models are utilized to analyse the experimental data of the MB dye adsorption on the SATCS surface at different initial MB concentration. The non-linear equations of the kinetic models PFO [44] and PSO [45] are expressed in Equations (3) and (4) as follows:

\[
q_t = q_e \left(1 - e^{-k_1t}\right) \quad (3)
\]

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

where \(q_e\) (mg/g) is the amount of MB dye adsorbed at equilibrium, and \(q_t\) (mg/g) is the amount of MB dye adsorbed at the time \(t\). \(k_1\) (1/min) is the rate constant of PFO, and \(k_2\) (g/mg min) is the rate constant of PSO. The kinetic data are also analysed by the coefficient of determination \(R^2\), and non-linear average relative error (ARE). The equations of \(R^2\) and ARE functions are presented as follows:

\[
R^2 = 1 - \frac{\sum_{n=1}^{N} (q_{t,meas} - q_{t,cal})^2}{\sum_{N=1}^{N} (q_{t,cal} - q_{t,cal})^2} \quad (5)
\]

\[
ARE = \frac{100}{n} \sqrt{\sum_{i=1}^{n} \left[\frac{q_{t,meas} - q_{t,cal}}{q_{t,meas}}\right]} \quad (6)
\]

where \(q_{t,meas}\) (mg/g) and \(q_{t,cal}\) (mg/g) are measured and calculated adsorption capacities of MB dye at time \(t\), while \(n\) is the number of observations.

The non-linear plots of PFO and PSO models are displayed in Figure 8. The parameters of kinetic models,
3.4. Adsorption isotherms

Non-linear equilibrium models of Langmuir, Freundlich, and Temkin are utilized to fit the experimental data. The non-linear equations of the equilibrium models Langmuir [47], Freundlich [48], and Temkin [49] are presented in Equations (7)–(9), respectively.

$$ q_e = \frac{q_{\text{max}} K_a C_e}{1 + K_a C_e} $$  \hspace{1cm} (7)

$$ q_e = K_f C_e^{1/n} $$  \hspace{1cm} (8)

$$ q_e = \frac{R T}{b T} \ln(K_T C_e) $$  \hspace{1cm} (9)

where $q_e$ (mg/g) is the amount of MB dye adsorbed at equilibrium, $C_e$ (mg/L) is the concentration of MB dye at equilibrium, $q_{\text{max}}$ (mg/g) is the maximum adsorption capacity, and $K_a$ (L/mg) is the Langmuir constant. $K_f$ (L/mg) is the Freundlich constant, $n$ is the dimensionless constant that indicates the adsorption intensity. $K_T$ (L/mg) is the Temkin constant, $T$ (K) is the temperature, $R$ (8.314 J/mol K) is the universal gas constant, and $b T$ (J/mol) is the heat of adsorption. The non-linear curves of the equilibrium models are shown in Figure 9. The parameters of equilibrium models are recorded in Table 3. According to the $R^2$ values (Table 3) obtained from the isotherm models, Freundlich isotherm shows the highest correlation ($R^2$ 0.97) which indicates the MB dye adsorption occurred on the heterogeneous surface [50]. The value of $1/n$ is less than 1, indicating the strong adsorption bond between MB dye molecules onto SATCS [51]. The maximum adsorption capacity ($q_{\text{max}}$) of SATCS for MB dye is 50.6 mg/g at 303 K. The $q_{\text{max}}$ of SATCS for MB dye is compared with other adsorbents of biomass materials treated with H$_2$SO$_4$ and presented in Table 4 which indicates the desirable adsorption property of the SATCS for the removal of cationic dye compared to other available biomass-based adsorbents.

3.5. Adsorption mechanism

There are three functional groups available on the surface SATCS can be involved in the adsorption mechanism of MB dye such as hydroxyl (OH), carboxyl (COOH), and carbonyl (C = O) as confirmed previously by FTIR spectral analysis. The sulphonation process is responsible for creating SO$_3$ acidic group on the surface of

| H$_2$SO$_4$-treated biomass | Adsorbent dosage (g) | pH | Temp. (K) | $q_{\text{max}}$ (mg/g) | Kinetic model | References |
|---------------------------|----------------------|----|-----------|--------------------------|--------------|------------|
| Coconut shell             | 0.1 g/100 mL         | 8  | 303       | 50.6                     | PSO          | This study |
| Mango peels               | 0.14 g/100 mL        | 5–6| 303       | 277.8                    | PSO          | [41]       |
| Rubber leaf               | 0.1 g/100 mL         | 5.6| 303       | 263.2                    | PSO          | [55]       |
| Banana peels              | 0.08 g/100 mL        | 10 | 303       | 250                      | PFO          | [56]       |
| Corn cob                  | 0.12 g/100 mL        | 5.6| 303       | 216.6                    | PFO          | [57]       |
| Bagasse                   | 0.4 g/100 mL         | 9  | 300–333   | 49.8–56.5                | PSO          | [58]       |
| Ficus carica              | 0.5 g/100 mL         | 8  | 298–323   | 47.62                    | PSO          | [59]       |
| Parthenium hysterophorus  | 0.4 g/100 mL         | 7  | 298       | 39.7                     | –            | [60]       |
| Dacton regia pods         | 0.2 g/100 mL         | 7  | 298       | 23.3                     | –            | [61]       |
| Wild carrot               | 0.05 g/100 mL        | 6  | 298       | 21                      | PSO          | [62]       |
| Sunflower oil cake        | 0.2 g/100 mL         | 6  | 288–318   | 16.43                    | PSO          | [63]       |
SATCS, which can play an important role in the adsorption process of MB dye through electrostatic attractions with the positively charged MB dye molecules. Generally, the adsorption mechanism of MB dye on the SATCS surface by different types of interactions is shown in Figure 10. An electrostatic attraction (Figure 10(a)) is considered from the most interaction that can occur between MB dye and the SATCS surface. This mechanism involves the electrostatic interaction between MB dye cations with negatively charged available on the SATCS surface. Adsorption mechanism also includes H-bonding interactions (Figure 10(b)) that occurred between H atom available on the surface of the SATCS, and N atoms in the MB dye structure. Finally, π-π interaction (Figure 10(c)) can occur between the hexagonal skeleton of SATCS and aromatic rings of MB dye. According to the above discussion, it can be concluded that these interactions are effective in enhancing the adsorption process of MB dye on the surface of the SATCS. Similar results were reported by other studies for the MB dye adsorption on multi-wall carbon nanotube [52], chemically treated carbon microspheres [53], wrapping carbon nanotube [54], and coal activated carbon [37].

4. Conclusion
The sulphuric acid-treated coconut shell (SATCS) was synthesized and applied for the removal of MB dye from the aqueous environment. The optimum conditions of adsorption process parameters were adsorbent dosage (0.1 g/100 mL), solution pH 8, and temperature (303 K). The kinetics and isotherms models data revealed that the adsorption was affected by chemisorption and heterogeneous mode of adsorption. The adsorption capacity of the SATCS was 50.6 mg/g at 303 K for MB dye. The adsorption mechanism included electrostatic attraction and H-bonding interaction, and π-π interactions. The adsorption results revealed that the SATCS is a feasible and low-cost biosorbent for the removal of MB dye.

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