

PAPER • OPEN ACCESS

Methylene blue dye removal using *Parkia speciosa* pod based activated carbon

To cite this article: A Aziz *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **765** 012104

View the [article online](#) for updates and enhancements.

You may also like

- [-keratin/Alginate Biosorbent for Removal of Methylene Blue on Aqueous Solution in a Batch System](#)
G Fadillah, E N K Putri, S Febrianastuti et al.
- [Kinetic and Thermodynamic Studies for Mebeverine hydrochloride Adsorption from Aqueous Solution using prepared chitosan polymer in delivery drug system](#)
Jubran G. Jabbar Almkhtar and Faiq F. Karam
- [Efficient removal of methylene blue by low-cost and biodegradable highly effective adsorbents based on biomass in the fixed bed column](#)
D Sasaengta, M Panapoy, N Chaiyut et al.

Methylene blue dye removal using *Parkia speciosa* pod based activated carbon

A Aziz¹, H Hassan^{1,2}, N K EM Yahaya³, J Karim³, M A Ahmad^{1*}

¹School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia

²Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia

³National Water Research Institute of Malaysia, 43300 Seri Kembangan, Selangor, Malaysia

* E-mail: chazmier@usm.my

Abstract. Critical environmental issues have emerged from wastewater of industrial textile effluent discharge which consists of refractory dyes. Effective methods such as activated carbon (AC) adsorption is extremely demanded for solving this environmental pollution. In this study, low-cost AC was developed from *Parkia speciosa* pods (PSP) using microwave-assisted activation technique for the methylene blue (MB) dye adsorption. Optimization on activating conditions in terms of MB removal and AC yield was performed using response surface methodology (RSM). The optimum microwave irradiation power (MIP) of 416.50 W was found to have significant effect on MB removal at 2 minutes activation. The *Parkia speciosa* pods activated carbon (PSPAC) possessed intermediate surface area and total pore volume of 51.3 m²/g and 0.0681 cm³/g, respectively. PSPAC surface morphology was microscopically observed with highly porous structure indicating characteristics of good AC. Batch adsorption studies with various initial concentrations discovered that MB adsorption increased with increasing initial concentrations and contact time. The experimental data was in close fit using Langmuir isotherm and followed pseudo-first-order kinetic models. The MB dye adsorption process was governed by simultaneous surface adsorption and intraparticle diffusion. The results of studies proved that PSPAC is a potential adsorbent for dye-contaminated wastewater.



1. Introduction

Textile industry has emerged as one of the important key trading profits for Malaysian economic growth. In 2017, this industry stood firm as the country's eleventh largest export earner, contributing approximately RM 15.3 billion to Malaysia's total export manufactured goods [1]. Textile and apparel industry alone in Malaysia generated a gross domestic production of GDP of 1.2 % in the year 2017 [2]. The main product of textile industry is textile fibers which are used primarily in the making of garments. Textile fibers can be broadly categorized into natural fibers and synthetic fibers. Natural fibers are originated from natural resources likes cotton, wool and silk whereas synthetic fibers are made from either natural polymer such as viscose and cellulose acetate or synthetic polymers such as polyester, nylon, spandex, acetate, acrylic, ingeo and polypropylene. However, the vast development of textile industry has led to the birth of modern environmental issues, especially the discharged liquid effluent which contains hazardous contaminants, including acidic or caustic dissolved solids, toxic compounds, and dyes [3].

Dyes have been used extensively to produce coloured products in various industries. Dyes are usually coloured organic compounds or a mixture that may be used to give colour to a substrate having resistance to normal laundry or cleansing procedures and stability to light [4]. Some common dyes being applied in industry include basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulphur dyes [5]. Over 100, 000 types of dyes are available commercially with an annual worldwide production of 700, 000–1, 000, 000 tons has been reported in the literature [6]. An estimation of 90 % of the dyes produced will end up in fabric products with the remaining 10 % shared by the production of leather, paper, plastic and chemicals [7]. Owing to these extensive consumptions of dyes in the textile industries, the discharged of huge amounts of dyes in the wastewater streams is inevitable. The presence of dyes in the water cycle system poses health concerns to both humans and animals as most of the dyes have found to be toxic or carcinogenic in nature to both aquatic organism and to human life. This is especially true for the most common dyes applied in textile industry namely methylene blue (MB). Furthermore, synthetic dyes are not easily eradicated in spite of being under aerobic conditions and has high chance of decomposing into carcinogenic aromatic amines in such conditions. As for reactive dyes, the removal by chemical coagulation is intricate due to the dyes' commending water solubility [8]. Consequently, the colours of dyes tend to persist in water due to their stability and resistance. Therefore, it is extremely important to treat the textile industry wastewater before it could pose severer adverse effect to our aquatic ecosystem.

Many treatment processes have been developed to treat this effluent efficiently and economically. Among them adsorption technique turns out to be a greatly promising treatment process due to its high efficiency for removing colours from wastewater stream for a wide variety of dyes [9]. Several criteria of absorbents such as high affinity, high adsorption capability and absorbent regeneration ability are the main considerations in selecting adsorbents. One of the most effective adsorbents which can work for a wide range of dyes is activated carbon (AC). However, commercial AC possesses limitations owing to high price and difficulty in regeneration [10]. Thus, the challenges in applying AC in the adsorption of dyes are to develop low-cost effective AC. Many researches have been developing AC from agricultural wastes such as capsicum annum seeds [11], tea waste [12], rice husk [13], etc. Since, agricultural wastes have little economic values, turning them into AC serves the purposes of eradicating textile wastewater pollution as well as reducing wastes. Therefore, utilizing agricultural wastes as potential low-cost AC appears to be a feasible solution as they are present in great amount in Malaysia.

The recent studies have been prioritized on the development of low-cost and potent adsorbents for dye removal from textile effluent. Many non-conventional low-cost and abundant adsorbents developed from agricultural wastes have been proposed including bamboo, oil palm empty fruit bunch, date stone, orange peel and rubber seed coat [14]. According to literature, AC derived from agro wastes is

in beneficial terms in providing a constructive, economically viable substitute for non-renewable coal-based AC as they offer promising performance [15]. Another agricultural waste that can be utilized in producing AC is *Parkia speciosa* pod (PSP). *Parkia speciosa* (PS) is a type of beans that can be found abundantly in Southeast Asian countries including Malaysia. It bears long and flat bean pod with green seeds. While the seeds are edible in either raw or cooked, and the pods are often considered as wastes. The disposal of these wastes could result environmental problem due to its abundance and under-utilization [16, 17]. Hence, PSP is proposed to be a potential precursor in the activated carbon preparation. Present study investigates the PSP based AC in optimizing the adsorption of MB dye using various activation parameters and their underlying kinetic-mechanism relationship.

2. Methodology

2.1 Materials

PSP as the raw material in synthesizing AC was collected from local market near Nibong Tebal, Pulau Pinang district. MB used as adsorbate in synthetic dye solution was supplied by Sigma-Aldrich (M) Sdn. Bhd. Nitrogen gas (N_2) and carbon dioxide gas (CO_2) with 99.99% and 99.80% purity used in activation process were supplied by MOX-Linde Gases Sdn Bhd.

2.2 *Parkia speciosa* pod-based activated carbon (PSPAC) preparation

Equipment used in the preparation of PSPAC include oven (model: Memmert 600, Germany) for drying the precursor, vertical tubular furnace (model: Carbolite, USA) for carbonization of dried PSP and microwave oven for the activation of PSP. Equipment setup for microwave-assisted activation process of PSPAC is shown in Figure 1.

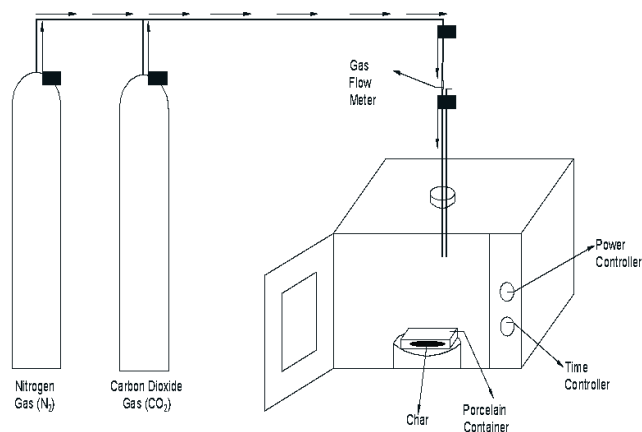


Figure 1. Schematic diagram of equipment setup of PSPAC activation process.

The PSP precursor samples were rinsed with distilled water and cut into smaller size. Moisture content of cleaned sample was removed by drying the sample in the oven for 24 hours. The oven-dried samples were then ground using an electric blender and sieved to the size between 355 μm to 1 mm. Carbonization of the sample was done by heating in the furnace at the temperature of 400 $^{\circ}C$ and heating rate of 10 $^{\circ}C/min$ for 1 hour. The product known as char, was then removed from the furnace and was allowed to cool down in a desiccator. The char was then placed in a commercial modified microwave oven at desired microwave irradiation power (MIP) and activation time under CO_2 flow rate of 1 cm^3/min to produce AC. Once the activation was done, the AC was cooled under N_2 flow and

then washed with hot distilled water to remove any dirt or color. The washed AC was oven-dried for 24 hours and stored for further characterization and batch adsorption studies.

2.3 Characterization of PSP precursor and PSPAC

The Brunauer–Emmett–Teller (BET) surface area, pore volume and average pore diameter of the samples were determined using volumetric adsorption analyzer (model: Micrometrics ASAP 2020). BET surface area was determined from the adsorption isotherm using BET equation; total pore volume was estimated to be liquid nitrogen volume under relative pressure of 0.98. Surface morphology of the samples was examined using scanning electron microscope (SEM) (model: Quanta 450 FEG, Netherland). The proximate analysis of the samples was carried out by sample capsulation inside a tin and pyrolysis process inside the combustion chamber under temperature of 975 °C using a simultaneous thermal analyzer (model: Perkin Elmer STA 6000, USA).

2.4 Batch adsorption system

Batch adsorption experiments of MB using PSPAC were carried out using a series of Erlenmeyer flasks under optimized activation conditions. Each Erlenmeyer flask was filled with 0.2 g of PSPAC, 200 mL of 50 mg/L to 300 mg/L initial concentrations of dye solution and sealed with aluminium foil. The Erlenmeyer flasks were then immersed in an isothermal water bath shaker (model: Protech, Malaysia) at 30 °C over 1 day for batch adsorption tests.

2.5 Design of experiment for PSPAC preparation

Optimization of activation conditions of PSPAC was carried out by Central Composite Design (CCD) of Response Surface Methodology (RSM) using Design-Expert® software version 12.0.1 (Stat-Ease, Inc, Minneapolis, MN 55413). Two parameters were optimized during PSPAC activation process namely, microwave irradiation power, x_1 (W) and activation time, x_2 (mins). The responses were MB removal, Y_1 (%) and AC yield, Y_2 (%). Each parameter was studied at a two-level and two factors CCD where the number of run of experiments is determined according to Equation 1.

$$N = 2^k + 2k + N_0 \quad (1)$$

Where, N = number of run of experiments, k = number of parameters, and N_0 = number of replicates at the center point.

CCD yields a total number of 13 run of experiments, with 4 factorial points; 4 axial points and 5 centroid replicate points. The matrix of studied range of parameters is shown in Table 1. The 13 experimental runs with the preparation parameters of PSPAC are listed in Table A1 in the Appendix.

Table 1. Studied range of parameters in coded and actual form for preparation of PSPAC.

Parameter (Factor)	Units	Low Level	0 Level	High Level
		+1	0	-1
Microwave Irradiation Power	W	264	440	616
Activation Time	Min	2	3	4

The empirical model which correlates the MB removal by PSPAC and PSPAC yield to the AC preparation variables can be represented by the second order (quadratic) polynomial equation. It is depicted by the following general empirical equation [18]:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} x_i x_j \quad (2)$$

where Y = modelled response

x_i, x_j = coded independent variables

β_0, β_i = constant coefficient and linear coefficient

β_{ii}, β_{ij} = quadratic coefficient and interactive coefficient

2.6 Sample analysis

Analysis of the sample was done by collecting the sample at desired time interval via a 10 ml disposable syringe. The dye concentration of each sample was determined by using UV-visible spectrometer. The desired wavelength was fixed at 663 nm after performing wavelength of maximum absorbance determination. The linear relationship between dye absorbance which has been adsorbed onto PSPAC and their respective concentration was determined using graphical method of absorbance versus concentration of the MB dye solutions to yield the calibration curve.

2.7 AC yield

AC yield was determined by measuring both the dry weight of the precursor and dry weight of final AC using an electronic balance (model: AND GF-3000, Australia). The calculation of AC yield was done according to Equation (3):

$$Yield (\%) = \frac{w_{AC}}{w_p} \times 100 \quad (3)$$

where w_{AC} = dry weight of final AC

w_p = dry weight of precursor

2.8 Studies of batch equilibrium, adsorption isotherm, kinetics and mechanism

For studying the batch equilibrium of MB dye adsorption on the PSPAC, similar method was used as in Section 2.4. The experiments were maintained at an adsorption temperature of 30 °C and agitation speed of 60 rpm over 1 day. The steps were repeated up to equilibrium stage. The amount of adsorption at equilibrium, q_e was calculated based on the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (4)$$

where C_o = Liquid-phase dye concentrations at initial stage (mg/L)

C_e = Liquid-phase concentrations of dye at equilibrium stage (mg/L)

V = Volume of dye solution (L)

W = Mass of adsorbent used (g)

MB dye removal, % C was determined using Equation (5):

$$\% C = \frac{(C_o - C_t)}{C_o} \times 100 \quad (5)$$

where C_t is liquid-phase dye concentrations at a particular time.

For isotherm studies, the collected experimental data was fitted with 3 isotherms; Langmuir, Freundlich and Temkin isotherms. Near unity correlation coefficient, R^2 was desired to determine which isotherm yielded the best fit to the experimental data. In kinetic adsorption study, the amount of adsorption at time t , q_t (mg/g) was determined using Equation (6) as follow:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (6)$$

where C_o = Liquid-phase dye concentrations at initial stage (mg/L)

C_e = Liquid-phase concentrations of dye at equilibrium stage (mg/L)

V = Volume of dye solution (L)

W = Mass of adsorbent used (g)

Pseudo-first and -second-order kinetic models were used to fit the experimental data. Similarly, the best-fit model was chosen based on the degree of closeness to unity of R^2 .

3. Results and discussion

3.1 Optimization of MB removal and AC yield

The overall design matrix, MB removal and AC yield data responses are listed in Table A2 in the Appendix. The maximum MB removal was found to be in the range of 69.65 % to 99.60 % whereas for maximum AC yield, it was found ranging from 32.77 % to 56.17 %. For MB removal, the selected model was quadratic model meanwhile for AC yield, the selected model was linear model based on the suggestion from the software. Final empirical models for the responses in coded factors form with insignificant terms excluded are demonstrated in Equation (7) and Equation (8), respectively.

$$\text{MB removal, } Y_1 = 92.20 + 5.43x_1 + 3.16x_2 - 1.23x_1x_2 - 15.22x_1^2 + 0.6776x_2^2 \quad (7)$$

$$\text{AC yield, } Y_2 = 43.67 - 8.64x_1 - 3.16x_2 \quad (8)$$

From the empirical equations, MB removal, Y_1 is influenced by the synergistic effect of the linear terms of factors x_1 and x_2 as well as quadratic effect of second-order term of factor x_2 . In addition, Y_1 is also influenced by the antagonistic effect of interaction term of x_1x_2 and quadratic effect of second-order term of factor x_1 . As for AC yield, Y_2 , the response is influenced by the antagonistic effect of linear terms of both factors x_1 and x_2 .

Validation of the developed models can be evaluated based on the correlation coefficients, R^2 . As R^2 is approaching unity, the model is able to predict the behaviour of responses better based on the parameters as it will give predicted values near to experimental values. From the results of fit statistics, the R^2 values for both Equation (7) and Equation (8) are 0.8665 and 0.9590 respectively. It signifies that 86.65% and 95.90% of the total variation in MB removal and AC yield were explained by the experimental-studied variables included in the developed model. In addition, standard deviations calculated for both models were 4.62 and 1.47 respectively. The relatively low standard deviations illustrate that the experimental values fell closer to the mean of experimental values. Since the R^2 values obtained for both models were relatively high (close to unity) and possessed low standard deviations, it is an indication of good agreement between predicted values and experimental values by the developed models. However, the R^2 value for MB removal (0.8665) is comparatively lower than that of AC yield (0.9590), which suggests that MB removal prediction might lead to larger variation as compared to AC yield. It could be deduced that the developed models provide convincingly good prediction for both responses, MB removal and AC yield within the experimental study range.

Analysis of variance (ANOVA) was carried out to further evaluate the adequacy and significance of the developed models. Table 2 and 3 show the ANOVA results for quadratic model of MB removal and linear model of AC yield, respectively.

Table 2. Analysis of variance (ANOVA) for quadratic model of MB removal using PSPAC.

Source	Sum of Squares	Degree of Freedom (DF)	Mean Square	F value	Prob > F
Model	967.83	5	193.57	9.08	0.0057
x_1	177.13	1	177.13	8.31	0.0235
x_2	59.91	1	59.91	2.81	0.1375
x_1x_2	6.05	1	6.05	0.28	0.6106
x_1^2	639.99	1	639.99	30.04	0.0009

x_2^2	1.27	1	1.27	0.06	0.8143
---------	------	---	------	------	--------

Table 3. Analysis of variance (ANOVA) for linear model of AC yield using PSPAC.

Source	Sum of Squares	Degree of Freedom (DF)	Mean Square	F value	Prob > F
Model	507.10	2	253.55	116.95	<0.0001
x_1	447.38	1	447.38	206.36	<0.0001
x_2	59.72	1	59.72	27.55	0.0004

The large Model F-value of 9.08 and low Prob > F value of 0.0057 in Table 2 implies that the generated model was significant. There is merely 0.57% possibility that this large F-value could occur because of noise. As for Prob > F value, low value of below 0.05 indicates that the result is not random and will attribute significant effect to the response [19]. Hence, from the ANOVA results for each term, Prob > F value of less than 0.05 shows that the model terms have significant effect to MB removal response. In this case, microwave irradiation power (x_1) and the quadratic term of MIP (x_1^2) were significant. Meanwhile, activation time (x_2), interaction term of MIP and activation time (x_1x_2) and quadratic term of activation time (x_2^2) were insignificant.

On the other hand, ANOVA results for linear model of AC yield using PSPAC is shown in Table 3. Similarly, the large model F-value and low Prob > F value of 116.95 and below 0.0001 respectively indicate that the generated model was significant as well. Only 0.01% possibility that this large F-value could occur because of noise. The results also show that the Prob > F values of less than 0.05 for all the terms involved in the model. Thus, MIP (x_1) and activation time (x_2) both having significant effects to AC yield response. It is deduced that MIP found to have prominent effect whereas activation time imposed insignificant effect on MB removal by PSPAC.

MB removal increases rapidly with increasing MIP up to a maximum value which is the optimum value as depicted in Figure 2 (a). Further increasing the MIP beyond the optimum value shows appreciable decrease in MB removal. Similar trend was observed in a study by Deng et al. (2010) [20] in MB dye removal using AC produced from cotton stalk. At power of 264 W with low MIP, pore structure of PSPAC was not well-developed and led to low MB removal. With increasing MIP from 264 W to 440 W, MB removal increased drastically with developing AC pore structure possibly due to expansion of AC structure and enhanced porosity as well as surface area under the integrated effect of internal and volumetric heating [21]. However, at high MIP of 616 W, excessive energy was adsorbed onto the PSPAC and caused extensive destruction of pore structure which led to gradual decrease in MB removal. On the other hand, increasing activation time only increases MB removal slightly. Sudaryanto et al. (2006) [22] obtained equivalent results using cassava peel-based AC and found that activation time resulted in negligible effect on the pore structure of AC. Slight increase in MB removal with increasing activation time could be caused by the increasing activation time brought about prolonged exposure to microwave irradiation and sped up the increment of temperature on PSPAC. This in turn accelerates the rate of reaction for the porous structure formation and therefore, increases MB removal to a small degree.

Figure 2 (b) shows the 3-D response curve of AC yield under the effect of MIP and activation time. It can be noticed from the plot that both MIP and activation time have significant effect on AC yield. AC yield decreases sharply with increasing MIP whereas AC yield decreases slightly with increasing activation time. Higher MIP promotes devolatilization rate of AC produced [22]. At the same time,

higher activation time will result in more energy being impinged on the AC. Therefore, decreasing AC yield with increasing MIP and activation time occurred due to more volatile matter released.

3.2 Validation of PSPAC preparing conditions

Validation of optimum conditions for PSPAC preparation was determined using Design-Expert® software version 12.0.1 (Stat-Ease, Inc, Minneapolis, MN 55413) where optimized parameters were selected based on the highest desirability. All the parameters were selected in range and both responses were maximized. The optimum conditions of MB dye removal using PSPAC were obtained at MIP and activation time of 416.50 W and 2 minutes. The model validation of optimized conditions for PSPAC preparation are shown in Table 4.

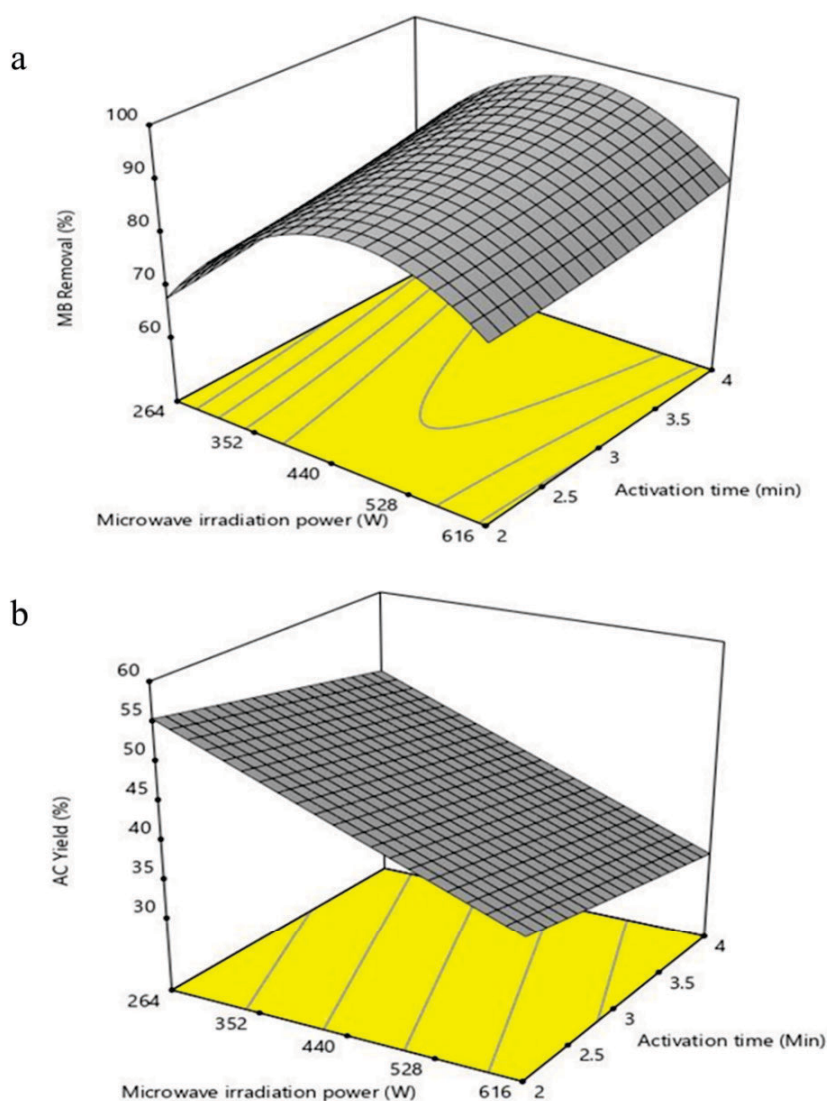


Figure 2. 3-D response surface plot of (a) MB dye removal and (b) AC yield by PSPAC (effect of MIP and activation time).

Table 4. Model validation of optimized conditions for PSPAC preparation.

Model Desirability	0.641
Microwave Irradiation Power, x_1 (W)	416.50
Activation Time, x_2 (min)	2

MB Removal (%)	
Predicted	88.56
Experimental	85.92
Error (%)	2.98
AC Yield (%)	
Predicted	47.99
Experimental	43.63
Error (%)	9.09

It is observed from the table that the experimental values produced agreed well with the predicted MB removal and AC yield. The errors calculated were relatively small, with less than 10 % for both MB removal and AC yield. Therefore, it can be proven that the optimized design parameters in PSPAC preparation resulted in reasonable performance for MB removal and AC yield.

3.3 Characterization of optimally prepared PSPAC

Characterization of optimized PSPAC were carried out using three characterization techniques; N₂ gas adsorption method, proximate analysis and scanning electron microscopy (SEM). Similar PSP precursor was used as a control in the characterization analysis.

3.3.1 Surface area and pore characteristics. The BET surface area obtained for both PSP precursor and PSPAC were 1.014 m²/g and 51.3 m²/g, respectively as shown in Table 5. The results obtained matched well with the pore characterizations by Foo and Lee (2010) [16] who also characterized PSPAC under various activation conditions. In general, the BET surface area of PSP precursor was relatively small due to the lack of pores in its structure whereas PSPAC showed drastic improvement in BET surface area since most of the volatile matters were removed during carbonization stage and further porosity development to create structure ordering of final highly porous product during activation stage [23]. The generation of PSPAC porous structure promotes higher surface area of PSPAC compared to PSP precursor. Similar trend is seen for mesopore surface area and total pore volume for both PSP precursor and PSPAC. This can be attributed to greater number of pores present in PSPAC than PSP precursor. The average pore diameter of PSP precursor and PSPAC were 5.32 nm and 5.98 nm respectively, which fall in the mesoporous region according to IUPAC classification [24]. The nature of PSPAC prepared consists primarily of mesopores which are highly favourable for large molecules adsorption such as MB [25]. Slightly higher average pore diameter is noticed for PSPAC as CO₂ activating gas produced etching effect on the pores during activation process, resulted in pore widening [26].

Table 5. Physical properties of PSP precursor and PSPAC.

Sample	BET surface area (m ² /g)	Mesopore surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
PSP	1.014	0.542	0.00001	5.32
PSPAC	51.3	26.4	0.0681	5.98

3.3.2 Proximate analysis. In view of the proximate analysis results (Table 6), PSP precursor has average moisture content (23.2%), high volatile matter (62.5%), average fixed carbon content (12.5%) and low ash content (2.2%). It is evident from the table that PSPAC having relatively lower moisture (13.1%) and volatile matter (53.9%) while simultaneously higher fixed carbon content (31.2%) and lower ash content (1.8%). As in carbonization and activation stages, bonds and linkages are broken due to instability caused by the action of heat. Subsequently, volatile matter is released as gas while moisture is evaporated off, leaving behind AC of high carbon content [27]. Another notable analysis result from Table 6 is the considerably low ash content of PSPAC makes it suitable to be used as AC

since high ash content can lower the adsorptive capacity of AC [28]. Although the average fixed carbon content of PSPAC presents a major holdback for AC, the low ash content of PSPAC which makes up for the average fixed carbon content, indicating that PSPAC presents a reasonably good AC selection.

Table 6. Proximate analysis values of PSP precursor and PSPAC.

Sample	Proximate analysis (%)			
	Moisture	Volatile	Fixed Carbon	Ash
PSP	23.2	62.5	12.5	2.2
PSPAC	13.1	53.9	31.2	1.8

3.3.3 Surface morphology. Surface morphology to verify the possible morphological changes of both PSP precursor and PSPAC are depicted in the SEM micrographs of Figure 3. The morphology surface of PSP precursor was observed smoother compared to PSPAC and seemed highly packed, porousless and no cavities available. In contrast, a rugged surface, highly porous structure with great number of pores and various pore sizes are observed over the PSPAC surface after activation process. This phenomenon can be attributed to the transformation of cellulose and lignin in the PSP precursor through dehydration, linkage breaking reactions and structural ordering of the residual carbon through heat generated by the microwave [29]. Similar results were observed from a study by Suyono et al. (2015) [30] where PSPAC showed highly porous structure and capable of adsorbing heavy metal ions. Therefore, it is evident that microwave radiation was highly capable for producing AC as it assisted in the formation of highly porous structure of PSPAC.

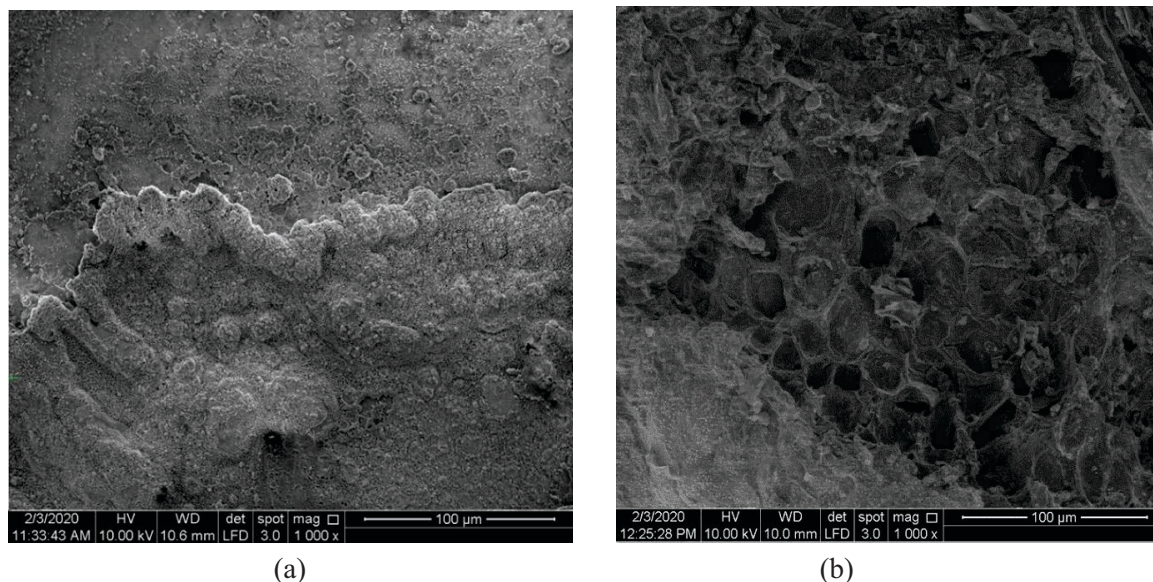


Figure 3. SEM micrographs of (a) PSP precursor and (b) PSPAC (magnification 1000x).

3.4 Batch adsorption system

3.4.1 Adsorption equilibrium. A series of experiments of MB adsorption using PSPAC were performed at various initial concentrations ranging from 50 to 300 mg/L and different contact time at 30 °C. Figure 4 portrays the results of adsorption capacity and removal of MB dye using PSPAC with different contact time at various initial concentrations.

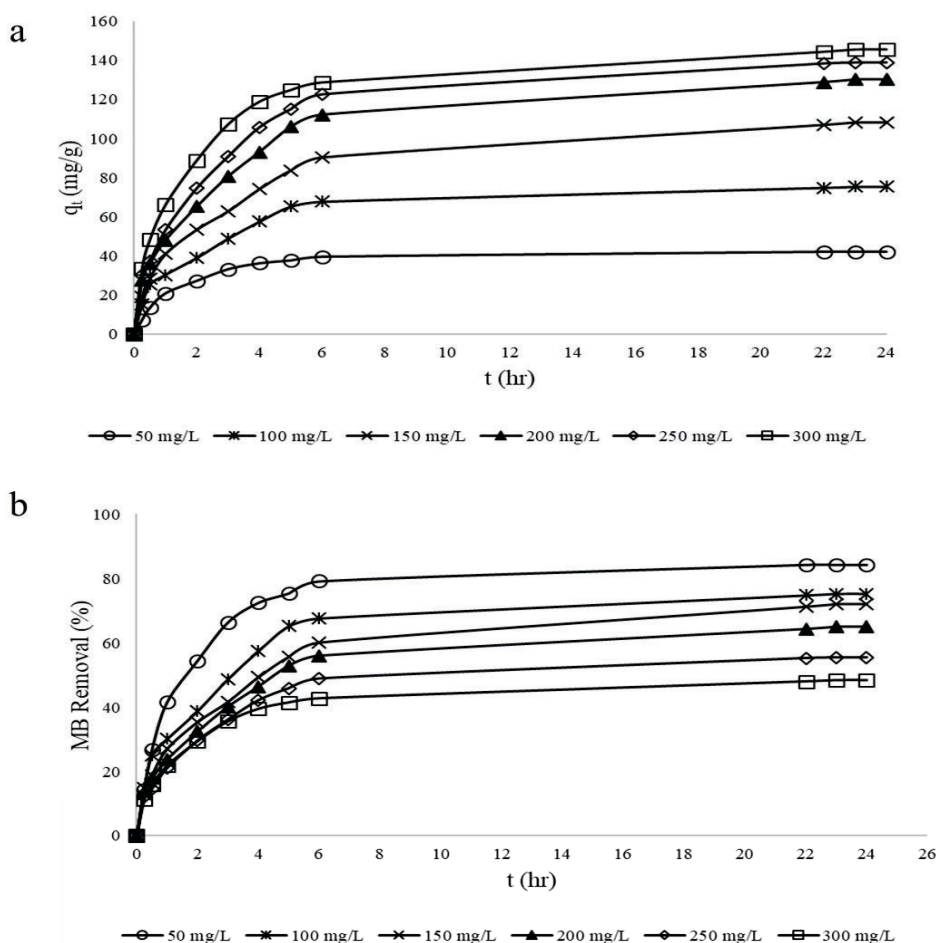


Figure 4. Variation of adsorption capacity of PSPAC using MB dye with different contact time (a) and MB dye removal by PSPAC with different adsorption time (b) using various initial concentrations at 30 °C.

Figure 4 (a) depicts MB adsorption on PSPAC that was rapid during the first 2 hours for all initial concentrations. Following that, the MB adsorption increased gradually from the 2nd to 6th hour and finally attained equilibrium within the 22nd to 24th hour, beyond where there is no significance increase in MB adsorption on PSPAC. Similar phenomenon was reported in the study by Heidarinejad et al. (2018) [31] for the adsorption of MB dye onto AC prepared from date press cake. The initial fast adsorption stage can be explained via the fast diffusion and adsorption process of MB dye molecules onto the external surface of PSPAC. During the initial stage, high number of vacant active sites on the surface of PSPAC were available for adsorption process and caused high adsorption rate. This was followed by the slower subsequent adsorption stage due to slow diffusion of MB dye molecules into PSPAC pores as occupation of most external active sites during the initial stage occurred [32]. Lower adsorption rate was seen as only fewer vacant external active sites were available and adsorption was difficult since MB dye molecules faced repulsive forces between the solute molecules in the bulk and adsorbed phases [33]. At the equilibrium stage, the adsorption rate was almost constant where the number of MB dye molecules absorbed was equivalent to the MB dye molecules desorbed.

As for the effect of initial concentration, it is seen from Figure 4 (a) that the amount of adsorbed MB dye on each unit mass of PSPAC increases with the increase of initial concentration. The equilibrium amount of MB dye absorbed increased from 42.19 mg/L to 145.44 mg/L with the increase of initial dye concentration from 50 mg/L to 300 mg/L. This can be accounted by the fact that an increase in

initial concentration will lead to an increase in concentration gradient of MB dye between the bulk phase and PSPAC surface. Thus, driving force for counteracting the mass transfer resistance between the bulk and adsorbed phases will increase and bring about increase in equilibrium amount of MB dye adsorbed [33]. The reduction in overall MB removal from 84.37% to 48.59% when initial concentration increases from 50 mg/L to 300 mg/L is seen from Figure 4 (b) possibly due to the saturation of adsorption onto PSPAC where there was relatively less available vacant active sites compared to the MB dye molecules.

3.4.2 Adsorption isotherm. The establishment of equilibrium data with isotherm is vital to obtain information regarding properties and mechanism of adsorption process [34]. An adsorption isotherm provides the relationship between the equilibrium adsorbed adsorbates and the concentration of adsorbates in the bulk liquid phase at constant temperature. In this study, 3 different isotherm models which are Langmuir, Freundlich and Temkin have been used to fit the experimental MB dye equilibrium adsorption data at 30 °C. Figure 5 (a), (b) and (c) illustrate the fitting of experimental adsorption data on all 3 linearized isotherm models while Table 7 summarizes the calculated isotherm constants and their respective fitting data.

Table 7. Parameters and fitting coefficients of isotherms for MB dye adsorption by PSPAC at 30 °C.

Isotherm	Langmuir	Freundlich	Temkin
Parameter	$q_m = 169.49 \text{ mg/g}$ $K_L = 0.0395 \text{ L/mg}$ $R^2 = 0.9966$ $S = 0.0215$	$K_f = 19.0897 \text{ (mg/g) (L/mg)}^{1/n}$ $n_f = 2.3348$ $R^2 = 0.9524$ $S = 0.0507$	$B_T = 36.73 \text{ J/mol}$ $A_T = 0.3965 \text{ L/mg}$ $R^2 = 0.9758$ $S = 7.0587$

As can be noticed from Table 7, the q_m value of 169.49 mg/g and K_L value of 0.0395 L/mg were determined for Langmuir isotherm. This q_m shows a reasonably good maximum adsorption of MB dye onto PSPAC and relatively weak interaction between the MB dye molecules and PSPAC due to small K_L value. As for the fitting of experimental data, R^2 value of 0.9966 and S value of 0.0215 show that Langmuir model is highly favourable in describing the adsorption process. For Freundlich isotherm, the calculated K_f and n_f values are 19.0897 (mg/g) (L/mg)^{1/n} and 2.3348, respectively. The high n_f value, greater than unity shows that the adsorption process is highly favourable [35]. The R^2 value of 0.9524 and S value of 0.0507 proved that Freundlich model provides satisfactory fitting to the experimental data. Meanwhile, Temkin isotherm constants, B_T and A_T values obtained were 36.73 J/mol and 0.3965 L/mg, respectively. The positive value of B_T indicates that MB dye adsorption on PSPAC is exothermic in nature [36]. Small A_T value indicates weak interaction between MB dye adsorbate and PSPAC surface. The R^2 value of 0.9758 and S value of 7.0587 signified that the model has a good fit on the data, but the fitting was relatively inaccurate due to high regression error obtained.

Based on the data calculated, the best isotherm model to describe the MB dye adsorption onto the PSPAC system was in the order of Langmuir > Freundlich > Temkin. The highest R^2 is observed in descending order from Langmuir followed by Temkin and Freundlich models. However, owing to the large regression error of Temkin model, the experimental data tend to fall away from the regression line and the inadequacy in adsorption property and mechanism prediction. Therefore, the mentioned order of fitting was proposed. This suggests that monolayer adsorption onto the PSPAC surface occurred. The results obtained were in good agreement with previous work reported by Vargas et al. (2011) [37] for MB adsorption on AC produced from flamboyant pods.

The essential features of Langmuir isotherm separation factor, R_L is able to verify the extent of the adsorption process where $R_L > 1$ denotes unfavourable; $R_L = 1$ denotes linear; $0 < R_L < 1$ denotes

favourable and $R_L = 0$ denotes irreversible processes accordingly. In the study range from 50 mg/L to 300 mg/L, the calculated R_L was between 0.078 and 0.336 which portrays favourable adsorption of MB dye onto PSPAC. In the meantime, the decrease in R_L with increasing initial concentration as indicated in Figure 5 (d) advocates that higher concentration is more preferable for MB dye on PSPAC adsorption system.

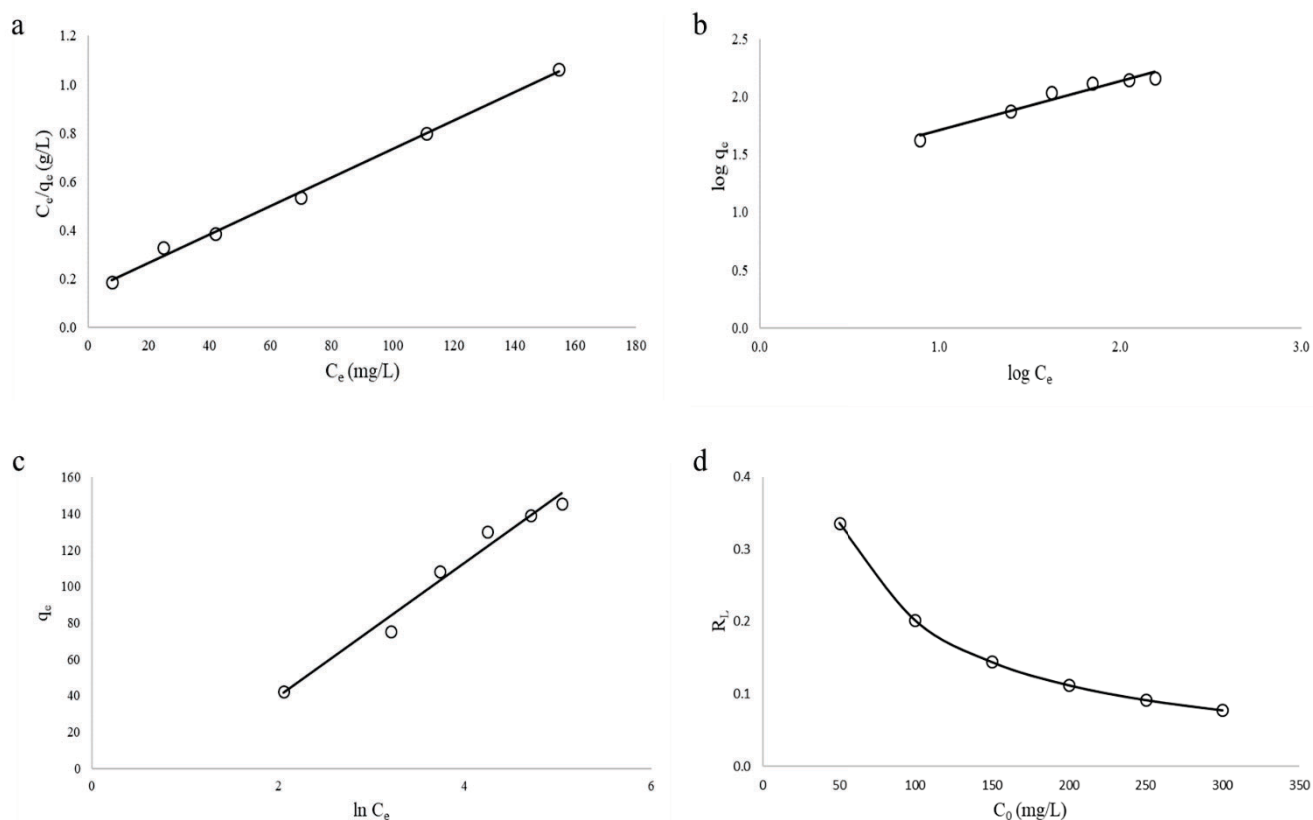


Figure 5. (a) Plots of Langmuir (b) Freundlich (c) Temkin isotherms for adsorption of MB dye onto PSPAC, and (d) MB dye separation factor with various initial concentrations at 30 °C.

3.4.3 Adsorption kinetics. Two kinetic models were applied in investigating MB dye adsorption process onto PSPAC; pseudo-first-order and pseudo-second-order kinetic models. Figure 6 (a) and (b) illustrate the plot of experimental adsorption data using linearized pseudo-first and -second-order models while Table 8 reports the models' constants and fitting data.

Table 8. Pseudo-first and -second-order constants and fitting data for MB dye onto PSPAC with various initial concentrations at 30 °C.

Initial dye concentration, C_0 (mg/L)		50	100	150	200	250	300
Exp, q_e (mg/g)		42.19	75.34	108.3	130.1	138.9	145.4
Pseudo-first-order	Predicted q_e	35.27	66.79	100.9	125.9	138.4	132.8
	(mg/g)			0	9	9	6
	k_1	0.435	0.395	0.295	0.340	0.379	0.372
	R^2	0.995	0.980	0.997	0.995	0.996	0.981
		1	0	7	8	9	0
		2	7	6	0	5	3

	Δq_e (%)	16.39	11.34	6.85	3.22	0.31	8.65
Pseudo-second-order	Predicted q_e	48.54	96.15	136.9	185.1	217.3	192.3
	(mg/g)			9	9	9	1
	k_2	0.014	0.004	0.002	0.001	0.001	0.002
		9	6	4	5	1	0
	R^2	0.998	0.987	0.988	0.991	0.973	0.981
		7	8	1	2	4	9
	Δq_e (%)	15.07	27.63	26.47	42.25	56.48	32.23

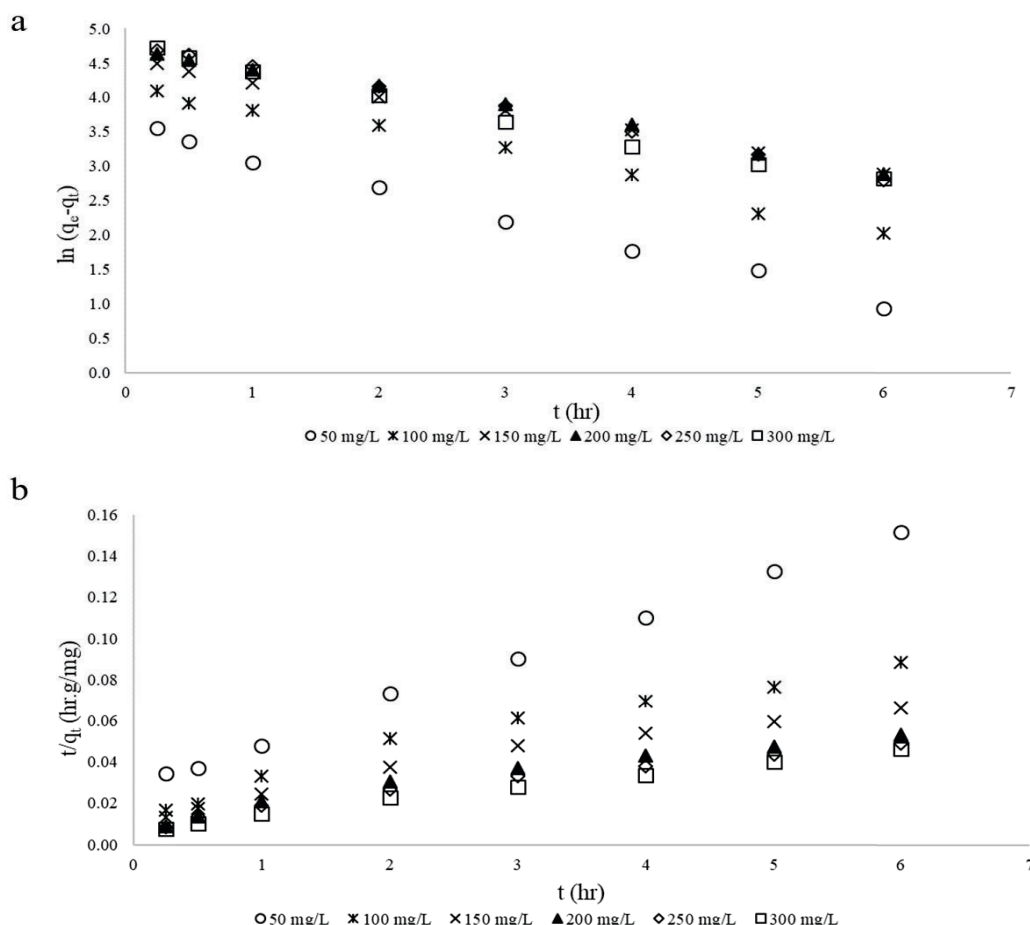


Figure 6. Plot of (a) pseudo-first and (b) pseudo-second-order kinetic models of MB dye adsorption onto PSPAC with various initial concentrations at 30 °C.

The fitting data for pseudo-first-order kinetic model calculated having R^2 values of close to unity and relatively small Δq_e values in the range of 3% to 16.4%. Thus, the predicted amount of MB dye adsorbed at equilibrium, q_e were in satisfactory match with the experimental data. On the other hand, pseudo-second-order model calculated as well having R^2 values close to unity. However, the Δq_e calculated were inconsistent and having larger range from 15% to 56.5%. It is obvious that q_e values possess larger deviations from the experimental data. Hence, it proposes that pseudo-first-order model describes better the MB dye adsorption onto PSPAC owing to the close R^2 values to unity and small Δq_e . The results suggest that MB adsorbate-PSPAC adsorbent system follows the assumption that rate of adsorption of MB dye adsorbates was governed by the number of vacant active sites [38].

However, the results of adsorption were in contradiction with most of the studies done on MB dye adsorption on AC where the adsorption process fits well with the pseudo-second-order process as reported by Aljeboree et al. (2017), Zhou et al. (2017) and Danish et al. (2018) [39-41]. This phenomenon can possibly be ascribed to the distortion of experimental kinetics caused by linearization of kinetic equations in linear forms [42]. Aichour et al. (2018) [43] showed similar result where pseudo-first-order model fitted well for MB dye adsorption using lemon peel AC. The range of initial concentration used in this study (50 to 300 mg/L) can be categorized into low initial concentration [44], therefore, the capability of pseudo-first-order kinetic model in modelling MB dye adsorption is demonstrated feasible for our PSPAC.

3.4.4 Adsorption mechanism. Adsorption mechanism of MB dye onto PSPAC was studied by introducing an intraparticle diffusional model so as to evaluate the possibility of MB dye adsorbates transport to PSPAC adsorbent via intraparticle diffusion mechanism. This model postulates the diffusion of adsorbate molecules into adsorbent internal pores. Figure 7 demonstrates the plot of intraparticle diffusional model of MB dye adsorption onto PSPAC with different initial concentrations at 30 °C whereas Table 9 shows the corresponding intraparticle diffusion rate constants.

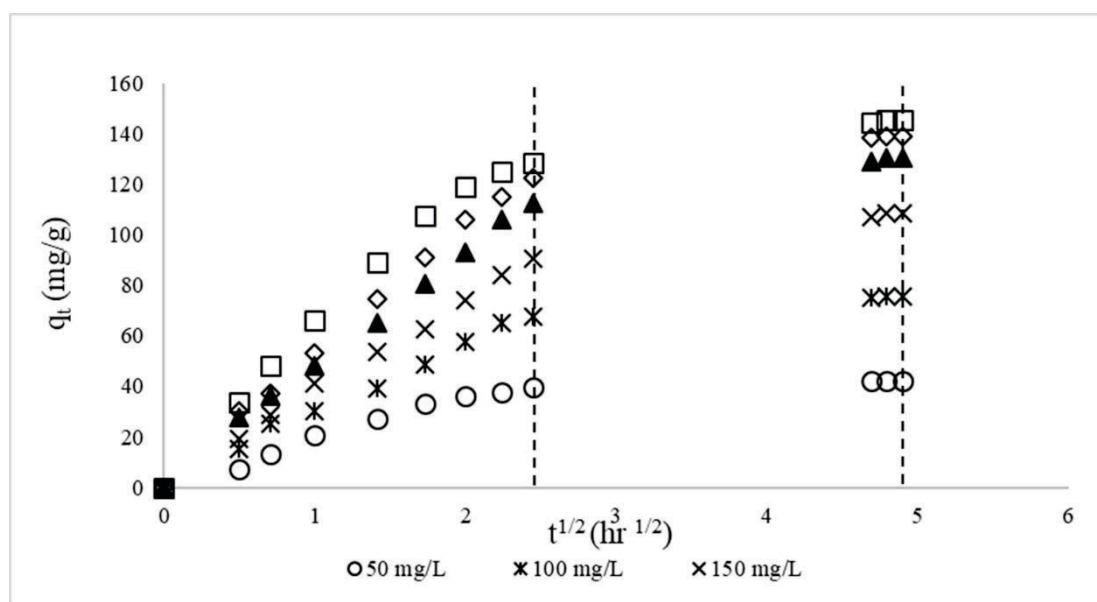


Figure 7. Plot of intraparticle diffusion model for adsorption of MB dye onto PSPAC with various initial concentrations at 30 °C.

Table 9. Intraparticle diffusion rate constants for adsorption of MB dye onto PSPAC with various initial concentrations at 30 °C.

Initial dye concentration, C_0 (mg/L)	$k_{d,1}$	$k_{d,2}$	$k_{d,3}$	c_1	c_2	c_3	R_1^2	R_2^2	R_3^2
50	14.54	17.54	1.09	0	1.14	36.96	1	0.9716	0.9948
100	16.34	27.22	3.18	0	2.90	59.59	1	0.9893	0.9987
150	18.13	35.25	7.45	0	3.25	72.18	1	0.9961	0.9987
200	23.15	43.30	7.46	0	5.09	93.95	1	0.9979	0.9986

250	30.42	49.02	6.85	0	5.43	105.86	1	0.9985	0.9979
300	38.88	53.58	7.02	0	10.09	111.40	1	0.9903	0.9987

* k_d is in the unit of $\text{mg/gh}^{1/2}$ while C_0 is in the unit of mg/L .

The indication of intraparticle diffusion as the mere rate determining step is only valid when the obtained plots of q_t versus $t^{1/2}$ shows linear line that goes through the origin. An obvious observation from Figure 7 is that multiple linearity presents which do not pass through the origin proposes that intraparticle diffusion was not the sole rate controlling step and the presence of other mechanisms in the adsorption process [45].

The plot consists of 3 distinct stages of MB dye adsorption onto PSPAC; each stage can be fitted by a well-defined straight line. The early initial stage (within 0.25 hour) shows fast adsorption rate with steeper slope represents the instantaneous adsorption or external surface adsorption. The subsequent stage (within 4.5 hours) depicts gradual adsorption of MB dye adsorbates onto the mesopores of PSPAC where intraparticle diffusion was dominant [44]. The final levelled part demonstrates the equilibrium stage with intraparticle diffusion retardation owing to relatively low MB concentrations remained in the bulk solution [46]. It is evident that rate controlling step of the process consisted not solely intraparticle diffusion since the linear lines in former 2 stages gave intercepts at the vertical axis.

The tabulated results of intraparticle diffusion parameters of k_d and c represent the intraparticle diffusional constants and intercepts on the q_t versus $t^{1/2}$ plot which are associated with the boundary layer thickness for each stage respectively. For k_d , it can be observed that the values of k_{d1} are greater when initial concentration of MB dye increases from 50 to 300 mg/L . This can be possibly attributed to the increase in driving force due to higher initial concentration of MB adsorbates which promotes diffusion rate. Similar results were reported by Islam et al. (2017) who studied MB dye adsorption using *Pongamia pinnata* AC. The obtained values of c portray increasing trend with increasing initial concentration. This indicates the increase in boundary layer thickness with increasing initial concentration which might be ascribed to the boundary layer effect where the increase in boundary layer thickness can effectively reduce the rate of external diffusion and maximize the pore diffusion rate and thus comparatively higher MB dye adsorption rate at higher initial concentration [8].

Kinetic results in general showed that MB dye adsorption onto PSPAC was governed by both external surface adsorption and intraparticle diffusion. The R_1^2 values which are close to unity indicated that intraparticle diffusion was involved in the adsorption process but the high c values confirmed the significance of surface adsorption mechanism. Similar observation for MB dye adsorption were also found from previous work by Jia et al. (2018) and Ma (2017) [47, 48].

4. Conclusion

In this work, *Parkia speciosa* pod (PSP) was successfully converted into AC using microwave-assisted activation technique. Quadratic and linear models developed for process optimization and statistical experiment designs using response surface methodology (RSM) were proved to be useful in correlating the activating parameters to MB removal and AC yield. The optimum conditions obtained using PSPAC were microwave irradiation power (MIP) of 416.50 W and activation time of 2 minutes. The optimized AC showed MB removal of 85.92% and AC yield of 43.63%. Optimized PSPAC demonstrated mesoporous nature with intermediate high surface area (51.3 m^2/g) and intermediate high total pore volume (0.0681 cm^3/g). Favourable surface morphology of PSPAC was observed with high porous structure and great number of pores distributed on the surface. Batch adsorption studies at 30 °C using optimized PSPAC revealed that increasing initial concentration of MB and contact time would significantly increase the maximum MB adsorbed capacity. Isotherm study deduced that the

equilibrium MB adsorption data was well represented by Langmuir isotherm model with maximum monolayer adsorption capacity of 169.49 mg/g. The equilibrium MB adsorption data obeyed pseudo-first-order kinetic model with good correlation. Intraparticle diffusion analysis indicated that both surface diffusion and intraparticle diffusion are the rate-determining steps of MB dye adsorption on PSPAC. This study proved that PSPAC is a potential adsorbent for dye-contaminated wastewater.

Appendix

Table A1. Experimental design matrix for preparation of PSPAC.

Run	PSPAC Preparation Parameters	
	Microwave Irradiation Power, x_1 (W)	Activation Time, x_2 (min)
1	264	2
2	264	3
3	264	4
4	440	2
5	440	3
6	440	3
7	440	3
8	440	3
9	440	3
10	440	4
11	616	2
12	616	3
13	616	4

Table A2. Experimental design matrix and MB removal and AC yield optimization responses.

Run	PSPAC Activation Parameters		MB Removal, Y_1 (%)	AC Yield, Y_2 (%)
	Microwave Irradiation Power, x_1 (W)	Activation Time, x_2 (min)		
1	264	2.00	69.65	56.17
2	616	2.00	82.48	39.00
3	264	4.00	75.08	50.37
4	616	4.00	82.99	32.77
5	264	3.00	71.26	52.06
6	616	3.00	83.12	35.02
7	440	2.00	86.58	47.90
8	440	4.00	99.60	41.00
9	440	3.00	95.70	43.24
10	440	3.00	85.23	44.78
11	440	3.00	98.06	43.60
12	440	3.00	93.57	40.54
13	440	3.00	88.02	41.31

References

- [1] *Malaysian Investment Development Authority: Textiles and Textile Products* (no date). Available at: <https://www.mida.gov.my/home/textiles-and-textile-products/posts/> (Accessed: 18 December 2019).

- [2] Ali A and Haseeb M 2019 *Uncertain Supply Chain Management* **7** pp 215–226.
- [3] Kumar Popuri A and Guttikonda P 2015 *Treatment of Textile Dyeing Industry Effluent Using Activated Carbon Prepared From Agriculture Waste (Sawdust)* **6** p 1165.
- [4] Coman V and Copaciu F 2014 *Analysis of Dyes and Inks, Instrumental Thin-Layer Chromatography* (United States: Elsevier).
- [5] Djilani C *et al.* 2015 *J. Taiwan Inst. Chem. E.* **53** pp 112–121.
- [6] Pang Y L and Abdullah A Z 2013 *Clean - Soil, Air, Water* **41** pp 751–764.
- [7] Hameed B H, Ahmad A A and Aziz N 2007 *Chem. Eng. J.* **133** pp 195–203.
- [8] Ahmad M A, Ahmad Puad N A and Bello O S 2014 *Water Resour. Ind.* pp 18–35.
- [9] Holkar C R *et al.* 2016 *J. Environ. Manage.* pp 351–366.
- [10] Galán J *et al.* 2013 *Chem. Eng. J.* **219** pp 62–68.
- [11] Tunali Akar S *et al.* 2011 *Chem. Eng. J.* **168** pp 125–133.
- [12] Auta M and Hameed B H 2011 *Chem. Eng. J.* **171** pp 502–509.
- [13] Han R *et al.* 2007 *J. Hazard. Mater.* **141** pp 713–718.
- [14] Ahmad M A and Alrozi R 2011 *Chem. Eng. J.* **171** pp 510–516.
- [15] Amirza M A R, Adib M M R and Hamdan R 2017 *MATEC Web of Conf.* **103** pp 32–34.
- [16] Foo P and Lee L 2010 *Proceedings of the World Congress on Engineering and Computer Science II* pp 1–17.
- [17] Chhikara N *et al.* 2018 *Agric. Food Security*, **7** pp 1–9.
- [18] Houshmand A, Daud W M A W and Shafeeyan M S 2011 *Bull. Chem. Soc. Jpn* **84** pp 1251–60.
- [19] Ahmad M A, Afandi N S and Bello O S 2017 *Appl. Water Sci.* **7** pp 717–727.
- [20] Deng H *et al.* 2010 *Chem. Eng. J.* **163** pp 373–381.
- [21] Foo K Y and Hameed B H 2012 *Bioresour. Technol.* **111** pp 425–432.
- [22] Sudaryanto Y *et al.* 2006 *Bioresour. Technol.* **97** pp 734–739.
- [23] Budi E *et al.* 2014 *AIP Conference Proceedings*, American Institute of Physics Inc. pp 130–133.
- [24] Rouquerol J *et al.* 1994 *Pure Appl. Chem.* **66** pp 1739–58.
- [25] Nsami J N and Mbadcam J K 2013 *J. Chem.* 2013.
- [26] Balanay J and Lungu C 2012 *Adsorpt. Sci. Technol.* **30** pp 355–367.
- [27] Ahmad M A and Alrozi R 2010 *Chem. Eng. J.* **165** pp 883–890.
- [28] Anisuzzaman S M *et al.* 2015 *Int. J. Ind. Chem.* **6** pp 9–21.
- [29] Sharif Y M *et al.* 2018 *Anal. Lett.* **51** pp 2731–44.
- [30] Suyono T *et al.* 2015 *J. Chem. Pharm. Res.* **7** pp 100–106.
- [31] Heidarinejad Z *et al.* *J. Mol. Liq.* **264** pp 591–599.
- [32] Liu Q X *et al.* 2019 *Adsorpt. Sci. Technol.* **37** pp 312–332.
- [33] Wanyonyi W C, Onyari J M and Shiundu P M 2013 *Bull. Environ. Contam. Toxicol.* **91** pp 362–366.
- [34] Dural M U *et al.* 2011 *Chem. Eng. J.* **168** pp 77–85.
- [35] Benderdouche N, Bestani B and Hamzaoui M 2018 *J. Mater. Environ. Sci.* **9** pp 1110–18.
- [36] Batool F *et al.* 2018 *Bioinorganic chemistry and applications.*
- [37] Vargas A M M *et al.* 2011 *Chem. Eng. J.* **168** pp 722–730.
- [38] Ghasemi M *et al.* 2014 *Int. J. Environ. Sci. Technol.* **11** pp 1835–44.
- [39] Aljeboree A M, Alshirifi A N and Alkaim A F 2017 *Arab. J. Chem.* **10** pp S3381–93.
- [40] Zhou L *et al.* 2017 *Ecol. Eng.* **102** pp 443–450.
- [41] Danish M *et al.* 2018 *Bioresour. Technol. Rep.* **3** pp 127–137.
- [42] Lin J and Wang L 2009 *Front. Environ. Sci. Eng. China*, **3** pp 320–324.
- [43] Aichour A *et al.* 2018 *J. Mol. Liq.* **256** pp 533–540.
- [44] Baysal M *et al.* 2018 *J. Environ. Chem. Eng.* pp 1702–13.
- [45] Patawat C *et al.* 2020 *RSC Adv.* **10** pp 21082–91.
- [46] Krishni R R, Foo K Y and Hameed B H 2014 *Desalin. Water Treat.* **52** pp 6104–12
- [47] Jia P *et al.* 2018 *Appl. Sci.* **8** p 1903.
- [48] Ma Y 2017 *Waste Biomass Valori.* **8** pp 549–559.

Acknowledgments

The authors thankfully acknowledge the research grant support obtained from the Universiti Sains Malaysia (304/PJKIMIA/6315247) and National Water Research Institute of Malaysia (NAHRIM).