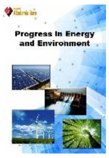
**Progress in Energy and Environment**

Journal homepage: http://www.akademiabaru.com/submit/index.php/progee

**Volume 14 No 1 (2020) 1-12**



Original Article

# Feasibility Study of Methylene Blue Adsorption Using Magnetized Papaya Seeds

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## Abstract

Adsorption is widely used in wastewater treatment due to its ease of operation and relatively low operational cost. Wastes from agricultural or food industrial sector have been idealized as a sustainable solution in the synthesis of adsorbent for this purpose. Magnetized adsorbents are gradually gaining attention since the hassle of further purification following the adsorption process can be avoided compared to the conventional adsorbents. In the present study, the potential of magnetized papaya seeds (MPS) to adsorb dye is investigated as a replacement to other adsorbents. The removal of methylene blue (MB) from aqueous solution using MPS was conducted. It was found that 80.47 % removal of MB could be achieved by MPS. The adsorption performance of MPS was further investigated under the effects of different parameters, which were pH of solution (2 – 12), adsorption temperature (25˚C – 65˚C), adsorbent dosage (0.25g – 1.25g), MB initial concentration (10 mg/L – 50mg/L) and contact time (30min – 180min). In terms of the adsorption isotherm, a comparison between the Langmuir, Freundlich and Temkin models was performed and the results revealed that the adsorption of MB onto MPS obeyed Langmuir adsorption isotherm model with the highest regression coefficient value ($R^2$= 0.9983). With such exploratory approach, the findings in this research are beneficial to suggest MPS as an inexpensive adsorbent that is effective for MB dye removal in a more realistic adsorption system.

**Article Info**

Received 29 April 2020
Received in revised form 21 May 2020
Accepted 22 May 2020
Available online 28 May 2020

**Keywords**

Adsorption
Methylene Blue
Magnetized Papaya Seeds
Isotherm Models

## 1 Introduction

Effluents from textiles, dyeing, painting, and papermaking industries are commonly containing highly colored species. It is reported that approximately 10 – 15% of the dyes end up in industrial effluents during the manufacturing and processing operations [1]. Serving as colorants in these industrial processes, dyes reduce the oxygen content in water since colored wastewater prevents the penetration of sunlight for photosynthesis of aquatic plants, hence disturbing the aquatic ecosystem and lives. Besides, dyes are also extremely stable in aqueous form due to its complex structure and non-biodegradability in nature [1]. Methylene blue (MB), a cationic dye is widely used in many industries such as food, paper, leather, plastics, cosmetics, and textiles for colouring purpose [2]. If the discharged coloured wastewater from these industries contains MB without proper wastewater treatment, it will cause many significant problems to the environment and human health. Therefore, the removal of such dye from wastewater prior to its discharge is of great interest based on both environmental and economical perspectives [3].

Various approaches had been attempted to treat dye-containing wastewater. These include adsorption, coagulation and flocculation, advanced oxidation, microbial degradation, membrane filtration and liquid–liquid extraction [4]. Advantages and disadvantages of every removal technique

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have been extensively reviewed in the literature. Scientists and environmentalists are still studying viable methods to treat dyes efficiently and economically. Adsorption is by far the most preferable method among all due to its ease of design, simple operation and resilience to toxic constituents. It is also possible to recover and reuse adsorbents after the pollutant removal, making the process more economically viable [5]. In common adsorption processes, activated carbon and synthetic resins are usually used to gain high removal efficiency. In recent years, a number of industrial inorganic wastes such as ash, or natural inorganic materials such as clay and zeolite, as well as living or non-living biomass have been extensively explored as cheap adsorbents capable of replacing the well-known, but more expensive ones [6-7].

Papaya seeds (PS) are abundantly found in Malaysia as crop wastes. Malaysia produces up to 72,000 tonnes of papaya annually. The discarded portion of seeds is between 15 – 20% of its overall weight [8]. Since papaya is a local staple fruit in Malaysia, the wastes create increasing disposal and potentially severe environmental problems. In this context, papaya seeds can be converted to adsorbents in wastewater treatment which provide both economical and waste handling advantages [8]. Even with the recognized efficiency of adsorbents to remove potentially harmful dyes from wastewater, conventional filtration method employed is difficult to separate, retrieve and regenerate the used adsorbent and could even cause blockage of filter that may lead to the loss of adsorbents. Moreover, centrifugation for large-scale applications suffers from high power consumption that leads to economic concern [9]. Hence, it is very challenging to develop highly effective adsorbents with minimal cost to separate pollutants particularly MB from wastewater in a continuous flow system [10].

In view of that, magnetic field assisted separation technology has gradually been improved to tackle these issues. Used magnetized adsorbents could potentially be recovered at once to produce clarified treated water after the water treatment processes. Its advantages in terms of convenience, economic feasibility and efficiency have been evidenced in many reports in the literature [10]. Magnetic adsorbents whereby the base adsorbents are embedded with magnetic particles (metal oxides) such as Co, Ni, Fe and Cu have gradually been explored recently [11]. In this study, the possibility of magnetizing papaya seeds to produce adsorbent that can be easily recovered from the treated solution by an external magnetic field was investigated. This research aims to reduce the hassle of filtration process and energy consumption associated with the centrifugation process in retrieving the used papaya seed adsorbent. The adsorption performance of magnetized papaya seed was also investigated under the effects of different adsorption parameters. Finally, the kinetic model for the prediction of MB removal using magnetically modified papaya seed was proposed.

## 2 Methodology and Experiment Setup

### *2.1 Preparation of the Papaya Seed*

Fully ripened and edible papaya fruits were bought from the night market at Taman Connaught, Cheras. The papaya seeds (PS) were removed from the fruit, washed with distilled water, oven dried at 85ºC for half an hour, before crushing and sieving to obtain uniform particle size between 350 and 450 μm.

### *2.2 Preparation of Magnetized Papaya Seed (MPS)*

The procedures performed in the magnetization of PS were according to the report of Madrakian et al. [3]. Briefly, 5.2 g of $FeSO_4 \cdot 7H_2O$ and 7.4 g of $FeCl_3 \cdot 6H_2O$ were dissolved in 80 ml of distilled water with vigorous stirring. When the solution was heated to 80ºC, 20 ml of ammonium hydroxide (25%) was gradually added in. Then, 10 g of PS was added to the solution and the reaction was allowed for one hour at 85ºC under constant stirring. Following that, the sample was cooled to room temperature and then repeatedly washed with distilled water and ethyl alcohol to remove the unreacted chemicals. The washed MPS was then dried in an oven at 60ºC for 10 hours and kept until further usage.

### 2.3 Preparation of Methylene Blue

Methylene Blue (MB) stock solution, without further purification, was prepared by dissolving accurately weighed samples of 0.25 g MB powder in 500 ml of distilled water. The desired MB concentrations in subsequent experiments were prepared by further diluting the stock solutions with suitable volumes of distilled water [13].

### 2.4 Adsorption of Methylene Blue Using Magnetized Papaya Seed

The adsorption process was carried out by adding 2.0 g of MPS into a 250 ml Erlenmeyer flask containing 100 mg/L MB solution without changing the solution pH [14]. Subsequently, the flask was placed on a rotary shaker at a pre-set speed of 300 rpm for 2 hours at 30°C. Upon completion, the flask was removed from the shaker, and the used adsorbent (MPS) was separated from the treated solution using an external magnet [15]. The final concentration of MB dye in the solution was analysed by a double beam UV-vis spectrophotometer (Hitashi U2900) at the wavelength of 673 nm [12]. The MB removal percentage was computed using Eq. (1):

$$\text{MB removal percentage (\%)} = \frac{C_0 - C_t}{C_0} \tag{1}$$

where, $C_o$ was the initial concentration of MB and $C_t$ was the concentration of MB after the adsorption process.

### 2.5 Effects of Adsorption Parameters on Methylene Blue Removal

The effects of five different adsorption parameters on the MB removal using MPS were investigated. These parameters included solution pH, adsorption temperature, adsorbent dosage, initial concentration of MB and contact time. The adsorption efficiency of MPS under the influence of different adsorption parameters was calculated by determining the removal percentage (Eq. 1) as well as the amount of MB adsorbed per unit mass of MPS ($Q_e$) according to Eq. (2).

$$Q_e = \frac{(C_0 - C_e)V}{W_0} \tag{2}$$

where, $C_o$ was the initial concentration of MB, $C_e$ was the equilibrium concentration of MB, V was the volume of the solution, and W was the mass of MPS used.

#### 2.5.1 Effect of Solution pH

The MB adsorption process was conducted as described in Section 2.4, with the exception that the solution pH was varied across pH 2, 4, 6, 8 and 10. The adjustment of pH was performed using 0.1 M HCl or 0.1 M NaOH accordingly. The adsorption process was performed for 3 hours and the MB concentration in the solution was measured by a double beam UV–vis spectrophotometer at 673 nm at the intervals of 30 minutes for every solution pH. The percentage removal of MB from aqueous solution of different pH was then calculated and compared.

#### 2.5.2 Effect of the Adsorption Temperature

The MB adsorption process was conducted as described in Section 2.4, with the exception that the adsorption temperature was manipulated to identify its effects towards the MPS adsorption efficiency. The MB solution temperature was varied from 25˚C, 35˚C, 45˚C, 55˚C to 65˚C for the adsorption process. The pH was fixed at 8 and the adsorption process was conducted for 2 hours. The MB concentration in the solution was measured by a double beam UV–vis spectrophotometer at 673 nm every 20 minutes for each adsorption temperature. The percentage removal of MB from aqueous solution of different temperature was then calculated and compared.

### 2.5.3 Effect of Adsorbent Dosage

The adsorption process was performed as described in Section 2.4, with the exception that different amount of MPS ranging from 0.25 g, 0.5 g, 0.75 g, 1.0 g to 1.25 g was used. The pH was fixed at 8 and the adsorption process was conducted for 2 hours at 25°C. The MB concentration in the solution was measured every 20 minutes by a double beam UV–vis spectrophotometer at 673 nm for each adsorbent dosage. The percentage removal of MB from aqueous solution of different MPS dosage was then calculated and compared.

### 2.5.4 Effect of Methylene Blue Initial Concentration and Contact Time

The adsorption process was performed as described in Section 2.4, with the exception that the experiments were repeated at different MB concentrations of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L for 3 hours using 0.25 g of MPS. The pH was fixed at 8 and the adsorption process was conducted at 25°C. The MB concentration in the solution was measured by a double beam UV–vis spectrophotometer at 673 nm at the intervals of 30 minutes for every initial concentration studied.

### 2.6 Adsorption Isotherms

In this study, three parametric kinetic models namely Langmuir, Freundlich, and Temkin models were used to analyse the experimental data of MB removal percentages. Results from the experimental runs were fitted into the linearized equation of Langmuir, Freundlich and Temkin isotherms as listed in Table 1. The graph of every isotherm was constructed accordingly. The best fit isotherm was determined based on the highest correlation coefficients, $R^2$. The model parameters of each isotherm were calculated by linear regression method.

**Table 1** Linearized equation for Langmuir, Freundlich and Temkin isotherm.

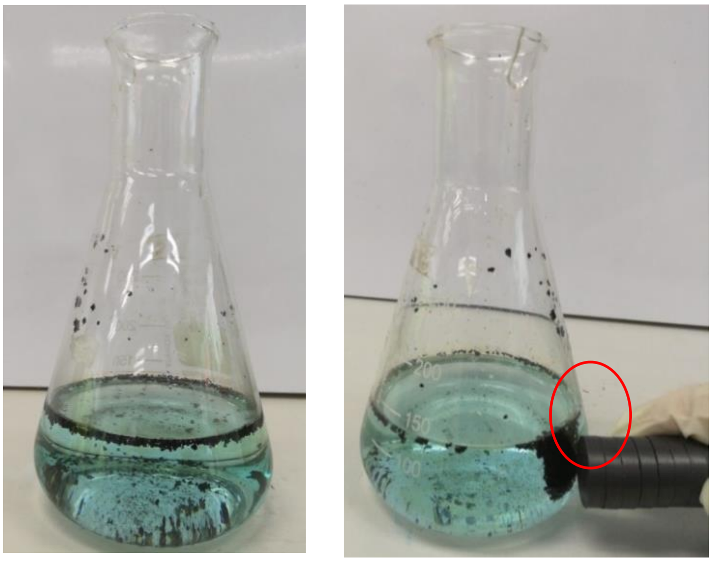
| Isotherms | Equation | Linearized Equation |
|---|---|---|
| **Langmuir** | $q_e = \dfrac{q_m K C_e}{1 + K_L C_e}$ | $\dfrac{c_e}{q_e} = \dfrac{1}{K_L q_m} + \dfrac{1}{q_m} C_e$ |
| **Freundlich** | $q_e = K_F C_e^{1/n}$ | $\log(q_e) = \log(K_F) + \dfrac{1}{n}\log(C_e)$ |
| **Temkin** | $q_e = \dfrac{R_T}{b_T}\ln(A_T C_e)$ | $q_e = B_T \ln(A_T) + B_T \ln(C_e)\Big\|_{B_T = \frac{R_T}{b_T}}$ |

In Table 1, $C_e$ is the equilibrium concentration of adsorbate (mg/L); $q_e$ is the adsorption capacity at equilibrium (mg/g); $K_L$ is the Langmuir constant related to the affinity of the binding sites (L/mg); $q_m$ is the maximum amount of adsorbed MB per gram of adsorbent (mg/g); $K_F$ is the Freundlich isotherm constant (mg/g); $n$ is the adsorption intensity under different experimental conditions; $1/n$ is the heterogeneity of the sorption sites and an indicator of isotherm nonlinearity; $A_T$ is the Tempkin isotherm equilibrium binding constant (L/mg); $b_T$ is the Tempkin isotherm constant; $R$ is the universal gas constant (8.314 J/mol/K); $T$ is the absolute temperature (K); and $B_T$ is the constant related to heat of sorption (J/mol).

## 3 Results and Discussion

### 3.1 Adsorption of Methylene Blue using Magnetized Papaya Seeds

A preliminary MB adsorption process was performed to evaluate the feasibility of magnetizing papaya seeds for the application of methylene blue removal from aqueous solution. It was observed that the used MPS adsorbent that was initially suspended and dispersed in the treated MB solution was successfully separated to a side (red circle) by using an external magnet after the adsorption process (Fig 1).



(a) (b)

**Fig. 1** The treated MB solution after adsorption process (a) with suspended MPS; (b) MPS separated to a side by using an external magnet.

The colour of the treated MB using MPS became light blue at the end of the experiment, which evidenced the effectiveness of MPS to remove MB from the aqueous solution. Based on calculation as depicted in Eq. 1, the MB removal was recorded as 80.47 %. This high percentage removal achieved could be correlated to the favourable electrostatic interactions between the positively charged MB dye molecule and the oppositely charged MPS surface. Lignocellulosic plant materials such as papaya seeds contained many negatively charged surface sites, which included the hydroxyl and carboxyl groups on the cellulose fibres and those in proteins and phenolic compounds [16-17]. Therefore papaya seed was proven to reduce or mitigate MB dye as a result of its chemical composition.

Magnetization technology offered the advantage in which the used biosorbent could be separated from the treated aqueous solution using an external magnet easily. Agro-industrial wastes of defective green coffee (DGC), coffee silverskin (CS) and spent coffee grounds (SCG) were possible to be transformed into low-cost magnetic adsorbents for the removal of cationic MB dye from aqueous solution and were easily recovered from the solution by a permanent magnet [18]. In addition to that, magnetically modified activated carbon had also been reported to show considerable potential for the removal of Crystal Violet and the magnetic adsorbent could be simply removed from treated solution by using magnet or appropriate magnetic separator after adsorption process [19]. Therefore, in terms of the recovery of used adsorbents after adsorption process, magnetization treatment showed that it possessed the practical potential to overcome the difficulty of separating them from wastewater in a continuous flow system, which was always faced by the conventional adsorption treatment. In this study, it was observed that magnetization of papaya seeds to be utilized as MB removal adsorbent is a feasible approach in easing the subsequent separation process.

### 3.2 Effects of Adsorption Parameters on Methylene Blue Removal

#### 3.2.1 Effect of Solution pH

In the present study, the effect of solution pH on the adsorption of MB is presented in Fig 2 over the pH range of 2 to 10 for initial MB concentration 10 mg/L at 25˚C. It was clearly observed that the removal of the MB dye from aqueous solution increased significantly as the pH was increased from 2 to 10. The cationic MB dyes produced positively charged ions when dissolved in water. Thus, in acidic mediums (lower pH), there was the possibility that positive charges were induced on the MPS surface and hence opposed the adsorption of cationic dyes [20]. On the other hand, as the pH of MB solution was increased, the adsorbent surface was slowly becoming negatively charged, resulting in the enhancement of MB adsorption due to an increase in the electrostatic attraction between the negatively charged MPS and positively charged MB dye. Based on Fig 2, the lower adsorption of MB at acidic pH could be also due to the presence of excess $H^+$ ions competing with dye cations for the available adsorption sites on MPS [21]. Therefore, basic conditions were found to be more favorable for the adsorption of MB from aqueous solution using MPS. In fact, the influence of solution pH towards the efficiency of MPS in the removal of MB was evidenced since the beginning of the process whereby a significant difference was noted in terms of the removal percentage as early as 30 minutes. Subsequently, it was observed that the improvement in the removal efficiency was not more than 10 % for each solution pH though the adsorption process was prolonged up to 180 minutes.

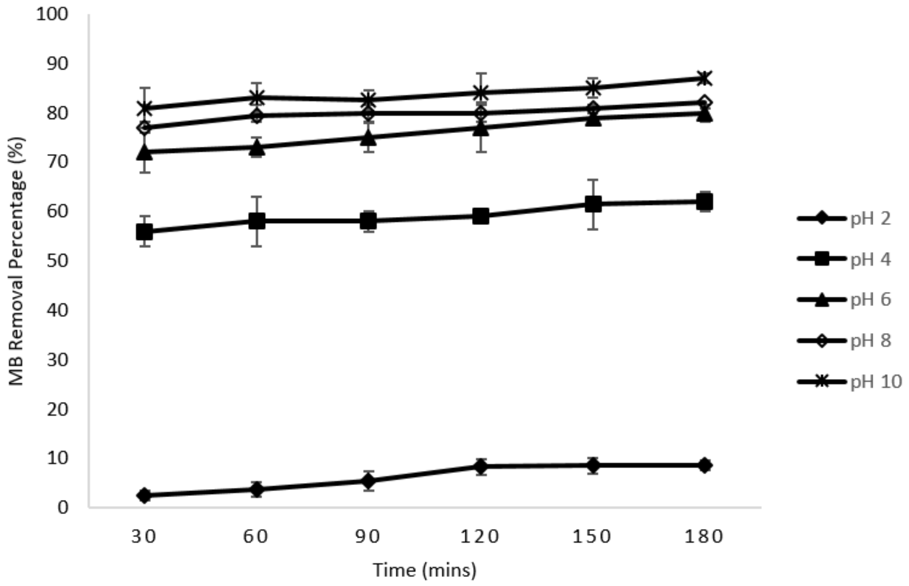


**Fig. 2** The effect of pH on the removal of MB using MPS.

#### 3.2.2 Effect of Adsorption Temperature

The effects of temperature variation on the adsorption rate of 10 mg/L MB were investigated within the range of 25˚C to 65˚C. The results are presented in Fig 3. Based on adsorption results, it was apparent that as the adsorption temperature was increased from 25˚C to 65˚C, the highest percentage removal of MB on papaya seeds was attained at the temperature of 55˚C with 81.59 % MB removal. Generally, in adsorption process, increasing the temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle as solution viscosity drops [22]. The increase of the adsorption efficiency and adsorption capacity at elevated temperature indicated that the adsorption of MB molecules onto MPS was endothermic in nature. Hence, in this study, increasing the temperature may produce a swelling effect within the internal structure of the MPS enabling MB dye particles to penetrate further and also due to enlargement of pore size or creation of some new active sites on the MPS surface due to rupture of bond. Mouni *et al.* [22] also suggested that this phenomenon may be due to a change in chemical potentials, correlated with adsorbate species solubility. However, based on Fig 3, it was found that there was a drop in the removal percentage of MB when the adsorption temperature was further increased to 65˚C. This could be due to the fact that temperature beyond 55˚C led to denature of the structure of papaya seeds and resulted in the weaker capability to adsorb the MB dyes. Another plausible explanation given by Bhaumik *et al.* [23] was that the reduction of removal percentages may be due to thinning of the boundary layer at higher temperatures. There was also higher tendency of the MB molecules to escape from the MPS surface to the solution phase, which resulted in a decrease in the adsorption capacity.

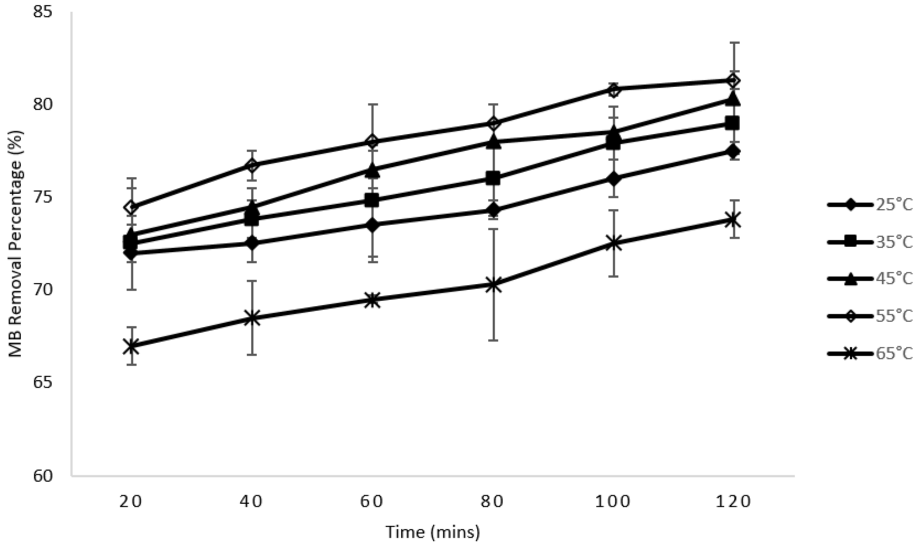


**Fig. 3** The effect of temperature on the removal of MB using MPS.

### 3.2.3 Effects of Adsorbent Dosage

In this study, the effect of adsorbent dosage on the adsorption of MB was studied over different amount of MPS used that ranged from 0.25 g to 1.25 g. The MB removal percentage profile is depicted in Fig 4. The MB removal percentage increased but remained almost constant, i.e. 2 % difference with the increase in the amount of MPS adsorbent beyond 1.0 g at the end of the adsorption process. Increase in the MB removal percentage with increasing adsorbent dosage using MPS was due to the split in the flux or the concentration gradient between MB concentration in the solution and the MB concentration on the surface of MPS. Umoren *et al.* [29] explained that the reason being the increment of adsorbate removal percentage on increasing adsorbent dosage was due to greater availability of the exchangeable sites or surface area at a higher concentration of the adsorbent. According to Kiew and Toong [5], increase in the amount of adsorbent leads to a substantial availability of active sites. However, at a point of saturation, the removal efficiency of the adsorbent will become steady and even start to decrease when the dosage is further increased beyond that. This phenomenon is contributed by the presence of adsorbent in excess that will in turn block the active sites, thus, reducing the total surface area of binding. In this study, the reduction of MPS adsorption efficiency however was not observed up to 1.25 g, but the MB removal rate increased insignificantly with further top-up of the MPS dosage beyond 1.0 g.

### 3.2.4 Effect of Methylene Blue Initial Concentration and Contact Time

The effect of MB initial concentration was examined in the range of 10 mg/L to 50 mg/L with 0.25 g MPS at 25˚C. The adsorption of MB on MPS was also studied as a function of contact time in order to identify the equilibrium time for the maximum adsorption efficiency. The effect of MB initial concentration with different adsorption time on the removal percentage is presented in Fig 5.

It was observed that the final MB percentage removal decreased with increasing initial concentration of MB solution. According to Bouaziz *et al.* [24], high removal percentage at lower dye concentration was observed due to the presence of high ratio of adsorbent sites to the dye molecules while the removal percentage decreased significantly at higher concentration of MB due to full occupation of the MPS pores on its surfaces. Subsequently, Marrakchi *et al.* [25] pointed out that with high dye concentration, the excess dye molecules in the adsorption system could not fully come in contact with the adsorbents. Dod *et al.* [26] and Ghosh and Reddy [27] also highlighted that although percentage removal decreased with an increase in the initial concentration, the dye uptake per unit weight of the adsorbent was found to increase with an increase in the initial dye concentration in all cases. This explanation was supported by Subramaniam and Ponnusamy [28] that the increase in initial dye concentration enhanced the interaction between MB and adsorbent molecules, thereby leading to more MB uptake by adsorbent molecules. The positive correlation in Fig 5 indicated the percentage removal of MB for all initial concentrations increased rapidly in the first 120 minutes and then gradually until the equilibrium was achieved.

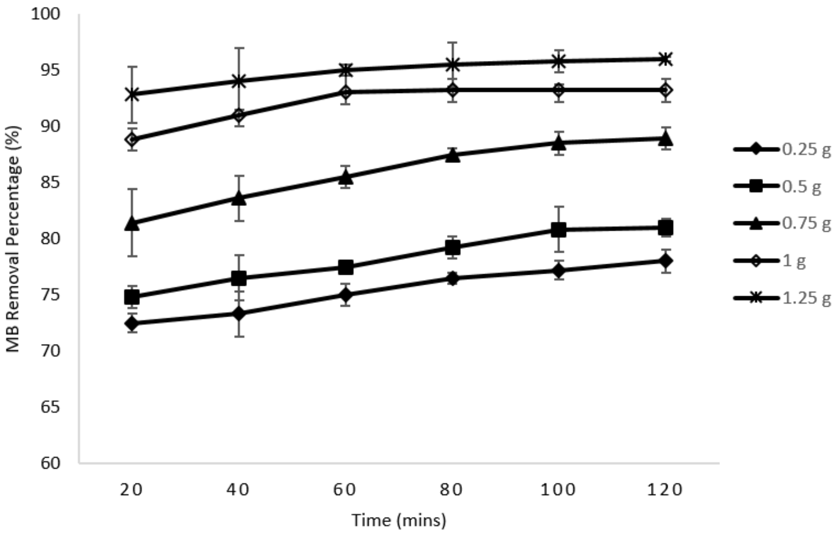


**Fig 4.** The effect of adsorbent dosage on the removal of MB using MPS.

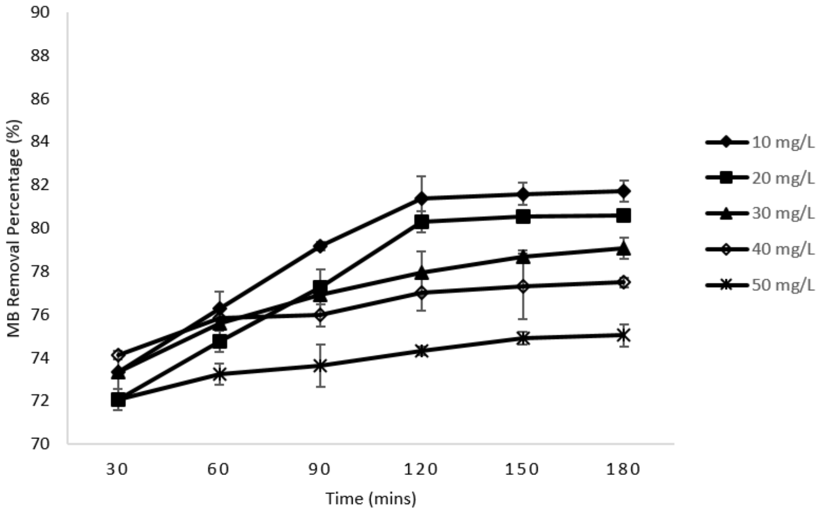


**Fig. 5** The effect of MB initial concentration and contact on the removal of MB using MPS.

### 3.3 Adsorption Isotherm

Fig 6 shows Langmuir, Freundlich and Temkin adsorption isotherm models of the magnetized papaya seeds adsorbent by linear regression analysis. Table 2 summarizes the parameters of each isotherm and their correlation coefficients ($R^2$). Based on the correlation value, Langmuir isotherm fitted the experiment data the best with $R^2$=0.9983 while Temkin fitted the least with $R^2$=0.9782.

Based on the plot linearity as shown in Fig 6, the Langmuir isotherm showed the best fit to the experimental data compared to Freundlich and Temkin models. Thus, the applicability of the Langmuir isotherm suggested that the adsorption of MB molecules on surface of the MPS was a monolayer adsorption over a homogenous surface. It also confirmed that adsorption of each molecule had equal activation energy and that sorbate–sorbate interaction was negligible. In addition, the essential characteristic of the Langmuir isotherm can be expressed in terms of a widely used dimensionless factor known as the equilibrium parameter ($R_L$), or the separation factor [27,30]. The $R_L$ factor can be calculated by the following expression:

$$R_L = \frac{1}{KC_i} \tag{3}$$

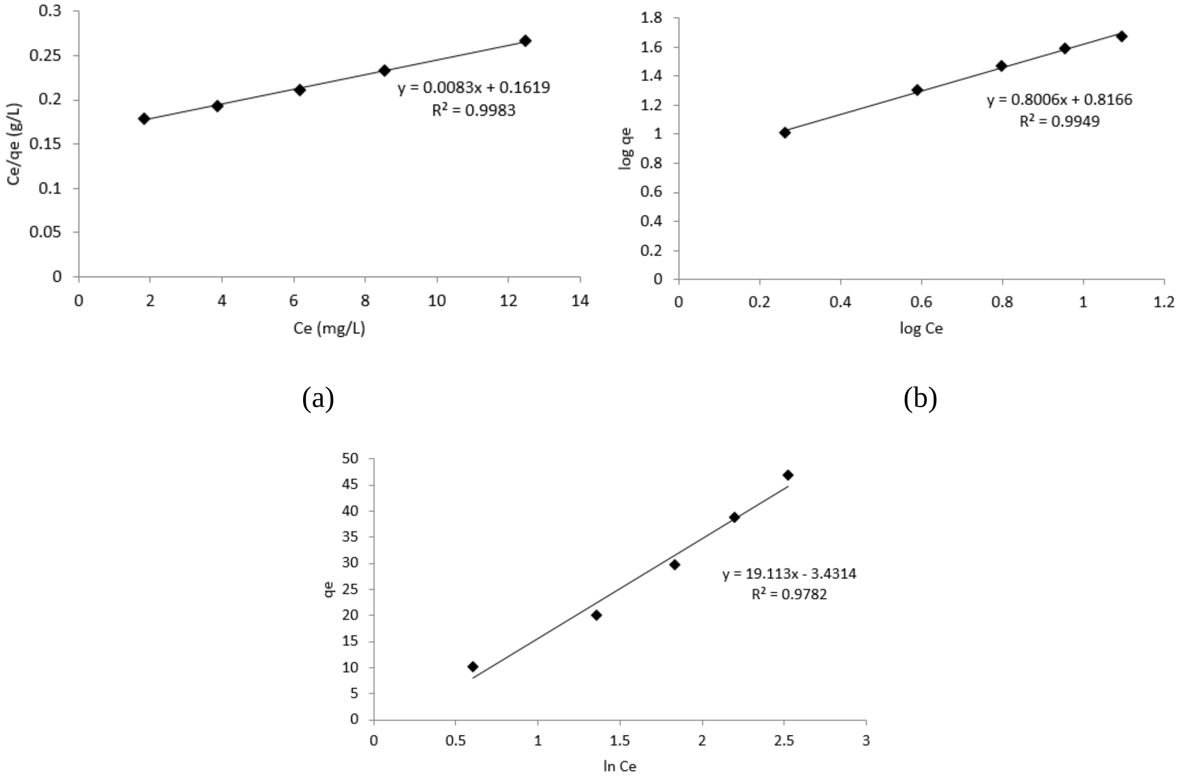
where k (in liters per milligram) was the Langmuir bonding energy coefficient, and $C_i$ was the highest initial dye concentration (in milligrams per liter). According to Webber and Chakkravorti [31], the value of $R_L$ indicated the feasibility of dye adsorption, in which the process was regarded as unfavorable when $R_L>1$, linear when $R_L=1$, favorable if $0<R_L<1$, or irreversible when $R_L=0$. In this study, $R_L$ value calculated from the MB adsorption on MPS was found to be 0.2085, which fell into the range of favorable adsorption system. The maximum adsorption capacity, $q_m$ of MPS towards the removal of MB in this study was determined to be 120.48 mg/g which was higher than other potential biosorbents that included fennel seed at 18.24 mg/g [32], acid-treated sago wastes at 36.8 mg/g [33] and masau stone at 65.1 mg/mg [34]. The performance is also comparable with the recently reported modified pyrolytic sludge at 149.05 mg/g [35] and modified Kaolin at 111.11 mg/g [36].

**Table 2** Langmuir, Freundlich, and Temkin model parameters for MB adsorption on MPS.

| Adsorption Isotherm Model | Langmuir | Freundlich | Temkin |
|---|---|---|---|
| **$R^2$** | 0.9983 | 0.9949 | 0.9782 |

## 4 Conclusion

The results of this study suggested that waste papaya seed, with its low cost and abundant availability has a potential to be used as an adsorbent for MB in wastewater. It was evidenced that the MPS could be easily recovered from the treated solution by an external magnetic field. Due to its paramount characteristic of short recovery time for the used adsorbent, magnetism technology was considered as a viable solution to replace the conventional filtration process and centrifugation in solid-liquid separation. Subsequently, various parameters were varied in the MB adsorption process, showing consistent trend between the adsorption performance of MPS with other conventional adsorbents. The adsorption results were also fitted into the isotherm equations of Langmuir, Freundlich and Temkin. The result demonstrated that this adsorption process was best fitted to the Langmuir isotherm. With the promising outcomes obtained in this study, further characterization study can be performed to investigate the changes in terms of physical surface morphologies and chemical functional groups following the magnetized modification on papaya seed to further correlate its adsorption performance to the magnetization process. The possibility of regenerating the used MPS can also be further explored.



(a) (b)

(c)

**Fig. 6** Linear fitting plots (a) Langmuir, (b) Freundlich and (c) Temkin isotherms model for adsorption process.

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