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New Application of Pomegranate Peel Waste: The Decontamination of Toxic Methylene Blue Dye from Textile Wastewater

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ABSTRACT

The textile wastewater contains different dyes which are harmful to the environment. Therefore, wastewater from textile industry need to be treated before being discharged into the environment. The removal of dyes from effluent via adsorption process using pomegranate peel waste provides an attractive alternative treatment. The present work describe the application of biomaterial, pomegranate peel waste (PPW) for the treatment of cationic dye, methylene blue from the surface of water. The main parameters affecting the adsorption of methylene blue i.e., sorption time, mass of sorbent and pH of water were optimized. Dye removal test performed with PPW revealed that it performed at pH 11 with contact time 30 min and 1.0 g of adsorbent dosage. The biosorption kinetic followed pseudo-second order model and Langmuir isotherm model for the isotherm analysis.

Keywords: Pomegranate Peel Waste, Adsorption, Methylene Blue.

1. INTRODUCTION

Food colouring, cosmetics, paper and textiles industries that discharge from effluent are impure by dyes. Allergic as eczema, skin irritation, cancer and mutation are the example of adverse result kind dye [1]. This dyes found within the discharges could be a major concern caused by their adverse effects to several varieties of life as an example the aquatic life. For the textiles industries in Malaysia, the COD production is 1189 mg/L and pH 13 [2] which cause pollution to the river. The conventional steps for treating dye-containing wastewaters are coagulation and flocculation [3], reverse osmosis [4] and activated carbon absorption [5]. These technologies do not show significant successful or benefit in economic. It will take a long time period if we take a low cost treatment compare the current method as more technologies.

A number of non-conventional, low-cost adsorbents have been tested for dye removal. These include garlic peel [5], macauba (Acrocomia aculeata) kernel oil [6], natural textile fiber [7], and jackfruit seed [8]. The present investigation is undertaken to test the use of pomegranate peel for the removal of methylene blue dye.

Methylene blue that is scientifically referred to as tetramethylthionine chloride may be a cationic dye with mass 373.9 g. it is a heterocyclic aromatic substance with the formula $C_{16}H_{18}ClN_3S$. Although the term methylene blue is used generally and often just refers to the colored cation. Adsorption by using pomegranate peel is one alternative way to reduce waste and decontaminate toxic dye from polluted water.

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2. MATERIAL AND METHODS

2.1 Materials

Methylene blue (MB), HCl and NaOH were purchased from Sigma Aldrich (Missouri, MO, USA) and pomegranate peel waste was collected from a fruit stall near the Main campus UniMAP located at Pauh, Perlis Malaysia.

2.2 Preparation of PPW

The pomegranate peels were washed thoroughly by using tap water and rinsed with distilled water to remove any dirt and dust on the pomegranate peels surface. The cleaned pomegranate peels were cut into small pieces and dried in binder heating oven at a temperature of 100 °C for 24 hours to ensure all the moisture content in the peel have been removed [9]. The dried peels pieces then grinded into powder to 10 micrometre particle size [10]).

2.3 Characterization of Adsorbent

The morphology of PPW was observed by scanning electron microscopy (SEM) (Hitachi S-4200, Japan). The functional groups of the PPW were investigated by Fourier Transform Infrared (FTIR) (Perkin Elmer, Inc., Billerica, USA).

2.4 Sorption Experiment

Batch adsorption experiments were carried out to determine the adsorption equilibrium and kinetics studies. Experiments were carried out to study the effect of parameters, such as solution pH, initial dye concentration, biosorbent dosage, and contact time.

2.4.1 Effect of pH

In order to study the effect of pH against contact time, the experiment was conducted over a pH range pH 2 to 11 such as pH 2, 3, 5, 7, 9 and 11 [2]. The solution pH was adjusted progressively by adding in 0.1 M HCl and 0.1 M NaOH using dropper. The solution pH was measured using Starter 300 pH meter (Ohaus Instruments Co., Ltd, Shanghai, China). Methylene blue solution with initial concentration of 50 mg/L was agitated with 0.1 g of pomegranate peels powder. The agitation speed of the incubator was set at 150 rpm and the temperature is control at 30°C at every 30 minutes. The absorbance of dye solution was measured using spectrophotometer (Thermo Electron Corporation, Madison, USA) at predetermined maximum wavelength at 665 nm.

2.4.2 Effect of Initial Dye Concentration

In order to study the effect of initial concentration against contact time, 10, 20, 30, 40, 50 mg/L [2] of aqueous dye solution at different initial concentration were prepared and added separately into 250 mL Erlenmeyer flasks. The methylene blue solution containing 200 ml with different initial concentration that is added to the flasks containing 0.1 g of pomegranate peel powder at optimum pH. The flasks then were placed in shaking incubator at 150 rpm and 30 °C. The concentration of dye solutions were measured by using spectrophotometer at 665 nm.

2.4.3 Effect of Adsorbent Dosage

The effects of adsorbent mass on the amount of methylene blue adsorbed by different amount of pomegranate peels were examined. The 250 ml flasks containing 200 ml methylene blue solutions at same concentrations were added with 0.1 g, 0.3 g, 0.5 g, 0.7g and 1.0 g of pomegranate peels powder [11]. The experiments were conducted using Thermo line Scientific Orbital Shaker Incubator. The shaker was set at a temperature of 30 °C and a constant speed of 150 rpm. The absorbance of dye solution was measured every 30 minutes using a UV spectrometer at 665 nm.

2.4.4 Effect of Contact Time

All the optimized parameters (i.e., pH, adsorbant dosage and initial dye concentration) were used to conduct the experiment. The samples were collected every 30 minutes until the absorbance of dye concentration remain constant.

2.5 Adsorption Kinetics

The adsorption kinetics of the Methylene Blue removal was analyzed by using pseudo-first order, and pseudo-second order model to study the performance of adsorption system in relation to time and was re-arranged into linearized form for linear regression analysis.

2.5.1 Pseudo-First Order Kinetic Model

The linear equation for pseudo-first order model is given by equation (1) below where, qt is the amount of adsorption at time t, and K_1 (L/min) is pseudo-first-order rate constant.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (1)$$

where q_t is the amount of dye adsorbed per unit of adsorbent (mg/g), t is contact time (min) and k_1 is the pseudo-first-order constant which can be determined from the plot of log ($q_{\_e}$-q_t) versus t.

2.5.2 Pseudo-Second Order Kinetic Model

The linear equation for pseudo-second order model is given by equation (2). Below, q_e and k_2 (g/mg min) is pseudo-second-order rate constant obtained from intercept and gradient of linear graph t/q_t against t.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

where k2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}). q_e and k_2 can be obtained by linear plot of t/q_t versus t.

2.6 Isotherm Analysis

The equilibrium data were examined by using Langmuir and Freundlich isotherms model. The adsorption quality at equilibrium, q_e (mg/g) was calculated by using equation (3). C_o and C_e (mg/L) are the initial and equilibrium concentration of dye solution obtained from the equilibrium curve.

$$Adsorption\ capacity, q = \frac{(c_o - c_e)v}{w} \tag{3}$$

Where V is the volume of the aqueous solution (L), W is the weight of adsorbent used. The percentage of dye removal was calculated by using equation (4) where C_t (mg/L) is the aqueous dye concentration at time t (min)

$$Percentage\ of\ removal = \left(\frac{C_o - C_t}{C_o}\right) x\ 100 \tag{4}$$

2.6.1 Langmuir Isotherm

The linear equation for Langmuir isotherms is given by equation (5) below, where, q_e is the amount of adsorbed dye in equilibrium (mg/g), C_e is the equilibrium concentration. Linear graph C_e/q_e is plotted against C_e to find out the Langmuir constant K_L (mg/g) and q_m (L/mg).

$$q_e = \frac{q_m K_L C_e}{1 + KC_e} \tag{5}$$

where q_m is the maximum adsorption amount with complete monolayer coverage on adsorbent surface, C_e is the dye concentration at equilibrium, K_L is the Langmuir constant.

2.6.2 Freundlich Isotherm

The linear equation for Freundlich isotherms is given by equation (6) below K_F, the Freundlich constant and 1/n, the adsorption intensity is obtained from the intercept and gradient of linear graph ln q_e against ln C_e

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{6}$$

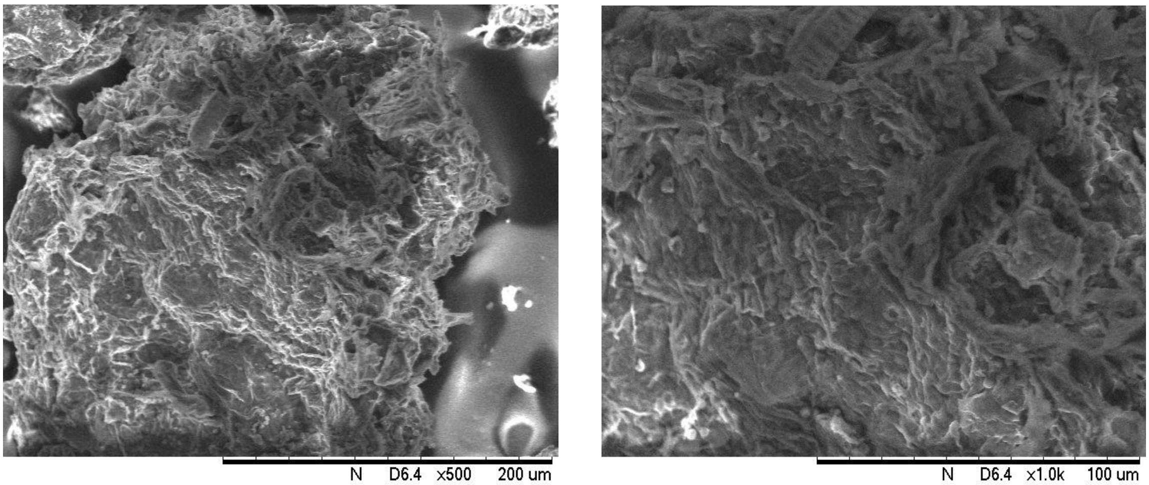
where Q_e is amount of dye adsorbed per unit of adsorbent, C_e is dye concentration at equilibrium, K_F and n are Freundlich constant which can be determined from the intercept and slope of Freundlich plot respectively.

3. RESULTS AND DISCUSSION

3.1 Morphological Study

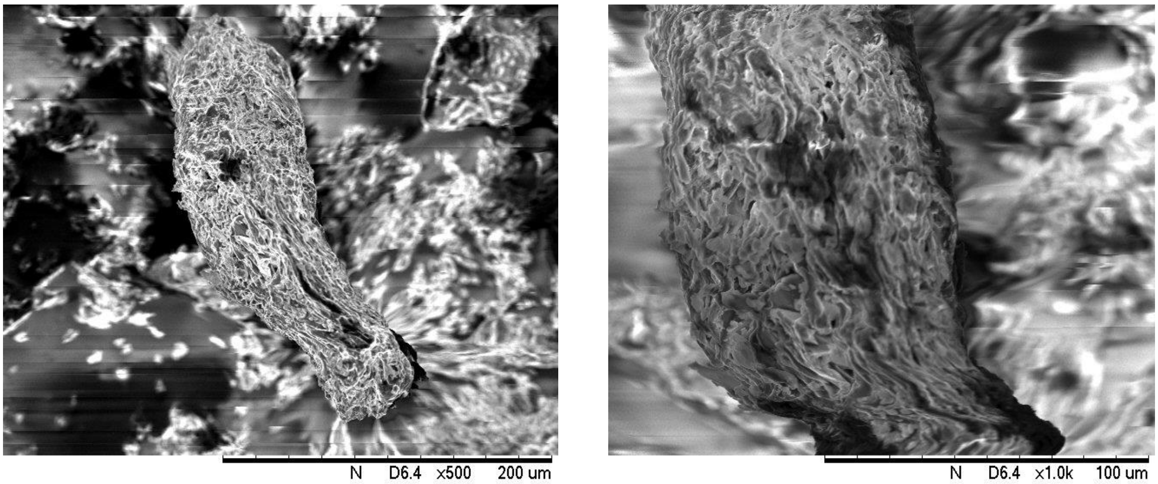
Surface morphology of PPW was investigated using Scanning Electron Microscope (SEM). SEM is an important tool for studying the surface morphology and the physical properties of biosorbent. Figure 1 and Figure 2 shows the surface images of biosorbent before and after adsorption process under magnification of 500x and 1000x. From the observation, the surface of the biosorbent before adsorption was rough, uneven and consists of porous structure [4]. Large surface area was exposed for adsorption process due to the heterogeneous surface. The presence of pores and cavities provide a high chance for the uptake of dye molecules to be adsorbed and attached onto the surface of biosorbent [12].

The structure of biosorbent changes after adsorption of Methylene Blue. The pore appeared on the surface of biosorbent are filled and the surface appears to be smoother compared to biosorbent before adsorption [5]. The observation shows that the cationic dye was adsorbed to the functional group on the surface of the biosorbent. Also, it shows a decrease in heterogeneity after adsorption process [5].



(a) (b)

Figure 1. SEM images of PPW before adsorption process at different magnifications (a) 500x; (b) 1000x.



(a) (b)

Figure 2. SEM images of PPW after adsorption process at different magnifications (a) 500x; (b) 1000x.

3.2 Functional group

FTIR spectroscopy offers important information related to the nature of the bonds and allows identification of different functional groups on the cell wall structure. The functional group is one of the factors resulting in the mechanism of binding and possible functional group that involved in the interaction between pomegranate peel with methylene blue. Table 1 shows the present of functional group in the adsorbent before and after adsorption process. The table showing a total of 6 different peaks showed the complex structure in the PPW.

Table 1 FTIR peak differences before and after biosorption process

IR peak	Frequency (cm^{-1})			Assignment
	Before adsorption	**After adsorption**	**Differences**	
1	3274.74	3289.14	-14.14	O-H stretch
2	2919.81	2919.47	0.34	C-H stretch
3	2172.66	2165.13	7.53	-C=C stretch
4	1609.62	1603.83	5.79	N-H stretch
5	1322.25	1325.57	-3.32	C-N stretch
6	1029.91	1028.10	1.81	C-F stretch

3.3 Optimization of Effective Parameters on Removal of Methylene Blue

3.3.1 Effect of Solution pH

The effectiveness of methylene blue removal is strongly dependent on the pH of methylene blue solution. From graph plotted in Figure 3 and 4, both of the removal percentage and adsorption capacity increase with increasing pH of dye solutions. Both of the removal percentage and adsorption capacity reach the highest values, which is 99.52% and 90.0 mg/g respectively.

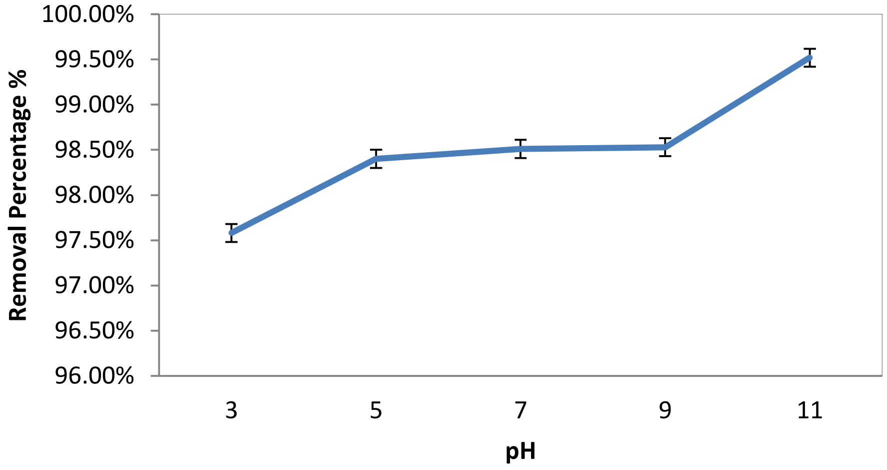


Figure 3. Effect of pH on dye removal percentage by PPW.

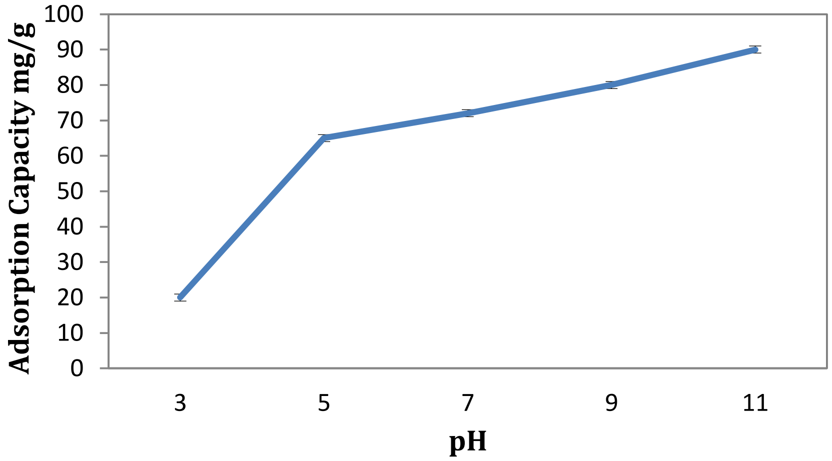


Figure 4. Effect of pH on adsorption capacity of methylene blue at equilibrium by PPW.

From this data, it means that PPW powder can adsorb methylene blue better under alkaline solution because the dye is acidic where the pH is 4.5. The highest percentage of removal recorded at pH 11. From FTIR analysis of pomegranate peels powder, there are many anionic functional groups can be found on its surface. At lower pH, protonation of these functional groups occur and behave as positive charge. On top of that, the research carried out by [13] further prove that higher pH enable more efficient adsorption of methylene blue. This phenomenon is explained by using the terms of electrostatic forces. At higher pH, less protonation occurs on lotus leaf powder, thus increasing the electrostatic force between molecules with opposite charges [13]. Thus, the uptake of cationic methylene blue particles by PPW is limited. At higher pH, less protonation occurs. The anionic functional group is available for the attraction of cationic dye. Hence, pH 11 is used for the next parameters.

3.3.2 Effect of Initial Dye Concentration

The effect of initial dye concentration on dye removal is study using pH 11, 0.1g of pomegranate peels powder and dye concentration from 10 to 50 mg/L at 30°C. Figure 5 shows the dye removal percentage while Figure 6 shows the adsorption capacity at equilibrium.

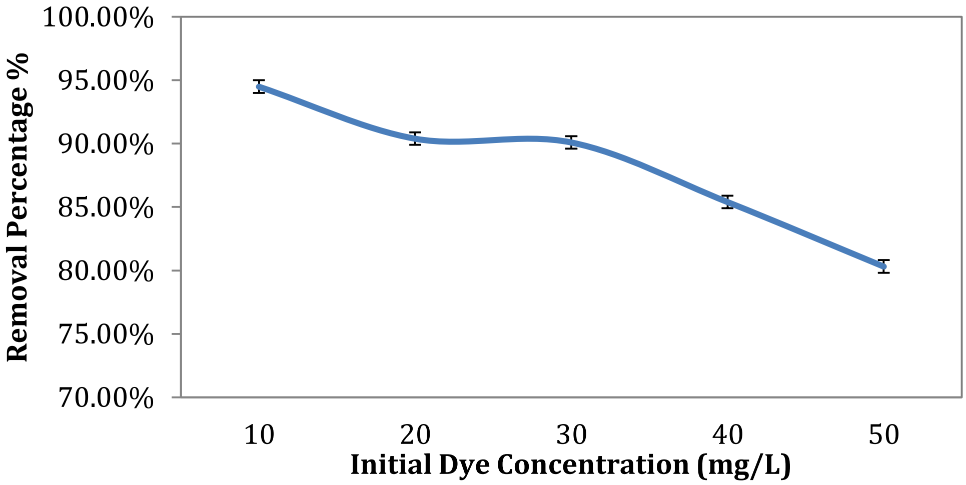


Figure 5. Effect of initial dye concentration on dye removal percentage by PPW.

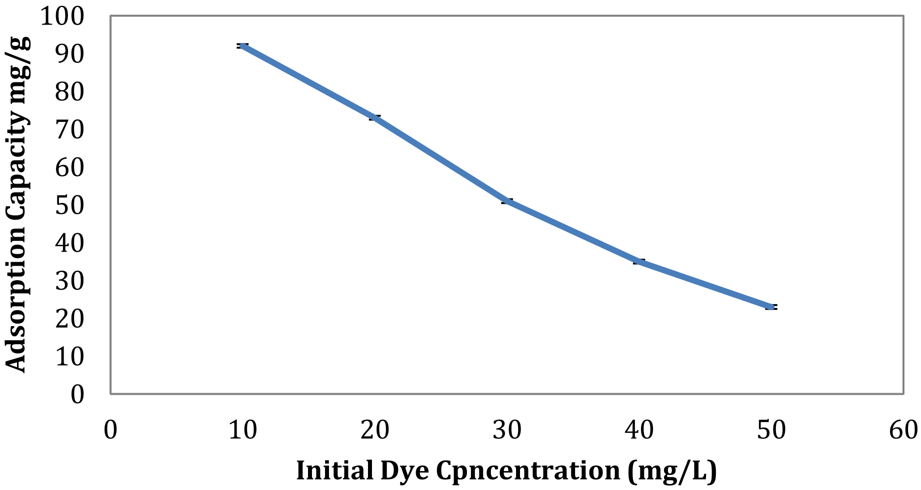


Figure 4. Effect of initial dye concentration on adsorption capacity of methylene blue at equilibrium by PPW.

The removal percentage of dye decrease with increasing initial dye concentration. This is because initial dye concentration acts as the driving force for adsorption process. The initial rapid adsorption of dye can be explained by the high number of active sites available on the surface. The driving force to solve the problem with the resistance to mass transfer of dye effect on increase in concentration enhances the interaction between the dye and adsorbent apart it. From Figure 4, adsorption capacity also decreases with increasing initial dye concentration. [5] have reported that the same trend of adsorption capacity of methylene blue onto garlic peels. The study showed that decreasing in dye concentration increase the mass transfer resistance between adsorbents and methylene blue in dye solution, thus resulting in such trend of result.

3.3.3 Effect of Adsorbent Dosage

Biosorbent dosage also affect significantly on biosorption performance. The effect of biosorbent dosage has been studied by varying biosorbent dosage from 0.1 g to 1.0 g using 50 mg/L methylene blue solution at pH 11. Figure 5 shows the dye removal percentage while Figure 6 shows the adsorption capacity at equilibrium.

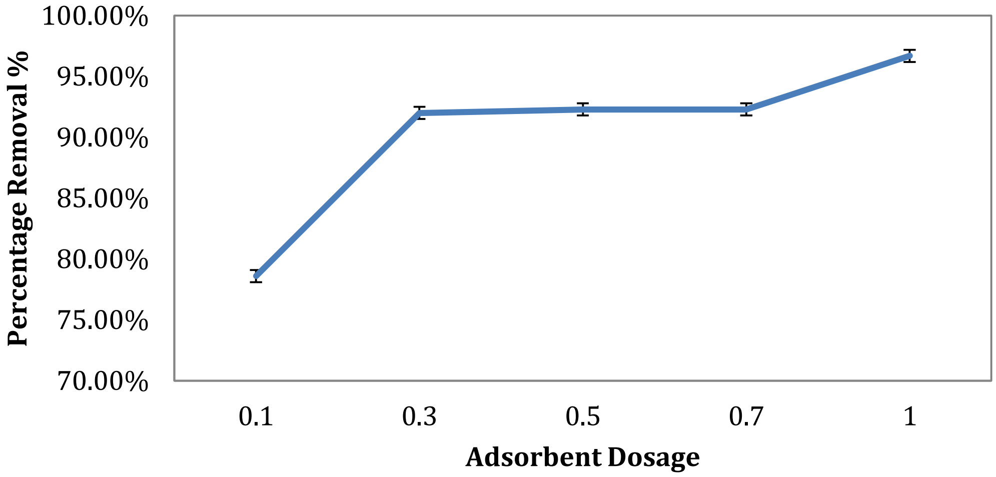


Figure 5. Effect of adsorbent dosage on dye removal percentage by PPW.

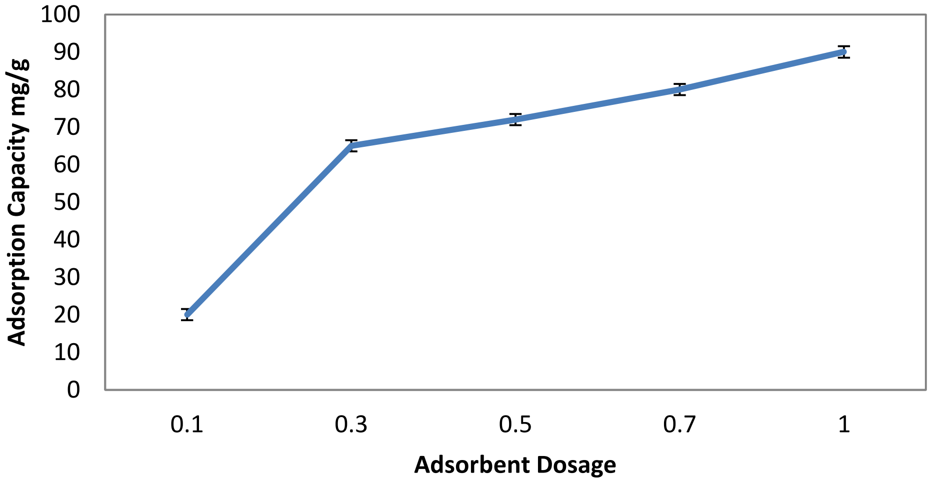


Figure 6. Effect of adsorbent dosage on adsorption capacity of methylene blue at equilibrium by PPW.

Biosorbent dosages also have significant impact on removal percentage and adsorption capacity. From graphs above, both of the dye removal percentage and adsorption capacity increase as the biosorbent dosage increase. The reason causing increase in removal of dye is because an increase in biosorbent dosage provide more active sites on the biosorbent, in turn the total sorption surface area for the adsorption of dye become larger [2]. This is because at higher biosorbent dosage, less pores or active sites on biosorbent are shielded, thus more methylene blue adsorbed onto pomegranate peels powder. In contrast, at lower biosorbent dosage, the biosorbent active sites are shielded with each other. In addition, the adsorption of dye particles per gram of PPWs powder also increased, hence increasing the adsorption capacity.

3.3.4 Effect of Contact Time

The study of the change in dye concentration over time is studied using 50 mg/L of methylene blue solution with 0.1 g of pomegranate peels powder at pH 11 and temperature of 30°C. Figure 7 shows the dye removal percentage while Figure 8 shows the adsorption capacity at equilibrium. The change in dye removal percentage was investigated until the adsorption process reach equilibrium. From the graph as shown in Figure 7 the dye concentration increased for the first 30 minutes. After that, the dye concentration remains constant. In the first 30 minutes, the adsorption of dye by pomegranate peels occurs. This is due to the biosorption of methylene blue onto pomegranate peels powder. As the biosorption occurs, the removal of methylene blue from dye solution occurs simultaneously where the time required to reach equilibrium is dependent on the types of adsorbate and adsorbent used. For treated biosorbent, usually the equilibrium can be reached in very short time, usually less than one hour. Removal percentage reaches as high as 99.8% at equilibrium. Figure 8 shows the amount of dye adsorbed per gram of pomegranate peels powder. From the graph plotted, the adsorption capacity reaches as high as 102.25 mg/g at equilibrium where all of the pores on biosorbent are assumed to be saturated by adsorbed dye particles [14].

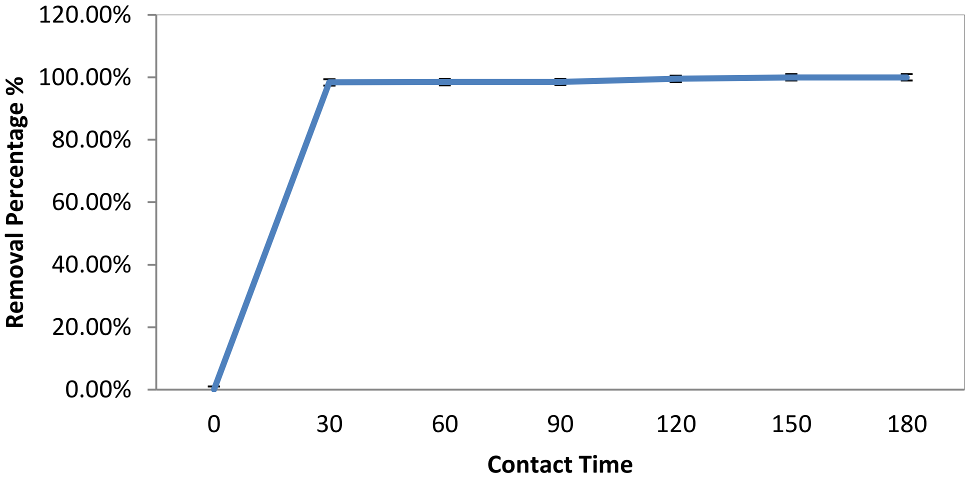


Figure 7. Effect of contact time on dye removal percentage by PPW.

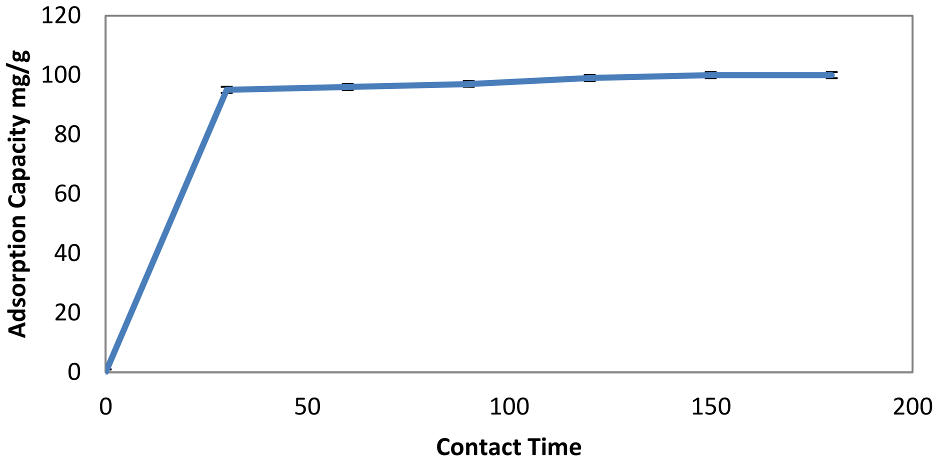


Figure 8. Effect of contact time on adsorption capacity of methylene blue at equilibrium by PPW.

3.4 Adsorption Kinetic

Pseudo-first and –second order kinetic models are plotted as following to find out the most suitable adsorption mechanism utilized by PPW to adsorb methylene blue. Figure 9 shows the kinetic model.

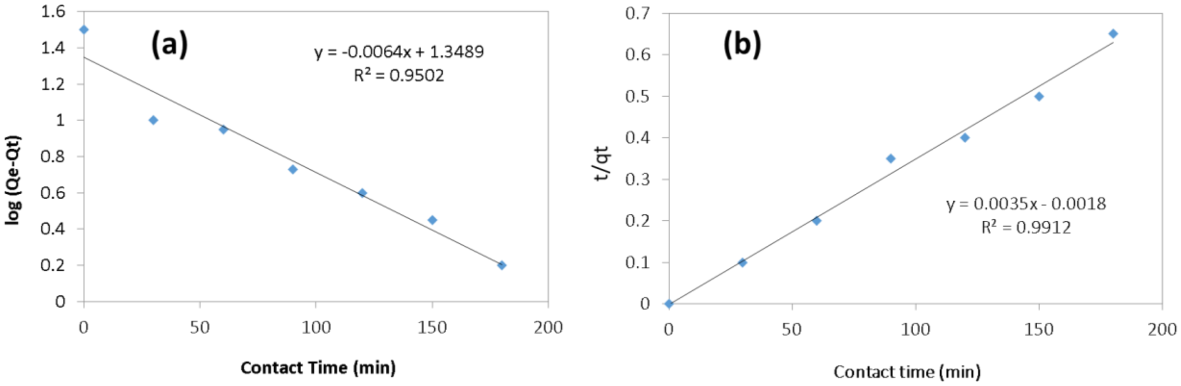


Figure 9. Kinetic models **(a)** Pseudo-first-order kinetic model **(b)** Pseudo-second-order model.

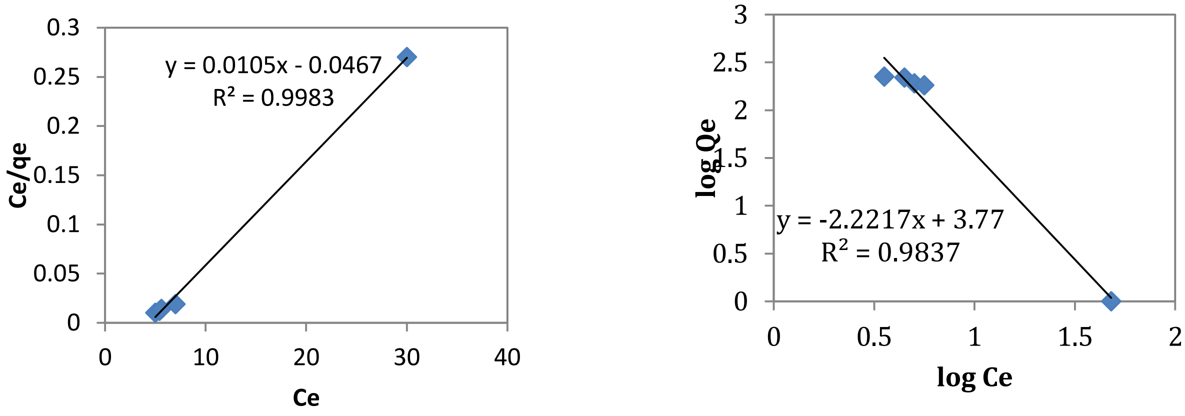
Pseudo-first-order kinetic model is plotted by using log (Qe-Qt) as y-axis and contact time as x-axis, while pseudo-second-order kinetic model is plotted by using t/qt as y-axis and contact time as x-axis. From Table 2, the value of R^2 for pseudo-second order model is 0.9912, which is much closer to 1 compared with the pseudo-first-order model with R^2 of 0.9502. Thus, pseudo-second-order kinetic model is more suitable to be used to represent the adsorption mechanism. Adsorption mechanism of methylene blue onto pomegranate peels powder is more prone to chemisorption rather than physiosorption, which means that the adsorption process might involve some covalent bonds of functional groups in both methylene blue and pomegranate peels powder [15].

Table 2 Important values of pseudo-first and–second order kinetic models

Pseudo-first-order model	Pseudo-second-order model
$R^2 = 0.9502$	$R^2 = 0.9912$
$k_1 = 0.0147$	$k_2 = 2.2085 \times 10^{-3}$

3.5 Isotherm Analysis

The isotherm study for the biosorption of Methylene Blue by pomegranate peel was conducted at different initial concentration (10, 20, 30, 40 and 50 mg/L). The experimental results were studied using Langmuir, and Freundlich isotherms. Figure 10 were show plotted as a result of linear regression analysis, which that are Langmuir plot (C_e/q_e vs C_e) and Freundlich plot (log q_e vs log C_e).



(a) (b)

Figure 10. Adsorption isotherms (a) Langmuir isotherm, (b) Freundlich isotherm.

As seen in Figure 10, the experimental data has been approved fitted into the Langmuir isotherm as indicated by the correlation coefficient, R^2 = 0.9983. From the R^2 value, it can be concluded that Langmuir isotherm is more suitable to represent the adsorption of methylene blue onto pomegranate peels powder since its R^2 value is closer to 1. This is due to the homogeneous distribution of binding sites on the pomegranate peels surface as Langmuir isotherm presumes the surface is homogeneous. The linear plot verifies the monolayer formation for the adsorption system [19]. Identical studies were reported for adsorption using Tea Waste [16]. This implies that methylene blue adsorbed onto pomegranate peels surface as monomolecular and homogeneous layer. There is no stalking of methylene blue particles on pomegranate peels. This means that only surface coverage is occurring [9]. In other words, only surface of pomegranate peels powder is available for biosorption. The Important values for Langmuir and Freundlich isotherms can be seen in Table 3.

Table 3 Important values for Langmuir and Freundlich isotherms

Langmuir isotherm	Freundlich isotherm
$R^2 = 0.9983$	$R^2 = 0.9837$
$K_L = 5.2 \times 10^{14}$	$K_F = 43.3801$
Q_m = 95.2381 mg/g	n = -0.4501

4. CONCLUSION

The present study shows that PPW possess the capability as an effective adsorbent for removal of cationic dye from aqueous solution. The effect on the adsorption process proven by operation parameters. The most suitable conditions for the biosorption of 100 mL of methylene blue onto pomegranate peels powder was pH 11, 10 mg/L, biosorbent dosage of 1.0 g. Most of the adsorption of methylene blue onto pomegranate peels powder consumed 120 minutes to reach equilibrium. The highest dye removal percentage and adsorption capacity were 99.8 % and 102.25 mg/g respectively. Methylene blue adsorption onto pomegranate peels can be explained by Freundlich and Langmuir isotherm model. Implying homogeneous adsorption took place during the adsorption process Langmuir isotherm model demonstrated the highest goodness of fit. The biosorption kinetic followed pseudo-second order model and showing chemisorption involved during adsorption process. By taking into account of all the results from the studies, it can be deduced that pomegranate peels may be used for removal of dyes in wastewater and the intra-particle diffusion is not the only rate-determining factor during adsorption.

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