

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Removal of Methyl Red from Aqueous Solution by *Nephelium lappaceum*.

Rahmiana Zein*, Ayu Widya Astuti, Dilla Wahyuni, Firda Furqani, Khoiriah, and Edison Munaf.

Laboratory of Analytical Environmental Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Padang 25163, Indonesia.

ABSTRACT

Removal of methyl red by rambutan (*Nephelium lappaceum*) seed as biosorbent by biosorption has been studied in the laboratory. Biosorption is done through batch method, and the result was used to study biosorption kinetics of Langmuir and Freundlich. Biosorbent was activated using HNO_3 0.1 N. Removal of methyl red was at optimum in pH 3, initial methyl red 690 mg/L, biosorbent dose of 0.1 g, agitation speed of 50 rpm, contact time of 20 minutes, and heating biosorbent temperature of 30°C. The biosorption capacity for biosorbent with optimum conditions is 62.6645 mg/g. R^2 value of the Freundlich isotherm is higher than that of the Langmuir isotherm – 0.236 and 0.914, respectively. The Freundlich isotherm indicates that biosorption is a physical process.

Keywords: Biosorption, methyl red, *Nephelium lappaceum*.

*Corresponding author

INTRODUCTION

Industrial effluents are one of the major causes of environmental pollution because effluent discharges from dyeing industries are highly colored with a large amount of suspended organic solid¹. Untreated disposal of this colored water into the receiving water body either causes damage to aquatic life or to human beings through mutagenic and carcinogenic effect. As a matter of fact, the discharges of such effluents are something to worry about for both toxicological and environmental reasons^{2,3}.

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical, and biological methods, such as coagulation and flocculation⁴, biosorption⁵, ozonation⁶, electrochemical techniques⁷, and fungal decolonization⁸. Among these methods, biosorption has gained more popularity in recent years due to its proven efficiency in the removal of pollutants from effluents. Use of seeds has already been widely researched in removing dye from aqueous solutions. Examples of these seeds are *Annona squamosa* seed⁹, avocado pear (*Persea americana*) seed¹⁰, *Polyalthia longifolia* (ashoka) seed¹¹, *Hevea brasiliensis* seed¹², mango seed¹³, *Ziziphus jujube* seed and *Mango kernel*¹⁴, date seeds¹⁵, and *Moringa oleifera* seeds¹⁶. Percent removal of methyl red from aqueous solutions by activated carbon prepared from the annona squamosa seed by adsorption with adsorbent dose of 0.6 g in pH 4, initial methyl red at 100 mg/L, and contact time of 100 minutes was 68%⁹.

Cultivation of *Nepthelium lappaceum* is possible in almost every tropical wet area such as in Asia, Amerika, Afrika, and Australia. After fruit consumption, the seeds are discarded as they are not edible. Thus, *Nepthelium lappaceum* seeds are available free of cost. Therefore, the main objective of this study was to evaluate the possibility of using dried *Nepthelium lappaceum* seed to develop a new low-cost biosorbent and to study its application in removing methyl red from simulated wastewater. Systematic evaluation of the involved parameters, such as pH, biosorbent dose, initial dye concentration, agitation speed, contact time, and heating biosorbent temperature, was carried out.

EXPERIMENTAL

In this study, biosorption experiments were conducted using *Nepthelium lappaceum* seed, methyl red (Merck), KBr (Merck), HNO₃ (Merck), HCl (Merck), NaOH (Merck), and dan aquadest.

Methods

FTIR spectra measurement

Fourier Transform InfraRed (Unican Mattson Mod 7000 FTIR Spectrometer using KBr pellets). The sample *Nepthelium lappaceum* seeds weighing 1–10 g were placed in contact with 100 mg KBr and pressed with thin disk or pellet. These spectra were recorded as absorbance values at each data point in duplicate.

Preparation of Biosorbent from *Nepthelium lappaceum* seed

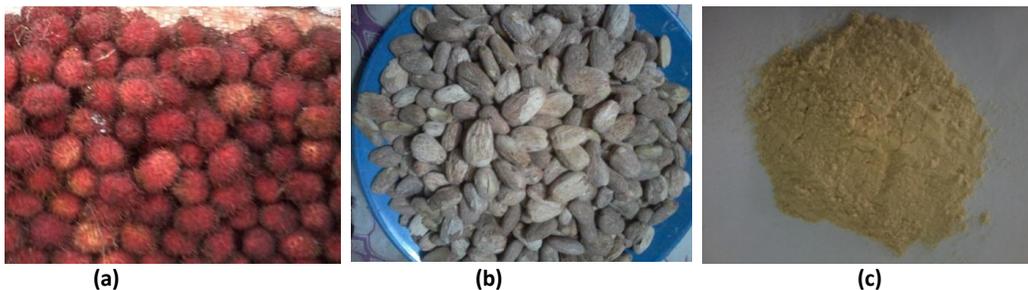


Figure 2.1.2 (a) *Nepthelium lappaceum* (b) *Nepthelium lappaceum* seed (c) *Nepthelium lappaceum* powder

The *Annona squamosa* seeds were air-dried and powdered in a grinder. They were soaked in concentrated HNO_3 for 2 hours and washed thoroughly with distilled water until neutral pH was attained. The dry biomass was crushed into granules, sieved to one particle size, and then preserved in desiccators for use.

Preparation of synthetic solutions

A stock solution of $1,000 \text{ mg L}^{-1}$ was prepared by dissolving an appropriate 250 mg of MR in 250 mL of distilled water. Different concentrations of 5, 10, 15, 20, 25, 40, 60, and 80 mg L^{-1} of MR were prepared from the stock solution. All the chemicals used throughout this study were analytical-grade reagents. Double-distilled water was used in preparing the solutions and reagents. The initial pH was adjusted with 0.1 M HCl or 0.1 M NaOH. All the biosorption experiments were carried out at room temperature ($27^\circ\text{C} \pm 2^\circ\text{C}$).

Batch biosorption studies

Effect of pH on MR biosorption

The effect of pH on the equilibrium uptake of dyes was investigated by employing an initial concentration of MR (60 mg/L) at 10 mL and 0.1 g of adsorbent. The initial pH values were adjusted with 0.1 M HCl or NaOH to form a series of pH levels from 2 to 9. The suspensions were shaken at room temperature ($27^\circ\text{C} \pm 2^\circ\text{C}$) using agitation speed (100 rpm), the minimum contact time required to reach the equilibrium (10 min), and the amount of the determined adsorbed MR.

Effect of initial dye concentration on MR biosorption

The effect of initial dye on the equilibrium uptake of MR ($30\text{--}720 \text{ mg L}^{-1}$) 10 mL and 0.1 g of adsorbent was investigated. The initial pH values were adjusted with 0.1 M HCl or NaOH to optimum pH. The suspensions were shaken at room temperature ($27^\circ\text{C} \pm 2^\circ\text{C}$) using agitation speed (100 rpm), the minimum contact time required to reach the equilibrium (10 min), and the amount of the determined adsorbed MR.

Effect of biosorbent dose on MR biosorption

The effect of biosorbent dose on the equilibrium uptake of MR with optimum initial dye concentration at 10 mL was investigated with adsorbent doses of 1, 1.5, 2, and 2.5 g. The initial pH values were adjusted with 0.1 M HCl or NaOH to optimum pH. The suspensions were shaken at room temperature ($27^\circ\text{C} \pm 2^\circ\text{C}$) using agitation speed (100 rpm), the minimum contact time required to reach the equilibrium (10 min), and the amount of the determined adsorbed MR.

Effect of agitation speed on MR biosorption

The effect of agitation speed on the equilibrium uptake of MR with optimum initial dye concentration at 10 mL was investigated with adsorbent dose of 1 g. The initial pH values were adjusted with 0.1 M HCl or NaOH to optimum pH. The suspensions were shaken at room temperature ($27^\circ\text{C} \pm 2^\circ\text{C}$) using different agitation speeds (30, 50, 100, 150, 200, and 250 rpm), the minimum contact time required to reach the equilibrium (10 min), and the amount of the determined adsorbed MR.

Effect of contact time on MR biosorption

The effect of contact time on the equilibrium uptake of MR with optimum initial dye concentration at 10 mL was investigated with adsorbent dose of 1 g. The initial pH values were adjusted with 0.1 M HCl or NaOH to optimum pH. The suspensions were shaken at room temperature ($27^\circ\text{C} \pm 2^\circ\text{C}$) using optimum agitation speed, the minimum contact time required to reach the equilibrium (5, 10, 15, 20, and 25 min), and the amount of the determined adsorbed MR.

Effect of heating biosorbent temperature on MR biosorption

The effect of heating biosorbent temperature on the equilibrium uptake of MR with optimum initial dye concentration at 10 mL was investigated with adsorbent dose of 1 g at different heating temperatures of 28°C, 30°C, 50°C, 70°C, and 90°C. The initial pH values were adjusted with 0.1 M HCl or NaOH to optimum pH. The suspensions were shaken at room temperature (27°C ± 2°C) using optimum agitation speed, optimum contact time required to reach the equilibrium, and the amount of the determined adsorbed MR.

Regeneration biosorbent

About 0.1 g of biosorbent after treatment and 10 mL of HNO₃ (0,001 N, 0,01 N, and 0,1 N) were shaken at room temperature (27°C ± 2°C) using optimum agitation speed, optimum contact time, and the amount of the determined desorbed MR.

Application on laboratory wastes

About 10 mL of laboratory waste was investigated with adsorbent dose of 1 g. The initial pH values were adjusted with 0.1 M HCl or NaOH to optimum pH. The suspensions were shaken at room temperature (27°C ± 2°C) using optimum agitation speed, optimum contact time required to reach the equilibrium, and the amount of the determined adsorbed MR.

The concentration of MR in the solution was measured by direct UV-vis spectrophotometric method using a Genesis 20 Thermo Scientific at optimum wavelength. All the experiments were duplicated, and only the mean values were reported. The amount of dye adsorbed at equilibrium onto carbon, q_e (mg/g), was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e)V/W \quad (2.1.6)$$

where C_0 and C_e (mg/L) are the initial and equilibrium liquid-phase concentrations of MR, respectively, V is the volume of the solution (L), and W is the weight of biosorbent used (g).

RESULTS AND DISCUSSION

Effect of system pH on MR uptake

The pH of the system has profound influence on the adsorptive uptake of adsorbate molecules presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule. The effect of system pH on MR uptake with rambutan seed activated with 0.1 N HNO₃ in pH level 2–9 was investigated. Figure 3.1 shows variations of removal of methyl red in solutions with different pH levels.

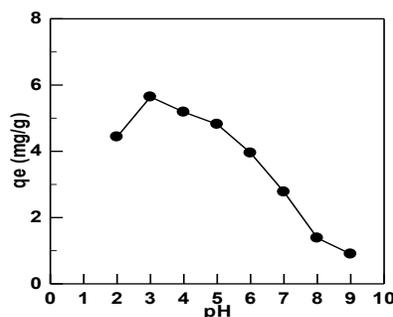


Figure 3.1 Effect of system pH on adsorption of MR, MR concentration (60 mg L⁻¹) at 10 mL onto biosorbent (0.1 g) at room temperature (27°C ± 2°C), and agitation speed at 100 rpm for the minimum contact time required to reach the equilibrium (10 min)

In Figure 3.1, the adsorption capacity for MR is 5.643 mg/g in pH 3. The adsorption capacity increased from 4.4355 mg/g to 5.643 mg/g from pH 2 to pH 3 and decreased to 5.1835 mg/g in pH 4. The adsorption capacity decreased pH dari 4 ke 9. Low pH value (1.0 to 2.0) leads to an increase in H^+ ion concentration in the system, and the surface of the biosorbent acquires positive charge by absorbing H^+ ions¹⁷. High pH value was observed and the adsorption capacity decreased because MR divestment of H^+ ions made methyl red negatively charged and could not interact with biosorbent¹⁸. Mas Rosemal and Kathiresan investigated the removal of methyl red from aqueous solutions using banana pseudostem fibers at optimum pH of 3¹⁹, and T. Santhi investigated removal of methyl red from aqueous solutions using activated carbon prepared from the annona squamosa seed by adsorption at optimum pH of 4⁹.

Effect of initial MR concentration

Effect of initial MR concentration by biosorption was investigated with varying initial MR concentrations of 30 mg/L, 60 mg/L, 120 mg/L, 240 mg/L, 480 mg/L, 690 mg/L, and 720 mg/L.

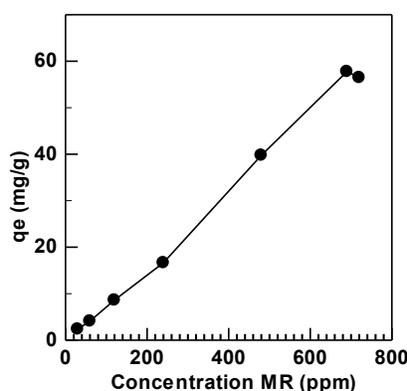


Figure 3.2 Effect of initial MR concentration of 10 mL onto biosorbent (0.1 g) at room temperature ($27^{\circ}\text{C} \pm 2^{\circ}\text{C}$), agitation speed of 100 rpm, and the minimum contact time required to reach the equilibrium (10 min)

Figure 3.2 shows the results of the experiments conducted in a range of dye concentrations (30–720 mg/L) at constant biosorbent dose (0.1 g), pH (3), and temperature ($27^{\circ}\text{C} \pm 2^{\circ}\text{C}$). The obtained results reveal that percent removal of dye depends on the initial dye concentration. The adsorption capacity for MR is 57.772 mg/g in dye concentration of 690 mg/L. The adsorption capacity decreased to 56.4855 mg/g in dye concentration of 720 mg/L. It obtained optimum dye concentration at 690 mg/L. These observations can be explained by the fact that sufficient biosorption sites are available to accommodate an increasing number of dye molecules. In other words, the number of molecules available for sorbing onto the sorbent surface is relatively lower than the ones available for the biosorption sites. Higher dye concentrations are capable of affecting the chemical equilibrium between dye molecules in the liquid phase and the ones adsorbed onto the biosorbent surface resulting in a further biosorption process. Moreover, this sorption behavior can be attributed to higher chance of effective interaction between adsorbate molecules and biosorbent surface as the concentration of dye increases¹⁶. Mas Rosemal and Kathiresan found optimum dye concentration at 500 kg/L¹⁹, and Paul had optimum dye concentration at 0.001 mol/dm^{3,20}.

Effect of biosorbent dose on MR biosorption

Effect of biosorbent dose on MR biosorption was investigated with varying biosorbent dose, from 0.1, 0.2, 0.3, 0.4, and 0.5 g. Figure 3.3 shows the variation removal of methyl red in the solution with different biosorbent dose.

The adsorption capacity decreased from 57.086 mg/g to 12.4915 mg/g as the biosorbent dose increased from 0.1 g to 0.5 g at equilibrium time (10 min). The adsorption capacity decreased as the adsorbent dose increased, but the MR concentration remained constant and the biosorbent caused an agglutination. T. Santhi observed the optimum biosorbent dose at 0.2 g⁹.

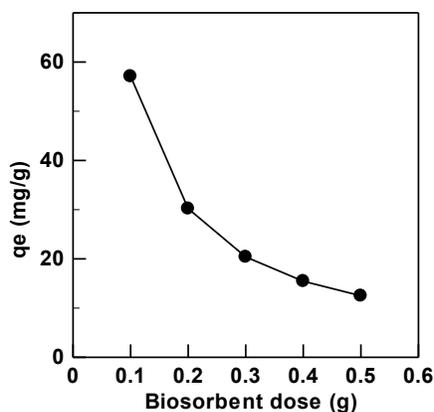


Figure 3.3 Effect of biosorbent dose on MR biosorption, MR concentration (690 mg L^{-1}) 10 mL onto biosorbent pH 3 at room temperature ($27 \pm 2^\circ\text{C}$), agitation speed of 100 rpm, and minimum contact time required to reach the equilibrium (10 min).

Effect of agitation speed on MR biosorption

The effect of agitation speed on MR biosorption was investigated with varying agitation speed that is from 30 rpm, 50 rpm, 100 rpm, 150 rpm, 200 rpm, and to 250 rpm. Figure 3.4 shows the variation removal of methyl red in solution with different agitation speed.

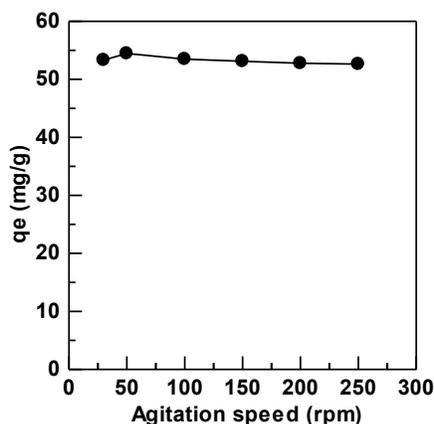


Figure 3.4 Effect of agitation speed on MR biosorption, MR concentration (690 mg L^{-1}) 10 mL onto biosorbent (0.1 g), pH 3 at room temperature ($27 \pm 2^\circ\text{C}$), and minimum contact time required to reach the equilibrium (10 min)

When the agitation speed increased from 30 rpm to 50 rpm, the adsorption capacity also increased. The optimum agitation speed was 50 rpm, with an adsorption capacity of 54.4575 mg/g. After that, the agitation speed increased to 100 rpm, but the adsorption capacity decreased to 53.486 mg/g. Increase in agitation speed caused the enduring capacity of thin layer biosorbent to decrease, which indicated that the dye interacted with the biosorbent. The adsorption capacity decreased because the biosorbent active sites were filled with dye at the optimum agitation speed.

Effect of contact time on MR biosorption

Effect of contact time on MR biosorption was investigated with varying contact time, from 5–25 minutes. Figure 3.5 shows the variation removal of methyl red in solution with different contact time.

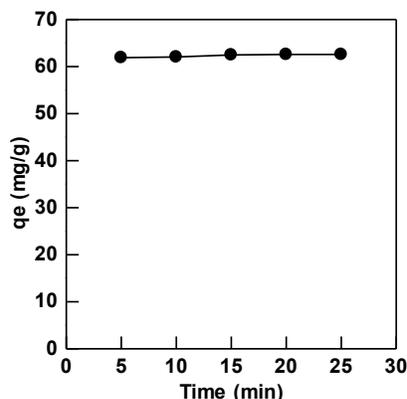


Figure 3.5 Effect of contact time on MR biosorption, MR concentration (690 mg L^{-1}) 10 mL onto biosorbent (0.1 g), pH 3 at room temperature ($27 \pm 2^\circ\text{C}$), agitation speed 50 rpm, and the optimum contact time required to reach the equilibrium

The effect of contact time on the amount of MR adsorbed was investigated using 690 mg/L initial concentration of MR with 0.1 g biosorbent at pH 3. The extent of removal of MR by the biosorbent was found to increase, and it reached a maximum value with increase in contact time, as shown in Fig. 3.5. The equilibrium time was found to be 20 minutes. It was observed that with initial dye concentration of 690 mg/L, the amount of dye adsorbed per unit mass of adsorbent increased from 61.386 mg/g to 62.5785 mg/g. Higher concentration resulted in a higher driving force of the concentration gradient. This driving force accelerated the diffusion of dye from the solution into the adsorbent. It is clear that the efficiency of dye removal depends on the initial dye concentration. The amount of dye adsorbed increased as the dye concentration increased, but it remained constant after reaching the equilibrium time²¹. T. Santhi observed the optimum contact time as 100 minutes⁹.

Effect of heating biosorbent temperature on MR biosorption

The effect of heating biosorbent temperature on MR biosorption was investigated with varying heating biosorbent temperature from 28°C, 30°C, 50°C, 70°C, and to 90°C. Figure 3.5 shows the variation removal of methyl red in solution with different heating biosorbent temperature.

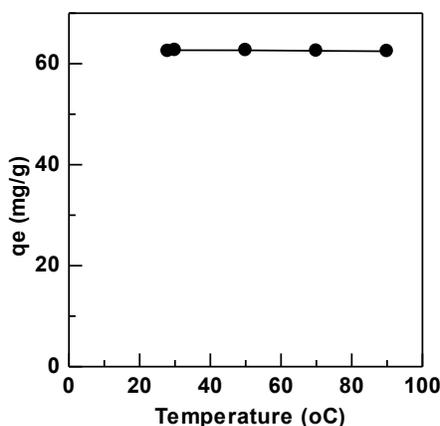


Figure 3.6 Effect of heating biosorbent temperature on MR biosorption, MR concentration (690 mg L^{-1}) 10 mL onto biosorbent (0.1 g), pH 3 at room temperature ($27 \pm 2^\circ\text{C}$), agitation speed 50 rpm, and contact time of 20 minutes.

The highest adsorption capacity of heating biosorbent temperature in 30°C is 62.6645 mg/g, but its effect wasn't different. This shows that the heating biosorbent temperature didn't affect MR biosorption with rambutan seed.

Regeneration biosorbent process

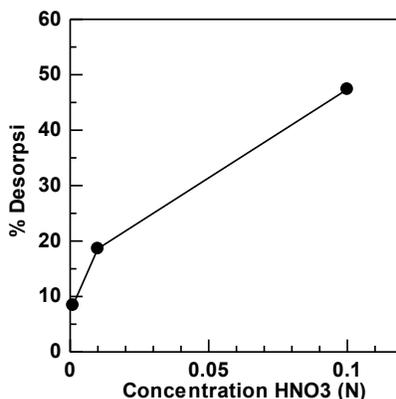


Figure 3.7 Regeneration biosorbent process of methyl red from rambutan seed with concentration of HNO₃ in 0.001 N, 0.01 N, and 0.1 N.

Figure 3.7 shows the regeneration biosorbent process with different concentrations of HNO₃ in 0.001 N, 0.01 N, and 0.1 N.

Figure 3.7 shows that 0.1 N HNO₃ removed methyl red from rambutan seeds better than 0.001 N, and 0.1 N HNO₃. Percent regeneration with 0.1 M HNO₃ was 47.37%, with 0.001 M HNO₃ was 8.415%, and with 0.01 M HNO₃ was 18.625%. Regeneration with 0.1 M HNO₃ had the highest percent regeneration, as 0.1 M HNO₃ is the highest concentration among the three concentrations, thus signifying that it had a lot of H⁺ ion to remove methyl red from rambutan seeds. After the regeneration biosorbent process, biosorbent can be used to remove methyl red dye or other kinds of dyes.

Application with laboratorium waste

Table 3.8 Hasil biosorpsi terhadap sampel alam (limbah laboratorium) menggunakan biji buah rambutan.

C _o (mg/L)	C _e (mg/L)	Q (mg/g)	% Penghilangan
475	298.57	17.643	37.03

In the table, the rambutan seeds that efficiently removed methyl red in laboratorium wastes had the adsorption capacity of 17.643 mg/g and percent removal of 37.03%. The adsorption capacity was lower in the experiment because the laboratorium wastes had other compounds that competed to interact with the biosorbent.

Adsorption isotherms

An adsorption isotherm indicates how adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step in finding the suitable model that can be used for design purposes. Adsorption isotherm is important to describe how solutes interact with adsorbents, and it is critical in optimizing the use of adsorbents. In this study, adsorption isotherm study was carried out on two isotherm models: Langmuir and Freundlich. The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficients, R² values¹⁹. Figure 3.9a and 4.9b show Langmuir isotherm model and Freundlich from methyl red.

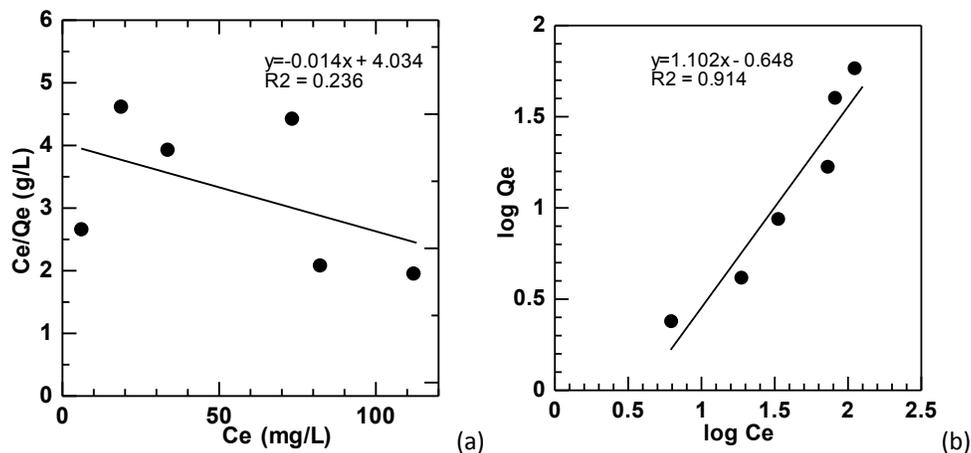


Figure 3.9 (a) Langmuir Isotherm model methyl red, (b) Freundlich Isotherm model methyl red

Table 3.9 Parameter-parameter Langmuir Isotherm and Freundlich isotherm

Langmuir Isotherm			Freundlich Isotherm		
q_m (mg/g)	K_a (L/mg)	R^2	K_F	$1/n$	R^2
71.4286	0.0035	0.236	4.4463	1.102	0.914

Langmuir Isotherm

The theoretical Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir nonlinear equation is commonly expressed as follows:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \quad (3.9.1.1)$$

where Q_m is a constant and reflect a complete monolayer (mg g^{-1}); K_a is adsorption equilibrium constant (L mg^{-1}) that is related to the apparent energy of sorption. The Langmuir isotherm Equation 1 can be linearized as shown in Equation 2:

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \quad (3.9.1.2)$$

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_a Q_m)$ ⁹. The results obtained from the Langmuir model for the removal of MR onto biosorbent are shown in Table 3.9. The applicability of the linear form of Langmuir model to biosorbent had the low correlation coefficients R^2 0.236. The maximum monolayer capacity Q_m obtained from the Langmuir is 71.4286 mg/g .

Freundlich Isotherm

The Freundlich isotherm model is the earliest known equation to describe the adsorption process. It is an empirical equation, and it can be used for non-ideal sorption that involves heterogeneous adsorption. The

Freundlich isotherm can be derived by assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites, and it is commonly given by the following nonlinear equation:

$$q_e = K_F C_e^{1/n} \quad (3.9.2.1)$$

where K_F is a constant for the system that is related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient, and it represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n$ indicates the adsorption intensity of dye onto the adsorbent or surface heterogeneity, and it becomes more heterogeneous as its value gets closer to zero. A value for $1/n$ that is below 1 indicates a normal Langmuir isotherm while a value for $1/n$ that is above 1 is an indication of cooperative adsorption. Equation 3 can be linearized in the logarithmic form (Equation 4), and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3.9.2.2)$$

The applicability of the Freundlich adsorption isotherm was also analyzed using the same set of experimental data by plotting $\log q_e$ versus $\log C_e$. The data obtained from linear Freundlich isotherm plot for the adsorption of the MR onto biosorbent are presented in Table 3.9. The correlation coefficients (0.914) showed that the Freundlich model is comparable to the Langmuir model. The adsorption of methyl red fits the Freundlich equations well.

SEM analysis

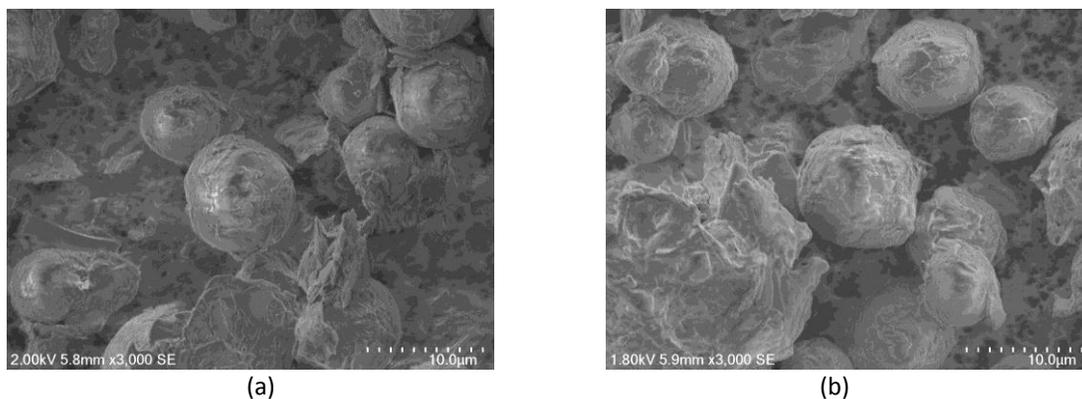


Figure 3.10 SEM Rambutan (*Nephelium lappaceum*) seed before biosorption (a) after biosorption (b)

The SEM analysis was performed to observe the surface morphology of the biosorbents before and after dyes adsorption. Figure 3.10a shows the SEM image in 3,000 X magnification, and it also shows that the *Nephelium lappaceum* seeds are highly porous and are small in size, thus indicating the possibility that it has good adsorption properties. After contacting with methyl red, the layer of adsorbed dye were clearly visible, molecules of *Nephelium lappaceum* became larger in size after its contact with methyl red (figure 3.10b). SEM analysis revealed that there were significant changes on the surface of biosorbents after interaction with dyes.

FTIR analysis

The spectrum for *Nephelium lappaceum* seeds before adsorption (Figure 3.11a) demonstrated the distinct peak at $3,330.61 \text{ cm}^{-1}$, representing O-H bond in alcohol; peak at $2,850.01 \text{ cm}^{-1}$, representing C-H stretching; peak at $1,709.85 \text{ cm}^{-1}$, representing C=O in carboxylic acid; peak at $1,463.39 \text{ cm}^{-1}$, representing C=C; peak at $1,155.45 \text{ cm}^{-1}$, $1,077.58 \text{ cm}^{-1}$, and $1,015.72 \text{ cm}^{-1}$ representing C-O in alcohol; peak at gelombang 860.96 cm^{-1} , 766.31 cm^{-1} , and 719.30 cm^{-1} , representing C-H in meta benzene²². Several shifts of peak were observed after activation (figure 3.11b). Peak displaced from $3,330.61 \text{ cm}^{-1}$ to $3,280.39 \text{ cm}^{-1}$ and from $1,709.85 \text{ cm}^{-1}$ to $1,710.40$

cm⁻¹ were indications of metal getting loose from biosorbent. Several shifts of peak were observed after adsorption (figure 3.11c); peak displaced from 3,280.39 cm⁻¹ to 3,335.13 cm⁻¹ and from 1,710.40 cm⁻¹ to 1,711.39 cm⁻¹ indicate the interaction between methyl red and the biosorbent. FTIR spectra reveal that the hydroxyl and carbonyl are the main functional groups that are present on the surface of the biosorbents involved in the biosorption process.

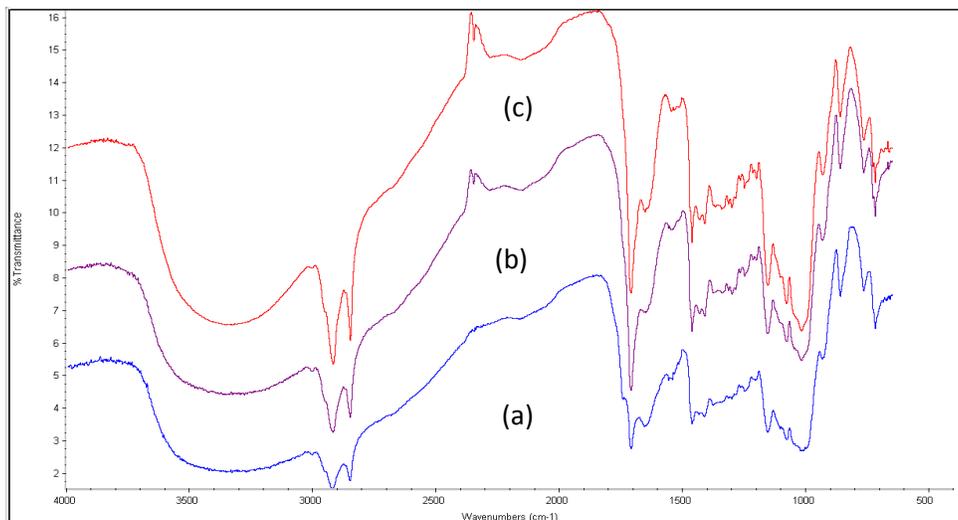


Figure 3.11 FTIR spectra of *Nephelium lappaceum* seed (a) before activation (b) after activation with 0.1 N HNO₃ (c) after biosorption

CONCLUSION

FTIR spectra of *Nephelium lappaceum* seed revealed the presence of O-H and C=O stretching in the adsorbent. These groups were responsible in the process of methyl red uptake as there was some shifting in those peaks. Biosorption of methyl red using *Nephelium lappaceum* seeds showed that the optimum condition of biosorption occurred at pH 3, initial concentration of methyl red 690 mg/L, biosorbent dose at 0.1 g, agitation speed at 50 rpm, contact time at 20 minutes, and biosorbent temperature at 30°C. *Nephelium lappaceum* seeds activation with 0.1 M HNO₃ give the maximum biosorption capacity, which is 62.6645 mg/g. Fitting of Freundlich isotherm data showed that the biosorption of methyl red tended to physisorption with R² value 0.914. This study revealed that *Nephelium lappaceum* seeds can be considered as an alternative biomass for removal of methyl red from aqueous solution, as it is highly stable, relatively high in biosorption capacity, is low cost, and can be regenerated.

REFERENCES

- [1] Crini, G: Non-Conventional Low-Cost Adsorbents for Dye Removal: A Review. *Bioresource Technology* 2006, 97(9): 1061-1085.
- [2] Robinson, T., McMullan G., Marchant R., Nigam P: Remediation of Dyes in Textile Effluent: A Critical Review on Current Treatment Technologies with a Proposed Alternative. *Bioresource Technology* 2001, 77(3): 247-255.
- [3] Aksu, Z: Application of Biosorption for the Removal of Organic Pollutants: A Review. *Process Biochemistry* 2005, 40(3-4): 997-1026.
- [4] Han, R., Zhang J., Zou W., Shi J., Liu H: Equilibrium Biosorption Isotherm for Lead Ion on Chaff. *Journal of Hazardous Materials* 2005, 125(1-3): 266-271.
- [5] Gupta, V. K., Ali I., Suhas, Mohan D: Equilibrium Uptake and Sorption Dynamics for the Removal of a Basic Dye (Basic Red) Using Low-Cost Adsorbents. *Journal of Colloid and Interface Science* 2003, 265(2): 257-264.

- [6] Ho Y. S., Chiu W. T., Wang C. C: Regression Analysis for the Sorption Isotherms of Basic Dyes on Sugarcane Dust. *Bioresource Technology* 2005, 96(11): 1285-1291.
- [7] Kumar, K.V: Comparative Analysis of Linear and Non-Linear Method of Estimating the Sorption Isotherm Parameters for Malachite Green onto Activated Carbon. *Journal of Hazardous Materials* 2006, 136(2): 197-202.
- [8] Ho Y. S: Second-Order Kinetic Model for the Sorption of Cadmium onto Tree Fern: A Comparison of Linear and Non-Linear Methods. *Water Research* 2006, 40(1): 119-125.
- [9] Santhi, T., S. Manonmani, T. Smitha: Removal of Methyl Red from Aqueous Solution by Activated Carbon Prepared from the *Annona squamosa* Seed by Adsorption. *Chemical Engineering Research Bulletin* 2010, 14: 11-18.
- [10] Asiaqwu, A. K., P. E. Omuku, C. O. Alisa: Kinetic Model for the Removal of Methyl Orange (Dye) from Aqueous Solution Using Avocado Pear (*Persea americana*) Seed. *An International Peer Review E-3 Journal of Sciences* 2013, 3(1): 48-57.
- [11] KS., Mundhe, Gaikwad AB, Kale AA, Deshpande NR, Kashalkar RV: *Polyalthia longifolia* (Ashoka) Seeds: An Effective Adsorbent for Methylene Blue Removal. *International Journal of Research in Pharmaceutical and Biomedical Sciences* 2012, 3(1): 180-186.
- [12] Hameed, B. H., F. B. M. Daud: Adsorption Studies of Basic Dye on Activated Carbon Derived from Agricultural Waste: *Hevea brasiliensis* Seed Coat. *Chemical Engineering Journal* 2007, 139: 48-55.
- [13] Itodo, H. U., Itodo A. U: Surface Coverage and Adsorption Study of Dye Uptake by Derived Acid and Base-Treated Mango Seed Shells. *J. Chem. Pharm. Res* 2010, 2(3): 673-683.
- [14] Pandharipade, S. L., Y. Moharkar, R. Thakur: Synthesis of Adsorbents from Waste Materials such as Ziziphus Jujube Seed & Mango Kernel. *International Journal of Engineering Research and Applications (IJERA)* 2012, 2: 1337-1341.
- [15] Yakubu, M. K., M. S. Gumel, A. M. Abdullahi: Use of Activated Carbon from Date Seeds to Treat Textile and Tannery Effluents. *African Journal of Science and Technology (AJST) Science and Engineering Series* 2008, 9(1): 39-49.
- [16] Marandi, R., S. M. B. Sepehr: Removal of Orange 7 Dye from Wastewater Used by Natural Adsorbent of *Moringa oleifera* Seeds. *American Journal of Environmental Engineering* 2011, 1(1): 1-9.
- [17] Santhi, T., S. Manonmani, T. Smitha, K. Mahalakshmi: Adsorption Kinetics of Cationic Dyes from Aqueous Solution by Bioadsorption onto Activated Carbon Prepared from *Cucumis sativa*. *Journal of Applied Sciences in Environmental Sanitation* 2009, 4 (3): 263-272.
- [18] Isiuku, B. O., M. Horsfall Jnr, A. I. Spiff: Colour Removal from a Simulated Methyl Red Wastewater by Adsorption on Carbon in a Fixed Bed. *Research Journal of Applied Sciences* 2014, 9 (4): 201-207.
- [19] Rosemal, H. M., Mas H, Kathiresan S: The Removal of Methyl Red from Aqueous Solutions Using Banana Pseudostem Fibers. *American Journal of Applied Sciences* 2009, 6(9): 1690-1700.
- [20] DIM, Paul E: Adsorption of Methyl Red and Methyl Orange Using Different Tree Bark Powder. *Academic Research International* 2013, 4(1): 330-338.
- [21] Shrivastava, V. S: Removal of Congo Red Dye from Aqueous Solution by *Leucaena leucocephala* (Subabul) Seed Pods. *International Journal of ChemTech Research* 2012, 4(3): 1038-1043.
- [22] Pavia, D. L., Gary M. L, George S. K, James R. V: *Introduction to Spectroscopy, Fourth Edition*, Department of Chemistry Western Washington University, Washington, 2009, 25-30.