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CHEMICALLY MODIFIED KAPOK SAWDUST AS ADSORBENT OF METHYL VIOLET DYE FROM AQUEOUS SOLUTION

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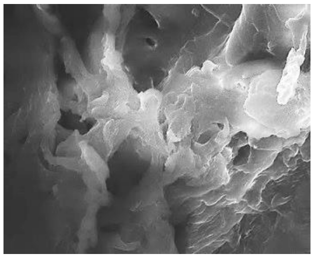
Graphical abstract



Abstract

In this study, chemically modified Kapok sawdust was used as an adsorbent for the removal of methyl violet from aqueous solution. Batch studies were performed to address various experimental parameters including pH, contact time, and initial concentration for the removal of this dye. Effective pH for methyl violet removal was 5. A greater percentage of dye was removed with a decrease in the initial concentration of dye. Quasi-equilibrium reached in 30 min. Equilibrium isotherms were analyzed by Langmuir, Freundlich, and Redlich-Peterson isotherm equations using correlation coefficients and two different error functions. Freundlich equation is found to best represent the equilibrium data for methyl violet-modified Kapok sawdust system.

Keywords: Kapok sawdust, methyl violet, dye, adsorbent, isotherm

1.0 INTRODUCTION

The disposal of synthetic dyes from paint, textile, leather and paper industries into the environment is an important source of water pollution. The dyes not only reduce the self-purification ability of rivers but also cause the bad effect to aquatic life. These compounds are quite stable and have low biodegradability [1]. Dyes can be classified as anionic, cationic and nonionic. The cationic dye such as methyl violet is even more toxic because it can pass through the entire food chain and form a protein-dye complex.

Numerous physicochemical and biological methods have been used to decolorize dyes in wastewater including aerobic [2] and anaerobic [3] microbial degradation, filtration [4], coagulation [5], and adsorption [1]. Among of these, adsorption process is one of the effective techniques that has been successfully employed for dye removal from wastewater due to its simplicity of design and easy to operate. A number of organic and inorganic adsorbents have been used to remove it, including various types of activated carbon [6-8] and polymer [9]. However, these adsorbents are generally expensive. As an alternative way to reduce costs, many agricultural wastes and byproducts of wood and forest industries of cellulose origin have been utilized, including sawdust [1,10-13], cashew nut shell [14], peanut husk [15], rambutan peel [16], and wheat straw [17]. Sawdust can be used in the adsorption of anionic dyes [1,18], but to enable binding of the cationic dyes such as methyl violet, the appropriate chemical modification is required.

The objective of the present study is to investigate the feasibility of alternative sawdust as an adsorbent for the removal of methyl violet from aqueous solution. Sawdust of Kapok, the indigenous crops in Indonesia, is reacted with sodium hydroxide (NaOH). It removes pectin, lignin, and hemicellulose and produces new adsorption sites on the sawdust surface that might be useful for binding methyl violet [19]. Batch experiments were carried out for equilibrium studies on the removal of methyl violet from aqueous solution. The influence of various contributing parameters including pH, contact time, and initial methyl violet concentration was investigated. Three adsorption isotherm models (Langmuir, Freundlich, and Redlich-Peterson) were used to study the fit of the experimental equilibrium data obtained in the study.

2.0 EXPERIMENTAL

2.1 Sample Preparation and Characterization

The sawdust of Kapok was sieved and the fractions with the particle size less than 0.149 mm were used for experiments. Further, it was washed with deionized water and dried. Kapok sawdust was further treated with sodium hydroxide solution (concentration 0.1 and 0.3 N) at 26°C for one hour. The ratio of sawdust weight to sodium hydroxide volume was 30 gram of sawdust to 500 mL of sodium hydroxide (NaOH). Finally, the sawdust was filtered, washed several times with deionized water until pH of the filtrate was around 7, dried at 110°C for one hour, characterized and used as an adsorbent in the sorption experiments. The FTIR spectra of raw and modified Kapok sawdust were recorded using an FTIR technique (Perkin Elmer, USA) by the KBr pellet method. The spectrum was scanned in the range of 400 to 4000 cm^{-1} wavenumbers. The photomicrography of the exterior surface of raw and modified Kapok sawdust was obtained by SEM (JEOL, Japan).

2.2 Batch Adsorption Experiment

Methyl violet (chemical grade reagent) was used as an adsorbate without further purification. The dye contains NH_2^+ functional group as shown in Figure 1.

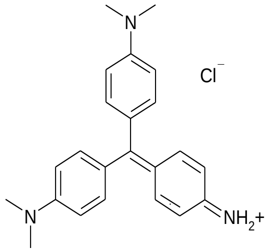


Figure 1 Structure of methyl violet

Isothermal adsorption experiments were performed by batch technique. Approximately 0.5 g of raw or modified Kapok sawdust was put into an Erlenmeyer filled with 50 mL of methyl violet solution (concentration of 60 mg/L). The adsorption was carried out at pH 5 with the addition of 0.1 N HCl and 0.1 N NaOH. The Erlenmeyer containing the mixture was further placed in a water bath and shaken mechanically at 26°C for 1 to 30 minutes at 115 rpm. Subsequently, suspended solid was filtered and the filtrate was analyzed to determine methyl violet concentration using a UV-Visible spectrophotometer at λ_{max} = 581 nm.

For pH study, 0.5 g of raw or modified Kapok sawdust was added into an Erlenmeyer filled with 50 mL of methyl violet solution (concentration of 2 mg/L). The pH was adjusted with the addition of 0.1 N HCl and 0.1 N NaOH to an appropriate pH (pH range of 3, 5, 7, 9). The Erlenmeyer containing the mixture was further placed in a water bath and shaken mechanically at 26°C for 120 minutes at 115 rpm. The sawdust was further separated from the solution and the filtrate was analyzed to determine methyl violet concentration using a UV-Visible spectrophotometer at λ_{max} = 581 nm.

To investigate the effect of initial concentration of methyl violet on the adsorption, 0.5 g of raw or modified Kapok sawdust was put into an Erlenmeyer filled with 50 mL of methyl violet solutions with varying concentration (1-100 mg/L). The sawdust-methyl violet system was maintained at pH 5 using 0.1 N HCl and 0.1 N NaOH. The Erlenmeyer was further placed in a water bath and shaken at 115 rpm at 26°C. After 120 minutes, suspended solid was filtered and the filtrate was analyzed for residual methyl violet using a UV-Visible spectrophotometer at λ_{max} = 581 nm. The percentage dye removal was calculated using equation (1) as follows:

$$\text{dye removal (\%)} = \frac{C_o - C_e}{C_o} \; x\,100 \tag{1}$$

where C_o (mg/L) is the initial concentration of methyl violet and C_e (mg/L) is the concentration of methyl violet at equilibrium [11]. The amount of dye adsorbed per unit weight of adsorbent at equilibrium (q_e, mg/g) was calculated using equation (2) as follows [12]:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where V (L) is the volume of methyl violet solution and m (g) is the dry weight of the adsorbents.

2.3 Adsorption Isotherm

To optimize the design of an adsorption system, it is important to prove the most appropriate correlation for the equilibrium curves. In this study, three isotherm models were used to describe the equilibrium nature of adsorption, including Langmuir, Freundlich, and Redlich-Peterson. The Langmuir isotherm model is suitable for monolayer adsorption on the adsorbent surface, which supposes that all the adsorption sites are energetically uniform and adsorption occurs on a structurally homogeneous adsorbent [17]. This model can be expressed as Eq. (3) and rearranged to the linear form is given by Eq. (4) as follows:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_e} \frac{1}{C_e} \tag{4}$$

where K_L is the adsorption equilibrium constant in L/mg related to the energy of adsorption, q_{max} is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent in mg/g and q_e is the amount dye adsorbed on unit mass of the adsorbent (mg/g) when the equilibrium concentration is C_e (mg/L). A plot of $1/q_e$ versus $1/C_e$ should yield straight line if Langmuir isotherm is obeyed by the adsorption equilibrium. The value of q_{max} and K_L can be calculated from the intercept and slope of the graphed line, respectively. The Freundlich equation is an indication of surface heterogeneity of the adsorbent and thus is responsible for multilayer adsorption due to the presence of energetically heterogeneous adsorption sites. This leads to the conclusion that the surface of adsorbent is made up small heterogeneous adsorption patches which are very much similar to each other in respect of adsorption phenomenon [20]. The Freundlich isotherm is described by Eq. (5) where K_F ($mg^{1-1/n}\ L^{1/n} g^{-1}$) and n are the Freundlich equilibrium constants which can be determined from the plot of log q_e versus log C_e on the linear form of Freundlich equation [17]. The higher value for K_F, indicates the higher affinity for adsorbate and the value of the empirical parameter n, indicates favorable adsorption.

$$q_e = K_F C_e^n \tag{5}$$

$$\log q_e = \log K_F + n \log C_e \tag{6}$$

The Redlich-Peterson isotherm approaches the Freundlich model at high concentration and is in accordance with the low concentration limit of the Langmuir equation. The Redlich-Peterson equation can be applied either in homogeneous or heterogeneous systems due to the high versatility of the equation [21]. The Redlich-Peterson isotherm can be represented as:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{7}$$

where K_R (L/g) and a_R (L/mg) are the Redlich-Peterson isotherm constants and β is the Redlich-Peterson isotherm exponent, which lies between 0 and 1. Eq. (7) can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln \alpha_R + \beta \ln C_e \tag{8}$$

Plotting the left-hand side of Eq. (8) versus ln C_e to obtain the isotherm constants is not applicable due to there are three unknowns constants (α_R, K_R, and β). Therefore, a minimization procedure was used to solve Eq. (7) by maximizing the correlation coefficient between the theoretical data for q_e predicted from Eq. (7) and the experimental data. The solver add-in function of the Microsoft excel was used to determine the parameters of the equations by minimizing the distance between the experimental data points and the theoretical model predictions.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Kapok Sawdust

To confirm the presence of functional groups in the adsorbent which are capable of adsorbing dye ions, FT-IR analysis was conducted. The FT-IR spectra of raw and modified Kapok sawdust are shown in Figure 2.

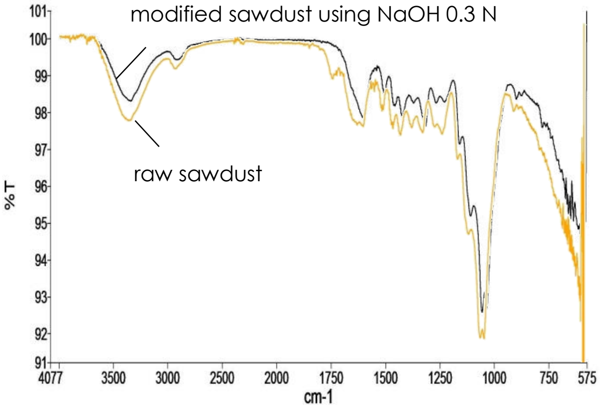


Figure 2 FTIR spectra of raw and modified Kapok sawdust

For raw sawdust, it can be seen that there is a broad and strong band from 3000 to 3600 cm^{-1}, which indicates the presence of carboxylic acid (RCOOH), alcohol (ROH) and amino (RNH_2) groups [1]. This is consistent with the peaks at 1037 and 1350 cm^{-1} due to alcoholic C-O and C-N bending vibration [22]. The broad absorption peak at 3360 cm^{-1} indicates the existence of bonded hydroxyl groups on the surface of sawdust. This band is associated with the OH stretching of the phenolic group of cellulose and lignin [11]. The peaks observed at 2930 and 1371 cm^{-1} are assigned to the stretch and bending vibration of the C-H bond in the methylene groups, respectively [22]. The spectrum also displays a strong band at 1735 cm^{-1}, which is assigned to the carbonyl group stretching from ester or the carboxylic acid group [1]. The peak at 1596 cm^{-1} may be attributed to N-H bending or C=C stretching of the aromatic rings while peaks located at 1508 and 1457 cm^{-1} are the characteristic of amine deformation [1]. The peak at 1422 cm^{-1} is attributed to the stretch vibration of C-O associated with the carboxylic group [11]. The band at 1400-1600 cm^{-1} is assigned to aromatic skeletal vibrations. The strong peak observed at 1037 cm^{-1} might represent the C-O-C of an ether group. [1]. The peak located at 595 cm^{-1} is assigned to the bending modes of the C-H group. After reaction with sodium hydroxide, the position and intensity of some peaks being changed. Peak indicating the existence of hydroxyl groups becomes narrower, shallower and shifts from 3360 to 3345 cm^{-1}. It may be due to the degradation of lignin by nucleophile strong base. The intensity of the peaks at 1400-1600 cm^{-1} was reduced, possibly due to the removal of aromatic or lignin. The peak at 1735 cm^{-1} disappeared because reaction with sodium hydroxide resulted in the conversion of carboxylic acid or esters to carboxylate as follow [1]:

hydroxyl:
$-ROH + NaOH \rightarrow -RO^{-}Na^{+} + H_2O$ (9)
carboxylic acid:
$-RCOOH + NaOH \rightarrow -RCOO^{-}Na^{+} + H_2O$ (10)
ester:
$-RCOOR' + NaOH \rightarrow -RCOO^{-}Na^{+} + R'-OH$ (11)

SEM micrograph of raw and modified Kapok sawdust are shown in Figure 3, 4 and 5. The surface texture of raw Kapok sawdust is smooth due to the high amount of lignin in the compound middle lamellae between the cell walls [11], as can be seen in Figure 3. After reaction with sodium hydroxide, the surface of modified Kapok sawdusts are rougher than that of raw Kapok sawdust and full of holes, mainly on the use of 0.3 N NaOH concentration, as can be seen in Figure 4 and 5. It is caused by the degradation of lignin, as described previously. Thus, there is a good agreement between the result of FT-IR analysis and SEM micrograph.

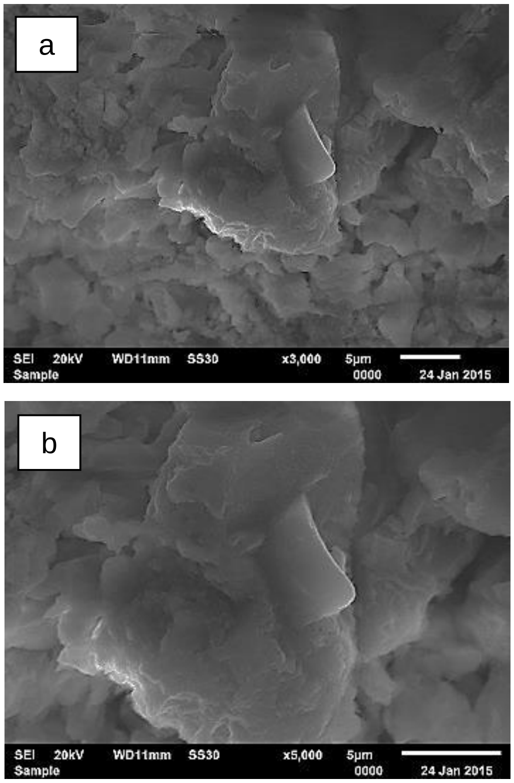


Figure 3 Scanning electron microscope (SEM) micrograph of raw Kapok sawdust, magnification: (a) 3000 x (b) 5000

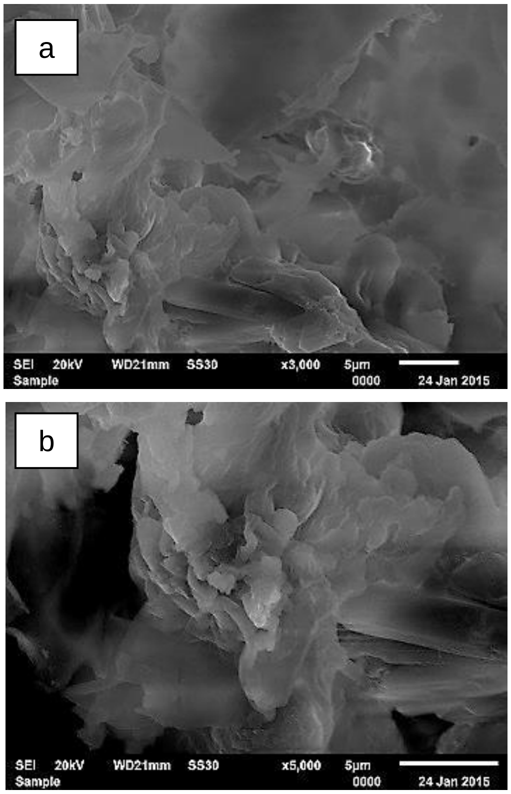


Figure 4 SEM micrograph of modified Kapok sawdust using NaOH 0.1 N, magnification: (a) 3000 x (b) 5000 x

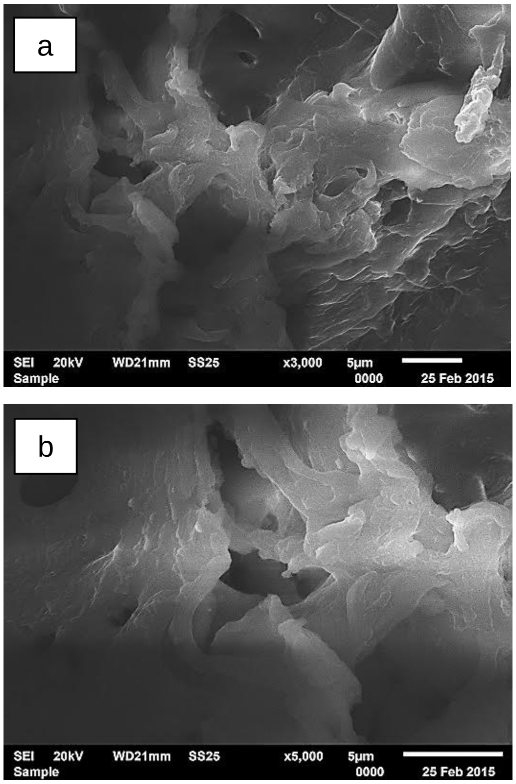


Figure 5 SEM micrograph of modified Kapok sawdust using NaOH 0.3 N, magnification: (a) 3000 x (b) 5000 x

The BET surface area of raw Kapok sawdust is 6.59 m^2/g while that of modified Kapok sawdust using NaOH 0.3 N is 7.42 m^2/g. Therefore, it can be concluded that sodium hydroxide treatment did not cause a significant increase in surface area. The average pore diameter of modified Kapok sawdust using NaOH 0.3 N determined by Barret-Joyner-Halenda (BJH) method is 130 Å.

3.2 Adsorption of Methyl Violet

The effect of initial pH of methyl violet solution was analysed over the range from 3 to 9. The result is shown in Figure 6. As seen there, the amount of dye adsorbed increase until pH 5 and then decrease with the increase of pH. The increase may be related to the formation of negative surface charges on the adsorbent which is influenced by the solution pH. In the acid medium, the positively charged species start dominating and surface tends to acquire positive charge while the adsorbate species are still positively charged. The increase of solution pH lead to the decrease of positively charged species and surface tends to acquire the negative charge. As the adsorbent surface is negatively charged, the increase of electrostatic attraction between positively charged of adsorbate species and negatively charged of adsorbent particles lead to the increase of methyl violet adsorption. The decrease in adsorption beyond pH 5 is due to the formation of soluble hydroxy complexes between the adsorbent and the dye [23]. Therefore, pH 5 was selected to be the optimum pH.

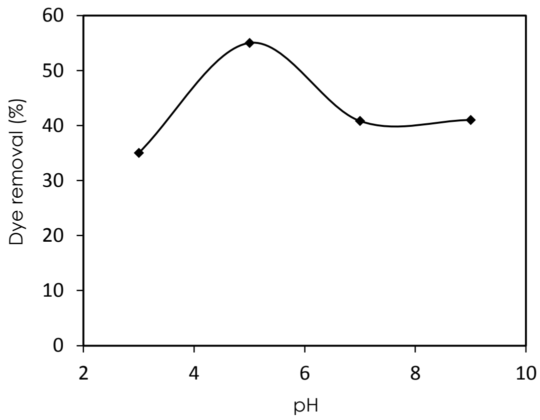


Figure 6 Effect of pH on the removal of methyl violet by modified Kapok sawdust using NaOH 0.3 N (condition: adsorbent dose = 0.5 g/50 mL solution, initial concentration = 2 mg/L, T = 26°C, contact time = 120 min)

The effect of contact time on the removal of methyl violet by modified Kapok sawdust using NaOH 0.3 N at initial concentration 60 mg L^{-1} is shown in Figure 7. The time curve describes that the removal of adsorbate is rapid but it gradually slows down until it reaches the equilibrium. This is due to the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Once equilibrium was attained, the percentage sorption of dye did not change with the further increase of time.

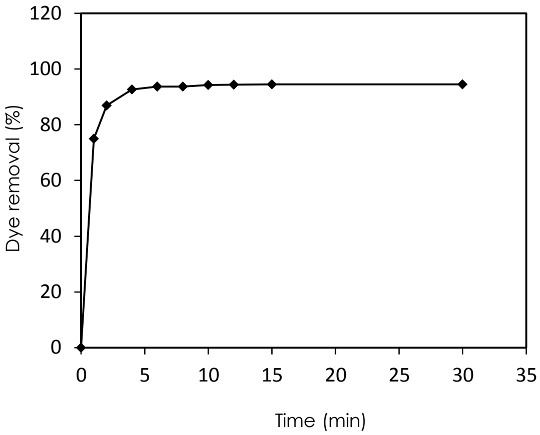


Figure 7 Effect of contact time on the removal of methyl violet by modified Kapok sawdust using NaOH 0.3 N (condition: adsorbent dose = 0.5 g/50 mL solution, initial concentration = 60 mg/L, T = 26°C, pH = 5)

Figure 8 illustrates that the percentage methyl violet adsorbed increases with the increase of methyl violet concentration and remain constant after equilibrium reached. The initial concentration provides an important driving force to overcome all mass transfer resistance of methyl violet between aqueous and solid phase. Hence, the higher initial concentration of methyl violet will enhance the adsorption process [20].

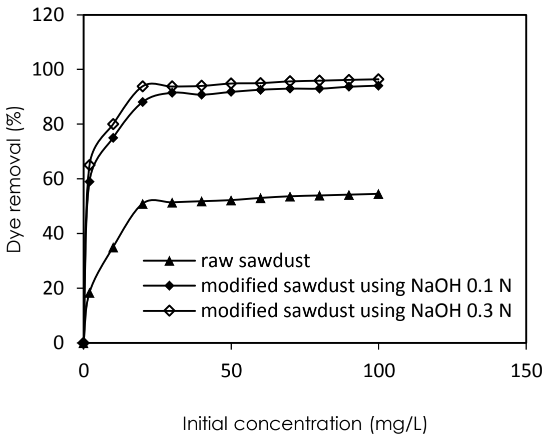


Figure 8 Effect of initial concentration on the removal of methyl violet by raw and modified Kapok sawdust (condition: adsorbent dose = 0.5 g/50 mL solution, pH = 5, T = 26°C, contact time = 120 min)

3.3 Adsorption Isotherm

The adsorption isotherm revealed the specific relation between the concentration of the adsorbate and its adsorption degree onto the adsorbent surface at a constant temperature. The analysis of the adsorption isotherm data by fitting them to different adsorption isotherm model that can be used for design purpose [20]. In the present study, the Langmuir, Freundlich, and Redlich-Peterson isotherm models were applied to describe the adsorption equilibrium. Figure 9 and 10 show the Langmuir ($1/q_e$ versus $1/C_e$) and Freundlich (log q_e versus log C_e) plot, respectively, for the removal of methyl violet by modified Kapok sawdust. The data was analysed by two correlation coefficients. The linear R^2 coefficients for linearised plots described in Figure 9 and 10 are 0.9729 for Langmuir isotherm and 0.9948 for Freundlich isotherm (Table 1).

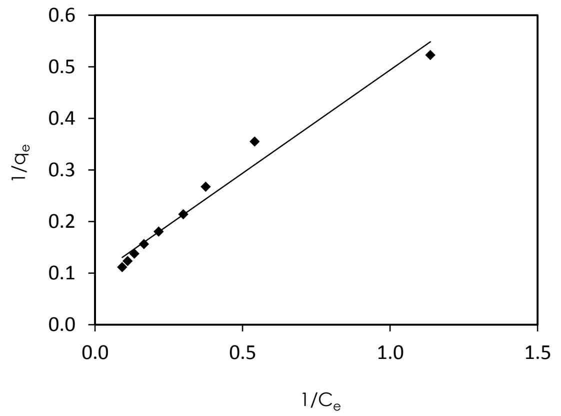


Figure 9 Langmuir isotherm plots for the removal of methyl violet by modified Kapok sawdust using NaOH 0.3 N (temperature = 26°C, contact time = 120 min)

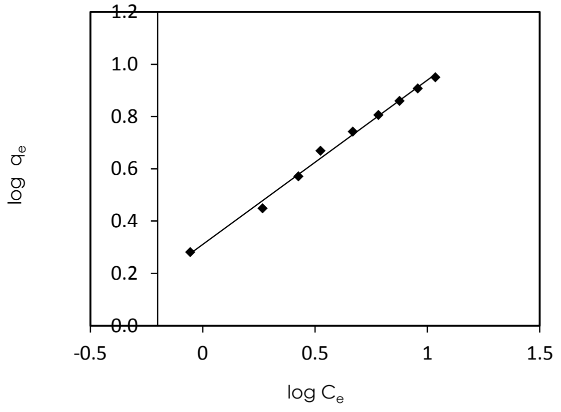


Figure 10 Freundlich isotherm plots for the removal of methyl violet by modified Kapok sawdust using NaOH 0.3 N (temperature = 26°C, contact time = 120 min)

The nonlinear R^2 values are based on the actual deviation between the experimental points and the theoretically predicted data points and are a better correlation of experimental data. The nonlinear correlation coefficients for the Langmuir and Freundlich isotherm analyses are presented in Table 1. In this case, the Freundlich equation represents a better fit of experimental data than the Langmuir equation due to the correlation coefficient for the Freundlich isotherm is closer to unity than Langmuir isotherm. The values of parameters for Langmuir and Freundlich isotherms are given in Table 1. A similar result has been reported for adsorption of basic dyes by modified bentonite clay [24]. The linearised from Redlich-Peterson isotherm plot is presented in Figure 11 while the Redlich-Peterson constants and the correlation coefficient, R^2 are listed in Table 1. The correlation coefficient is significantly lower than the Freundlich isotherm R^2 value so Freundlich isotherm is found to the best represent the equilibrium data for methyl violet-modified Kapok sawdust system.

Table 1 Isotherm parameters for the removal of methyl violet by modified Kapok sawdust using NaOH 0.3 N

Isotherm	**linear**	**nonlinear**
Langmuir		
K_L	0.2345	0.1216
q_{max}	10.6609	15.3293
R^2	0.9729	0.9984
Freundlich		
K_F	2.0446	2.0696
n	0.6284	0.6194
R^2	0.9948	0.9989
Redlich-Peterson		
K_R	8.8919	8.8884
a_R	3.3845	3.2764
β	0.4392	0.4559
R^2	0.9851	0.9985

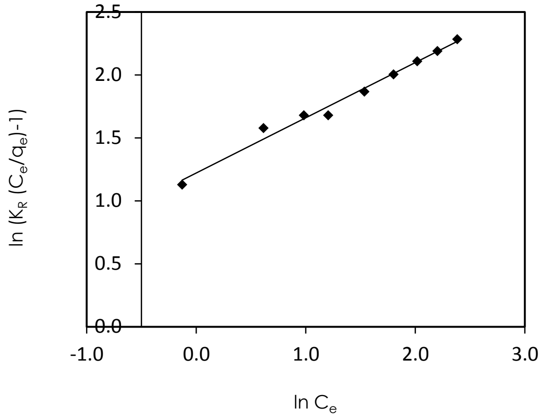


Figure 11 Redlich-Peterson isotherm plots for the removal of methyl violet by modified Kapok sawdust using NaOH 0.3 N (temperature = 26°C, contact time = 120 min)

Due to the inherent bias result from linearisation, two different error functions of nonlinear regression were employed to evaluate the isotherm constants including the sum of the square of the errors (SSE) and the sum of the absolute errors (SAE), as shown by Eq. (12) and (13), respectively.

$$\sum_{i=1}^{n}\left(q_{e,calc}-q_{e,meas}\right)_i^2 \tag{12}$$

$$\sum_{i=1}^{n}\left|q_{e,calc}-q_{e,meas}\right|_i \tag{13}$$

The values of two error measurements were presented in Table 2. These values show that the Freundlich isotherm best fits for methyl violet-modified Kapok sawdust system. This is same as predicted by R^2 (nonlinear) analysis. Figure 12 depicts the comparison of the experimental and predicted amount of methyl violet adsorbed on modified Kapok sawdust for all the isotherm models studied.

Table 2 Values of two different error analyses of isotherm models of methyl violet on modified Kapok sawdust

Isotherm	SSE	SAE
Langmuir	0.3041	1.1414
Freundlich	0.1553	0.8310
Redlich-Peterson	0.1961	1.0034

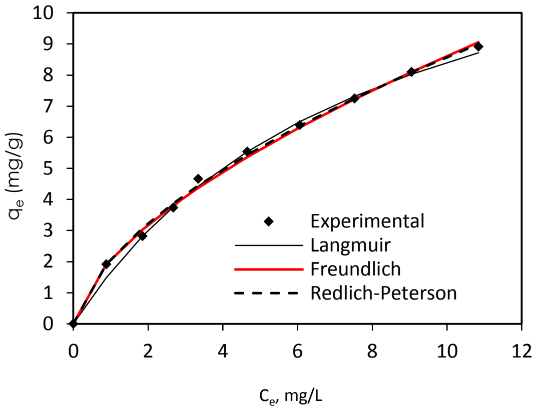


Figure 12 Equilibrium isotherms for methyl violet adsorption on modified Kapok sawdust using NaOH 0.3 N

4.0 CONCLUSION

The present study shows that modified kapok sawdust is an effective adsorbent for the removal of methyl violet from aqueous solution. The effective pH for methyl violet removal was 5. A fast removal of methyl violet was noticed as more than 90% of methyl violet was removed in 30 min. An error analysis showed that Freundlich isotherm best fits equilibrium data for methyl violet-modified Kapok sawdust system.

Acknowledgement

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