

CHEMICALLY MODIFIED KAPOK SAWDUST FOR ADSORPTION OF METHYL VIOLET DYE FROM AQUEOUS SOLUTION

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Abstract. The potential of chemically modified Kapok sawdust for methyl violet adsorption was investigated in a batch adsorption process. Various physicochemical parameters such as pH, contact time and initial dye concentration were studied. The adsorbent was characterized with Fourier transform infrared spectrophotometer, scanning electron microscope and Brunauer, Emmett and Teller (BET) analysis. The optimum conditions for methyl violet adsorption were pH 5 and contact time 30 min. Langmuir, Freundlich and Redlich-Peterson isotherm model were used to analyze the equilibrium data. The experimental data fitted well with the Redlich-Peterson model, with the value of constants are 41.001 L g^{-1} for K_R , $0.523 \text{ L}^{0.799} \text{ mg}^{-0.799}$ for a_R and 0.799 for β .

Keywords: kapok sawdust, methyl violet, dye, adsorption

INTRODUCTION

The release of synthetic dyes from the dyestuff manufacturing, textile, leather and paper industries into the environment is an important sources of water pollution and can be harmful to aquatic life. Dyes impede light penetration, retard photosynthetic activity, inhibit the growth of biota and have a tendency to chelate metal ions . The removal of color synthetic organic dyestuff from waste effluents becomes environmentally important since most dyes are stable to light and heat, high in organic content, have a complex aromatic structures and not biodegradable .

Numerous physicochemical and biological methods have been used to decolorize dyes in wastewater, often in combinations as one single treatment may not be sufficient to remove certain classes of synthetic dyes . Adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater. A number of organic and inorganic adsorbents have been used to remove it, including various types of activated carbon - and polymer . 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 , - , cashew nut shell , peanut husk and rambutan peel . Wood powder

does not noticeably swell in water and does not decompose upon prolonged contact with water. It can be used as a low cost adsorbent due to its lignocellulosic composition. It contains abundant lignin, cellulose, hemicellulose and some functional groups such as carboxyl, hydroxyl, phenolic and amide groups in its structure, which make the adsorption processes possible .

Generally, the sorption capacities of crude agricultural by-products are low. To improve the adsorption capacity, chemical modification has been used. Argun et al. modified oak sawdust with HCl and obtained adsorbents with good performance to adsorb Cu, Ni and Cr . Kapok fiber has been modified with diethylenetriamine pentaacetic acid after hydrophilicity treatment and used to adsorb Pb^{2+} , Cd^{2+} and Cu^{2+} from aqueous solution . Wheat straw has been reacted with citric acid and the adsorption properties of copper ion and methylene blue were investigated .

The objective of this work was to modify kapok sawdust with a strong alkaline solution(NaOH) to remove pectin, lignin and hemicelluloses and liberate new adsorption sites on the sawdust surface .Modified kapok sawdust was further used to adsorb methyl violet dye in aqueous solution. The influences of pH, adsorption time and initial concentration of methyl violet in the adsorption behaviour were investigated.

METHODS

Sample Preparation and Characterization.The sawdust of kapok was sieved and the fractions with particle sizes less than 0.149 mm was used for experiments.Further, it was washed with deionized water and dried. Kapok sawdust was further treated with sodium hydroxidesolution (concentration 0.1 and 0.3N) 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 were obtained by SEM(JEOL, Japan).

Batch Adsorption Experiment.Approximately 0.5 g of raw or modified kapok sawdust was put into an erlenmeyer filled 50 mL of methyl violet solution (concentration of 60 $mg.L^{-1}$). Structure of this dye is shown in Fig. 1. The adsorption was carried out at pH 5. The erlenmeyer contained the mixture was placed in a waterbath at 26°C and shaken mechanically for 1 to 30 minutes. Subsequently, suspended solid was filtered and the filtrate was analyzed to determine methyl violet concentration using a UV-Visible spectrophotometerat $\lambda_{max} = 581$ nm.To investigate the effect of pH on adsorption, 0.5 g of original or modifiedkapok sawdust was added to an erlenmeyer filled 50 mL of methyl violet solution (concentration of 2 $mg.L^{-1}$). The

pH was adjusted with base/acid to an appropriate pH (pH range of 3, 5, 7, 9). The erlenmeyer filled the mixture was placed in a waterbath at 26°C and shaken mechanically for 180 minutes. The sawdust was separated from the solution and the filtrate was analyzed to determine methyl violet concentration using a UV-Visible spectrophotometer at $\lambda_{\max} = 581 \text{ nm}$. The percentage dye removal were calculated using equation (1) as follows:

$$\text{dye removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 (mg.L⁻¹) is the initial concentration of methyl violet and C_e (mg.L⁻¹) is the concentration of methyl violet at equilibrium .

Isotherm Adsorption. To evaluate the adsorption capacities of kapok sawdust, batch adsorption test were conducted for the adsorption of methyl violet dye. The initial concentrations of methyl violet were selected in the range of 0 to 1000 mg.L⁻¹. The amount of dye adsorbed per unit weight of adsorbent at equilibrium (q_e , mg.g⁻¹) were calculated using equation (2) as follows :

$$q_e = \frac{(C_0 - C_e)v}{m} \quad (2)$$

where v (L) is the volume of methyl violet solution and m (g) is the dry weight of the adsorbents. The experimental isotherm data were interpreted by the non linear forms of Langmuir, Freundlich and Redlich-Peterson isotherm models. 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 homogenous adsorbent . This model can be expressed as:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (3)$$

where C_e (mg L⁻¹) is the equilibrium concentration of methyl violet on the solution, K_L (L mg⁻¹) is the Langmuir constants related to the affinity of the binding sites and energy of adsorption, and q_{\max} (mg g⁻¹) is the maximum adsorption capacity related to monolayer coverage. The higher the K_L value, the higher the affinity of the binding sites. 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 . The Freundlich model can be

expressed as:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (4)$$

where $K_F(\text{mg g}^{-1})(\text{mg L}^{-1})^{-1/n}$ is the Freundlich constant related to the adsorption capacity and n is an indicator of adsorption intensity. Higher value for K_F , indicates higher affinity for adsorbate and the value of the empirical parameter n , indicates favorable adsorption. The Redlich-Peterson model can be represented as:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (5)$$

where $K_R (\text{L g}^{-1})$, and $a_R (\text{L mg}^{-1})^\beta$ are the Redlich-Peterson isotherm constants and β is the Redlich-Peterson isotherm exponent, which lies between 0 and 1. Redlich-peterson model is a compromise between Langmuir and Freundlich models. For $\beta=1$, Eq. (5) converts to the Langmuir form. The value of q_{max} , K_L , $K_F n$, K_R , β and a_R can be determined by trial and error method which gives a minimum Sum of Square Error (SSE).

RESULTS AND DISCUSSION

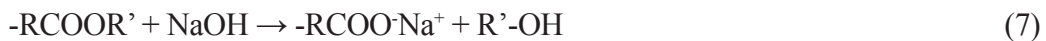
To confirm the presence of functional groups in the adsorbent which are capable to adsorb dye ions, FT-IR analysis was conducted. The FT-IR spectra of raw and modified kapok sawdust are shown in Figure 2. For raw sawdust, it can be seen that there is a broad and strong band from 3000 to 3600 cm^{-1} , which indicates the presence of carboxylic acid (RCOOH), alcohol (ROH) and amino (RNH_2) groups. This is consistent with the peaks at 1037 and 1350 cm^{-1} due to alcoholic C-O and C-N bending vibration. The broad absorption peaks at 3360 cm^{-1} indicate the existence of bonded hydroxyl groups on the surface of sawdust. This band is associated with the OH stretching of phenolic group of cellulose and lignin. The peak 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. 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. 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. The peak at 1422 cm^{-1} is attributed to the stretch vibration of C-O associated with the carboxylic group. The band at 1400-1600 cm^{-1} are assigned to aromatic skeletal vibrations. The strong peak observed at 1037 cm^{-1} might represent the C-O-C of an ether group. The peak located at 595 cm^{-1} is assigned to the bending modes of C-H group. After reaction with sodium hydroxide, the position and intensity of some peaks being changed. Peak indicating the existence of hydroxy 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. The reaction that took place can be represented as follows :

carboxylic acid :



ester :



SEM micrograph of raw and modified kapok sawdust are shown in Figure 3. 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. 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 0.3N NaOH concentration, as can be seen in Figure 3e and 3f. 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.

The effect of initial pH of methyl violet solution was analyzed over the range from 3 to 9. The results is shown in Figure 4. 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 negative charge. As the adsorbent surface is negatively charged, the increase of electrostatic attraction between positively charged adsorbate species and negatively charged 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. Therefore, pH 5 was selected to be the optimum pH for further studies.

The effect of contact time on the removal of methyl violet by modified kapok sawdust using NaOH 3 N, at initial concentration 60 mg.L^{-1} is shown in Figure 5. 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 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 further increase of

time.

Figure 6 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, higher initial concentration of methyl violet will enhance the adsorption process .

The adsorption isotherm revealed the specific relation between the concentration of the adsorbate and its adsorption degree onto 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 . In the present study, the Langmuir, Freundlich and Redlich-Peterson isotherm models were applied to describe the adsorption equilibrium. Comparison between the value of q_e for Langmuir, Freundlich and Redlich-Peterson models with experimental data is described in Figure 7, while the value of Langmuir, Freundlich and Redlich Peterson constants are given in Table 1. Table 1 also summarizes the applicability of the isotherm was judge by the value of average deviation of q_e models toward experimental data. Data in Table 1 shows that Redlich-Peterson model is in agreement with experimental data because it has the lowest average deviation. The Redlich-Peterson isotherm exponent, β , calculated as 0.799, is indicative of a favourable adsorption of methyl violet onto modified kapok sawdust.

Table 1 Isotherm constants and average deviation of q_e models toward q_e data

Constants	Value	Average deviation
Langmuir		12.563
K_L	0.349	
q_{max}	125.000	
Freundlich		35.542
K_F	15.707	
n	1.004	
Redlich-Peterson		7.950
K_R	41.069	
a_R	0.523	
g	0.799	

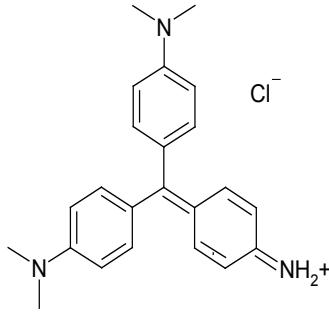


Figure 1 Structure of methyl violet dye

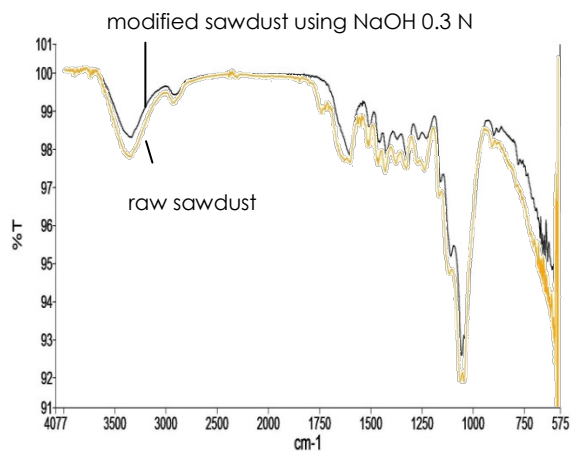
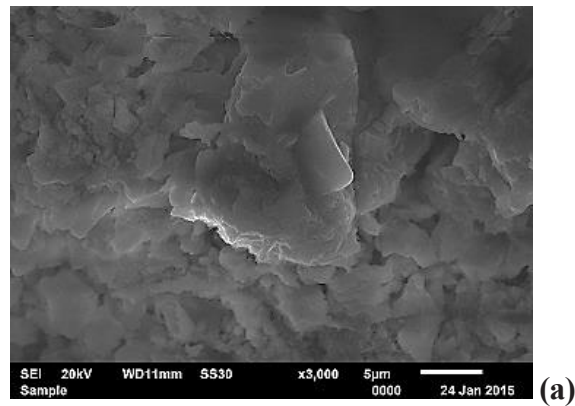


Figure 2 FTIR spectra of raw and modified kapok sawdust



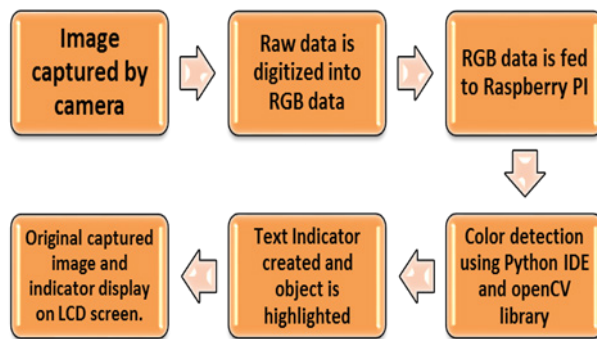
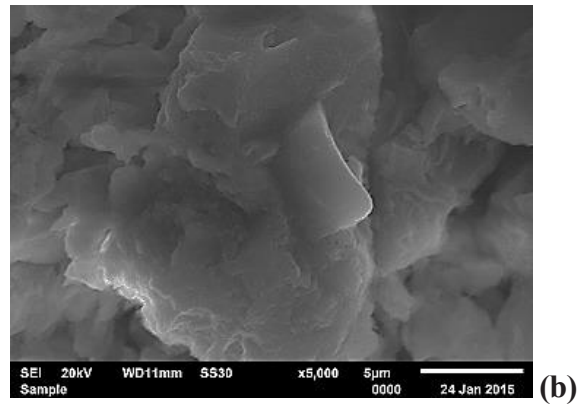
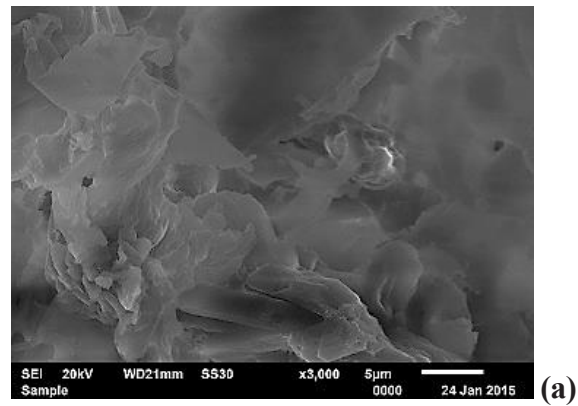


Figure 3 SEM micrograph of raw kapok sawdust, magnification: (a) 3000 x (b) 5000 x



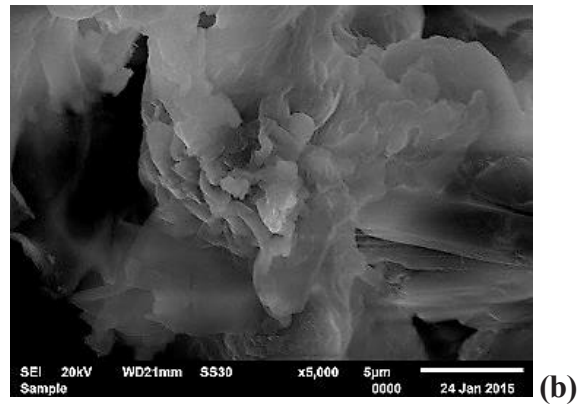


Figure 4 SEM micrograph of modified kapok sawdust using NaOH 0.1N, magnification: (a) 3000 x (b) 5000 x

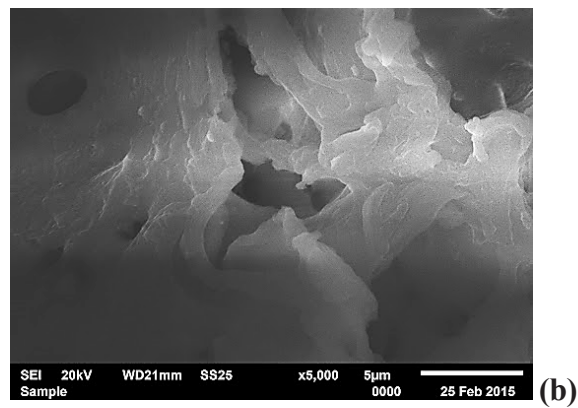
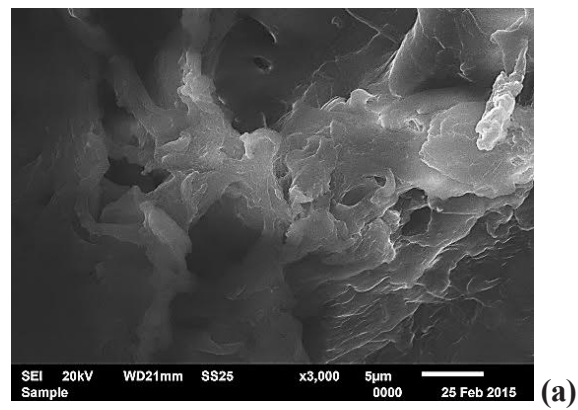


Figure 5 SEM micrograph of modified kapok sawdust using NaOH 0.3 N, magnification: (a) 3000 x (b) 5000 x

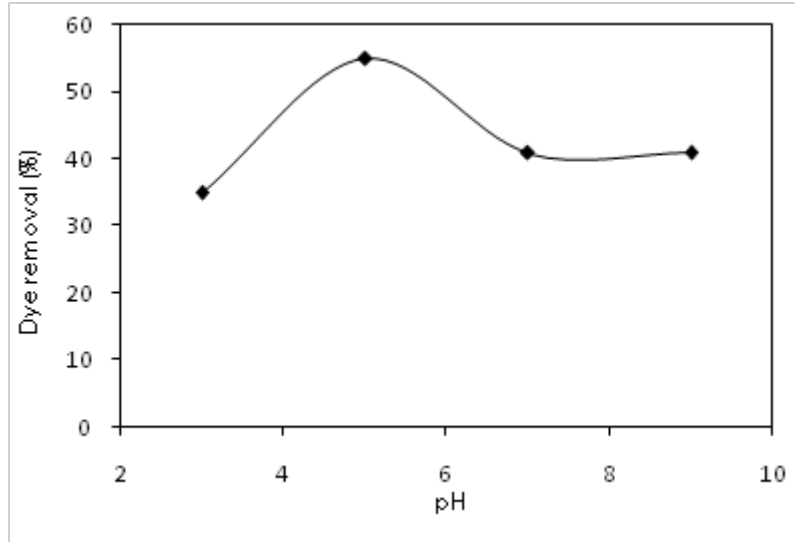


Figure 6 Effect of pH on the removal of methyl violet by modified kapok sawdust using NaOH 0.3 N

(condition: adsorbent dose = 0.5 g/50 mL solution, initial concentration = 2 mgL⁻¹, T = 26°C, contact time = 120 min)

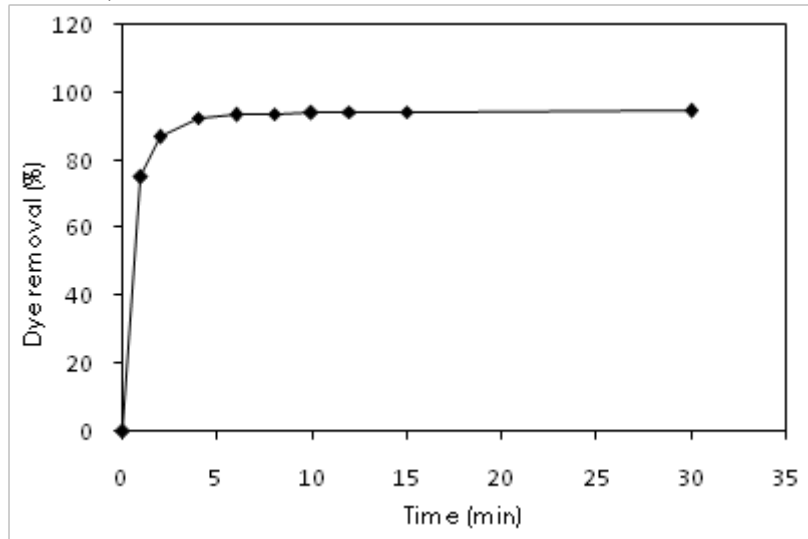


Figure 7 Effect of contact time on the removal of methyl violet by modified kapok sawdust using NaOH 3 N (condition: adsorbent dose = 0.5 g/50 mL solution, initial concentration = 60 mgL⁻¹, T = 26°C, pH = 5)

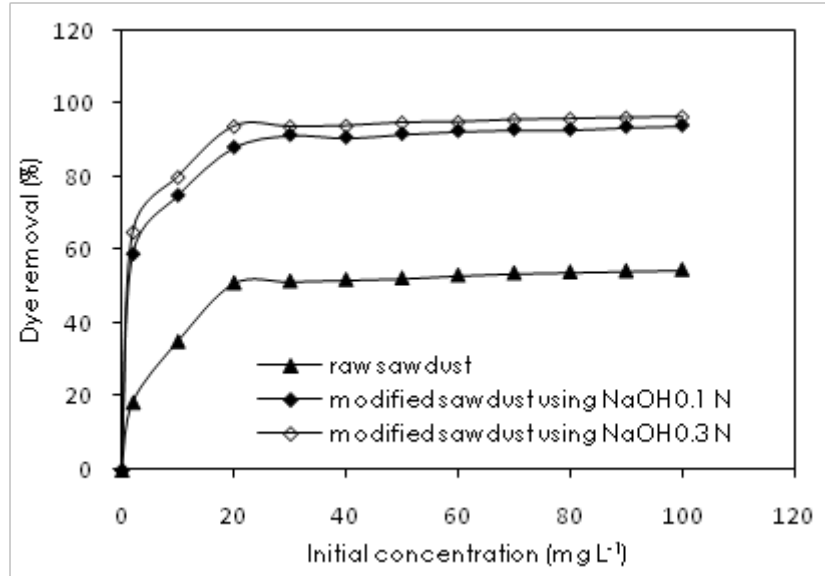


Figure 8 Effect of initial concentration on the removal of methyl violet by raw and modified kapok sawdust (condition: adsorbent dose = 0.5 g/50 mL solution, pH = 5, T = 26°C, contact time = 120 min)

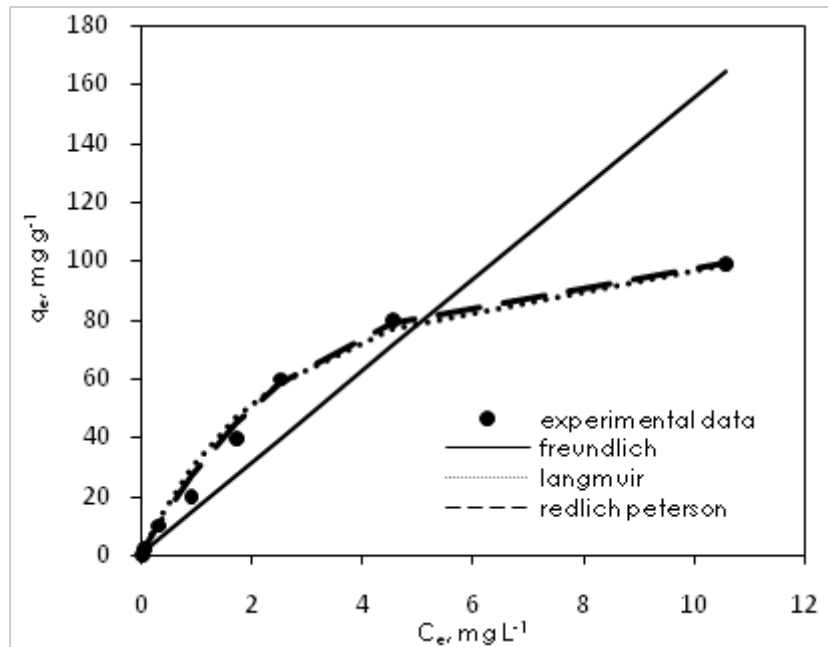


Figure 8 The non linear fitted curves with different equilibrium models

CONCLUSION

In this study, adsorption of methyl violet on raw and modified kapok sawdust using NaOH

has been investigated. The data obtained through this work support the statement that the sawdust is an effective low cost biosorbent for the removal of methyl violet in aqueous solution. The sorption of methyl violet is heavily dependent on pH, contact time and concentration of methyl violet. Maximum removal of methyl violet on sawdust occur at pH 5. The adsorption capacity of modified sawdust is greater than that of raw sawdust. The equilibrium adsorption data is seen in accordance with Redlich-Peterson isotherm model.

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