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Equilibrium and Kinetics of Adsorption of Methyl Violet from Aqueous Solutions Using Modified *Ceiba pentandra* Sawdust

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Modified *Ceiba pentandra* sawdust has been investigated as an adsorbent for the removal of methyl violet from aqueous solutions. Batch experiments were carried out to investigate the effect of pH, contact time and methyl violet concentration on sorption efficiency. The favourable pH for maximum methyl violet adsorption was 5. For the investigated methyl violet concentration (0-100 mg/L), maximum adsorption rates were achieved almost in 10-20 min of contact. The experimental data fitted well with the Freundlich isotherm while the kinetics of methyl violet adsorption was well described by the pseudo-second order kinetic model.

Keywords: *Ceiba pentandra*, Adsorption, Methyl violet, Equilibrium, Kinetics.

INTRODUCTION

Since the dyeing technique was invented, colour effluents are considered as the important source of water pollution. The discharge of coloured wastes into receiving streams not only interferes with the transmission of sunlight into streams and reduces photosynthetic activity [1] but also increases damage to natural ecosystems, because some of these dyes may be highly toxic, potentially carcinogenic, mutagenic and allergenic on exposed organisms [2]. Wastewater offer considerable resistance for their biodegradation due to the presence of these heat and light stable dyes [1].

Dyes can be classified as anionic, cationic and non-ionic [1]. Methyl violet, a typical cationic dye has been widely applied in textile, ink, paint, leather and paper industries. Although not strongly hazardous, methyl violet causes some harmful effect including heart beat increase, vomiting, shock, jaundice cyanosis, quadriplegia and tissue necrosis in humans because as a cationic dye, methyl violet can easily interact with negatively charged of cells membrane surfaces and can enter into cells and concentrate in the cytoplasm [2]. Therefore, in recent years, colour removal from industrial wastewater by adsorption techniques has become prominent. The adsorption process is a favourable treatment because of the chemical and biological stability of dyes to the conventional wastewater treatment methods [3]. As an alternative way to reduce costs, many agricultural wastes and by-products of wood and forest industries of cellulose origin have been utilized, including mansonia wood sawdust [4] and pinus radiata [5].

Ceiba pentandra belongs to the family of Bombaceae and grow in Asia including Indonesia, Africa and South America. *Ceiba pentandra* wood is variable in colours from white to light brown [6]. The major components of the wood are cellulose 40-55 %, lignin 15-35 % and hemicelluloses 20-35 %, called as lignocellulosic materials. Cellulose is the most abundant polysaccharide. It is a high molecular weight stereoregular linear polymer of repeating α-D-glucopyranose units. The hemicelluloses of woods are generally considered to be consist of several types of amorphous polymeric carbohydrates that occur through the woody structure of plants [6]. Lignin, as the most abundant natural aromatic polymer, has a highly branched three-dimensional phenolic structure including three main phenylpropane units, namely *p*-coumaril, coniferyl and sinapyl [7]. It makes the adsorption processes possible.

The adsorption capacity of *Ceiba pentandra* can be enhanced by modifying the physico-chemical properties of its surface. The modification has been carried out using various reagents such as diethylenetriamine pentaacetic acid [8] and sodium hydroxide [9]. Sodium hydroxide is a well-known fibre-swelling agent of woods and agricultural residues. It acts primarily on the hemicellulose fraction and brings about the swelling of the cell wall. A mild alkaline treatment produced chemical changes in the wood resulting in acid groups release and acetyl groups elimination [9]. The degree of change is dependent on the time, temperature and alkali concentration [9].

The objective of the present study is to investigate the feasibility of *Ceiba pentandra* modified with sodium hydroxide as an adsorbent for the removal of methyl violet dye in aqueous solutions. Batch experiments are carried out for the kinetic studies. The influence of various contributing parameters such as pH, contact time and initial methyl violet concentration are investigated. Three adsorption isotherm models including Langmuir, Freundlich and Redlich-Peterson are used to study the fit of the experimental equilibrium data obtained in the study and several kinetic models including pseudo first-order and pseudo-second order are used to evaluate the mechanism of adsorption.

EXPERIMENTAL

Synthesis of adsorbent: Sawdust of *Ceiba pentandra* was sieved through a 0.149 mm sieve, washed repeatedly with distilled water to remove soluble impurities and dried at 110 °C to constant weight. The dried sawdust was further reacted with 0.1 and 0.3 N sodium hydroxide solution at 26 °C for 1 h. The ratio of sawdust weight to sodium hydroxide volume was 30 g of sawdust to 500 mL of sodium hydroxide. The sawdust was further filtered, washed with distilled water until pH of the filtrate was around 7 and dried at 110 °C to constant weight.

Batch experiments: Batch adsorption experiments were carried out at constant temperature (26 ± 1 °C) by adding 0.5 g of raw or modified *Ceiba pentandra* sawdust to 100 mL Erlenmeyer flask containing 50 mL aqueous solutions with varying initial methyl violet concentration (1-100 mg/L). pH values of sawdust-methyl violet aqueous solution were adjusted to desired levels (pH 3-9) using 0.1 N HCl or 0.1 N NaOH. The Erlenmeyer flask was shaken at 115 rpm for varying duration (0-120 min) to study the influence of contact time between adsorbent and methyl violet on the adsorption efficiency. After specified contact times, suspended solids were filtered through Whatman paper No. 5 and the filtrates were analyzed for residual methyl violet using a UV-visible spectrophotometer at λ_{max} = 581 nm for adsorption efficiency assessment and isotherm analysis. Adsorption efficiency was expressed as a percentage of methyl violet adsorbed compared to initial methyl violet concentration as given by eqn. 1, whereas adsorption capacity was expressed as the amount of methyl violet adsorbed per mass unit of sawdust as given by eqn. 2 [10]:

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

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

where C_i and C_e are the initial and residual concentration of methyl violet in mg/L, q_e is the adsorption capacity in mg/g, V is the volume of methyl violet solution (L) and m is the adsorbent mass in g.

Adsorption isotherm models: Adsorption isotherms are important to describe the adsorption mechanism of solute on the adsorbent surface [10]. In this study, the equilibrium data obtained for methyl violet removal using raw and modified *Ceiba pentandra* sawdust were tested with three isotherm models, including Langmuir, Freundlich and Redlich-Peterson, to reveal the best fitting isotherm.

The Langmuir isotherm is based on the fact that the monolayers adsorption occurs in homogeneous sites on the adsorbent surface. Langmuir isotherm is represented in terms of fractional coverage (θ) as given by eqn. 3. The amount of dye adsorbed (q_e) given by eqn. 4 [10].

$$\theta = \frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (3)$$

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

where K_L is the adsorption equilibrium constant in L/mg related to the energy of adsorption, q_m 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 minimization procedure was used to solve eqn. 4 by maximizing the correlation coefficient between the q_e predicted from eqn. 4 and the experimental data. The solver add-in function of the Microsoft excel was used to determine the value of K_L and q_m by minimizing the distance between the experimental data points and the theoretical model predictions.

The Freundlich isotherm is described by eqn. 5 where K_F ($mg^{1-1/n} L^{1/n} g^{-1}$) and n_F are the Freundlich equilibrium constants which can be determined by minimizing the distance between q_e predicted from eqn. 5 and experimental data using the solver add-in function of Microsoft excel.

$$q_e = K_F C_e^{n_F} \quad (5)$$

The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It 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 [1]. The Redlich-Peterson isotherm can be expressed as:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \quad (6)$$

where K_R is Redlich-Peterson isotherm constant (L/g), a_R (L/mg) is Redlich-Peterson isotherm constants and β is the exponent which lies between 1 and 0, where β = 1 it becomes a Langmuir equation as given by eqn. 7.

$$q_e = \frac{K_R C_e}{1 + a_R C_e} \quad (7)$$

Eqn. 6 becomes eqn. 8 where β = 0, *i.e.* Henry's law equation.

$$q_e = \frac{K_R C_e}{1 + a_R} \quad (8)$$

A minimization procedure was used to solve eqn. 6 by maximizing the correlation coefficient between the q_e predicted from eqn. 6 and the experimental data. The value of K_R, a_R and β were determined using the solver add-in function of the

Microsoft excel by minimizing the distance between the experimental data points and the theoretical model predictions.

Adsorption kinetic models: In order to clarify the adsorption kinetics of methyl violet onto modified *Ceiba pentandra* sawdust, pseudo-first order and pseudo second order kinetic models were applied to the experimental data.The pseudo-first order equation by Lagergren is given as:

$$\frac{d_{q_t}}{dt} = k_f(q_e - q_t) \quad (9)$$

where q_e and q_t are amounts of methyl violet adsorbed at equilibrium (mg/g) at time t (mg/g), respectively, k_f is the rate constant of pseudo-first order model (min^{-1}) and t is time (min). After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$, the equation becomes [11]:

$$\ln(q_e - q_t) = \ln q_e - k_f t \quad (10)$$

The plots of $\ln(q_e - q_t)$ *versus* t should yield straight line if pseudo-first order model is obeyed by the adsorption kinetic. The constants were obtained from the slope and intercept. The pseudo-second order equation is expressed as:

$$\frac{d_{q_t}}{dt} = k_s(q_e - q_t)^2 \quad (11)$$

where k_s is the rate constant of pseudo-second order model (g/mg min). After integrating eqn. 11 for boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the following form of the equation can be obtained:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (12)$$

The plots of t/q_t *versus* t should yield straight line if pseudo-second order model is obeyed by the adsorption kinetic. The constants were obtained from the slope and intercept.

Desorption study: In order to clarify the mechanism of adsorption, desorption studies were performed. Initially, batch equilibrium experiments were carried out. The dye-loaded adsorbent was filtered using filter paper (Whatman No. 5) and dried. Furthermore, 0.5 g of dye-loaded adsorbents was added into 50 mL of distilled water and agitated for 180 min at 115 rpm. After specified contact times, suspended solids was filtered through Whatman paper No.5 and the filtrate was analyzed for methyl violet using a UV-visible spectrophotometer at $\lambda_{max} = 581$ nm.

RESULTS AND DISCUSSION

Factors affecting methyl violet adsorbed on sawdust

Effect of sodium hydroxide concentration toward methyl violet adsorbed: The amount of methyl violet adsorbed by sodium hydroxide modified sawdust is higher than that of raw sawdust (Fig. 1). It can be explained by the fact that adsorption occurs mainly by means of ion-ion interaction operating between methyl violet having NH_2^+ as a functional group and the anionic groups within the sawdust. Cellulose behaves as a very weak acid and will ionize according to the normal basic dissociation equation to generate cellulosate ions, which are many times more reactive than cellulose itself [12]:

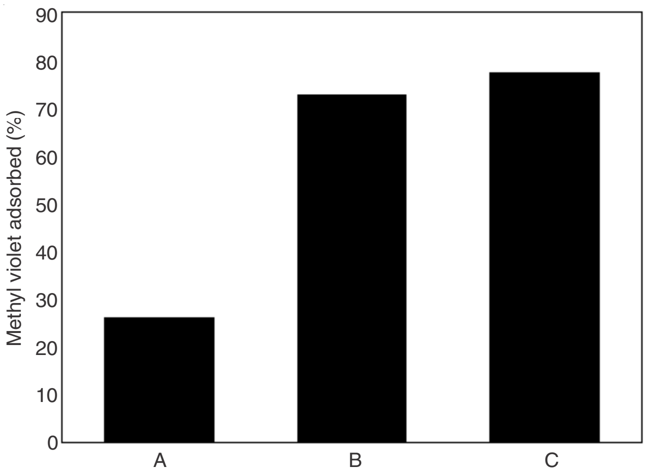

Fig. 1. Effect of sodium hydroxide treatment on *Ceiba pentandra* sawdust toward methyl violet adsorbed (A = raw sawdust, B = modified sawdust with 0.1 N NaOH, C = modified sawdust with 0.3 N sodium hydroxide)

$$\text{Cell-OH} + OH^- \rightleftharpoons \text{Cell-O}^- + H_2O \quad (13)$$

$$\text{Cell-O}^- \text{ — Dye-}NH_2^+ \text{ (electrostatic attraction)} \quad (14)$$

The presence of the carboxylic group (-COO-) in the hemicelluloses structure may have enhanced the affinity of *Ceiba pentandra* sawdust to methyl violet molecules that are electron deficient (*i.e.* positively polarized), thus the adsorption process can be explained by electrostatic attraction between two counter ions [12].

$$\text{Hemicell-COO}^- + \text{dye-}NH_2^+ \rightarrow \text{hemicell-COO-}NH_2 \quad (15)$$

Effect of initial pH of suspension toward methyl violet adsorbed: In previous studies, pH has been referred as an important influencing factor for dyes adsorption [13,14]. Solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent. In a certain pH range (3-9), most dyes adsorption increases with increasing pH up to a certain pH value and then decreases with further increasing pH. Therefore, there is a favourable pH range for the adsorption of every dye on a specific adsorbent. In this study, the effect of pH on methyl violet adsorption by 0.3 N sodium hydroxide modified *Ceiba pentandra* sawdust is investigated by varying the pH of methyl violet solution-sawdust suspension from 3 to 9. The results are described in Fig. 2. The amount of methyl violet 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 pH. In the acid medium, the positively charged species start dominating and sawdust 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 sawdust surface tends to acquire the negative charge. The increase of electrostatic attraction between positively charged of adsorbate species and negatively charged of sawdust lead to the increase of the adsorption of methyl violet dye. The decrease in adsorption beyond pH 5 is due to the formation of soluble hydroxy complexes between the adsorbent and the dye [15].

Effect of contact time toward methyl violet adsorbed: The effect of contact time toward the amount of methyl violet

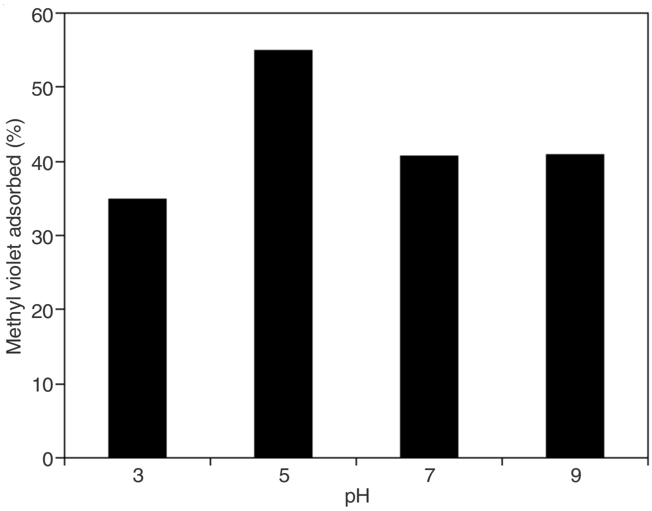

Fig. 2. Effect of pH toward methyl violet adsorbed by modified *Ceiba pentandra* sawdust using NaOH 0.3 N (condition: adsorbent dose = 0.5 g/50 mL solution, initial concentration of 2 mg/L, temperature of 26 °C, time of 120 min)

adsorbed by 0.3 N sodium hydroxide modified *Ceiba pentandra* sawdust is investigated to study the rate of methyl violet removal (Fig. 3). The removal of methyl violet is rapid but it gradually slows down until it reaches the equilibrium. This is due to 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 further increase of time.

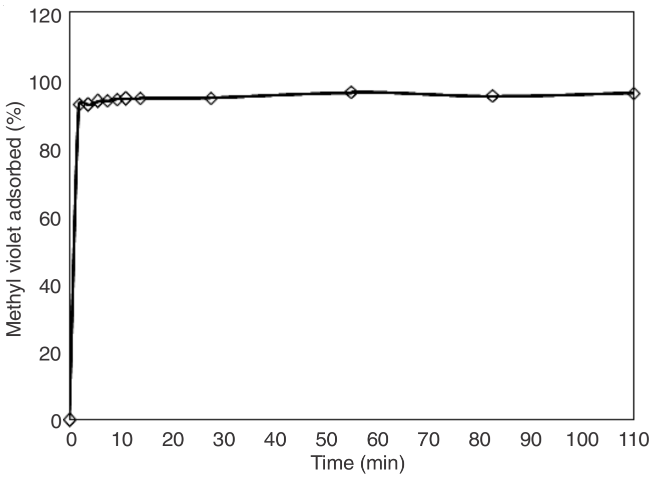

Fig. 3. Effect of contact time on the removal of methyl violet by modified *Ceiba pentandra* sawdust using NaOH 0.3 N (condition: adsorbent dose = 0.5 g/50 mL solution, initial concentration = 60 mg/L, T = 26 °C, pH = 5)

Effect of initial methyl violet concentration on sorption efficiency: The effect of initial methyl violet concentration (1-100 mg/L) was investigated at pH of 5 in the presence of 0.5 mg/50 mL sawdust and recorded outcomes are illustrated in Fig. 4. The percentage methyl violet adsorbed increases with the increase of methyl violet concentration and remain constant after equilibrium reached. The initial concentration

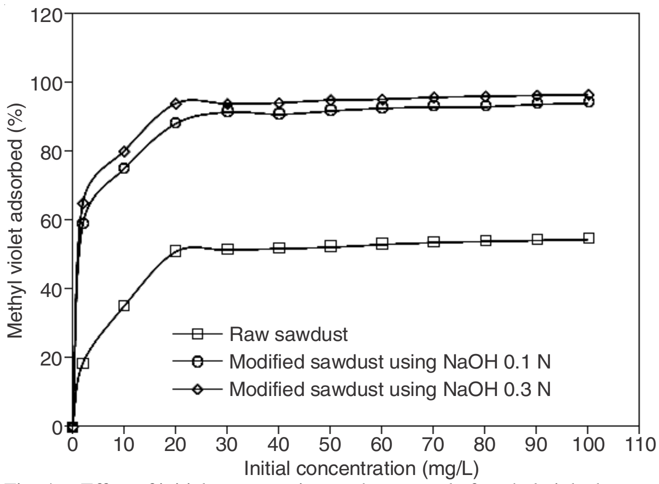

Fig. 4. Effect of initial concentration on the removal of methyl violet by raw and modified *Ceiba pentandra* sawdust (condition: adsorbent dose = 0.5 g/50 mL solution, pH = 5, T = 26 °C, contact time = 120 min)

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.

Adsorption isotherm study: As previously mentioned, adsorption isotherm assist in describing the adsorption mechanism of methyl violet dye on the surface of modified *Ceiba pentandra* sawdust. Adsorption isotherms are characterized by specific constants that express the surface properties and affinity of adsorbent towards the adsorbed pollutant [10]. In this study, three equilibrium models are analyzed including Langmuir, Freundlich and Redlich-Peterson. The applicability of the isotherms was judged of the value of the correlation coefficients (Table-1). Table-1 shows that Freundlich model is seen in accordance with experimental data due to the correlation coefficient for the Freundlich isotherm is closer to unity than that of Langmuir and Redlich-Peterson isotherms. It 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. The value of Langmuir, Freundlich and Redlich-Peterson constants are given in Table-2 while the comparison of the experimental and predicted methyl violet adsorbed for all isotherm models studied is described in Fig. 5.

TABLE-1
CORRELATION COEFFICIENTS (R^2) OF LANGMUIR, FREUNDLICH AND REDLICH-PETERSON ISOTHERM MODELS

Models	R^2
Langmuir	0.9984
Freundlich	0.9989
Redlich-Peterson	0.9985

Adsorption kinetics study: The experimental data were tested with pseudo-first order and pseudo-second order kinetic models in order to understand the kinetics of methyl violet removal using modified *Ceiba pentandra* sawdust as an adsorbent.

Pseudo-first order model: Methyl violet adsorption kinetics onto *Ceiba pentandra* sawdust was tested with the pseudo-first order kinetic model by plotting ln ($q_e - q_t$) *versus* t, as can be seen in Fig. 6. From this plot, the first order constant, k_f, the

TABLE-2
ISOTHERM CONSTANS FOR METHYL VIOLET ADSORPTION ONTO MODIFIED *Ceiba pentandra* SAWDUST USING 0.3 N NaOH SOLUTION

Constants	Value
Langmuir model	
K_L	0.1216
q_{max}	15.3293
Freundlich model	
K_F	2.0696
n_F	0.6194
Redlich-Peterson model	
K_R	8.8884
a_R	3.2764
β	0.4559

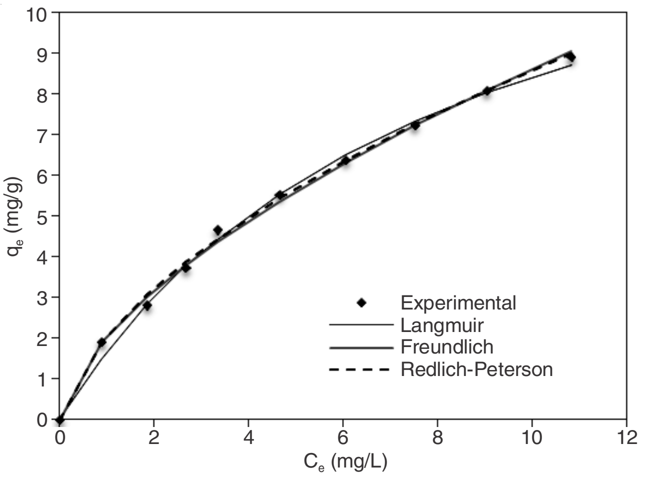

Fig. 5. Comparison of experimental and predicted methyl violet adsorbed for all isotherm models studied by modified *Ceiba pentandra* sawdust using 0.3 N NaOH

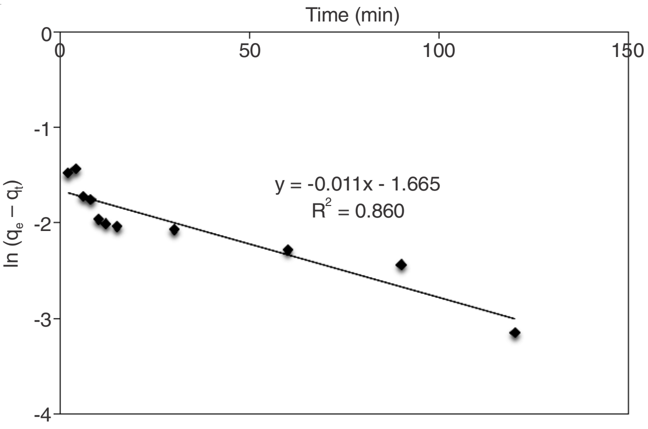

Fig. 6. Pseudo-first order plot for methyl violet adsorption onto modified *Ceiba pentandra* sawdust using 0.3 N NaOH

estimated equilibrium capacity, q_e and the coefficient of determination (R^2) were calculated for initial methyl violet concentration of 60 mg/L. It was found that calculated q_e value was not suitable with the experimental values with R^2 values of 0.8608.

Pseudo-second order model: Adsorption kinetics model of methyl violet dye onto *Ceiba pentandra* sawdust was also tested with the pseudo-second order kinetic model by plotting t/q_t *versus* t, as described in Fig. 7. The pseudo second order constant, k_s, the estimated equilibrium capacity, q_e and the

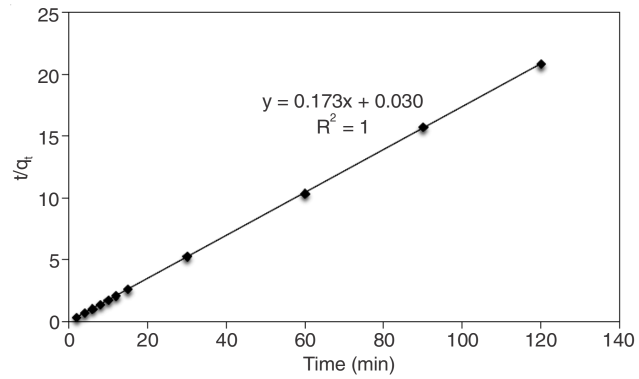

Fig. 7. Pseudo-second order plot for methyl violet adsorption onto modified *Ceiba pentandra* sawdust using 0.3 N NaOH

coefficient of determination (R^2) were calculated for initial methyl violet concentration of 60 mg/L. The calculated q_e values show a very good agreement with the experimental values with R^2 values exceeding 0.999. This indicates that the pseudo-second order kinetics model describes well methyl violet removal using *Ceiba pentandra* sawdust under study.

Desorption study: Desorption is an important issue to clarify the mechanism of adsorption. Desorption study of methyl violet onto raw and modified *Ceiba pentandra* sawdust was performed using distilled water. If methyl violet can be desorbed by distilled water, it indicates that methyl violet adsorption occurs with weak interaction (physisorption). Otherwise, if methyl violet can not be desorbed by distilled water, it indicates that methyl violet adsorption occurs in stronger interaction (chemisorption). Fig. 8 shows that 25.6 % of methyl violet adsorbed into the raw sawdust can be desorbed by distilled water. It indicates that most of the adsorption occurs through a chemisorption mechanism. Reaction of *Ceiba pentandra* sawdust with sodium hydroxide solution lead to the decrease of methyl violet desorbed. It may be caused by stronger interaction of methyl violet dye molecules with functional groups, which may be formed during the reaction.

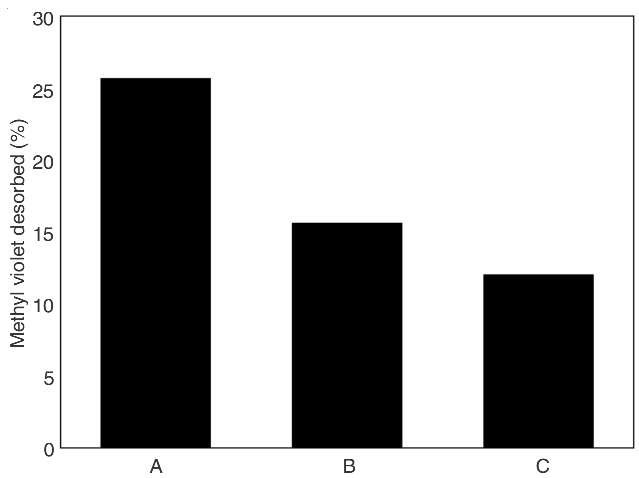

Fig. 8. Amount of methyl violet desorbed by raw sawdust (A), modified sawdust with NaOH 0.1 N (B), modified sawdust with 0.3 N NaOH (C)

Conclusion

Modified *Ceiba pentandra* sawdust has proven to be a promising adsorbent for methyl violet removal from aqueous solutions. Adsorption efficiency may be influenced by pH, contact time and initial concentration. pH 5 was determined as the optimum pH for adsorption. A fast removal of methyl violet was noticed as more than 90 % of methyl violet was removed in 60 min. The equilibrium adsorption data were tested with three isotherm models and were best fitted with Freundlich isotherm. The kinetics of methyl violet adsorption was very well described by the pseudo-second order kinetic model with R^2 values exceeding 0.999.

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