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The **3rd FIRST 2019** (Forum in Research, Science, and Technology) **International Conference** was initiated and organized by State Polytechnic of Sriwijaya in collaboration with Management and Science, University (MSU), Malaysia and National Chin-Yi University of Technology, Taiwan. The theme of the conference was “*Integration of Advanced Technology to Enhance Social Welfare*”.

The **3rd FIRST 2019** International Conference facilitated the participants from all over the world to meet face to face to open chances in establishing connection and collaboration among them. It was not only for the researchers in academics, but also in industries and governments. This conference became an effective media to link the researchers from many parts of the world conference, for exchanging, sharing, following up and discussing the results of the latest researches, industries needs, and government regulatory policies.

The **3rd FIRST 2019** International Conference became worthwhile platform for researchers to present their finding in the areas on multidisciplinary of Engineering and Science (Track 1), Computer Science and ICT (Track 2), and Social Science (Track 3). It has also provided an opportunity for the professionals and researchers to learn and share about the latest development and research in those 3 tracks.

The **3rd FIRST 2019** International Conference attracted so many authors not only from Indonesia but also from other countries, such as Japan, Taiwan, and Malaysia. There were 180 papers were accepted in the **3rd FIRST 2019** International Conference, including 89 papers for Track 1 (Engineering and Science), 46 papers for Track 2 (Computer Science and ICT), and 45 papers for Track 3 (Social Science).

In The **3rd FIRST 2019** International Conference, there were 4 keynote speakers and 3 invited speakers. As the keynote speakers, there were Prof. Yasushi Kiyoki, Ph. D from KEIO University, Japan, Prof. Nurul Taufiqu Rochman, M. Eng, Ph. D, From LIPI, Indonesia, Prof. Tjiptohadi Sawarjuwono, M. Ec., Ph. D., Ak, from Universitas Airlangga, Indonesia, and Prof. Win-Jet Luo, from National Chin-Yi University of Technology, Taiwan. As the invited speakers, there were Dr. R. Wisnu Nurcahyo, DVM from Universitas Gadjah Mada, Indonesia, and Assoc. Prof. Dr. Intan Zaurah binti Mat Darus from Universiti Teknologi Malaysia.

The **3rd FIRST 2019** International Conference committee would like to say thank you very much for all the participants and their respected institution that have supported for the success of the **3rd FIRST 2019** International Conference, and all of the guess and sponsors of the **3rd FIRST 2019** International Conference.



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Adsorption of Synthetic Dye by Betel Nuts Activated Carbon in a Fixed-bed Column, Experiments and Prediction of Breakthrough Curves

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Abstract. Wastewater produced from textile industry contains synthetic dye that couldn't degrade naturally. The dye waste adsorbed in a continuous fixed-bed column by betel nuts activated carbon. The fixed-bed column had 60 cm of height and 2 inches of ID. The synthetic dye solution fed to the top of column with flow 10 ml/min. The column performance was evaluated with varying bed height in 5,10, and 15 cm. The outlet analyzed using UV-Vis spectrophotometer. The increased of bed height indicated longer of breakthrough time and column life. The 15 cm of bed height result column maximum capacity (q_{exp}), % total removal, and total adsorbed dye solute (q_{total}) in the amount of 21.99 mg/g, 68.17%, dan 3299.62 g respectively. The prediction of breakthrough curve has been done using kinetic adsorption study the of Thomas, Yoon-Nelson, Adam Bohart, and Bed Depth Service Time (BDST) model. The result of the experiment indicates the kinetic model of Thomas and Yoon-Nelson are the fit models, with the coefficients of regression (R^2) are 0.98 and 0.95 at the bed heights of 10 and 5cm.

1. Introduction

Water pollution is an environmental problem that must be avoided because it causes losses. Water pollution usually comes from industrial waste, household waste, and geographical effects. The example of industrial waste is Jumputan dye waste. The industry of jumputan cloth is usually a household industry that does not have waste processing.

The industrial waste of jumputan contains the dyestuff of organic compounds of the procion, erionyl, auramin, and rodhamin species. Dyestuff organic compounds that are channeled into the waters can reduce the dissolved oxygen levels needed by aquatic organisms because oxygen is used as an oxidizing dye organic compound [1].

One effort to overcome jumputan dye waste is by using adsorption method. Adsorption is a process that takes place when a fluid (liquid or gas) is bonded to a solid and ultimately forms a thin film on the surface of the solid. In general, the adsorbent used is activated carbon. One of the active ingredients that develop by authors is Betel nuts. Betel nuts are used as activated carbon due to carbohydrate content of 60.86% which will become the main carbon component of the activated carbon [2].

Activated carbon of betel nuts made by carbonization and activation process. The major components are carbon with 86.27% [2].

The adsorption kinetics show the rate adsorption by the adsorbent. In continuous-system adsorption, the calculation of the adsorption kinetics is often referred as the calculation of the adsorption column performance. The performance can be pointed out by breakthrough curve. The time and shape of



breakthrough curve represented the effectiveness of the adsorbent and the dynamic response behavior of the column [3-5]). In the calculation of the performance of columns, there are several commonly used modeling models namely Thomas, Yoon Nelson, Adam-Bohart, and Bed Depth Service Time (BDST) model.

2. Research Methodology

Activated carbon from betel nut is Adsorbent used in this research. The carbonized betel nuts use a furnace with a temperature of 500°C, uniformed the size to 60 mesh, and activated with 0.5 M HCl solution [2].

Preparation The dye solution is carried out by dissolving 10 g of powdered synthetic dye and 10 ml acetic acid 15% v/v in 10 L of water with a temperature of 80-90°C.

The adsorption column used has an inside diameter of 2 inches, a height of 60 cm and made from polyvinylchloride (PVC). The activated carbon set in the middle of wool cloth-aluminum plate layer. The dye solution fed to the top of column by using peristaltic pump with a flow rate of 10 ml/min. To evaluate the effect of bed height, the adsorbent mass in the adsorption column was varied to 50, 100, and 150 g. The variation of the adsorbent mass indicates a bed height of 5, 10, and 15 cm. The out solution from the column analyzed with UV-Vis spectrophotometer.

The adsorption column performance was evaluated using the breakthrough curve achieved through C_t/C_o versus t , where C_t and C_o were color concentrations of output and feed in milligrams per liter [68]. Where Q is the volumetric flow rate (ml/min), t_{total} is the total time of dye absorption (min), and X is the mass of an adsorbent in column (g).

The total weight of the adsorbed dye (q_{total}) can be calculated by the equation (1)

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t_{total}} C_{ad} dt \quad (1)$$

The total dye transferred to the column (W_{total}) can be calculated by the equation (2)

$$W_{total} = \frac{C_o Q t_{total}}{1000} \quad (2)$$

Total dye removal (% removal) can be calculated by the equation (3)

$$\% \text{ removal} = \frac{q_{total}}{W_{total}} \times 100 \quad (3)$$

The adsorption capacity (q_{eq}) can be calculated by the equation (4)

$$q_{eq(\text{exp})} = \frac{q_{total}}{X} \quad (4)$$

Ordinary adsorption kinetic models that develop was Thomas, Yoon-Nelson, and Adam Bohart. The description of each models and the equation referred to many articles [6-12].

This model is often used to describe fixed bed columns and parameters of a column system. Thomas model has been represented by the second law of reaction kinetics without axial dispersion. Thomas model can be calculated by equation (5). Where C_t is the concentration of outlet (mg/l), m is the mass of adsorbent (g), K_{th} is the Thomas kinetic coefficient (ml/min mg), Q is flow rate (ml/min), and q_o is the adsorption capacity (mg/g). The value of K_{th} and q_o is obtained from the plot $\ln \left[\frac{C_o}{C_t} - 1 \right]$ versus t .

$$\ln \left[\frac{C_o}{C_t} - 1 \right] = \frac{K_{th} q_o m}{Q} - K_{th} C_o t \quad (5)$$

This model is developed based on the adsorption theory. The Yoon-Nelson model is based on column and data parameters, and used for system per unit of component, following equation (6). K_{YN} is Yoon-Nelson adsorption constant (min^{-1}) and τ is the time required for 50% adsorption (minutes), other physical parameters are not required for this model, K_{YN} and τ values can be obtained from plot $\ln \left[\frac{C_t}{C_0 - C_t} \right]$ versus t .

$$\ln \left[\frac{C_t}{C_0 - C_t} \right] = k_{YN} t - \tau k_{YN} \quad (6)$$

This model was chosen based on the description of the fixed bed column for the initial part of the operation, this model states that the reaction is not as fast as the surface reaction theory, the following equation (7). K_{AB} is the kinetic constant of Adam-Bohart ($\text{l/mg}\cdot\text{min}$), N_0 and Z is concentration in mg/l and column length (cm), respectively, U_0 represents linear velocity (cm/min) determining the calculation of excessive volumetric flow rate from area bed. The values of

K_{AB} and N_0 are obtained from plot $\ln \left[\frac{C_t}{C_0} \right]$ versus t .

$$\ln \left[\frac{C_t}{C_0} \right] = K_{AB} C_0 t - \frac{K_{AB} N_0 Z}{U_0} \quad (7)$$

BDST (*Bed Depth Service Time*) is a simple model to predict the relationship between bed depth and time. In process concentration and adsorption parameters, this model is only used to describe from the initial part of the absorption curve, based on a breakpoint with 10-15% saturation point. BDST focuses on parameter estimation such as maximum adsorption capacity and kinetic constant, this model assumes based on adsorption speed controlled by surface reaction between adsorbate and unused capacity of adsorbent. Where C_0 is the solute concentration (mg/l), C_B is the concentration of the solute at a time of absorption (mg/l), k_a is the value of the adsorption constant ($\text{l/mg}\cdot\text{h}$), N_0 is the adsorption capacity (mg/l), H is the column size (cm), u is the linear flow rate from material to bed (cm/h), t is the service time of the column below and above a condition in units (h).

$$t = \frac{H N_0}{u C_0} - \frac{\ln \left(\frac{C_0}{C_B} - 1 \right)}{k_a C_0} \quad (8)$$

3. Results and Discussion

The performance of the adsorption column can be seen from the resulting breakthrough curve data, where the breakthrough curve is the ratio of the dye concentration at time t and at initial (C_t/C_0) versus time (t). The column performance test is done by varying the height of the bed. The bed height used is 5, 10, and 15 cm; comparable to 50, 100, and 150 g of adsorbent.

At figure 1, the 5 cm bed height of the breakthrough occurs most rapidly. The slowest breakthrough takes place with saturation time of 480 minutes. The results obtained have similarities to the study of Lim and Ahmad [13] and Nidheesh et.al [14] which states the higher the bed the longer the breakthrough happens. Thus the height of bed 15 cm is the optimal variable in the operational efficiency of the column. This is because the longer the breakthrough occurs the less the replacement of the adsorbent is done.

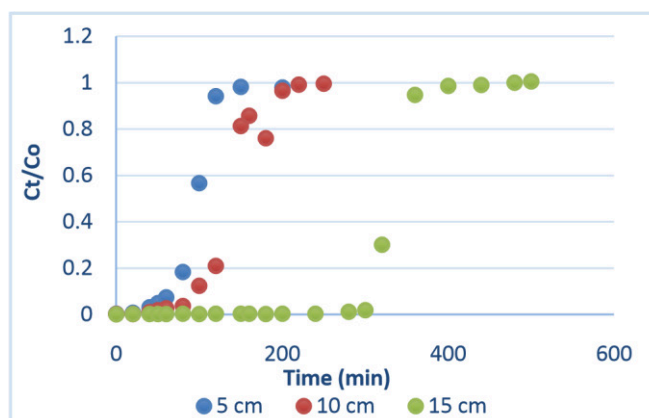


Figure 1. Effect of bed height on the breakthrough curve

The adsorption column parameter is one of the performance reviews of adsorption columns. The parameters reviewed are dye absorption (q_{total}), total dye transferred to column (W_{total}), dye removal, and maximum column capacity (q_{eq}). The maximum column capacity is the most important parameter to review. This is because the maximum column capacity represents the number of solutes attached to a certain amount of adsorbent.

From the calculation of column parameters (Table 1), increased bed depth increases the time and total dye absorption (q_{total}), the dyestuff that transferred to the column (W_{total}), and the total removal of dye. The increase in W_{total} value is due to an increase in adsorption time at each bed height (Table 1). The largest dye removal occurred at a bed height of 15 cm with a value of 68.17%.

Table 1. Adsorption Column Performance : Experimental Data

Bed Height (cm)	C_o (mg/L)	q_{total} (mg)	W_{total} (mg)	Dye removal (%)	$q_{\text{exp}} = q_{\text{eq}}$ (mg/g)
5	968	970.74	1936	50.14	19.41
10	968	1308.25	2420	54.06	13.08
15	968	3299.62	4840	68.17	21.99

However, in the parameters of maximum column capacity (q_{eq}), the higher the bed does not mean getting better results. This is indicated by the maximum value of column capacity at bed height 10 cm smaller than bed height 5 cm with the value of 13.08 mg/g and 19.41 mg/g respectively. The maximum value of column capacity is obtained at a bed height of 15 cm of 21.99 mg/g. The results of this study have similarities with the research Lim and Ahmad [13] in Cd(II) adsorption using dead calcareous skeletons with variations in the height of bed 1.1; 1.65; and 2.2 cm. Value (q_{eq}) at the height of bed 1.1; 1.65; and 2.2 cm by 20.47; 15.68; and 26.45 mg/g respectively.

Thomas kinetic model is a widely used adsorption kinetic model. This model aims to describe the performance of the column and predict the breakthrough curve. Thomas model follows Langmuir adsorption kinetics. The Thomas model ignores axial dispersions in the adsorption column during driving force following the rules of the second-order reversible kinetics reaction.

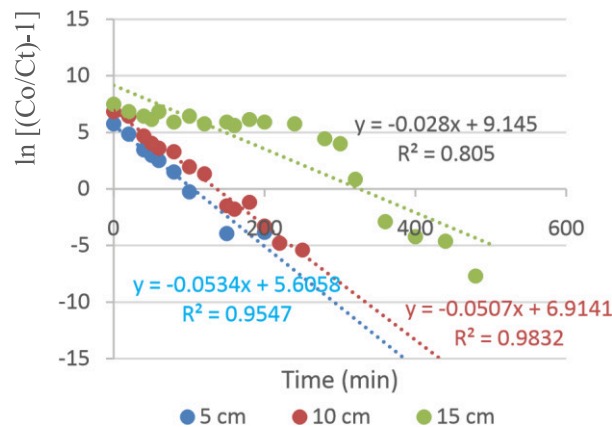


Figure 2. Thomas Kinetic Model

Based on Figure 2, Thomas is a good model that used in variations in bed height of 5 cm and 10 cm because it has a regression coefficient (R^2) ≥ 0.9 . While at variable height of 15 cm bed, Thomas model is not good to use because it has regression coefficient (R^2) ≤ 0.9 . Table 2 shows the Thomas kinetics (k_{th}) getting smaller with increasing bed height.

The adsorption capacity (q_o) in the Thomas model has the same graph as the experimental result where the bed height of 15 cm has the greatest value followed by the bed height of 5 cm and 10 cm. This result has the same trend as Lim and Ahmad [13], which is the value of adsorption capacity has the same graph between experimental data and Thomas modeling predictions. However, the opposite result had shown by the study of Lopez-Cervantes et.al [15], the value of adsorption capacity has unequal graphs between experimental data and predictions of Thomas models. This can be caused by the low regression coefficient value obtained that is equal to 0.818; 0.832; and 0.503 for height variations of 3, 6, and 12 cm [15]. The predicted parameter of Thomas model can be seen in Table 2.

Yoon-Nelson model was developed based on the theory of adsorbent ability to adsorb the solute. This modeling can be calculated directly by involving fewer data and column parameters. The Yoon-Nelson model can also be applied to a single component system. The k_{YN} and τ values denote Yoon-Nelson kinetics constants (min^{-1}) and the time it takes to reach 50% breakthrough adsorption (min) [13].

Based on Figure 3, the value of the regression coefficient (R^2) equals the Thomas model. Therefore, Yoon-Nelson is good for bed height variables of 5 cm and 10 cm. Table 2 shows suitability of the estimated predictive value of the half-life breakthrough (τ) and the experimental results, where the fastest breakthrough occurs in variations in bed height 5 cm, then 10 cm, and 15 cm. Meanwhile, the increase in bed height will decrease the value of Yoon-Nelson kinetics constant (k_{YN}).

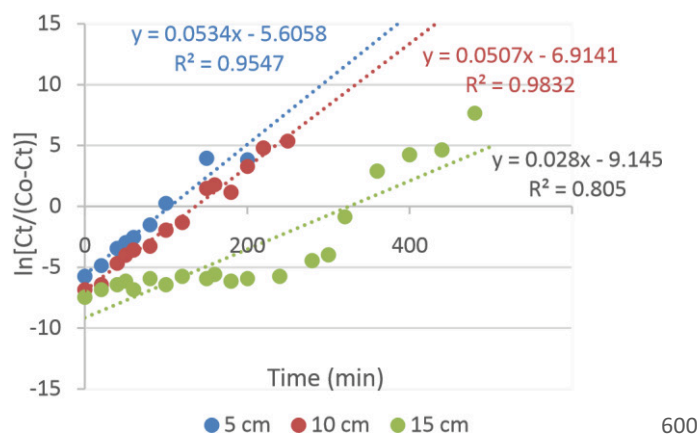


Figure 3. Yoon-Nelson Kinetic Model

Adam Bohart model was chosen to describe the breakthrough curve in the initial state of operation. In the Adam-Bohart model, no immediate reaction occurs such as surface reaction theory [13]. This model can be used to calculate the value of adsorption capacity (N_o) and the Adam-Bohart kinetics constant.

Figure 4 shows the resulting regression coefficient ($R^2 \leq 0.9$). The Adam-Bohart model is considered imprecise to describe the adsorption kinetics [16]. The predicted values obtained from the Adam-Bohart model show a decrease in the value of the Adam-Bohart kinetics constant (k_{AB}) and adsorption capacity (N_o) with increasing bed height (Table 2).

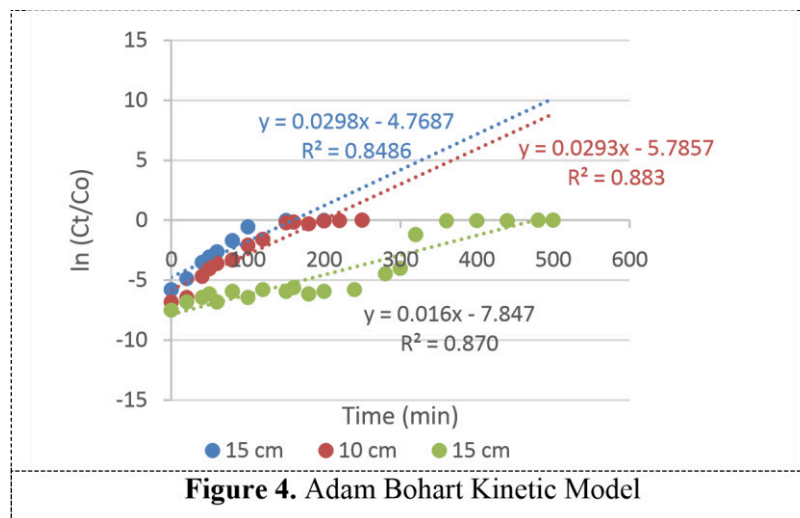


Table 2. Adsorption Kinetic Model Parameter

Bed Height (cm)	Thomas		Yoon-Nelson		Adam-Bohart	
	k_{Th} (ml/min mg)	q_o (mg/g)	k_{YN} (min^{-1})	τ (min)	k_{AB} (l/mg min)	N_o (mg/l)
5	0.055	20.32	0.053	101.98	0.0000307	40760
10	0.052	13.35	0.050	137.78	0.00003006	39210.67
15	0.029	21.01	0.028	325.46	0.00001704	14723.33

The Bed Depth Service Time (BDST) model is a simple model to predict the relationship between bed height and service time (t) [6]. This model is only used to describe the beginning of the breakthrough curve up to 10-50% saturation. The BDST model assumes that the adsorption rate is controlled by the surface reaction between the adsorbate and the adsorbent.

The value of service time on the BDST kinetics model curve (Figure 5) is the saturation point of the research. The service time data will produce prediction parameters in the form of kinetics model BDST (K_a) and adsorption capacity (N_o). From Figure 5 visible curve in the model of BDST is not good used as a model in this study because it has a regression coefficient value ≤ 0.9 . The prediction of BDST

kinetics value obtained is 0.0151 L / mg hour and the adsorption capacity of column is 59.18 mg/cm³. By entering a C_B value of 40% breakthrough, resulting critical height value (H_o) of 5.5 cm.

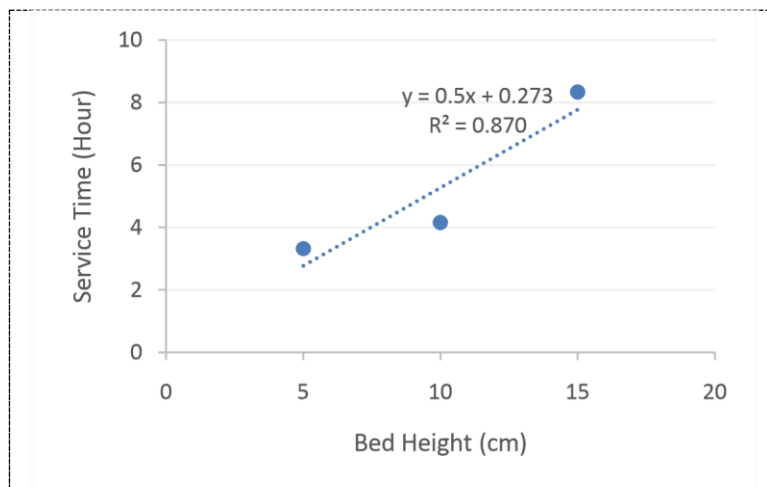


Figure 5. Bed Depth Service Time (BDST) Kinetic Model

Table 3. Prediction Parameter of Bed Depth Service Time (BDST) Model

C _o (mg/l)	Q (ml/menit)	u (cm/jam)	N _o (mg/cm ¹)	K _a (l/mg hr)	R ²	H _o (cm)
968	10	122.28	59.18	0.015	0.87	5.5

regression value in all three modeling. From Figure 6 and 7, the model of Thomas and Yoon-Nelson model has almost the same value. Model Thomas and Yoon-Nelson models are also close to experimental data. This is due to the regression value of both models ≥ 0.98 . The Adam-Bohart model has a predictive value that is far from the experimental data, this may be due to the regression value in the Adam-Bohart model <0.9 .

After viewing the model that is by the experiment, then next choose the modeling based on the existing needs. Each model has its advantages. If the study aims to determine the maximum value of column capacity, the appropriate model used is Thomas. The Yoon-Nelson model is used when looking for time for 50% breakthrough and the Adam-Bohart model aims to determine the value of adsorption capacity.

The prediction of the breakthrough curve can be seen in Figure 6, 7, 8 below. The prediction of the breakthrough curve is done at bed height 5 and 10 cm because both equations have the greatest

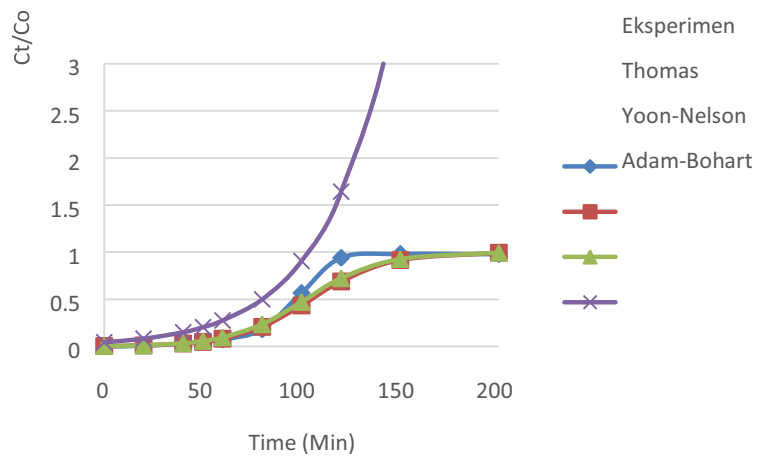


Figure 6. The prediction of the breakthrough curve uses the Thomas, the YoonNelson, and the Adam-Bohart model at a bed height of 5 cm

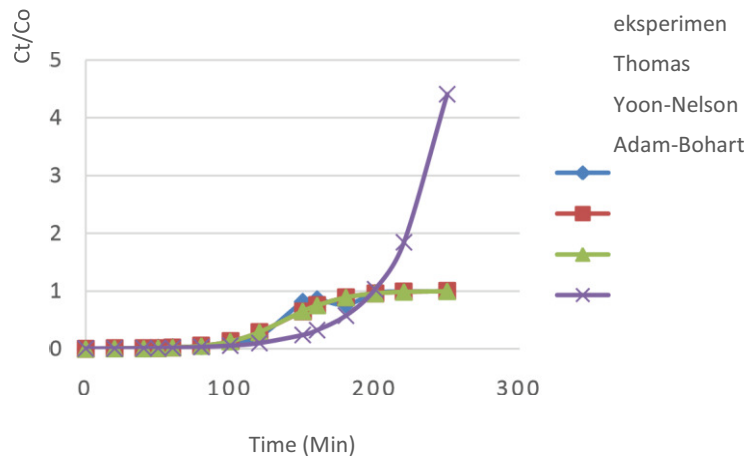


Figure 7. The prediction of the breakthrough curve uses the Thomas, the YoonNelson, and the Adam-Bohart model at a bed height of 10 cm

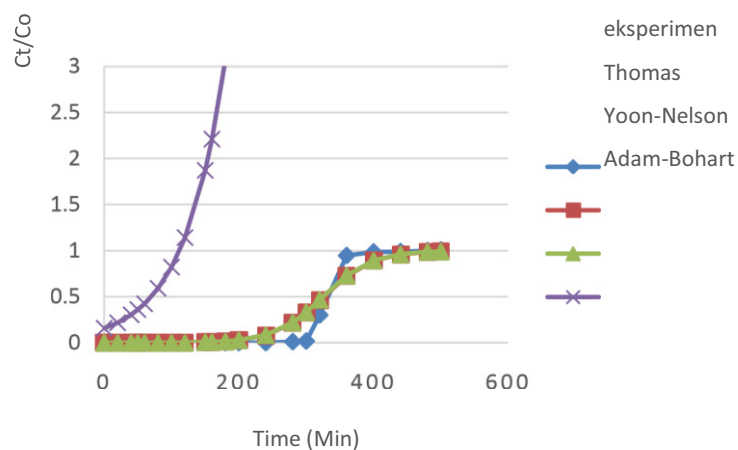


Figure 8. The prediction of the breakthrough curve uses the Thomas, the YoonNelson, and the Adam-Bohart model at a bed height of 15 cm

Table 4. Prediction Breakthrough Curve: Regression Value Model Thomas, Yoon-Nelson, and Adam-Bohart

Bed Height (cm)	R ²		
	Thomas	Yoon-Nelson	Adam-Bohart
5	0.95	0.95	0.85
10	0.98	0.98	0.88
15	0.81	0.81	0.87

4. Conclusion

The increase in bed height will retard the breakthrough time so that longer saturation occurs. The longest saturation point is obtained at bed height 15 cm with saturated time 480 minutes. The bed height of 15 cm is the optimum variable to produce maximum adsorption capacity (q_{exp}), percentage of dye removal (%), and total dye absorption (q_{total}) in the fixed-bed column by the value of 21.99 mg/g, 68.17%, and 3299.62 g respectively.

Thomas and Yoon-Nelson kinetics models are the best models that can be used as a dye adsorption model using activated carbon made from betel nuts. The prediction of the breakthrough curve is fitted with the experimental data at bed height 5 and 10 cm with the regression coefficient (R^2) value of 0.95 and 0.98 respectively.

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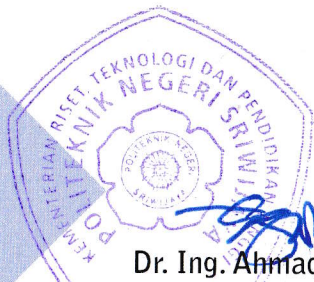
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