Prediction of continuous adsorption performance of cellulose acetate butyrate/poly(L-lactid acid) composite beads for dye removal

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Abstract. Continuous adsorption of methylene blue (MB) from aqueous solution was studied by using cellulose acetate butyrate (CAB) and poly(L-lactic acid) (PLLA) composite beads. Various parameters such as PLLA composition (0 wt.% and 30 wt.%) and flowrate (7, 13, 23 ml/min) were applied in this experiment. Three different kinetic models, such as Adam-Bohart, Thomas, and Yoon Nelson were applied to the experimental data to analyze the column performance and predict the breakthrough curve of MB adsorption onto adsorbent beads. The value of adsorption capacity increased with the increase of flowrate. The highest maximum capacity was reached by adsorbent of pure CAB (0 wt.% of PLLA) at flowrate of 23 mL/min. Statistical methods such as Sigma Squared Error (SSE), Sigma Absolute Error (SAE) and percentage error were utilized to evaluate the obtained prediction data with the experimental data and to find out the fitted kinetic model for this continuous adsorption. The prediction results indicated that Thomas and Yoon-Nelson models fit well to the experimental data based on the correlation coefficient and error analysis.

1. Introduction
Water pollution is one of the crucial problems for our environment today. Water pollution is also one of the leading causes of death and disease worldwide. Textile industry waste is one of the contributors of water pollution. World Bank data showed that it is estimated about 20% of total water pollution is generated from textile industry waste. This is very dangerous for the survival of living things because water is one of the important resources [1]. Various methods to reduce textile industry waste have been carried out such as coagulation, flocculation, and chemical oxidation. However, these methods have disadvantage of being expensive and ineffective at reducing large-scale waste. One of the effective ways is using the adsorption method. This method is effective for removing various types of dyes from wastewater because it provides good results, high waste removal efficiency and simplicity of design [2].

The adsorbent which is most widely used is activated carbon. However, activated carbon has non-biodegradable properties that in the end of adsorption process may cause another problem for the
environment. Therefore, utilization of biodegradable adsorbent is preferred than the non-biodegradable one. In this case, there are biodegradable materials which can be used as adsorbent and one of that is cellulose. Cellulose also has high temperature resistance, abundant availability, and affordable price. However, cellulose also has disadvantage such as brittleness and low softening temperature, so that additional materials are needed to strengthen the structure of cellulose. Material that can be added is Poly(L-lactic acid) (PLLA).

PLLA has biodegradable properties and has good mechanical properties [3]. For purposes as an adsorbent, cellulose is generally in the form of beads. Cellulose beads are round, porous and have a higher specific surface area compared to fibrous cellulose. Cellulose beads have a high porosity, interesting functional properties and have good swelling properties [4].

This research focused on the prediction of dye adsorption performance continuously by using the neat cellulose acetate butyrate (CAB) bead and CAB/PLLA composite bead with 30 wt.% of PLLA. The adsorption was carried out in continuous system because it will give accurate scale-up data that can be used for large scale of treatment [5]. For performance prediction, three kinetic models of continuous adsorption were derived from experimental data and were used to predict the breakthrough curve and adsorption performance such as maximum capacity and saturated time. From this research, it is expected to know the ideal breakthrough curve of the continuous adsorption of methylene blue using pure CAB and CAB/PLLA (70/30) beads as adsorbents. The prediction data from three kinetic models were evaluated in term of error analysis between prediction data and experimental data to reveal the suitable kinetic model for the adsorption process.

2. Kinetic models of continuous adsorption

The fixed bed column design involves estimating the shape of the breakthrough curve and displaying the breakpoint, which are important factors in determining the feasibility of using the adsorbent in real applications. To explain the behavior of fixed bed columns and to scale them up to industrial scale applications, an appropriate model is needed. Several simple mathematical models have been developed to describe and estimate the dynamic behavior of the performance in bed column. Three mathematical models of continuous adsorption, Adam-Bohart, Thomas and Yoon Nelson models, were used in this study to describe the adsorption performance. Thomas model assumes plug flow behavior in the bed. This is the most general and widely used kinetic model to describe the performance of the adsorption process in fixed-bed column [6]. This equation is expressed as following:

$$\ln \left[ \frac{(C_0 \text{m})}{(C_t \text{m})} \right] = \frac{k_\text{Thomas} q \epsilon m}{q} - (k_\text{Thomas} C_0 t)$$

(1)

Yoon-Nelson model was used to describe the column adsorption data. Utilization of this model could minimize the error resulted from Thomas model, especially at lower or higher time periods of the breakthrough curve. This equation is expressed as following:

$$\ln \left[ \frac{(C_\text{t})}{(C_0 \text{m} - C_\text{t})} \right] = k_\text{YN} t - \tau k_\text{YN}$$

(2)

Bohart and Adams describe the relationship between $C_t/C_0$ and $t$ in a continuous system. It is used for describing the initial part of the breakthrough curve. This equation is expressed as following:

$$\ln \left( \frac{C_t}{C_0} \right) = k_\text{AB} C_0 t - \frac{k_\text{AB} N_0 Z}{F}$$

(3)

3. Error analysis

To find out the best applicable model to the experimental data, the error analysis between prediction data and experimental data was studied. A number of error analysis methods such as the sum of the square of the error (SSE), the sum of the absolute error (SAE), percentage error were used in this
present study to find out which model fitted well to the experimental observations [7]. The expressions for some error functions are as follows:

\[
\text{SSE} = \sum_{i=1}^{n}(y_e - y_i)^2 \tag{4}
\]

\[
\text{SAE} = \sum_{i=1}^{n} |y_c - y_e| \tag{5}
\]

Percentage error = \frac{y_e - y_c}{y_e} \times 100\% \tag{6}

where \(y_e\) is the predicted (calculated) data and \(y_c\) is the experimental data and \(y\) represents the ratio \(C_t/C_0\). The above statistical error expressions were applied to all the kinetic model equations.

4. Experimental Section

4.1. Materials

Poly(L-lactic acid) (PLLA) (Mw of 166,000 kg/kmol (GPC)) was obtained from Zhejiang Hisun Biomaterials Co., Ltd (China). Cellulose Acetate Butyrate (CAB) (Mn = ~30,000; ≥49 wt.% Butyryl; 1.4-2.4 wt.% Hydroxyl) was supplied from Sigma-Aldrich (USA). All the materials were used as received without any purification.

4.2. Experimental Procedure

The cellulose beads were synthesized through a process of solution blending followed by solution injection to a coagulant bath, as described in detail our previous work [8]. The pure CAB bead and CAB/PLLA (70/30) 15 wt.% were utilized as the adsorbents for methylene blue (MB) removal. The adsorption was carried out in continuous system in fixed-bed column with a height of 3 cm. A solution of methylene blue with concentration of 10 ppm was feed to the column continuously with various flow rates of 7 mL/min, 13 mL/min and 23 mL/min. In this study, the data obtained experimentally were processed to derive kinetic models and then developed the calculated breakthrough curve. The maximum time of adsorption was 90 minutes. The kinetic models applied in this experiment were Thomas model, Yoon-Nelson model, and Adam-Bohart model.

4.2.1. Breakthrough curve prediction and adsorption capacity. From the experimental data, we have initial concentration of methylene blue (\(C_0\)) of 10 ppm and various final MB concentration (\(C_t\)) as function of time. From that data, a graph was made from each models t vs. ln(\(C_t/C_0\)) was plotted for Thomas model, t vs ln(\(C_t/C_0\)) for Yoon-Nelson model and t vs ln(\(C_t/C_0\)) for Adam-Bohart model. An equation of \(y=ax+b\) from each graph was obtained and used for calculating the final concentration of methylene blue (prediction data). The \(y=ax+b\) equation was also used to find the capacity of adsorption by calculating the intercept and slope of the graph.

4.2.2. Error Analysis Calculation. After calculating the predictive data, the error of the prediction result can be compared using statistical data. Sigma Squared Error (SSE), Sigma Absolute Error (SAE) and Percentage Error can be used to determine the error analysis. From this statistical data, the evaluation of models can be analyzed to get the better operation system of continuous adsorption.

5. Results and Discussion

The provided data can be used to determine the breakthrough curve from plotting the final concentration (\(C_t\)) vs. time. The breakthrough curve from provided data with each variable is shown in figure 1. With increasing of time, the adsorbent surface is filled with dye and reduces the surface area of the adsorbent, causing an increase in the concentration of adsorbate at the column output [9]. In this experiment, the breakthrough curve profile was completed faster at flow rate of 23 mL/min for all beads of neat CAB and CAB/PLLA (70/30) 15 wt.%). This is due to the low residence time which causes the adsorbate does not have enough time to absorb methylene blue maximally so that the
methylen blue leaves the column before equilibrium occurs. So, the higher flow rate, the faster breakthrough curve is formed [10].

![Breakthrough curve](image)

**Figure 1.** Breakthrough curve from experimental data provided on (a) CAB/PLLA (100/0) and CAB/PLLA (70/30) with various inlet flow.

The addition of PLLA is expected to increase the performance of the methylene blue dye adsorption. In addition, there is a variable flow rate of 7 mL/min, 13 mL/min and 23 mL/min, respectively. From the experimental data, a breakthrough curve was obtained, and it can be applied to 3 models, which are the Adam-Bohart model, the Thomas model, and the Yoon-Nelson model.

### 5.1. Adsorption Kinetic Models

#### 5.1.1. Thomas model. The Thomas model is a widely used theoretical method to describe column performance which assumes a plug flow treatment within the bed. Thomas model adsorption capacity curves of CAB/PLLA (70/30) and CAB/PLLA (100/0) beads were used to obtain linear graph equations for each flow rate of 7 mL/min; 13 mL/min; and 23 mL/min at initial MB concentration of 10 ppm. The results of the adsorption prediction data can be seen in the table 1. From the data table, the breakthrough curve of the predicted adsorption is presented in figure 2 and figure 3 for each flow rates. As seen in the graph, ideally the breakthrough curve has 3 phases, namely the breakpoint phase, the breakthrough phase, and the exhausted phase. The graphical form can touch C\textsubscript{t}/C\textsubscript{0} up to 1 which is then close to saturation and even saturation. This is because at the beginning of the adsorption process, the adsorbent surface is still empty so that it can attract the molecules to be absorbed [11].

Based on the results for all beads and flow rates variable, the higher the flow rate, the faster the beads will reach saturated condition. This is because the faster the inflow rate, the mass transfer rate will increase which causes the amount of dye adsorbed to the column to increase and saturate more quickly at high flow rates [12].

In this experiment, a breakthrough curve profile that occurs faster at a high flowrate or flow rate of 23 mL/min for all CAB/PLLA (100/0) and CAB/PLLA (70/30) beads. This is because of the lower residence time of the feed entering the column, which reduces the contact time between methylene blue and CAB/PLLA beads. The higher input flow rate, the mass transfer rate will increase which causes the amount of dye adsorbed to the column also increase and saturate faster at high flow rates. In addition, at high flow rates, the adsorption capacity is lower due to insufficient solute residence time in the column as well as diffusion of the solute into the pores of the adsorbent. Therefore, the solute leaves the column before equilibrium occurs [11]. Meanwhile, for the adsorption capacity (q\textsubscript{0}), the higher the flow rate, the higher the q\textsubscript{0}. The adsorption capacity is shown in table 4. The highest adsorption capacity calculated by using Thomas model is 46.733 mg/g at a flow rate of 23 mL/min for CAB/PLLA beads (100/0) 15 wt.%. 

![Adsorption Kinetic Models](image)
Table 1. Prediction data of MB adsorption on CAB/PLLA (70/30) and CAB/PLLA (100/0) beads in Thomas model for various flow rates.

| t (min) | CAB/PLLA (70/30) | 23 mL/min | 13 mL/min | 7 mL/min | CAB/PLLA (100/0) | 23 mL/min | 13 mL/min | 7 mL/min |
|---------|------------------|------------|------------|-----------|------------------|------------|------------|-----------|
| 0       | 0.0353           | 0.0237     | 0.0418     | 0.0246    | 0.0241           | 0.0303     |            |           |
| 3       | 0.0512           | 0.0349     | 0.0547     | 0.0360    | 0.0340           | 0.0395     |            |           |
| 6       | 0.0737           | 0.0510     | 0.0714     | 0.0523    | 0.0478           | 0.0512     |            |           |
| 9       | 0.1050           | 0.0741     | 0.0927     | 0.0755    | 0.0668           | 0.0662     |            |           |
| 12      | 0.1474           | 0.1063     | 0.1194     | 0.1078    | 0.0926           | 0.0853     |            |           |
| 15      | 0.2030           | 0.1503     | 0.1526     | 0.1515    | 0.1270           | 0.1091     |            |           |
| 18      | 0.2730           | 0.2083     | 0.1931     | 0.2089    | 0.1719           | 0.1386     |            |           |
| 21      | 0.3563           | 0.2812     | 0.2411     | 0.2808    | 0.2284           | 0.1745     |            |           |
| 24      | 0.4493           | 0.3678     | 0.2968     | 0.3661    | 0.2968           | 0.2174     |            |           |
| 27      | 0.5459           | 0.4639     | 0.3592     | 0.4606    | 0.3757           | 0.2674     |            |           |
| 30      | 0.6392           | 0.5627     | 0.4268     | 0.5581    | 0.4619           | 0.3241     |            |           |
| 33      | 0.7231           | 0.6568     | 0.4972     | 0.6512    | 0.5504           | 0.3865     |            |           |
| 36      | 0.7938           | 0.7400     | 0.5677     | 0.7341    | 0.6358           | 0.4529     |            |           |
| 39      | 0.8502           | 0.8089     | 0.6356     | 0.8033    | 0.7134           | 0.5210     |            |           |
| 42      | 0.8932           | 0.8629     | 0.6985     | 0.8579    | 0.7802           | 0.5883     |            |           |
| 45      | 0.9250           | 0.9035     | 0.7547     | 0.8993    | 0.8350           | 0.6525     |            |           |
| 48      | 0.9478           | 0.9330     | 0.8034     | 0.9296    | 0.8783           | 0.7116     |            |           |
| 51      | 0.9640           | 0.9539     | 0.8444     | 0.9513    | 0.9115           | 0.7642     |            |           |
| 54      | 0.9753           | 0.9686     | 0.8782     | 0.9665    | 0.9362           | 0.8098     |            |           |
| 57      | 0.9831           | 0.9786     | 0.9054     | 0.9771    | 0.9544           | 0.8484     |            |           |
| 60      | 0.9885           | 0.9855     | 0.9271     | 0.9844    | 0.9676           | 0.8803     |            |           |
| 63      | 0.9921           | 0.9902     | 0.9441     | 0.9894    | 0.9770           | 0.9062     |            |           |
| 66      | 0.9947           | 0.9934     | 0.9573     | 0.9928    | 0.9838           | 0.9270     |            |           |
| 69      | 0.9964           | 0.9956     | 0.9675     | 0.9951    | 0.9886           | 0.9434     |            |           |
| 72      | 0.9975           | 0.9970     | 0.9754     | 0.9967    | 0.9920           | 0.9564     |            |           |
| 75      | 0.9983           | 0.9980     | 0.9813     | 0.9978    | 0.9944           | 0.9664     |            |           |
| 78      | 0.9989           | 0.9986     | 0.9859     | 0.9985    | 0.9960           | 0.9742     |            |           |
| 81      | 0.9992           | 0.9991     | 0.9893     | 0.9990    | 0.9972           | 0.9803     |            |           |
| 84      | 0.9995           | 0.9994     | 0.9919     | 0.9993    | 0.9980           | 0.9849     |            |           |
| 87      | 0.9996           | 0.9996     | 0.9939     | 0.9995    | 0.9986           | 0.9885     |            |           |
| 90      | 0.9998           | 0.9997     | 0.9954     | 0.9997    | 0.9990           | 0.9912     |            |           |
5.1.2. Yoon-Nelson model. The Yoon-Nelson model is a simple model and does not require detailed data on the characteristics of the adsorbate, the type of adsorbent, and the physical properties of the bed of the adsorption column. Yoon-Nelson model adsorption capacity curves of CAB/PLLA (70/30) and CAB/PLLA (100/0) beads were used to obtain linear graph equations for each flow rate of 7 mL/min; 13 mL/min; and 23 mL/min at initial MB concentration of 10 ppm. The results of the adsorption prediction data can be seen in the table 2.

From the data in table 2, the breakthrough curve of the predicted adsorption is presented in figure 4 and figure 5 for each flow rate. For all beads and flow rates variable, the higher the flow rate, the faster the beads will saturate. This is due to the faster the inflow rate, the mass rate will increase which causes the amount of dye adsorbed onto the adsorbent increase and saturate faster at high flow rate [12]. As seen in the graph, ideally the breakthrough curve has 3 phases, which are the breakpoint phase, the breakthrough phase, and the exhausted phase. The graphical form can reach \( C_t/C_0 \) up to 1 which is then close to saturation and even saturation [11].

This experiment resulted in a breakthrough curve profile that occurred faster at a high flow rate or flow rate of 23 mL/min for all CAB/PLLA (100/0) and CAB/PLLA (70/30) beads. This is because of the lower residence time of the feed entering the column, which reduces the contact time between methylene blue and CAB/PLLA beads. The higher the inflow rate, the mass rate will increase which causes the amount of dye adsorbed into the adsorbent beads increase and saturate faster at high flow rate. In addition, at high flow rate, the adsorption capacity is lower, due to insufficient solute residence time in the column and the diffusion of the solute into the adsorbent pores, because the solute leaves the column before equilibrium occurs [11]. The highest adsorption capacity calculated from the Yoon-Nelson model is 46.733 mg/g at a flowrate of 23 mL/min for CAB/PLLA beads (100/0) 15 wt.%. All the results of adsorption capacity are shown in table 4.
Table 2. Prediction data of MB adsorption on CAB/PLLA (70/30) and CAB/PLLA (100/0) beads in Yoon-Nelson model for various flow rates.

| t (min) | 23 mL/min | 13 mL/min | 7 mL/min | 23 mL/min | 13 mL/min | 7 mL/min |
|---------|-----------|-----------|----------|-----------|-----------|----------|
| 0       | 0.0353    | 0.0237    | 0.0418   | 0.0246    | 0.0241    | 0.0303   |
| 3       | 0.0512    | 0.0349    | 0.0547   | 0.0360    | 0.0340    | 0.0395   |
| 6       | 0.0737    | 0.051     | 0.0714   | 0.0523    | 0.0478    | 0.0512   |
| 9       | 0.105     | 0.0741    | 0.0927   | 0.0755    | 0.0668    | 0.0662   |
| 12      | 0.1474    | 0.1063    | 0.1194   | 0.1078    | 0.0926    | 0.0853   |
| 15      | 0.203     | 0.1503    | 0.1526   | 0.1515    | 0.1270    | 0.1091   |
| 18      | 0.273     | 0.2083    | 0.1931   | 0.2089    | 0.1719    | 0.1386   |
| 21      | 0.3563    | 0.2812    | 0.2411   | 0.2808    | 0.2284    | 0.1745   |
| 24      | 0.4493    | 0.3678    | 0.2968   | 0.3661    | 0.2968    | 0.2174   |
| 27      | 0.5459    | 0.4639    | 0.3592   | 0.4606    | 0.3757    | 0.2674   |
| 30      | 0.6392    | 0.5627    | 0.4268   | 0.5581    | 0.4619    | 0.3241   |
| 33      | 0.7231    | 0.6568    | 0.4972   | 0.6512    | 0.5504    | 0.3865   |
| 36      | 0.7938    | 0.74      | 0.5677   | 0.7341    | 0.6358    | 0.4529   |
| 39      | 0.8502    | 0.8089    | 0.6356   | 0.8033    | 0.7134    | 0.5210   |
| 42      | 0.8932    | 0.8629    | 0.6985   | 0.8579    | 0.7802    | 0.5883   |
| 45      | 0.925     | 0.9035    | 0.7547   | 0.8993    | 0.8350    | 0.6525   |
| 48      | 0.9478    | 0.93      | 0.8034   | 0.9296    | 0.8783    | 0.7116   |
| 51      | 0.964     | 0.9539    | 0.8444   | 0.9513    | 0.9115    | 0.7642   |
| 54      | 0.9753    | 0.9686    | 0.8782   | 0.9665    | 0.9362    | 0.8098   |
| 57      | 0.9831    | 0.9786    | 0.9054   | 0.9771    | 0.9544    | 0.8484   |
| 60      | 0.9885    | 0.9855    | 0.9271   | 0.9844    | 0.9676    | 0.8803   |
| 63      | 0.9921    | 0.9902    | 0.9441   | 0.9894    | 0.9770    | 0.9062   |
| 66      | 0.9947    | 0.9934    | 0.9573   | 0.9928    | 0.9838    | 0.9270   |
| 69      | 0.9964    | 0.9956    | 0.9675   | 0.9951    | 0.9886    | 0.9434   |
| 72      | 0.9975    | 0.997     | 0.9754   | 0.9967    | 0.9920    | 0.9564   |
| 75      | 0.9983    | 0.998     | 0.9813   | 0.9978    | 0.9944    | 0.9664   |
| 78      | 0.9989    | 0.9986    | 0.9859   | 0.9985    | 0.9960    | 0.9742   |
| 81      | 0.9992    | 0.9991    | 0.9893   | 0.9990    | 0.9972    | 0.9803   |
| 84      | 0.9995    | 0.9994    | 0.9919   | 0.9993    | 0.9980    | 0.9849   |
| 87      | 0.9996    | 0.9996    | 0.9939   | 0.9995    | 0.9986    | 0.9885   |
| 90      | 0.9998    | 0.9997    | 0.9954   | 0.9997    | 0.9990    | 0.9912   |
5.1.3. Adam-Bohart model. The Adam-Bohart model is a model that describes the relationship between $\frac{C_0}{C_t}$ and time in a continuous system and is used to describe the beginning of the breakthrough curve. Adam-Bohart model adsorption capacity curves of CAB/PLLA (70/30) and CAB/PLLA (100/0) beads were used to obtain linear graph equations for each flow rate of 7 mL/min; 13 mL/min; and 23 mL/min at initial MB concentration of 10 ppm. The results of the predicted adsorption data can be seen in the table 3.

From the data table, the breakthrough curve of the predicted adsorption data is presented in figure 6 and figure 7 for each flow rates. Ideally the breakthrough curve has 3 phases, which are the breakpoint phase, the breakthrough phase, and the exhausted phase. However, the Adam-Bohart model graph is theoretically not ideal because it does not have the three phases of the ideal breakthrough curve [11].

This experiment resulted in a breakthrough curve profile that occurred faster at a high flow rate or flow rate of 23 mL/min for all CAB/PLLA (100/0) and CAB/PLLA (70/30) beads. This is because of the lower residence time of the feed entering the column, which reduces the contact time between methylene blue and CAB/PLLA beads. The higher the inflow rate, the mass rate will increase which causes the amount of dye adsorbed onto the adsorbent increase and saturate faster at high flow rate [12]. In addition, at high flow rate, the adsorption capacity is low due to insufficient solute residence time in the column and the diffusion of the solute into the adsorbent pores, because the solute leaves the column before equilibrium occurs [11]. Table 4 shows that the higher the flow rate, the Adam-Bohart velocity constant value decreases, while the adsorption capacity increases with the increasing of flow rate for all beads. The highest adsorption capacity calculated from Adam-Bohart model is 4.487 mg/gr at flowrate 23 mL/min for CAB/PLLA beads (100/0) 15 wt.% This phenomenon shows that the overall kinetic system is dominated by external mass transfer [7].
Table 3. Prediction data of MB adsorption on CAB/PLLA (70/30) and CAB/PLLA (100/0) beads in Adam-Bohart model for various flow rates.

| t (min) | CAB/PLLA (70/30) | CAB/PLLA (100/0) |
|---------|------------------|-------------------|
|         | 23 mL/min | 13 mL/min | 7 mL/min | 23 mL/min | 13 mL/min | 7 mL/min |
| 3       | 0.2440    | 0.1891    | 0.1484   | 0.198216 | 0.155953 | 0.108968 |
| 6       | 0.2602    | 0.2037    | 0.1615   | 0.213141 | 0.169416 | 0.119948 |
| 9       | 0.2774    | 0.2195    | 0.1757   | 0.229191 | 0.18404  | 0.132033 |
| 12      | 0.2958    | 0.2364    | 0.1912   | 0.246449 | 0.199928 | 0.145337 |
| 15      | 0.3154    | 0.2547    | 0.2081   | 0.265007 | 0.217186 | 0.159981 |
| 18      | 0.3364    | 0.2743    | 0.2265   | 0.284962 | 0.235935 | 0.176101 |
| 21      | 0.3587    | 0.2955    | 0.2465   | 0.30642  | 0.256302 | 0.193844 |
| 24      | 0.3824    | 0.3184    | 0.2683   | 0.329493 | 0.278427 | 0.213376 |
| 27      | 0.4078    | 0.3429    | 0.2919   | 0.354304 | 0.302462 | 0.234875 |
| 30      | 0.4348    | 0.3694    | 0.3177   | 0.380983 | 0.328572 | 0.258541 |
| 33      | 0.4637    | 0.3980    | 0.3458   | 0.409671 | 0.356936 | 0.284592 |
| 36      | 0.4944    | 0.4287    | 0.3763   | 0.44052  | 0.387748 | 0.313267 |
| 39      | 0.5272    | 0.4618    | 0.4095   | 0.473691 | 0.42122  | 0.344831 |
| 42      | 0.5621    | 0.4975    | 0.4457   | 0.50936  | 0.457582 | 0.379576 |
| 45      | 0.5994    | 0.5359    | 0.4850   | 0.547715 | 0.497082 | 0.417822 |
| 48      | 0.6392    | 0.5773    | 0.5278   | 0.588958 | 0.539993 | 0.459921 |
| 51      | 0.6815    | 0.6219    | 0.5744   | 0.633307 | 0.586607 | 0.506262 |
| 54      | 0.7267    | 0.6699    | 0.6251   | 0.680995 | 0.637246 | 0.557273 |
| 57      | 0.7749    | 0.7217    | 0.6803   | 0.732274 | 0.692256 | 0.613423 |
| 60      | 0.8263    | 0.7774    | 0.7404   | 0.787415 | 0.752014 | 0.675231 |
| 63      | 0.8811    | 0.8374    | 0.8057   | 0.846707 | 0.816932 | 0.743267 |
| 66      | 0.9395    | 0.9021    | 0.8769   | 0.910465 | 0.887453 | 0.818158 |
| 69      | 1.0018    | 0.9718    | 0.9543   | 0.979023 | 0.964062 | 0.900595 |

Figure 6. Breakthrough curve of predicted data of MB adsorption on CAB/PLLA (70/30) 15wt.% beads in Adam-Bohart model.

Figure 7. Breakthrough curve of predicted data of MB adsorption on CAB/PLLA (100/0) 15wt.% beads in Adam-Bohart model.
### Tabel 4. Comparison of adsorption capacity, SSE, SAE, and percentage error between three kinetic models

#### Adam-Bohart

| Flow rate (mL/min) | k      | q₀     | SSE   | SAE   | Percentage error (%) |
|--------------------|--------|--------|-------|-------|----------------------|
| 23                 | 0.0032 | 1.432  | 0.449 | 2.905 | 38.240               |
| 13                 | 0.0028 | 2.588  | 0.411 | 2.714 | 35.230               |
| 7                  | 0.0024 | 4.550  | 0.382 | 2.620 | 38.757               |

CAB/PLLA (100/0) 15%

| Flow rate (mL/min) | k      | q₀     | SSE   | SAE   | Percentage error (%) |
|--------------------|--------|--------|-------|-------|----------------------|
| 23                 | 0.0028 | 1.400  | 0.422 | 2.721 | 33.256               |
| 13                 | 0.0025 | 2.582  | 0.482 | 2.936 | 40.219               |
| 7                  | 0.0021 | 4.487  | 0.288 | 2.311 | 45.194               |

Adam-Bohart’s average error = 38.483

#### Thomas

| Flow rate (mL/min) | k      | q₀     | SSE   | SAE   | Percentage error (%) |
|--------------------|--------|--------|-------|-------|----------------------|
| 23                 | 12.930 | 9.553  | 0.253 | 1.919 | 14.038               |
| 13                 | 12.930 | 17.742 | 0.338 | 2.274 | 18.578               |
| 7                  | 13.230 | 34.479 | 0.125 | 1.374 | 12.486               |

CAB/PLLA (100/0) 15%

| Flow rate (mL/min) | k      | q₀     | SSE   | SAE   | Percentage error (%) |
|--------------------|--------|--------|-------|-------|----------------------|
| 23                 | 13.040 | 10.538 | 0.259 | 2.046 | 17.429               |
| 13                 | 11.830 | 21.707 | 0.155 | 1.665 | 14.709               |
| 7                  | 9.100  | 46.733 | 0.118 | 1.553 | 15.618               |

Thomas’s Average error = 15.476

#### Yoon-Nelson

| Flow rate (mL/min) | k      | q₀     | SSE   | SAE   | Percentage error (%) |
|--------------------|--------|--------|-------|-------|----------------------|
| 23                 | 0.129  | 9.553  | 0.253 | 1.919 | 14.038               |
| 13                 | 0.132  | 19.488 | 0.338 | 2.274 | 18.578               |
| 7                  | 0.095  | 40.647 | 0.125 | 1.374 | 12.486               |

CAB/PLLA (100/0) 15%

| Flow rate (mL/min) | k      | q₀     | SSE   | SAE   | Percentage error (%) |
|--------------------|--------|--------|-------|-------|----------------------|
| 23                 | 0.130  | 10.538 | 0.259 | 2.046 | 17.429               |
| 13                 | 0.118  | 21.707 | 0.155 | 1.665 | 14.709               |
| 7                  | 0.091  | 46.733 | 0.118 | 1.553 | 15.618               |

Yoon-Nelson’s average error = 15.476
5.2. Error Analysis
Statistical calculations have been carried out to determine the best kinetics model in continuous adsorption. This experiment used SSE, SAE, and percentage error analysis for determining the best model. The result of each statistical equation is shown in table 4.

As shown in table 4, it can be concluded that the SSE, SAE, and percentage error values of the Adam-Bohart model are, on average, higher than those of the Thomas and Yoon-Nelson models. For the specific values of each variable composition and flow rate, it cannot be concluded which is the best because the resulting value is fluctuating. What can be concluded from the calculation of the error analysis is that the Thomas and Yoon-Nelson models is more appropriate than the Adam-Bohart model for continuous adsorption of dye with cellulose-based adsorbent. Adam-Bohart model is not a suitable choice because the error value obtained is pretty much high of 38.483%, which is much different from other models with an average error value of 15.476%. This is because the operating conditions of the research conducted by Adam-Bohart have high complexity, such as temperature and pressure variables that are considered in adsorption so that this model is still not suitable for this study [13]. Even in theory, the Adam-Bohart model is applied only during the initial condition of the breakthrough curve [6]. Therefore, the overall breakthrough curve of Adam-Bohart model is still not suitable to this study.

Thomas model has a smaller error analysis value because theoretically Thomas model assumes continuous plug flow behavior in the bed [11]. Thomas model is also one of kinetic models that has been generally applied to adsorption. Therefore, Thomas model is suitable for continuous dye adsorption experiment using cellulose-based adsorbent. The Yoon-Nelson model theoretically assumes that the reduction ability of the adsorbate to absorb will decrease with time [14]. This is a general adsorption concept so that this model can fit well into continuous dye adsorption experiment using cellulose-based adsorbent.

6. Conclusion
The prediction of methylene blue (MB) adsorption with composite beads in a continuous system has been carried out. At the same flow rate, CAB/PLLA (70/30) composite bead showed faster saturation time compared to CAB/PLLA (100/0). The higher the feed flow rate, the faster the beads will saturate. The longest saturation time, which is 90 minutes, was reached by CAB/PLLA (100/0) adsorbent bead at a flowrate of 7 mL/min. In overall, CAB/PLLA (100/0) has a higher adsorption capacity (q_0) when compared to CAB/PLLA (70/30). The higher the feed flow rate, the greater the adsorption capacity (q_s) will be achieved. The highest adsorption capacity of 46.733 mg/g was reached by CAB/PLLA (100/0) adsorbent bead at a flowrate of 23 mL/min. The error analysis revealed that the smallest error value between the predicted and experimental data were found in the Thomas and Yoon-Nelson adsorption kinetic model which is in average of 15.476%. It can also be stated that the Thomas and Yoon-Nelson models fitted well to the MB adsorption in continuous system onto cellulose-based adsorbent.

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