

## Mass Transfer Model for Basic Blue Adsorption onto Pillared Bentonite Clay by Taking Into Account the Intra Particle Concentration Gradient

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### Abstract

Bentonite clay, which was composed of alumina-silicate, is a low price commodity, widely available, and considered to be an effective sorbent having a high added value. Due to its large porosity, beside its potential as an adsorbent, bentonite is also very suitable to be used as catalysts and ion exchange materials. However, although it is very useful in many areas of application, it has limitations in maintaining its shape, due to its nature of easy to swell. Bentonite clays can swell due to hydration, deflate and even the structure of the clay can be damaged by dehydration and heating. To prevent this deformation, the interlayer region should be supported by a stable pillar. The other purpose of such modification is to create a large pore volume. In addition, it was also addressed to increase its ability of maintaining the porosity of bentonite clay despite hydration and dehydration occur. This process is called pillarization.

Volume element mass balance was developed for basic blue adsorption onto pillared bentonite clay by taking into account the intra particle concentration gradient. The relationship between the concentration of the adsorbate in the pore walls and the concentration of the adsorbate in the pore cavity was described by linear equilibrium equation which was expressed by Henry's law.

The aim of this research work is to develop a mass transfer model which is suitable for basic blue adsorption onto pillared bentonite clay by taking into account the intra particle concentration gradient and applying linear equilibrium equation. The suitability of the model was examined by using the data of laboratory experiments and analyzed quantitatively.

The effect of the bentonite pillarization was shown by the different surface appearance between original and pillared bentonite which was found on the scanning electron microscope images. In addition, the formation of basal spacing and area of intermellar was identified in the pillared bentonite. It was found that after pillarization the aluminium oxide content in bentonite clay increase to some significant extent, i.e. from 18.23 %w to 54.16 %w, which indicated that the pillarization process has strongly incorporated and tied the pillaring agent into the bentonite solid sheets.

Furthermore, larger pore volume was indicated by pillared bentonite which reflect increasing the surface area after pillarization. There has been a tremendous shift of pore size distribution dominates, from 0-20 Angstroms for the original bentonite to 20-500 Angstrom for pillared bentonite.

This research work has proven that the developed mass transfer model are suitable for basic blue adsorption onto pillared bentonite clay.

**Keywords:** Adsorption; Basic Blue; Bentonite; Clay; Modeling; Pillarization

### 1. Introduction

Bentonite clay, which was composed of alumina-silicate, is a low price commodity, widely available, and considered to be an effective sorbent materials having a high added value. Based on the mineral content, the clay can be divided into: smectite (montmorillonite), kaolinite, halloysite, chlorite and illite [Olphen et al., 1977]. Bentonite is a type of clay which has the ability to adsorb water and its cation exchange power much greater than the ordinary clay. Components of the dominant clay mineral in bentonite is montmorillonite. Montmorillonite has the chemical formula  $[Na_xAl(2-x)Mg_x(Si_4O_{10})(OH)_2] \cdot (H_2O)_m$ .

Montmorillonite clay minerals are a group that has a good ability to adsorb both the metal and the organic molecules. It also has an ability to inflate and deflate (swelling) and an exchangeable cation

[Pinnavaia, 1983]. Bentonite is a clay composed of alumina-silicate which consists of 3 layers, where a layer containing octahedral aluminum flanked between the other two layers containing tetrahedral silicate. This three layers form a sheet structure [Astrology, 2000].

Due to its large porosity, beside its potential as an adsorbent, bentonite clay is very suitable to be used as catalysts and ion exchange material. However, although bentonite clay is very useful in many areas of application, it has limitations in maintaining its shape, due to its nature of easy to swell. Clays can swell due to hydration, deflate and even the structure of the clay can be damaged by dehydration and heating. To prevent this deformation, the interlayer region should be supported by a stable pillar. The other purpose of such modification is to create a large pore volume. In addition, it was also addressed to increase its ability of maintaining the porosity of clay despite hydration and dehydration occur. This process is called pillarization [Robert et al., 1999].

Two main steps of the pillarization process were as follows, 1). Inserting a pillaring agent to the layer between the clay sheets, 2). Calcining the material to make the pillaring agent incorporated and tied into the solid sheets strongly. The so-called pillaring agent is any substance that can form the pillars on sheets of clay, so the clay becomes porous. While the insertion of these substances into the space between the sheets (interlayer), without changing the structure of the sheet called intercalation stage. Bentonite that has undergone a process of pillarization is called pillared bentonite clay [Robert et al., 1999].

To form a stable pillared bentonite with permanent porosity, the process of heating (calcination) need a great consideration. The best temperature range for calcination is between 300-500 °C [Barrer et al, 1978]. Pinnavia described that the calcination process at the temperature range makes the pillaring agent strongly bind to the bentonite clay sheets. This is indicated by the spectral data A1 MAS-NMS on smectite clays pillared with Al (Barrer et al, 1978). After experiencing pillarization, the pillared bentonite clay has expands vertically compared to prior pillarization, and can not return to the original form despite the dehydration happen [Robert et al., 1999].

Besides being able to expand vertically due to dehydration, other characteristics of pillared bentonite is having basal spacing at least 0.315 to 0.353 nm. The pillaring agent molecules are laterally in the area of intermellar which has porous characteristic. However, the basic criteria of pillared bentonite is having a good thermal and chemical stability and having a good distribution of the pillars in the intermellar region [Robert et al., 1999].

The aim of this research work is to develop a mass transfer model which is suitable for basic blue adsorption onto pillared bentonite clay by taking into account the intra particle concentration gradient and applying linier equilibrium equation. The suitability of the model was examined by using the data of laboratory experiments and analyzed quantitatively.

## 2. Theory and Experimental

### 2.1 Modeling

Since the pillared bentonite clay particles used in this research work is sphere-like shape, it was considered appropriate to assume the shape of pillared bentonite to be spherical shape, then the mass transfer model was developed using volume element mass balance for sphere:

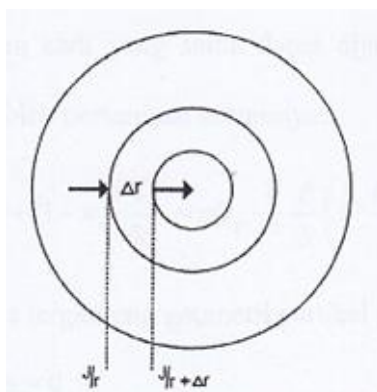


Figure 1. Volume element mass balance

$$M.in - M.out = M.acc \quad (1)$$

In differential form the mass balance could be expressed as:

$$\left( -De.4\pi r^2 \frac{\partial C}{\partial r} \right) - \left( -De.4\pi(r + \Delta r)^2 \frac{\partial C}{\partial r} \right) = 4\pi r^2 \Delta r \frac{\partial}{\partial t} (\epsilon C + C_{\mu} \rho_{ads}) \quad (2)$$

The Henry equilibrium relationship was expressed as:

$$C^* = HC_{\mu}; \quad C_{\mu} = \frac{C^*}{H} \quad (3)$$

Combination of equation (2) and (3) result in:

$$\frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) = \frac{\left( \epsilon + \frac{\rho_{ads}}{H} \right) \partial C}{De} \frac{\partial C}{\partial t} \quad (4)$$

Equation (4) is the general form of differential equation for adsorption of solut from liquid phase to solid sphere which was taken into account the intra particle concentration gradient. The above differential equations was solved using the finite dference approximation which its general form was expressed as:

$$C_{i,j+1} = \frac{\left(1 - \frac{1}{i}\right)}{P} C_{i-1,j} + \left(1 - \frac{2}{P}\right) C_{i,j} + \frac{\left(1 + \frac{1}{i}\right)}{P} C_{i+1,j} \quad (5)$$

$$P = M \left( \epsilon + \frac{\rho_{ads}}{H} \right) \quad (6)$$

$$M = \frac{(\Delta r)^2}{D_e \cdot \Delta t} \quad (7)$$

For a certain position in spherical shape, it is necessary to modify the general finite difference equations as follow:

At the centre of the sphere (i = 0),

$$C_{i,j+1} = \left(1 - \frac{6}{P}\right) C_{i,j} + \frac{6}{P} C_{i+1,j} \quad (8)$$

At the surface of the sphere (i = N (the number of the differential increament)),

$$C_{N,j} = \left( \frac{\beta}{1 + \beta H} \right) C_{AL} + \frac{1}{1 + \beta H} C_{N-1,j} \quad (9)$$

$$\beta = \left( \frac{k_c \cdot \Delta r}{D_e} \right) \quad (10)$$

Solute concentration in the liquid phase ( $C_{AL}$ ) was calculated using the equation:

$$C_{AL,j+1} = C_{ALo} - 4\pi \cdot N_p \int_0^R r^2 (C_{i,j}) dr \quad (11)$$

There are several methods available to solve the finite difference approximation such as explicit (forward), implicit ( backward) and Crank-Nicolson [Wahyudi Budi Sediawan and Agus Prasetya, 1997]. In this research work, the finite difference approximation equation was solved using explicit method. The suitability of the model was examined by evaluating the sum of squares of errors (SSE) which was expressed as:

$$SSE = \Sigma (C_{model} - C_{experimental})^2 \quad (12)$$

## 2.2 Experiment

Bentonite clay, which was originate from Pacitan, East Java – Indonesia, was treated following intercalation and pillarization method. The measurement of some physical properties such as density, total porosity, macro and micro pore size and surface area BET (Brunauer, Emmet, Teller) was conducted afterward. Cationic surfactant (HDTMA-Cl) was used in intercalation while sodium hydroxide and  $AlCl_3$  was used during pillarization process. The C.I. Basic Blue 41 under the trade name T/A Blue RGN-T 200% was used as adsorbate.

Intercalation is performed by preparing bentonite suspensions in which the ratio of bentonite/water = 1 gram/50 ml was applied and was diluted using distillate water to 1000 ml of total mixing volume. Surfactant was then added to the bentonite suspension and was stirred for 5 hours at a temperature of 80 °C. The weight ratio of surfactant/bentonite used was 1: 25. After being stirred for 5 minutes the solution was cooled briefly and was separated from the filtrate by a vacuum pump and then was dried in a laboratory scale oven at 100°C for 1 hour.

Pillaring agent was made by mixing NaOH and  $AlCl_3$ , in which the ratio of OH/Al was 0.8, at a temperature of 80 °C and was stirred until homogeneous mixing was reached. Intercalated bentonite suspensions was stirred and heated until the temperature reaches 80 °C. After that pillaring agent, ratio of Al/bentonite = 10 mmol/gram, was added gradually to a suspension of intercalated bentonite and stirred for 5 hours at 80 °C. After 5 hours, bentonite was separated from the filtrate using a vacuum pump and dried in an oven at 100 °C for 1 hour. Finally the bentonite was calcined at 500 °C in a laboratory scale furnace for 4 hours with a gradual increase to the calcination temperature every 15 minutes to avoid a collapse in the structure of pillared bentonite. To ensure uniformity, cool pillared bentonite powder then passed 100 mesh sieve prior the analysis of surface area BET and other physical and chemical characterization. Pore radius, pore surface area and pore volume was analyzed using NOVA Data Analysis Package Ver. 2.00, Quantachrome Corporation.

Adsorption test of Al pillared bentonite powder was performed using an artificial waste which was prepared by dissolve a basic blue dye in 500 ml distilled water. Experiments were conducted by varying the initial dye concentration and bentonite weight / solution volume ratio. During the batch experiment, the dye concentration change in liquid phase was detected by taking samples and measure the concentration using an UV spectrophotometer.

## 3. Results and Discussion

The scanning electron microscope (SEM) image of original and pillared bentonite was shown on Figure 2 and Figure 3, respectively. The effect of the pillarization treatment was shown by the different surface appearance of the two images. The pillared bentonite image showed clearly the formation of basal spacing and area of intermellar where the pillaring agent molecules are laterally distributed.

The result of the composition analysis of the original and pillared bentonite was shown on Table 1. It could be seen from the table that the mass fraction of aluminum oxide increased to some significant extent, i.e. from 18.23 %w to 54.16 %w. The increasing aluminum oxide content due to the infiltration of pillaring agent  $AlCl_3$ . Then, it indicated that the pillarization process has strongly incorporated and tied the pillaring agent into the bentonite solid sheets. While the mass fraction of some components including silicon dioxide, calcium oxide and ferro oxide decreased as consequent of increasing the aluminum oxide content.

Larger pore volume was detected on pillared bentonite which reflect increasing the surface area after pillarization. Accumulated pore volume and pore surface area were presented on Figure 4 and Figure 5, respectively. The figures showed clearly that the pillarization increased pore volume and pore surface, significantly. There has been a tremendous shift of pore size distribution dominates, from 0-20 Angstroms for the original bentonite to 20-500 Angstrom for pillared bentonite.

Figure 6 and Figure 7 displays basic blue concentration in the liquid phase by comparing the experimental data to the calculated value from the model for variations in the initial concentration. While Figure 8 and Figure 9 displays the same thing for variations in the ratio of mass of bentonite to volume of solution.

The parameters associated with the calculation of dye concentration, which include the distribution constant, external mass transfer coefficient and diffusivity coefficient, generated during solving the finite difference approximation were presented in Table 2 and Table 3.

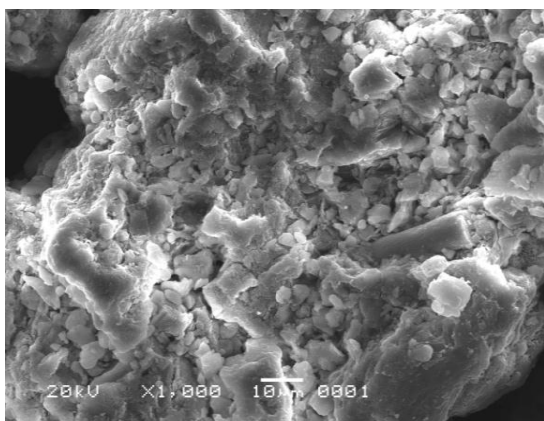


Figure 2: Scanning electron microscope image of original bentonite at magnification 1000x

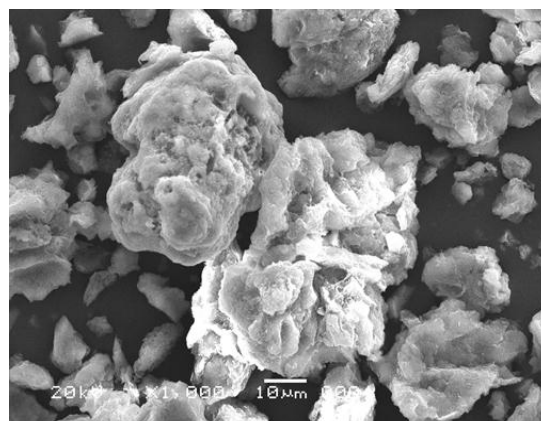


Figure 3: Scanning electron microscope image of pillared bentonite at magnification 1000 x

Table 1: The result of the composition analysis of original and pillared bentonite

Component	Original bentonite , %w	Pillarred bentonite , %w
Na <sub>2</sub> O	0,05	0.54
MgO	3.70	2.32
Al <sub>2</sub> O <sub>3</sub>	18.23	54.16
SiO <sub>2</sub>	68.69	40.91
CaO	3.90	0.06
TiO <sub>2</sub>	0.59	0.16
FeO	4.83	1.85

Analysis methode : SNI 0449-2010

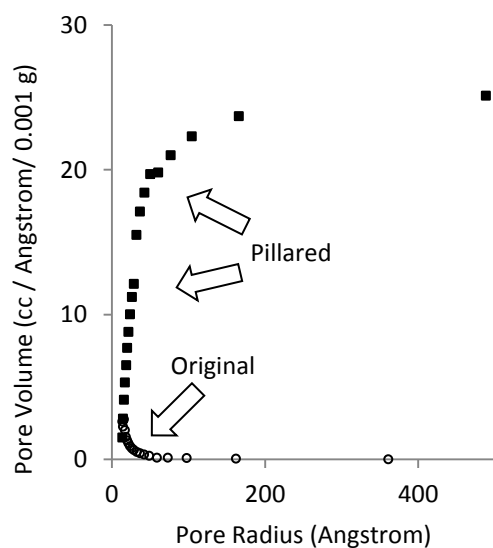


Figure 4: Accumulated pore volume versus pore radius of original and pillared bentonite clay.

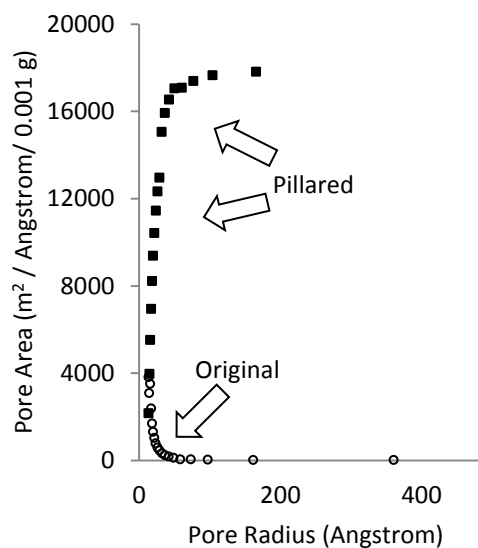


Figure 5: Accumulated pore surface area versus pore radius of original and pillared bentonite clay.

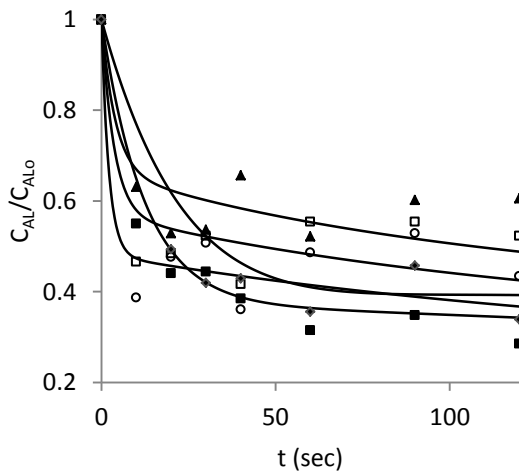


Figure 6: Basic blue concentration ratio in liquid phase versus time. The experimental data symbol for related initial concentration: ■ 100 ppm, ○ 200 ppm, ▲ 300 ppm, □ 400 ppm, ◆ 500 ppm. The curved line expressed the calculated result from the model. The mass ratio of bentonite/solution : 0.10 g/100 ml.

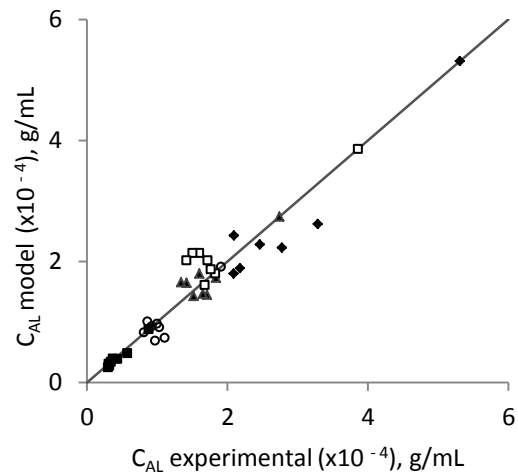


Figure 7: Basic blue concentration in liquid phase, model versus experimental data. The experimental data symbol for related initial concentration: ■ 100 ppm, ○ 200 ppm, ▲ 300 ppm, □ 400 ppm, ◆ 500 ppm. The mass ratio of bentonite/solution: 0.10 g/100 ml.

The distribution constants obtained from the experiments were in the range of  $0.9 \cdot 10^{-5}$  -  $1.9 \cdot 10^{-4}$  g/ml. Distribution constants for dye adsorption by bentonite was apparently not affected by the dye concentration in solution, while an increase in the ratio of bentonite/solution slightly lowering the distribution constant value as was shown on Table 2 and Table 3.

The external mass transfer coefficient ( $k_c$ ) vary in the range of 1.90 – 22.00 cm/s. It wasn't found a clear correlation between the external mass transfer coefficient and the initial dye concentration as well as the bentonite/solution ratio.

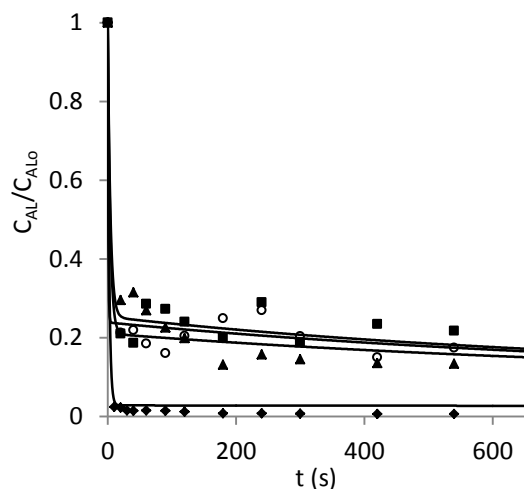


Figure 8: Basic blue concentration ratio in liquid phase versus time. The experimental data symbol for related bentonite/solution ratio: ■ 0.20 g/100 ml, ○ 0.25 g/100 ml, ▲ 0.35 g/100 ml, ◆ 0.40 g/100 ml. The curved line expressed the calculated result from the model. The initial concentration of basic blue 600 ppm.

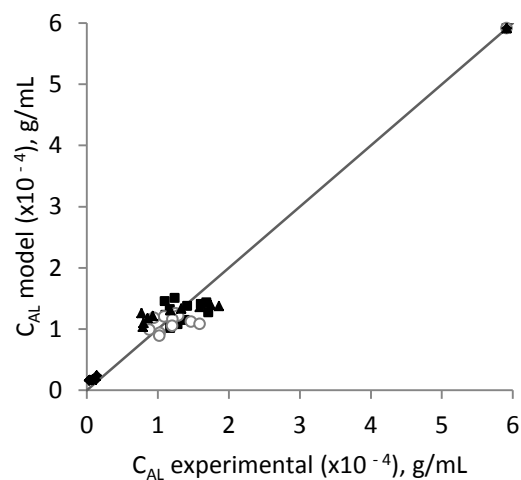


Figure 9: Basic blue concentration in liquid phase, model versus experimental data. The experimental data symbol for related bentonite/solution ratio: ■ 0.20 g/100 ml, ○ 0.25 g/100 ml, ▲ 0.35 g/100 ml, ◆ 0.40 g/100 ml. The curved line expressed the calculated result from the model. The initial concentration of basic blue 600 ppm.

Table 2: Distribution constant, external mass transfer coefficient, diffusivity coefficient and SSE at various initial dye concentration for bentonite/dye solution ratio 0.1g/100 ml

$C_{ALo}$ ppm	H g/ml	$k_c$ cm/s	$D_e$ cm <sup>2</sup> /s	SSE
100	$1.2 \cdot 10^{-4}$	7.60	$1.59 \cdot 10^{-3}$	$1.4 \cdot 10^{-10}$
200	$1.3 \cdot 10^{-4}$	17.98	$1.59 \cdot 10^{-3}$	$3.8 \cdot 10^{-10}$
300	$1.9 \cdot 10^{-4}$	19.00	$1.59 \cdot 10^{-3}$	$2.8 \cdot 10^{-9}$
400	$0.9 \cdot 10^{-4}$	22.00	$1.59 \cdot 10^{-3}$	$1.2 \cdot 10^{-8}$
500	$1.8 \cdot 10^{-4}$	6.43	$1.59 \cdot 10^{-3}$	$1.1 \cdot 10^{-8}$

Table 3: Distribution constant, external mass transfer coefficient, diffusivity coefficient and SSE at various bentonite/dye solution ratio for initial dye concentration 600 ppm

B/D g/ 100 ml	H g/ml	$k_c$ cm/s	$D_e$ cm <sup>2</sup> /s	SSE
0.20	$6.1 \cdot 10^{-5}$	6.50	$4.03 \cdot 10^{-4}$	$5.8 \cdot 10^{-9}$
0.25	$4.9 \cdot 10^{-5}$	5.85	$4.03 \cdot 10^{-4}$	$4.2 \cdot 10^{-9}$
0.35	$5.0 \cdot 10^{-5}$	18.00	$4.03 \cdot 10^{-4}$	$8.2 \cdot 10^{-9}$
0.40	$0.9 \cdot 10^{-5}$	1.90	$4.03 \cdot 10^{-4}$	$0.1 \cdot 10^{-9}$

Varying the initial concentration of dye at constant bentonite/solution ratio and varying the bentonite/solution ratio at constant initial dye concentration mean varying the dye concentration during the batch adsorption process. In fact, value of the diffusivities calculated from the experimental data was constant at  $1.59 \cdot 10^{-3}$  cm<sup>2</sup>/s for variation of the initial concentration in the range of 100 - 500 ppm at constant bentonite/solution ratio 0.1 g/100 ml and constant at  $4.03 \cdot 10^{-4}$  cm<sup>2</sup>/s for variation of bentonite/solution ratio in the range of 0.20 – 0.40 g/100 ml at constant initial concentration 600 ppm.

While value of the external mass transfer coefficient calculated from the same experimental data source vary, as shown in Table 2 and Table 3. It mean that a change of dye concentration might be result in a change of an eddy diffusivity and/or the thickness of liquid phase interface film, since an external mass transfer coefficient depend on both the eddy diffusivity and the thickness of liquid phase interface film.

The sum of squares of errors which was used to examine the suitability of the developed model was presented in Table 2 for initial dye concentration variation and in Table 3 for bentonite/solution ratio variation. The value were in the range of  $1.4 \cdot 10^{-10}$  -  $1.2 \cdot 10^{-8}$ . This low value of SSE indicates that the developed mass transfer model are suitable for basic blue adsorption onto pillared bentonite clay.

#### 4. Conclusion

The effect of the bentonite pillarization was shown by the different surface appearance which was found on the scanning electron microscope images. The formation of basal spacing and area of intermellar was identified in the pillared bentonite.

After pillarization, the mass fraction of aluminum oxide increased to some significant extent, i.e. from 18.23 %w to 54.16 %w. The increasing aluminum oxide content due to the infiltration of pillaring agent AlCl<sub>3</sub>. It indicated that the pillarization process has strongly incorporated and tied the pillaring agent into the bentonite solid sheets.

Larger pore volume was indicated by pillared bentonite which reflect increasing the surface area after pillarization. There has been a tremendous shift of pore size distribution dominates, from 0-20 Angstroms for the original bentonite to 20-500 Angstrom for pillared bentonite.

This research work has proven that the developed mass transfer model are suitable for basic blue adsorption onto pillared bentonite clay.

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## Nomenclature

$B/D$	bentonite/dye solution ratio (g / 100 ml)
$CAL$	solut concentration in liquid phase (mol/ml)
$CAL_0$	initial solut concentration in liquid phase (mol/ml)
$C^*$	solut concentration in liquid phase interface (mol/ml)
$C_{i,j}$	solut concentration at position $i$ at time $j$
$C_\mu$	solut concentration in solid (g/g solid)
$D_e$	diffusivity coefficient (cm <sup>2</sup> /s)
$H$	distribution constant (g/ml)
$k_c$	external mass transfer coefficient (cm/s)
$M.in$	rate of mass inflow (mol/s)
$M.out$	rate of mass outflow (mol/s)
$M.acc$	rate of mass accumulated (mol/s)
$N$	total number of particle
$R$	sphere radius (cm)
$r$	distance from the sphere center in radial direction (cm)
$t$	time (s)
<i>Greek letters</i>	
$\varepsilon$	particle porosity
$\rho_{ads}$	adsorbent density (g/ml)

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