



Modeling and Simulation of Methylene Blue Batch Adsorption Using *Jatropha Curcas L.* Residue-Based Activated Carbon by Shrinking Core Model

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Abstract

Physic nut residue is one of bio-wastes which contains enough carbon can be processed further into other products with higher usage and economical value. One of the products is activated carbon which used commonly in chemical industry. Information regarding the kinetics describing mechanism and characteristic of adsorption using physic nut residue-based activated carbon can be obtained through modeling. Model used in this research are Pore-Surface Diffusion Model (PSDM) and Film-Pore Diffusion Model (FPDM) derived based on shrinking core model. This research begins with estimating the value of k_f , D_s , and D_p parameters which later will be validated and simulated using various correlations and the model. Variations are done towards three variables: initial aqueous phase concentration (C_0), pH value, and adsorbent types. The result shows PSDM is more accurate in representing the mass transfer characteristics of methylene blue adsorption using activated carbon synthesized from physic nut residue because the model prediction fit the experimental data better than the FPDM. The value of D_s ranged from 3, 99E-14 to 7, 66 E-14 while the value of D_p ranged from 9, 98E-13 to 2, 82E-12 . It is also found that value of D_s and D_p are affected by variables mentioned before.

Keywords: adsorption, carbon, model, shrinking

Introduction

Adsorption is a separation process which plays a key role in modern industries, especially in the field of environmental engineering. Adsorption processes are being employed for large scale chemical recovery and purification applications. Adsorption operations are mainly concerned with the ability of adsorbents to selectively concentrate substances from solution onto their surfaces, such as the moisture removal of gasoline, decolorization of petroleum products, and the removal of pollutants from effluents. (Seader, *et.al.*,2010)

The design stage of adsorption system requires information regarding the kinetics of the adsorption process, usually obtained through experiments. Model implementation to adsorption process is done to understand the equilibrium, kinetics, and capacity of the adsorbent based on equation that will be constituted and used.

Models that will be used in this study are two-resistance diffusion model based on shrinking core model. Shrinking core model itself assumes the saturation layer (pores that were already occupied by fluid molecules) will move towards the center of the adsorbent particle for a certain amount of time, leaving an infinitely small, shrinking unreacted core. The first model assumes the rate determining steps are pore and surface diffusion; hence the model is called *Pore-Surface Diffusion Model* (PSDM). The other model assumes film and pore diffusion are the rate determining steps; hence the model is called *Film-Pore Diffusion Model* (FPDM). The study is conducted in order to acquire the best model which is capable of representing the batch adsorption of methylene blue using activated carbon synthesized from physic nut residue.

Methodology

Adsorption is a process which a fluid is bound in the surface of a solid (adsorbent). The mass-transfer mechanisms on a typical adsorption process are happened on four steps:

- Convective transport of fluid to interphase boundary layer (film).;
- External mass transport of fluid from film to the outer surface of adsorbent;
- Internal transport of fluid from the outer surface of adsorbent to the inner surface of adsorbent through pores.

This process consists of two sub-steps:

- Pore diffusion, in which the fluid diffuses towards the interior of the adsorbent's pores;
 - Surface diffusion, in which the fluid diffuses towards the inner surface of the adsorbent through the pores.
- Adsorption of the fluids on the adsorbent's surfaces. (Worch, 2012)

Pore Surface Diffusion Model (PSDM)

The basic assumptions in establishing this mass-transfer-based model are: (Chen *et.al.*, 2001.)



- The mass-transport resistance in the particle external boundary layer is negligible.
 - Pore and surface diffusion are the two rate-controlling mechanisms in this model.
 - The adsorption process itself is done rapidly and is not involved in the rate-controlling mass-transfer process.
- The equations used in the PSDM based on shrinking core model are represented:

- Fluid mass balance at time t

$$W \frac{K_L C_{s,t} R^3 - r^3}{1 + \alpha_L C_{s,t} R^3} = V(C_0 - C_{s,t}(t)) \quad (1)$$

$$C_{s,t}(t) = C_{(t),model} \quad (2)$$

- Molecular diffusion rate in terms of shrinking core radius

$$dr = \frac{D_{eff} R(1 + \alpha_L C_{s,t}(t))}{r \rho_s K_L (r - R)} dt \quad (3)$$

$$t = 0, r = R$$

- Correlation between D_{eff} with D_p and D_s

$$D_{eff} = D_p + \rho_s D_s \frac{K_L}{(1 + \alpha_L C_{s,t}(t))^2} \quad (4)$$

Film-Pore Diffusion Model (FPDM)

The basic assumptions in establishing this mass-transfer-based model are: (Cheung, *et.al*, 2002.)

- Film and pore diffusion are the two rate-controlling mechanisms in this model.
 - The adsorption process itself is done rapidly and is not involved in the rate-controlling mass-transfer process.
- The equations used in the FPDM based on shrinking core model are represented:

- Fluid mass balance at time t

$$C_{s,t}(t) = \left\{ \left(\alpha_L C_0 - \left(\left[1 + \frac{D_{eff} r}{k_f R (R-r)} \right] + K_L R_m \right) \right) + \left[\left(\alpha_L C_0 - \left(\left[1 + \frac{D_{eff} r}{k_f R (R-r)} \right] + K_L R_m \right) \right)^2 + 4 \alpha_L \left[1 + \frac{D_{eff} r}{k_f R (R-r)} \right] C_0 \right]^{\frac{1}{2}} \right\} / 2 \alpha_L \left[1 + \frac{D_{eff} r}{k_f R (R-r)} \right] \quad (5)$$

$$R_m = \left(1 - \left(\frac{r}{R} \right)^3 \right) \left(\frac{W}{V} \right) \quad (6)$$

$$C_{(t),model} = \left[1 + \frac{D_{eff} r}{k_f R (R-r)} \right] C_{s,t}(t) \quad (7)$$

- Molecular diffusion rate in terms of shrinking core radius

$$dr = \frac{D_{eff} R(1 + \alpha_L C_{s,t}(t))}{r \rho_s K_L (r - R)} dt \quad (3)$$

$$t = 0, r = R$$

$$D_{eff} = D_p \quad (8)$$

Kinetics and isotherms parameter data used in this study are obtained from experiment conducted by Kurniawan and Ismajji, 2011. Adsorbent that will be used are parent activated carbon which is not thermally or chemically activated (coded as JAC-1) and the other one which chemically activated using nitric acid (coded as JAC-2). Kinetics experiment is done at 30°C using adsorbent dosage of 0,6 gram and conducted for 7 hours in stirred batch vessel agitated at 500 rpm. Variations are done towards three initial aqueous phase concentration values (0,2; 0,5; 0,8 kg/m³) and three pH values (3, 7, and 11) using both adsorbents.

This study is consisted of three main steps: 1) parameters estimation which will be used in the 2) validation step, then the validated parameters will be used in 3) simulation step. Parameters that will be studied are surface diffusivity (D_s) and pore diffusivity (D_p) for PSDM and film diffusion coefficient (k_f) and pore diffusivity (D_p) for PFDM.

The parameter estimation is done on both adsorbents at concentration value of 0,2 and 0,8 kg/m³ and all pH value. Validation step is done on both adsorbent at concentration value of 0,5 kg/m³ and pH value of 7 and 11. Lastly, the simulation is done on all estimated and validated data.

The equations in this study are integrated numerically to obtain the value of aqueous phase concentration predicted by model. The parameters are obtained after evaluation through numbers of iteration performed to

minimize the error (sum of squares of differences between the value of aqueous phase concentration predicted by model and the value of aqueous phase concentration from the data).

Result and Discussion

Parameter Estimation Using PSDM

Parameters for JAC-1 and JAC-2 are estimated using PSDM for initial aqueous phase concentration values (C_0) of 0,2 and 0,8 kg/m^3 and pH values of 3,7, and 11.

Table 1. Parameters Estimation Using PSDM

	JAC-1				JAC-2			
	D_s (m^2/s)	D_p (m^2/s)	Error	R^2	D_s (m^2/s)	D_p (m^2/s)	Error	R^2
pH 3								
0.2	5,23E-14	1,98E-12	1,10E-03	0,9677	5,56E-14	1,71E-12	1,07E-03	0,9988
0.8	6,76E-14	2,12E-12	9,33E-04	0,9767	7,02E-14	2,04E-12	1,13E-03	0,9976
pH 7								
0.2	6,01E-14	1,99E-12	1,21E-04	0,9999	3,99E-14	9,98E-13	1,14E-03	0,9787
0.8	7,22E-14	2,21E-12	1,14E-04	0,9998	5,79E-14	2,82E-12	8,91E-04	0,9979
pH 11								
0.2	9,46E-15	2,15E-12	2,91E-04	0,9697	6,53E-14	1,99E-12	1,02E-03	0,9980
0.8	5,25E-14	2,71E-12	1,92E-04	0,9997	7,66E-14	2,21E-12	1,01E-03	0,9967

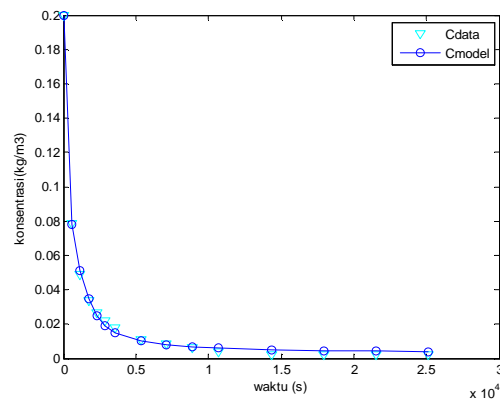


Figure 1. Estimation curve using PSDM for JAC-1 at $C_0=0,2 \text{ kg/m}^3$ and pH 7.

Figure 1. shows that the model prediction fits the experimental data. This result implies that PSDM can represent the adsorption mechanism of methylene blue in activated carbon synthesized from *Jatropha curcas L.* According to the condition used in the model, the diffusion in this adsorption system is controlled by the pore and surface diffusion step. (Chenet.*al.*, 2001)

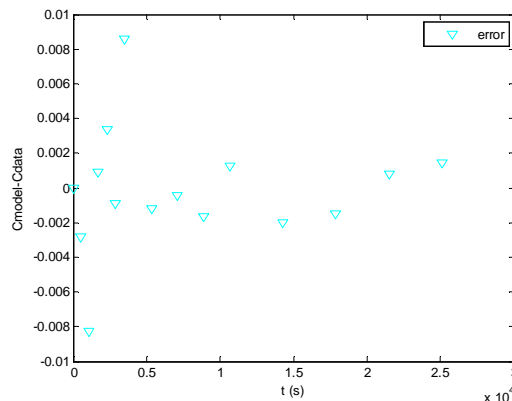


Figure 2. Residual plot of PSDM for JAC-1 at $C_0=0,2 \text{ kg/m}^3$ and pH-7.

In order to analyze the model's accuracy further, error analysis is done by using residual plot. It is shown in **Figure 2**. that the error produced by model can be classified as random error. Random error implies that the model is sufficient in describing the characteristics of adsorption system's mechanism. (Chapra, 2002)

Parameter Validation Using PSDM

Estimated parameters are then validated using the set of data at $C_0=0,5 \text{ kg/m}^3$ for pH value of 7 and 11 for both type of adsorbents.

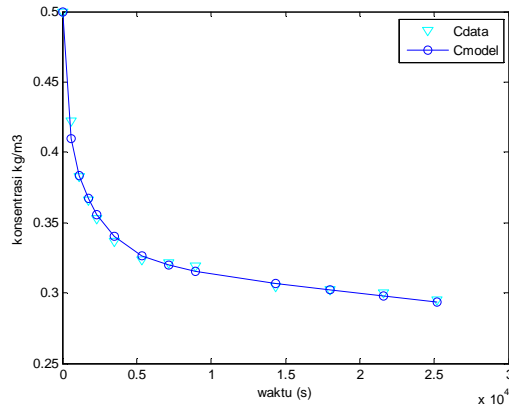


Figure 3. Validation curve using PSDM for JAC-1 at $C_0=0,5 \text{ kg/m}^3$ and pH 7.

Figure 3. shows that the parameter values estimated by the PSDM are valid for the three C_0 values because the aqueous phase concentration value predicted by the model fits the data. Estimated parameters value (both D_s and D_p) at initial aqueous phase concentration value of 0,2 and 0,8 kg/m^3 are correlated using the following equation: (Dannyet. al, 2002)

$$\log D_s = \log D_{s,w} + n \log C_0 \quad (9)$$

to acquire the parameter value at initial aqueous phase concentration value of 0,5 kg/m^3 .

Adsorption Simulation Using PSDM

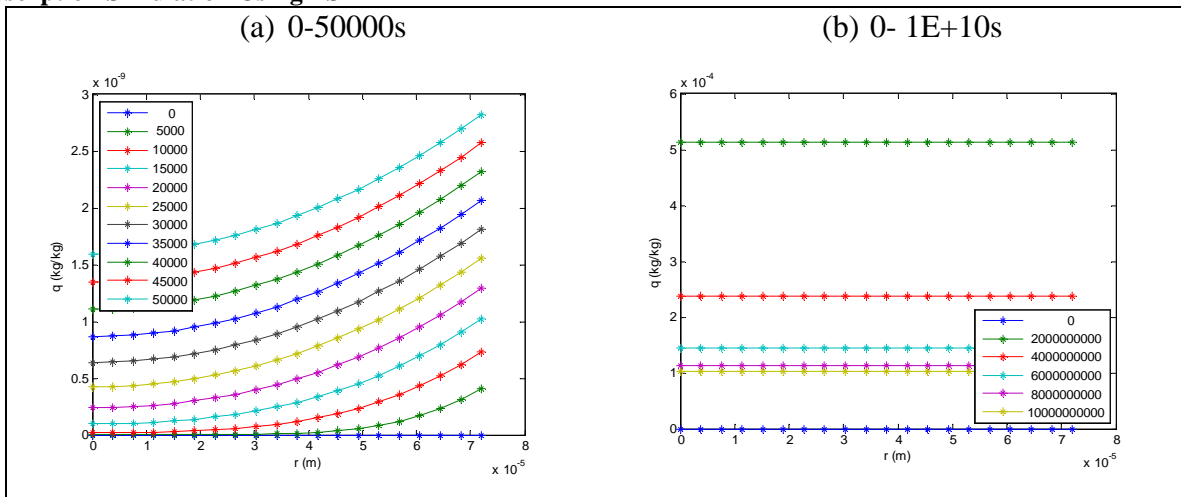


Figure 4. Solid phase concentration vs radius for various times at $C_0=0,2 \text{ kg/m}^3$ & pH 7 for JAC-1 for early time. (a) shorter time, (b) longer time

Figure 4(a). shows that the diffusion is slow at the beginning of the adsorption and gradually increasing its rate and becoming faster as the time went by. It is also found that that the solid phase concentration values are larger in the outer parts (surface) of the adsorbent, indicated by the bigger value of radius (r). This indicates that plenty solute molecules are held at the surface than the adsorbent's interior at the beginning stage of the adsorption. This justifies surface diffusion as the rate-controlling in this adsorption system's mass-transfer mechanism. (Seader. et.al., 2010)

Figure 4(b). is same as **Figure 4(a).** but for a longer period of time, assumed reaching the equilibrium. It is shown that there is no difference in the solid phase concentration at equilibrium for different values of radii. This result indicates the equilibrium is reached when the adsorbent is saturated, filled completely with fluid molecules in every

possible adsorption sites. It is also shown that the curve's gradient value will get larger over time and will become smaller again until the gradient's value reaches zero, implying the system has reached equilibrium and no more solute diffusing from aqueous phase (solution) to the solid phase (adsorbent). (Seader *et al.*, 2010)

Parameter Estimation using FPDM

The same data sets estimated using PSDM are also estimated using FPDM. The result is shown at **Figure 7**.

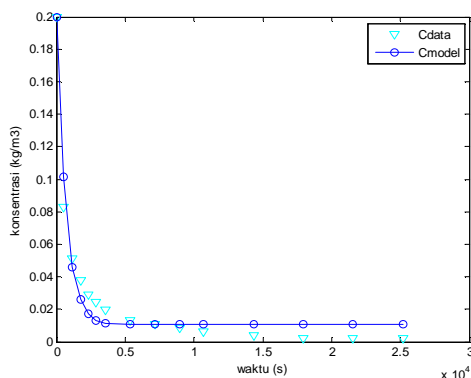


Figure 5. Estimation Curve using FPDM for JAC-2 at $C_0=0,2 \text{ kg/m}^3$ and pH 7.

It is shown **Figure 5**, that the C_0 values predicted by FPDM don't sufficiently fit the experimental data. Deviations (errors) are observed at the curve's turning point and also the equilibrium tail. Assumption used in FPDM is the rate-controlling steps are employed by film diffusion and pore diffusion. The inaccuracy showed by FPDM prediction can be contributed by the mismatching assumption. In the real experiment condition, the adsorption mixture in the vessel is agitated at 500 rpm for 7 hours. Agitation will cause the mass-transfer resistance caused by interphase film layer between methylene blue solution and JAC adsorbent become minimal to the degree its magnitude is negligible, allowing the fluid molecules diffuse quickly through the film towards the adsorbent's surface and interior (Kurniawan, Ismadji, 2011).

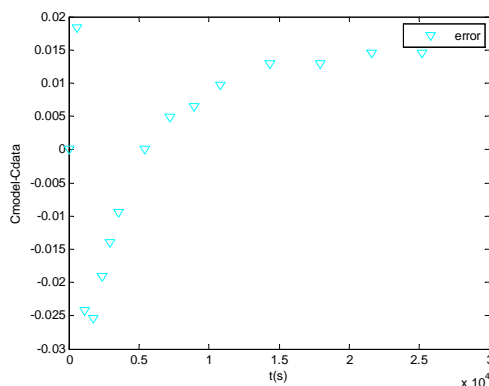


Figure 6. Residual plot of FPDM for JAC-1 at $C_0=0,2 \text{ kg/m}^3$ and pH-7.

Further analysis using residual plot is also done towards aqueous phase concentration values predicted by FPDM. As shown in **Figure 7**, the errors follow a certain pattern. The errors start as negative error followed by positive error. It is also observed that the errors have an increasing trend in its value. This so-called error is categorized as systematic or formulation error. This kind of error indicates there is a lacking or mismatching assumption or mechanism in constituting or formulating the model. The lacking mechanism is assumed to be the surface diffusion step. The accuracy of FPDM can be improved by incorporating the surface diffusion part to the FPDM equations. (Chen, *et al.*, 2001)

Effect of C_0 and pH on D_s and D_p

Results shown in **Table 1** indicates certain tendencies between the diffusivities parameters with C_0 and pH values. It is shown that the value of D_s and D_p are proportional to the value of C_0 . This result agrees with the experiment conducted by Danny, *et al.* (whose correlation is used in this study), as shown by equation (9).

It is also found that the value of D_s and D_p are also proportional to the value of pH. At higher value of pH, methylene blue (which are basic in nature) is easier to be bound in activated carbon's adsorption site which is acidic in nature. The acidic nature of activated carbon (especially chemically activated JAC-2 using nitric acid) is contributed by its surface chemistry which rich in carboxylic functional group. The acidic JAC is easier to bind the



basic methylene blue molecules thanks to the additional electrostatic interaction due to differences in the pH of both phases. The higher the value of the pH, the greater the electrostatic interaction generated. Kinetically, this phenomenon is shown in the increasing value of D_s and D_p . (Kurniawan, Ismadji, 2011)

Conclusion

1. Pore and surface diffusion is the rate-controlling steps in mass-transfer of methylene blue adsorption using activated carbon synthesized from *Jatropha curcas L.*
2. The value of D_s and D_p are proportional to C_0 and pH value.
3. The value of D_s and D_p are also affected by the type of the adsorbent.

Nomenclature

a_L	Langmuir constant	(m^3/kg)
C_0	initial aqueous phase concentration	(kg/m^3)
$C_{e,(t)}$	equilibrium aqueous phase concentration at time t	(kg/m^3)
$C_{(t)}$	aqueous phase concentration at t	(kg/m^3)
D_{eff}	effective diffusivity	(m^2/s)
D_p	pore diffusivity	(m^2/s)
D_s	surface diffusivity	(m^2/s)
$D_{s,0}$	surface diffusivity at $C_0=0$	(m^2/s)
k_f	film diffusivity	(m/s)
K_L	Langmuir constant	(m^3/kg)
$q_{(t)}$	solid phase concentration at t	(kg/kg)
R	adsorbent radius	(m)
R_m	fraction of unreacted core radius	(m)
$r_{(t)}$	unsaturated adsorbent radius at t	(m)
t	time	(s)
V	solution volume	(m^3)
W	adsorbent mass	(kg)
Greek letter		
ρ_s	adsorbent density	(kg/m^3)

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Lembar Tanya Jawab

Moderator : Didi Dwi Anggoro (Universitas Diponegoro Semarang)

Notulen : Susanti Rina Nugraheni (UPN "Veteran" Yogyakarta)

1. Penanya : Didi Dwi Anggoro (Teknik Kimia Universitas Diponegoro Semarang)
- Pertanyaan :
- Cara mengukur methylene blue?
 - Model grafik untuk *shrinking core* yang seharusnya ditampilkan adalah di padatan.
 - R dan r apa bedanya?
- Jawaban :
- Dari penelitian sebelumnya di dalam reaktor batch 7 jam, diambil menggunakan pipet kemudian dicek menggunakan spektrofotometer.
 - Diagram yang digunakan pada cairan.
 - R : radius
r : posisi pada saat t, saat t=0 R=r.

