Breakthrough Adsorption Study of Crude Oil Removal Using Buffing Dust

L W N Setyaningsih¹, A T Yuliansyah¹, A Prasetyo², S K Arimanintan² and D R Putri²
¹Department of Chemical Engineering, Islamic University of Indonesia, Yogyakarta, INDONESIA
²Department of Chemical Engineering, Gadjah Mada University, Yogyakarta, INDONESIA
lucky.nuzulia@uii.ac.id

Abstract. The utilization of leather industry solid waste as adsorbent to separate oil from water emulsions of surfactant flooding process is a solution that is relatively inexpensive. This study was conducted aiming to obtain a mathematical model that is appropriate for the adsorption process of crude oil by buffing dust in emulsion phase with a continuous adsorption method. Variations in the column adsorption experiments were carried out, such as: flow rate of feed of water-crude oil-surfactant, the concentration of crude oil in the feed, and mass of adsorbent used. Data were evaluated using three models: Adams Bohart, Thomas and Yan. Best results are obtained on the following conditions, the feed flow rate of 60 mL/minute, the crude oil concentration in feed is 1.5% volume and the mass of adsorbent used was 10 g. The values of kinetic constant and adsorption capacity obtained from Yan Model was 21.7774 mL/mg/minute and 220.9581 mg/g with the relative error obtained is 5.4424%.

1. Introduction
Buffing dust is another issue faced by every leather industry, therefore it need an effort to deal with the solid waste pollution. This solid waste contains chromium as 27 g/kg of buffing dust, synthetic fats, oils, tanning agents, chemical dyes. Buffing dust is a microfined solid particulate impregnated with trivalent chromium (Cr³⁺) and potentially converted into hexavalent chromium (Cr⁶⁺) during the incineration at temperature 800°C[1]. This waste causes clinical problems like respiratory disease, allergic dermatitis, kidney malfunction and lung cancer if ingested or inhaled by human [2]. Disposal of buffing dust should not be done carelessly, because there is a standard of maximum chromium concentration that permitted, which is in soil were 714 mg / kg of soil and in groundwater were 0.25 mg / L[1].

The density of buffing dust is relatively small, 0.05 g/cm³, which indicates that the buffing dust has a large pore volume. Buffing dust generated from the leather industry has a porous surface and a good candidate to be used as an adsorbent [3]. Buffing dust can be used as an adsorbent to separate oil from water emulsions of surfactant flooding process. The utilization of leather industry solid waste as adsorbent is a solution that is relatively inexpensive because the adsorbent used is waste that has been unused and can obtained at a low price or even free, and the process is simple. Similar studies done by Gammoun [3] was analyzed factors that affect the sorption of crude oil using buffing dust in batch systems. The study resulted several conclusions as follows, buffing dust has high selectivity to crude oil sorption than water sorption, adsorption of crude oil into buffing dust occurs spontaneously and was not influenced by time, the sorption capacity of crude oil by buffing dust about
0.9844 g / g adsorbent. Other results showed that the salinity in sea water has no effect on the adsorption process.

This study was conducted aiming to obtain a mathematical model that is appropriate for the adsorption process of crude oil by buffing dust in emulsion phase with a continuous adsorption method. Variations in the column adsorption experiments were carried out, such as: flow rate of feed of water-crude oil-surfactant, the concentration of crude oil in the feed, surfactant concentration, and mass of adsorbent used. The kinetic and dynamic behaviours of the adsorption process were then evaluated to study the adsorption mechanism of crude oil molecules onto buffing dust.

2. Material and Method

The material used in this research were buffing dust that were supplied by PT. Nike Indonesia, this solid waste was not purified prior to use, crude oil used in this research was obtained from wells P-14 Rantau, Sumatera, Indonesia, Sodium Lauryl Sulfate were supplied by CV. Brataco Chemical, Yogyakarta, Indonesia.

The research method is as follows, the feed with certain concentration of crude oil (1%, 1,5% and 2% volume) and surfactants (2% volume) as much as 4 L was loaded into the container and then flowed with the desired flow rate of (60 mL/min, 100 mL/min, 125 mL/min) into adsorption pond with a diameter of 4 cm containing buffing dust and marbles. Every few minutes 10 mL sample was taken to measure the crude oil concentration by using spectrophotometer UV-Vis. The flow was stopped when the column has been saturated. All the experiments were carried out at room temperature. Data were evaluated using three models: Adams Bohart, Thomas and Yan. Model Adams-Bohart written in linear form as follows[4]:

\[
\ln \frac{C}{C_0} = k_{AB} C_0 t - k_{AB} q_{AB} \frac{z}{U}
\]  

(1)

Where \( C \) is the concentration of crude oil in the effluent after passing through the adsorption column, \( C_0 \) is the concentration of crude oil in the effluent before adsorption, \( k_{ab} \) is the kinetic constant on the model of Adams-Bohart, \( t \) is time of draining waste, \( q_{ab} \) is the adsorption capacity, \( z \) is the position of the axial direction in columns and \( U \) is the flow rate of the waste through the column. Thomas Model is written as follows[5]:

\[
\ln \left( \frac{C_0}{C} - 1 \right) = \frac{k_{Th}}{Q} q_{Th} W - k_{Th} C_0 t
\]  

(2)

Where \( k_{th} \) is the kinetic constant of Thomas model, \( Q \) is the discharge of liquid through the column, \( q_{th} \) is the adsorption capacity and \( W \) is mass of buffing dust. Yan Model in pokhrel and viraraghavan[6] proposed an empirical equation that can overcome Thomas model weaknesses, especially thomas models in predicting the effluent concentration at time of zero. Yan Model is written as follows:

\[
\ln \left( \frac{C}{C_0 - C} \right) = a \ln V - a \ln f
\]  

(3)

\[
f = \frac{k_Y q_Y W}{Q}
\]  

(4)

\[
a = \frac{k_Y C_0}{Q}
\]  

(5)

Where \( V \) is the volume of waste, \( k_Y \) is the kinetic constant on Yan model, and \( q_Y \) is the adsorption capacity.
3. Result and Discussion
The result of oil sorption on buffing dust using continuous system presented in form of curves between ratio of the outlet crude oil concentration to inlet crude oil concentration as a function of time (C/C₀ vs t).

3.1. Effect of initial crude oil concentration
The effect of crude oil concentration in the feed is shown in figure 1. It shown that the lower concentration of crude oil provides breakthrough curve which increasingly ramps, it indicates that the volume of solution that can be passed through the column until the occurrence of the saturation was higher as the decreasing concentrations of crude oil. This is due to a decrease in the concentration of crude oil in the feed led to more displacement than the adsorbate molecules from body fluids to the surface of the adsorbent so that the mass transfer coefficient and diffusion will decrease. At the highest crude oil concentration which is 2% by volume, the adsorbent reached saturation in the shortest period of time which is less than 20 minutes. The higher the concentration of crude oil in the feed will give acceleration to reach saturated conditions by buffing dust. This is due to the increasing number of adsorbent surface which is covered by adsorbate molecules. Adsorption capacity will rise with increasing concentration of crude oil in the feed, due to large differences in concentrations that produce a driving force of the adsorption process. At the beginning of the curve it shows that C/C₀ incline sharply, suggesting that in these experiments the axial diffusion is quite affecting.

![Figure1. Breakthrough curves for crude oil sorption on buffing dust at different initial crude oil concentration](image)

3.2. Effect of emulsion flowrate
The effect of solution flowrate shown in figure 2. The increasing flow rate of the feed stream generating capacity in reducing crude oil was higher and the time to reach saturation was faster. Figure 2 show that the greater the velocity of solution will produce a ramps breakthrough curve. The amount of solution that can be streamed in the column until it reaches saturation will increase along with rising mass used buffing dust. This is because the molecules adsorbed crude oil increased. At low flow rates adsorption capacity is also low due to the retention time in the column is not sufficient for the diffusion of crude oil into the pores of buffing dust. It is because the molecules of crude oil left column before equilibrium conditions occur.
3.3. Effect of mass of adsorbent

The effect of mass of adsorbent shown in figure 3. Figure 3 shows that the greater the mass of buffing dust used, the longer time required to reach the saturation and the greater the volume of solution that may be passed through would be. This is due to the greater mass of adsorbent, the surface area available for adsorption of crude oil on the surface of the adsorbent more. The mass of adsorbent used will affect the high bed, the lower the mass of adsorbent used the height of the bed will be decreased so that the residence time of molecules of crude oil in the column is shorter and therefore the time available was not enough for the molecules of crude oil to diffuse into the pores of the adsorbent.

3.4. Breakthrough curve study

The data were fitted to three kinetics models and verified with the sum of error squares (SSE %). Comparison between the experimental data with the three models shows that Yan Model fit to a whole range of values of $C/C_0$. Thomas Model is just fit for the area of final breakthrough curves, whereas the Adams Bohart model is not good enough to describe the region early breakthrough curve. The calculation result of $k_{ab}$ and $q_{ab}$ from equation 1, $k_h$ and $q_h$ from equations 2 and $k_y$ and $q_y$ from equation 3 are summarized in Table 1. Table 1 show that the concentration of crude oil increased the value of adsorption capacity of the column using Yan and Thomas Models ($q_a$ and $q_y$) decreased, while the Adams-Bohart Model has tendency to increase. In another study showed the different trend, where adsorption capacity increase with increasing solute concentration. It is because that in high difference concentrations provide greater driving force to the adsorption process in order to achieve higher capacity. Similarly, the kinetic constant for Yan and Thomas Models ($k_h$ and $k_y$) decreased.
when the crude oil concentration increased, while the kinetic constant of Adams-Bohart Model increased. This may occur because of the emulsion solution characteristic. The emulsion contains surfactant that make emulsion become more stable, which decreases the adsorption capacity of adsorbent. Also emulsion becomes less hydrophobic and therefore the contact between adsorbent and solute decreases[7].

**Table 1. Parameter of Yan, Thomas and Adams-Bohart Model for Crude oil Concentration Variation**

| Crude Oil Concentration (%vol) | Yan | Thomas | Adams-Bohart |
|-------------------------------|-----|--------|--------------|
|                               | $k_Y$ | $q_Y$ | SSE % | $k_Th$ | $q_Th$ | SSE % | $k_{AB}$ | $q_{AB}$ | SSE % |
| 2%                            | 15.25 | 15.04 | 8.05  | 0.01   | -206.36 | 271.37 | 0.003   | 171.69   | 15.07 |
| 1.5%                          | 21.78 | 20.96 | 5.44  | 0.02   | -42.29  | 233.40 | 0.004   | 145.37   | 10.90 |
| 1%                            | 36.53 | 40.11 | 7.65  | 0.03   | 83.73   | 168.50 | -0.0001 | -3260  | 32.01|

SSE 7.05  SSE 224.43  SSE 19.33

The SSE of Yan Models is 7.048%. smaller than SSE resulted in Thomas and Adams-Bohart Models. Table 2 shows that the kinetic constant of Adams-Bohart, Thomas and Yan Model increases with the increasing of flow rate of the solution stream. This indicates that the kinetic constant of Adams-Bohart, Thomas and Yan showed that mass transfer resistance in the liquid is not negligible. On the other hand, with flowrate increasing the adsorption capacity using Yan and Adams-Bohart increase while the Thomas model result different trend where lower flow rate would increase the adsorption of crude oil on the buffing dust.

**Table 2. Parameter of Yan, Thomas and Adams-Bohart Model for Flowrate Variation**

| Flowrate (mL/min) | Yan | Thomas | Adams-Bohart |
|-------------------|-----|--------|--------------|
|                   | $k_Y$ | $q_Y$ | SSE % | $k_Th$ | $q_Th$ | SSE % | $k_{AB}$ | $q_{AB}$ | SSE% |
| 60                | 15.2866 | 15.0731 | 6.7355 | 0.0145 | -169.021 | 266.8574 | 0.0033   | 159.8112 | 11.5702 |
| 80                | 34.6530 | 34.1430 | 11.1886 | 0.0227 | -201.646 | 92.1001  | 0.0033   | 220.8782 | 14.1670 |
| 120               | 63.5292 | 57.8637 | 8.8749 | 0.0303 | -534.428 | 59.9419  | 0.0017   | 315.6504 | 7.8136 |

SSE 8.9321  SSE 139.6331  SSE 11.1836

As the mass of adsorbent increased, the value of adsorption capacity increased for both of Thomas and Adams-Bohart Model, while the value of adsorption capacity for Yan Model decreased. This was due to the greater mass of adsorbent the closer the distance between the grains buffing dust would be. Thus there were overlaps resulting adsorbent surface in contact with the liquid is getting smaller. The kinetic constant for Yan and Thomas Models decreased with increasing of mass of adsorbent, but increased for Adams-Bohart Models.

The assumptions used in the Adams-Bohart Model that axial dispersion is negligible cannot be applied in this experiment. The experimental results show that the macroscopic properties of the buffing dust affect the kinetic constant so that the phase in the column cannot be considered pseudo homogeneous. Likewise, the assumptions used in Thomas model, in which the axial dispersion is negligible and Thomas model derivation are based on a second order reaction kinetics cannot be applied in this experiment because the mass transfer of prisoners greatly influence the determination of kinetic constants. Meanwhile the model formulated to improve Thomas model in describing the area of early breakthrough curve.

Best results are obtained on the following conditions, the feed flow rate of 60 ml/min, the crude oil concentration 1.5% volume and the mass of adsorbent used was 10 g. The values of kinetic constant and adsorption capacity obtained from Yan Model were 21.7774 mL/mg/minute and 220.9581 mg/g with the relative error obtained is 5.4424%.
Table 3. Parameter of Yan, Thomas and Adams-Bohart Model for Mass of Adsorbent Variation

| Mass of buffing dust (grams) | Yan  | Thomas | Adams-Bohart |
|------------------------------|------|--------|--------------|
|                              | k_Y | q_Y   | SSE %  | k_m | q_m | SSE. % | k_AB | q_AB | SSE. % |
| 7.5                          | 30.177 | 34.9355 | 9.1653 | 0.0289 | -233.183 | 304.4891 | 0.0025 | 167.384 | 8.2739 |
| 10                           | 21.0065 | 19.7754 | 8.8695 | 0.0161 | -65.258 | 258.2961 | 0.0036 | 164.7672 | 11.7994 |
| 12.5                         | 13.7276 | 15.4143 | 9.7012 | 0.0119 | 93.0787 | 179.5293 | 0.0038 | 192.7947 | 16.4755 |

4. Conclusion
Comparison between the experimental data with the three models shows that Yan Model fit to a whole range of values of C/C_0. Thomas Model is just fit for the area of final breakthrough curves. Whereas the Adams Bohart model is not good enough to describe the region early breakthrough curves.

References
[1] Sekaran G, Shanmugasundaram K A, Mariappan M 1998 Characterization and Utilisation of Buffing Dust Generated by the Leather Industry J. Hazard Mater B 63 53-68
[2] Swarnalatha S, Srinisvasulu S, Srimurali M and Sekaran G 2008 Safe Disposal of Toxic Chrome Buffing Dust Generated from Leather Industries J. Hazard Mater 150 290-299
[3] Gammoun G, Soufiane T, Abderrahman A, Mohammed A, and Miguel D L G 2007 Decontamination of Water Polluted with Oil Through The Use of Tanned Solid Wastes J. Environ Eng Sci 6 553-559
[4] Ghomshe S M, Mousavi S M, Soltanieh M and Kordi AK. 2011 Batch and column study of haloacetic acids adsorption onto granular activated carbon Sci Res Essays 6 3553-3560
[5] Sekhula M M, Okonkwo J O, Zvinowanda C M, Agyei N N, and Chaudhary A J 2012 Fixed bed column adsorptions of Cu (II) onto maize tassel-PVA beads Journal of Chemical Engineering and Process Technology, 3 1-5
[6] Pokhrel D and Viraraghavan T 2008 Arsenic removal in an iron oxide-coated fungal biomass column: analysis of breakthrough curves Bioresource Technol 99 2067-2071
[7] Wang D, Elisabeth M, Robert P, and Lin Y S 2012 Adsorption of Oils from Pure Liquid and Oil-Water Emulsion on Hydrophobic Silica Aerogels Sep Purif Technol 99 28-35