

Adsorption of Alkyl Benzene Sulfonate Surfactant on Activated carbon For Biobarrier Purpose

Anondho Wijanarko*, Praswasti Pembangun Dyah Kencana Wulan, Willy Chandra,
Dianursanti, Song Seung Koo, Mahmud Sudibandriyo and Misri Gozan

*Department of Chemical Engineering, Faculty of Engineering, University of Indonesia
Kampus Universitas Indonesia, Depok 16424, Indonesia.*

Abstract

Simultaneous adsorption and biodegradation process in fluidized biobarrier reactor is one of emerging methods for eliminating surfactant in waste water. This paper discusses the adsorption process on activated carbon as a part of a biobarrier system. Surfactant used in these experiments is branched sodium dodecyl benzene sulfonate branched in various concentrations of 400, 700, 1000 and 1500 mg/L placed in 250 mL closed-erlenmeyer container (in batch system). Adsorption took part in a glass column of 30 cm length and 2 cm diameter. Total surfactant concentration was measured with COD-chromate analysis and surface tension measurement. Adsorption equilibrium curves in solid (dC/m) and liquid phase (C_e) as well as surfactant concentration versus surface tension were performed. The results showed that surfactant adsorption equilibrium curve rose within equilibrium concentration (C_e) 0 – 533.4 mg/L, then reached plateau with increasing C_e . Critical Micelle Concentration (CMC) Sodium Dodecyl Benzene Sulfonate was 533.4 mg/L. Freundlich equilibrium constants were $(1/n) = 1.91$ and $K_f = 9.97 \cdot 10^{-5}$ in C_e range of 252.6 to 481.2 mg/L. The equilibrium time for adsorption was 24 hours and the minimum fluidization velocity was predicted to be 0.717 cm/s.

Keywords: adsorption, surfactant concentration, COD-chromate, surface tension.

1.0 Introduction

Surface active agent is a compound that has polar and non polar functional groups enabling to bond with other non polar as well as polar compounds. This ability favour surfactant applications in industrial and house hold as cleaning agents, polymerization process emulsifiers, textile colour agents, paint stripper, personal care products for food industry and petroleum field, etc. [1, 2] Alkyl Benzene Sulphonate (ABS) is among popular anionic surfactant. Indonesian ABS industry production volume is relatively large with ca. 192,500 tons annual production capacity [3]. In the future, this high ABS utilization will probably be enormous considering the population of Indonesian.

High surfactant utilization relates with negative impacts to the human health if released or disposed to environment. Diarrhoea, emaciation, skin irritation, necroscopy, hard breath and death (mice

* Corresponding authors: Tel: 62-21-786 3516, 786 5335, Fax: 62-21-786 3515, Email: anondho@che.ui.edu and mgozan@che.ui.edu

experiment results) have been reported to be strongly related to the presence of ABS in surface waters [2]. ABS content in commercial products could be around 60-90% and in consumption goods around 5-30% [2].

Currently, several technologies are applied to minimize the extent of surfactant in the environment such as ozonation and adsorption. Natural biodegradation is the common treatment method. However, branched alkyl structure causes difficulty for microbial degradation process. Other treatment such as ozonation is more expensive. Simultaneous adsorption and regeneration seems to be a promising technology.

Activated carbon is widely used in water and wastewater treatment due to high adsorption capacity [4]. Nevertheless, ABS adsorption by active carbon is rarely done. Effectiveness of ABS adsorption was examined in this paper through variation of surfactant concentration in constant active carbon amount. Calculation of minimum fluid velocity was also carried out.

2.0 Materials & Method

Experiments were carried out in 200 ml Erlenmeyer, auto shaker, callipers and picnometer. Meanwhile, the experimental reagents and materials are sodium dodecyl benzene sulphonate branched surfactant (0, 400, 700, 1000, and 1500 mg/L), COD reagent, reverse osmosis water, local market activated carbon, potassium hydrogen phthalate (PHP; 500, 1000, and 1500 mg/L).

ABS surfactant physical properties such as viscosity and density were measured by 'Redwood' viscosity method and picnometer. Physical properties of active carbon for calculation of minimum fluidize rate such as active carbon porosity measurement was performed by measuring the left empty space (void volume, ϵ_M) on the packed active carbon.

Spectra calibration curve at 612 nm for COD measurement was performed based on PHP standard solution appropriate to standard method No.5220 B 3 G. [5]. COD was measured according to standard method No. 5520 [5] which uses chromate COD reagent at 150°C (2 hours) in closed reflux COD reactor before spectrofotometry measurement. Surfactant solution surface tension was measured by 'Kruss' interfacial tension meter.

Experimental began by COD and surface tension measurement of several ABS solutions [400, 700, 1000, and 1500 ppm] and then 5.0 or 10 g active carbon was added each sample prior to shaking. Shakings were carried for 1, 2, 3, 24, 48 and 72 hours followed by COD and surface tension re-measurement for calculation of minimum fluidize rate.

3.0 Results and Discussion

3.1 Contact time effects on adsorption of ABS surfactant

Contact time effect to absorbed ABS on activated carbon at various surfactant initial concentrations is depicted in Fig. 1. The curves show that both experimental results in Fig. 1a and 1b share the same trends. In the first 3 hours of contact time between activated carbon and surfactant, adsorption

was very high as shown by the steep inclining slope. During the initial 3 to 24 hours, the rate of adsorption increases until it reaches a plateau.

The adsorption rate during the first 3 hours is much higher than the adsorption rate after 3 hours. These results explain that the adsorption rate is controlled by the external mass transfer and diffusion into macro pores, and this occurs rapidly. Next, the internal diffusion into meso - and micro pores happens slowly [6]. Adsorbed molecules or ions can only enter into adsorbent pores if those ions or molecules diameters are smaller than adsorbent pores diameter [7]. Adsorption rate was highly influenced by the activated carbon pores diameter.

Fig. 1a shows that the maximum amount of surfactant absorbed for the same activated carbon mass, is different for each initial concentration (400, 700, 1000, 1500 ppm). It is caused by the differences between initial surfactant concentrations (bulk phase) and surfactant concentration in solid phase. Higher concentration difference creates higher driving force for external and internal diffusion processes within adsorbent pores so that surfactant adsorption rate is higher for the higher initial surfactant concentration.

Fig. 1b shows that the maximum amount of surfactant adsorbed on 10 grams of activated carbon was similar between initial concentration 1000 and 1500 ppm. Similarity occurs because the maximum adsorption limit was reached. Maximum adsorption limit was defined by the constant value of $(C_e - C_0)/m$ for C_e (equilibrium concentration) is higher than Critical Micelle Concentration (CMC) value of that surfactant [8, 9, 10].

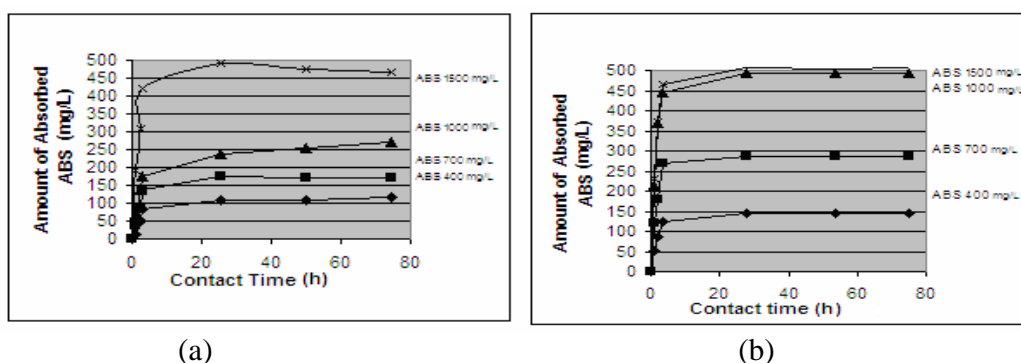


Figure 1 Contact time effect on amount of absorbed ABS; a. 5 grams activated carbon; b. 10 grams activated carbon.

3.1 ABS concentration effect on surface tension

The effect of increasing ABS concentration on solution surface tension is shown in Fig. 2 which shows that the presence or the increasing concentration of ABS surfactant reduces solution surface tension. Surface tension sharply decreases and then remains constant at approximately 35 mN/m. Solution surface tension becomes relatively constant when ABS concentration is above their CMC. This is due to the fact that the surfactant solution consists only of the monomeric form that contributes to stop the decrease of solution surface tension [8].

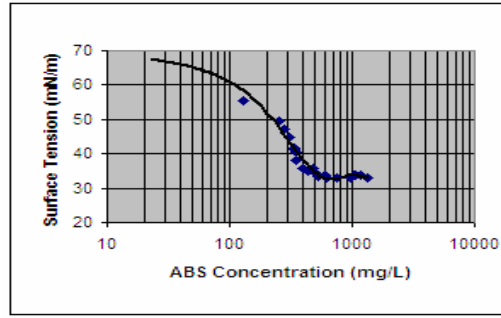


Figure 2 Effect of initial ABS concentration on surface tension

According to the experiments, the CMC is ca. 533.4 mg/L. Other experiments showed that the CMC was 557.6 mg/L [2], which is only 4.4 %.

3.2 Isotherm adsorption and determination of Freundlich Equilibrium Constants

The adsorption equilibrium between liquid and solid phase is shown in Fig. 3. At the beginning of the curve the tendency for adsorbed surfactant molecules per unit mass of activated carbon (q_e) increased until equilibrium surfactant concentration (C_e) reached 481.6 mg/L. At equilibrium concentration higher than that the q_e curve follows a constant trend. The CMC value is 533.4 mg/L and it located between 481.6 and 649.5 mg/L of C_e of the experimental data.

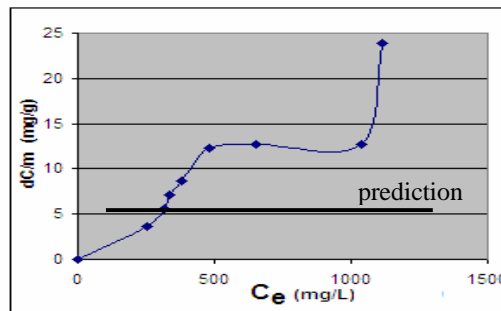


Figure 3 Isotherm Adsorption Curve

Due to the flattening curve on $C_e > \text{CMC}$, then Freundlich and Langmuir isotherm adsorption analysis were only done on C_e below CMC value (within equilibrium concentration between 252.6 and 481.2 mg/L) as shown in Fig. 4.

$$\text{Langmuir : } \frac{1}{q} = \frac{1}{q_m} + \frac{1}{q_m \cdot K_L} \cdot \frac{1}{C_e} \quad (1)$$

$$\text{Freundlich : } \log q = \log K_f + (1/n) \log C_e \quad (2)$$

Where,

q , amount of adsorbed solute per gram adsorbent

C_e , equilibrium concentration

K_f , Freundlich constant with $(1/n) > 1$

K_L , Langmuir constant relating with adsorption enthalpy

q_m , amount of adsorbed solute mass per gram adsorbent to create a single layer

$q_e = dC/m$, amount of surfactant molecule adsorbed per mass unit activated carbon

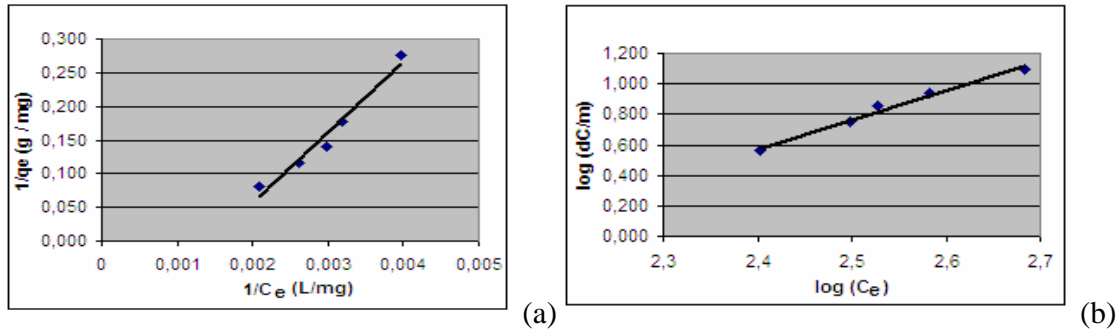


Figure 4 Isotherm adsorption result a. Langmuir Isotherm Adsorption b. Freundlich Isotherm Adsorption
($252.6 < C_e < 481.2$)

Abbreviate:

$q_e = dC/m$, amount of surfactant molecule adsorbed per mass unit activated carbon

C_e , surfactant concentration on liquid phase in equilibrium

Langmuir isotherm constants are obtained by this experiment and it can be concluded that $1/q_m$ is -0.153 and $1/q_m \cdot K_L$ is 105.1 with $R^2 = 0.96$. On the other hand, Freundlich isotherm constants are calculated and results are $1/n$ is 1.91 and K_f is $9.97 \cdot 10^{-5}$ with $R^2 = 0.98$. This experimental study finds that the ABS adsorption phenomenon follows better Freundlich isotherm adsorption.

3.3 Calculation of fluidization minimum velocity for fluidized bed bioreactor

The formula, which was used to calculate particulate fluidization velocity is shown in following equation.

$$\frac{150\mu V_{o,M}}{\Phi s^2 D_p^2} \frac{(1-\varepsilon_M)}{\varepsilon_M^3} + \frac{1.75 \cdot \rho \cdot V_{o,M}^2}{\Phi s \cdot D_p} \frac{1}{\varepsilon_M^3} = g \cdot (\rho_p - \rho) \quad (3)$$

Where,

μ fluid viscosity

$V_{o,M}$ fluidization minimum velocity

D_p particulate diameter

Φs sphericity, ratio between spherical area and the real area of that particulate (adsorbent)

ε_M minimum porosity (initial fluidization)

ρ_p solid particulate density

ρ fluid density

Reynolds Number (N.Re) was a number, which showed fluid flow characteristic of flowing fluid. The formula used to calculate Reynolds number is:

$$N.Re = \frac{\rho_p \cdot V_{o,M} \cdot D_p}{\mu} \quad (4)$$

Table 1 show the result of minimum velocity calculation that is needed to keep activated carbon bed still fluidizes.

Table 1 Fluidization Minimum Velocity

| ABS Concentration (mg/L) | V _{o,M} (cm/s) | N.Re |
|--------------------------|-------------------------|------|
| 0 | 0.717 | 15.3 |
| 100 | 0.717 | 15.3 |
| 400 | 0.717 | 15.3 |
| 700 | 0.717 | 15.3 |
| 1000 | 0.717 | 15.3 |
| 1500 | 0.717 | 15.3 |

As can be observed, for ABS concentration between 0 – 1500 mg/L the minimum fluidization velocities are similar, approximately 0,717 cm/s. The Reynolds number of 15.3 (2 < N.Re < 500) indicates that the fluid flows in the transition region [5, 11].

4.0 Conclusion

The highest ABS adsorption in this batch process occurs during the initial contact time between 0 – 3 hours and the efficiency time for maximum adsorption is 24 hours. The solution surface tension decreased when the initial ABS concentration is increased and became relatively constant in case of ABS concentration above their CMC. CMC value of *Sodium Dodecyl Benzene Sulphonate* (ABS) is 533.4 mg/L. Maximum adsorption capacity in this experiment is 50.6% for 10 grams activated carbon and 311 % for 5 grams activated carbon. This study reveals that the ABS adsorption phenomenon follows Freundlich isotherm adsorption. Adsorption equilibrium constants obtained are 1/ n is 1.91 with K_f equals to 9.97.10⁻⁵. Minimum fluidization velocities are similar, approximately 0,717 cm/s. and breakthrough time is estimated 50 seconds.

References

- [1] Anonym, Surfactants; *The Ubiquitous Amphiphiles*, http://www.chemsoc.org/chembytes/ezone/2003/hargreaves_jul03.htm, (visiting date, November 1, 2005)
- [2] Anonym, *Hazard Data Availability and Assessment Report for Linear and Branched Alkylbenzene Sulphonic Acids and Derivatives*, <http://www.epa.gov/chemrtk/alkylbenz/c14187tp.pdf> (visiting date, November 1, 2005)
- [3] Anonym, 2001, *Pengembangan Industri Petrokimia di Indonesia*, Jakarta: Indonesian Chemical Industries Club
- [4] Zamora R. M. R., A. D. Pilotzi, R. D. Mora and A. D. Moreno 2004, Removal of Detergents by activated petroleum coke from a clarified waste water treated for reuse, *Water Science and Technology*, Vol. 50, No. 2, pp. 91-98
- [5] Clesceri, LS. et. al., 1998, *Standard methods for The Examination of Water and Wastewater*, 20th ed., Washington DC: American Public Health Association
- [6] Sontheimer, C. et. al., 1988, *Activated Carbon for Water Treatment*, 2nd ed., Berlin: DVGW-Forschungsstelle

- [7] Nugroho, S., 2001, *Aplikasi Karbon Aktif Sebagai Adsorben Dalam Pengendalian Kadar Cu Dalam Limbah Cair Dengan Proses Adsorpsi Sistem Batch*, Depok: Universitas Indonesia
- [8] Rosen, M.J. 1989. *Surfactants and Interfacial Phenomena*, New York: John Wiley & Sons, Inc.,
- [9] Huibers P.D.T., V.S. Lobanov, A.R. Katritzky, D.O. Shah and M. Karelson 1996, Prediction of Critical Micelle Concentration using Quantitative Structure – Property Relationship Approach, *Langmuir*, Vol. 12, pp. 1462-1470
- [10] Lisensky, G., 2005, *Critical Micelle Concentration*. <http://mrsec.wisc.edu/Edetc/nanolab/micelle/text.html> (visiting date, November 20, 2005)
- [11] Bird, R.B. et. al., 1960, *Transport Phenomena*, New York: John Wiley & Sons Inc.