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Adsorption kinetics of surfactants on activated carbon

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Abstract. A study on the adsorption of both cationic and anionic surfactants using activated carbon as well as the investigation of the adsorption isotherms and adsorption kinetics has been conducted. The results showed that the adsorption of sodium lauryl sulfate (SLS) by activated carbon was Langmuir's adsorption isotherm while its adsorption kinetics showed pseudo-second order with an adsorption rate constant of 2.23 x 10^3 g mg^{-1} $hour^{-1}$. Meanwhile, the adsorption of HDTMA-Br by activated carbon showed that the isotherm adsorption tended to follow Freundlich's isotherm and was pseudo-second order with an adsorption rate constant of 89.39 g mg^{-1} $hour^{-1}$.

1 Introduction

Activated carbon is a porous material composed of carbon with a surface area and pores growing well in the presence of an activator. The well-developed surface and pores on carbon may be used as adsorbent [1, 2]. One of the raw materials in the production of activated carbon is rice husk due to its high content of organic compounds [3, 4]. Research on carbon activation using H_3PO_4 has been undertaken by Huang et al [5] , which indicated that the carbon pores were more open. Consequently, the adsorption ability of the activated carbon would increase.

The adsorption of surfactants is necessary to be undertaken since the pollution generated by surfactants as a result of their use now shows an increase in proportion to the increase in the human's population. The pollution is caused by surfactants in the environment such as the foam emergence and their limited biodegradation by bacteria or microorganisms resulting in the disturbance of the water ecosystems.

Schouten et al [6] have studied the kinetics of adsorption of surfactant linier alkylbenzene sulfonate (LAS) by granular activated carbon derived from norit (Netherlands). The result showed that the kinetics order of this adsorption process was first order while Yakout et al [7] reported that the order reaction of the CTAB surfactant adsorption on carbon (from corn cob and char) activated by KOH was a pseudo-second order.

This research studied the adsorption isotherm and adsorption kinetics of sodium lauryl sulfate (SLS) and hexadecyltrimetilammonium bromide (HDTMA-Br) surfactant adsorbed by activated carbon made from rice husks. By determination of adsorption isotherm and adsorption kinetics, the adsorption order, adsorption rate constant and adsorption isotherm models can be specified. Order adsorption and adsorption rate constant associated with the rate of adsorption of surfactant by activated carbon. It is known that the factors affecting the rate of adsorption, such as the concentration of adsorbate and

adsorbent, temperature, the surface area of adsorbent and catalyst, can be used to accelerate the rate of adsorption. Adsorption isotherm was studied to estimate that the adsorbate was trapped onto the adsorbent in monolayer or multilayer pattern.

2 Materials and Method

2.1 Materials. Materials used in this research were rice husks, H_3PO_4, H_2SO_4, NaOH, phenolphthalein, phosphate-washing solution, SLS and HDTMA-Br surfactants, distilled water, bromophenol blue, phosphate buffer pH 8 and chloroform. All the reagents are analytical grade and were purchased from Merck, Indonesia.

2.2 Adsorption of surfactants by activated carbon. This research experiment consisted of several stages. The first stage was carbonization of rice husk, the second step was activation of carbon, and the last stage was adsorption of surfactants onto the activated carbon. Carbonization of rice husk was conducted at 300°C by pyrolysis (decomposition process of organic substances resulting in tar, charcoal (carbon) and volatile compounds by heating with or without oxygen). The carbon generated had been then activated using H_3PO_4 60% at 420°C for 1 hour. This step aimed to remove impuritities covering the pores of the adsorbent so that pores become bigger. The adsorption process was conducted by contacting 1 g of activated carbon with 25 ml of SLS surfactant (60 ppm) in different times 3, 4, 5, 6 and 7 hours at room temperature. The mixture was then separated by simple filtration using filter paper (Whatmann no. 1, diameter 15 mm, pore zise 11 μm). The filtrate was then analyzed using methylen blue active substance (MBAS) method to determine the concentration of SLS that was not adsorbed [3]. This method is applied for determination of anionic surfactant unadsorbed by adsorbent. This procedure was also applied to the adsorption of 300 ppm HDTMABr by 1 gram of activated carbon. However, the concentration of unabsorbed HDTMABr surfactant was determined using the bromphenol blue method [8] (method applied for determiantion of cationic surfactant concentration).

3 Results and Discussion

Surfactant adsorption on activated carbon was conducted by contacting the activated carbon with both SLS and HDTMABr surfactants in the range of time 3, 4, 5, 6 and 7 hours. The data obtained were in the form of correlation between adsorption contact time and adsorbed-surfactant concentration and also adsorption capacity. The data were then used to determine the adsorption types and adsorption kinetics of both surfactants trapped onto activated carbon. Table 1 indicates that the adsorption SLS and HDTMA-Br by activated carbon occurred at the optimum time of 4 hours. The adsorption of both surfactants increased insignificantly after 4 hours. It shows that at the time of 4 hours, the activated carbon optimally absorbed surfactants.

Table 1. The concentration of surfactant adsorbed by activated carbon

No.	Time (Hours)	Adsorbed surfactant (ppm)		Adsorption capacity (mg / g)	
		HDTMABr	SLS	HDTMABr	SLS
1.	3	298.79	59.95	7.47	1.4987
2.	4	299.11	59.98	7.48	1.4995
3.	5	299.11	59.98	7.48	1.4996
4.	6	299.22	59.97	7.48	1.4992
5.	7	299.28	59.96	7.48	1.4991

3.1 Adsorption isotherms

Determination of the types of adsorption occurring in the adsorption of surfactants by activated carbon used Langmuir (1) and Freundlich (2) equations.

$$\frac{C}{N} = \frac{C}{N_m} + \frac{1}{K}N \qquad \text{..... (1)}$$

N = moles of surfactant adsorbed per gram of activated carbon; C = final concentration of surfactant in moles/liter; K = Langmuir's constant and Nm = the number of moles required to make a single layer of surfactants on the activated carbon.

$$\frac{X}{m} = kC^n \longrightarrow \log\frac{X}{m} = \log k + n\log C \qquad \text{..... (2)}$$

X = weight of substances (solute) adsorbed (g); m = weight of adsorbent (g); C = concentration of the solution after adsorption (after equilibrium); k = Freundlich's constant; n = another constant in which k and n are related with mass of adsorbent and temperature of adsorbate, respectively.
Tables 2 and 3 show the data that will be used to determine the type of adsorption occurred in the SLS adsorption process by activated carbon. This data was obtained from data calculation in Table 1. Plotting data between N vs. C / N (Figure 1) and log C vs. log X/m (Figure 2) is then applied to determine the type of adsorption (Langmuir or Freundlich) by looking at the linearity of the curve (R^2).

Table 2. The component data of SLS surfactant adsorbed on the activated carbon for the determination of Langmuir's kinetics.

C (mol / liter)	C / N	N (mol / g)
$1.73\text{x}10^{-7}$	$3.33\ \text{x}10^{-2}$	$5.1970\text{x}10^{-6}$
$6.93\text{x}10^{-8}$	$1.33\ \text{x}10^{-2}$	$5.1990\text{x}10^{-6}$
$6.93\text{x}10^{-8}$	$1.33\ \text{x}10^{-2}$	$5.1990\text{x}10^{-6}$
$1.04\text{x}10^{-7}$	$2.00\ \text{x}10^{-2}$	$5.1988\text{x}10^{-6}$
$1.39\text{x}10^{-7}$	$2.67\ \text{x}10^{-2}$	$5.1980\text{x}10^{-6}$

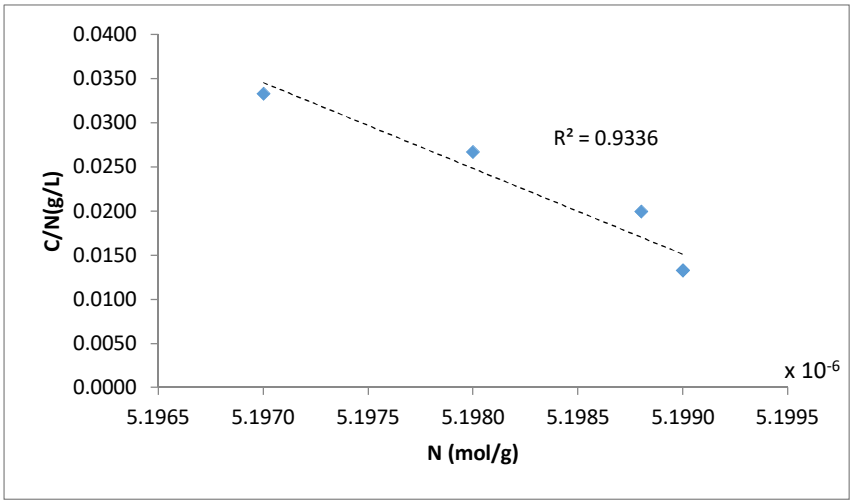

Figure 1. The Langmuir adsorption isotherms model of SLS adsorption on the activated carbon.

Table 3. The component data of SLS surfactant adsorbed on the activated carbon for the determination of Freundlich's kinetics.

C (mol)	X **(g)**	m **(g)**	X / m (g / g)	log C	log X / m
$4.33x10^{-9}$	$1.49870x10^{-3}$	1	$1.50x10^{-3}$	-8.36351	-2.82429
$1.73x10^{-9}$	$1.49930x10^{-3}$	1	$1.50x10^{-3}$	-8.76195	-2.82412
$1.73x10^{-9}$	$4.99220x10^{-3}$	1	$4.99x10^{-3}$	-8.76195	-2.30171
$2.60x10^{-9}$	$1.49890x10^{-3}$	1	$1.50x10^{-3}$	-8.58503	-2.82423
$3.46x10^{-9}$	$1.49813x10^{-3}$	1	$1.50x10^{-3}$	-8.46092	-2.82445

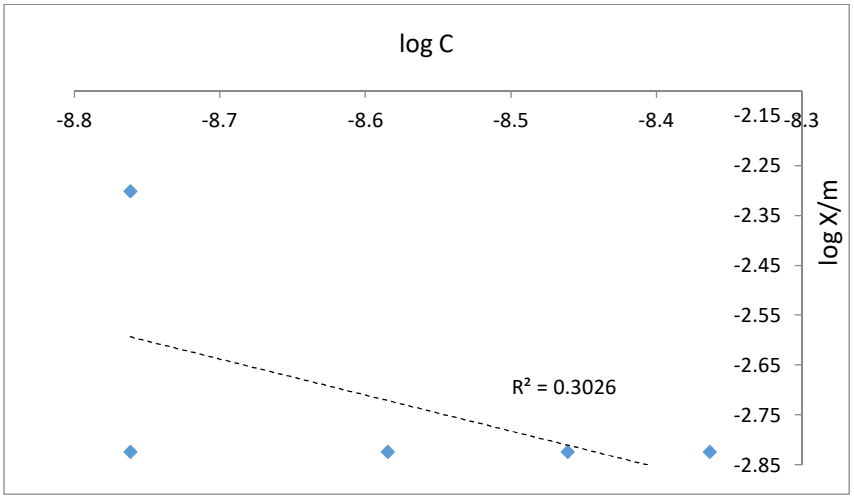

Figure 2. The Freundlich adsorption isotherms model of SLS adsorption on activated carbon.

Figures 1 and 2 show the model of the adsorption isotherms. Langmuir's adsorption isotherm model in Figure 1 provides a linearity (R^2) of 0.9336 greater than the linearity of Freundlich adsorption isotherm (R^2 = 0.3026) (Figure 2). **The Figures 1 and 2** indicate that the SLS adsorption by activated carbon followed the Langmuir's isotherm rather than Freundlich's isotherm. Based on the hypothesis of the Langmuir's adsorption, SLS surfactant was adsorbed by activated carbon by forming a monolayer.

Tables 4 and 5 are the data used to determine the type of adsorption occurred in the adsorption process of HDTMABr by activated carbon. In the same way as the determination of adsorption SLS, Figures 3 and 4 show the type of Langmuir's and Freundlich's adsorption isotherms in the adsorption HDTMABr.

Table 4. The component data of HDTMABr surfactant adsorbed on the activated carbon for the determination of Langmuir's kinetics.

C (mol / liter)	C / N	N (mol / g)
$3,20x10^{-6}$	0,156	$2,050x10^{-5}$
$2,44x10^{-6}$	0,119	$2,051x10^{-5}$
$2,44x10^{-6}$	0,119	$2,051x10^{-5}$
$2,14x10^{-6}$	0,104	$2,052x10^{-5}$
$1,97x10^{-6}$	0,096	$2,053x10^{-5}$

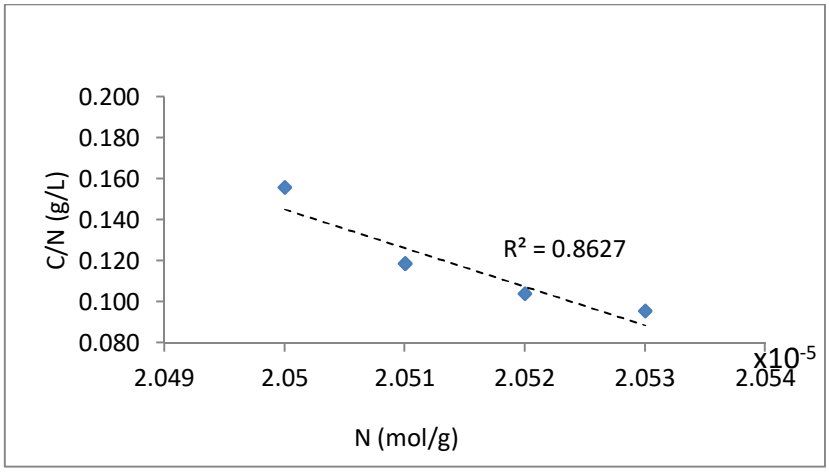

Figure 3. The Langmuir's adsorption isotherms model of the adsorption of HDTMABr on the activated carbon

Table 5. The component data of HDTMABr surfactant adsorbed on the activated carbon for the determination of Freundlich's kinetics.

C (mol)	**X (g)**	**m (g)**	X / m (g / g)	log Csisa	log X / m
$8{,}3x10^{-8}$	$1{,}2x10^{-3}$	1	$1.20x10^{-3}$	-7.08092	-2.92082
$6.1x10^{-8}$	$8{,}9x10^{-4}$	1	$8.9x10^{-4}$	-7.21467	-3.05061
$6{,}1x10^{-8}$	$8{,}9x10^{-4}$	1	$8.90x10^{-4}$	-7.21467	-3.05061
$5{,}35x10^{-8}$	$7{,}8x10^{-4}$	1	$7.80x10^{-4}$	-7.27165	-3.10791
$4{,}93x10^{-8}$	$7{,}1x10^{-4}$	1	$7.10x10^{-4}$	-7.30715	-3.14874

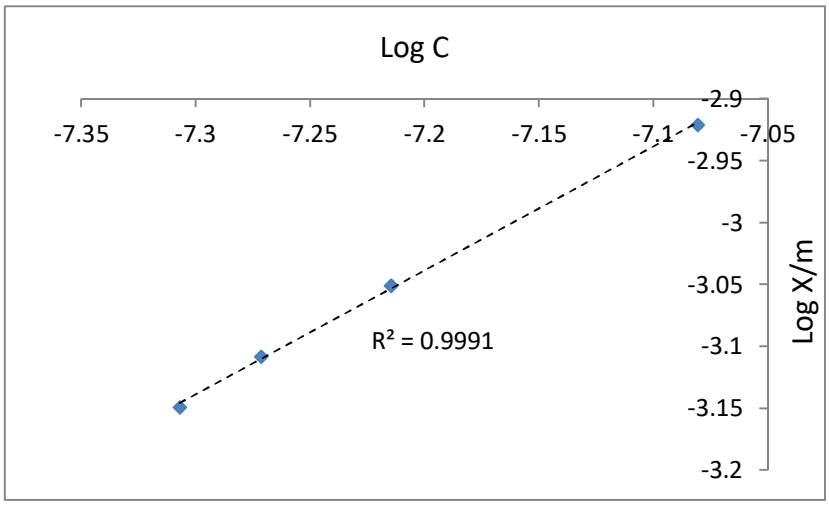

Figure 4. The Freundlich's adsorption isotherms model of the adsorption of HDTMABr on the activated carbon

It can be seen in Figures 3 and 4 that HDTMA-Br adsorption on the activated carbon followed Freundlich's isotherm with R^2 of 0.999. Compared to SLS adsorption process, the HDTMABr adsorption was in the form of multilayer, which means that after HDTMABr molecules were adsorbed and formed a monolayer, they attracted their neighboring molecules.

3.2 Adsorption Kinetics

The data in Table 6 and 7 were then used to determine the adsorption kinetics of SLS and HDTMABr adsorption process by activated carbon. By using the kinetics equation of Lagergren's pseudo second-order $\frac{t}{q_t} = \frac{1}{k q_{e^2}} + \frac{1}{q_e} t$ the linear graphs between t/qt vs. t as presented in Figures 5 and 6 were generated.

Table 6. The component data of SLS surfactant adsorbed on the activated carbon for the determination of Lagergren's kinetics.

Kinetics of the adsorption of SLS by activated carbon			
Time (hours)	[SLS] adsorbed (mg / L)	t/qt	qt
3	55.95	2:00	1:50
4	55.98	2.67	1:50
5	55.98	3:33	1:50
6	55.97	4:00	1:50
7	55.93	4.67	1:50

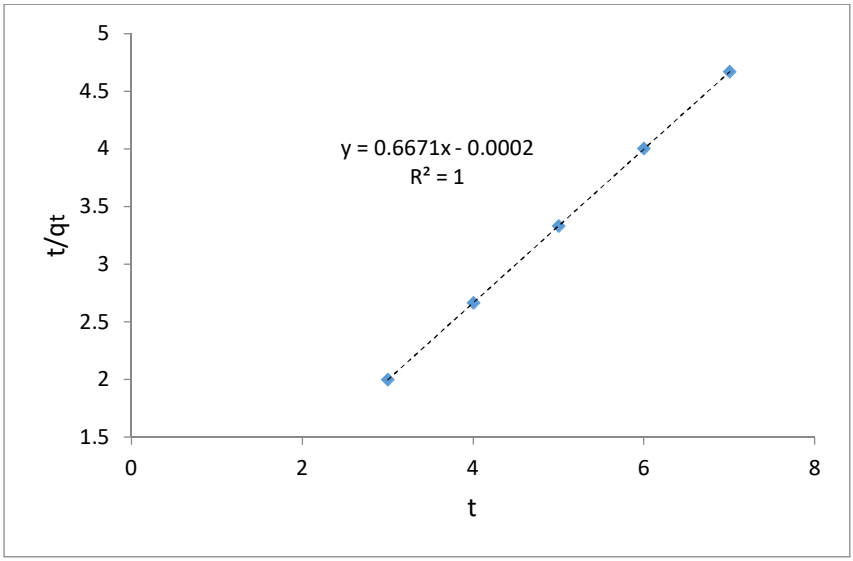

Figure 5. The pseudo second-order kinetics of the adsorption of SLS on activated carbon

Table 7. The component data of HDTMABr surfactant adsorbed on the activated carbon for the determination of Lagergren's kinetics.

Adsorption kinetics HDTMA-Br activated carbon			
Time (hours)	[HDTMA-Br] adsorbed (mg/L)	t/qt	qt
3	298.79	0.400534045	7.4900
4	299.11	0.535475234	7.4700
5	299.11	0.669344043	7.4700
6	299.22	0.802139037	7.4800
7	299.28	0.935578722	7.4820

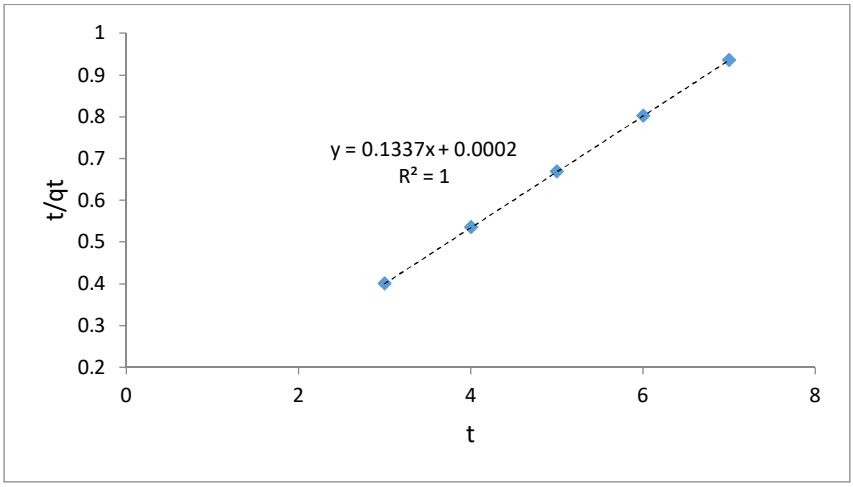

Figure 6. The pseudo second-order kinetics of HDTMA-Br adsorption on activated carbon

Based on the Lagergren's kinetics equation, the adsorption kinetics of both SLS and HDTMA-Br adsorption by the activated carbon were pseudo-second order because both adsorptions showed a linearity (R^2) of 1. By equation of a simple second-order reaction rate, $v = k [A]^2$, the concentration of the reactant A is magnified two times if the rate of reaction is four times of the original rate. Also, based on the Lagergren's formula, the rate constant of adsorption for SLS and HDTMABr adsorption can be calculated. The result showed that the adsorption rate constant of the adsorption of SLS and HDTMABr by activated carbon was $2.23x10^3$ $gmg^{-1}hour^{-1}$ and 89.39 $gmg^{-1}hour^{-1}$, respectively. This result suggests that the adsorption rate of SLS on the activated carbon is more effective than HDTMABr.

4 Conclusion

Surfactant adsorption process both SLS and HDTMABr by activated carbon shows that the process followed the model of Langmuir and Freundlich adsorption isotherms, respectively. The adsorption kinetics of both surfactants showed pseudo second order with a rate constant for adsorption of SLS and HDTMABr is consecutively $2.23x10^3$ $gmg^{-1}h^{-1}$ and 89.39 $gmg^{-1}h^{-1}$.

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