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# Kinetic study of adsorption carboxylic acids of used cooking oil using mesoporous active carbon

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**Abstract.** This study investigates the reduction of free fatty acids from the problem of used cooking oil in the food industry with bio-waste adsorbents such as banana peels—experimental conditions at the activation temperature of making activated carbon. Adsorption kinetics and temperature of activated effects were studied. Bio-char activated at 600, 650, and 700°C. The used cooking oil and activated carbon were analyzed using Fourier transform infrared spectroscopy, transmission electron microscopy, X-ray energy-dispersive, and BET analysis. Activated carbon has a surface area of 548 m<sup>2</sup>/g, with an average pore diameter of 35 nm (range of mesopore). As a result, bio-char activated at 700°C is best presented by a linear pseudo-second-order kinetic model suitable for describing the adsorption kinetic. The maximum adsorption capacity was 62 mg/g at 303 K. Carboxylic groups as free fatty acid was removed from used cooking oil used surface of activated carbon. Models best described the experimental data as with the higher values of the correlation coefficient ( $R^2$ ). The results of this study prove that the banana peel bio-waste ingredient, which is food waste, is a potential adsorbent to reduce free fatty acid levels to the standard of 0.3

## 1. Introduction

Increased population growth is comparable to a dramatic increase in industrial activity. The increase in an industry also increases the amount of pollution, one of which is the pollution of household waste, such as used cooking oil [1]. Used Cooking oil contains high free fatty acids (FFA) and tends to be thrown away. The urgency if cooking oil is continuously used and not treated properly can cause cancer and death.

Most of the used cooking oil is collected and arises from kitchens and food vendors who use cooking oil. The strategy for collecting and disposing and managing waste is utilized in other products. Used cooking oil proceeds into bio-lubricants [2] and animal feed [3].

Used cooking oil undergoes a frying process and produces derivatives of triglycerides such as FFA, heterocycles, and Maillard reaction products. The specific composition of other products from FFA waste can be exploited as a useful source of chemicals for bio-plasticizers and syngas production. The real content in used cooking oil is the high content of free fatty acids with a carboxylic group's characteristic as one of the parameters for assessing cooking oil quality. The emergence of free fatty acids indicates decreased cooking oil quality due to hydrolysis, oxidation, and polymerization. Cooking oil used repeatedly is found in the field increasing in acid number, which reaches 1.4 mg KOH/g. Meanwhile, the required acid number is at least 0.3, which is the fried oil's quality requirement.



The ability of banana peels as adsorbents do not doubt because they contain carbon in the form of pectin (10-21%), lignin (6-12%), cellulose (7.6-9.6%), and hemicelluloses (6.4-9.4%) [4]. Banana peel adsorbents had been studied, including reducing levels of heavy metals such as copper [5], Cadmium [6], Lead [7]. Many reports on FFA adsorption from several materials, such as clay and banana peel [8]. With banana peels, particle size has been researched. Adsorption using activated carbon with technical KOH presents a hydroxyl group in addition to the hydroxyl group, which is carried from biomass raw materials, which has strength.

It is essential to know the rate of adsorption kinetics with a batch system for optimizing contact time and the design of adsorption units in FFA treatment systems in industrial cooking oil users. The kinetics study was conducted to determine the adsorption capacity of the adsorbent and evaluate the rate of constants in the form of a model approach.

## 2. Methods

Practical work and analysis in the laboratory were carried out in the Chemical Engineering Laboratory of Universitas Negeri Semarang and Kasetsart University. Activated carbon was made in Indonesia. The cooking oil used is cooking oil for manufactured products in Thailand. Frying was worn on French fries shoestring. Used cooking oil was served in cooking oil, which is then used for frying potatoes several times until the initial concentration of carboxylic acid in cooking oil is higher than 0.3% of the cooking oil requirement. This process was carried out by mixing the banana peel charcoal in powder with a technical KOH activator with a carbon and KOH ratio of 1: 6 (w/w) in 600 mL aqua dest. The mixture was then heated at 60 °C until slurry was formed. The slurry had been formed is then refined at a temperature variation of 600°C, 650°C, and 700°C for 1 hour until it becomes activated carbon. If the carbonation takes 2 hours, it is feared that much carbon will form graphite [9]. The activated carbon was washed using a 0.1 M HCl solution until a pH of 7 is obtained using a universal indicator and rinsed using distilled water. After obtaining neutral activated carbon, it was dried using an oven at 105°C until a constant weight was obtained. Activated carbon was powdered with a pass size of 200 mesh.

Analysis of free fatty acid levels was done by taking a sample of 10 mL of cooking oil, put it in the Erlenmeyer, and adding 50 mL of ethanol. It is heated on a hot plate while stirring until a homogeneous solution was formed. Then lift and drop with the indicator phenolphthalein by three drops. Titrate with 0.1 N NaOH solution until the color turns pink and does not disappear within 30 seconds. The calculation of FFA levels uses equation 1. Where A is the molecular weight of fatty acids 269.73 g.gmol<sup>-1</sup>, B is the volume of NaOH (mL), C is the normality of NaOH (N), and D is the weight of the sample tested (g)

$$\% \text{ FFA} = (\text{A.B.C}) \times 100\% / (\text{D} \times 1000) \quad (1)$$

The model FFA adsorption on the Activated Carbon of banana peels is analyzed. This equation (2) represents an integrated rate law for a pseudo-first-order reaction. The correlation coefficient ( $R^2$ ) value was calculated from the plot of  $\log(q_e - q_t)$  vs.  $t$ .

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where  $k_1$  is the rate constant, the correlation coefficient ( $R^2$ ) value was calculated from the plot of  $\log(q_e - q_t)$  vs.  $t$ . Pseudo second-order-kinetics model: The linear form of the pseudo-second-order kinetic model is given by equation (3). The  $q_e$  and  $k_2$  can be calculated from the slope and intercept of the  $t$  vs.  $t/q_t$  linear plot. The experimental  $q_e$  value is used to match the predicted  $q_e$  value by plotting it with the correlation coefficient value ( $R^2 = 1$ ).

$$\frac{t}{q_1} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where  $k_2$  ( $\text{g mg}^{-1}\text{min}^{-1}$ ) is the rate constant of the pseudo-second-order equation,  $q_e$  is the adsorption capacity of adsorbent at equilibrium, and  $qt$  is the amount of FFA adsorbed by an adsorbent at time  $t$ . The  $q_e$  and  $k_2$  can be calculated from the slope and intercept of the  $t$  vs.  $t/qt$  linear plot. The experimental  $q_e$  value is used to match the predicted  $q_e$  value by plotting it with the correlation coefficient value ( $R^2 = 1$ ), which indicates that the second-order kinetic model is more suitable for describing the adsorption kinetics, while the Evolich model is shown in equation 4. Where  $q_i$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the same parameters as the above mentioned,  $\alpha$  ( $\text{mg}/(\text{g}\cdot\text{min})^{-1}$ ) is the initial adsorption rate,  $\beta$  ( $\text{g}\cdot\text{mg}^{-1}$ ) is associated with the fraction of surface coverage and activation energy for chemisorptions.

$$qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (4)$$

Nitrogen adsorption experiments at 77 K were conducted to determine the test samples' specific surface area using 3Flek Physisorption Micromeritics. The samples were outgassed overnight at 180°C before adsorption measurements. The BET model was applied to fit the nitrogen adsorption isotherms and evaluate the samples' specific surface area. The chemical functional groups in the bulk phase and on the carbon surface were characterized using a Fourier Transform IR spectrophotometer (Perkin Elmer type Frontier) in 4000 to 400  $\text{cm}^{-1}$ . The samples were examined as KBR Disk. The crystallographic structure of the activated carbon samples was studied using a powder X-Ray diffraction analyzer PanAlytical type Xpert 3 Power with  $\text{CuK}\alpha$  X-ray source with a secondary monochromator (Germany), which operated at 40 kV and 40 mA in the  $2\theta$  range of 4 to 80.

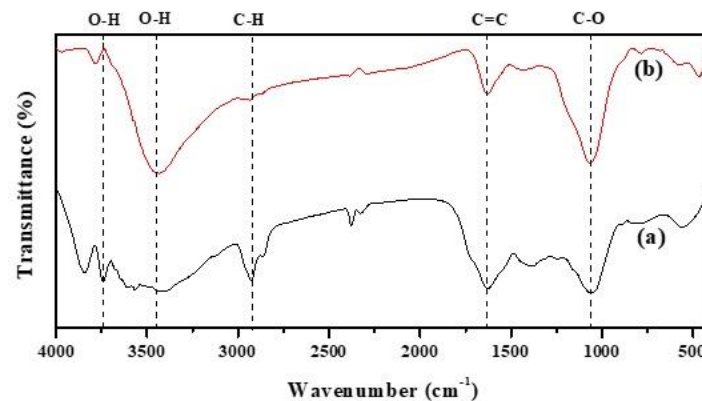
### 3. Result and discussions

Based on Table 1, the results of BET analysis with different temperatures in the sample of activated carbon from banana peels show that the activation temperature of 700°C is the highest and best-activated carbon temperature for adsorbing adsorbate with a surface area of 548  $\text{m}^2/\text{g}$ , a pore volume of 0.48  $\text{cm}^3/\text{g}$ , and pore size of 35 Å. The pore size indicates that the pores which have activated carbon in banana peels by this process are mesoporous. When banana peel acts as an adsorbent, its adsorption capacity was limited by its surface structure and pore volume.

**Table 1.** Analysis of BET of Activated Carbon Banana Peel

The temperature for making activated carbon (°C)	Surface Area ( $\text{m}^2/\text{g}$ )	Pore of Volume ( $\text{cm}^3/\text{g}$ )	Pore Size (Å)
600	114	0.29	101
650	411	0.53	51
700	548	0.48	35

Based on Figure 1, there were two FTIR graphs of banana peel powder in dry conditions by the sun, and after turning into activated carbon by heating at 600°C. The FTIR spectrum showed that at the 3740  $\text{cm}^{-1}$  peaks, it forms OH bonds classified in water, which appear billowing when the dry powder was a banana peel and becomes thinner when it becomes activated carbon by heating 600°C. The bands at 3432 and 1080  $\text{cm}^{-1}$  were assigned the O-H bond and the C-OH stretch, respectively, characteristic of the phenolic group. The visible spectrum in the observed band area in the region between 1680  $\text{cm}^{-1}$  was asymmetric C = C group from the pyrone group as an ether group, and at 1470  $\text{cm}^{-1}$ , it was found that C = O as a lactone group as a carboxylate group. The two dominant groups proved that the activated carbon has an aromatic functional group in the presence of phenols and carboxylates, acid groups, while the base group is pyrone. The phenol functional group, namely the hydroxyl on the carbon's surface, is also found in carbon activated using KOH in bamboo biomass [10]. Banana peel powder is almost similar to other biomass, which shows the presence of lignocellulosic material. Several functional groups are in the O-H strain vibration of the hydroxyl functional groups, including hydrogen bonds at a bandwidth of 3200-3400  $\text{cm}^{-1}$ , which indicates the presence of alcohol, phenol, or carboxylic acid [11]

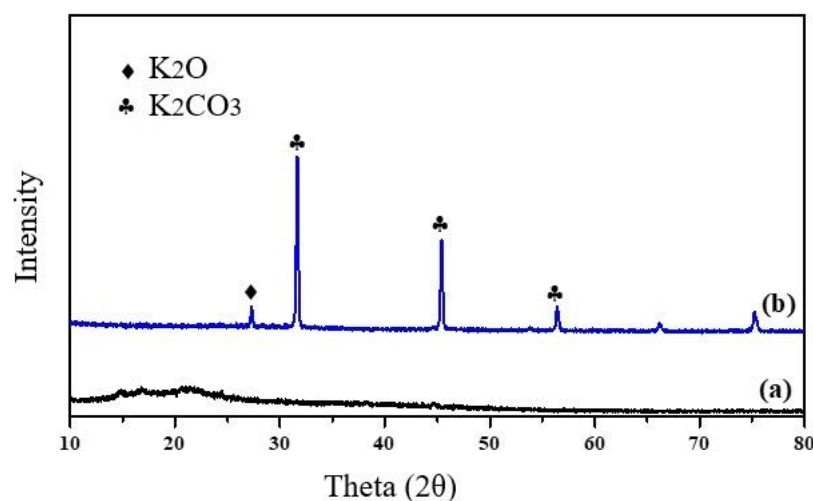


**Figure 1.** The FTIR spectra of powder banana peel powder a) dried and b) Activated Carbon

Figure 2 illustrates the X-ray diffraction profile of a banana peel and its activated carbon. This activated carbon showed a vast diffraction peak, and the absence of sharp peaks reveals a dominant amorphous structure. There are broad peaks around  $2\theta$  peaks at around 14 to 27. At sharp peaks ( $27^\circ$ ,  $32^\circ$ , and  $46^\circ$ ) on the  $600^\circ\text{C}$  activated carbon graph. Compared with the banana peel powder chart, the sharp peak was not found in the chart of banana peel powder. Activation using KOH can find residual KOH reactions on the carbon surface Tseng et al., (2008), as follows:

Based on research by Mopoung et al. [12], at the peak of  $27^\circ$ , it showed that  $\text{K}_2\text{O}$  was formed at a temperature of  $500^\circ\text{C}$ . The peaks of  $32^\circ$ ,  $46^\circ$ , and  $58^\circ$  showed  $\text{K}_2\text{CO}_3$  in the activated carbon sample, activated with KOH.

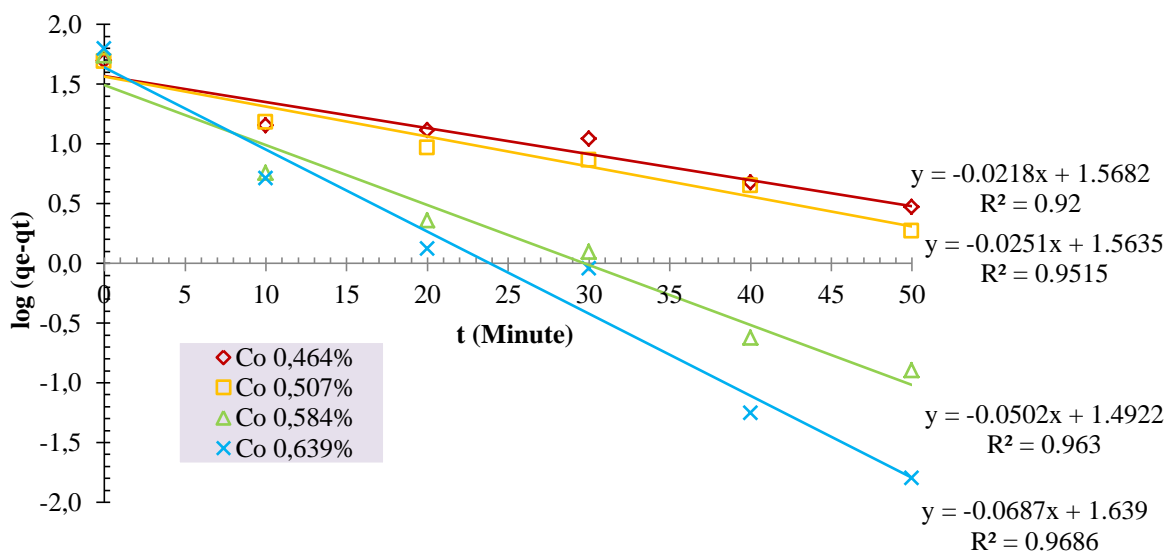
The difference in the crystal structure of banana peel powder and activated carbon can use the XRD analysis presented in Figure 2. Based on Figure 2, it can be concluded that activated carbon has a higher crystallization rate than banana peel powder. It was shown by the sharp peaks ( $27^\circ$ ,  $32^\circ$ ,  $46^\circ$ , and  $58^\circ$ ) on the  $600^\circ\text{C}$  activated carbon graphs. Compared with the banana peel powder graph, the sharp peak is not found in the graph of banana peel powder. Based on research by Mopoung [12], at the peak of  $27^\circ$ , it showed that  $\text{K}_2\text{O}$  was formed at a temperature of  $500^\circ\text{C}$ . The peaks of  $32^\circ$ ,  $46^\circ$ , and  $58^\circ$  indicate  $\text{K}_2\text{CO}_3$ . The peak intensity increased in proportion to the increase in activation temperature ( $600^\circ\text{C}$ ). According to the other case peaks at  $27^\circ$ ,  $32^\circ$ , and  $74^\circ$  indicate carbon (monoclinic), peak intensity increases in proportion to the increase in carbonization temperature at  $600^\circ\text{C}$  [11, 13].



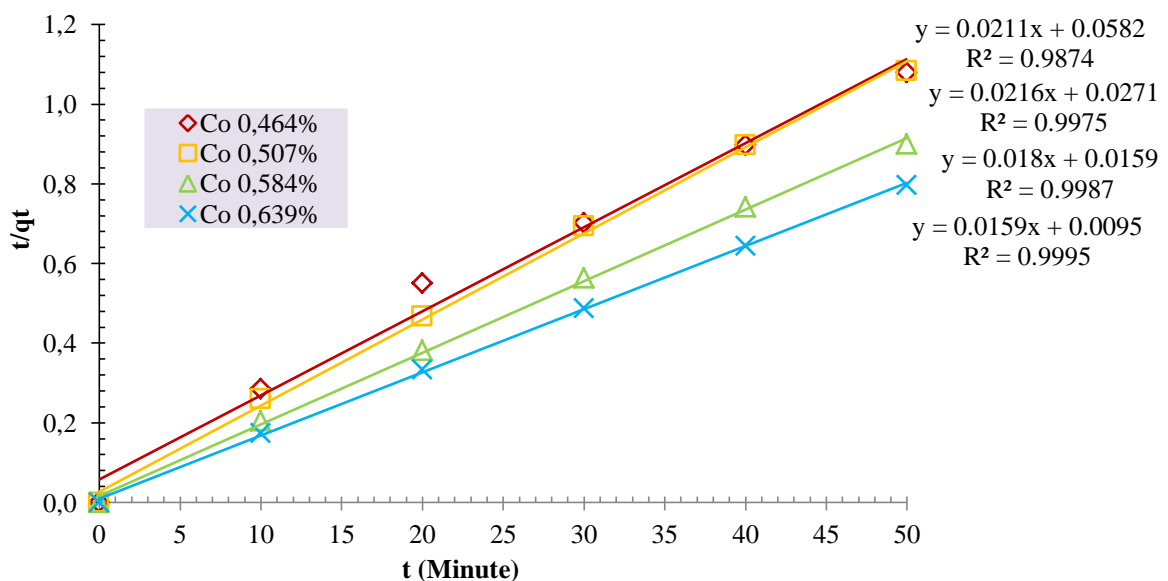
**Figure 2.** XRD Pattern for FFA (a) dry banana peel powder and activated carbon with an activation temperature of 600°C

The graphical relationship can be seen in Figure 3, it is obtained a linear equation  $y = -0.0691x + 1.639$  pseudo first order on free fatty acid adsorption at the initial concentration variation of FFA 0.639% with  $R^2$  0.9686, so we get  $k_1 = 0.1582$  and the value of  $q_e = 62.7040$  mg / g.

The second-order pseudo equation can be graphed for the relationship  $(t/qt)$  versus  $(t)$  time, as shown in Figure 4. The relationship graph shows that the value of  $R^2$  is 0.9995 with the linear equation  $y = 0.0159x + 0.0095$  with  $R^2$  of 0.9995. From the linear equation, the value of  $K_2 = 0.0266$  and the value of  $q_e = 62.9308$  mg/g. Analysis of modelling errors was carried out with the % error value. The value of % error was obtained from modelling and calculation data. The FFA concentration is 0.639%, the % error value is 1.0362%.



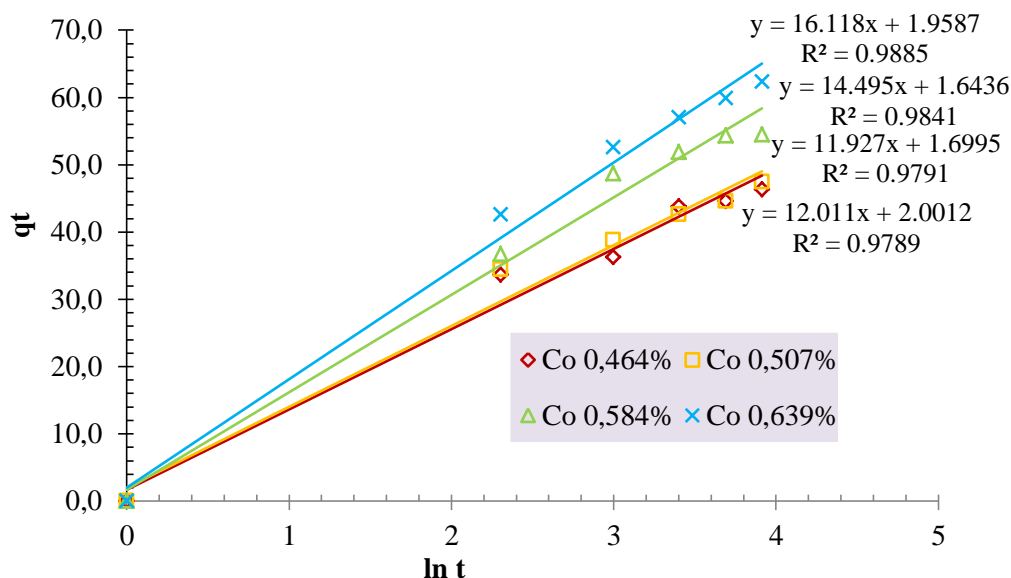
**Figure 3.** Pseudo-First-Order Linearity of Free Fatty Acid Adsorption



**Figure 4.** Pseudo-Second-Order Linearity of Free Fatty Acid Adsorption**Table 2.** Model of FFA Pseudo First Order Adsorption Kinetics Approach

The concentration of FFA (%)	Parameters	Activation Temperature 600 °C	Activation Temperature 650 °C	Activation Temperature 700 °C
<i>Pseudo First Order</i>				
0.464	qe (mg/g)	43.1119	43.8502	49.2700
	k <sub>1</sub> (min <sup>-1</sup> )	0.0737	0.0856	0.0993
	R <sup>2</sup>	0.9035	0.9194	0.9200
0.508	qe (mg/g)	47.1310	46.8618	49.0196
	k <sub>1</sub> (min <sup>-1</sup> )	0.0707	0.0804	0.0762
	R <sup>2</sup>	0.9298	0.9329	0.9515
0.584	qe (mg/g)	54.3308	54.5850	54.5907
	k <sub>1</sub> (min <sup>-1</sup> )	0.1173	0.1243	0.1460
	R <sup>2</sup>	0.9422	0.9652	0.9630
0.639	qe (mg/g)	60.7356	62.5678	62.7040
	k <sub>1</sub> (min <sup>-1</sup> )	0.1282	0.1322	0.1582
	R <sup>2</sup>	0.9664	0.9669	0.9686
<i>Pseudo Second Order</i>				
0.464	qe (mg/g)	44.8430	45.0450	47.3933
	k <sub>2</sub> (mg/g min)	0.0057	0.0059	0.0076
	R <sup>2</sup>	0.9756	0.9779	0.9874
0.508	qe (mg/g)	45.8716	45.6621	46.2963
	k <sub>2</sub> (mg/g min)	0.0102	0.0144	0.0172
	R <sup>2</sup>	0.9935	0.9970	0.9975
0.584	qe (mg/g)	54.9450	54.6448	55.5555
	k <sub>2</sub> (mg/g min)	0.0103	0.0143	0.0204
	R <sup>2</sup>	0.9953	0.9972	0.9987
0.639	qe (mg/g)	61.7284	62.1118	62.8930
	k <sub>2</sub> (mg/g min)	0.0113	0.0116	0.0266
	R <sup>2</sup>	0.9974	0.9978	0.9995
<i>Elovich Model</i>				
0.464	α (mg/g min)	200.0050	401.1985	450.0016
	β (mg/g)	1.2215	1.1387	1.0355
	R <sup>2</sup>	0.9775	0.9784	0.9791
0.508	α (mg/g min)	324.0009	460.0021	500.0020
	β (mg/g)	1.0541	1.0378	1.0378
	R <sup>2</sup>	0.9783	0.9784	0.9789
0.584	α (mg/g min)	421.0050	475.8947	513.3837
	β (mg/g)	0.8775	0.8798	0.8605
	R <sup>2</sup>	0.9827	0.9831	0.9841
0.639	α (mg/g min)	460.9904	481.8482	532.9647
	β (mg/g)	0.7616	0.7172	0.7188
	R <sup>2</sup>	0.9866	0.9880	0.9885

The elovich model equation could be graphed for the relationship (qt) versus (t) time shown in Figure 5. The R<sup>2</sup> value of 0.9885 is obtained in the equation  $y = 16.118x + 1.9587$  at the FFA concentration variation of 0.634%. The equation at the variation of the concentration of FFA 0.634%, the value of  $\alpha = 532.9647$  mg / g min and  $\beta$  0.7188 mg / g is obtained. In other variations of the FFA, concentration can be seen in the table.



**Figure 5.** Elovich Linearity of Free Fatty Acid Adsorption

Table 2 shows the adsorption kinetics parameters in which the pseudo-second-order model has  $R^2 = 0.9995$  and evolich, where  $R^2 = 0.9885$ . Both models show a better evaluation of the pseudo-first-order. Thus, the FFA adsorption kinetic model that best fits the experimental data ( $R^2 > 0.995$ ) is the pseudo-second-order model. FFA and activated carbon show the most significant amount of adsorption by suggesting that chemisorption is a rate-limiting step in the adsorption process. The adsorption strength of FFA on activated carbon activated by the KOH base indicates that the carbon surface has several functional groups from the hydrophobic region containing oxygen functional groups. Therefore, FFA is adsorbed in certain parts to interact with activated carbon mainly through hydrophobic bonds, followed by hydrogen bonds and ion-ion interactions. In this activated carbon material, a large surface area also has a significant role in adsorption.

#### 4. Conclusion

Kepok banana peels dried to remove long-chain carboxylic acids from used cooking oil have shown good efficiency. The FTIR spectrum of banana peels shows an increasing functional group such as hydroxyl and carboxyl. Experimental data have been installed well into the kinetic model showing the pseudo-second-order nature of the adsorption process. Biomass waste from harmless and readily available fruit peels such as Kepok banana peels can be used successfully as an adsorbent to reduce the amount of carboxylic acid from cooking oil at low concentrations.

#### 5. Acknowledgment

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