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Kinetic Study of Biodiesel Purification from Used Cooking Oil Using Activated Carbon

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Abstract. Used cooking oil (UCO) is a hazardous pollutant that leads to environmental problems. In general, UCO was discharged directly into the water, although it has the potential to be processed. One alternative process of UCO is its potency as the main material of biodiesel production. Biodiesel is produced via a transesterification process, during which the reaction between UCO and alcohol occurs. The results obtained from this reaction include biodiesel and glycerol. In this study, pure biodiesel was obtained by purification using the adsorption process. The adsorbent was activated carbon from coconut shells that were contacted at a certain concentration and contact time. The adsorbent concentrations were varied from 3, 6, 9, and 12(w/w) addition, while the contact times were 30, 45, 60, 75, and 90 min. The crude biodiesel adsorption was carried out at 90°C. FFA removal increased with increasing adsorbent concentration and contact time. With 12% adsorbent addition, FFA was removed up to 64.91% in a 90 min adsorption process. The kinetics of the adsorption process were analyzed using several kinetics models, either in the linear or nonlinear form. The best kinetic fit in this process was obtained using a nonlinear pseudo-second-order model.

Keywords: Adsorbent, Biodiesel, Kinetics, Waste Cooking Oil

INTRODUCTION

Biodiesel demand in Indonesia has increased over several years due to the Indonesian government's fossil fuel energy replacement policy. Fossil-based fuels are mixed with biodiesel by up to 20% and are targeted to 30% in 2025 for the transportation sector (DEN, 2019). Biodiesel is produced from various feedstocks such as edible oil (soybean, rapeseed, palm, cottonseed, sunflower, and coconut oil) and non-edible oil (jatropha, neem, rubber seed, jojoba, castor, Pongamia oil) (Shafeeq *et al.*, 2013).

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Another potential raw material in biodiesel production is used cooking oil (UCO). Direct disposal of UCO can cause various environmental problems. Recycling UCO into biodiesel is a promising solution to reduce the negative effects of UCO and fulfill the raw material demand for biodiesel production at a lower cost (Kawentar and Budiman, 2013; Simasatitkul *et al*., 2012).

The main production process of biodiesel from UCO involves several processes, such as esterification (Buasri *et al*., 2023; Neumann *et al*., 2016), transesterification, electrolysis, and pyrolysis (Cerón Ferrusca *et al*., 2023). The biodiesel production method commonly used is transesterification, which has several advantages in terms of conversion and cost. The transesterification process produces high-conversion biodiesel at low production costs. The operating conditions in this process are mild and produce biodiesel with characteristics similar to petroleum diesel (Suzihaque *et al*., 2022). Transesterification is a reversible reaction that occurs in three stages. First, the oil containing triglycerides is converted into diglycerides. Then, the diglycerides convert to monoglycerides and, lastly, become glycerol. In this reaction, the alcohol to oil ratio remains excessive, usually around 3:1. The reaction produces a biodiesel phase on the top layer and a glycerol-rich phase on the bottom layer (Chozhavendhan *et al*., 2020). The top-layer product or crude biodiesel mainly consists of methyl esters and several impurities such as spent alcohol, glycerin, and catalysts. If the crude is not treated, it can influence the fuel properties and cause problems in the application of the machine (Predojević, 2008).

A simple method to purify the crude biodiesel is by water washing. However, this method releases liquid effluent with high values of total suspended solid (TSS), volatile suspended solid (VSS), and mineral suspended solid (MSS). Alternative methods include ion exchange and magnesium silicate (Magnesol). However, these processes do not significantly affect glyceride content, water content, acid value, or oil stability index (OSI) (Atadashi *et al*., 2011; Berrios and Skelton, 2008). Moreover, resin regeneration is not recommended by suppliers that could generate more solid waste (Stojković *et al*., 2014). Crude biodiesel purification using activated carbon gave higher yields and better properties than water washing (Fadhil and Dheyab, 2015).

The purification process of biodiesel produced from UCO was performed using activated carbon. The activated carbon was synthesized from spent tea waste and compared with silica gel and water washing methods. Using activated carbon gave a higher yield of 97% than other methods (Fadhil *et al*., 2012). Another purification process was studied using rice husk ash (RHA) with a concentration of 1% to 5% (w/w) and compared with other methods (using 1% H_3PO_4 solution and 1% Magnesol). Adding 4% RHA in the crude biodiesel at 65°C gave effective performance in biodiesel impurities removal (Manique *et al*., 2012). The purification process was completed using 1% to 5% (w) of bio-adsorbent from oil palm empty fruit bunch (OPEFB). 30% of the FFA was successfully removed with the addition of 5% bio-adsorbent (Farid *et al*., 2017).

The work aimed to study the kinetics of purification in crude biodiesel produced from UCO using activated carbon as the adsorbent. These studies were conducted at different concentrations of activated carbon adsorbent and contact times. The adsorption kinetics were evaluated using several kinetic models, including linear and nonlinear correlation.

MATERIALS AND METHODS

Materials

In this study, the materials used for biodiesel production were UCO from a local fried chicken merchant and activated carbon powder produced from coconut shells with 100 mesh sizes. KOH and Methanol (99% purity Merck, Germany) were also needed as catalyst and reactant, respectively.

Methods

The pretreatment process was performed before the transesterification process to reduce the UFO's Free Fatty Acid (FFA) concentration. 350 g of UFO was contacted with 6% (w/w) of activated carbon. The mixture was homogenized at 90°C for 90 min.

Biodiesel production was started with 2.3 g of KOH diluted in 62.5 ml methanol. The solution reacted with 250 ml of treated UFO that had heated up to 60°C. The mixture was stirred at 500 rpm for 60 min. After the reaction, the mixture was inserted into a separating funnel to separate the biodiesel and crude glycerol.

The upper product obtained from the separation funnel contained biodiesel and other byproducts. To purify it, the biodiesel was contacted with activated carbon. The adsorption process was varied using different concentrations of the adsorbent (3%, 6%, 9%, and 12% w/w) and adsorption contact time (30, 45, 60, 75, and 90 min). The adsorption process took place at 90°C.

Data Analysis

The properties of crude biodiesel were determined using FFAs determined using the titration method. Palmitic acid was the most abundant FFA in UFO biodiesel. The concentration of FFAs in biodiesel was calculated using Eq. (1).

$$C = \frac{V \times N \times 256}{W} \tag{1}$$

where C is the FFAs concentration expressed as mg/g, V is the volume of the KOH solution consumed during the titration process (mL), N is the normality of the KOH solution (mol/L), 256 is the molecular weight of palmitic acid (g/mol) which is a major saturated fatty acid in palm oil (Lim *et al*., 2018), and W is the weight of biodiesel (g).

The activated carbon's equilibrium adsorption uptake (q_e) was calculated using Eq. (2), where q_e is expressed in mg/g. C_0 and C_e represent the initial and equilibrium FFA concentration, respectively. W is the mass of biodiesel in g, and m is the mass of the adsorbent in g.

$$q_e = \frac{(C_0 - C_e)W}{m} \tag{2}$$

The efficiency of FFAs was calculated by Eq. (3), which represents the FFA removal.

$$FFA\ Removal = \frac{(C_0 - C_e)}{C_0} 100\% \tag{3}$$

The kinetic studies were evaluated using linear and nonlinear models. The adsorption kinetics correlations used were the pseudo-first-order model, pseudo-second-order model, nonlinear pseudo-first-order model, nonlinear pseudo-second-order model, and nonlinear pseudo-*n*th-order. Lagergren (1898) proposed the linear pseudo-first-order. Hence, the linear pseudo-second-order model, used equation from Ho and McKay (1999). The kinetic models used are listed in Table 1.

Table 1. General Equations of Kinetic Models Used in This Study

Pseudo-first-order $\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_e - q_t)$	(4)
Pseudo-second-order $\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	(5)
Nonlinear pseudo-first-order $q_t = q_e[1 - e^{-k_1 t}]$	(6)
Nonlinear pseudo-second-order $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	(7)
Nonlinear pseudo-*n*th-order $q_t = q_e - \left[(n-1)k_n t + q_e^{(1-n)}\right]^{\frac{1}{1-n}}$	(8)
Note: k_i=constant; q_e=equilibrium adsorption uptake (mg/g); q_t=adsorption uptake at time t (mg/g); t=time (min)	

For nonlinear modeling, the estimation of model parameters was facilitated using the objective function (OF). The OF is the sum of the square of differences between the experimental and calculated data of the response variable as stated in Eq. (9).

$$OF = \sum_{n=1}^{n} \left(q_{t,exp,n} - q_{t,cal,n}\right)^2 \tag{9}$$

Error analyses between experimental data and calculations using the model were evaluated using the coefficient of determination (R^2), root mean square deviation (RMSE), and chi-square statistic ($\mathcal{X}^2$) that represented by Eq. (10)-(12), respectively. The best-fitted model would have R^2 with a value near 1 and minimum values of RMSE and $\mathcal{X}^2$.

$$R^2 = 1 - \frac{\sum_{n=1}^{n}\left(q_{t,exp,n} - q_{t,cal,n}\right)^2}{\sum_{n=1}^{n}\left(q_{t,exp,n} - \overline{q_{t,exp,n}}\right)^2} \tag{10}$$

$$RMSE = \sqrt{\frac{1}{n-1}\sum_{n=1}^{n}\left(q_{t,exp,n} - q_{t,cal,n}\right)^2} \tag{11}$$

$$\mathcal{X}^2 = \sum_{n=1}^{1} \frac{\left(q_{t,exp,n} - q_{t,cal,n}\right)^2}{q_{t,cal,n}} \tag{12}$$

Here, $q_{t,exp}$ is experimental adsorption capacities at time *t* (mg/g), $q_{t,cal}$ is theoretical adsorption capacities at time *t* (mg/g), and *n* is the number of data.

RESULTS AND DISCUSSION

FFA Removal

In this study, an activated carbon adsorbent was applied to crude biodiesel produced from UCO. FFA had to be removed because it could provoke corrosion and lessen the oxidation stability of the fuel (Berrios and Skelton, 2008). From Fig. 1, the FFA removal increased over time for all adsorbent concentrations. These conditions occurred because the longer adsorption time prolonged the contact between the adsorbent and the crude biodiesel. The binding of the impurities into the adsorbent pores also would increase. This study showed the optimum time of the adsorption process was 90 min.

Fig. 1 also shows the effect of the adsorbent concentration. The lowest FFA removal was achieved using 3% activated carbon. With higher adsorbent concentrations, the amount of FFA removed increased due to the greater contact area. The highest FFA removal was obtained at 12% adsorbent and a contact time of 90 min, with a value of 64.91%.

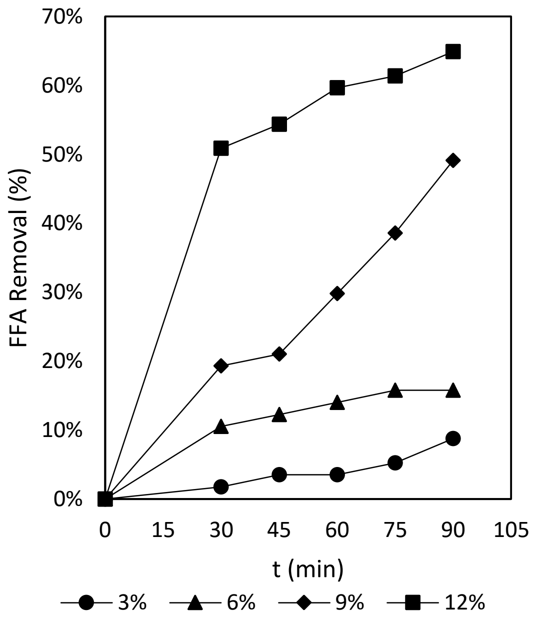

Fig. 1: Effect of Adsorbent Concentration on FFA Removal Over Time

The adsorption uptake of the adsorbent increased over time (Fig. 2). Initially, FFA adsorbed on the activated carbon surface rapidly. The adsorption rate gradually decreased because the adsorbent surface reached saturation condition and the adsorbate entered the pores that took a relatively long contact time (Baccar *et al*., 2010; Rahayu *et al*., 2019).

Adsorption Kinetics

Kinetics evaluation of the batch adsorption process is important for defining the sorption type between the FFA and the adsorbent. The pseudo-first-order kinetic model assumes that the rate of adsorbate uptake is limited to one mechanism. The pseudo-second-order kinetic model assumed that the adsorption rate is limited by chemical sorption or that electrons change between the sorbate and adsorbent (Waskita *et al*., 2012).

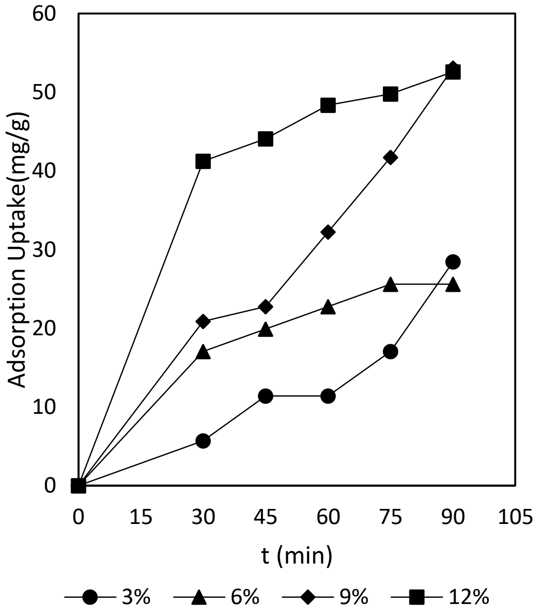

Fig. 2: Effect of Adsorbent Concentration on Adsorption Uptake

First, the experimental kinetic data of FFA adsorption on crude biodiesel using activated carbon were fitted to linear pseudo-first-order and pseudo-second-order. The linear pseudo-first-order kinetic constant and theoretical q_e were calculated from the plots of $\ln(q_e-q_t)$ versus t in Fig. 3. Hence, the linear pseudo-second-order was calculated from the plots of t/q_t versus t in Fig. 4. The values of the kinetic constant, theoretical q_e, and error analysis for the linear model were listed on Table 2.

For nonlinear model evaluation, the values of the kinetic constant and theoretical q_e were obtained from trial-error analysis using an objective function that was set to the minimum value. The calculation obtained the kinetic constant, theoretical q_e, and the *n*th-order for the pseudo-*n*th-order kinetic model. The values and error analysis results for all adsorbent concentration are listed in Table 3.

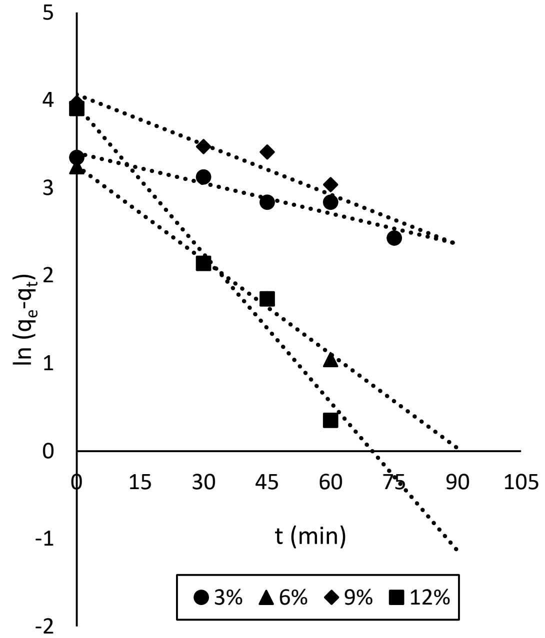

Fig. 3: Linear Form of Pseudo-First-Order Model

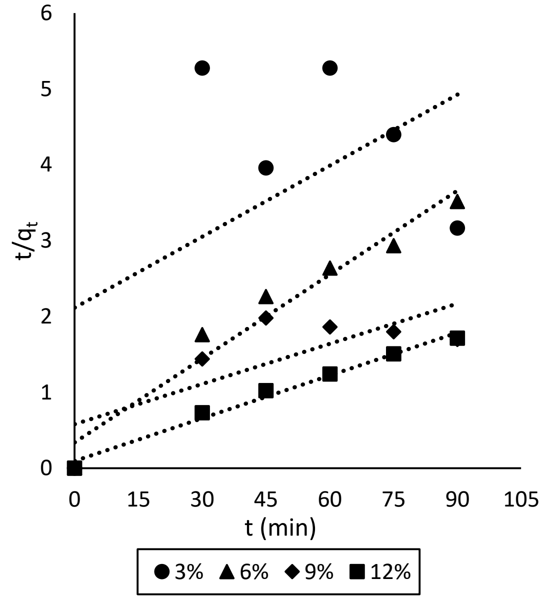

Fig. 4: Linear Form of Pseudo-Second-Order Model

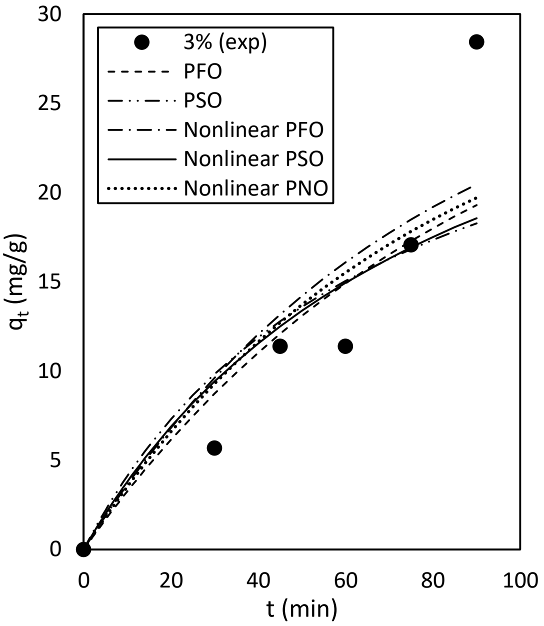

Fig. 5: Experimental Data and Fitted Kinetic Models for FFA Removal from Crude Biodiesel at 3% Adsorbent

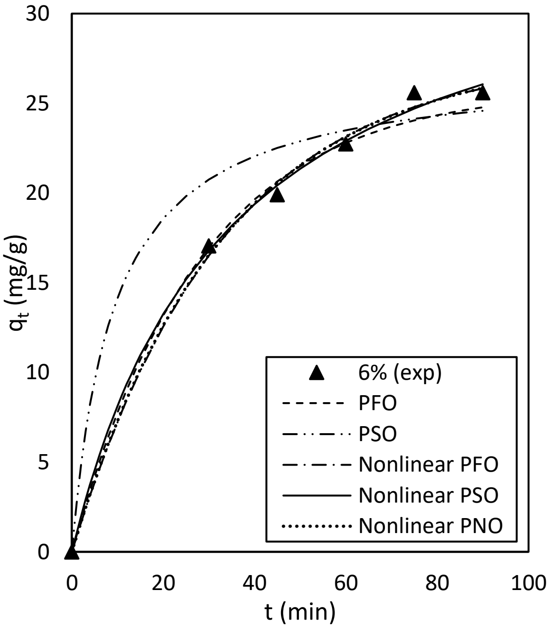

Fig. 6: Experimental Data and Fitted Kinetic Models for FFA Removal from Crude Biodiesel at 6% Adsorbent

The evaluation of the linear and nonlinear kinetic models for each adsorbent concentration were presented in Fig. 5–8, respectively. With the addition of

3% activated carbon, the adsorption mechanism was fitted to a linear pseudo-first-order kinetic model that occurred on one mechanism. For higher adsorbent concentrations, nonlinear models showed better results than linear kinetic models. Generally, the nonlinear pseudo-second-order fitted well with 6-12% addition of adsorbent. In the pseudo-second-order model, the kinetic rate was limited on the surface of the adsorbent and the chemisorption mechanism involved in this adsorption system. The impurities are removed from the mixture by physicochemical interaction between those two phases (Ersali *et al*., 2013). The surface of activated carbon contains several hydrophobic functional groups containing oxygen. Therefore, FFA adsorbed on hydrophobic binds (Phetrungnapha *et al*., 2023; Rengga *et al*., 2021).

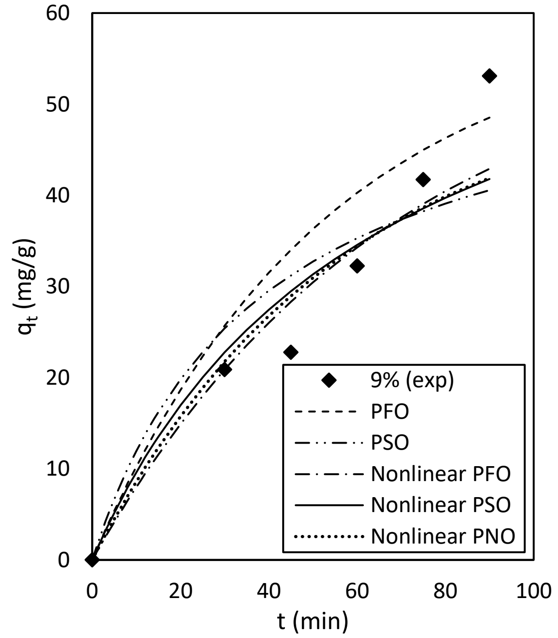

Fig. 7: Experimental Data and Fitted Kinetic Models for FFA Removal from Crude Biodiesel at 9% Adsorbent

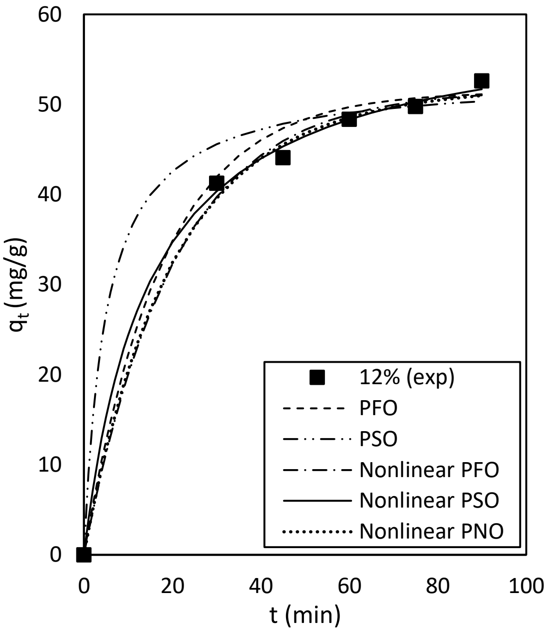

Fig. 8: Experimental Data and Fitted Kinetic Models for FFA Removal from Crude Biodiesel at 12% Adsorbent

CONCLUSIONS

Activated carbon from coconut shells effectively removed FFA in crude biodiesel. The adsorption process was effectively run for longer contact times to give better sorption on the adsorbent. The highest FFA removal was achieved using a 12% adsorbent concentration in a 90 min process. The kinetic model of these adsorption processes followed a nonlinear pseudo-second-order that the chemisorption process limited the sorption process.

Table 2. Parameters of Linear Kinetic Models (Pseudo-First-Order and Pseudo-Second-Order) for FFA Adsorption at Different Activated Carbon Concentrations

Model	Adsorbent Concentration % (w/w)			
	3	6	9	12
Pseudo-First-Order				
$q_{e,cal}$ (mg/g)	29.9233	25.8113	58.2275	51.4403
k_1 (min^{-1})	0.0115	0.0358	0.0190	0.0564
R^2	0.7794	0.9922	0.8553	0.9916
RMSE	4.2013	0.7780	6.3989	1.6476
$\mathcal{X}^2$	6.2731	0.1540	6.8930	0.3388
Pseudo-Second-Order				
$q_{e,cal}$ (mg/g)	32.0286	27.0929	56.6309	53.1178
k_2 (g/mg.min)	0.0005	0.0040	0.0005	0.0038
R^2	0.7166	0.9482	0.8408	0.9799
RMSE	4.7617	2.0037	6.7112	2.5473
$\mathcal{X}^2$	8.4553	1.1099	7.5439	0.8275

Table 3. Parameters of Nonlinear Kinetic Models (Pseudo-First-Order, Pseudo-Second-Order, and Pseudo-*n*th-Order) for FFA Adsorption at Different Activated Carbon Concentrations

Model	Adsorbent Concentration % (w/w)			
	3	6	9	12
Nonlinear Pseudo-First-Order				
$q_{e,cal}$ (mg/g)	29.4844	27.6465	58.4611	51.6589
k_1 (min^{-1})	0.0132	0.0303	0.0147	0.0489
R^2	0.7779	0.9965	0.9141	0.9954
RMSE	4.2157	0.5192	4.9304	1.2138
$\mathcal{X}^2$	6.4533	0.0756	3.8102	0.1934
Nonlinear Pseudo-Second-Order				
$q_{e,cal}$ (mg/g)	36.0807	36.0033	71.7822	60.1546
k_2 (min^{-1})	0.0003	0.0008	0.0002	0.0011
R^2	0.7386	0.9970	0.8869	0.9982
RMSE	4.5730	0.4806	5.6572	0.7569
$\mathcal{X}^2$	7.6852	0.0594	5.1657	0.0750
Nonlinear Pseudo-*n*th-Order				
$q_{e,cal}$ (mg/g)	28.4444	27.9063	52.6222	52.1632
k_n (g/mg.min)	0.0128	0.0267	0.0171	0.0346
n	1.010	1.0395	1.010	1.0977
R^2	0.7736	0.9966	0.8948	0.9960
RMSE	4.2563	0.5137	5.4559	1.1360
$\mathcal{X}^2$	6.5391	0.0733	4.7331	0.1723

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