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Bulletin of Chemical Reaction Engineering & Catalysis, 11 (1), 2016, 93-99

Research Article

Kinetic Study on the SO_2 Adsorption using $CuO/\gamma\text{-}Al_2O_3$ Adsorbent

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Received: 10th November 2015; Revised: 29th February 2016; Accepted: 29th February 2016

Abstract

Adsorbent $CuO/\gamma\text{-}Al_2O_3$ for adsorption of SO_2 were prepared by impregnating $Cu(NO_3)_2.3H_2O$ solution. Five types of adsorbent were obtained 5Cu (intended Cu concentration of 5%, actual of 4.92%, 8Cu (7.68%), 15Cu(14.13%), 22Cu (20.80%) and 27Cu (25.80%). For activity test, model gas containing SO_2 with a concentration of about 0.757 $mol.m^{-3}$ were passed through the bed of 1 gram adsorbent at a flow rate in the range of 1.4-1.8 $mL.s^{-1}$. Adsorption of SO_2 were carried out at a constant temperature of 300, 350, 400 or 450 °C. Increasing sulfur loadings (gram of sulfur per gram of adsorbent) were observed with increasing adsorption temperatures, but not with increasing Cu content in the adsorbent. Among those types, adsorbent of 8Cu was considered as the best with respect to the sulfur loading (3.71 g of sulfur per 100 g of adsorbent). Adsorbent 5Cu had actually a better sulfur loading, but it was suspected being contributed also by adsorption of SO_2 on $\gamma\text{-}Al_2O_3$. The shrinking core model was used in the kinetic study of adsorption using 8Cu and with additional assumption of a spherical particle. Compared to film diffusion and pore diffusion controlling step models, the reaction rate limitation was the best to fit the experimental data. The reaction rate constant for this model at temperatures of 300, 350, 400 and 450 °C were 0.015, 0.027, 0.030 and 0.042 $kg.m.mol^{-1}.min^{-1}$, respectively. The activation energy was 21.37 $kJ.mol^{-1}$ and the frequency factor was 1.45 min^{-1}. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: SO_2 adsorption; $CuO/\gamma\text{-}Al_2O_3$ adsorbent; CuO conversion; shrinking core model

How to Cite: Bahrin, D., Subagjo, S., Susanto, H. (2016). Kinetic Study on the SO_2 Adsorption using $CuO/\gamma\text{-}Al_2O_3$ Adsorbent. *Bulletin of Chemical Reaction Engineering & Catalysis*, 11 (1): 93-99. (doi:10.9767/bcrec.11.1.425.93-99)

Permalink/DOI: http://dx.doi.org/10.9767/bcrec.11.1.425.93-99

1. Introduction

Increasing the use of low grade coal with a relatively high sulfur content for power plant will increase the emission SO_2. This gas is poisonous that causes acid rains, corrosion at equipments and very harmful to human health. Depending on the excess air during the combustion, the concentration of SO_2 in the flue gas can be in the range of 294-747 $mg.Nm^{-3}$. Increasing consumption of coal with the high sulfur content of more than 0.5%.wt (dry basis), the SO_2 content may exceed the environmental standard of 750 $mg.Nm^{-3}$ in Indonesia [1].

Conventional FGD (flue gas desulfurization) technologies, such as absorption using lime/limestone slurry or sea water are claimed to have an efficiency of SO_2 removal up to 99%. But these techniques discharge other forms of waste. So it has been considered since long time ago to develop a method to adsorb SO_2, then desorp it as SO_3, which may finally be

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converted to H_2SO_4. The main reaction is presented in Equation (1).

$$CuO_{(s)} + SO_{2(g)} + 1/2O_{2(g)} \rightarrow CuSO_{4(s)} \quad (1)$$

For this technique, a regenerable adsorbent CuO/γ-Al_2O_3 has been proposed by many researchers [2-5]. Various CuO content in γ-Al_2O_3 were reported by previous researchers [6-10]. The effective CuO content on γ-Al_2O_3 was in the range of 4-8 % by mass [1, 5, 11], though more CuO could be impregnated [1, 6, 8, 11]. Increasing CuO of course increase the sulfur loading of adsorbent CuO/γ-Al_2O_3. This correlation is not linear, due probably to a blocking of pores of the support by CuO [1, 8, 12, 13].

Further explorations on preparation, characterization and activities test of CuO/γ-Al_2O_3 as a regenerable adsorbent is reported in this paper. A special attention was paid to the kinetic study of SO_2 adsorption on a CuO/γ-Al_2O_3 having a CuO content of 8%, which was the most effective adsorbent [1]. Hopefully, the kinetic model may be used for designing an adsorption columns.

The shrinking core model was used to represented the experimental data with the following assumptions: (a) constant particle size of adsorbent; (b) inwards movement of reaction surface. The shrinking core model is a popular model since it is clear physicochemical, easily applied with a good approximation for many gas-solid reacting system [14, 15]. The shrinking core model is already used for FGD to describe the behavior of sulfation of limestone [14]. Other kinetic of SO_2 such as pore and grain models can be found in some literatures [16, 17].

2. Materials and Methods

2.1. Preparation and characterization of adsorbent

Adsorbent CuO/γ-Al_2O_3 was prepared using the dry impregnation method with a solution of $Cu(NO_3)_2.3H_2O$ as a source of active site. The γ-Al_2O_3 support has the following pore properties: spesific surface area of 218.43 $m^2.g^{-1}$, pore volume of 0.46 $cm^3.g^{-1}$ and average pore diameter of 83.3 Å. The $Cu(NO_3)_2$ impregnated support was dried in two steps: at a temperature of 50°C for 8 h, and at 120 °C for 5 h. Finally, the dry impregnated support was calcined at a temperature of 400 °C for 8 h to obtained CuO on the support.

The impregnation might be carried out more than once to get desired CuO contents up to 30% by mass (see Table 1). Detailed procedure of the impregnation was reported in our previous paper [1]. The CuO content in the adsorbent were analyzed using Atomic Absorption Spectroscopy (Varian Spectra AA 220). The pore properties of the adsorbent were analyzed using BET method (Nova 3200e Quanta Chrome).

2.2. Activity test of adsorbent

The activity tests of CuO/γ-Al_2O_3 were con-

Table 1. Characteristics of adsorbent

Adsorbent	Cu content (mass fraction)	Pore characteristics			Ref.
		Surface area (m^2/g)	Pore volume (cm^3/g)	Mean diameter (Å)	
0Cu	0%	218.43	0.46	83.33	this study
0Cu	0%	207.39	0.48	91.69	[1]
5Cu	4.92%	211.23	0.43	81.14	this study
8Cu	7.68%	196.11	0.41	83.20	this study
8Cu	7.93%	190.49	0.44	91.47	[1]
15Cu	14.13%	157.30	0.37	94.84	this study
15Cu	14.76%	160.57	0.37	92.76	[1]
Cu-1	11.20%	153.00	0.48	-	[8]
Cu-2	14.10%	150.00	0.48	-	[8]
22Cu	20.80%	149.37	0.30	88.40	this study
Cu-3	17.40%	141.00	0.47	-	[8]
Cu-4	21.30%	137.00	0.47	-	[8]
27Cu	25.80%	124,23	0.28	90.13	this study
30Cu	28.98%	128.62	0.29	88.51	[1]
Cu-5	26.50%	134.00	0.47	-	[8]

ducted in an electrically heated tubular reactor (see Figure 1). Adsorptions were carried out for 60 minutes, at a constant temperature of 300, 350, 400 or 450 °C. The amount of adsorbent was 1.0 gram. The gas was a mixture of SO_2 and air, having a SO_2 concentration of about 0.757 mol.m^{-3}. The gas flowrate was adjusted in the range of 1.4-1.8 mL.s^{-1}.

Concentration of SO_2 in the gas was measured by bubbling the gas into a series of three bottle containing 15 mL H_2O_2 (20% v/v). The absorbed SO_2 in H_2O_2 converted to H_2SO_4 which was then titrated using NaOH (0.1 M). In order to get the progress of adsorption of SO_2 on CuO, the solution of H_2O_2 was replaced with the fresh one every five minutes.

The amount of reacted CuO was calculated from the removal of SO_2 from the gas stream (see Equation (1)). Then, the conversion of CuO was calculated by Equation (2).

$$X = \frac{reacted\ CuO\ (mol)}{initial\ CuO\ (mol)} \tag{2}$$

2.3. The shrinking core model

In our case, we took the following assumption of spherical particle and constant size, and isothermal reaction inside the particle. Furthermore, the SO_2 concentration was assumed constant. The following three possible phenomena were examined in this study:

For film diffusion limitation:

$$X = k_m.t \tag{3}$$

$$k_m = \frac{3k_g C}{\rho R} \tag{4}$$

For pore diffusion limitation:

$$1 - 3(1-X)^{2/3} + 2(1-X) = k_d t \tag{5}$$

$$k_d = \frac{6DC}{\rho R^2} \tag{6}$$

For surface chemical reaction limitation:

$$1 - (1-X)^{1/3} = k_r t \tag{7}$$

$$k_r = \frac{k_s C}{\rho R} \tag{8}$$

For chemical reaction limitation, the Arrhenius equation may be applied:

$$\ln k_s = \ln A - \frac{E_a}{RT} \tag{9}$$

where, t = reaction time (minute); ρ = density of solid reagent (kg.m^{-3}); C = concentration of fluid reagents (mol.m^{-3}); k_g = mass transfer coefficient (m^2.s^{-1}); k_s = reaction rate constant (kg.m.mol^{-1}.min^{-1}); R = radius of solid particle (m); D = diffusion coefficient, (m^2.s^{-1}); X = conversion of CuO; A = frequency factor (min^{-1}); E_a = activation energy (kJ.mol^{-1}); R = ideal gas constant (8.314 J.mol^{-1}.K^{-1}); and T = absolute temperature (K). Using an appropriate linearization, the above each reaction rate equation can be drawn as a straight line, with k_m, k_d and k_r as constants, respectively.

3. Results and Discussion

3.1. Characteristics of CuO/γ-Al_2O_3 adsorbent

The desired Cu contents in the adsorbent CuO/γ-Al_2O_3 were successfully obtained using dry impregnation method (see Table 1). The specific surface area of the adsorbent were found to decrease with increasing of Cu content. This was due probably to coverage of pores by CuO. These phenomena were reported already in our paper [1] and also by other previous researcher [8].

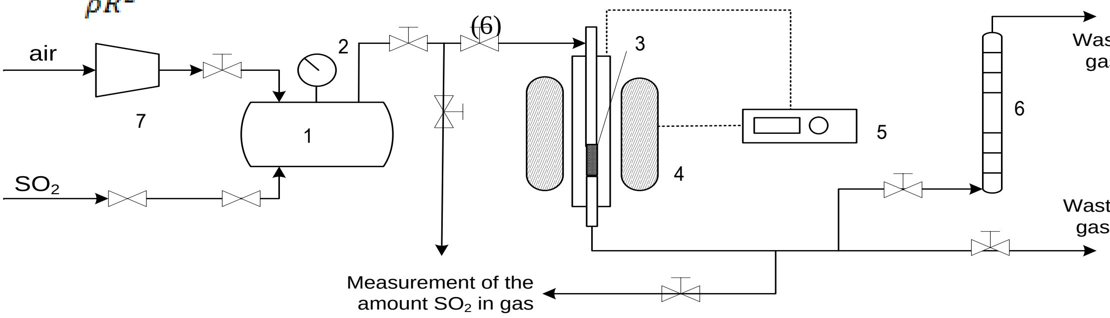


Figure 1. Experimental set up: (1) Feed gas storage; (2). Manometer; (3). Adsorbent; (4). Furnace; (5). Temperature controller; (6). Bubble soap meter; (7). Air compressor

3.2. Sulfur Loading

The increase in CuO content in did not affect the maximum sulfur loading, or gram of sulfur per 100 gram of adsorbent (see Figure 2). On the other hand, the sulfur loadings were influenced by the adsorption temperature, the higher temperature the higher loading. Unfortunately, the maximum sulfur loadings were far below the stoichiometric yield, and were more less the same as those obtained by by previous researcher [8]. This incomplete utilization of CuO indicated that some active site of CuO could not be reached by SO_2, as CuO were not evenly distributed and a possible formation of a multilayer CuO on the surface of pores [1, 13].

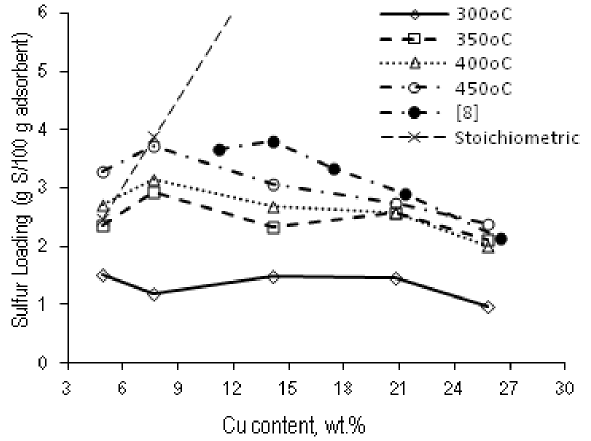


Figure 2. Maximum sulfur loading as a function of Cu content in adsorbent (see also Table 1)

Progress in CuO conversions were measured for five types adsorbent: 5Cu, 8Cu, 15Cu, 22Cu and 27Cu (see Figure 3), including experimental data reported by [8]. Adsorbents with a lower CuO content had significantly a better CuO conversion. This confirmed the effectivity of CuO distribution on the internal surface, and the gas and solid reaction took place only on the top layer active site.

Unrealistic CuO conversions exceeding 100% were observed from the adsorbent 5Cu, at temperatures of 400 and 450 ^{o}C. These were probably due to additional SO_2 reaction with the support, γ-Al_2O_3. Please note that CuO conversion was calculated from the decrease of SO_2 concentration across the adsorbent bed. Meanwhile part of internal surface in the adsorbent 5Cu was not covered CuO yet. This phenomenon is also reported by previous researchers [4, 5, 7, 11, 12]. Probability of reaction between SO_2 and Al_2O_3 had been checked using XRD analysis on adsorption of SO_2 using original support γ-Al_2O_3 [1, 8].

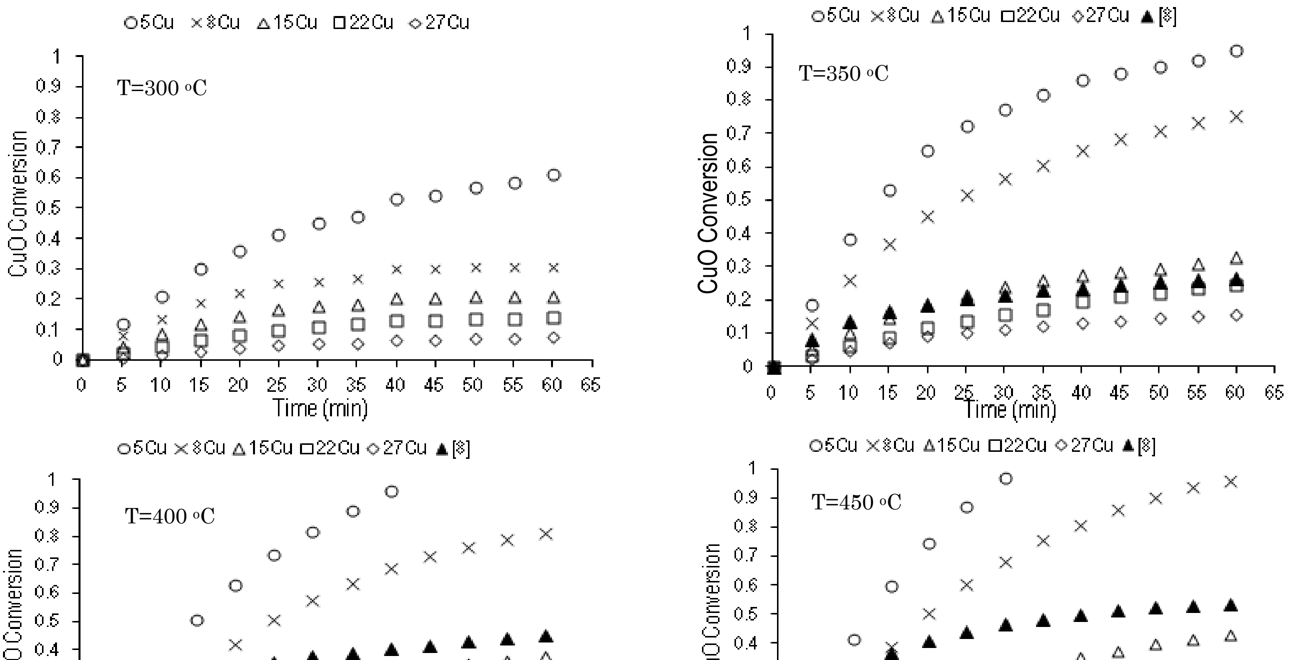


Figure 3. Progress in adsorption test

3.3. Model validation

Although the sulfur loadings were far from the stoichiometry (Figure 2), the conversion rate already decreased towards zero (Figure 3). These lead to a hypothesis that the overall rate of reaction between SO_2 and CuO was controlled either by pore diffusion or by surface reaction, not by film diffusion. As the above discussion, the adsorbent 8Cu was considered the best among five type adsorbents. So, its experimental data was used in the kinetic study.

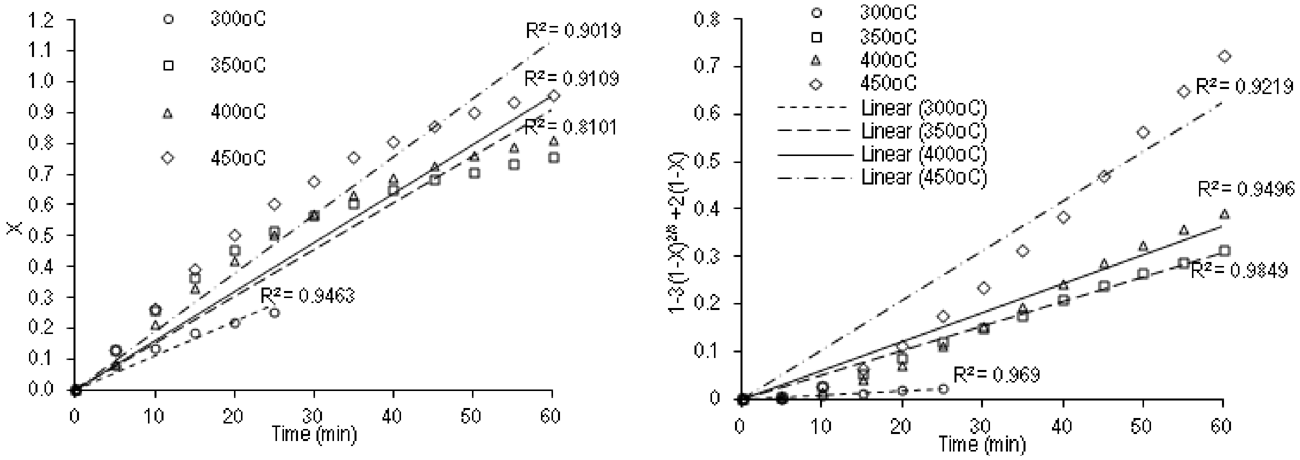
With an additional assumption of particle diameter of 2 mm, the experimental data were fitted very well using the shrinking core model with surface reaction as controlling step (Figure 4, including the correlation coefficient). Blocking pore or covering active site of CuO by $CuSO_4$ might explain the reason of this finding.

Further evaluation on the shrinking core model with reaction limitation resulted the reaction rate constant of k_r and k_s at various temperatures for adsorbent 8Cu. Finally, the kinetic parameters for surface reaction were found as follows: (a) activation energy: E_a = 21.37 kJ.mol^{-1}; (b) frequency factor: A = 1.45 min^{-1}.

The above activation energy was slightly lower than the common value for kinetic of reaction regime, i.e. in the range of 25-35 kcal.mol^{-1}. Thus, the overall process in the adsorption of SO_2 with CuO/γ-Al_2O_3 actually dictated not only by surface chemical reaction, but also by physical phenomena. The validation of the model using the above kinetic parameters was very satisfactory (Figure 6).

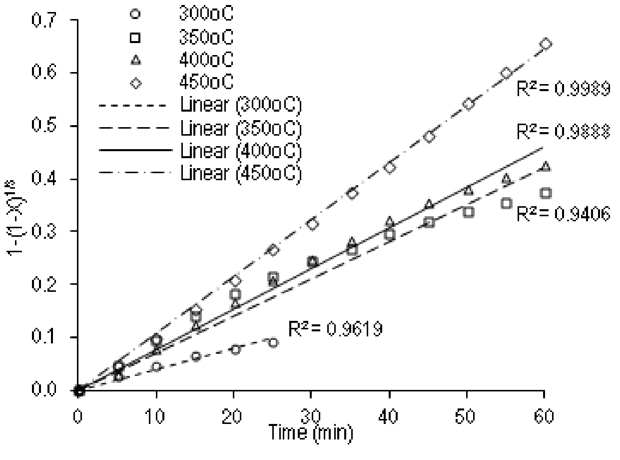
4. Conclusions

The CuO concentration in adsorbent affected significantly to the pore properties of adsorbent CuO/γ-Al_2O_3. Unfortunately, its increase did not enhance the sulfur loading, and even decreased the CuO conversion. Adsorb-



(a) film diffusion limitation

(b) pore diffusion limitation



(c) chemical reaction limitation

Controlling step	Correlation coefficient (R^2)			
	300 °C	350 °C	400 °C	450 °C
(a) film diffusion	0.946	0.810	0.911	0.902
(b) pore diffusion	0.969	0.985	0.950	0.922
(c) chemical reaction	0.962	0.941	0.989	0.999

Figure 4. Fitting shrinking core models on experimental data of adsorption using 8Cu

ent 8Cu was considered as the best. Adsorption process could be represented by shrinking core model with reaction limitation.

Acknowledgements

This research is a part of doctoral research in Chemical Engineering FTI-ITB. This research on development of regenerable adsorbent are financed by PT. Pupuk Sriwidjaja, Palembang.

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Table 2. The value of k_r and k_s at various temperatures for adsorbent 8Cu (C_{SO2} = 0.757 mol.m^{-3} and $\rho_{adsorbent}$ = 2911.6 kg.m^{-3})

Parameters	Temperatures (°C)			
	300	350	400	450
k_r (min^{-1})	0.004	0.007	0.0077	0.0108
k_s (kg.m.mol^{-1}.min^{-1})	0.015	0.027	0.0300	0.0420

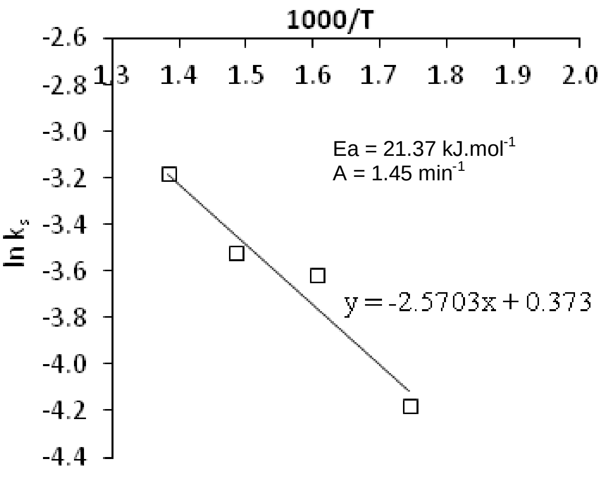

Figure 5. ln k_s versus 1/T for adsorbent 8Cu (see Table 2, based on Equation (9))

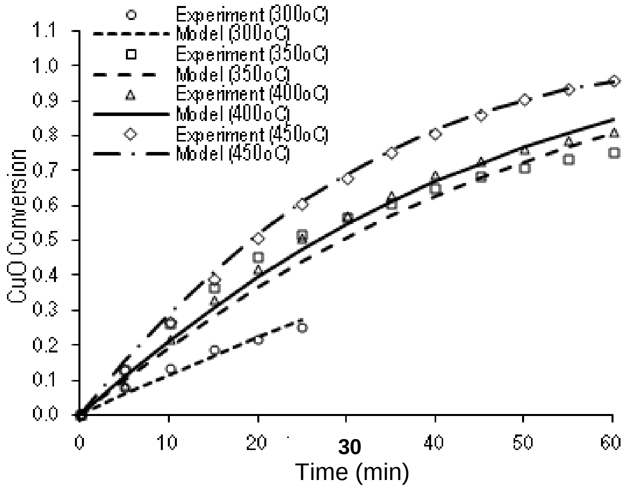

Figure 6. Fitting chemical reaction limitation model to experiment data of adsorbent 8Cu

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