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by Agus Mirwan

Submission date: 07-Mar-2021 05:42PM (UTC-0800)

Submission ID: 1526793674

File name: Artikel_Hairullah_revisi_-_HAIRULLAH_MHS_ULM.docx (196.26K)

Word count: 2147

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A modified shrinking core model for microwave-assisted leaching of aluminum from peat clay

Hairullah, A Mirwan*, M D Putra, B H Ilmanto, H S H Putri, M B Ulum, M R Haka

Chemical Engineering Department, Faculty of Engineering, Lambung Mangkurat University, Banjarbaru, South Kalimantan, 71714, Indonesia

*Corresponding author's email: agusmirwan@ulm.ac.id

Abstract. Aluminum oxide in peat clay has the potential to be used as a catalyst, coagulant, and adsorbent for the water treatment process. The usefulness of aluminum oxide in peat clay is enhanced by the leaching process. Aluminum was leached from peat clay in a variety of microwave power, HCl concentrations, and particle size during the stirring process with the microwave-assisted leaching for 1 hour. The effect of the microwave leaching parameters on aluminum leaching rate was observed. The leaching process is then modeled using the shrinking core (SC) model. The SC model used in microwave-assisted leaching was assumed a pseudo steady state with chemical reactions. Effective diffusivity (D_e), mass transfer coefficient (k_c), and reaction rate constants (k) are used as fitting parameters. The best fitting parameters D_e , k_c , and k obtained 0.0049 cm²/s, 2.49 cm/s, and 0.5 cm/s, respectively. The comparison of experimental data and model calculations shown that the SC model can describe experimental data well for all microwave-assisted leaching conditions.

1. Introduction

Peat clay is collected at a depth of about 150 to 300 centimeters from surface soil. Peat clays are found in Indonesia, especially in South Kalimantan [1]. Mirwan et al. [2] reported that peat clay has high mineral content of iron oxide (Fe₂O₃), silicon oxide (SiO₂), titanium oxide (TiO₂), aluminum oxide (Al₂O₃), calcium oxide (CaO), and other oxides in significant amounts small. The content of aluminum oxide (Al₂O₃) in peat clay is around 7.20% which by calcination process can increase the percentage of its content to 17.90%. Aluminum oxide has the potential to be used as a catalyst, coagulant, and adsorbent for the water treatment process [1], [2]. Therefore, increasing the leaching process of aluminum oxide from peat clay should be of interest to industries related to the various potentials of aluminum oxide compounds.

Microwave-assisted leaching (MAL) method has been used to increase the level of leaching process for mineral and secondary resources, especially nickel, copper ore, fly ash, sewage sludge, and also industrial dust [4]. The MAL method has several advantages over conventional methods, especially in the fields of hydrometallurgy, food, pharmacological medicine, and natural medicine [6]–[7]. Aluminum leaching from peat clay using acidic solvents with the microwave-assisted has been considered as a possible field of MAL because of shorter processing times, high recovery values, and environmentally friendly.

Although the leaching process equipment with microwaves requires high maintenance costs than conventional process equipment [8], energy costs are reduced to one-tenth of conventional processes and can increase selectivity so as to reduce the energy and solvents used in the leaching process [9]. To improve the efficiency of MAL, there are several mathematic models that have been postulated for effective diffusion and mass transfer parameter. In engineering, mathematical modeling can simplify process control, optimize, design a process, and provide correct information about equipment scale up procedures. Moreover, mathematic models provides better information about leaching behavior [10].

The proposed mathematical model is based on the integration of the mass balance differential. These models are based on the macro scale mass transfer mechanism. The shrinking core (SC) model illustrates that the reaction occurs first in the outer shell of the particle and then the reaction area moves to areas that don't react more deeply. The reaction area occurs at ash layer assumed to be inert [11]. Macro-scale shrinking core models have been used in solid-liquid reactions with conventional heating and applied to experimental data for aluminum leaching from water treatment sludge and peat clay successfully [3], [12]. Macro scale mass transfer mechanism of aluminum leaching from peat clay has been applied by Mirwan et al. [3] however, the research just provide information about the effect of temperature condition to leaching process. Aluminum was located in the solid core particles of shrinking peat soils as leached solutes, and assumed that the structure of the surface particles unchanged, linear equilibrium at the solid-liquid interface, and kinetic mechanism based on first-order reaction. Effective diffusivity, mass transfer coefficient, and reaction rate constants are used as fitting parameters.

In this research, microwave-assisted leaching aluminum from peat clay is running on various microwave power, HCl concentration, and particle size. The novelty of this work is the application of the macro scale SC model to aluminum leaching from peat clay using microwave to modelling the microwave-assisted leaching aluminum process based on experimental data.

2. Materials and Methods

2.1. Materials

Peat clays was collected from Peat Village, South Kalimantan with approximately 300 centimeters in the depths from the surface of the earth. Peat clays are cleaned of small logs and other impurities, and dried by sunlight directly. Grinding and sieving are carried out to reduce particle size (0.0074 and 0.0149 cm) and calcined at 700 °C for 120 min.

2.2. Microwave-assisted aluminum leaching

The microwave-assisted leaching devices are arranged in advance as shown in Figure 1. 5 grams of sieved peat clay and 1 M HCl solution that has been made are inserted into a three-neck flask. The microwave power is set at 100 W and 60 min the operating time. The stirring motor with 300 rpm is turned on. The sample solution is taken using a syringe in the span of 5, 10, 15, 20, 25, 30, 40, 50 and 60 minutes.

Sample solution was stored in a glass sample bottle. The stages of the leaching process are repeated for 2 M and 4 M HCl solutions, microwave power of 80 W, and particle size of 0.0074 and 0.0149 cm. The aluminum content was determined using an inductively coupled plasmacluster optical emission spectrometer (ICP-OES, 9060-D Teledyne Leeman Labs, USA) instrument. Each aluminum analysis was repeated three times to obtain an average value.

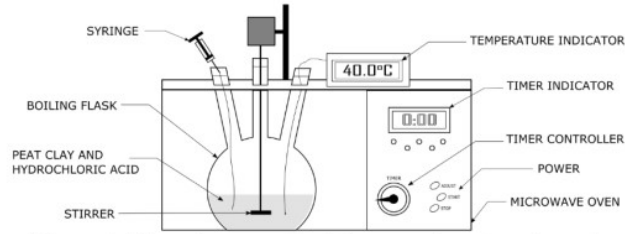


Figure 1. The microwave leaching experiment equipment

2.3. ¹ Shrinking core (SC) model

The macro scale **shrinking core** (SC) model was adopted from Mirwan et al. [13] with several assumption. Peat clay has a shape spherical particle. Temperature was fixed during the microwave-assisted leaching process. The particles are perfectly mixed and the spherical shape of the particles unchanged; although it has an effect on some cases. Based on assumptions and considerations that the microwave-assisted leaching process occurs in a stirred with reaction process, the mass balance equation is described as:

$$\frac{dC_{Al}}{dt} = \frac{k_c(1-\varepsilon)}{R} (C_{A(R)} - C_{Al}) \quad (1)$$

Concentration of solute (aluminum) in the solid phase (peat clay) are related to liquid phase mass transfer coefficient:

$$\frac{d\bar{q}}{dt} = \frac{4\pi R^2 k_c \rho_p}{3m} (C_{A(R)} - C_{Al}) \quad (2)$$

Diffusion equation outside the particle:

$$-\frac{d}{dr} \left(-D_e 4\pi r^2 \frac{dC_{A(R)}}{dr} \right) = 0 \quad (3)$$

The initial conditions of microwave-assisted leaching process was given by equation (4) and boundary conditions by equation (5 and 6):

$$r_c = R \text{ and } \bar{q} = q_u \text{ at } t=0 \quad (4)$$

$$r = r_c \rightarrow D_e \frac{dC_{A(R)}}{dr} = kC_{A(R)} \quad (5)$$

$$-D_e \frac{dC_{A(R)}}{dr} = k_c (C_{A(R)} - C_{Al}) \quad (6)$$

The average value ¹⁵ of the solute (aluminum) concentration in the solid phase:

$$\frac{\bar{q}}{q_u} = \left(\frac{r_c}{R} \right)^3 \quad (7)$$

Equation (3) was integrated to produce an equation (8):

$$C_{A(R)} = -\frac{K_1}{r} + K_2 \quad (8)$$

Equation (5) was substituted into the equation (8) to obtain equation (9):

$$K_1 = \frac{kK_2 r_c^2}{(D_e + kr_c)} \quad (9)$$

Equation (8) was substituted into the equation (6) so that the equation is obtained (10)

$$K_2 = \frac{k_c C_{Al} (D_e + kr_c) R^2}{D_e (kr_c^2 + R^2 k_c) + k_c k (r_c R^2 - r_c^2 R)} \quad (10)$$

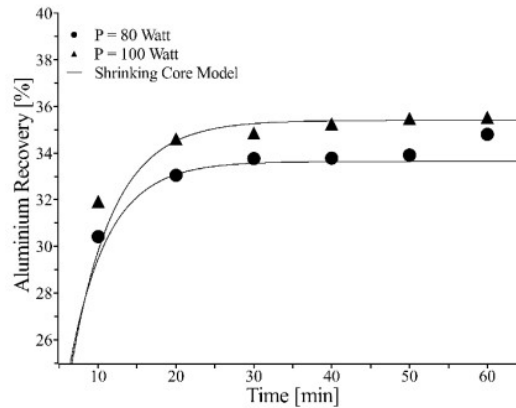
Equation (10) was substituted into the equation (9). These equations are substituted into the equation (8) to obtain equation (11):

$$C_{A(R)} = \frac{kk_c C_{Al} R^2 r_c^2 + k_c C_{Al} (D_e + kr_c) R^2}{D_e (kr_c^2 + R^2 k_c) + k_c k (r_c R^2 - r_c^2 R)} \quad (10)$$

12 3. Results and Discussions

3.1. Effect of microwave power

Figure 2 shown that aluminum recovery increases with increasing microwave power. Mass transfer coefficient was decreased, but the rate of formation reaction increases with increasing microwave power (Table 1). At the same time, mass transfer resistance increases while mass transfer coefficient decreases. The shrinking core model was modelling experimental data well and SC model give a small error value.



7 Figure 2. Effect of microwave power (80 and 100 W) on aluminum recovery by SC models at 0.0074 cm particle size and 1 M HCl concentration.

Table 1. Values of fitting parameters in SC mode

		SC model		
		D_e (cm ² /s)	k (cm/s)	k_c (cm/s)
Microwave power P (Watt)	80	0.002708	1.28	2.756
	100	0.00139	3.58	0.99
HCl concentration C_{HCl} (M)	1	0.00137	6.85	0.929
	2	0.003369	3.8	2.03
	4	0.009308	3.6	4.119
Particle size d_p (cm)	0.0074	0.01516	6.2	6.289
	0.0149	0.00358	1.2	0.909

3.2. Effect of HCl concentration

Figure 3 shown that the effect of HCl concentrations (1, 2, and 4 M) on recovery aluminum of microwave leaching. Recovery aluminum leaching increases with an increase HCl concentration. Increasing HCl concentration was caused an increase the amount of HCl to particle of peat clay, then increasing inter-molecular interactions between HCl and solutes (aluminum), and increasing solubility of solutes. Mass transfer is influenced by increasing HCl concentration, mass transfer coefficient and effective diffusivity. According to Figure 3, the SC model give a good fit of experimental data because it has a small error value.

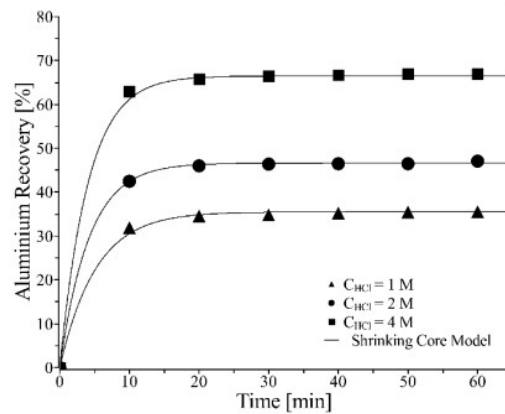


Figure 3. Effect of HCl concentrations (1, 2, and 4 M) on aluminum recovery by SC model at 0.0074 cm particle size and 100 W of microwave power

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3.3. Effect of particle size

The effect of particle size (0.0074 and 0.0149 cm) on aluminum recovery for SC model is shown in Figure 4. The milling process increases surface area, making solutes more accessible to solvents with reducing mass transfer resistance, and consequently, increasing aluminum recovery. Mirwan et al. [1] obtained similar results for aluminum leaching using HCl solvents under conventional heating. Smaller particle sizes can make large contact surface areas by increasing aluminum recovery. The SC model can describe experimental data well at larger particle sizes of 0.0149 cm.

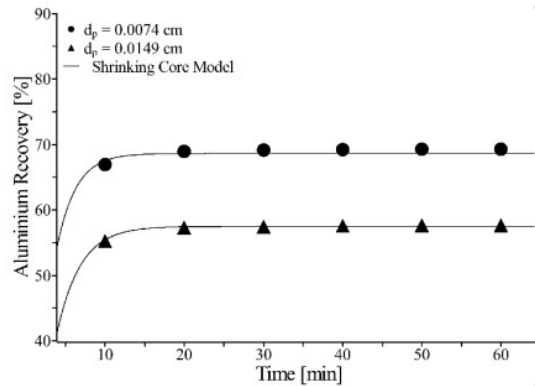


Figure 4. Effect of particle size (0.0074 and 0.0149 cm) on aluminum recovery by SC model at 4 M HCl concentration, 40 °C temperature, and 100 W microwave power

4. Nomenclature

\bar{q}	average value of q (g/L)
C_{Al}	solvent concentration (g/L)
r	radial coordinates
$C_{A(R)}$	aluminum leaching concentration (g/L)
D_e	effective diffusivity (cm^2/s)
k	reaction rate constants (cm/s)
t	time (s)
k_c	liquid phase mass transfer coefficient (cm/s)
K_1	first partition constant (g/cm^3)
K_2	second partition constant (g/cm^3)
m	solid mass (g)
R	particle radius (cm)

Greek letters

π	circle ratio (3,14159)
ε	empty fraction (-)
ρ_p	solid density (g/cm^3)

7 Conclusions

Aluminum from peat clay was leached using microwave-assisted leaching to observe the effects of microwave power, HCl concentration, and particle size. Aluminium recovery increase with increasing microwave power, HCl concentration, and particle size. The shrinking core model can illustrate experimental data well for all leaching conditions. The best fit of parameters is $0.0049 \text{ cm}^2/\text{s}$, $10.5 \text{ cm}/\text{s}$ and $2.49 \text{ cm}/\text{s}$ for D_e , k , and k_c , respectively.

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Acknowledgments

The authors are thankful for the financial support from the Ministry of Research and Technology/National Research and Innovation Agency, Republic of Indonesia No. B/87/E3/RA.00/2020 (Master's Thesis Research Grant 2020)

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