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

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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. The effect of the microwave leaching parameters on the aluminum leaching rate was observed. The shrinking core (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 cm$^2$/s, 2.49 cm/s, and 10.5 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. Precious information on the results of this research can be given for the goal of the scaling-up and design of the microwave assisted leaching process.

1. Introduction

Peat clay used in this study is located at a depth of about 1.5 to 3.0 meters 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 silicon oxide (SiO$_2$), iron oxide (Fe$_2$O$_3$), titanium oxide (TiO$_2$), calcium oxide (CaO), and aluminum oxide (Al$_2$O$_3$), and other oxides in significant amounts small. The content of aluminum oxide (Al$_2$O$_3$) 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) has been used to increase the level of leaching process for mineral and secondary resources, especially copper ore, nickel ore, sewage sludge, fly ash, and industrial dust [5]. The MAL method has several advantages over conventional methods, especially in the fields of hydrometallurgy, food, pharmacological medicine, and natural medicine [6]–[8]. 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 [9], 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 [10]. To improve the efficiency of MAL, there are several kinetic models that have been postulated for effective component diffusion. In engineering, mathematical modeling can simplify process control, optimize, design a process, and provide correct information about equipment scale up procedures. Moreover, the kinetic law provides better information about leaching behavior [11].

The proposed mathematical model is based on the integration of the balanced mass balance differential. These models are based on the mass transfer mechanism which is reviewed on a macro scale. 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 [12]. Macro-scale shrinking core models have been used in solid-liquid reactions with conventional heating and successfully applied to experimental data for aluminum leaching from water treatment sludge and peat clay [3], [13]. Aluminum leaching from peat clay has been modeled by Mirwan et al. [3] however, the model is only applied to temperature condition of the process. Aluminum was located in the solid core particles of shrinking peat soils as extracted solutes, and assumed that the structure of the particles changed, the kinetic mechanism of first-order leaching, and linear equilibrium at the solid-liquid interface. In their model, effective diffusivity, mass transfer coefficient, and reaction rate constants are used as fitting parameters.

In this work, microwave-assisted leaching aluminum from peat clay is carried out at various microwave power, acid concentration, and particle size. The novelty of this work is the application of the SC model to aluminum leaching from peat clay using microwave-assisted to describe the aluminum leaching process based on experimental data.

2. Materials and Method

2.1. Materials
The peat clay was collected from Peat Village, South Kalimantan, Indonesia and approximately 3.0 meters 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 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). Each analysis was repeated three times to obtain an average value.

![Figure 1. The microwave leaching experiment equipment](image-url)
2.3. Mathematical model of shrinking core (SC)

The shrinking core (SC) model was adopted and modified from Mirwan et al. [13] with several to assume. Peat clay has a shape spherical particle. Fixed temperature during the microwave-assisted leaching process. Other compounds found in peat clay do not have a significant effect on process kinetics. The particles are perfectly mixed and the spherical shape of the particles can be maintained; although it has an effect on some cases. Based on assumptions and considerations that the microwave leaching process occurs in a stirred with reaction process, the mass balance equation is described as:

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

(1)

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

$$\bar{dq} = \frac{4\pi R^2 k_c p_e}{3m}(C_{A(R)} - C_{Al})$$

(2)

Diffusion equation outside the particle:

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

(3)

The initial conditions in the equation (4) and boundary conditions in the equation (5 and 6):

$$r_c = R \text{ and } q = q_u \text{ at } t = 0$$

(4)

$$r = r_c \rightarrow D_e \frac{dC_{A(R)}}{dr} = k C_{A(R)}$$

(5)

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

(6)

The average value of the solute concentration in the solid phase:

$$\bar{q} = \frac{r_c^3}{q_u R}$$

(7)

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

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

(8)

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

$$K_1 = \frac{k C_{Al} r_c^2}{(D_e + k r_c)}$$

(9)

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

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

(10)

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

3.1. Effect of microwave power

Figure 2 shown that leaching 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 with decreasing mass transfer coefficient. The shrinking core model was illustrated experimental data and SC model good fit with small error value.

\[ C_{Al}(R) = \frac{k_c A_{Al} R^2 c^2 + k_c C_{Al}(D_c + k_c R^2)}{D_c (k_c R^2 + R^2 k_c) + k_c (r_c R^2 - r_c^2 R)} \]  

(11)

![Figure 2](image)

**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 | \( D_c \) (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 in acid concentration.
Increasing acid concentration was caused an increase in the amount of acid mass per unit volume to enter the particle, thereby increasing inter-molecular interactions between acid and solutes, and increasing solubility of solutes. For this condition, mass transfer is influenced by increasing acid concentration, mass transfer coefficient and effective diffusivity. According to Figure 3, the SC model more good fit illustrates experimental data because it has a relatively 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.]

3.3. Effect of particle size
The effect of particle size (0.0074 and 0.0149 cm) on recovery leaching for SC model is shown in Figure 4. A reduction in recovery leaching for an increase in particle size is observed. The milling process increases surface area, reducing mass transfer resistance, making solutes more accessible to solvents, and consequently, increasing recovery aluminum leaching. 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 thereby increasing recovery leaching. 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

- $q$ average value of $q$ (g/L)
- $C_{al}$ solvent concentration (g/L)
- $r$ radial coordinates
- $C_{al(R)}$ aluminum leaching concentration (g/L)
- $D_e$ effective diffusivity (cm²/s)
- $R$ particle radius (cm)
- $k$ reaction rate constants (cm/s)
- $t$ time (s)

- $k_c$ liquid phase mass transfer coefficient (cm/s)
- $K_1$ first partition constant (g/cm³)
- $K_2$ second partition constant (g/cm³)
- $m$ solid mass (g)
- $\pi$ circle ratio (3.14159)
- $\varepsilon$ empty fraction (-)
- $\rho_0$ solid density (g/cm³)

5. Conclusions

Aluminum from peat clay was leached using microwave assisted leaching to observe the effects of microwave power, HCl concentration, and particle size. Aluminum recovery increase with increasing microwave power, HCl concentration, and particle size. The shrinking core model can illustrate experimental data well for all extraction conditions except for particle size. The best fit of parameters is 0.0049 cm²/s, 10.5 cm/s and 2.49 cm/s for $D_e$, $k$, and $k_c$, respectively.

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Reviewers' comments 1

C1: Research contribution is quite significant
R1: We are very grateful to the Reviewer for his comments.

C2: More study is needed regarding the aluminum leaching model approach
R2: We are grateful to Reviewer for their comments which helped improve the revised version of this manuscript. We learn more about the microwave-assisted aluminum leach model approach.

Reviewers' comments 2

The paper is quite interesting which discuss about modified shrinking core model for microwave-assisted leaching of aluminum from peat clay. However, some improvements need to address as follows:

C1: Please refer to the IOP template how to write author name etc.
R1: We gratefully acknowledge reviewers for their comments. We have adjusted the standard of IOP template as suggested in http://cms.iopscience.iop.org/alfresco/d/d/workspace/SpacesStore/f67538ae-18b2-11e4-831a-29411a5deefe/WordGuidelines.zip

C2: The abstract is too short, I suggest to add in the abstract research background, aims, method, results, and the implication of the benefits.
R1: We thank reviewers for their comments. We've added the abstract section as requested.