Mirwan_vol72_oke.docx

Temperature-dependent Kinetics of Aluminum Leaching from Peat Clay

Agus Mirwan[a,*], Susianto[b], Ali Altway[b], Renanto Handogo[b]

[a]Department of Chemical Engineering, Faculty of Engineering, Lambung Mangkurat University, Banjarbaru 70714, Indonesia
[b]Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia
agusmirwan@ulm.ac.id

The leaching kinetics of aluminum from peat clay using 4 M HCl at dissimilar leaching temperatures (30–90 °C) was investigated. The maximum of aluminum recovery is 91.27% after 60 min of leaching in agitated Pyrex reactor at 90 °C. The model involves the concept of shrinking core to describe aluminum is located inside the core solid particle of peat clay that shrinks as the extracted solute, and assumes unchanged particle structure, a first-order leaching kinetics mechanism and a linier equilibrium at the interface of solid-liquid. The proposed model is corresponding to fit experimental data and to simulate the aluminum leaching from peat clay with four fitting parameters of temperature, which was confirmed with the mass transfer coefficient (k_c, cm/s), diffusion coefficient (D_e, cm^2/s), and reaction rate constants (k, cm/s) following an increasing trend with increasing temperature. Moreover, it was validated by the correlation coefficient ($c_{coef} \geq 0.9794$), the root mean square error ($RMSE \leq 0.485$), the mean relative deviation modulus ($E \leq 3.290\%$), and the activation energy value is 19.15 kJmol^{-1}. This model could describe the aluminum leaching kinetics from peat clay suitable with experiment parameters and statistical criteria giving useful information for optimization, scaling-up, and design.

1. Introduction

The clay minerals are naturally aluminum silicate composed essentially of silica, alumina, iron, magnesium and water in varying levels, and the other compounds frequently present as well in small quantity (Ajemba and Onukwuli, 2012). While, peat clay located at a depth of about 1.5 to 3.0 meters from the peat soil is clay soil which mostly contains a major chemical composition in shape of aluminum oxide, silica oxide, and iron oxide (Mirwan et al. 2018). Aluminum in form aluminum oxide has potential as a coagulant, adsorbents and catalysts for water and wastewater treatment (Karjalainen et al. 2016). In general, clay has several remarkable advantages such as good acid tolerance, low cost, good mechanical properties, easy solid-liquid separation, and very good reusability (Iannicelli Zubiani et al. 2015).

The readability in the aluminum leaching from peat clay materials is currently concentrated on increasing the aluminum content for scientific goals only. Acid leaching is one of the most common chemical modifications applied to peat clay minerals. Previously, the peat clay is actived using a thermal treatment or calcination for increase reactivity the dehydrhydration transformation of kaolinite to amorphous meta kaolinite and straightforward to leached with acid solution (Brown and Hrishikesan, 1962; Wendt and O'Connor, 1989).

According to Estokova et al. (2015) that leaching is the process of dissolving and removing soluble components from a material using solvent media. This process is initial act in the utilization of aluminum from natural resources in obtaining valuable material such as coagulant, adsorbent, and catalysts. The leaching process is the mass transfer process from solid to liquid in which the solute can be leached out based on the solubility, pores, and particle surface. Gertenbach (2002); Schwartzberg & Chao (1982) explain that partition constants and kinetic parameters are related to equilibrium which will be used in the calculation of mathematical models. In the engineering and separation process, mathematical modeling is necessary because it provides quick and inexpensive calculations and minimizes the number of required experiments. Mass transfer mechanisms are very easy to understand with the analysis of model parameters that will be needed for process optimization, simulation, and reactor design.

The shrinking core (SC) model is the most widely used model for the leaching of different constituents from natural mineral materials or hydrometallurgy to acquire metal or other precious material (Safari et al. 2009; Mirwan et al. 2017). In addition to papers on the kinetics of leaching aluminum from metallurgical materials such as clay, peat clay, and water treatment sludge (Cheng et al. 2012; Mirwan et al. 2018), to greats of science, only one study has been published on the aluminum leaching kinetics of water treatment sludge, which also uses SC model. Prior paper (Mirwan et al., 2018) indicated that the aluminum leaching from peat clay was influenced the acid concentration, particle in small size, and leaching temperature. The increase of aluminum rate in leaching process followed by the increase of acid concentration, leaching temperature, and particle in the small size. The highest aluminum leaching yield is reached at 90 °C, +200-325 mesh, and 4M HCl. A well appropriate model on aluminum leaching peat clay was accomplished; nevertheless, the paramaters of model do not have bodily sense. While for industrial scale, leaching kinetics data for optimization process, reactor design, and suitable model are not existing.

The major purpose of this research was to investigate the temperature effect varied between 30 and 90 °C on the aluminum leaching rate from peat clay and to evolve the leaching kinetics model depending on temperature parameters.

2. Experimental

2.1 Material

Peat clay from Peat Village, District of Banjar, South Kalimantan and in depths about 3.0 meters from surface of the earth was used. Manually, peat clay was cleaned and dried for 48 hours in direct sunlight. After crushing and grinding, the peat clay was sieved to the size fraction of 0.044–0.210 mm and calcined for thermal treatment at 700 °C for 2 h. From Sigma-Aldrich with a purity of 37%, 1.18 g/ml, HCl was used as the leaching solution. Desired HCl concentrations were diluted with de-ionized water.

2.2 Leaching procedure

Aluminum leaching was carried out in an atmospheric Iwaki Pyrex two-neck reactor; for the thermometer and for the inlet and/or outlet of the sample periodically. Magnetic stirrer (300 rpm) with heating indirectly through a water bath was used for mixing reaction. 5 g of calcined peat clay was added and reacted into 250 ml of HCl solution at specific temperature. The solid/liquid ration was kept constant at 0.02 g/ml. Sample was taken using a syringe at selected time interval and filtered using filter paper for analysis of aluminum content determination by inductively coupled plasmacluster optical emission spectrometer (ICP-OES) (9060-D Teledyne Leeman Labs. USA). Repetition of each analysis is carried out three times and represented by the average value. The equation of $x = (X/X_0) \times 100$, states the aluminum recovery (x); the total aluminum achieved through the acid leaching process is expressed as X_0, and the amount of aluminum obtained at different conditions (mg/g) is expressed by X.

In solid-phase amorphous in peat clay, aluminum hydroxide can be leached out by acid. Beacuse, aluminum oxide at ambient temperature cannot react in acidic condition. Chemical reaction of aluminum oxide with acid is stated as follow $Al(OH)_{3\,(s)} + 3HCl_{(aq)} \rightarrow AlCl_3\,(aq) + 3H_2O$

2.3 Mathematical modelling of leaching kinetics

The principle of SC model from the previous paper (Mirwan et al., 2017) explains that firstly the HCl ions were diffused through film surrounding the surface of peat clay particles. The untreated core surface was continuously penetrated and diffused through the blanket of product layer by the acid ions, and reacted with the aluminum precipitate. Eventually, all aluminum ions in the peat clay particles are diffused out to the surrounding liquid. Furthermore, the SC model assumes that peat clay particles are spherical and their spherical shape can be maintained during completely reacting.

The overall mass balance equation for leaching is

$$\frac{dC_{AL}}{dt} = \frac{k_c}{R}\frac{\left(1-\varepsilon_L\right)}{\varepsilon_L}\left(C_{A(R)} - C_{AL}\right) \tag{1}$$

Here, C_{AL} was concentration in the solvent (kmol/m^3), $C_{A(R)}$ was concentration of aluminum leaching (kmol/m^3), k_c was mass transfer coefficient (cm/s), ε_L was void fraction, and R was particle radius (m). The mass transfer rate of solute is related to aluminum concentration in peat clay particle (time variation of the solid phase)

$$\frac{d\overline{q}}{dt} = \frac{4\pi R^2 k_c \rho_s}{b \times solid\ mass}\left(C_{A(R)} - C_{AL}\right) \qquad (2)$$

where $\overline{q}$ was average value of q (mol/m^3), b was stoichiometric coefficient, ρ_s was sludge solid waste density (kg/m^3), and π was the ratio of a circle's (3.14159). The outer particle diffusion is used

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

Here, D_e was effective diffusivity (m^2/s) and r was radial coordinate. The solute concentration average value

$$\frac{\overline{q}}{q_0} = \left(\frac{r_c}{R}\right)^3 \qquad (5)$$

where q_0 was initial solid-phase concentration (mol/m^3) and r_c was critical radius of core (m). Boundary conditions and initial conditions

$$r = r_c \rightarrow D_e \frac{C_{A(R)}}{dr} = kC_{A(R)} \qquad (6)$$

$$-D_e \frac{C_{A(R)}}{dr} = k_c\left(C_{A(R)} - C_{AL}\right) \qquad (7)$$

$r_c = R$ and $\overline{q} = q_o$ at $t = 0$

k was reaction rate constant (cm/s). Fitting the experimental data to Eq.(6) to (8) can obtain the model parameter i.e. k_c, k, and D_e. Through the integration of Equation 4 obtained

$$C_{A(R)} = \frac{k_1}{r} + k_2 \qquad (8)$$

The substitution of Equation 6 to Equation 9 is obtains

$$k_1 = \frac{kk_2 r_c^2}{\left(D_e + kr_c\right)} \qquad (9)$$

Here, k_1 and k_2 were first and second partition constant (kg/m^3). The incorporation of equations 7, 9, and 10 is yielded the solute mass of the aluminum recovery. Eq.(11) is substituted into Eq.(10). The k_1 and k_2 variables are obtained from the solution of Eq.(9) to obtain concentration of aluminum leaching (kmol/m^3) or $C_{A(R)}$.

$$k_2 = \frac{k_c C_{AL}\left(D_e + kr_c\right)R^2}{D_e\left(kr_c^2 + R^2 r_c\right) + k_c k\left(r_c R^2 - r_c^2 R\right)} \qquad (10)$$

$$C_{A(R)} = \frac{kk_c C_{AL} R^2 r_c^2}{D_e\left(kr_c^2 + R^2 k_c\right) + k_c k\left(r_c R^2 - r_c^2 R\right) r} + \frac{k_c C_{AL}\left(D_e + kr_c\right)R^2}{D_e\left(kr_c^2 + R^2 k_c\right) + k_c k\left(r_c R^2 - r_c^2 R\right)} \qquad (11)$$

2.4 Statistical analysis

The experimental data was used to determine the proposed model parameters through nonlinear regression. The sufficiency of the appropriate model with experimental data would be evaluated by three statistic results, i.e. correlation coefficient (c_{coef}), root mean square error (*RMSE*), and modulus of mean relative deviation (*E*). A good fit between the model and the data is indicated by $c_{coef} \rightarrow 1$, $RMSE \rightarrow 0$, and $E < 10\%$ (Mirwan et al. 2017). c_{coef}, *RMSE*, and *E* were computed as:

$$c_{coef} = \sqrt{1 - \frac{\sum_{i=1}^{N}\left(C_{pred,i} - C_{\exp,i}\right)^2}{\sum_{i=1}^{N}\left(C_{\exp,i} - C_{\exp,sr}\right)^2}} \qquad (12)$$

$$RMSE = \sqrt{\frac{1}{N} \cdot \sum_{i=1}^{N}\left(C_{pred,i} - C_{\exp,i}\right)^2} \qquad (13)$$

$$E = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{C_{\exp,i}-C_{pred,i}}{C_{\exp,i}}\right| \qquad (14)$$

where $C_{pred,i}$ was predicted aluminum recovery calculated with the model, particle core (%), $C_{exp,i}$ was experimental value of aluminum recovery, particle core (%), $C_{exp,sr}$ was experimental value of aluminum recovery, solid phase (%), and N was number of experimental points.

3. Results and Discussion

Figure 1 illustrates that the total aluminum rate in the leaching yield evaluated at a leaching temperature of 30, 50, 70 and 90 °C. The increasing leaching temperature followed by the increasing leaching yield; aluminum recovery value was 91.267 % at 90 °C and 60 min of leaching. The form of leaching curve is equal to the form of curve informed by Mirwan et al. (2017) for aluminum leaching from water treatment sludge.
The experimental data has been tested and appropiated with Eq. (12) through minimizing the root mean square distinction. The adjusting model parameters were showed: the temperature-dependent reaction rate constant, mass transfer coefficient, and effective diffusivity, which the values were written in Table 1 along with the statistic results. The radius of the R particle and the ratio of solid to solvent were fixed at 0.0295 cm (262.5 mesh) and 0.02 g/mL, respectively. The correlation coefficient ($c_{coef} \geq 0.9602$), *RMSE* values (≤ 0.854) are comparatively low, and *E* values are under 3.2903 % for every temperature. The model is appropriate to prophesy the aluminum leaching kinetics from peat clay.

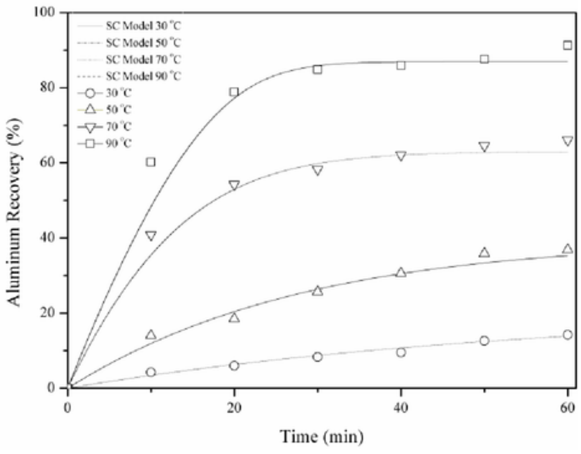

Figure 1: Aluminum recovery from experimental data and model curves

Table 1: Fitting model parameters and statistical criteria at distinct leaching temperatures (T)

T (°C)	30	50	70	90
k (cm/s)	12.4	18.5	30.8	42.2
k_c (cm/s)	0.0003	0.0014	0.0050	0.0063
$D_e.10^{-5}$ (cm^2/s)	0.21	1.69	10.38	25.08
c_{coef}	0.9602	0.9860	0.9906	0.9794
RMSE	0.0330	0.0863	0.2211	0.4854
E (%)	3.1693	2.5095	2.2074	3.2903

The connections of the mass transfer coefficient, the reaction rate constants, the diffusion coefficient, and and the leaching temperature that is numerically using the Arrhenius equation in the form of a logarithm can be explained by the activation energy (Mirwan et al. 2017):

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (15)$$

where the pre-exponential factor is symbolized by A, the activation energy (J/mol) is E_a, the global gas constant (8.314 J/K mol) is *R*, and the absolute temperature (K) is *T*. Based on the calculation of the graph slope of ln k to the inverse absolute temperature, activation energy value can be obtained. The *k* value is inversely proportional to the temperature. Figure 3 exhibits that the activation energy result is 19.15 kJ/mol.

The expected *RMSE* criterion increase following the effective diffusion coeficients minimizing because the temperature effect is increased.

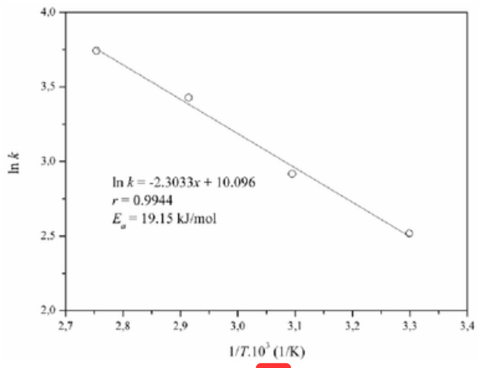

Figure 2: Arrhenius graph: k is the reaction rate constant, cm/s, and T is the absolute leaching temperature, K

4. Conclusions

The results in the this research obtain that the aluminum leaching from peat clay with HCl solution at temperatures 30-90 °C occurred in two stages: the fast initial stage of leaching out reachable subtances from surface zone of particles and the sluggish diffusion stage to the surface of particle. The offered model is appropriate to depict the aluminum leaching kinetics from peat clay in conformation with the tested conditions, which was verifyed by statistical criteria. The physical purpose of model kinetic parameter provides good concept of mass transfer phenomena through the the batch aluminum leaching from peat clay. Thus, valuable information needed for simulation, optimization, scale-up and leaching process design can be obtained from this study outcomes.

Acknowledgments

The authors convey appreciation to the Directorate General of Higher Education, Ministry of Education and Culture Republic of Indonesia (No. 23428/A4.2/2014) for financially supporting this work.

References

Ajemba R.O., Onukwuli O.D., 2012, Application of the Shrinking Core Model to the Analysis of Alumina Leaching from Ukpor Clay Using Nitric Acid. Int. J. Eng. Res. Technol., 1, 3, 1–13.

Brown W.H., Hrishikesan K.G., 1966, Process for the production of alumina. United States Patent Online, No. 3, 240, 562.

Cheng W.-P., Fu C.-H., Chen P.-H., Yu, R.-F., 2012, Dynamics of Aluminum Leaching from Water Purification Sludge, J. Hazard. Mater., 217–218, 149–155.

Estokova A., Oravec J., Kovalcikova M., 2015, Environmental Impact Assessment of the Concrete Composites in Terms of the Selected Toxic Metals Leaching, Chemical Engineering Transactions, 43, 1915–1920.

Gertenbach D., 2002, Solid–liquid extraction technologies for manufacturing nutraceuticals. In J. Shi, G. Mazza, & M. Le Maguer (Eds.), Functional foods: Biochemical and processing aspects, Boca Raton FL: CRC Press, 331 – 366.

Iannicelli Zubiani E.M.I., Cristiani C., Dotelli G., Stampino P.G., Pelosato R., 2015, Recovery of Rare Earths and Precious Metals from Waste Electrical and Electronic Equipment by Acid Leaching and Immobilized Chelating Agents, Chemical Engineering Transactions, 43, 2413–2418.

Karjalainen S.M., Ronkanen A.-K., Heikkinen K., Kløve, B., 2016, Long-Term Accumulation and Retention of Al, Fe and P in Peat Soils of Northern Treatment Wetlands. *Ecol. Eng.* 93: 91-103.

Mirwan A., Susianto S., Altway A., Handogo, R., 2017, A Modified Shrinking Core Model for Leaching of Aluminum from Sludge Solid Waste of Drinking Water Treatment, Int. J. Technol., 8,1, 19.

Mirwan A., Susianto S., Altway A., Handogo, R., 2018, Kinetic Model for Identifying The Rate Controlling Step of The Aluminum Leaching from Peat Clay, J. Teknologi, 80, 2, 37–44.

Safari V., Arzpeyma G., Rashchi F., Mostoufi N., 2009, A Shrinking Particle—Shrinking Core Model for Leaching of a Zinc Ore Containing Silica. Int. J. Miner. Process., 93, 1, 79–83.

Schwartzberg H.G., & Chao, R.Y., [illegible]82, Solute diffusivities in leaching processes. Food Technology, 73–86.

Wendt H., O'Connor D.J., 1989. Alumina Extraction from Non Bauxitic Materials, Aluminium-Verlag GmbH, Düsseldorf. 1988. 370 Seiten, Preis: DM 160, Berichte Bunsenges, Für Phys. Chem., 93, 5, 639–639.

Mirwan_vol72_oke.docx

ORIGINALITY REPORT

22%

SIMILARITY INDEX

PRIMARY SOURCES

1	ijtech.eng.ui.ac.id Internet	112 words	4%
2	Ana Bucić-Kojić, Helena Sovová, Mirela Planinić, Srećko Tomas. "Temperature-dependent kinetics of grape seed phenolic compounds extraction: Experiment and model", Food Chemistry, 2013 Crossref	91 words	3%
3	www.aidic.it Internet	80 words	3%
4	imwa.de Internet	31 words	1%
5	Bucić-Kojić, Ana, Helena Sovová, Mirela Planinić, and Srećko Tomas. "Temperature-dependent kinetics of grape seed phenolic compounds extraction: Experiment and model", Food Chemistry, 2013. Crossref	31 words	1%
6	www.ijert.org Internet	29 words	1%
7	www.syke.fi Internet	28 words	1%
8	Cacace, J.E.. "Mass transfer process during extraction of phenolic compounds from milled berries", Journal of Food Engineering, 200310 Crossref	27 words	1%

9 Mahmoud M. Fouad, Taha M. A. Razek, Ahmed S. Elgendy. "Utilization of Drinking Water Treatment Slurry to Produce Aluminum Sulfate Coagulant", Water Environment Research, 2017
Crossref
25 words — 1%

10 Ikechukwu A. Nnanwube, Okechukwu D. Onukwuli. "Hydrometallurgical Processing of a Nigerian Galena Ore in Nitric Acid: Characterization and Dissolution Kinetics", Journal of Minerals and Materials Characterization and Engineering, 2018
Crossref
25 words — 1%

11 free-doc-lib.com
Internet
21 words — 1%

12 Teeradet Supap, Raphael Idem, Paitoon Tontiwachwuthikul, Chintana Saiwan. "The Roles of O2 and SO2 in the Degradation of Monoethanolamine during CO2 Absorption from Industrial Flue Gas Streams", 2006 IEEE EIC Climate Change Conference, 2006
Crossref
18 words — 1%

13 www.scribd.com
Internet
18 words — 1%

14 Meilana Dharma Putra, Chairul Irawan, Udiantoro, Yuli Ristianingsih, Iryanti Fatyasari Nata. "A cleaner process for biodiesel production from waste cooking oil using waste materials as a heterogeneous catalyst and its kinetic study", Journal of Cleaner Production, 2018
Crossref
16 words — 1%

15 Lewerenz, H. J.. "K. S. V. Santhanam, M. Sharon: Photoelectronical solar cells, studies in physical and theoretical chemistry, Vol. 50, Elsevier, Amsterdam, Oxford, New York, Tokyo 1988. 372 Seiten, Preis: Dfl. 275", Berichte der Bunsengesellschaft für physikalische Chemie, 1989.
Crossref
15 words — 1%

16 artemis.library.tuc.gr
Internet
14 words — 1%

17	Ajchariyapagorn, A.. "Predicting the extraction yield of nimbin from neem seeds in supercritical CO"2 using group contribution methods, equations of state and a shrinking core extraction model", The Journal of Supercritical Fluids, 200911 Crossref	12 words — < 1%
18	open.uct.ac.za Internet	10 words — < 1%
19	uad.portalgaruda.org Internet	10 words — < 1%
20	Xin-wei Liu. "Recovery of valuable metals from a low-grade nickel ore using an ammonium sulfate roasting-leaching process", International Journal of Minerals Metallurgy and Materials, 05/2012 Crossref	7 words — < 1%
21	"Light Metals 2013", Springer Nature, 2016 Crossref	7 words — < 1%

EXCLUDE QUOTES	OFF	EXCLUDE MATCHES	OFF
EXCLUDE BIBLIOGRAPHY	OFF		