

Kinetic model for identifying the rate controlling step of the aluminum leaching from -ref.docx

Kinetic model for identifying the rate controlling step of the aluminum leaching from peat clay

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Abstract

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The aluminum leaching kinetics from peat clay was investigated using hydrochloric acid as solvent. Aluminum leaching experiments were performed with various acid concentrations, particle sizes and temperatures. They all have significant effects on aluminum leaching process. The aluminum leaching recovery was found to be 91.3 % at 4 M hydrochloric acid, using particle size of +200 -325 with solid to liquid ratio of 0.02 g·ml⁻¹. Leaching kinetic study was applied to the two rate equations proposed that is acid diffusion via product layer and surface chemical reaction using the shrinking core (SC) model to analyze the leaching data. The model used spherical particles to represent the model. The short period of time, the acid diffusion through the product layer as a rate controlling, while surface chemical reactions as a rate controlling on the long period of time. The apparent activation energy in the two rate equations were found to be 82.79 kJ mol⁻¹ and 27.08 kJ mol⁻¹, respectively.

Keywords: aluminum leaching kinetics; peat clay; rate controlling step; short and long period of time; shrinking core model

1. Introduction

Owlilaie et al., (2006); Velde and Meunier (2008) ; Cebon et.al (2015) claimed that clay mineral was widely dispersed on the earth crust. They significantly affect the physical, chemical and biological properties of the soil. Furthermore, clay minerals undergo modification and transformation spontaneously to changing environmental conditions as indicated by the structures and types of clay minerals (Turpault et al., 2008). Natural clay minerals are a highly effective and robust adsorbent because they have a high surface area, the structure of the molecular sieve, chemical and mechanical stability, and a variety of surface and structural properties (Sparks, 2003; Srinivasan et al., 2015). In addition, their low cost, high sorption and potential as ion exchangers (Crini, 2006). In Indonesia, especially in South Kalimantan, peatlands are very spacious and they have not been utilized optimally. Indirectly, their existence shows that there are a lot of clay peat in the region. Peat clays are in the depths about 1.5-3.0 meters from the surface of earth. Further, the main mineral peat clays generally consists of kaolinite, pyrite, illite, and halloysite (Notodarmojo, 2005) and they have a major chemical composition in the form of aluminum oxide (Al₂O₃) in which it has the ability as a coagulant, adsorbents and catalysts (Hulbert and Huff, 1970; Park et al., 1997; Al-Ajeel and Al-Sindy, 2012; Al-Zahrani and Abdel-Majid, 2004, 2009; Ibrahim et al., 2013). The various countries in the world, quantitatively, the chemical composition of all types of clays are shown in **Table 1**.

Aluminum leaching process of clay require prior activation process because its inactive and stable structure. A very common method to activate the clay by thermal

treatment at a temperature range of 500-900 °C and 15-180 minutes for aluminum oxide soluble (Phillips and Wills, 1982; Eisele et al., 1983; Gajam and Raghavan, 1985; Al-Zahrani and Abdel-Majid, 2004; Al-Ajeel and Al-Sindy, 2012; Numluk and Chaisena, 2012; Ajemba and Onukwuli, 2012). This process is expected to increase the clay reactivity that influence the dehydrhydration transformation of kaolinite to amorphous metakaolinite (Al_2SiO_7), which is more reactive and easy to extracted with acids or alkali (Phillips and Wills, 1982; Wendt, 1989). Various mineral acid for leaching aluminum oxide has been investigated, namely sulfuric acid (H_2SO_4) (Hulbert and Huff, 1970; Al-Zahrani and Abdel-Majid, 2004; Numluk and Chaisena, 2012), nitric acid (HNO_3) (Hulbert and Huff, 1970; Phillips and Wills, 1982; Ajemba and Onukwuli, 2012), dan hydrochloric acid (HCl) (Hulbert and Huff, 1970; Eisele et al., 1983; Park et al., 1997; Al-Ajeel and Al-Sindy, 2012; Al-Zahrani and Abdel-Majid, 2009; Ajemba and Onukwuli, 2012; Ibrahim et al., 2013). Among these acids, hydrochloric acid has several advantages, especially for the treatment of pure kaolinitic clay (Wendt, 1989). Furthermore, aluminum recovery percentage is obtained using hydrochloric acid ranging from 62.9-95% (Hulbert and Huff, 1970; Eisele et al., 1983; Park et al., 1997; Ajemba and Onukwuli, 2012; Ibrahim et al., 2013).

The aluminum leaching process with acid is represented as a non-catalytic solid-liquid reactions. The main various models expanded for first order reaction are shrinking core (SC), shrinking particle, homogeneous and grains model (Gbor and Jia, 2004), among which the SC model has been greatly recognized for the leaching kinetics of solid-liquid system (Su et al., 2010; Song et al., 2013). SC is the model which assumes that the solute inside the solid particle is located within a core that shrinks as the extracted solute (Machmudah et al., 2006) and assumes first order reaction and unchanged structure of the particles (Froment and Bischoff, 1979; Wen, 1968). Furthermore, this model describes that the situation of irreversible desorption was followed by diffusion process in the porous solid particle through the pores (Goto et al., 1996; Machmudah et al., 2006). According to Gbor and Jia, (2004) that SCM is applicable to an initially non-porous particle, which reacts with a reagent leaving a reacted layer around the unreacted core. SC model is still applicable if the particle is completely porous and the reaction is fast compared to the inward diffusion of the gaseous reagent (Melchiori and Canu, 2014). The various studies have been conducted on aluminum leaching kinetics of kaolin and clay using SC model which describe the effect of thermal treatment, acid concentration, temperature, time, particle size, and solid/liquid ratio on the leaching process (Beolchini et al., 2001; Gbor and Jia, 2004; Lee et al., 2005; Safari et al., 2009; Santos et al., 2010; Tang et al., 2010; Senanayake, 2011; Safarzadeh et al., 2011; Xue et al., 2011; Li et al., 2013).

The present study is organized to investigated aluminum leaching kinetics from peat clay using hydrochloric acid. The effects of four different acid concentration, three different particle sizes, and four different of reaction temperature as the time function on aluminum leaching recovery were evaluated. Leaching kinetics of aluminum were examined according to non-catalytic fluid-solid reaction using SC model for determining the rate controlling steps at short and long period of leaching time.

2. Material and Methods

2.1. Materials

Peat clay samples were collected from Peat Village, Subdistrict of Peat, District of Banjar, South Kalimantan, Indonesia with a longitude coordinates of location between 3°23'55.3"S and 114°42'14,6"E and in the depths about 3.0 meters from the surface of earth.

Table 1
Elemental composition of some clays from different locations in the world

Location	Chemical composition (% weight)														LOI	CEC	Reference
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	CaO	MgO	MnO	TiO ₂	K ₂ O	P ₂ O ₅	Cr ₂ O ₃	ZnO	NiO	CuO			
S. Carolina, USA	42.90	0.4	na	na	na	na	na	1.8	na	na	na	na	na	na	na	na	Hulbert and Huff (1970)
South-West Devon, UK	50.30	32.70	2.4	na	0.1	0.4	na	0.1	5.3	na	na	na	na	na	8.3	na	Phillips and Wills (1982)
Sandersville, GA	51.80	43.00	1.260	0.032	0.034	0.087	0.004	3.270	0.063	0.087	0	0.012	0.008	0.005	na	na	Eisele et al., (1983)
Hadong-Sancheong, Korea	44.50	38.26	1.48	0.33	0.86	0.79	0.20	1.55	0.09	na	na	na	na	na	na	na	Park et al., (1992)
Sancheong, Korea	44.03	37.86	1.46	0.33	1.85	0.78	0.02	2.0	1.53	na	na	na	na	na	na	na	Park et al., (1997)
Hasandede, Turkey	52.28	8.13	3.10	5.45	3.50	12.77	0.05	0.33	1.73	0.10	na	na	na	na	na	na	Demirci et al., (1998)
Keskin, Turkey	49.11	18.66	10.95	1.01	3.12	2.98	0.02	0.67	0.26	0.03	na	na	na	na	na	na	Demirci et al., (1998)
Samas, Turkey	61.43	17.32	3.73	2.49	3.16	1.98	0.11	0.32	1.01	0.17	na	na	na	na	na	na	Demirci et al., (1998)
Cambransan, Turkey	61.83	17.36	5.38	2.24	1.39	2.64	0.1	0.73	0.95	na	na	na	na	na	na	na	Demirci et al., (1998)
Ceylan, Turkey	55.35	16.63	9.32	1.90	3.26	2.29	0.1	1.32	0.68	0.1	na	na	na	na	na	na	Demirci et al., (1998)
Toullant, Mongolia	74.3	15.1	1.63	1.06	3.32	3.59	na	na	0.95	na	na	na	na	na	na	na	Temujin et al., (2004)
Maghnia, Algeria	69.39	14.67	1.16	0.50	0.30	1.07	na	0.16	0.79	na	na	na	na	na	11.00	na	Zermame et al., (2005)
Az-Zabirah, Saudi Arabia	47.25	29.4	2.87	2.11	0.59	0.35	<0.05	1.17	0.17	<0.05	na	na	na	na	16.02	na	Al-Zahrani and Abdel-Majid, (2004)
Erzurum, Turkey	46.3	23.7	21.6	na	8.4	na	na	na	na	na	na	na	na	na	na	na	Gurses et al., (2004)
Hattar ind. estate, Pakistan	61.46	18.74	3.55	0.00	2.05	5.42	0.13	0.49	0.93	0.11	na	na	na	na	7.56	na	Tahir and Rauf, (2006)
Duwaikha Mine, Iraq	50.5	33.3	na	na	na	na	na	0.98	na	na	na	na	na	na	na	na	Al-Ajeel and Al-Sindy (2006)
Caltek, Turkey	59.46	14.92	5.18	0.98	4.75	1.98	na	0.73	2.45	na	na	na	na	na	8.73	na	Sari et al., (2007)
Azraq, Jordan	59.60	13.70	8.34	0.68	1.15	2.33	na	1.61	2.07	na	na	na	na	na	10.47	na	Salman et al., (2007)
Madiya Pradesh, India	28.98	14.08	1.201	2.547	0.183	0.638	0.036	0.875	0.382	na	na	0.005	0.003	0.003	na	na	Nayak and Singh, (2007)
Landasan Ulin 1, Indonesia	80.03	4.29	2.36	0.70	0.14	0.40	na	0.47	0.36	na	na	na	na	na	11.25	11.20	Mahmud and Notodarmojo, (2007)
Landasan Ulin 2, Indonesia	72.24	13.64	2.41	0.41	0.28	0.32	na	0.64	0.67	na	na	na	na	na	9.39	12.80	Mahmud and Notodarmojo, (2007)
Landasan Ulin 3, Indonesia	70.07	14.59	3.07	0.80	0.21	0.78	na	0.45	0.62	na	na	na	na	na	9.41	1	Mahmud and Notodarmojo, (2007)
Landasan Ulin 4, Indonesia	60.03	22.65	2.63	1.23	0.56	0.41	na	1.20	1.54	na	na	na	na	na	9.45	1	Mahmud and Notodarmojo, (2007)
Ds Paminggir, Indonesia	44.48	19.47	5.07	0.201	0.361	0.598	0.014	0.77	1.14	0.33	0.017	0.047	0.014	0.009	27.24	na	Diana and Notodarmojo (2010)
Lampang clay, Thailand	66.30	22.70	0.63	0.49	0.05	0.15	na	0.03	4.05	na	na	na	na	na	5.10	na	Numluk and Chaisena (2012)
Ukpor clay, Nigeria	48.6	26.9	20.13	na	0.08	0.329	0.033	2.06	na	0.20	0.084	0.008	0.011	0.064	na	na	Ajemba and Onukwuli (2012)
Imbabah Giza, Mesir	65.32	13.89	7.51	2.61	1.09	0.95	na	1.46	0.75	0.28	na	na	na	na	5.87	na	Hegazy et al., (2012)
Ds Gambut, Indonesia	65.54	18.78	1.57	0.298	0.087	0.609	0.009	0.991	0.651	0.055	na	na	na	na	10.88	na	Darnas et al., (2013)

na = not analyzed

LOI = lost of ignition

CEC

=

cation

exchange

capacity

Peat clay was washed and dried under direct sunlight 48 hours and then it was crushed and screened with size fraction of +70-120, +120-200, +200-325 mesh (0.044-0.210 mm) based on standard sieve of the American Society for Testing and Materials (ASTM) and calcined at 700 °C for 2 hours for thermal treatment. Hydrochloric acid was gained from Sigma-Aldrich with a purity of $\geq 32\%$, $1.16 \text{ g}\cdot\text{ml}^{-1}$. Required concentrations of hydrochloric acid were arranged along with dilution of deionized water.

Characterization of peat clay was analyzed with XRD (Philips X-pert powder model, Netherlands) using powder diffraction data base file-2 (PDF-2) 1996 which shows the major mineral phases i.e. kaolinite (aluminum silicate hydrate ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) compounds), quartz (silica oxide (SiO_2) compound), hematite (iron oxide (Fe_2O_3) compounds), and corundum (aluminum oxide (Al_2O_3) compounds) (Fig.1). Identification of variations mineral form of each functional group which brought distinctive properties of the compounds in the peat clay using FTIR (Shimadzu, Japan) with band in the range $500\text{-}4000 \text{ cm}^{-1}$ and transmittance in percent (%). The possibility of the compounds of quartz, kaolinite, illite, hematite, calcite based on FTIR analysis is described in Fig. 2 and Table 2.

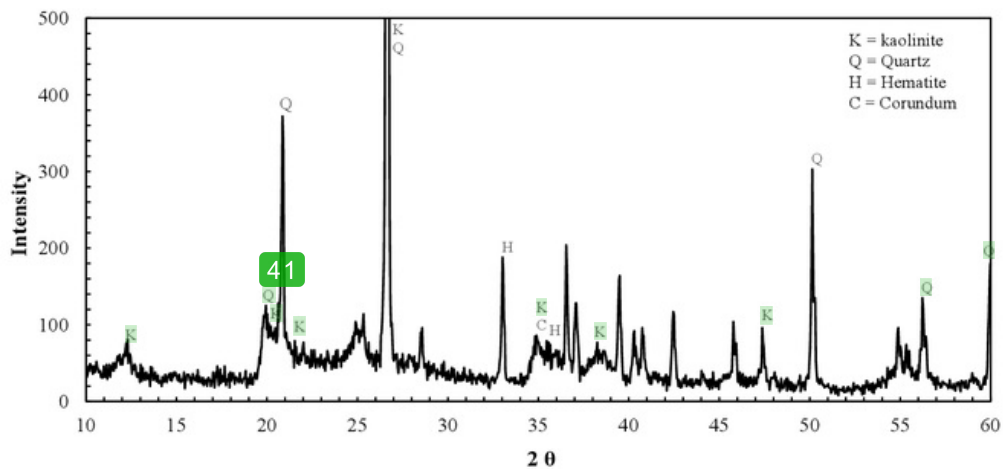


Fig. 1. XRD pattern of peat clay from Peat Village, Subdistrict of Peat, District of Banjar, South Kalimantan, Indonesia

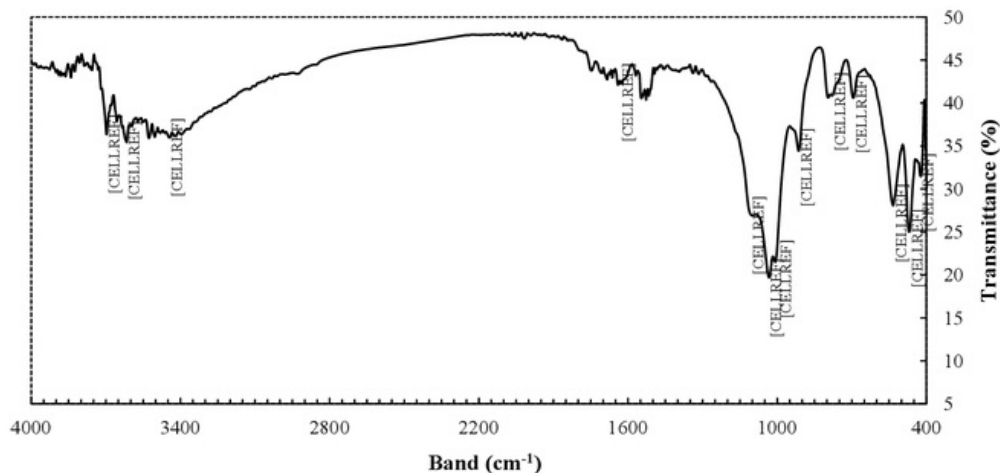


Fig. 2. FTIR spectrum of peat clay from Peat Village, Subdistrict of Peat, District of Banjar, South Kalimantan, Indonesia

Flake structure of peat clay was analyzed by SEM-EDX (SEM EVO MA 10, Germany) that showed the presence of the same dominant elements, namely Al, Si, Fe (color difference) with a composition of 31.21%wt, 50.18%wt, 18.61%wt respectively (**Fig. 3**). The chemical composition of peat clay based on XRF (PANalytical miniPAL4, Netherlands) analysis is listed in **Table 3**.

Table 2

Infrared spectroscopy (IR) band of peat clay from Peat Village, Subdistrict of Peat, District of Banjar, South Kalimantan, Indonesia

Infrared Band (cm ⁻¹)	Transmittance (%)	Assignment
3697.29	36.350	Al-O-H str (kaolinite, illite)
3616.28	35.428	Al-O-H (kaolinite, illite, calcite)
3444.63	35.979	H-O-H str (kaolinite, illite)
1623.95	42.233	H-O-H str (illite, calcite)
1099.35	26.901	Si-O str (kaolinite, quartz)
1033.77	19.707	Si-O-Si, Si-O str. (kaolinite, illite)
1008.7	21.507	Si-O str (kaolinite, quartz)
914.2	34.436	Al-O-H str (kaolinite, illite, hematite)
779.19	40.861	Al-O-Al str (kaolinite, illite)
694.33	40.595	Al-O-Al str., Si-O-Al str (quartz, kaolinite)
534.25	28.083	Al-O-Al str., Si-O-Al str (kaolinite)
468.67	25.018	Si-O str., Si-O-Fe str. (quartz, kaolinite)
422.38	31.474	Si-O str (quartz)

source: Tuddenham and Lyon, 1960; Gadsden, 1975; Marel and Beutelspacher, 1976; Nayak and Singh, 2007; Thambavani and Kavitha, 2014.

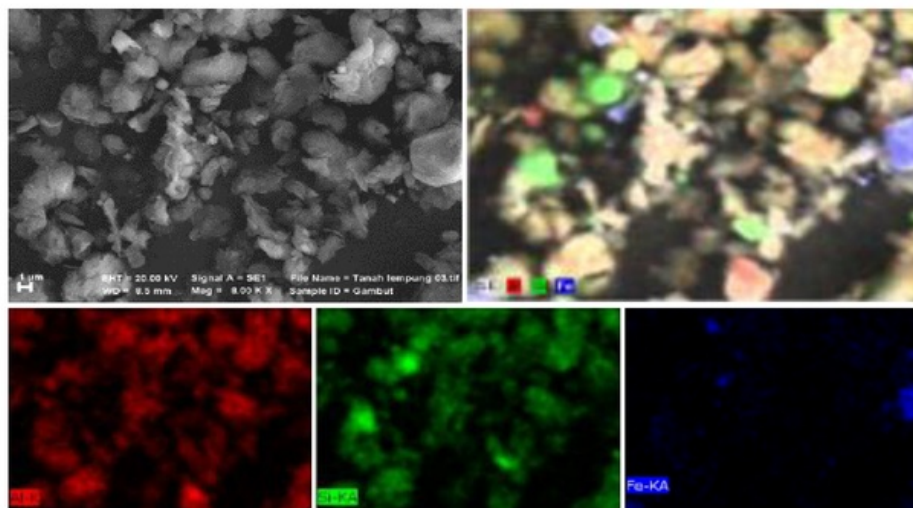


Fig. 3 Morphology SEM of peat clay from Peat Village, Subdistrict of Peat, District of Banjar, South Kalimantan, Indonesia

2.2. Leaching process

The leaching trials had been done at 10 atmospheric pressure in an Iwaki Pyrex reactor which it had two neck for a thermometer and for the inlet of the sample or for withdrawal of samples at regular time intervals. The reaction mixture was agitated at 300 r·min⁻¹ using a stirrer and heated indirectly via a water bath. Aluminum leaching from the calcined peat clay was performed in the reactor using hydrochloric acid solutions at three different particle sizes, and four different reaction temperatures as function of times. 5 g of calcined peat clay was added to 250 ml agitated hydrochloric acid solution (solid/liquid ratio is 0.02 g·ml⁻¹) at

particular temperature. The effect of particle size (+70-120, +120-200, and +200-325 mesh), and reaction temperature (30, 50, 70, and 90 °C) on aluminum leaching were studied and performed at 60 min. At selected time interval, all samples were collected using a syringe and filtered for analysis determine aluminum content in solution using inductively coupled plasmacluster optical emission spectrometer (ICP-OES) (9060-D Teledyne Leeman Labs. USA). Each analysis was repeated three times and deputized with average values.

According to Cheng et al., (2012) total of aluminum can be leached out in the acid condition and calculated based on the standard methods for examination of water and wastewater and the standard method of the Taiwan environmental agency (N R353.00C). Calcined peat clay was added in nitric acid with a ratio of 1:1 and filtered. The filtrate was analyzed to determine the amount of soluble aluminum using ICP-OES. The result indicates that approximately 81.78 mg of aluminum ions can leach from 1 g of SSW, and the aluminum leaching recovery (x) can be stated as

$$x = (X/X_0) \times 100 \quad (1)$$

where X_0 denotes total aluminum obtained through acid leaching process and X is the amount of aluminum obtained at different conditions (mg/g).

Table 3

Chemical composition of peat clay from Peat Village, Subdistrict of Peat, District of Banjar, South Kalimantan, Indonesia

Compound	Mass composition %
SiO ₂	38.80
Al ₂ O ₃	11.00
Fe ₂ O ₃	27.00
K ₂ O	1.16
MnO	0.10
CaO	0.83
TiO ₂	2.57
V ₂ O ₅	0.11
Cr ₂ O ₃	0.20
ZnO	0.06
NiO	0.93
CuO	0.16
MoO ₃	6.50
Re ₂ O ₇	0.10
LOI	10.48

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2.2. Shrinking core (SC) model

SC model for spherical particles of unchanging structure and size of particles (Froment and Bischoff, 1979; Wen, 1968) describes kinetic characteristics of reaction mechanisms throughout the noncatalytic heterogeneous solid liquid reaction. Based on Wen, (1968), there are six steps process system in the surface reaction of solid-liquid system. The SC model involves the three reaction mechanisms which comprises of the following steps: first, film diffusion control or diffusion of the leachant through the liquid film surrounding the particle; second, inert-layer diffusion control or diffusion of the leachant through the inert-layer (product layer) at the surface of the unreacted core; and third, surface chemical reaction control or chemical reaction of the leachant at the surface of the core Nazemi et al., (2011). For the aluminum leaching kinetics, however, only two reaction mechanisms would be used at previously established SC model (Levenspiel, 1972; Abdel-Aal and Rashad, 2004; Liddell, 2005; Ong et al., 2012; Ju et al., 2015; Raza et al., 2015). The kinetics equation for leaching process controlled by a surface chemical reaction is as follows:

$$\frac{t}{\tau_c} = 1 - (1-x)^{1/3} \quad (2)$$

If the leaching process is controlled by diffusion through a product layer, the kinetics equation is as follows:

$$\frac{t}{\tau_i} = 1 - 3(1-x)^{2/3} + 2(1-x) \quad (3)$$

with time for complete leaching by chemical reaction control $\tau_c = \rho_B R / b M_w k_c C_A$ and the time for complete leaching by product layer diffusion control $\tau_i = \rho_B R^2 / 6 b M_w D_e C_A$, where x denotes the fraction of aluminum leaching recovery; t is the reaction time; ρ_B is the solid density; R is the initial radius of the particle; b is the stoichiometric coefficient; M_w is the molecular weight of the solid (g/mol); k_c is the factor of mass transfer; C_A is the concentration of hydrochloric acid; and D_e is the product layer diffusion coefficient.

Eq. (2) and (3) can be applied to the short time leaching process. If the model follows the experimental data, then a long period of leaching time can be used. However, for a long period of time, the boundary condition is different with the condition of short period of time. In the case of surface chemical reaction control and product layer diffusion control, other equations can be formulated as follows Aarabi-Karasgani et al., (2010):

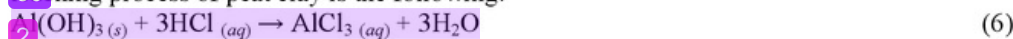
$$\frac{t-t_1}{\tau_c} = 1 - \left(\frac{1-x}{1-x_1} \right)^{1/3} \quad (4)$$

$$\frac{t-t_1}{\tau_i} = 1 - 3 \left(\frac{1-x}{1-x_1} \right)^{2/3} + 2(1-(1-x_1)^{1/3})(x-x_1) \quad (5)$$

with time for complete leaching by surface chemical reaction control $\tau_c = \rho_B R (1-x_1)^{1/3} / b k_c C_A$ and the time for complete leaching by product layer diffusion control for long period of time leaching process $\tau_i = \rho_B R^2 (1-x_1)^{2/3} / 6 b D_e C_A$, where t_1 and x_1 values are not zero and its value from experimental data should be regarded as an initial condition (rather than 0 in the short period of time leaching process).

3. Results and Discussion

According to chemical analyses data, aluminum is a major element of the peat clay sample which has a similar composition to water treatment sludge. Its major elements are silica oxide and aluminum oxide (Wu et al., 2004). At normal temperature, the aluminum oxide cannot react with acid. However, only $\text{Al}(\text{OH})_3$ shaped amorphous solid in the sludge can be leached under acidic conditions (Cheng et al., 2012). Consequently, the major reaction in the leaching process of peat clay is the following:

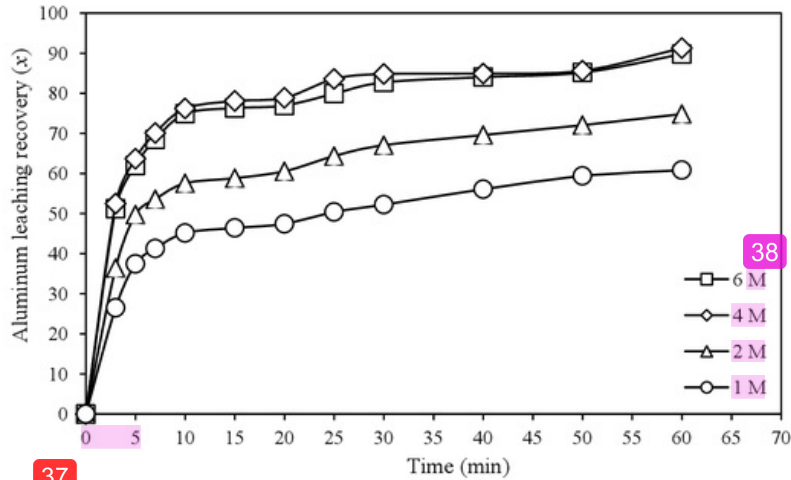


3.1. Effect of acid concentration on the aluminum leaching recovery

Fig. 4 shows the influence of acid concentration on the aluminum leaching recovery at a temperature of 90 °C, stirring rate of 300 r·min⁻¹, particle size of +200-325 mesh, and solid to liquid ratio 0,02 g·ml⁻¹, with all experiment conducted with adequate acid. The aluminum leaching recovery increase with time and acid concentration from 1 mol·L⁻¹ to 6 mol·L⁻¹. 91.3% of aluminum leaching recovery was achieved at hydrochloric acid of 4 mol·L⁻¹ and 60 min. At 6 M of hydrochloric acid, however, aluminum leaching recovery decreased little in all leaching time, leading to a leaching recovery less than 90% in 60 min. This result could possibly be due to the precipitation of metal-chloride. A similar experiment has been reported by Baba et al., (2009) for the recovery of zinc from spent zinc carbon batteries after a prior leaching in hydrochloric acid.

Furthermore, leaching kinetics have an influence on the aluminum leaching recovery, while the leaching process is influenced by thermodynamics. The viewpoint of leaching kinetics that increasing the aluminum leaching recovery along with increasing concentrations of hydrochloric acid, but, the decrease in the solubility of aluminum chloride (AlCl_3) (Mahi et

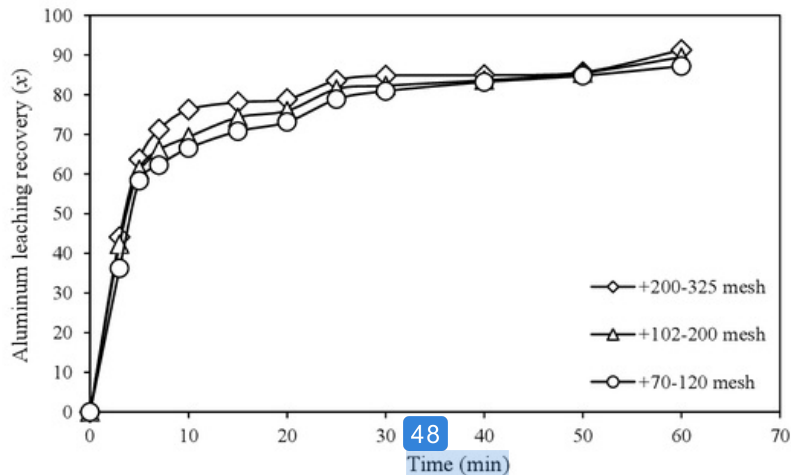
al., 1991; Cui et al., 2015). In accordance with Cui et al., (2015), when aluminum chloride is saturated dissolution and precipitation of aluminum oxide have been occurred a dynamic stability, wherein aluminum oxide dissolution percentage was reached a stable condition. This might describe the aluminum leaching recovery behavior in $6 \text{ mol}\cdot\text{L}^{-1}$ of hydrochloric acid solution.



37 **Fig. 4.** Effect of acid concentration on aluminum leaching recovery 38

3.2. Effect of particle size on the aluminum leaching recovery 5

Fig. 5 shows the influence of particle size on aluminum leaching recovery at acid concentration of 4 M, temperature of 90°C , string rate of $300 \text{ r}\cdot\text{min}^{-1}$, and solid to liquid ratio $0,02 \text{ g}\cdot\text{ml}^{-1}$. The aluminum leaching recovery increase with time and particle size decrease from +70-120 mesh to +200-325 mesh. Conversely, the aluminum leaching recovery decreased with time as the particle size increased. The smaller the particle size, the faster was its dissolution (Baba and Adekola, 2012) or the smaller particle sizes can create higher surface area for contact with the acid solution thereby improving the aluminum leaching recovery of the clay particles in the liquid medium. The particle size of +200-325 mesh was used for experiments in this study.



23 **Fig. 5.** Effect of three different particle sizes on aluminum leaching recovery 48

3.3. Effect of temperature on the aluminum leaching recovery

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Fig. 6 shows the effect of leaching temperature on aluminum leaching recovery at acid concentration 4 M and particle size of +200-325 mesh. The aluminum leaching recovery increased with time and temperature. About 91.30% of aluminum leaching recovery was achieved at hydrochloric acid of 4 M, 60 min, particle size of +200-325 mesh with solid to liquid ratio 0,02 g·ml⁻¹, and temperature of 90 °C. Aluminum leaching was more sensitive to boil temperature above 90 °C, which showed that the diffusion process could be a step not limiting because the layer can be gradually formed on the surface of the particles and not hinder acid from attaining the reactive area at temperature of 90 °C and above. This statement contradicts with Cui et al (2015) that aluminum oxide dissolution from coal mining waste was less sensitive to temperature between 90 °C and 106 °C, diffusion process is possible as the rate controlling. However, other researchers describe that the leaching rate increases with increasing temperature or influenced by temperature (Al-Zahrani and Abdel-Majid, 2009; Olanipekun, 2000; Ajemba dan Onukwuli, 2012; Cheng et al., 2012; Ju et al., 2015; Raza et al., 2015).

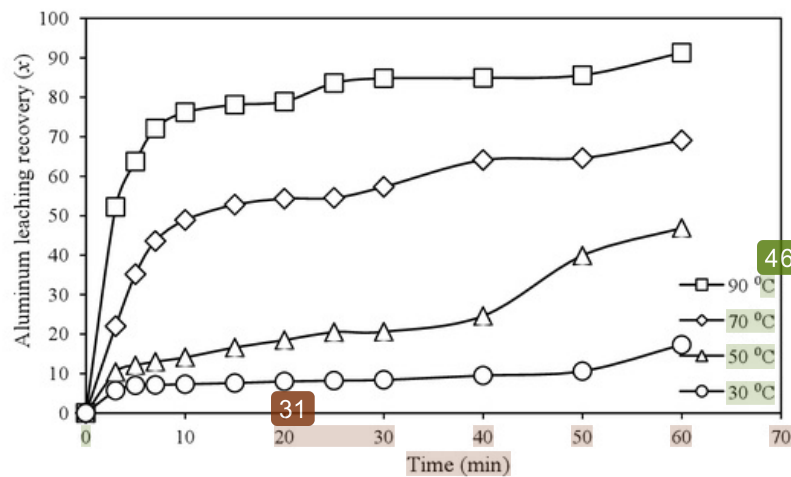


Fig. 6. Effect of four different temperatures on aluminum leaching recovery (at 30-90 °C, 4 M HCl, and particle size of +200-325 mesh)

3.4. Leaching kinetics

3.4.1. Effect of acid concentration

Aluminum leaching trial presents data for kinetic modeling. Based on Eqs. (2)-(3) for the short period of time and Eqs. (4)-(5) for the long period of time the rate constants determined at dissimilar concentrations are given in Table 4 according to aluminum leaching recovery data in Fig. 4. According to Table 4, the correlation coefficient value (R^2) of rate constant of product layer diffusion (K_i) is higher than the value of rate constant of surface chemical reaction (K_c) for both the short and long period of leaching time. For long period of time, Fig. 4 is used as the data to predict two control mechanisms that starts from time 15 min and the value of aluminum leaching recovery is not zero where the initial time used is $t_1 = 15$ min, and x_1 should be read from Fig. 4. Results indicate that the aluminum leaching recovery is dominated by an inert-layer diffusion on acid conditions from 1 mol·L⁻¹ to 6 mol·L⁻¹ at 90 °C for all period of leaching time.

Based on K_i , the logarithm of aluminum leaching rate constant is illustrated versus the concentration logarithm. The reaction order to acid concentration is gained from the slope in Fig. 7. It is indicated that the aluminum leaching is both pseudo first order reaction at short and long period of time. The reaction order describes the correlation between acid concentration and aluminum leaching rate. A higher reaction order denotes a more influential leaching to the alteration of hydrochloric acid concentration (Cui et al., 2015). According to

Fig. 7, Compared to the aluminum leaching rate for short period of time, the aluminum leaching rate for long period of time is more influence by the hydrochlorid acid concentration. The slope show that the reaction order is 0.7497 and 0.5318, with correlation coefficient of 0.9406 and 0.9678 for short and long period of time, respectively. Therefore, the reaction order with respect to H^+ ion concentration is near 1 for acid concentrations ≤ 4 M. A similar experiment has been reported by Baba et al., (2009) for order of reaction determination.

Table 4

Values of K_i , K_c and correlation coefficient (R^2) for aluminum leaching recovery at different acid concentrations (1–6 mol·L⁻¹) for the short and long period of time

Acid concentration (M)	The short period of time				The long period of time			
	Apparent rate constants (min ⁻¹)		Correlation coefficient (R^2)		Apparent rate constants (min ⁻¹)		Correlation coefficient (R^2)	
	K_i	K_c	K_i	K_c	K_i	K_c	K_i	K_c
1	0.0090	0.0179	0.9676	0.8808	0.0084	0.0024	0.9862	0.9843
2	0.0160	0.0244	0.9501	0.8595	0.0140	0.0033	0.9752	0.9747
4	0.0325	0.0366	0.9805	0.8834	0.0196	0.0049	0.8582	0.8518
6	0.0309	0.0355	0.9838	0.8865	0.0216	0.0051	0.9521	0.9500

3.4.2. Effect of particle size

Using the data shown in Fig. 5 and Eqs. (2)-(3) for the short period of time and equations (4)-(5) for the long period of time, the rate constants calculated at three different particle sizes are given in Table 5. According to Table 5, the correlation coefficient value (R^2) of the rate constant of product layer diffusion (K_i) is higher than the value of rate constant of surface chemical reaction (K_c) for the short long period of leaching time. The results indicate that the aluminum leaching recovery is dominated by a product layer diffusion process for the short period of time. For long period of time, Fig. 5 is used as the data to predict two control mechanisms that starts from time 15 min and the value of aluminum leaching recovery is not zero where the initial time used is $t_1 = 15$ min, and x_1 should be read from Fig. 5. For this condition, The surface chemical reaction control and product layer diffusion control mechanisms are used Eqs. (4) and (5). Based on Tabel 5, the R^2 value of K_i is lower than the value of K_c . It means that the aluminum leaching recovery is dominated by a chemical reaction under different particle size and 90 °C.

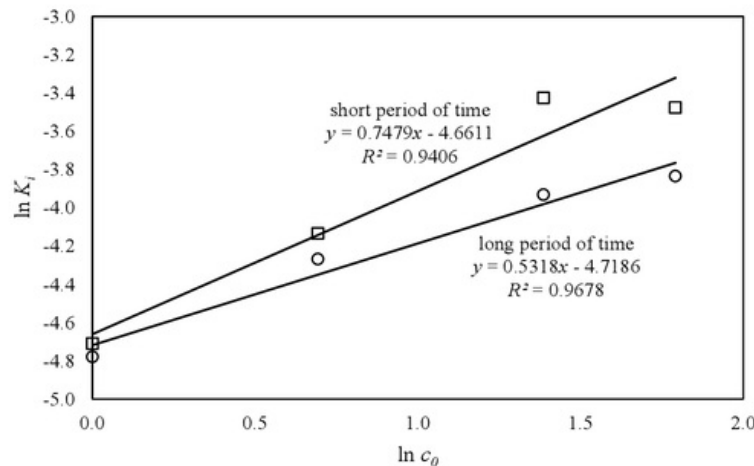


Fig. 7. Plots of $\ln K_i$ versus $\ln c_0$ giving the slope as reaction order which c_0 is hydrochloric acid concentration

Table 5

Values of K_i , K_c and correlation coefficient (R^2) for aluminum leaching recovery at four different particle size (+70-120; +120-200; and +200-325 mesh) for the short and long period of time

Particle size (mesh)	The short period of time				The long period of time			
	Apparent rate constants (min^{-1})		Correlation coefficient (R^2)		Apparent rate constants (min^{-1})		Correlation coefficient (R^2)	
	K_i	K_c	K_i	K_c	K_i	K_c	K_i	K_c
+70-120	0.0239	0.0311	0.9297	0.8840	0.0218	0.0051	0.8862	0.9279
+120-200	0.0265	0.0327	0.9330	0.8699	0.0209	0.0052	0.8971	0.9333
+200-325	0.0343	0.0284	0.9680	0.9171	0.0196	0.0049	0.8518	0.8582

3.4.3. Effect of temperature

Based on the data in Fig. 6, the rate constants calculated at four different temperatures using the right hand side of equation (2) and (3) against the short period of time for aluminum leaching are presented in Fig. 8 and Table 6. According to Table 6, the R^2 value of K_i is higher than the value of K_c for the short period of time. The right hand side of equation (3) as a function of short period of time provides good linear lines in the range of temperature which indicates that the acid diffusion via the product layer to the reaction surface is the rate controlling.

Again, based on the experimental data of Fig. 6, the right hand side of Eqs (4) and (5) versus time is provided in Fig. 9 and Table 6 for the long period of time. In previous section, the initial time used is $t_1 = 15$ min, and x_1 should be read from Fig. 6. The results indicate that the aluminum leaching recovery at the long period of time is controlled by surface chemical reaction. The R^2 value of K_c is higher than the value of K_i . This condition, chemical reaction through surface of the core becomes the rate determining of aluminum leaching process.

Table 6

Values of K_i , K_c and correlation coefficient (R^2) for aluminum leaching recovery at different temperature (30, 50, 70, and 90 °C) for the short and long period of time.

Temperature (°C)	The short period of time				The long period of time			
	Apparent rate constants (min^{-1})		Correlation coefficient (R^2)		Apparent rate constants (min^{-1})		Correlation coefficient (R^2)	
	K_i	K_c	K_i	K_c	K_i	K_c	K_i	K_c
30	0.0002	0.0023	0.8006	0.7005	0.0006	0.0007	0.6940	0.7541
50	0.0007	0.0046	0.9096	0.7663	0.0064	0.0031	0.8701	0.9034
70	0.0112	0.0205	0.9744	0.9554	0.0119	0.0030	0.9604	0.9607
90	0.0333	0.0372	0.9702	0.8817	0.0188	0.0049	0.7361	0.8554

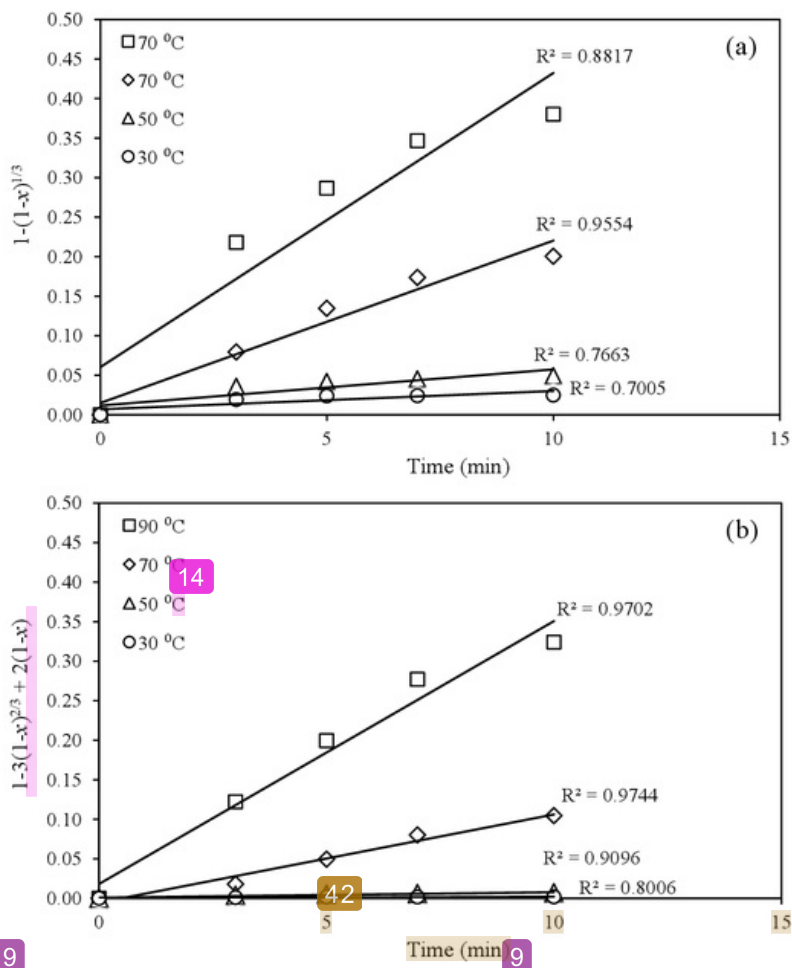


Fig. 8. (a) Right hand side of Eq. (2) versus time, and (b) right hand side of Eq. (3) versus time

The Arrhenius equation used to determine the apparent activation energy as follows:

$$K = Ae^{-E_a/RT} \quad (7)$$

linear shape is

$$\ln K = \ln A - \frac{E_a}{RT} \quad (8)$$

where K is the rate constant, A is the pre-exponential factor, E_a ($\text{kJ}\cdot\text{mol}^{-1}$) is the activation energy, R is the universal gas constant, $8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and T is the temperature (K). K values can be gained from the lines slope given in Table 5 at different temperatures.

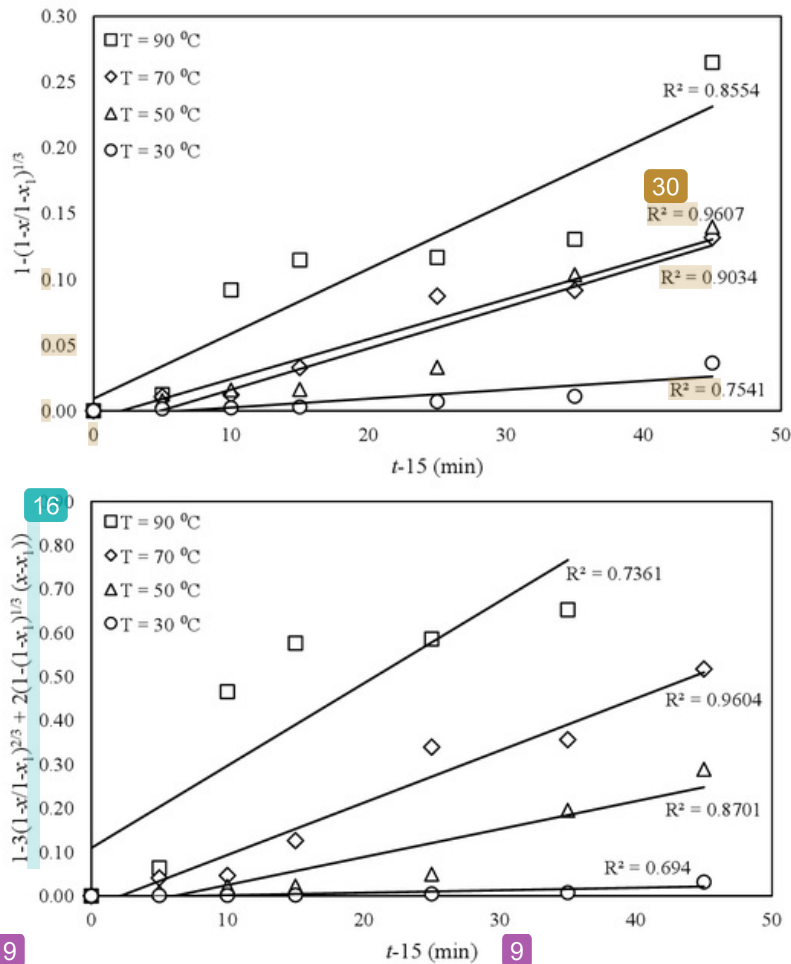


Fig. 9. (a) Right hand side of Eq. (4) versus time, and (b) right hand side of Eq. (5) versus time

From Table 6, it can be concluded that the R^2 value of K_i is higher than the value of K_c for short period of time. For long period of time, however, the R^2 value of K_c is higher than the value of K_i . In reality, the R^2 value of K_i and R^2 value of K_c in short and long period of time condition is different, proposing the probability of two dissimilar reactions take place in the time of leaching continues. This is possibly due to the presence of the other compounds besides aluminum compound in the peat clay particles. To ensure this hypothesis, the Arrhenius equation is used to determine the value of activation energy. Consequently, in this study, the K value of Arrhenius formula represents the K_i and K_c values for both short and long period of time, respectively.

As indicated in Fig. 10, the apparent activation energy at short and long period of time in the Arrhenius equation were estimated to be $82.79 \text{ kJ.mol}^{-1}$ and $27.08 \text{ kJ.mol}^{-1}$, respectively. In the present study, the results are not aligned with those given by Cui et al., (2015); Brantley et al., (2008); Abdel-Aal and Rashad, (2004); Aydogan et al., (2005). The activation energy compared with that described by Aarabi-Kasgani et al., (2010), a lower activation energy means that a surface reaction ($24\text{--}30.12 \text{ kJ.mol}^{-1}$) influences the leaching kinetics. Whereas a higher activation energy shows that product layer diffusion ($39\text{--}90 \text{ kJ.mol}^{-1}$) is the rate controlling step (Rath et al., 1981; Olanipekun, 2000; Xue et al., 2011; Ajemba and Onukwuli, 2012).

The kinetic model of aluminum leaching proses from peat clay at different temperature can be written as $1-3(1-x)^{2/3}+2(1-x)=2.95\times 10^{10}e^{-82.79/RT}t$ for short period of time and $1-(1-x)^{1/3}=43.715\times 10^{10}e^{-27.076/RT}t$ for long period of time.

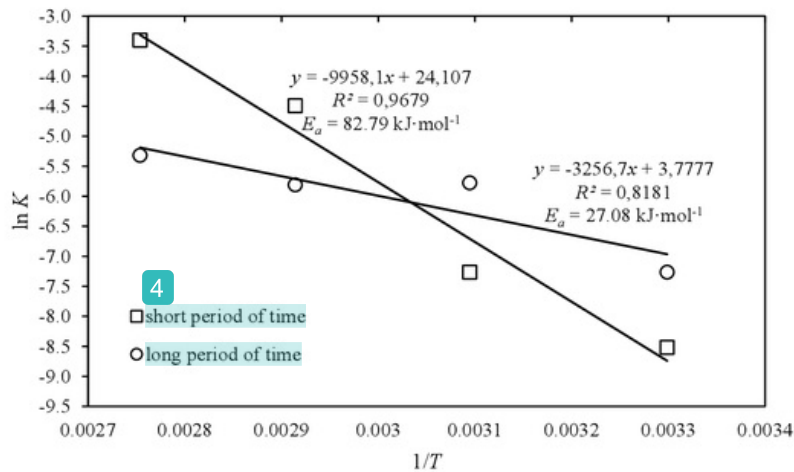


Fig. 10. The Arrhenius plot of $\ln K$ against T^{-1} for aluminum leaching at short and long period of time

4. Conclusions

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The aluminum kinetics from peat clay was investigated using hydrochloric acid as solvent. Leaching experiments were performed with four different acid concentration, three different particle size, and four different temperature. The conclusions can be made based on the results of the study, as follows:

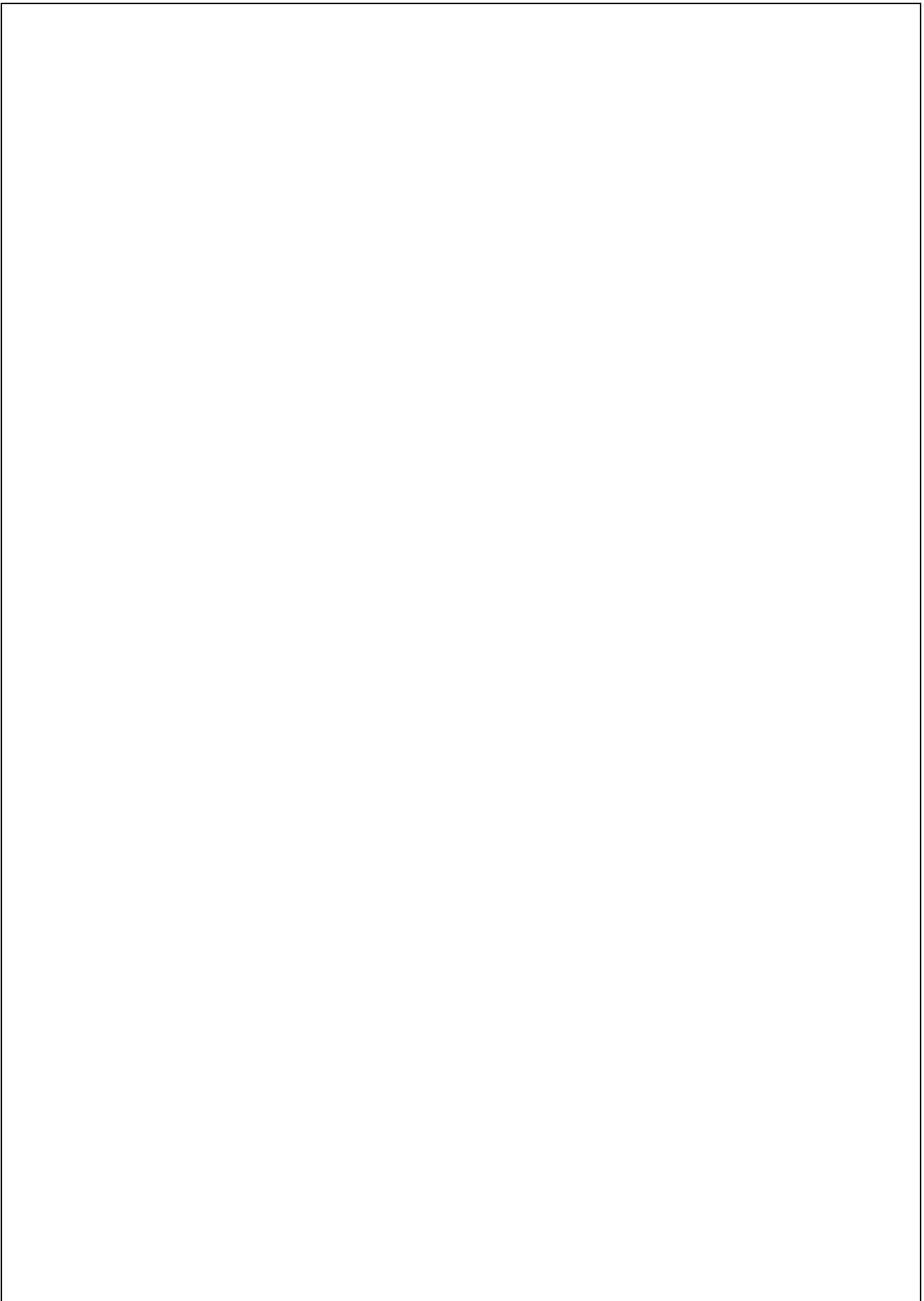
1. Acid concentration, particle size, and temperature have significant effect on aluminum leaching process.
2. About 91.30% of aluminum leaching recovery was achieved within 60 min at 4 M hydrochloric acid and temperature of 90 °C, using particle size of +200-325 mesh with solid to liquid ratio 0,02 g·ml⁻¹. The apparent activation energy at short and long period of time in the Arrhenius equation were estimated to be 82.79 kJ·mol⁻¹ and 27.08 kJ·mol⁻¹, respectively.
3. The aluminum leaching results indicated that the SC model for spherical particles is useable. The acid diffusion via the product layer to the reaction surface is the rate controlling in the range of temperature for short period of time. A similar condition, however, the surface chemical reaction has been defined to be rate-controlling step for long period of time. The kinetic model for aluminum leaching proses can be written as $1-3(1-x)^{2/3}+2(1-x)=2.95\times 10^{10}e^{-82.79/RT}t$ for short period of time and $1-(1-x)^{1/3}=43.715\times 10^{10}e^{-27.076/RT}t$ for long period of time.

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