



Article

Dissolution of aluminium from metakaolin with oxalic, citric and lactic acids

Danyal Karbalaie Saleh¹, Hadi Abdollahi^{1*}, Mohammad Noaparast¹ and Alireza Fallah Nosratabad²

¹School of Mining Engineering, College of Engineering, University of Tehran, PO Box 1439957131, Tehran 1417466191, Iran and ²Soil and Water Research Institute, The Research, Education and Agricultural Extension (AREEO), PO Box 31785-311, Karaj 31779-93545, Iran

Abstract

This study examines the leaching of aluminium from calcined kaolin (metakaolin) with citric, oxalic and lactic acid and binary combinations of these organic acids. The investigated parameters were the pulp density, acid concentration, pH, agitation speed, temperature and contact time. The kinetics of aluminium dissolution from metakaolin in binary organic acid mixtures were determined and scanning electron microscopy examination and energy-dispersive spectrometry mapping of Si and Al of untreated kaolin and residual solids were also carried out. Aluminium dissolution increased with temperature, time, acid concentration, pulp density and acidity. At maximum dissolution, citric–oxalic (1:4 w/w) and lactic–oxalic (1:4 w/w) mixtures dissolved 77% and 78% aluminium, respectively, from metakaolin in 11 h. The activation energy ranged from 57.8 to 74.6 kJ/mol. The most effective parameter in the dissolution of aluminium was the temperature, indicating that the reaction was not diffusion-controlled. It was concluded on the basis of the activation energy values and the sensitivity of the reaction to temperature that the dissolution was under chemical-reaction control.

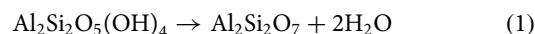
Keywords: aluminium dissolution, leaching kinetics, metakaolin, organic acids

(Received 10 October 2018; revised 17 March 2019; Accepted Manuscript online: 27 May 2019; Associate Editor: Joao Labrincha)

Aluminium is produced from bauxite *via* the Bayer process (Hosseini *et al.*, 2011). Non-bauxite sources of aluminium production include kaolin, alunite, sillimanite, kyanite, fly ash and micas (Altiokka & Hoşgün, 2003; Hosseini *et al.*, 2011). Kaolinite, with a relatively small particle size and large specific surface area, belongs to the group of hydrated aluminium silicates (Cuadros, 2017). Kaolinite (ideally $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is a 1:1-type phyllosilicate mineral that consists of one silicate tetrahedral sheet and one aluminium hydroxide octahedral sheet in each layer. Kaolinite has properties that are valued in the porcelain, cement, brick, paper and rubber industries, such as brightness, whiteness, a fine grain size and chemical stability. Rocks rich in kaolinite are known as kaolin or china clay (Aghaie *et al.*, 2009; Pohl, 2011; Phipps, 2014; Zhao *et al.*, 2018). Kaolin is composed of 35–38% Al_2O_3 and 42–45% SiO_2 and may be mined for the production of alumina (Al_2O_3) and aluminium (Tang *et al.*, 2010; Hosseini *et al.*, 2011).

The endothermic dehydroxylation of kaolinite begins at 550–600°C, producing disordered metakaolin, but continuous hydroxyl loss is observed up to 900°C. Although, historically, there has been much disagreement concerning the nature of the metakaolin phase, extensive research has led to a general consensus that metakaolin is not a simple mixture of amorphous silica (SiO_2) and alumina, but rather it has a complex amorphous structure that retains some longer-range order (but not strictly

crystalline) due to stacking of its layers. The reaction is presented as follows (Bellotto *et al.*, 1995):



Thermal treatment such as calcination at 750°C increases the dissolution rate of Al and impurities such as Fe (Groudev & Groudeva, 1986; Altiokka & Hoşgün, 2003). Kaolin dissolution occurs under both acidic and alkaline conditions. Bauer & Berger (1998) studied kaolinite dissolution using batch experiments in 0.1–4.0 M KOH solutions at 25°C and 80°C. Kaolinite dissolution was characterized by a linear release of SiO_2 and Al as a log function of time. This relationship may be explained by a reaction affinity effect that is controlled by octahedral-sheet dissolution. Aldabsheh *et al.* (2015) and Wang *et al.* (2016) showed that silicon extraction from kaolinite was mainly affected by alkali-leaching temperature, alkali concentration and alkali-leaching time, and increasing these parameters enhanced dissolution. In a previous study involving an exhaustive analysis of the solubility of several aluminosilicate minerals in alkaline media, Si and Al dissolved congruently (Cama & Ganor, 2015). The extent of dissolution was somewhat higher in NaOH than in KOH solution (Aldabsheh *et al.*, 2015).

Hulbert & Huff (1970) examined the acid leaching of calcined kaolin with 5.9 and 8.6 N solutions of hydrochloric, nitric and sulfuric acids. Kaolin was calcined at 732°C for 2 h and the leaching tests were carried out at 60°C, 80°C and 95°C. The dissolution could be expressed as $\ln \frac{1}{1-x} = kt^m$, where the parameter m varies between 1.10 and 1.55 and is process specific, x

*E-mail: h_abdollahi@ut.ac.ir

Cite this article: Karbalaie Saleh D, Abdollahi H, Noaparast M, Fallah Nosratabad A (2019). Dissolution of aluminium from metakaolin with oxalic, citric and lactic acids. *Clay Minerals* 54, 209–217. <https://doi.org/10.1180/clm.2019.28>

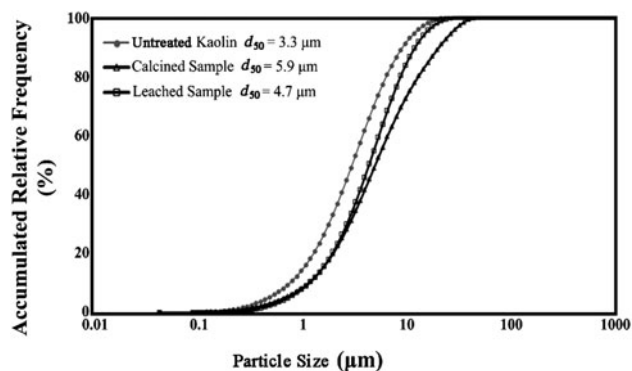
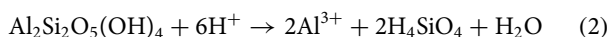


Fig. 1. Particle-size distribution of untreated kaolin (not calcined), calcined and leached samples. d_{50} = average particle size.

is the fraction reacted and t is the contact time. The activation energy was 121.4 kJ/mol and the dissolution of aluminium with HCl was the fastest, whereas HNO₃ had the lowest dissolution rate. Altioikka & Hoşgün (2003) and Lima & Angélica (2014) investigated the kinetics of kaolin dissolution in HCl and H₂SO₄, respectively. The activation energy was 79 kJ/mol for Al dissolution in HCl and 97 kJ/mol in H₂SO₄.

Organic acids may also be used to dissolve Al-silicates. Cama & Ganor (2006) showed that the dissolution of Al-silicates in oxalic acid and other carboxylic acids is much faster than inorganic acids under comparable pH conditions. Organic acids act as metal-chelating agents and thereby increase the solubility of minerals. Thus, the adsorption of organic acids and anions on the surfaces of clay minerals may accelerate and facilitate metal dissolution, leading to mineral weathering and degradation (Ganor & Lasaga, 1994; Cama & Ganor, 2006). Protonation caused by organic acids reduces the pH and may shift the equilibrium towards dissolution. The overall dissolution reaction of kaolinite under acidic conditions may be expressed as (Cama & Ganor, 2006):



The dissolution rate depends on the specific organic acid. Zinder *et al.* (1986) showed that the dissolution rate constants followed the following orders: $k_{\text{oxalate}} > k_{\text{malonate}} > k_{\text{succinate}}$ for dicarboxylic anions and $k_{\text{salicylate}} > k_{\text{phthalate}} > k_{\text{benzoate}}$ for aromatic ligands. Wang *et al.* (2005) showed that the dissolution of Si and Al from kaolinite increased with increasing concentration of citric, oxalic and malic acid and was most effective with oxalic acid.

The purpose of this study was to investigate the dissolution of aluminium from metakaolin using citric, oxalic and lactic acids in single and binary (citric–oxalic and lactic–oxalic) mixtures. The pulp density, acid concentration, pH, agitation speed, temperature and contact time were evaluated as process parameters and the kinetics of aluminium dissolution in binary organic acids systems and their respective activation energies were determined.

Materials and methods

Characterization and chemical composition

A representative kaolin sample from a concentrate was obtained from the Zonoz processing plant, located in East Azerbaijan

Table 1. XRF analysis results before and after heating (calcination). The results are expressed as wt.%.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	LOI
Untreated kaolin	63.0	24.0	0.55	1.2	0.55	0.3	9.0
Metakaolin	68.8	25.6	1.10	2.4	0.20	0.8	0.6

LOI = loss on ignition.

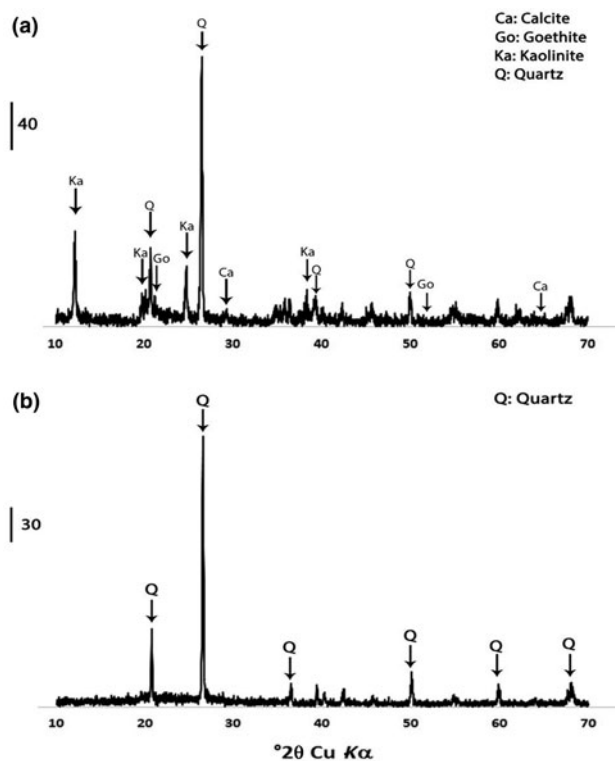


Fig. 2. XRD traces of (a) untreated kaolin and (b) metakaolin.

Province, Iran. The particle-size distribution of the kaolin sample was determined by a laser particle sizer (Analysette 22, Fritsch Nano-Tec, Idar-Oberstein, Germany) and it was comparable with results for the calcined and leached samples (Fig. 1). The kaolin sample had a median particle size (d_{50}) of 3.3 µm, d_{80} of 7 µm and d_{25} of 1.7 µm. Calcination and leaching did not change significantly the particle size, with the d_{50} of the calcined and leached samples being 5.9 and 4.7 µm, respectively.

The kaolin sample was heated at 750°C for 2 h to convert it to metakaolin before the dissolution experiments (Groudev & Groudeva, 1986; Altioikka & Hoşgün, 2003). The chemical analysis of the original material and the metakaolin, determined by X-ray fluorescence (XRF) spectroscopy (MagiX-PRO XRF spectrometer, PANalytical), is provided in Table 1. The original kaolin contained 63% SiO₂ and 24% Al₂O₃, while the metakaolin contained 68.8% SiO₂ and 25.6% Al₂O₃. The weight loss (loss on ignition) of the calcined sample was significantly reduced, but other oxides except MgO were slightly increased. Because the exact aluminium content was important and the chemical elemental analysis methods are more precise, an alkaline fusion method in addition to XRF was used to analyse the aluminium content. The chemical analysis of the metakaolin sample by the alkaline fusion method yielded an

Table 2. The effects of acid type and their mixtures on the dissolution of aluminium from metakaolin (50°C, 6 h, 150 rpm, total acid concentration 50 g/L, pulp density 20%, pH 0.5). Standard deviations are also indicated for the percentage dissolution.

Acid	Ratio	Al dissolution	
		g/L	% ± SD
Citric	-	2.11	12.6 ± 0.2
Oxalic	-	2.41	14.4 ± 0.2
Lactic	-	1.93	11.5 ± 0.2
Citric-oxalic	1:1	2.22	13.3 ± 0.2
Citric-oxalic	1:2	2.39	14.3 ± 0.2
Citric-oxalic	2:1	2.18	13.0 ± 0.2
Citric-oxalic	1:3	2.33	13.9 ± 0.2
Citric-oxalic	3:1	2.22	13.3 ± 0.2
Lactic-oxalic	1:1	2.31	13.8 ± 0.2
Lactic-oxalic	1:2	2.44	14.6 ± 0.2
Lactic-oxalic	2:1	2.19	13.1 ± 0.2
Lactic-oxalic	1:3	2.49	14.9 ± 0.2
Lactic-oxalic	3:1	2.22	13.3 ± 0.2
Citric-lactic	1:1	2.23	13.3 ± 0.2
Citric-lactic	1:2	2.09	12.5 ± 0.2
Citric-lactic	2:1	2.18	13.0 ± 0.2
Citric-lactic	1:3	2.16	12.9 ± 0.2
Citric-lactic	3:1	2.25	13.4 ± 0.2
Citric-oxalic	1:4	2.43	14.5 ± 0.2
Lactic-oxalic	1:4	2.50	14.9 ± 0.2

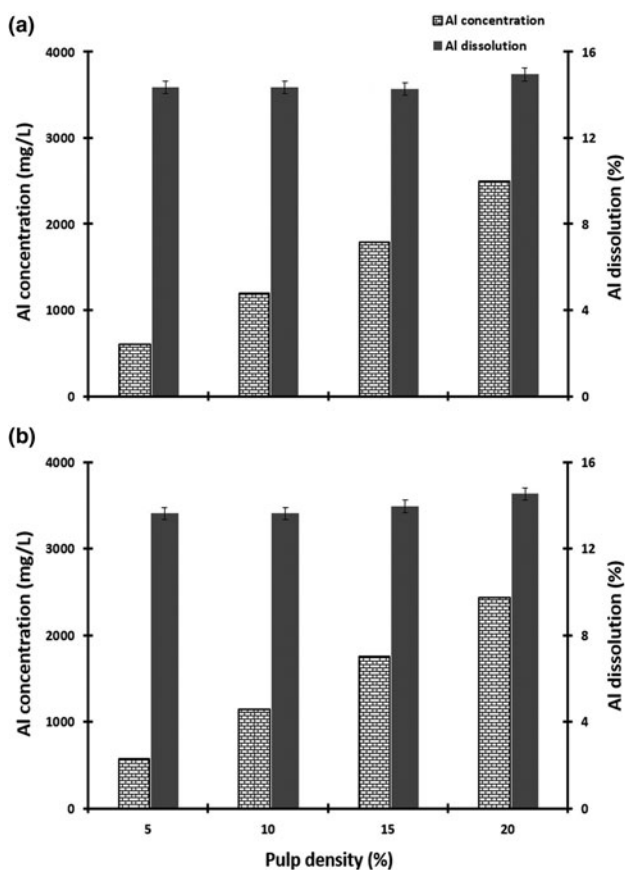


Fig. 3. The effect of pulp density on the dissolution of aluminium from metakaolin (50°C, 6 h, 150 rpm, total acid concentration 50 g/L). (a) Lactic-oxalic acid mixture and (b) citric-oxalic acid mixture at 1:4 ratios, pH 0.5.

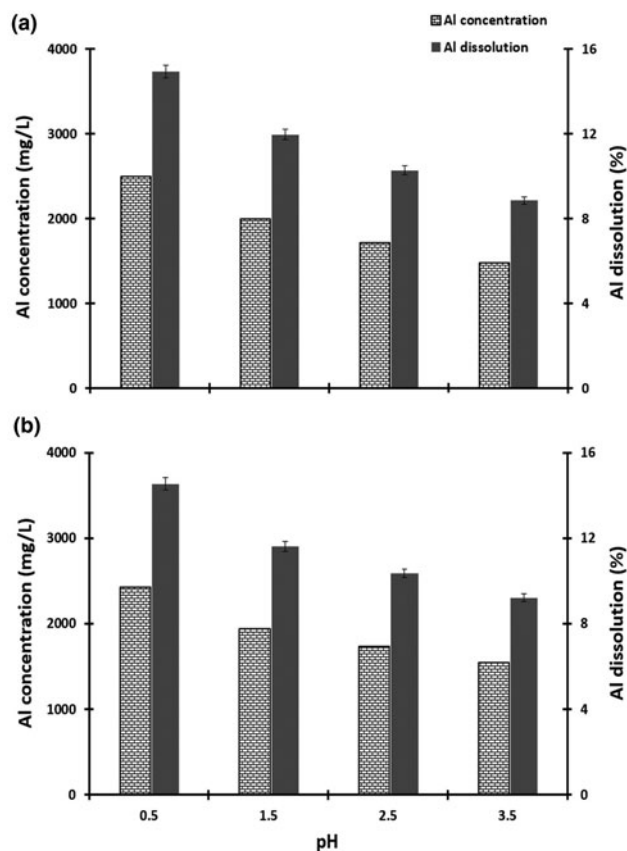


Fig. 4. The effect of pH on the dissolution of aluminium from metakaolin (50°C, 6 h, 150 rpm, concentration of acid 50 g/L). (a) Lactic-oxalic acid mixture and (b) citric-oxalic acid mixture at 1:4 ratios and 20% pulp density.

aluminium content of 12.5%, and this value was used in subsequent calculations.

Semi-quantitative X-ray diffraction (XRD) was used to identify the mineralogical composition of the sample. The XRD traces were obtained using a Siemens D-8 Advance diffractometer with Ni-filtered Cu-K α radiation, a goniometer speed of 1°2 θ /min and a scan step of 0.01°2 θ from 10 to 70°2 θ . Quartz (SiO₂), kaolinite (Al₂Si₂O₅(OH)₄), goethite (FeO(OH)) and calcite (CaCO₃) were the major phases of the original untreated sample. After calcination at 750°C for 2 h, the kaolinite peaks disappeared in the metakaolin sample. Figure 2 presents the result of the XRD analysis of the kaolin and metakaolin samples.

The morphology and elemental composition of gold-coated samples were examined with a scanning electron microscope (SEM; Philips XL30) equipped with an energy-dispersive spectrometer (EDAX).

Leaching tests and kinetic studies

The chemical leaching tests were performed by adding 20 g of the metakaolin sample to 100 mL of acid solution, which contained 50 g citric, oxalic or lactic acid/L (or their binary mixtures) in 250 mL conical flasks. The initial pH of 0.5 was adjusted with sulfuric acid (96–98% H₂SO₄). The reaction temperature, stirring speed and reaction time were 50°C, 150 rpm and 6 h, respectively. The leaching solution was removed by filtration and the solids were washed with 50 mL of deionized water before elemental analysis.

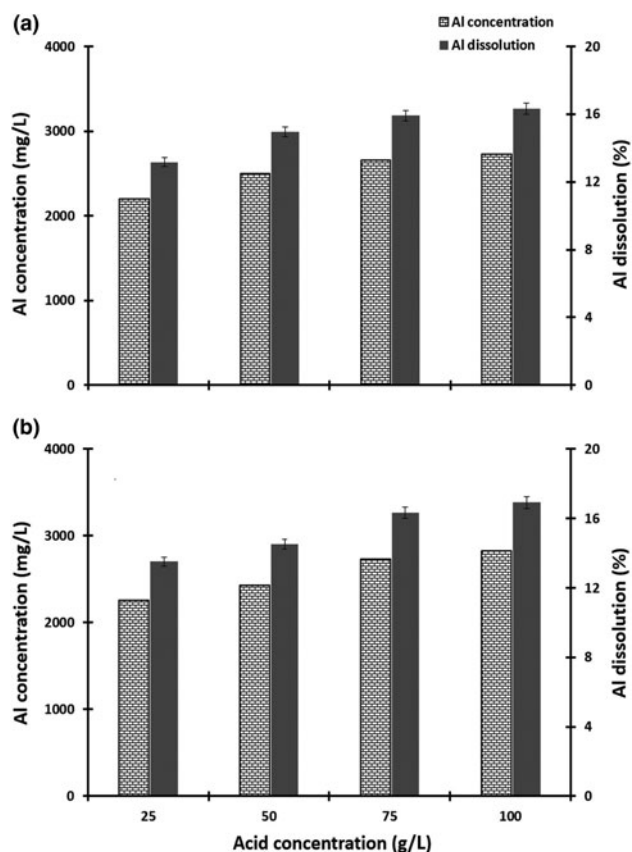


Fig. 5. The effect of acid concentration on the dissolution of aluminium from meta-kaolin (50°C, 6 h, 150 rpm, pH 0.5). (a) Lactic-oxalic acid mixture and (b) citric-oxalic acid mixture at 1:4 ratios.

Initially, aluminium dissolution from meta-kaolin was tested with citric, oxalic and lactic acid and their binary (citric-oxalic acid and lactic-oxalic acid) mixtures. The pulp density for further experiments was selected based on the greatest extent of aluminium dissolution. The initial pH values and acid concentrations were also tested for aluminium dissolution, followed by the agitation speed and the reaction temperature. These series of tests were carried out in 500 mL Erlenmeyer flasks with 200 mL of leach solution on a magnetic heater stirrer. Sample aliquots (2 mL) were taken at intervals for analysis of dissolved Al. All chemicals were of analytical grade, and deionized water was used to prepare the test solutions. The experiments were repeated twice and the average results are reported. Loss of volume due to evaporation was compensated for by adding deionized water. Deionized water was first heated up to the reaction temperature and then, after adjusting the pH, was added to the reaction vessel. Sample volumes were replaced with fresh leaching solution and this dilution was taken into account in the results.

In total, eight parameters (type and concentration of organic acid and binary ratios, pulp density, pH, agitation speed, temperature and contact time) were evaluated using the 'one factor at the time' methodology.

Results and discussion

Effect of acid type and their binary combinations

The results of the chemical leaching tests to determine the effects of the acid type (citric, oxalic and lactic acid) and their binary ratios

Table 3. The effect of stirring speed on aluminium dissolution from meta-kaolin (50°C, 6 h, pH 0.5, pulp density 20%, lactic-oxalic acid and citric-oxalic acid mixture at 1:4 ratio, total acid concentration 100 g/L). Standard deviations are also indicated for the percentage dissolution.

Acid type	Agitation speed (rpm)	Al dissolution	
		g/L	% ± SD
Lactic-oxalic	150	2.73	16.3 ± 0.2
Lactic-oxalic	250	3.40	20.3 ± 0.2
Lactic-oxalic	450	3.41	20.4 ± 0.2
Lactic-oxalic	600	3.19	19.1 ± 0.2
Citric-oxalic	150	2.83	16.9 ± 0.2
Citric-oxalic	250	4.21	25.2 ± 0.2
Citric-oxalic	450	3.30	19.7 ± 0.2
Citric-oxalic	600	3.25	19.4 ± 0.2

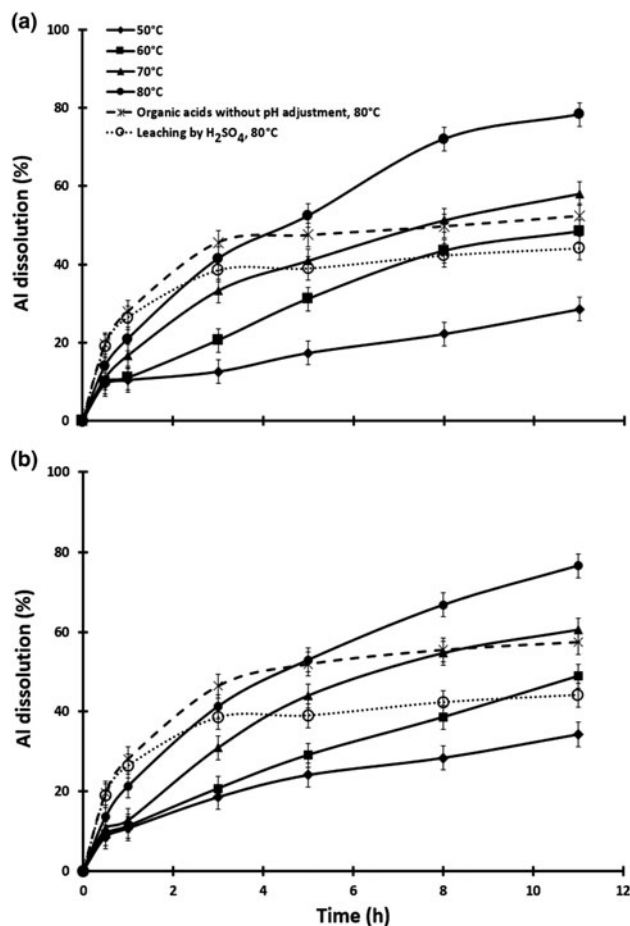


Fig. 6. The time course of aluminium dissolution in the temperature range of 50–80°C. (a) Lactic-oxalic acid 1:4 mixture and (b) citric-oxalic acid 1:4 mixture.

on aluminium recovery are listed in Table 2. The aluminium dissolution rates with respect to various ligands were in the following order: oxalic acid > citric acid > lactic acid. Oxalic acid had the highest level of aluminium dissolution among the acids, in accordance with previous studies (Zinder *et al.*, 1986; Chin & Mills, 1991). The binary 1:4 ratios of citric-oxalic and lactic-oxalic acids yielded the greatest extent of aluminium dissolution, reaching 2.43 g and 2.50 g Al/L and leaching yields of 14.5% and 14.9%, respectively. These binary 1:4 ratios of citric-oxalic and lactic-oxalic acids were used in the remainder of the leaching tests.

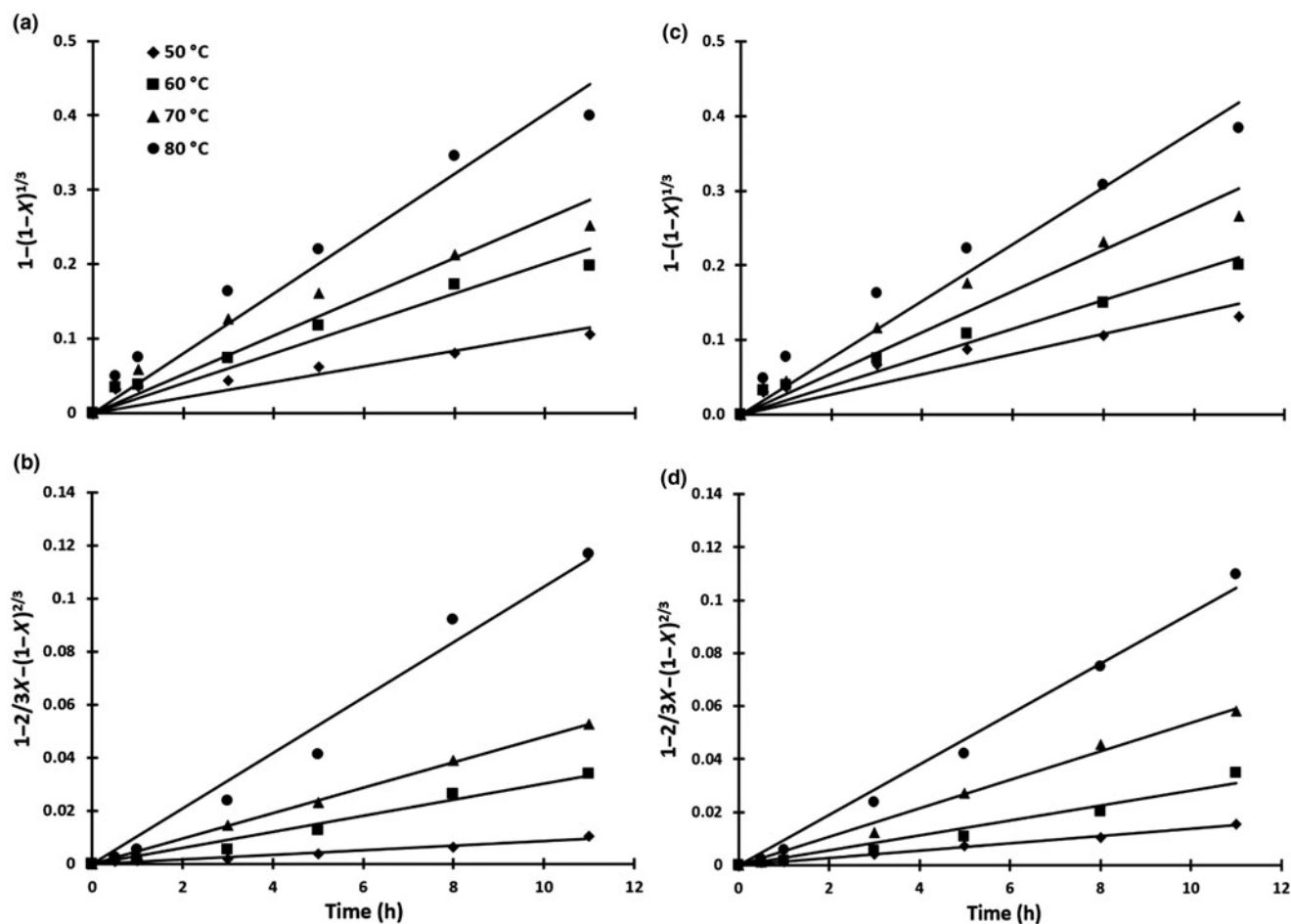


Fig. 7. Kinetic modelling of (chemical control and diffusion control) aluminium leaching from metakaolin at temperatures of 50–80°C. (a,b) Lactic-oxalic acid mixtures and (c,d) citric-oxalic acid mixtures at 1:4 ratios.

Table 4. The rate constants (*k*) and coefficients of determination for aluminium dissolution at various temperatures. The data were calculated from Fig. 7.

Temperature (°C)	Lactic-oxalic (1:4)				Citric-oxalic (1:4)			
	Diffusion		Chemical		Diffusion		Chemical	
	<i>k</i>	R ²	<i>k</i>	R ²	<i>k</i>	R ²	<i>k</i>	R ²
50	0.0104	0.96	0.0009	0.76	0.0014	0.99	0.0135	0.80
60	0.0200	0.97	0.0030	0.93	0.0028	0.95	0.0192	0.95
70	0.0260	0.99	0.0048	0.88	0.0054	0.98	0.0276	0.92
80	0.0401	0.97	0.0105	0.95	0.0095	0.99	0.0380	0.94

Effect of pulp density

Pulp densities were tested at 5%, 10%, 15% and 20% concentrations. The results are shown in Fig. 3. The dissolution of aluminium increased slightly with pulp density. The greatest Al-leaching yields were 14.9% and 14.5% obtained with lactic-oxalic and citric-oxalic acid mixtures and 20% pulp density (Fig. 3).

Effect of pH

The effect of pH over the range 0.5–3.5 was tested in suspensions with 20% pulp density. Sulfuric acid and Na-hydroxide were used

for pH adjustments. The results are shown in Fig. 4. Aluminium dissolution decreased with increasing pH. The greatest Al-leaching yields of 14.9% with the lactic-oxalic acid mixture and 14.5% with the citric-oxalic acid mixture were obtained at pH 0.5 (Fig. 4).

Effect of organic acid concentration

The effect of organic acid on Al dissolution was tested at concentrations of 25, 50, 75 and 100 g/L. The results are presented in Fig. 5. Aluminium dissolution increased with acid concentration. In the presence of organic ligands, the rates of Al dissolution were markedly increased, and this increase was directly related to ligand concentration (Chin & Mills, 1991; Cama & Ganor, 2006). The greatest extent of Al dissolutions of 2.73 g/L with the lactic-oxalic acid mixture and 2.83 g/L with the citric-oxalic acid mixture were obtained with an acid concentration of 100 g/L, corresponding to the respective Al-leaching yields of 16.3% and 16.9% (Fig. 5).

Effect of stirring speed

The effect of stirring speed on Al dissolution from metakaolin was tested at 150, 250 and 600 rpm. The results are presented in Table 3. The dissolution rate increased with the agitation speed,

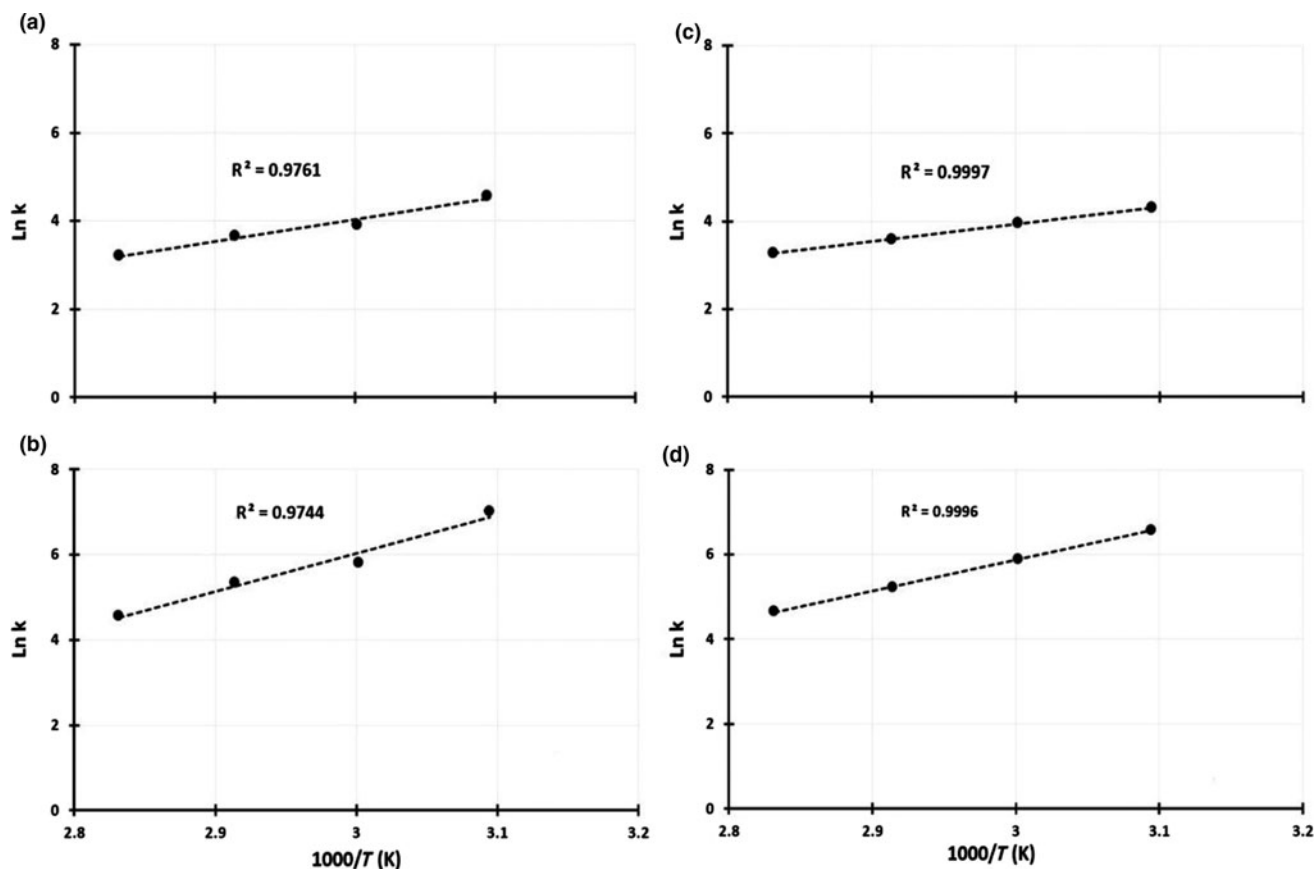


Fig. 8. Arrhenius plots of aluminium dissolution from metakaolin at 50–80°C (323–353 K). Lactic-oxalic acid (1:4) mixtures: (a) chemical reaction control model; (b) diffusion control model. Citric-oxalic acid (1:4) mixtures: (c) chemical reaction control model; (d) diffusion control model.

probably due to the decrease in the thickness of the metakaolin film layer or the formation of fine particles as a result of disaggregation or abrasion of metakaolin. These fine particles have a large ratio of reactive surface area to specific surface area and therefore the dissolution rate increased with stirring (Metz & Ganor, 2001; Ajemba & Onukwuli, 2012). Aluminium dissolution decreased across the stirring speed range of 250–600 rpm. High agitation speed may cause turbulence, forcing the fluid to rotate like a cyclone and thereby reducing the contact or residence time of the elements. Maximum Al dissolution was obtained at 250 rpm.

Effects of temperature and contact time

The effect of temperature was tested at 50, 60, 70 and 80°C. To reduce evaporation, experiments were carried out with 200 mL of solution and the pulp density (20%) was kept constant. Sulfuric acid was used to adjust the pH to 0.5. The results are presented in Fig. 6. After 11 h of contact time with the citric-oxalic acid mixture, the greatest Al-leaching yields increased from 34.3% at 50°C to 76.6% at 80°C. The Al-leaching yields with the lactic-oxalic acid mixture increased from 54.3% at 50°C to 78.3% at 80°C. Kaolinite dissolution is mainly affected by the alkali-leaching temperature, alkali concentration and alkali-leaching time (Aldabsheh *et al.*, 2015; Wang *et al.*, 2016). These parameters are also effective in acid leaching. The dissolution of Al increased with these parameters in the acid leaching of metakaolin.

In general, in the series of initial and optimization tests (except for those at 50°C and 50 g/L acid concentration), the initial pH of the solutions was ~0.7 on average. The amount of additional sulfuric acid for pH adjustment was very small and had no discernible effect on the dissolution rate of aluminium. After investigating the effect of acid concentration on the dissolution of aluminium and selecting a concentration of 100 g/L, the initial pH of the solution was ~0.5 and the amount of additional sulfuric acid used to adjust the pH during the leaching tests was negligible. In the final set of tests on the temperature effect, the pH increased and therefore sulfuric acid was titrated in order to adjust the pH during the contact time. Aliquots of 3, 6 and 7 mL of sulfuric acid were used to adjust the pH at 60, 70 and 80°C, respectively. Due to the considerable amount of additional sulfuric acid used in tests with a temperature of 80°C, this temperature was selected for two additional experiments in order to evaluate the effect of additional sulfuric acid on aluminium dissolution (Fig. 6). One test was performed with organic acids without the pH adjustment and the second was carried out with pH adjustment with sulfuric acid. The effect of additional sulfuric acid was lower at the other temperatures.

The concentration of sulfuric acid was the same as that used for pH adjustment. The combination of organic acids and sulfuric acid yielded maximum Al recovery. Organic acids without pH adjustment (*i.e.* no sulfuric acid) achieved the greatest extent of dissolution in the first 3 h, but the greatest overall aluminium dissolution was obtained with organic acids and pH adjustment with sulfuric acid to pH 0.5.

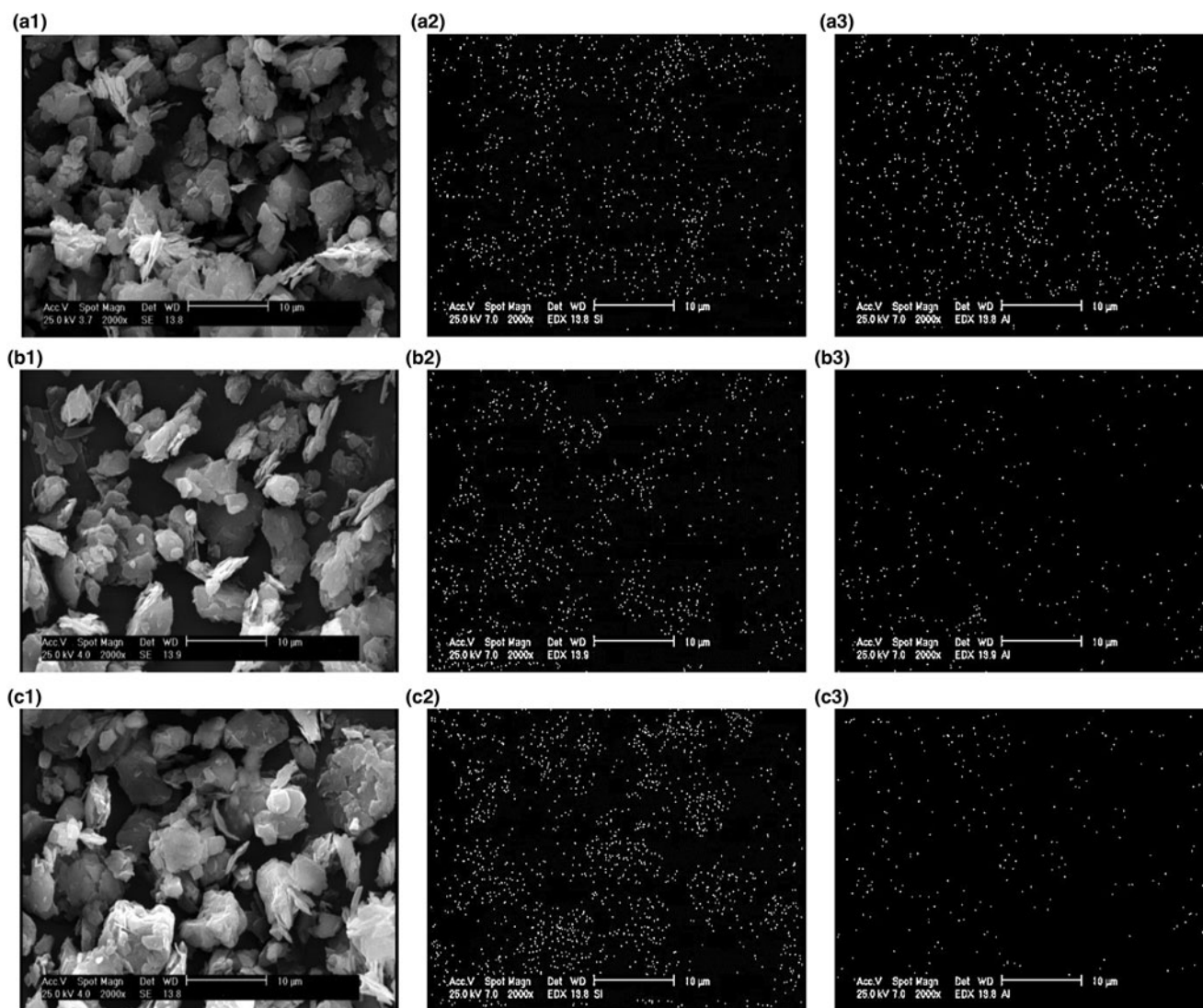


Fig. 9. SEM images and the corresponding EDAX mapping of Si and Al of (a) untreated metakaolin and residual solids from the leaching of the metakaolin sample with (b) the citric-oxalic acid (1:4) mixture and (c) the lactic-oxalic acid (1:4) mixture.

Kinetic study

Previous kinetic studies have mostly tested inorganic acids such as sulfuric acid and hydrochloric acids, but not organic acids. There is little to no general agreement on the dissolution mechanism and reaction kinetics for describing the dissolution of Al from metakaolin. Altıokka & Hoşgün (2003) and Lima *et al.* (2014, 2017) studied the application of the shrinking core model to spherical particles with a constant size. The dissolution was a chemically controlled process. However, Olsen *et al.* (1983) reported that the leaching of metakaolin in boiling HCl solution was a zero-order reaction with diffusion control. The results of the present study indicate that the dissolution was under chemical-reaction control because of the high values of the activation energy and the response of the reaction to temperature. A comparison of the activation energy obtained from the dissolution by organic acids with previous studies shows that the activation energy of organic acids was less than that with inorganic acids.

The reaction model is dependent on the particle size, which does not change upon leaching and calcination. The shrinking core model was applied in order to describe the leaching of spherical and flat particles with constant size (Gharabaghi *et al.*, 2009; Lima & Angélica, 2014). According to this model, the rate of the leaching is controlled by diffusion or a chemical reaction. Simplified equations of the shrinking core model for spherical particles with constant size are expressed as follows (Levenspiel, 1972; Souza *et al.*, 2007; Lima & Angélica, 2014).

$$kt = 1 - (1 - x)^{1/3} \quad (3)$$

$$kt = 1 - \frac{2}{3}x - (1 - x)^{2/3} \quad (4)$$

where x is the reacted fraction, k is the rate constant and t is the reaction time; Eq. (3) is the chemical control model and Eq. (4) is the diffusion control model.

Application of the kinetic models of surface chemical reaction and diffusion control is shown in Fig. 7 for specific ranges of particle size and acid concentration at 20% pulp density. The rate constants (k) and coefficients of determination (R^2) for the various temperatures are given in Table 4.

In the Arrhenius equation, $k = k_0 \exp(-E_a/RT)$, a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $-E_a/RT$ and an intercept of $\ln k_0$. Activation energy (E_a) values were calculated using the chemical and diffusion-control models (Fig. 8). The data fit better in the diffusion control model. Thus, the dissolution rate of aluminium from metakaolin is subject to diffusion control with activation energy values $E_{a(\text{lactic-oxalic})} = 74.6$ kJ/mol and $E_{a(\text{citric-oxalic})} = 57.8$ kJ/mol.

Although the diffusion model provided a better fit, the E_a values are high for diffusion control and are within the range of chemical control reactions. In general, the activation energy for diffusion control is <20 kJ/mol and is >40 kJ/mol for chemical reaction control (Habashi, 1999; Safarzadeh *et al.*, 2009; Uçar, 2009). The diffusion-control process depends only slightly on temperature, whereas the chemical control process is highly dependent on temperature. The activation energy values for the chemical control model (Fig. 8) are $E_{a(\text{lactic-oxalic})} = 41.0$ kJ/mol and $E_{a(\text{citric-oxalic})} = 32.9$ kJ/mol. These activation energy values suggest that both diffusion control and chemical control were effective at the leaching of aluminium from metakaolin.

SEM and EDAX analysis

The results of SEM and the corresponding EDAX mapping of Si and Al of untreated kaolin and residual solids from the leaching of metakaolin by organic acids in binary systems are presented in Fig. 9. Some particles were flat and some were rounded and spherical. The surfaces of the particles in the original sample were nearly smooth and even. After contact with organic acids, the particles showed a more robust, even eroded surface. The amount of Al in the solids after the leaching process was clearly reduced. In contrast, the elemental maps of Si before and after the leaching treatment were comparable.

Conclusion

Oxalic acid dissolved more Al from metakaolin than citric and lactic acids. The dissolution increased with the binary combination of oxalic acid with two other acids at w/w ratios of 1:4 (lactic or citric acid to oxalic acid). Aluminium dissolution was pH and temperature dependent. Pulp density of up to 20% did not increase Al dissolution significantly. The dissolution increased with agitation speed up to 250 rpm and then decreased. The optimal combination of the experimental parameters was: total acid concentration = 100 g/L, pulp density = 20%, pH = 0.5, stirring speed = 250 rpm and temperature = 80°C. Under these conditions, Al dissolution reached 78% and 77% with the lactic-oxalic and citric-oxalic acid mixtures, respectively. In the corresponding control test using only sulfuric acid, aluminium dissolution was 44%. The activation energy values and the temperature dependency indicated that the dissolution was under chemical reaction control, although diffusion also seemed to contribute to the overall kinetic control.

Author ORCIDs.  Hadi Abdollahi, 0000-0002-9099-7451.

Acknowledgements. The authors acknowledge with thanks the University of Tehran for financial support. The authors are also thankful to Mr Ali Rezaei for technical assistance.

References

- Aghaie E., Pazouki M., Hosseini M.R., Ranjbar M. & Ghavipankeh F. (2009) Response surface methodology (RSM) analysis of organic acid production for kaolin beneficiation by *Aspergillus niger*. *Chemical Engineering Journal*, **147**, 245–251.
- Ajemba R.O. & Onukwuli O.D. (2012) Application of the shrinking core model to the analysis of alumina leaching from Ukpok clay using nitric acid. *International Journal of Engineering*, **1**, 1–13.
- Aldabsheh I., Khoury H., Wastiels J. & Rahier H. (2015) Dissolution behavior of Jordanian clay-rich materials in alkaline solutions for alkali activation purpose. Part I. *Applied Clay Science*, **115**, 238–247.
- Altokka M.R. & Hoşgün H.L. (2003) Investigation of the dissolution kinetics of kaolin in HCl solution. *Hydrometallurgy*, **68**, 77–81.
- Bauer A. & Berger G. (1998) Kaolinite and smectite dissolution rate in high molar KOH solutions at 35° and 80°C. *Applied Geochemistry*, **13**, 905–916.
- Bellotto M., Gualtieri A., Artioli G. & Clark S.M. (1995) Kinetic study of the kaolinite-mullite reaction sequence. Part I: Kaolinite dehydroxylation. *Physics and Chemistry of Minerals*, **22**, 207–217.
- Cama J. & Ganor J. (2006) The effects of organic acids on the dissolution of silicate minerals: a case study of oxalate catalysis of kaolinite dissolution. *Geochimica et Cosmochimica Acta*, **70**, 2191–2209.
- Cama J. & Ganor J. (2015) Dissolution kinetics of clay minerals. *Developments in Clay Science*, **6**, 101–153.
- Chin P.K.F. & Mills G.L. (1991) Kinetics and mechanisms of kaolinite dissolution: effects of organic ligands. *Chemical Geology*, **90**, 307–317.
- Cuadros J. (2017) Clay minerals interaction with microorganisms: a review. *Clay Minerals*, **52**, 235–262.
- Ganor J. & Lasaga A.C. (1994) The effects of oxalic acid on kaolinite dissolution rate. *Mineralogical Magazine*, **58**, 315–316.
- Gharabaghi M., Noaparast M. & Irannejad M. (2009) Selective leaching kinetics of low-grade calcareous phosphate ore in acetic acid. *Hydrometallurgy*, **95**, 341–345.
- Groudev S.N. & Groudeva V.I. (1986) Biological leaching of aluminum from clays. *Biotechnology and Bioengineering Symposium*, **16**, 91–99.
- Habashi F. (1999) *Kinetics of Metallurgical Processes*. Métallurgie Extractive Québec, Québec, QC, Canada.
- Hosseini S.A., Niaei A. & Salari D. (2011) Production of $\gamma\text{-Al}_2\text{O}_3$ from kaolin. *Open Journal of Physical Chemistry*, **1**, 23–25.
- Hulbert S.F. & Huff D.E. (1970) Kinetics of alumina removal from a calcined kaolin with nitric, sulphuric and hydrochloric acids. *Clay Minerals*, **8**, 337–345.
- Levenspiel O. (1972) *Chemical Reaction Engineering*. Wiley, New York, NY, USA.
- Lima P.E.A., Angélica R.S. & Neves R.F. (2014) Dissolution kinetics of metakaolin in sulfuric acid: comparison between heterogeneous and homogeneous reaction methods. *Applied Clay Science*, **88**, 159–162.
- Lima P.E., Angélica R.S. & Neves R.F. (2017) Dissolution kinetics of Amazonian metakaolin in hydrochloric acid. *Clay Minerals*, **52**, 75–82.
- Metz V. & Ganor J. (2001) Stirring effect on kaolinite dissolution rate. *Geochimica et Cosmochimica Acta*, **65**, 3475–3490.
- Olsen R.S. (1983) *Leaching Rates for the HCl Extraction of Aluminum from Calcined Kaolinitic Clay. Report of Investigations 8744*. Bureau of Mines, US Department of the Interior, Washington, DC, USA.
- Phipps J.S. (2014) Engineering minerals for performance applications: an industrial perspective. *Clay Minerals*, **49**, 1–16.
- Pohl W. (2011) *Economic Geology: Principles and Practice: Metals, Minerals, Coal and Hydrocarbons – Introduction to Formation and Sustainable Exploitation of Mineral Deposits*. Wiley-Blackwell, Chichester, UK.
- Safarzadeh M.S., Moradkhani D. & Ojaghi-Ilkchi M. (2009) Kinetics of sulfuric acid leaching of cadmium from Cd-Ni zinc plant residues. *Journal of Hazardous Materials*, **163**, 880–890.

- Souza A.D., Pina P.S., Lima E.V.O., da Silva C.A. & Leão V.A. (2007) Kinetics of sulphuric acid leaching of a zinc silicate calcine. *Hydrometallurgy*, **89**, 337–345.
- Tang A., Su L., Li C. & Wei W. (2010) Effect of mechanical activation on acid-leaching of kaolin residue. *Applied Clay Science*, **48**, 296–299.
- Uçar G. (2009) Kinetics of sphalerite dissolution by sodium chlorate in hydrochloric acid. *Hydrometallurgy*, **95**, 39–43.
- Wang H., Feng Q. & Liu K. (2016) The dissolution behavior and mechanism of kaolinite in alkali-acid leaching process. *Applied Clay Science*, **132**, 273–280.
- Wang X., Li Q., Hu H., Zhang T. & Zhou Y. (2005) Dissolution of kaolinite induced by citric, oxalic, and malic acids. *Journal of Colloid and Interface Science*, **290**, 481–488.
- Zhao J., Gao W., Tao Z.-G., Guo H.-Y. & He M.-C. (2018) Investigation, using density function theory, of coverage of the kaolinite (001) surface during hydrogen adsorption. *Clay Minerals*, **53**, 393–402.
- Zinder B., Furrer G. & Stumm W. (1986) The coordination chemistry of weathering: II. Dissolution of Fe(III) oxides. *Geochimica et Cosmochimica Acta*, **50**, 1861–1869.