

REMOVAL OF Fe FROM KAOLIN BY CHEMICAL LEACHING AND BIOLEACHING

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Abstract—The use of microorganisms to remove Fe (oxyhydr)oxides from kaolins has the potential to be an effective method for upgrading the whiteness and brightness, and therefore the commercial value, of the kaolin. The purpose of the present study was to compare kaolin products obtained by currently used chemical leaching methods with a bioleaching treatment using *Aspergillus niger* in order to remove Fe from kaolin (from Canakkale, Turkey). The effects of pulp density, temperature, and oxalic acid concentration on the chemical leaching experiments were investigated using the ANOVA-Yates test. The greatest degree of removal of Fe from the kaolin sample (at 15% w/v pulp density, temperature of 80°C, oxalic acid concentration of 0.2 M, and a particle size of <63 μm) was found to be 94.89% in 120 min of leaching. The Fe content decreased from 1.723% Fe₂O₃ to 0.088% Fe₂O₃. In a shake flask, bioleaching of kaolin by *Aspergillus niger* resulted in removal of 77.13% of the total Fe, suggesting that this strain is effective at removing Fe impurities from kaolin. The removal efficiency generally decreased with increased pulp density. The Fe content of the kaolin decreased from 1.723% Fe₂O₃ to 0.394% Fe₂O₃ (at 1% w/v pulp density, temperature of 25°C, *Aspergillus niger* 3 × 10⁷ spores, and particle size of <63 μm) after 21 days of bioleaching.

Key Words—*Aspergillus niger*, Bioleaching, Chemical Leaching, Kaolin, Yates' Technique.

INTRODUCTION

Kaolin (Al₂O₃·2SiO₂·2H₂O) is essential in the manufacture of porcelain and ceramic goods, and in the production of paper, pigments, and fillers. Fe hydroxides (usually Fe³⁺ forms) are commonly precipitated or adsorbed on the kaolin surfaces or admixed as a separate phase rendering much of the kaolin unusable for commercial application due to insufficient whiteness or loss of some refractory properties (Avgustinik, 1983; Murad, 1987; Štyriaková and Štyriak, 2000). Raw kaolin is usually associated with various impurities including quartz, anatase, rutile, pyrite, siderite, feldspar, mica, etc., depending on the origin and depositional environment (Grimshaw, 1971).

The refinement of low-grade clay is a viable and necessary alternative resource to high-grade clay. Various physical and chemical (and recently microbiological) techniques have been developed with the purpose of removing the ferric Fe present as oxide or hydrated oxide in the clay. The techniques generally include magnetic separation, froth flotation, selective flocculation, size separation by hydrocyclones, and chemical leaching (Lee *et al.*, 2002). Separating all of the Fe from kaolin by any of these methods, however, has yet to be achieved. Fe-reducing microorganisms can be used effectively for the refinement of kaolins (Kostka *et al.*, 1999). Chemical methods, currently the most

commonly used, use strong reducing agents (*e.g.* sodium dithionite) at low pH, to remove the majority of the Fe and leave very white kaolin. Such methods have drawbacks, however: they involve extreme working conditions and are expensive (Conley and Lloyd, 1970). An alternative to the classical chemical methods is the use of organic acids, produced by fermentation with filamentous fungi such as *Aspergillus* and *Penicillium*, using residues with large organic carbon contents as substrates (whey, molasses, etc.) (Cleland and Johnson, 1955; Strasser *et al.*, 1994). The ability of heterotrophic microorganisms to dissolve metals from solid materials could be useful for improving the quality of mineral raw materials, such as kaolins, clays, and sands (Groudev, 1987; Barker *et al.*, 1998).

One of the most effective techniques for studying process behavior is the factorial-design test with analysis of variance (ANOVA) from which information can be utilized for optimization purposes. Statistical design is an important tool in understanding process behavior. The statistical-design concept has been used successfully in leaching studies (Cochran and Cox, 1957; Daniel, 1976; Box *et al.*, 1978; Davis, 1978; Veglio *et al.*, 1993; Datta *et al.*, 1995).

The purpose of the present work was to compare chemical leaching and biological leaching methods for removal of Fe from kaolin. In the chemical-leaching tests, using the ANOVA-Yates test technique, the effects of pulp density, temperature, and oxalic acid concentration on the chemical leaching experiments were investigated. In the biological leaching tests, the ability of *Aspergillus niger* to remove Fe hydroxides from a

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Table 1. Chemical composition (wt.%) of kaolin before treatment and after leaching.

Sample	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	P ₂ O ₅	SiO ₂	TiO ₂
Untreated	18.06	0.231	1.723	0.207	0.221	77.11	0.578
Bioleached	18.54	0	0.394	0.211	0.254	71.23	0.398
Chemically leached	23.65	0	0.088	0.218	0.281	70.08	0.214

contaminated kaolin, and the influence of pulp density on the removal efficiency were studied.

MATERIALS AND METHODS

Kaolin sample

The kaolin sample was obtained from Kale Mining Company, Canakkale (Dardanelles), Turkey. The particle-size distribution of the sample was measured by laser radiation scattering on a Laser-Particle-Sizer (Malvern Mastersizer 2000). The main particle diameter, d_m , ($d_{90} = 43.37 \mu\text{m}$) was calculated from granulometric data. The kaolin sample consisted of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and quartz (SiO_2). Iron was present as magnetite (Fe_3O_4) and as amorphous oxides and oxyhydroxides with various compositions (Table 1). The sample was identified using scanning electron microscopy (Figure 1). Before analysis, all samples were coated with carbon and subsequently examined in a Tesla BS 340 scanning electron microscope. The samples were analyzed by X-ray diffraction (XRD) using a Philips X-Pert SW-binary diffractometer with $\text{CuK}\alpha$ radiation (40 kV, 50 mA), equipped with an automatic divergence slit, sample spinner, and a diffracted-beam graphite monochromator (Figure 2). The whiteness index was determined by light reflection at 457 nm (Keet C-100) (Hui and Wei, 1993; Gou *et al.*, 1993).

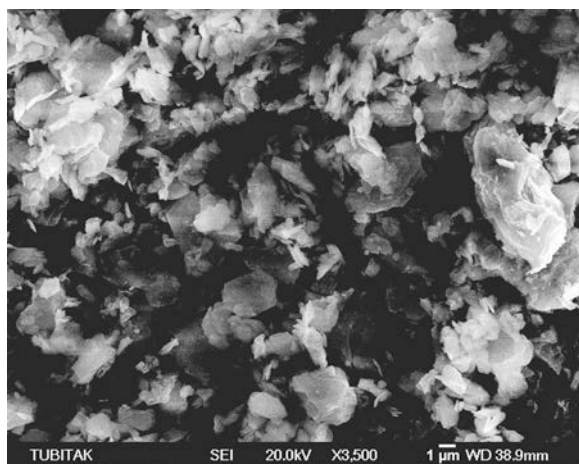


Figure 1. SEM image of the kaolin.

Microorganism and culture media

The microorganism used in this study was a strain of *Aspergillus niger* provided by the Department of Biology, Cukurova University, Adana, Turkey. The medium utilized for growth of the culture was based on the method of Bosshard *et al.* (1996) in which a culture was inoculated on a potato dextrose agar (3.9% (w/v)). In order to obtain sufficient numbers of spores, the culture was kept in this medium at 26°C for 7 days. Afterward, the spores were recovered using 0.2% (w/v) sodium dodecyl sulfate. The spores were counted using a Petroff-Hausser counting chamber where 1 mL of spores ($\sim 3 \times 10^7$ spores) was obtained. The spores were then added to a 250 mL flask containing 150 mL of prepared medium.

A synthetic medium containing sucrose, 120 g/L; NH_4NO_3 , 450 mg/L; KH_2PO_4 , 100 mg/L; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 300 mg/L; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 mg/L; and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.25 mg/L was employed as the culture medium in all experiments. The pH of the medium was adjusted to 7.0 with 0.1 M NaOH solution (Cameselle *et al.*, 2003).

Determination of organic acids produced by *Aspergillus niger*

The concentrations of citric and oxalic acids were determined in the test solutions by a Shimadzu Prominence model, high-performance liquid chromatograph (HPLC). Numerous other acids such as gluconic, tartaric, malic, and phytic were assayed but were not

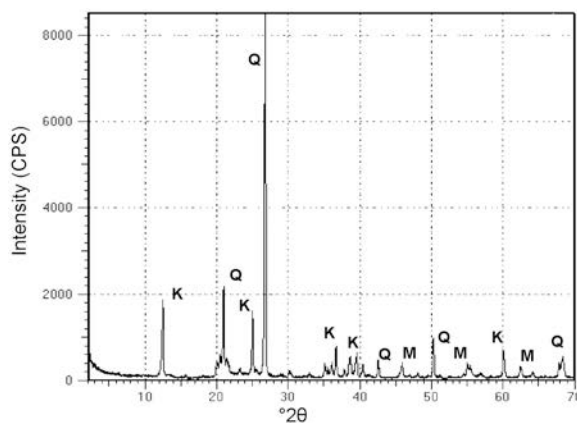


Figure 2. XRD pattern of the kaolin sample.

found in detectable amounts. The method included pump LC-20AT, atomic preventive SIL-20AC, column furnace SPD-M20A, communication bus module CTO-20AC, and a HPLC column prodigy 5 μm ODS(2) (150 mm × 4.60 mm) at a flow rate of 0.5 cm³ min⁻¹ (room temperature with a mobile phase of 50 mmol dm⁻³ mono-ammonium phosphate adjusted to pH 2.4 with phosphoric acid). The signal was monitored using a CBM-20A detector at 210 nm.

Chemical leaching experiments

Three concentrations of oxalic acid (0.2, 0.6, and 1 M) were stirred and heated (30, 55, and 80°C) in 250 mL flasks. When the solution reached the desired temperature, 5.26 g, 11.11 g, or 17.65 g of sample was added and stirred for 120 min. The rate of agitation was kept constant for all the experiments. A watch glass was fitted to the flask to minimize evaporation. After each experiment, the samples were filtered and the residue was washed with distilled water. The leach liquor was analyzed for Fe using atomic absorption spectroscopy (AAS) (PerkinElmer Model AS-800).

Bioleaching experiments

Bioleaching experiments were carried out in 250 mL flasks. Experimental samples at different pulp densities (corresponding to 1–8% w/v solids concentration) were added. The flasks were then autoclaved at 120°C for 20 min, after which each flask was inoculated under aseptic conditions with a 10 mL aliquot of the selected culture to produce a final slurry volume of ~150 mL. To facilitate mixing of the contents and transfer of O₂ and CO₂, the flasks were agitated at 150 rpm on an orbital shaker controlled at a growth temperature of 30±2°C for a period of 21 days. Each flask was sampled daily by removing a 1 mL aliquot of the leach solution, which was then used for analysis of Fe by AAS and to monitor the pH, redox potential, and temperature. In all experiments, chemical-grade reagents and distilled water were used, except in the chemical analysis where double distilled water was used. A control flask containing no microorganisms was used for each experiment and the analysis performed in duplicate. The results were reproducible within 5%.

Kinetics study

For the bioleaching treatment, a kinetic model was used, the equation for which is (Froment and Bischoff, 1979; Blancarte-Zurita *et al.*, 1987):

$$-dC_{Fe}/dt = k(C_{Fe-max} - C_{Fe}) \quad (1)$$

where C_{Fe} is the dissolved Fe concentration; k , the kinetic coefficient; and C_{Fe-max} , the maximum Fe concentration attainable. The C_{Fe} value can be limited by the bioleaching capacity or by the Fe available in the solid and by t , the bioleaching time. By integrating equation 1 between the initial state (where $t = 0$ and C_{Fe}

Table 2. Results of statistical analysis on response (Fe removal).

TC ^a	IR ^b (%)	Yates' analysis 1	Yates' analysis 2	Total effect (%)	[TE] ² /8	DF ^c	F (calculated)	F (table)	Decision	X ₁	X ₂	X ₃	Y (calculated)
1	0.088	0.168	0.325	0.479						-1	-1	-1	
A	0.080	0.157	0.154	-0.013	2.11 × 10⁻⁵	1	7.04	5.32	E^d	1	-1	-1	0.078
B	0.082	0.077	-0.015	-0.011	1.51 × 10 ⁻⁵	1	5.04	5.32	NE ^e	-1	-1	-1	0.085
AB	0.075	0.077	0.002	0.005	3.13 × 10 ⁻⁶	1	1.04	5.32	NE ^e	1	1	-1	0.078
C	0.039	-0.008	-0.011	-0.171	3.66 × 10⁻³	1	1218.40	5.32	E^d	-1	-1	1	0.038
AC	0.038	-0.007	0	0.017	3.61 × 10⁻⁵	1	12.04	5.32	E^d	1	-1	1	0.039
BC	0.037	-0.001	0.001	0.011	1.51 × 10 ⁻⁵	1	5.04	5.32	NE ^e	-1	1	1	0.038
ABC	0.040	0.003	0.004	0.003	1.13 × 10 ⁻⁶	1	0.375	5.32	NE ^e	1	1	1	0.039
Total	0.060												

^a TC: treatment combination (A – oxalic acid; B – pulp density; C – temperature); ^bIR: Fe removal; ^cDF: degree of freedom; ^dE: effective; ^eNE: ineffective.

Table 3. 2³ factorial designs for kaolin chemical leaching.

Variables	Low level (-)	Base level	High level (+)
Oxalic acid concentration (M)	0.2	0.6	1
Pulp density (w/v, %)	5	10	15
Temperature (°C)	30	55	80

= 0) and the state at time t , equation 2 is obtained, from which the value of the kinetic coefficient can be deduced:

$$\ln[C_{\text{Fe-max}}/(C_{\text{Fe-max}} - C_{\text{Fe}})] = kt \quad (2)$$

RESULTS AND DISCUSSION

Chemical leaching results

The success of oxalic acid leaching of kaolin depends on the selection of suitable parameters (concentration of the oxalic acid, pulp density, and temperature). The optimization of these parameters necessitates many tests. The Yates technique (Yates, 1976) for 2³ experiments was used for statistical design and analysis of the results. Combining the Yates technique with ANOVA (Table 2) simplifies the determination of significant differences. In the present study, treatment ABC is the experimental run in which the variables A (oxalic acid concentration), B (pulp density), and C (temperature) were set at their highest levels. The variables and levels of 2³ full factorial designs are presented in Table 3. The higher level was designated as '+' and lower level as '-'. The regression equation with interactive terms can be written as:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1X_2 + b_5X_1X_3 + b_6X_2X_3 + b_7X_1X_2X_3 \quad (3)$$

The model created for removal of Fe using the effects of variable significance at the 95% or greater confidence interval are given below:

$$Y = 0.195 - 0.0389X_2 - 0.1091X_3 + 0.0354X_2X_3 \quad (4)$$

$$R^2 = 0.968$$

The correlation coefficient, R^2 , is used to check the model's ability to predict the response (Fe removal) accurately. The empirical models were found to estimate accurately the response variable, as indicated by the R^2 value, which was 0.968. The residual analysis for removal of Fe is given in Figure 3.

The degree of removal of Fe from kaolin was determined to be 94.89% under optimum chemical-leaching conditions (temperature 80°C; oxalic acid concentration 0.2 M; pulp density 15% w/v; leaching time 120 min, and particle size of <63 μm). The Fe content in the kaolin sample was decreased from 1.723% Fe₂O₃ to 0.088% Fe₂O₃.

Bioleaching results

Aspergillus niger can segregate some organic acids depending on the medium composition and pH value. Production of oxalic acid can be improved by use of a culture medium rich in N and with a pH close to neutrality (Kubicek *et al.*, 1988; Cameselle *et al.*, 1998). During the bioleaching experiments, the initial pH was set to 5–5.5 for *Aspergillus niger* in order to minimize the detrimental effect of precipitation of Fe. Changes in pH with time (no change in the control samples) in the bioleaching experiments (Figure 4) revealed that the solution pH decreased rapidly over the first 6 days. The initial decrease in pH within the first 6 days could be attributed to solubilization of Fe. The decrease in pH continued until the 15th day of bioleaching after which the pH became stable. The solubilization of Fe slowed after 15 days. At the end of the bioleaching experiments (21st day), the pH of the solution was determined as 1.50 at 1% w/v pulp density. As suggested in Figure 4, if the pulp density increases, the rate of decrease of the pH also decreases. For the extraction of Fe, oxalic acid was five times more effective than citric acid, and is capable of complexing and removing Fe. In order to dissolve a mole of Fe, three equivalents of oxalic acid are required (Cameselle *et al.*, 1997; Mulligan *et al.*, 2004).

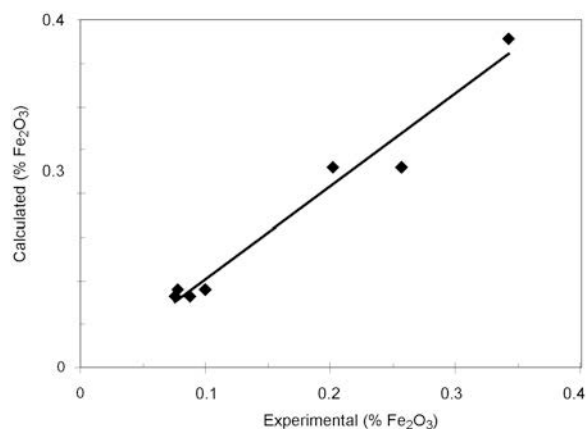
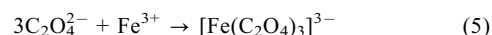


Figure 3. Residual analysis for removal of Fe.

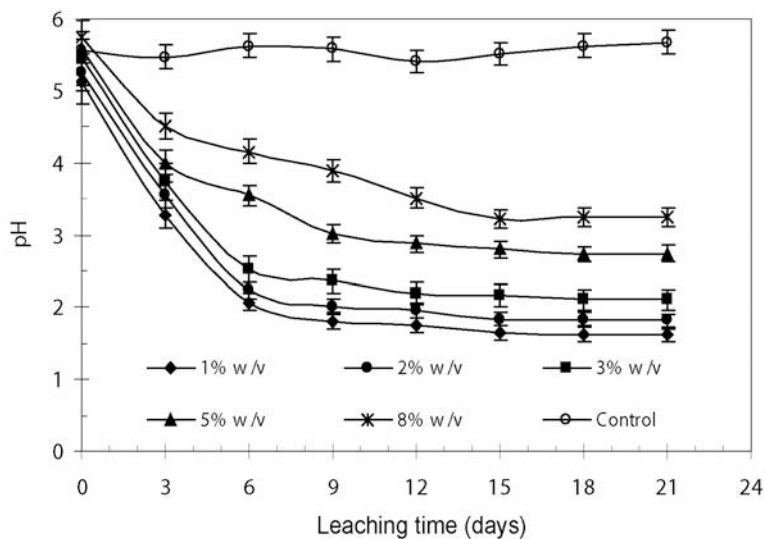


Figure 4. Evolution of pH during bioleaching experiments.

The final oxalic and citric acid concentrations of the experiments (Figure 5a,b) reveal, for those experiments in which the clay was added at the beginning of cultivation, that the average organic-acid concentrations were: oxalic acid – 15 g/L and citric acid – 3.25 g/L for 1% w/v pulp density. When the pulp density increases, the concentration of organic acids decreases.

Bioleaching tests using *Aspergillus niger* at 1–5% w/v showed that increasing the pulp density adversely influenced the removal of Fe (Figure 6). The Fe-reduction rates increased with decreasing pulp density. The maximum Fe-reduction rate was 77.13% at 1% w/v pulp density. The Fe content in the kaolin sample decreased from 1.723% Fe₂O₃ to 0.394% Fe₂O₃.

Kinetics study

From the results of bioleaching experiments at optimum pulp density, the kinetics of the process with *Aspergillus niger* was studied. The greatest rates of dissolution were obtained at the beginning of the experiment, after which the rate decreased and the amount of Fe dissolved decreased, until the maximum Fe concentration was attained. In the present case, the process consists of a reaction between a solid (kaolin, Fe oxide) and a liquid (leaching solution), and a model (equation 1) was used to describe the kinetics of leaching of Fe oxides. Because of the great porosity of kaolin, the transport through both reacted and unreacted structures was rapid compared with the true reaction rate, and this means that the situation could be called truly homogeneous. The model was formulated with these characteristics and the experimental results at optimum pulp density with *Aspergillus niger* (Figure 7) fitted it well. Under these conditions, the maximum Fe recovery was 77.13%. The values for the kinetic

coefficient (k) and the correlation coefficient (R^2) were determined to be 0.094 day⁻¹ and 0.9989, respectively.

Comparison of whiteness before treatment and after the chemical and biological leaching

The colors of the raw kaolin sample affect the color of the ceramic product after the coloring process in porcelain and pottery manufacture. The red color of kaolin becomes stronger as the amount of Fe oxide increases, resulting in the impurities which reduce the refractory property and lead to the formation of cracks during firing. The color of kaolin is, therefore, the most important factor in determining the quality of the clay. White clay was classified as ‘high quality’ (Povlov and Meshcheryakova, 1983; Ratzenberger, 1988; Stepkowska and Jefferis, 1992). In the present study, the whiteness indexes were determined as 47.20%, 81.10%, and 90.60% for the raw kaolin, bioleached kaolin, and chemically leached kaolin, respectively.

CONCLUSIONS

In light of the chemical leaching experimental results achieved by the factorial experimentation, the best conditions for the removal of Fe from kaolin, after chemical leaching tests, are: temperature of 80°C, oxalic acid concentration of 0.2 M, pulp density of 15% w/v, leaching time of 120 min, and a particle size of <63 μm. The degree of removal of Fe from kaolin under optimal chemical-leaching conditions was 94.89%. The Fe content decreased from 1.723% Fe₂O₃ to 0.088% Fe₂O₃ in the kaolin sample.

Bacterial leaching is a suitable means of improving the qualitative properties of kaolins used in the ceramic

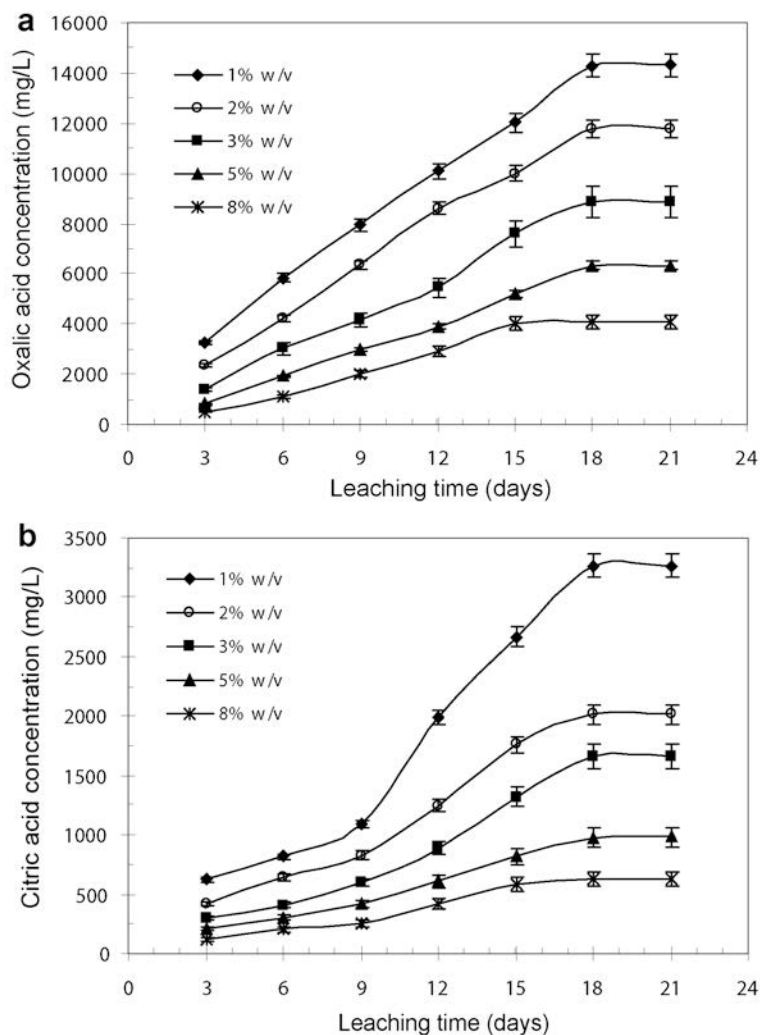


Figure 5. (a) Oxalic acid concentration during bioleaching experiments; (b) citric acid concentration during bioleaching experiments.

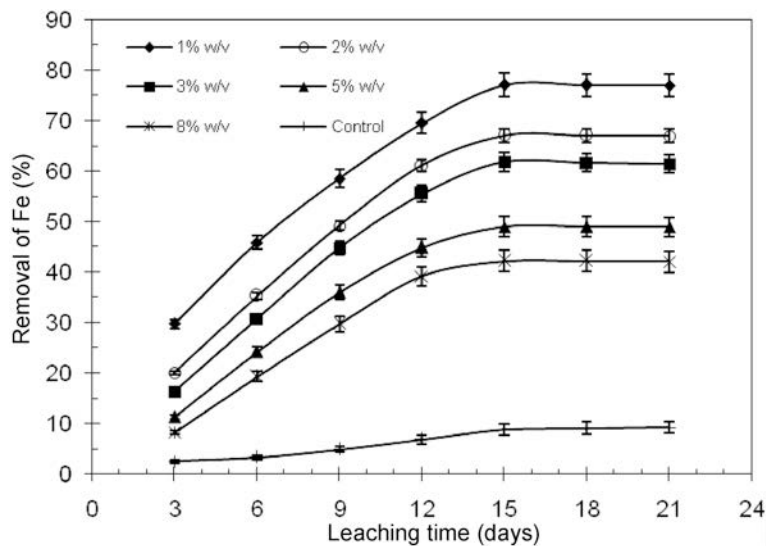


Figure 6. Removal of Fe during bioleaching experiments.

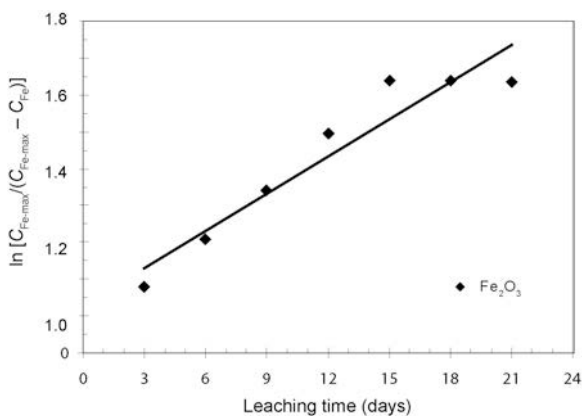


Figure 7. Kinetic modeling, using equation 1, of bioleaching at 1% w/v.

industry. Bacteria of *Bacillus spp.* can decrease the amount of free Fe, and of Fe bound in mica, which often contaminates kaolins. Increasing the proportion of fine-grained fraction also has a positive influence on the degree of success of the bacterial leaching. The process is time consuming, from a technological viewpoint, but advantageous in ecological and economic terms. The bioleaching of Fe oxides by *Aspergillus niger* resulted in the removal of 77.13% of the total Fe in the kaolin sample, and suggested that this strain has the ability to remove Fe impurities from kaolin. The Fe content decreased from 1.723% Fe₂O₃ to 0.394% Fe₂O₃. The whiteness indexes were determined as 47.20%, 81.10%, and 90.60% for raw, bioleached, and chemically leached kaolin samples, respectively, values which are acceptable in the ceramics industry.

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