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# REMOVAL OF Fe FROM KAOLIN USING DISSIMILATORY Fe(III)-REDUCING BACTERIA

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**Abstract**—LongYan kaolin has a large Fe content which affects the coloring. Bioleaching treatments to remove Fe impurities were conducted here using indigenous dissimilatory Fe(III)-reducing bacteria. The factors that affect bioleaching efficiency include bioleaching time, carbon source, pH, temperature, pulp density, and inoculum density and these were examined. Environmental scanning electron microscopy and X-ray diffraction were used to examine any textural or mineralogical changes at the surface of the kaolin that may have occurred during the bioleaching. Iron impurities in the kaolin were reduced from 0.88% to 0.48% with an increase in the natural whiteness index from 60.8% to 81.5% after 7 days of bioleaching treatment. A granulometric analysis of dispersed kaolin demonstrated that the bioleaching resulted in a decrease in particle size. The results demonstrated that the bioleaching was very effective at improving the quality of the kaolin, where insoluble Fe(III), either adsorbed to the kaolin surfaces or admixed as amorphous forms, was leached out by micro-organisms as water-soluble Fe(II).

**Key Words**—Bioleaching, Dissimilatory, Fe(III)-reducing Bacteria, Iron Impurity, Kaolin.

## INTRODUCTION

Kaolin has been used in many industries, *e.g.* porcelain and pottery, paper, pigment, filler manufacture, and insecticide manufacture (Murray, 1963; Ryu *et al.*, 1995; Štyriaková and Štyriak, 2000; Hosseini *et al.*, 2007). Iron impurities are present in kaolin as Fe (oxyhydr)oxides (*e.g.* hematite and goethite) or pyrite, either adsorbed to the kaolin surfaces or coordinated into kaolinite (Shelobolina *et al.*, 2005). The Fe impurities have a considerable effect on the quality and industrial value (Zheng, 2007) of the kaolin because kaolin refractoriness and whiteness decline with increasing Fe content (de Mesquita *et al.*, 1996). Kaolin used for whiteware, sanitaryware, and fiberglass have strict allowable levels of Fe (Murray, 2000) and kaolin must be refined extensively to remove the Fe (oxyhydr)oxides in order to enhance use in commercial and industrial applications (Inoue and Yoshida, 1984; Lee *et al.*, 2002).

Several physical methods have been used to improve the quality of the raw kaolin, including froth floatation, gravity separation, and magnetic separation. Two types of chemical bleaching techniques are used for kaolin processing. Reduced-acid leaching is performed using sodium hydrosulfite to remove Fe oxide and reduce the degree of yellowness (Inoue and Yoshida, 1984; Kimura and Tateyama, 1989; Mandal and Banerjee, 2004), while oxidative bleaching is performed using ozone or other oxidative treatments to remove discoloring organic matter adsorbed on the surfaces of kaolinite particles (Inoue and Yoshida, 1984; Kimura and Tateyama, 1989). Because of technological and environmental disadvantages (*e.g.* $SO_2$) associated with these methods (Russell *et al.*, 1979; Schwertmann *et al.*, 1998; Kostka *et al.*, 1999; Lee *et al.*, 2002; Hosseini *et al.*, 2007), however, bioleaching using bacteria is now being considered as an alternative to reduced-acid leaching with sodium hydrosulfite, due to its low cost and eco-friendliness together with good commercial and industrial results (Mandal and Banerjee, 2004; Hosseini *et al.*, 2007).

Some micro-organisms oxidize or reduce Fe *via* metabolic products acting as Fe-complexing agents, as well as participating in enzymatic and non-enzymatic Fe reduction-oxidation reactions (Lee *et al.*, 2002). *Thiobacillus ferrooxidans*, for example, has been used as Fe(II)-oxidizing micro-organisms to remove pyrite from low-grade clay (Ryu *et al.*, 1995). More recently, *Bacillus. spp* (Štyriaková *et al.*, 2007) and *Shewanella oneidensis* (O'Reilly *et al.*, 2006) were used as Fe(III)-reducing micro-organisms to leach Fe impurities *via* the organic acids produced through oxidation of organic matter in clay minerals. The filamentous fungus, *Aspergillus niger*, displays remarkable selectivity for Fe extraction and has been used to remove Fe impurities from kaolin and simultaneously produce organic acids (especially oxalic acids) during metabolism (Inoue and Yoshida, 1984; Cameselle *et al.*, 2003; Mandal and Banerjee, 2004; Hosseini *et al.*, 2007). In addition, microbial refinement of kaolin by mixed cultures of Fe-reducing bacteria from kaolin has also been reported (Lee *et al.*, 2002). A bioleaching method to remove Fe impurities and to improve the brightness of kaolin has attracted much attention because less energy is consumed, smaller operation costs are involved, and less harm is caused to the environment than with the

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chemical bleaching techniques (Ryu *et al.*, 1995; Mulligan *et al.*, 2004; Hosseini *et al.*, 2007).

The aim of the present study was to evaluate a bioleaching method to remove $Fe_2O_3$ from kaolin using cultured Fe-reducing bacteria mixtures initially isolated from a sludge sample. The factors that affected bioleaching efficiency, including bioleaching time, carbon source, pH, temperature, pulp density, and inoculum density were examined in order to determine whether the Fe-reducing bacteria mixtures could be used to remove Fe impurities from LongYan kaolin. In addition, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to examine whether any textural or mineralogical changes had taken place during the bioleaching treatments. A granulometric analysis of dispersed kaolin was also carried out so that changes in kaolin particle size during bioleaching could be assessed.

## MATERIALS AND METHODS

### *Kaolin samples*

The kaolin examined was a processed product supplied by LongYan Kaolin Company, Fujian, China. The kaolin was dried at 105ºC and cooled to room temperature in a desiccator to ensure that no moisture was adsorbed. The dried kaolin was passed through a <46 μm sieve prior to use. The sample contained 0.88% Fe (expressed as $Fe_2O_3$) with a natural whiteness index of 60.8%.

### *Micro-organisms and media*

Indigenous Fe(III)-reducing bacterial consortia cultured from sludge collected at the LongYan kaolin deposit, Fujian, P.R. China, were used. The sludge sample was collected between the upper soil and lower kaolin at a depth of 10 cm, and placed in sterile plastic bags before being transported to the laboratory. Sludge (25 g) containing Fe(III)-reducing bacterial consortia was added to a 250 mL sterilized (aseptic autoclave: 0.13 MPa, 121ºC, 20 min) Erlenmeyer flask containing 100 mL of medium with the following composition: 10 g $L^{-1}$ of glucose and 0.1 g $L^{-1}$ of $Fe_2O_3$. The head space of the flasks was purged with $N_2$ before the flasks were sealed tightly with a butyl rubber stopper. The flasks were then incubated at 30ºC for several days until sufficient fermentative gases ($CO_2$) were collected using a 20 mL syringe installed on each flask to indicate the existence of active micro-organisms. From each flask, solution (5 mL) was transferred into 1 L of medium with the following composition: 10 g $L^{-1}$ of peptone, 5 g $L^{-1}$ of NaCl, and 5 g $L^{-1}$ of beef extract. The micro-organisms were incubated on a rotary shaker (150 rpm) at 30ºC for 24 h and then harvested in the middle exponential phase (Optical Density (OD) at 600 nm = 0.5). This mixed culture broth was subsequently used to inoculate the source for subsequent bioleaching experiments.

### *Bioleaching experiments*

All bioleaching experiments were carried out in 250 mL Erlenmeyer flasks containing 10 g of kaolin, 100 mL of glucose medium (10 g $L^{-1}$), and 5 mL of mixed culture broth. Slurries were autoclaved (0.13 MPa, 121ºC, 20 min) before incubation in the same manner as described for the cultivation of the micro-organisms. All samples were incubated at 30ºC for 7 days unless otherwise specified and all experiments were conducted in triplicate. To avoid particle segregation, clay deposited at the bottom of the flasks was mixed daily during the incubation.

To investigate the effect of inoculation on the efficiencies of removal of Fe impurities as a function of time, two samples containing culture medium of 10% w/v of glucose and 10% w/v pulp density were added to 5 mL of either washed or unwashed mixed Fe(III)-reducing bacteria and incubated at 30ºC for 10 days, together with an aseptic autoclaved (121ºC, 20 min) control sample with no inoculation.

To understand better the actions of different carbon sources on the removal of Fe impurities from the kaolin, various sugars, including glucose, sucrose, and maltose, were added to cultures and the effect of sugar concentrations, ranging from 1% to 12% (w/w, sugar/clay), on the removal of Fe impurities were examined.

The effect of pH (4.3, 5.0, 6.1, 7.1, and 7.5), incubation temperature (15, 20, 25, 30, 35, and 40ºC), pulp density (10%, 15%, 20%, 25%, and 30% $w/w_T$), and inoculum density (10%, 30%, 50%, 70%, and 90% v/w) on Fe removal efficiency were also tested to obtain optimum bioleaching conditions. Subsequently, bioleaching experiments with kaolin using the Fe(III)-reducing bacterial consortia were conducted under these optimum conditions to evaluate the bioleaching efficiency.

### *Analysis and characterization of kaolin before and after bioleaching*

The pH of the culture medium during bioleaching was monitored using a pH meter (PHS-3C, Shanghai, China). Iron leached from the kaolin ($Fe^{2+}$) was determined using the 1,10-phenanthroline colorimetric method (Amonette and Templeton, 1998). Under strict anaerobic conditions ($N_2$ protected), the medium was concentrated by centrifugation. Supernatant (0.5 mL) was added with 1 mL HCl (1:1, v/v), 5 mL of NaAc-HAc buffer (pH = 4.6), 3 mL of 1,10-phenanthroline (5%, w/v), and diluted to 25 mL. The mixture was capped tightly and mixed thoroughly and then allowed to stand for at least 15 min. Absorbance was measured at 510 nm and the amount of Fe leached was calculated based on a standard curve that was constructed using dilutions of ferrous ammonium sulfate, $C_{Fe(II)} = 25$ μg $mL^{-1}$, stock. Bioleached kaolin samples were filtered and collected on filter paper and rinsed with distilled water prior to drying at 105ºC and cooling to room temperature in a

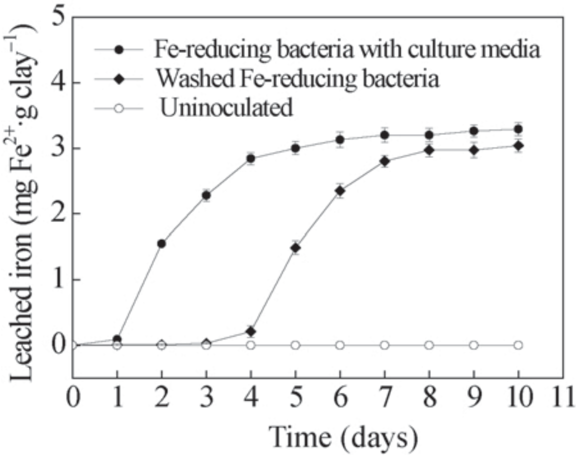

Figure 1. Effect of inoculation of Fe(III)-reducing bacteria on the removal of Fe impurities from the kaolin sample.

desiccator. The method used to measure Fe in the kaolin samples was described in the National Standard of China (1993 – GB/T14565-93). The whiteness indexes of the kaolin samples before and after bioleaching were measured using a colorimeter (WSB-IIIA, Beijing, China) according to National Standard of China (1996, GB/T5950-1996). The whiteness of the kaolin was compared to that of a sample calcined to 1280ºC for 1 h. The kaolins, before and after bioleaching, were characterized using an X-ray diffractometer (Philips X'Pert PW1710 with CuK$\alpha$ radiation operated at 40 kV and 40 mA), equipped with an automatic divergence slit, sample spinner, and a graphite diffracted-beam monochromator. Data were collected from the scan range 10−80º2θ with step-scan size of 0.1º. The kaolins before and after bioleaching were also examined using SEM (Philips-FEI XL30 ESEM-TMP) to check whether any textural changes to the surfaces of the kaolin due to bioleaching had occurred. Change in kaolin particle size during bioleaching was determined by granulometric analysis using a centrifugal sedimentation particle size analyzer (BT-1500) (Bettersize Instruments Ltd, Dandong, China).

## RESULTS AND DISCUSSION

### *Bioleaching treatments with and without inoculation*

Experimental measurements of the effect of inoculation revealed that no Fe was leached from the control sample and that little Fe was leached from kaolin following addition of 5 mL of washed Fe(III)-reducing bacteria during the first 3 days of incubation (Figure 1). The removal rate increased rapidly during the incubation period from day 4 to day 7 and reached a maximum of 2.8 mg of Fe g$^{-1}$ of clay after 7 days of incubation. A significantly greater rate of removal of Fe, 3.2 mg of Fe g$^{-1}$ of clay after 7 days of incubation, was obtained following addition of 5 mL of Fe(III)-reducing bacteria. This clearly indicated that the removal of Fe impurities from the kaolin depended significantly on inoculation with the Fe(III)-reducing bacteria and the initial population of the organisms with particular nutrients included in the culture medium. During incubation, insoluble Fe(III), trapped within the kaolin, was reduced to water-soluble Fe(II) under anaerobic conditions, resulting in Fe impurities being removed from the sample (Lee *et al.*, 2002) and the consequent change in color from pink to white, while the pH of the medium decreased from 6 to 4.5. The decrease in pH was due to fermentation of glucose, leading to the formation of gases and organic acids (Lee *et al.*, 2002).

The change in kaolin color, before and after the bioleaching treatment, as quantified by the whiteness indexes (Table 1) revealed that, after bioleaching, kaolin was graded based on whiteness index after calcining at 1280ºC and subsequently classified as 'special grade' (above 70%) (Lee *et al.*, 1999). The observed increase in whiteness index from 60.8% (before) to 81.5% (after) following bioleaching indicates that the quality of the kaolin had been improved. The results reveal that Fe(III)-reducing bacteria may be useful in the removal of Fe impurities from the kaolin used for many commercial and industrial purposes.

### *Effect of carbon source on the removal of Fe*

Study of the Fe contents leached from kaolin using different sugars as a function of bioleaching time (Figure 2a) revealed that the micro-organism responded better to sucrose and glucose than to maltose for the removal of Fe impurities. During bioleaching over 7 days, the amount of Fe leached from the kaolin was 3.3 mg of Fe$^{2+}$ g$^{-1}$ of clay (equivalent to 53% of the total Fe present in the kaolin sample) for sucrose and glucose and only 2.8 mg of Fe$^{2+}$ g$^{-1}$ of clay (46%) for maltose. The difference may be related to different metabolic reactions of the micro-organisms to the different carbon resources, leading to different rates of

Table 1. Comparison of the whiteness index for the kaolin samples before and after calcining and before and after bioleaching treatment.

| | – Before firing – | | – After firing at 1280ºC – | |
|---|---|---|---|---|
| | Raw clay | Bioleached clay | Raw clay | Bioleached clay |
| Whiteness index (%) | 60.8±0.5 | 81.5±0.5 | 83.8±0.5 | 92.0±0.5 |

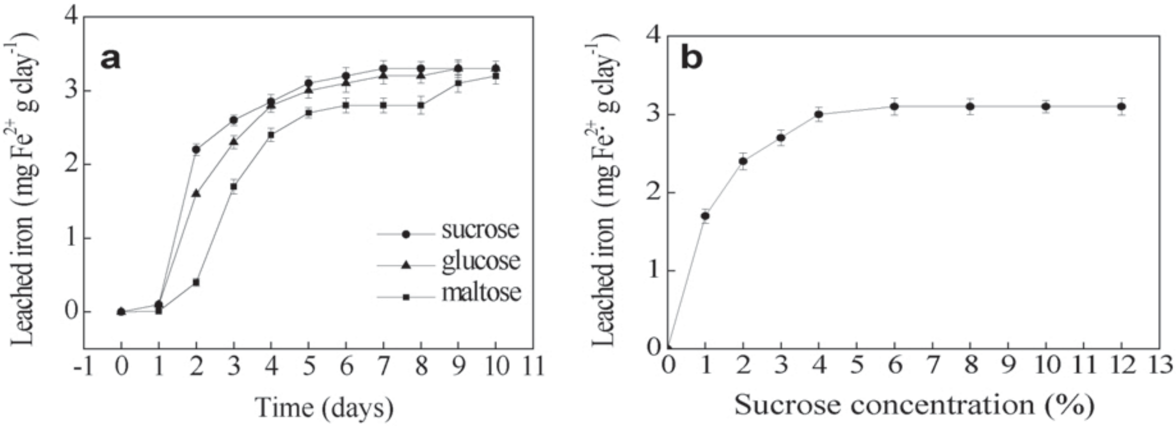

Figure 2. Effect of the (a) carbon source and (b) sucrose concentration on the removal of Fe impurities from the kaolin sample.

Fe removal. Similar results were obtained by Lee *et al.* (2002) in the microbial removal of Fe(III) impurities from clay using sucrose and glucose as the substrates. The presence of Fe(III) (oxyhydr)oxides (free Fe) in kaolin was identified by the visible brown-red color of the material (Štyriaková and Štyriak, 2000). Fe(III) in both the tetrahedral and *trans*-octahedral sites of the kaolinite can easily be extracted and reduced by bacteria; *cis*-octahedral Fe(III), however, is not easily reduced by bacteria (Jaisi *et al.*, 2005). A limited number of active sites in contact with the mineral surface on the cells can influence the Fe solubility and availability (Bonneville *et al.*, 2004). In addition, Fe(II) biosorption by dissimilatory Fe-reducing bacteria may also affect the rate and extent of Fe(III) reduction (Urrutia *et al.*, 1998). The Fe(III) reduction rate was limited, therefore, reaching only 53%.

Sucrose was the preferred carbon source in the present bioleaching experiment. As sucrose concentration increased, the removal of Fe impurities also increased, reaching 3.0 mg of Fe$^{2+}$ g$^{-1}$ of clay at a sucrose concentration of 4% and a maximum of 3.1 mg of Fe$^{2+}$ g$^{-1}$ of clay at a sucrose concentration of 6% (Figure 2b). The small increase in the extent of removal of Fe impurity at sucrose concentrations in the range 4–6% suggests that the sucrose concentration reached the saturation constant for the consortium and consequently reduced the activities of Fe(III)-reducing bacteria (Lee *et al.*, 2002).

### *Effect of pH and temperature on the removal of Fe*

The effect of pH on the removal of Fe from kaolin was studied, where the pH of the medium was initially adjusted to 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, or 9.0 using dilute NaOH or HCl solution prior to autoclaving and was measured as 4.3, 5.0, 6.1, 7.1, 7.5, or 7.9, respectively, after autoclaving (Figure 3a). No test was conducted at pH <3 because at that level Fe dissolves from the kaolin sample. The amount of Fe impurities leached from kaolin was greater but relatively consistent, ~3.0 mg of

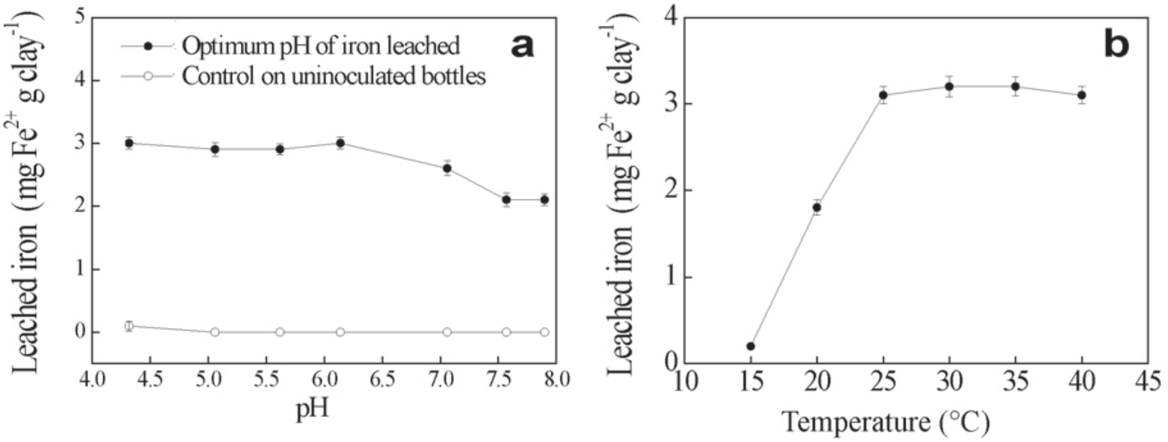

Figure 3. Effect of (a) pH and (b) temperature on the removal of Fe impurities from the kaolin sample after 7 days of the bioleaching experiment.

$Fe^{2+}$ $g^{-1}$ of clay for pH in the range 4.3–6.0, suggesting that Fe(III)-reducing bacteria are physiologically active in this optimum pH range (Kostka *et al.*, 1996). The pH values are indicative of a fermentative process (Lovley and Phillips., 1989). Removal of Fe impurities from kaolin decreased, however, with increase of the pH from 6 to 7.5 and reached a minimum between pH 7.5 and 7.9, either because Fe(III) precipitates as ferric hydroxide or Fe(II) becomes inherently unstable in the presence of $O_2$ under neutral to alkaline pH conditions and is oxidized to Fe(III) (Atlas and Bartha, 1993).

The effect of incubation temperature (15 to 40ºC) on Fe removal indicated that the preferred temperature range was 25–40ºC with a maximum removal of 3.2 mg of $Fe^{2+}$ $g^{-1}$ of clay obtained at 35ºC (Figure 3b). An enzymatically catalyzed reaction may occur in the pH range 4.3–6.0 and in the temperature range 25–40ºC (Kostka *et al.*, 1996).

### *Effect of pulp density and inoculum density on Fe removal*

The effect of clay pulp density on the efficiency of Fe removal from kaolin is significant because the clay pulp density affects slurry mixing, which is closely related to the operating cost of the refinement process. The variation in Fe concentrations in the culture broth with pulp densities ranging from 10% to 30% was investigated (Figure 4a). With an increase in pulp density, Fe impurity removal rates were reduced from 3.1 mg of $Fe^{2+}$ $g^{-1}$ clay at a pulp density of 10% to 2.3 mg of $Fe^{2+}$ $g^{-1}$ of clay at a pulp density of 30%, indicating that removal of Fe impurities from the kaolin sample depended on the clay pulp density. This may be due to the agglomeration of kaolin particles at a high clay pulp density, and inhibitory effects of some organic compounds dissolved from the clay (Andrews *et al.*, 1988).

The effect of inoculum density on the removal of Fe impurities from the kaolin was also tested by adding different volumes of inocula (1, 3, 5, 7, or 9 mL) into the medium and incubating for 7 days (Figure 4b). The rate of removal of Fe from the kaolin increased significantly with increasing inoculum density and reached a maximum of 3.0 mg $Fe^{2+}$ $g^{-1}$ clay at an inoculum density of 30% (v/w). The rate of removal of Fe remained constant with further increasing inoculum density, suggesting that extensively crystallized Fe present may be difficult to remove.

### *Optimum conditions for bioleaching kaolin*

Bioleaching experiments for kaolin using Fe(III)-reducing bacterial consortia under optimum conditions were performed to evaluate the bioleaching efficiency. The experimental conditions were 4% sucrose, 20% ($w/w_T$) pulp density, pH 5–6, and incubation temperature at 35ºC for up to 7 days. During this time the maximum leaching rate was 3.2 mg of $Fe^{2+}$ $g^{-1}$ of clay and Fe impurities in the original kaolin sample were reduced from 0.88% to 0.48% with a corresponding increase in the natural whiteness index from 60.8% to 81.5%. The main chemical compositions of the kaolin did not change and the Fe(III) impurities were removed selectively after the biological treatment (Table 2). The optimum conditions for bioleaching of Fe from kaolin may well be feasible to improve the quality of kaolin on an industrial scale.

### *Characterization of kaolin by SEM, granulometric analysis, and XRD*

Scanning electron microscopy images of the kaolin sample before and after bioleaching showed that the kaolin had undergone textural and mineralogical changes resulting in a decrease in particle size after bioleaching (Figure 5a,b). The removal of amorphous Fe during leaching (Phillips *et al.*, 1993), leading to the formation of fine particles, may have been the cause. Distribution of the fine-grained fraction (particle size 1.50–4.00 µm

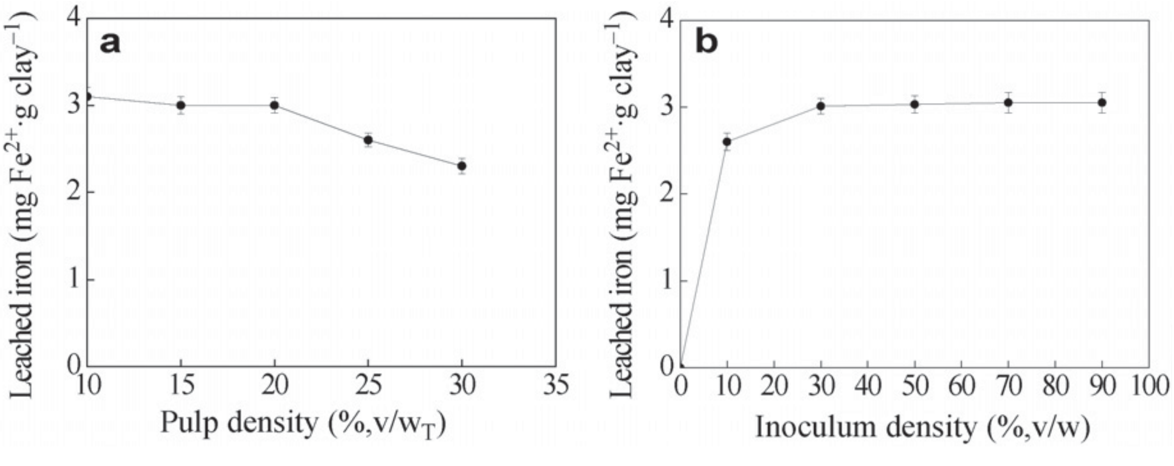

Figure 4. Effect of (a) pulp density and (b) inoculum density on the removal of Fe impurities from the kaolin sample after 7 days of the bioleaching experiment.

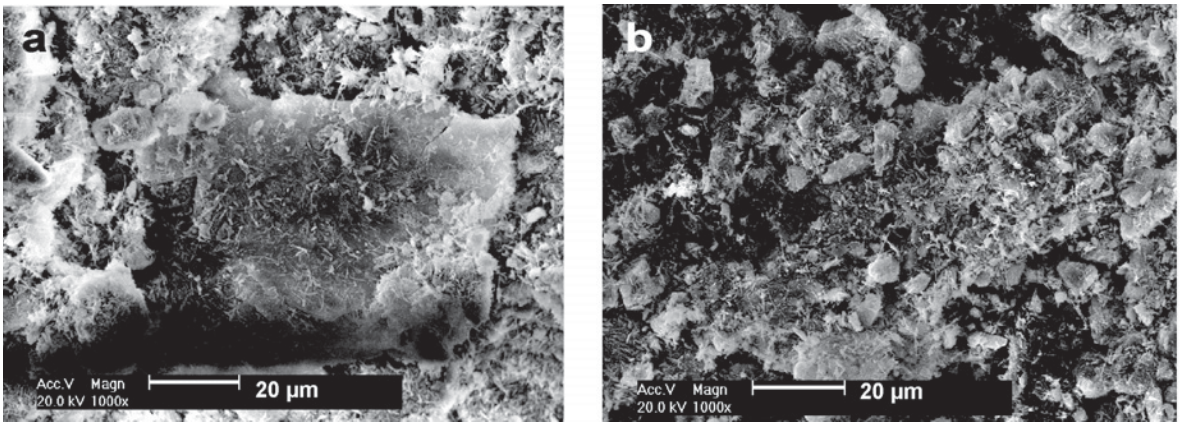

Figure 5. ESEM images of the kaolin sample before (a) and after (b) bioleaching treatment.

and 6.00–10.00 µm) was increased significantly after bioleaching (Figure 6). X-ray diffraction results revealed that the major mineral compositions remained unchanged for the kaolin sample after bioleaching (Figure 7). As the kaolin sample was only bioleached for 10 days, no secondary minerals were formed. Kaolin bioleached for >100 days, however, can be transformed into secondary mineral phases such as illite (Štyriaková and Štyriak, 2000).

## CONCLUSIONS

Bioleaching experiments showed that cultures of mixed Fe(III)-reducing bacteria could remove Fe impurities from a raw kaolin mineral. The Fe impurities in the initial kaolin sample were reduced from 0.88% to 0.48% with a corresponding increase in whiteness index from 60.8% to 81.5%. The SEM images revealed that the kaolin had undergone textural and mineralogical transformations, while X-ray diffraction (XRD) showed that the major mineral compositions remained unchanged after the treatment. Bioleaching resulted in a decrease in kaolin particle size.

Preliminary bleaching experiments using Fe(III)-reducing bacteria show that improving clay quality without changing the major mineral composition is possible. More Fe impurities can be removed when as little as 4% (w/w) sucrose is used as a carbon source and this is significant because reduction of the carbon source is a key cost issue associated with refining low-grade kaolin minerals for industrial applications.

Table 2. Chemical compositions (wt.%) of the kaolin samples before and after bioleaching treatment under optimum conditions.

| | Before bioleaching | After bioleaching |
|---|---|---|
| $Al_2O_3$ | 38.24 | 38.26 |
| $SiO_2$ | 46.31 | 46.33 |
| $Fe_2O_3$ | 0.88 | 0.48 |

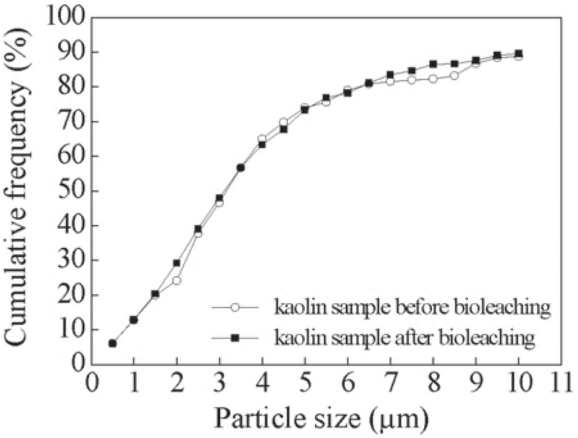

Figure 6. Particle-size distribution of the kaolin samples during bioleaching.

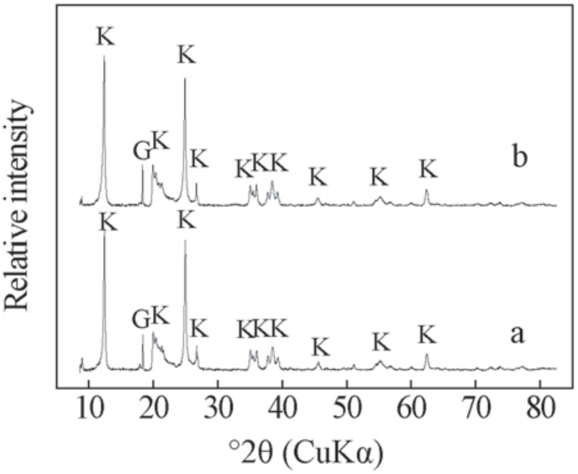

Figure 7. XRD patterns of the kaolin sample (a) before and (b) after bioleaching (K – kaolinite, G – gismondine).

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