Iron leaching from China clay with oxalic acid: effect of different physico-chemical parameters[☆]

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Abstract

China clay is an important mineral, which is used in the manufacture of ceramics and refractory, as also in other industries. Mined China clay contains iron oxides and silicates as impurity; if present in excess of a threshold level, the impurities affect the commercial value of the products. Currently available processes for lowering the iron content in China clay to the desired level ($< 0.8\%$) are energy- and cost-intensive, not sufficiently flexible, and may cause environmental pollution. An alternative approach for iron removal consists in the development of a biotechnological process which is expected to be cost-effective, less complex and eco-friendly. We reported earlier that several fungi, especially *Aspergillus niger*, and their culture filtrates could leach sufficient amount of iron from a China clay sample; oxalic acid was found to be the most active component of the culture filtrate (Trans. Indian Inst. Met. 55 (2002) 1). We now report the rates of iron leaching from another China clay sample by oxalic acid and by the culture filtrate of *A. niger* NCIM 548 that was found to be the most active strain in our previous study (Trans. Indian Inst. Met. 55 (2002) 1). The iron-leaching rates increased with temperature (T) and followed biphasic kinetics. The effect of oxalic acid concentration (C), pH (H), solids concentration or pulp density (P), time and mode of agitation on the rate of iron leaching is described. The rate of leaching with oxalic acid (R_{ox}) can be calculated theoretically from the following relationship: $R_{ox} \sim (C)^{0.76}(T)^{1.76}(H)^{0.80}(P)^{0.20}$ under the specified set of conditions. Using the same concentration of oxalic acid in *A. niger* culture filtrate, the relationship of the rate differed; this may be due to the influence of other metabolites present in the culture filtrate on the rate.
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1. Introduction

The importance of China clay in the manufacture of pottery, ceramics and refractory, as also in paper, rubber and other industries is well known (Goetz, 1985). The common impurities of the natural mineral are iron oxides and silicates, which impart poor quality to the finished. products and cause other problems, if present in excess. For the production of high quality materials, the iron content in China clay should be lower than 0.8% (w/w). Many methods, such as froth floatation, gravity separation, acid treatment, reductive roasting and magnetic separation are used for the beneficiation of China clay (Grim, 1968;

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Kumar, 1994). Based on these physico-chemical methods, several industrial processes (and related patents) have been developed (Danilova et al., 1982; Bonney, 1994; Veglio, 1997). However, these operations are expensive, energy-intensive and not sufficiently flexible, and give rise to environmental pollution. On the other hand, suitable biotechnological methods are expected to produce low-iron clay at lower cost under environmentally safe and relatively less complex conditions (Groudev and Groudeva, 1985; Toro et al., 1992; Strasser et al., 1993).

Iron is an essential element for growth. Though it is abundant in nature, it remains mostly in the insoluble state. Microorganisms have therefore evolved special mechanisms for extracting it from nature. One of them is the production of metabolites like organic acids and siderophores (Powell et al., 1980; Winkelmann et al., 1987; Strasser et al., 1994). Compared to abiotic processes, these mechanisms help microorganisms in extracting more iron from several minerals (Barker et al., 1983). Commercial feasibility of iron removal by bioleaching was first studied in the late 1970s (Groudev et al., 1978; Groudev and Groudeva, 1985, 1986). A process was developed for the removal of iron at high temperature (90 °C) from quartz sands, kaolins and clays using the culture filtrates of acid producing fungi, mainly *Aspergillus niger* (Groudev, 1987). Recently, a bacterial consortium occurring in kaolins and kaolin-containing rocks was utilized for removing iron from such materials. Microbial treatment followed by iron removal through subsequent magnetic separation resulted enrichment of kaolins and other minerals (Shelobolina et al., 1999). The percentage of iron in most of the China clay deposits in India is high and this cannot be lowered by conventional processes to the level required for the production of high quality materials (Kumar, 1994; Wadia, 1994). We observed that several fungi and their culture filtrates could leach iron from an iron-rich clay sample (Mandal et al., 2002). At ambient condition, the highest iron-leaching activity was observed with the culture filtrate of an oxalic acid producing *A. niger* strain. It is well established that oxalic acid is a potential leaching agent for dissolving heavy metals from various minerals including clay and kaolin, and biohydrometallurgy groups are now considering processes for removal of heavy metals depending on this property of oxalic acid (Bonney, 1994; Strasser et al., 1994;

Taxiarchou et al., 1997a,b; Dudeney et al., 1999; Veglio et al., 1999). Therefore, a study on the effect of various environmental parameters on the rate of iron leaching by oxalic acid from iron-rich China clay is necessary. Veglio et al. (1996) studied the effects of main factors which can potentially influence the iron-dissolution process by oxalic acid using a relatively low iron containing (0.84% as Fe_2O_3) kaolin. The use of culture filtrate of an oxalic acid producing *A. niger* strain for removing iron from a China clay containing only 0.11% iron was also reported (RoyChaudhury and Das, 1990). However, the rate equations derived for low-iron containing China clay may not be applicable for a sample having high content of iron. Further, the rates calculated with culture filtrates containing other components besides oxalic acid, which might have influenced the iron-leaching rate, may be different from those for pure oxalic acid solution. Thus, evaluation of the iron-dissolution rate equations from clay using oxalic acid or *A. niger* culture filtrate with respect to variables like temperature, pH, solids concentration and oxalic acid concentration is necessary. This report describes the results of such a study.

2. Materials and methods

2.1. Fungal strain and growth conditions

The *A. niger* NCIM 548 strain was obtained from Prof. A.K. Guha, Indian Association for the Cultivation of Science, Kolkata. The strain was grown for 7 days at 30 °C on a rotary shaker (215 rpm) in a modified medium (Strasser et al., 1993) of the following composition (in g/l): glucose, 105.5; $NaNO_3$, 1.5; KH_2PO_4, 0.5; $MgSO_4.7H_2O$, 0.025; KCl, 0.025; yeast extract, 1.6; and universal indicator solution, 2% (v/v). The medium pH was adjusted to 6 initially and maintained within 5.5–6.0 throughout the culture period by adding 4 M NaOH at intervals. The strain was maintained in Czapek–Dox medium (Mandal et al., 2002).

2.2. China clay

The China clay sample (particle size − 300 mesh BSS) was mined from a deposit near Mukdumnagar,

Birbhum district, West Bengal, India. Elemental composition (w/w as oxide) of the clay was SiO_2 (45.72%), TiO_2 (1.52%), Al_2O_3 (35.96%), Fe_2O_3 (1.87%), CaO (0.33%), MgO (trace), Na_2O (0.18%), K_2O (0.19%), and the loss on ignition (LOI) was 13.79%. The clay was reddish white in colour suggesting that the iron was partly present as free iron oxyhydroxide.

2.3. Treatment of China clay with oxalic acid and culture filtrate

The culture filtrate was made 100 mM with respect to oxalic acid by adding the requisite amount of the acid. The clay sample was taken either in screw-capped bottles (30-ml capacity) or in Erlenmeyer flasks (100-ml capacity). The bottles containing 5 ml slurry of oxalic acid solution or *A. niger* culture filtrate with clay were rotated (cyclic) in a hybridization oven (Stuart, UK) at 60 rpm, and the flasks containing 25 ml of the slurry were shaken (orbital or reciprocating) at 215 rpm in an environmental incubator (Rosi 1000; Thermolyne, USA). Oxalic acid concentration (C), pH (H), solids concentration (P) and temperature (T) were varied from 10–300 mM, 0.75–4.0, 5–50% (w/v) and 40–80 °C, respectively. After a specified time, either an aliquot from the containers or the whole content of a vessel was centrifuged, and the supernatant was collected for iron estimation.

2.4. Analytical methods

Iron content was measured following a modified method of May and Fish (Fish, 1988; May and Fish, 1978) described in detail previously (Mandal et al., 2002). In practice, a small volume of sample solution containing less than 5 µg of iron was diluted to 1 ml with 0.5 ml of 0.02 N HCl and water. This solution was incubated at 60 °C for 2 h after adding 0.5 ml of freshly prepared Reagent A (0.6 N in HCl and 0.142 M in $KMnO_4$). The temperature was brought down to ambient, and 0.1 ml of Reagent B (5 M in ammonium acetate, 2 M in ascorbic acid, 6.5 mM in ferrozine, and 13.1 mM in neocuproine) was added to the mixture. Absorbance at 562 nm was measured after 20 min but before 20 h. Oxalate in the culture filtrate was precipitated with $CaCl_2$ and estimated by $KMnO_4$ titration.

2.5. Scanning electron microscopy

A scanning electron microscope (Model No. S440) of Leo Electron Microscopy Limited (UK) was used for this purpose.

2.6. Determination of iron-leaching rates

Plots were drawn with the values of log (rate of iron dissolution) on the *y*-axis versus log of the variable parameter *X* (viz. concentration, pH, temperature or solids concentration) on the *x*-axis. Rates (R) were determined from the slope (m) in each case and the relation between the leaching rate and the variable parameter was expressed as $R \alpha X^m$.

3. Results and discussion

The leaching experiments were normally conducted under the following conditions: concentration of oxalic acid, 100 mM; temperature, 60 °C; pH, 1.5; pulp density, 10% (w/v); and time, 4 h. The rates of iron leaching were calculated with change in oxalic acid concentration, temperature, pH, pulp density, reaction time and shaking conditions and are described in the respective sections. All the experiments and analyses were replicated. The rate of iron dissolution was observed to be very fast during the first hour. As this might be due to the dissolution of freely available iron oxyhydroxide, the rates were calculated from the data obtained after the first hour of reaction.

3.1. Effect of oxalic acid concentration on the iron dissolution rate

The experiment was carried out in 100-ml Erlenmeyer flask on an orbital shaker (16-mm throw) at 215 rpm using concentrations of oxalic acid varying from 10 to 300 mM. Iron dissolution rate (R) was slow up to 40 mM, but increased above this concentration. From the plot of log (rate of iron dissolution) versus log (concentration), the slope was calculated as 0.76 above 40 mM (Fig. 1). Therefore, the rate equation for oxalic acid, i.e. amount (%) of iron leached/minute can be written as $R_{ox} \sim (C)^{0.76}$, where C is expressed in mM.

The culture filtrate of *A. niger* was estimated to be 89 mM in oxalic acid. Since the rates for pure oxalic
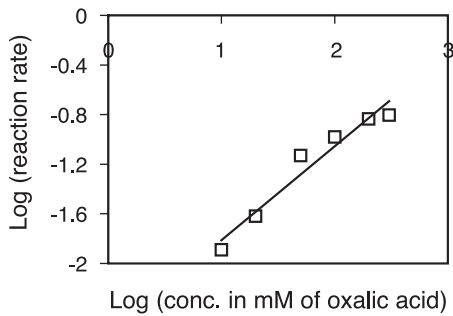
Fig. 1. Correlation between oxalic acid concentration and iron leaching rate.

acid were determined at 100 mM concentration, the culture filtrate was enriched with additional oxalic acid to the same concentration (100 mM). It was noted that at the same oxalate concentration, much less iron was leached with culture filtrate than oxalic acid (5.4% vs. 24.9%). The result suggests that the culture filtrate of *A. niger* strain contains such materials (other than the medium components) that strongly inhibit the iron dissolution process under the conditions (short period leaching at temperature higher than ambient). It may be mentioned that on prolonged incubation for 15 days at ambient temperature (37 °C), more iron was leached by the culture filtrate compared to oxalic acid (Mandal et al., 2002).

3.2. Temperature effect on the iron dissolution rate

The experiments were conducted in screw-capped bottles in a hybridisation oven (cyclic rotation) at 40–80 °C. After the first hour, iron dissolution occurred at a constant rate, which increased with temperature (Fig. 2). During short-period leaching, little iron dissolution occurred with culture filtrate even at 50 °C.

The rates of iron dissolution for different temperatures were calculated after the first hour of leaching. From the plot of log (rate of iron dissolution) versus log of temperature (in absolute scale as T), the slope was derived as 1.76 for oxalic acid and 3.72 for culture filtrate (Fig. 3A). Therefore, the rate equations can be written as $R_{ox} \sim (T)^{1.76}$ and $R_{cf} \sim (T)^{3.72}$ for oxalic acid and culture filtrate, respectively. When log values of the reaction rates at different temperatures were drawn against $1/T$, the slope was derived as -1.76 and -3.72 for oxalic acid and culture filtrate, respectively. Using the Arrhenius rate equation, activation energy of iron dissolution was calculated 8.1 and 17.2 kcal/T/mol for oxalic acid and culture filtrate, respectively (Fig. 3B), suggesting a faster reaction rate for oxalic acid than the culture filtrate. The result further indicated that the rate of oxalic acid reaction with iron was inhibited by one or more compounds present in the culture filtrate; these may be either medium components or products of the fungus. In a previous report (RoyChaudhury and Das, 1990), where culture filtrate of another *A. niger* strain and a low-iron China clay sample were used, the rate equation was derived as $R_{cf} \sim (T)^{1.25}$ and the activation energy was calculated as 2.31 kcal/T/mol. Low activation energy in this case might be due to the low iron content of the mineral.
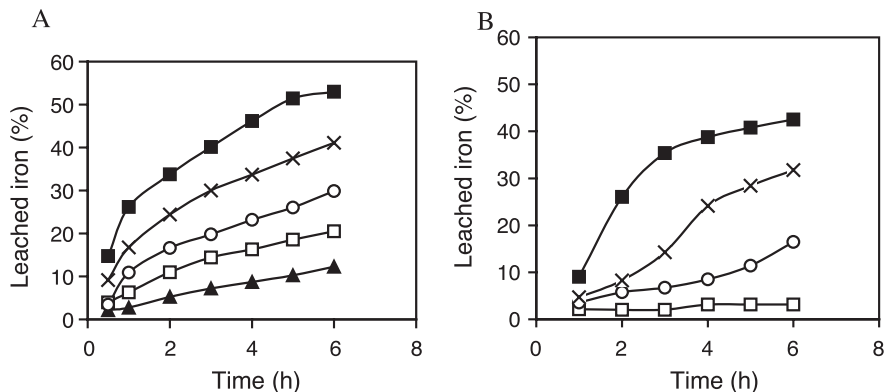

Fig. 2. Leaching of iron from China clay at (■) 80 °C, (×) 70 °C, (○) 60 °C, (□) 50 °C and (▲) 40 °C by 100 mM oxalic acid (A) and *A. niger* culture filtrate (B).
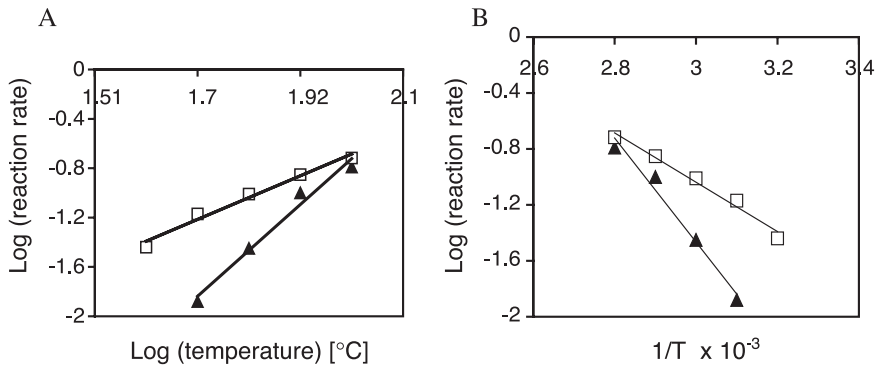
Fig. 3. Correlation between iron leaching rate and temperature (°C) [A], and evaluation of activation energy [B] by 100 mM oxalic acid (□) and *A. niger* culture filtrate (▲).

3.3. Effect of pH on the iron dissolution rate

Initial pH of the oxalic acid solution was allowed to vary from 0.75 to 4.0 in this experiment that was carried out in Erlenmeyer flasks placed in a reciprocal shaker (25.5-mm throw). It was observed that above pH 2.0, the amount of dissolved iron in the leached solution decreased rapidly; this was probably due to precipitation of iron at pH>2 (Fig. 4A). The highest rate of iron leaching was noted at pH 1.75, which is higher than the pK_1 of oxalic acid. From the plot of log (rate of iron dissolution) versus log (pH), the slope was calculated to be 0.8 (Fig. 4B). Therefore, the rate equation can be written as $R_{ox} \sim (H)^{0.8}$, H being the initial pH of oxalic acid solution. With culture filtrate as the leaching solution, iron leaching was highest at

pH 1.25 and dropped above this pH. An almost similar observation was reported previously with culture filtrate where iron dissolution was highest at the lowest pH (0.5) tested; the rate equation was presented as $R_{cf} \sim (H)^{0.4}$ (RoyChaudhury and Das, 1990).

3.4. Effect of solids concentration on the iron dissolution rate

This experiment was conducted by varying the pulp density from 5% to 50% (w/v), and was performed in the hybridisation oven. The rate of iron dissolution was observed to increase with increase in pulp density, reaching a maximum at 15%, and then declining slowly (Fig. 5). With culture filtrate, the rate
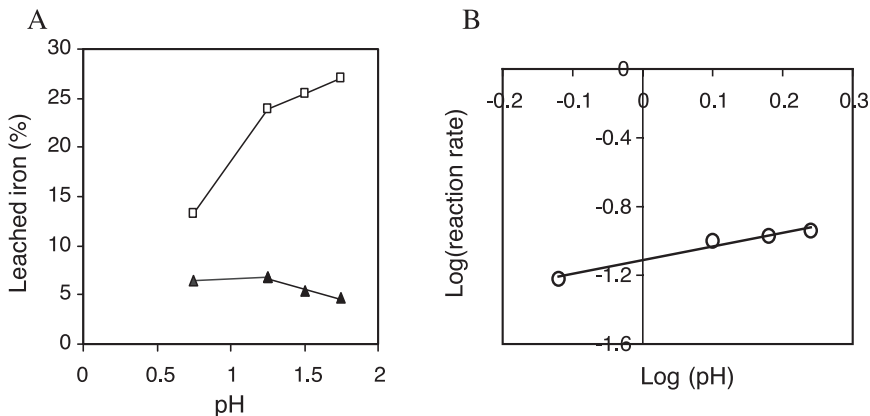

Fig. 4. Effect of pH on the iron leaching rate by oxalic acid (□) and *A. niger* culture filtrate (▲) (A), and correlation of iron dissolution rate with initial pH of the oxalic acid solution (B).
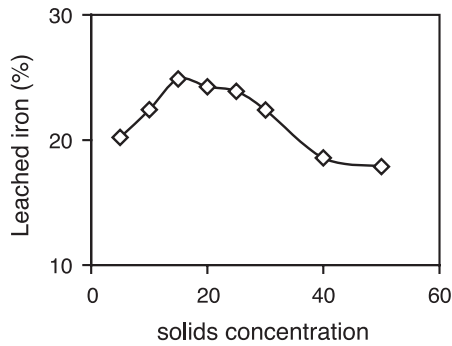
Fig. 5. Effect of solids concentration variation on the rate of iron leaching with oxalic acid.

of iron dissolution also increased up to 15% (w/v) solids concentration. At higher concentrations (>15%, w/v), the suspension probably becomes sufficiently thick restricting free mixing of clay particles with the leaching solution that results in decrease of the rate. From the plot of log (rate of iron dissolution) versus log (solids concentration) (Fig. 6), the slope was calculated as 0.2 for oxalic acid and 0.9 for culture filtrate; therefore, the rate equations are $R_{ox} \sim (P)^{0.2}$ and $R_{cf} \sim (P)^{0.9}$, respectively. It was derived as $R_{cf} \sim (P)^{0.27}$ in a previous report (RoyChaudhury and Das, 1990).

3.5. Effect of shaking condition on the iron dissolution rate

Leaching of iron was slightly better when clay suspension was agitated on a reciprocal rather than an orbital shaker; under a set of conditions, 26% and
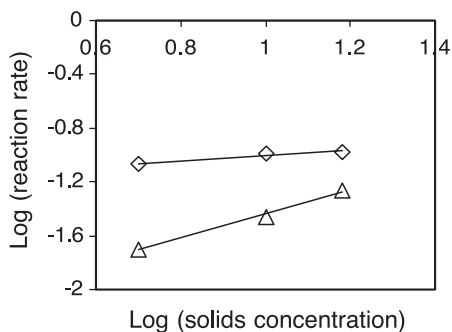

Fig. 6. Relationship on rate of iron removal and solids concentration by 100 mM of oxalic acid solution ($\diamond$) and *A. niger* culture filtrate ($\triangle$).
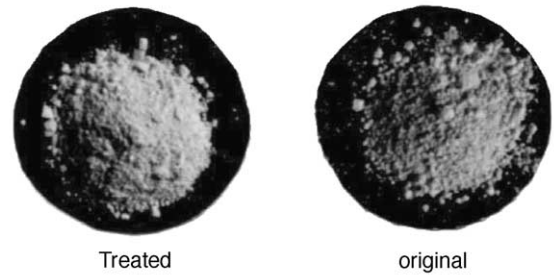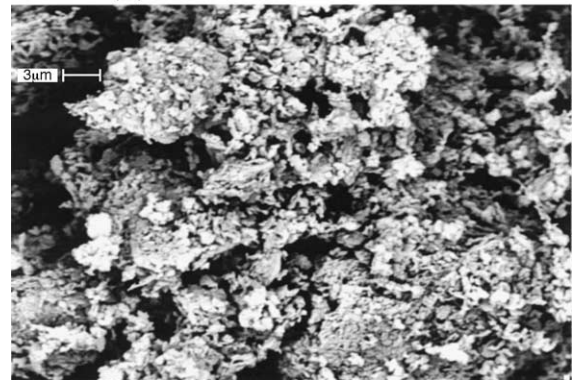

Fig. 7. Photograph of China clay before (right) and after (left) leaching with oxalic acid.

27.5% of iron was leached under orbital and reciprocal motion, respectively. Variation of the shaking speed (range of 60–250 rpm) did not have much effect on iron leaching. From the various results, however, it
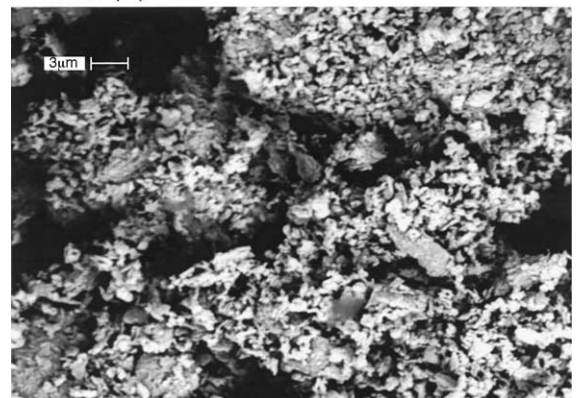

Fig. 8. Scanning electron micrograph of China clay after (A) and before untreated (B) oxalic acid treatment.

may be suggested that under the same conditions leaching must be much better under cyclic rotation.

4. Conclusion

This study was conducted with a China clay sample from which at least 40% (w/w) of total iron had to be removed to make it suitable for the production of quality materials. The reddish colour of the clay was almost completely removed after treatment with 0.1 M oxalic acid (pH 1.5) for 6 h at 80 °C under cyclic rotation (60 rpm) (Fig. 7). Electron micrographs of the materials indicated reduction in the number of clumps in the treated sample (Fig. 8A) compared to the untreated one (Fig. 8B). It may thus be concluded that the desired beneficiation of iron-rich China clay could be achieved using oxalic acid. The leaching rate can be calculated theoretically from the relationship: $R_{ox} \sim (C)^{0.76}(T)^{1.76}(H)^{0.8}(P)^{0.2}$ under a set of conditions. In spite of the higher activation energy, iron leaching from China clay continued at pH>1.25 when culture filtrate containing other component(s) was used.

Acknowledgements

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