



Research paper

Refinement of industrial kaolin by microbial removal of iron-bearing impurities[☆]Asfaw Zegeye^{*}, Sani Yahaya, Claire I. Fialips, Maggie L. White, Neil D. Gray, David A.C. Manning

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ABSTRACT

The commercial value of kaolin raw materials is greatly affected by the presence and content of iron-bearing impurities, which can have a detrimental effect on the whiteness and refractoriness of manufactured products. Because of the high cost and environmental impact of techniques currently used to remove these impurities, some effort is now targeted toward the development of alternative methods, such as biological processes. This paper reports a series of anaerobic microcosm experiments conducted to evaluate the suitability of iron-respiring bacteria (IRB) of the *Shewanella* species (*S. alga* BrY, *S. oneidensis* MR-1, *S. putrefaciens* CN32, and *S. putrefaciens* CIP 8040), in bioleaching iron-bearing impurities from raw kaolin. All tested bacterial strains were able to reduce and leach ferric iron present in the kaolin, thereby substantially improving its color properties. Among the tested bacteria, *S. putrefaciens* CIP8040 produced the greatest improvements, with increases in ISO brightness and whiteness from 74% to 79% and from 54% to 66%, respectively, in 5 days at 30 °C. Neither secondary mineral nor crystal-chemical alteration of the kaolinite was observed by X-ray diffraction and infrared spectroscopy. Observations of the biotreated kaolins by scanning electron microscopy showed that the original hexagonal shape of the clay particles became less regular. Further research and development should now focus on optimising the rate and extent of the bioleaching process before its application at a larger pilot or industrial scale. In particular, further studies should evaluate the environmental and economical benefits compared to currently used approaches, such as the chemical bleaching with sodium hydrosulfite.

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1. Introduction

Clay minerals are among the most important structural materials on the Earth's surface, being major components in soils and sediments, and the rocks formed from these (Moore and Reynolds, 1997). Clays play an important role in environmental, agricultural and industrial processes such as nutrient cycling, plant growth, petroleum production, and contaminant migration (Stucki, 2006; Stucki et al., 2002). Clay raw materials include kaolins, which are mined materials rich in kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), a clay mineral generally formed by the intense weathering or hydrothermal alteration of aluminosilicate minerals, such as feldspars and mica. Apart from kaolinite, kaolins as mined contain other mineral phases, such as quartz, micas and unaltered feldspars. They also contain minerals that act as pigments, including iron oxides or oxyhydroxides (lepidocrocite, goethite, and/or hematite), which give a brown colour, and the TiO_2 polymorphs anatase and/or rutile, which give a pink colour. Similarly to kaolinite,

iron oxides and oxyhydroxides are common products of intense weathering; their presence in kaolins is frequent but in low quantity (generally less than 5 m%).

Kaolins are exploited for a wide range of industrial applications, such as the production of paper (as a filler and/or a coating material), ceramics (to add strength, abrasion resistance, and rigidity), plastics (as a filler) and paints (as a filler and thickening agent). Before kaolin products can be used by manufacturing industry, the raw kaolins have to be refined to meet commercial specifications (Hosseini et al., 2007; Styriakova and Styriak, 2000). One of the key criteria for the industrial use of processed kaolins for paper manufacture and ceramics is a low content in iron-bearing minerals as such impurities substantially affect the whiteness and refractoriness of the product, affecting especially paper and ceramic applications. In particular, because of their particularly intense red or brownish color, it is essential that very low contents of the iron oxides and oxyhydroxides are achieved by processing following mining, either by blending or treatment during mineral production. Even a very low iron concentration in a kaolin may result in a significant reduction in the whiteness of a ceramic product as any coloration is intensified by the firing process (Lee et al., 2002).

Ferric iron (Fe^{III}) is only soluble at an acidic pH of 3 or below. Ferrous iron (Fe^{II}) is soluble over a wider range of pH but, at circum-neutral pH or above, it is only stable under reducing conditions. In the presence of oxygen, it is rapidly oxidised to the trivalent form and precipitated as an

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Fe(III)-bearing solid (Schwertmann and Taylor, 1989). The removal of Fe(III)-bearing impurities from industrial kaolins is generally achieved by the combination of physical techniques (magnetic separation, selective flocculation) with chemical treatments under acidic or reducing conditions. The reductive leaching of Fe from kaolins with sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), alternatively known as sodium dithionite, is particularly efficient and is currently employed by the kaolin industry, in some cases giving very low iron concentrations (below 0.3% Fe_2O_3) and very high brightness values (above 94%) required for high specification kaolin products (Thurlow, 2001). However, these chemical treatments have economical, technological, and environmental disadvantages. In particular, sodium hydrosulfite is an expensive and dangerous chemical requiring specific and costly storage and transport arrangements. Iron leaching with this chemical is also fairly complex, requiring careful monitoring of the pH, the density of the kaolin slurry, the oxygen level, and the amount of added sodium hydrosulfite as the reaction of reduction of Fe(III) may be impaired by concurrent reactions (Conley and Lloyds, 1970). Its use also produces large amounts of effluents that have high concentrations of dissolved sulfates, requiring chemical treatment, often in large ponds, before disposal.

Over the last decade or so, some effort has been targeted on the development of alternative refining methods, such as biological processes, to remove iron impurities from raw kaolins (Arslan and Bayat, 2009; Camselle et al., 2003; Guo et al., 2010a,b; Hosseini et al., 2007; Lee et al., 2002; Musial et al., 2011; Stucki, 1988). The capital and energy costs of bacterial leaching are likely to be low and no or minimal environmental impact is expected. Such an approach is therefore considered to be of great potential for future mineral treatments (Bosecker, 1997; Hosseini et al., 2007). Most studies on the biological leaching of metal impurities from mineral materials have focused on acid-producing microorganisms, such as *Bacillus* sp., (Guo et al., 2010a; He et al., 2011) and *Aspergillus niger* (Arslan and Bayat, 2009; Guo et al., 2010b; Hosseini et al., 2007; Musial et al., 2011). The organic acids produced by their metabolism abiotically dissolve metals from solid materials, improving to some extent the quality of the raw material. In particular, the organic acids produced by the filamentous fungus *A. niger* (principally oxalic but also citric and gluconic acids) resulted in an increase in whiteness of another kaolin from 56.5% to 80% in 40 h (Camselle et al., 2003). Several technological problems were however identified, such as the use of two separate stages, one for the culture of the *A. niger* and the second for kaolin acid-leaching, and the need to maintain the pH around 3 through the addition of acid. Experiments using direct addition of oxalic acid (not biologically produced) required heating to 84 °C for more than 5 h to remove 44 wt.% of Fe from a raw kaolin (Terrazas Calderon et al., 2005). In the UK, unpublished work in the 1990s indicated costs of around £30/kg for treating kaolin with oxalic acid in heated reactors, compare to around £7/kg using sodium hydrosulfite. To evaluate the effectiveness of microbiological treatments in economically improving the quality and value of raw kaolin, new studies have to focus on different bacterial metabolisms. Biogeochemical evidence supports the potential importance of crystalline or amorphous Fe-bearing minerals as electron acceptors for Fe-reducing bacteria in soils and subsurface sediments (Lovley, 2000; Lovley and Phillips, 1988). A phylogenetically and physiologically diverse group of bacteria has been isolated that is capable of iron-respiring reduction. Iron-respiring bacteria (IRB) gain energy by coupling the oxidation of organic compounds or hydrogen to the reduction of ferric Fe oxides (Nealson and Myers, 1992; Nealson and Saffarini, 1994). These bacteria have been shown to reduce Fe(III) within the structure of clay minerals and associated phases (Jaisi et al., 2007; Kostka et al., 1996, 2002; Vorhies and Gaines, 2009). Moreover, some IRB were isolated from subsurface kaolin lenses (sedimentary kaolins, Georgia, USA) indicating their presence associated with raw kaolins in natural settings (Sheilbolina et al., 2007). Thus, the use of IRB may be of industrial interest for the removal of iron impurities from kaolins.

In the present study, the Fe(III) removal efficiency from a kaolin from SW England has been evaluated using different *Shewanella* IRB species (*S. alga* BrY, *S. oneidensis* MR-1, *S. putrefaciens* CN32, and *S. putrefaciens* CIP 8040). The microbial reduction of Fe(III) was monitored in batch cultures under non-growth conditions. The rate and extent of Fe(III) reduction were examined as a function of the *Shewanella* species and cell/kaolin ratio. The bio-treated materials were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) to investigate any mineralogical transformation. The whiteness and brightness indices of the kaolins were also assessed by spectrometry.

2. Materials and methods

2.1. Kaolin materials

The kaolin sample used in this study was provided by Imerys Minerals Ltd. (St. Austell, Cornwall, UK). It is a processed product ('Remblend') derived ultimately from a large open pit in kaolinised granite near St. Austell, Cornwall, UK (Pysrillos et al., 1999). In this case, raw kaolin slurry was generated by washing the altered granite with a high-pressure water jet. The coarser grained and heavier sand, mica, feldspar, and other associated minerals were removed using a variety of processes combining gravity settling and subsequent mechanical separation to obtain a kaolinite-rich clay slurry. The kaolin slurry was then passed through hydrocyclones to collect the less than 53 μm fraction, consisting almost exclusively of kaolinite particles (Pysrillos et al., 1999). The final kaolin slurries have a mineral content of around 250 g L⁻¹ and chemical analysis using X-ray fluorescence spectroscopy (XRF) revealed a low iron content (~ 1.05 m% Fe_2O_3) and the presence of few other impurities, as TiO_2 , K_2O , and MgO (Table 1).

2.2. Preparation of iron respiring bacteria inocula

Pure lyophilised cultures of *S. oneidensis* strain MR-1, *S. alga* strain BrY, *S. putrefaciens* strain CN 32 (*S. p.* CN 32), and *S. putrefaciens* strain CIP 8040 were obtained from NCIMB Ltd. (Aberdeen, Scotland) and DSMZ (Braunschweig, Germany). The cells were cultured as described in (Zegeye et al., 2007). Briefly, frozen cells from a stock (20% glycerol at -80 °C) were revived under aerobic conditions on tryptic soy agar (TSA). They were sub-cultured twice, and then the colonies were used to prepare a suspension with a target optical density of 0.55 ± 0.01 ($\lambda = 600 \text{ nm}$). Twenty millilitres of this suspension was inoculated in 200 mL of tryptic soy broth (TSB) in order to initiate the liquid culture. Cells were grown to a stationary growth phase (24 h) and harvested by centrifugation, washed twice with sterile NaCl 0.9% and concentrated in the same medium. Cells were purged for 30 minutes by bubbling with N_2 to reach anoxic conditions, sterilised by filtration through a membrane of pore size 0.2 μm (Millex FG50, Millipore) and used to inoculate batches with kaolin.

Table 1
XRF and specific surface area data of the kaolin used in this study.

Composition	Kaolin
SiO_2 (%)	48.7
TiO_2 (%)	0.08
Al_2O_3 (%)	35.8
Fe_2O_3 (%)	1.05
CaO (%)	0.06
MgO (%)	0.25
K_2O (%)	1.94
Na_2O (%)	0.07
Specific surface area (m^2/g)	8.19
> 53 μm	< 0.1%
> 10 μm	10%
< 2 μm	39%

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