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Review article

Biological beneficiation of kaolin: A review on iron removal

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ABSTRACT

Application of mineral bio-beneficiation to remove iron oxyhydroxides from kaolinite clays has been the center of interest in recent decades, and many research works over the world have been dedicated to study the potential of this approach for upgrading the clay whiteness and refractoriness while preserving the inherent specifications and therefore improving the commercial value of kaolin. Microbial purification methods are preferred since they are environmentally benign (neither use nor release hazardous chemicals), not energy intensive, low in initial and operational costs, and they preserve the crystal structure of the clay. The present review offers the general concepts and fundamentals of the process along with an outline and critical assessment of the latest studies carried out on the biological dissolution of iron from kaolinite clays.

1. Introduction

Kaolin is a significant industrial clay that mainly contains a hydrated aluminum silicate mineral named as kaolinite ($Al_2Si_2O_5(OH)_4$) (de Mesquita et al., 1996; Murray, 2006b; Zegeye et al., 2013). Other kaolin minerals include dickite, nacrite, and halloysite. Pure forms of these minerals are not as ubiquitous as kaolinite, and are usually found along with kaolinite in hydrothermal deposits (Murray, 2006b). Kaolin may form in residual or sedimentary modes. In the former type, kaolinite is created by in-situ weathering or hydrothermal alteration of aluminosilicate parent rocks like granite; though, in the latter, the mineral is produced by the deposition of kaolinite formed elsewhere (Bloodworth et al., 1993; Zegeye et al., 2013).

Unique mineralogy, morphology, chemical and physical specifications of kaolin make it a versatile raw material appropriate for many different applications (Ryu et al., 1995; Kostka et al., 1999a; Štyriaková and Štyriak, 2000; Murray, 2006b), such as ceramic, paper coating and fillers, pigment extender in water-based interior latex paints and oil-based exterior industrial primer. In addition, kaolin is applied in non-black rubber, medicines and pharmaceuticals, cosmetics, crayons, fertilizers, detergents, pesticides, white cement, ink, catalysts, and many other products (Bloodworth et al., 1993; Ryu et al., 1995; Murray, 2006a,b). These properties are greatly affected by the mode of clay formation which controls the kaolin quality through varying the kaolinite and impurity contents. For instance, kaolinite content of the residual and sedimentary kaolins differs from 20% to 60%, respectively (Bloodworth et al., 1993). High quality kaolins are also low in iron-bearing minerals.

The existence of iron oxides in kaolin adversely affects the clay color, and reduces its brightness and refractoriness (Ryu et al., 1995; de Mesquita et al., 1996; Lee et al., 2002; Mockovčiaková et al., 2008). These cause a dramatic decrease in its commercial price (Guo et al., 2010). Even an amount of 0.4% of oxides, hydroxides and hydrated oxides of ferric iron may be enough to impart a red to yellow pigmentation to clay deposits. These iron oxide/hydroxides may be hematite (red), maghemite (reddish brown), goethite (brownish yellow), lepidocrocite (orange), ferrihydrate (brownish red), etc. (Ambikadevi and Lalithambika, 2000). Similarly, iron ores such as hematite may contain clays like kaolin as contamination which cause problems in the operation of blast furnaces. Therefore, the first beneficiation step to make these raw materials commercially valuable is to effectively eliminate iron oxides from kaolinite clays and vice versa (Poorni and Natarajan, 2013).

The iron removal processes can be categorized as physical, chemical, or a combination of both (Prasad et al., 1991; de Mesquita et al., 1996). Physical approaches include intense magnetic separation which is able to remove iron and titanium impurities, gravity separation, and hydrocyclones (Prasad et al., 1991; de Mesquita et al., 1996; Guo et al., 2010; He et al., 2011). Chemical methods involve leaching the iron content of clay by organic and inorganic acids such as oxalic, citric or hydrochloric acid (Prasad et al., 1991; Ambikadevi and Lalithambika, 2000; Musiał et al., 2011), and reductive leaching by potent reducers, like sodium dithionite plus aluminum sulfate, sulfur dioxide plus aluminum or zinc powder, sodium formaldehyde sulfoxylate, hydroxyl ammonium acid sulfate, and hydrazine (de Mesquita et al., 1996; Ambikadevi and

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Lalithambika, 2000; Štyriaková et al., 2003; Stucki, 2013; Zegeye et al., 2013). Also, combined remediation processes are froth flotation and flocculation (Prasad et al., 1991; Lee et al., 2002; Guo et al., 2010; He et al., 2011).

Among the above mentioned approaches, the reductive leaching of iron from kaolins is more useful and results in a significant removal of iron (Prasad et al., 1991; de Mesquita et al., 1996; Zegeye et al., 2013); however, it destructs the crystal structure of the clay and also, lessens the organic component of kaolin, which affects the clay plasticity and refractoriness (Kostka et al., 1999a; Lee et al., 2002; Andrade et al., 2011). On the other hand, these bleaching methods are high in capital and operating costs (Lee et al., 2002), require complex operating conditions (de Mesquita et al., 1996), and are environmentally hazardous (Guo et al., 2010).

Hence, in order to dispose of these technical, environmental, and economic problems, physical and chemical techniques should be substituted by biological methods (Ryu et al., 1995; Chen and Lin, 2010) which are supposed to play a trivial role in iron mobilization from clay minerals in nature. Iron oxide existence in kaolin is biologically induced, so it is better to apply a biological process for removing it from clays by exploiting microorganisms (Poorni and Natarajan, 2013). Interaction of microbes with clay minerals conserves the clay structure, fertility, and chemistry of the soil through the cation exchange and pH buffering (Kostka et al., 1999a). This also greatly affects the mineral weathering, degradation of organic material, development of aggregates, and the mobility of a wide variety of elements (Jiang et al., 2007) that cause microorganisms to be applied for several purposes such as valuable metal extraction, heavy metal removal from wastes to prevent environmental pollution, and beneficiation of industrial minerals (Kostka et al., 1999b; Cameselle et al., 2003).

Bio-beneficiation processes are more efficient in comparison to chemical routes, because they are environmentally benign as they neither use nor release hazardous chemicals, not energy intensive for they operate at room temperature, low in initial and operational costs, and to a large extent, maintain the crystal structure of clay.

In the present study, initially, the general concepts and fundamentals of the biological removal of iron from kaolinite clays are described, and then the literatures and findings published on this subject in the past two decades are concisely reviewed and assessed.

2. Iron impurities in clay minerals

Iron (Fe) comprises about 6% of the earth's mass, and therefore is the fourth most abundant element in the world after oxygen, silicon, and aluminum (Dong, 2012; Stucki, 2013). Biotite, pyroxene, amphibole, olivine, ilmenite, magnetite, and pyrite are the most important iron bearing minerals in soils which in all of them, iron is predominantly in bivalent state (Cornell and Schwertmann, 2004). Weathering causes the release of Fe^{II} from rocks and formation of Fe^{III} oxide/hydroxides which move through the crust mechanically or via complexation/reduction by organic compounds and microbes, and then mix with clay silicates by precipitating and coating soil grains or scatter throughout the bulk of the clay as a separate phase (Ambikadevi and Lalithambika, 2000; Cornell and Schwertmann, 2004; Štyriaková et al., 2012; Stucki, 2013). Also, iron may present in clays as structural style either in oxidized form bound the aluminosilicate lattice in both the octahedral and tetrahedral sheets or as a compensating iron ion which substitutes for aluminum in silicate structure (Štyriaková and Štyriak, 2000; Mockovčiaková et al., 2008; Štyriaková et al., 2012; Stucki, 2013). Iron oxide formation varies with the changing water and air content of soil. For example, hematite may be found as coatings at the dry surface of rocks, whereas goethite can occur near moist cracks or plant roots (Cornell and Schwertmann, 2004; Murray, 2006a). The higher the pH of the environment, the greater the iron oxidation rate, and depending on the type, maturity, and iron content of the parent rock, iron content varies between less than 0.1% to several 10% (Cornell and Schwertmann, 2004). Reduction of structural iron affects the swelling, cation exchange capacity, specific surface area, color, and magnetic exchange interactions. It also, causes the clay layers to collapse and trap cations in the mineral matrix, which makes the valuable nutrients unavailable for agricultural purposes (Xie and Walther, 1992; Kostka et al., 1999b; Stucki, 2013).

3. Biological leaching

Bioleaching processes are based on the ability of microorganism or their metabolites to transform solid compounds into soluble and extractable elements which can be recovered, subsequently. The following is a brief history of kaolin bioleaching using different kinds of bacteria and fungi.

3.1. Fungi

Fungi which are used in leaching processes must be able to excrete considerable amounts of organic acids and be resistant to heavy metals. Generally, fungi acidify the environment during growth because of the excretion of protons via the proton trans-locating plasma membrane, absorption of nutrients in exchange for protons, excretion of organic acids, and the carbon dioxide production by their respiration (Burgstaller and Schinner, 1993). This acidic medium and the metabolites contribute to biological solubilization of metal compounds through protonation (acidifying), complexation, or reduction (Burgstaller and Schinner, 1993; de Mesquita et al., 1996; Cornell and Schwertmann, 2004). A fungus may also accumulate the metal ion from the solution and cause metal detoxification. In the first mechanism, the oxygen atoms covering the surface of a metal compound are protonated and the metal then detaches from the surface. In complexation, a metal ion is solubilized by forming a soluble complex with a chelating molecule like oxalic or citric acid (Burgstaller and Schinner, 1993; Ambikadevi and Lalithambika, 2000; Saikia et al., 2003; Hernández et al., 2013). This is the most important characteristic of fungal leaching processes as the ultimate purpose of leaching is to extract metal ions in dissolved form. Additionally, reduction may also happen as reducing ferric iron or manganese to more soluble Fe^{II} or Mn^{II} by oxalic acid which is biologically excreted to the culture medium (Burgstaller and Schinner, 1993; de Mesquita et al., 1996; Cornell and Schwertmann, 2004; Lovley et al., 2004).

Among the microorganisms of interest, the fungus *Aspergillus niger* is often favored as the most efficient species producing oxalic acid (Mulligan et al., 2004; Hosseini et al., 2007; Musiał et al., 2011; Zegeye et al., 2013). The maximum oxalic acid production from saccharides by this fungus is obtained by setting the pH in the range of 6 to 7, but when the pH is lower, citric acid is dominant (Cameselle et al., 1998; Musiał et al., 2011). Application of oxalic acid produced by fungi for the dissolution of iron impurities from kaolinite clays has been the subject of many experimental research works which are summarized in Table 1. These experiments have been generally conducted in two forms of “in-situ” or “two-stage”. When the process is done in-situ, microbial growth and bioleaching proceed simultaneously that means microorganisms metabolize in the presence of clay; however, in the two-stage style, fungal fermentation is performed firstly, then the clay bioleaching stage is carried out using the metabolites separated from the fungal cells.

The idea of the presence of kaolin in the growing cultures (in-situ bioleaching) affects negatively both fungus development and active metabolite secretion. In contrast, two-stage bioleaching makes it possible to perform the process at higher temperatures which are not tolerable for the microorganisms in an in-situ approach. Therefore, applying a full factorial designs, Cameselle et al. (2003) tried to make a comparison between the kaolin bleaching efficiency through in-situ and two-stage processes by two different strains of *A. niger*, CBS 246-65 which had been used previously (Cameselle et al., 1995), and