Iron removal from a kaolinitic clay by leaching to obtain high whiteness index

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Abstract

Beige kaolin clays were crushed and sieved. The mineral was characterized by X-ray diffraction and chemically analyzed by atomic absorption spectrophotometry. The material below 37 microns was leached with oxalic acid. A study of main variables of the leaching process in different ranges was realized: time (0 to 120 min), temperature (25 to 100 °C) and acid concentration (0.01 to 0.5 M). Crystallographic analysis of the initial sample indicates the presence of kaolinite, iron oxides in the form of magnetite and iron-titanium oxides. By this method it was possible to obtain iron extraction percentages over 80% and whiteness index above to 90%.

Keywords: clays, kaolin, leached, oxalic acid.

1. Introduction

At present, kaolin minerals is a commonly used in the ceramics industry as raw material in various applications because of its refractory cement, glass fiber, etc. Also is widely used in other industries such as paint, paper, pesticides, pharmaceuticals and cosmetics (1).

Many parameters influence the industrial use of kaolin especially its impurities as these largely determine the quality of kaolinitic minerals, affecting negatively their thermal and optical properties (2, 3, 4). For example, amounts as low as 0.4% iron (ferric) may be sufficient to impart color to the clay deposits and reducing their refractoriness and whiteness. Some specific physical and chemical properties of kaolin depend on its geographical source and methods of their processing, (1, 6), within which is the leaching, which is based on the removal or reduction of iron oxides, resulting concentrates that can be competitive kaolinitic up with finer kaolin, of higher purity than the kaolins Chinese (1, 5, 6). The leaching of iron from the red clay of kaolin is important for the following reasons: (a) You can find application in the production of refractory materials, (b) it is possible to recover items such as nickel, cobalt and chromium, (c) can be exploited to produce alumina as the Bayer process, or to produce anhydrous aluminum chloride (7).

Some previous studies have reported the leaching of kaolin with various chemical reagents, such as oxalic acid and other organic acids (7, 8, 9), in the presence of a fermented medium, bioleaching (4, 5, 10), etc., And all them in order to reduce the iron content. Even in some it has been observed that has received considerable attention mechanism studies with synthetic minerals such as hematite, goethite and magnetite ignoring the complex interactions that can be set in the dissolution of iron from industrial minerals, as bauxite, kaolin, silica and feldspathic sands (8).

The Hidalgo state in the municipality owns the Agua Blanca Iturbide there is a large deposit that is not exploited or benefit properly, for these reasons it is necessary to provide research results based on an increase in the quality (purity) of mineral giving it an added value.

Therefore, it is considered that the data obtained from the leaching of iron from oxalic acid kaolinitic clays are important for the diversity of its potential industrial applications, which is why this paper presents the study of kaolin ore leaching with in order to obtain the experimental conditions such as temperature and concentration of oxalic acid, leading to a high mineral white kaolin with low iron content.
2. Material and methods

2.1 Material
The kaolin simple was (samples of particle size averaging 35µm) collected in the municipality of Agua Blanca de Iturbide, Hidalgo (México), with iron oxide content of 0.70% and a whiteness index of 87.80%, which was previously reduced in size and classified by ASTM mesh. In order to know the mineralogical composition, chemical and whiteness index of the samples of kaolin were used techniques X-ray diffraction (INEL mod. Equinox 2000), atomic absorption spectrophotometry (Perkin Elmer Co., Mod 2380 ) and reflectance spectrophotometer (GretagMacbeth, eye color model XTS).

2.2 Experimental procedure
The leaching tests were carried out in a round bottomed flask (500 mL) which was kept stirred in a heating mantle, For each run, 400 mL of oxalic acid solution (C$_2$H$_2$O$_4$, reagent grade) at different concentrations (0.01, 0.10 and 0.5 M) were added to the flask and the temperature was set to the desired value. Then, 40.0 g of clay was added to the flask while under 600 rpm magnetic stirring. Periodically (5, 15, 30, 60, 90 and 120 min), a 10 mL sample was taken from the leach slurry and was centrifuged immediately at 300 rpm during 15 min. A clear 5 mL aliquot of the solution was collected for total iron determination. All leaching tests were made at atmospheric pressure. In all experiments used a solid:liquid ratio of 10 g of kaolin and 100 mL of leaching solution. Experiments were done in duplicate. The variables studied were the concentration of oxalic acid (0.01, 0.10 and 0.50 M) and temperature (25, 40, 60 and 100 °C).

3. Results and discussion
The results of the mineralogical and chemical analyzes are shown in Figure 1 and Table 1, respectively. Was identified that the kaolinite (JCPDF 08956538) and silica in the form of quartz (065-0466) and tridymite (076-0894), are the main constituents. The iron is considered as an impurity and is present as magnetite (089-0951), hematite (089-2810), Di-iron titanium oxides (074-2084) and greigeite (089-1998).

![Image](image-url)

Figure 1. X-ray diffractogram of: a) kaolin ore with average particle size 35 µm. b) Leached kaolin.

Table 1. Chemical analysis of the sample of kaolin.

| Component  | Wt % |
|------------|------|
| SiO$_2$    | 65.00 |
| Al$_2$O$_3$| 27.00 |
| Fe$_2$O$_3$| 0.70  |
| CaO        | 0.40  |
| MgO        | 0.57  |
| Na$_2$O    | 2.65  |
| K$_2$O     | 2.42  |
| TiO$_2$    | 0.67  |
| LiO*       | 0.95  |

LiO* = Loss on ignition

It is important to make this identification because in several studies (2, 7, 8, 9, 11) has reported the dissolution of magnetite and greigeite using oxalic acid. In this regard, Mandal, S. K. and Banerjee (13), reported that the dissolution of the hematite is much slower than for the other magnetite and hydrated iron oxides such as goethite (α-FeOOH) and lepidocrocite (γ-FeOOH); and suggest the use of different chemicals and experimental conditions to explain the mechanism of dissolution of hematite and magnetite. Many researchers (2, 7, 8, 10) have shown that this acid is most efficient for the dissolution of iron in clay minerals. Moreover, being an organic compound is not aggressive to the environment. Fig. 1 shows the decrease of the peaks corresponding to the reflections of magnetite and hematite for (a) ore kaolin and (b) leached kaolin.
In solution, oxalic acid (H$_2$C$_2$O$_4$) dissociates releasing the bi-oxalate ion (HC$_2$O$_4^-$):

H$_2$C$_2$O$_4$ → H$^+$ + HC$_2$O$_4^-$ \[1\]

For its part, the bi-oxalate ion formed dissociates releasing the oxalate ion (C$_2$O$_4^{2-}$):

HC$_2$O$_4^-$ → H$^+$ + C$_2$O$_4^{2-}$ \[2\]

Of these species, it is considered that the bi-oxalate is responsible for the dissolution of the iron:

Fe$_2$O$_3$ + H$^+$ + 5HC$_2$O$_4^-$ → 2Fe(C$_2$O$_4$)$_2^{2-}$ + 3H$_2$O + 2CO$_2$ \[3\]

Therefore, the conditions in the medium should be suitable leachant for favoring the prevalence of HC$_2$O$_4^-$ ion. Reason it is important to evaluate the temperature and concentration of oxalic acid.

3.1 Effect of acid concentration

Figure 2 shows the dissolution of iron (%) versus time at 100 °C, using various concentrations of oxalic acid (0.01, 0.10 and 0.50 M), is observed that the dissolution of iron is increased as the concentration of oxalic acid in the range 0 to 120 minutes. Obtaining a maximum rate of dissolution of 98 % at a time of 2 hours. This behavior is attributed to increasing the acid concentration increases the concentration of oxalate and hydrogen ions. That is, with the increase in the amount of oxalate ion favors the formation of bi-oxalate (see reaction 2), which is the species responsible for the extraction of iron and increased the hydrogen ions which has a direct influence on the pH. That coincides with that reported by Ambikadevi and Lalithambika in 2000 that found that oxalic acid was the best acid for the dissolution of iron (which unlike this work was in the form of goethite and hematite) of a kaolin mineral and to increase the acid concentration (0.05 to 0.15) increases the efficiency of iron dissolution (2).

![Figure 2](image1.png)

Figure 2. Iron extraction at 100 °C versus time at different concentrations of oxalic acid.

3.2 Effect of reaction temperature

In Figure 3 presents the percentage of iron dissolution versus time, at a concentration of 0.5 M oxalic acid at various temperatures (25, 40, 60 and 100 °C). It is observed that the extraction of iron increases with increasing temperature in the range of 0 to 120 minutes. That is, the dissolution of iron with oxalic acid has to be thermally activated to be efficient. This, on the other hand, is an indicator that the system exhibits a chemical control. Similar results for kaolinitic minerals have been reported by several authors as Mandal and Banerjee (13) and Lee et al, (11, 12). Figure 4 shows the results of the percentage of iron removed, and the ratio or percentage of whiteness obtained at a concentration of 0.50 M oxalic acid at 100 °C. Can see that the whiteness index increases in the same way that increases the dissolution of iron ore, yielding a maximum whiteness index of 93.55% at a time of 2 hours. Confirming that a lower percentage of iron oxides, the whiteness index increases.

![Figure 3](image2.png)

Figure 3. Iron extraction with oxalic acid [0.50 M] versus time at different temperatures.
4. Conclusions

This study found that using oxalic acid as a leaching agent at a concentration of 0.50 M and 100 °C in a time of 2 hours was possible bleaching kaolin clays from the municipality of Agua Blanca de Iturbide, Hidalgo (Mexico), obtaining iron extraction percentages of 98% and a whiteness index of 93.55%. Oxalic acid concentration and temperature markedly influenced the rates of dissolution and the whiteness index of the mineral studied.

References

[1]. Murray, H. H. 2000. “Traditional and new applications for kaolin, smectite, and palygorskite: a general overview”, Applied Clay Science., vol. 17, pp. 207-221.
[2]. Ambikadevi., V.R., Lalithambika., M. 2000. “Effect of organic acids on ferric iron removal from iron-stained kaolinite”, Applied Clay Science., vol.16, pp. 133-145.
[3]. Chandrasekhar, Sathy, Ramaswamy, S., 2002. “Influence of mineral impurities on the properties of kaolin and its thermally treated products”, Applied Clay Science., Vol. 21, No.3-4, pp. 133.142.
[4]. Eun-You L., Kyung-Suk C., 1999. “Microbial removal of Fe (III) impurities from clay using dissimilatory iron reducers”, Bioscience and bioengineering, Vol. 87, No.3, pp. 397-399.
[5]. Lee Eun-Young, Cho Kyung-Suk., Ryu Hee Wook. 2002. “Microbial Refinement of Kaolin by iron-reducing bacteria”. Applied Clay Science, Vol. 22, pp. 47-53.
[6]. Saikia, N.J., Bharali, D.J., Sengupta, P., Bordoloi, D., Goswamee, R.L., Saikia, P.C., Borthakur, P.C., 2003. “Characterization, beneficiation and utilization of a kaolinite clay from Assam, India”, Applied Clay Science, Vol. 24, pp. 93-103.
[7]. Veglio F., Toro L., 1994. “Process development of kaolin pressure bleaching using carbohydrates in acid media”. Mineral processing, Vol. 41, pp. 239-255.
[8]. Veglio, F., Passariello, B., Toro, L., Marabini, A. M., 1996. “Development of a bleaching process for a kaolin of industrial interest by oxalic, ascorbic and sulphuric acids; preliminary study using statistical methods of experimental design”, Ind. Eng. Chem. Res., Vol. 35, pp. 1680-1687.
[9]. Groudev, S. N., 1999. “Biobeneficiation of mineral raw materials”. Miner Metall. Process., Vol. 16, no.4, pp 19-28.
[10]. De Mesquita, L.M.S., Rodríguez, T., Gomes, S.S, 1999. “Bleaching of brazilian kaolins using organic acids and fermented médium”. Miner. Eng., Vol. 9, No.9, pp. 965-971.
[11]. Sung Oh Lee, Tam Tran, Byoung Hi Jung, Seong Jun Kim, Myong Jun Kim 2007. “Dissolution of iron oxide using oxalic acid”. Science Direct Hydrometallurgy, No. 87, pp 91-99.
[12]. Ayala Perez G., Z., Vargas Rodríguez Y., C., Córdoba Tuta E., M., 2010. “Beneficio de una arcilla caolínítica de la región de Barichara (Santander) para la fabricación de refractarios”. Dyna No. 164, pp. 29-38.
[13]. Mandal, S. K. and Banerjee, P. C. 2004. “Iron leaching from China clay with oxalic acid: effect of different physicochemical parameters”, Int. J. Miner. Process, Vol. 74, pp. 263-270.