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Research paper

Characterization and electrochemical treatment of a kaolin

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ABSTRACT

In this work, studies on characterization and electrochemical treatment of kaolin from the municipality of Agua Blanca, Hidalgo, Mexico were carried out, in order to identify its properties and establish the operating conditions for an electrochemical purification treatment. Different characterization techniques were used in order to quantify this clay characteristics, such as X-ray diffraction, scanning electron microscopy, analysis of the whiteness index, particle size, FTIR, Induced Coupled Plasma Spectroscopy, Z potential, cyclic voltammetry, chronopotentiometry and chronoamperometry. This study shows that the tested clay had a high content of kaolinite, but also impurities, such as: quartz, iron oxides, and titanium oxides. These impurities have an influence on the surface charge of the kaolin particles and therefore on their properties. The clay with a heat treatment exhibited a thermal behavior characteristic of this type of clays. The particle size range was between 0.5 and 100 μm with an average particle size about 15 μm. The voltammetry study revealed that a reduction processes occur in a range of 0.07 to − 1.2 V (E *vs.* SCE) and, when a cell potential of 3.3 V for 24 h was imposed, there was a decrease of about 43% in the amount of iron oxides present in the ore. This reduction was of particular significance for the cleaning process.

1. Introduction

Nowadays, supplementary cementitious materials (SCMs) such as the metakaolin (amorphous material obtained after kaolinite dihydroxylation) (Wianglor et al., 2017) are a focus of attention in the alternatives to the Portland cement (PC) and this is a dehydroxylated form of kaolin. The main application of kaolin is in the manufacturing of ceramics and cement, but this versatile clay have been used for the manufacturing of many different products, such as paints, pharmaceuticals, cosmetics, rubber, plastics, water treatment, substrate for catalysis, mortar and concrete, and others (Murray, 2006; Nandi et al., 2009; Peter et al., 2015; Roy et al., 2015; Siddique and Klaus, 2009). Nonetheless, naturally occurring clays are very sandy and have different impurities (SGM, 2014), which represent important disadvantages. Thus, in order to be useful, clays and particularly kaolin and metakaolin requires a low amount of impurities (Murray, 2000). Therefore, a complete characterization study of the clays for specific applications is very important in order to know its properties and the ranges of composition for the different impurities.

The characterization, benefit, and purification of kaolin have been widely investigated. Purification techniques has been described in numerous works with the main aim of the diminishment of iron oxides (Aghaie et al., 2009; Asala et al., 2016; Cao et al., 2016; González and Ruiz, 2006; Martínez-Luévanos et al., 2011; Murray, 2006; Ondruška et al., 2015; Saikia et al., 2003; Taran and Aghaie, 2015; Xia et al., 2012), where leaching, flotation, flocculation and high-intensity magnetic separation were the most widely used techniques (Murray, 2006). Only some authors have studied the properties using unconventional techniques, such as: electroremediation, bioremediation and bioleaching (Aghaie et al., 2012, 2009; He et al., 2011; Hosseini and Ahmadi, 2015; Pazos et al., 2010, 2006; Wang et al., 2006; Zegeye et al., 2013), with important results. However, these techniques have a low efficiency as well as the need for further studies and sometimes require to carry out some post-treatments. Among electrochemical techniques, electrolysis is relevant due to its selectivity used in reduction and deposition of oxidized metal species.

There is a deposit of clay in the region of Agua Blanca de Iturbide, located to the East of the State of Hidalgo, Mexico, which extends to the municipality of Huayacocotla, Veracruz, Mexico. This site is the largest deposit of kaolin in the region. This work shows the use of electrolysis

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as an alternative treatment for iron reduction and consequently the purification of kaolin. Samples used in this work were collected from that region of México.

2. Materials and methods

2.1. Kaolin materials

Kaolin samples were from the mines of the municipality of Agua Blanca de Iturbide, Hidalgo, Mexico, which have been marketed by the company *Molinos y Moliendas de Pachuca S.A. de C.V.*, were studied. In this work, this kind of samples was denominated **BGK** (for "Beige Kaolin"). Also, for comparison purposes, a food-grade kaolin commercialized by *J.T. Baker*, was studied. This kind of samples was denominated **PK** (for "Pharmaceutical Kaolin").

2.2. Instrumental techniques

X-ray diffraction studies were performed with an Inel diffractometer, *EQUINOX 2000*, with a Co Kα1 radiation source and a Ge monochromator. The powdered samples were about 0.6 g for each measurement and were placed in a spinning sample holder. They were heat treated for 2 h in a furnace at 120 °C. The morphologies of the samples were observed by a Scanning Electron Microscope, model *Jeol* JSM-6300. For studying the whiteness index a spectrophotometer *Gretag Macbeth*, *ColorEye XTS* was used with its software for analysis of the data. To study reflectance a *Color IQC* equipment of the same brand was used. For particle size analysis, each sample was processed through scanner laser beam diffraction, *Beckman Coulter*, LS13320 model. Chemical analysis was carried out with a *Perkin-Elmer* spectrometer *Optima 3000XL*, ICP-OES; for this study, samples were previously digested in an acid medium of HF and H_3BO_3. For the measurements of Z potential (ζ), the samples were diluted in deionized water, setting the pH values between 1 and 11 by the controlled addition of HNO_3 and NH_4OH. For this study, a *Malvern International* analyzer, 3000Hsa, was used. The IR spectra study was performed with a *Perkin–Elmer System 2000 FTIR spectrometer*, as KBr pellets, 4000–400 cm^{-1} range and a resolution of 4 cm^{-1}. Cyclic voltammetry and electrochemical techniques were applied with a potentiostat-galvanostat *Princeton Applied Research* model 263A, and a typical three-electrode cell. The electrodes used were as follows: the working electrode was a plate of silver 99.9% of purity; a graphite bar as the counter electrode and as the reference a Calomel electrode (SCE).

3. Results and discussion

The diffractograms of the kaolin samples tested are shown in Fig. 1. In both samples, peaks of kaolinite (JCPDS 80-0885) were present. However, the non-basal PK sample peak intensities may be affected by preferential orientation of the sample and they are greater and better defined than the peaks of the BGK sample. This difference may be due to the impurities of the BGK sample, which were identified as quartz (JCPDS 45-0131), titanium-ferrous oxides (JCPDS 80-1213) and iron oxide (JCPDS 76-0955).

The presence of impurities in the BGK sample, iron generally, is the main cause of its pigmentation and this can be observed in its whiteness index, which was measured as 89.7%. The PK sample showed a whiteness index of 94.5%.

The presence of impurities was corroborated by means of chemical analysis ICP–OES as shown in Table 1 (Huang et al., 2009; Dogan et al., 2012). BGK sample had a high content of alumina and silicon oxide. The last was present in a higher amount than expected since the theoretical composition of kaolin is about Al_2O_3 39.50%, SiO_2 46.54% and H_2O 13.96% (Murray, 2006). Based on the XRD and ICP results, it was determined that the excess of SiO_2 was present in the form of quartz crystals. Also, the BGK sample presents a high amount of iron oxide and

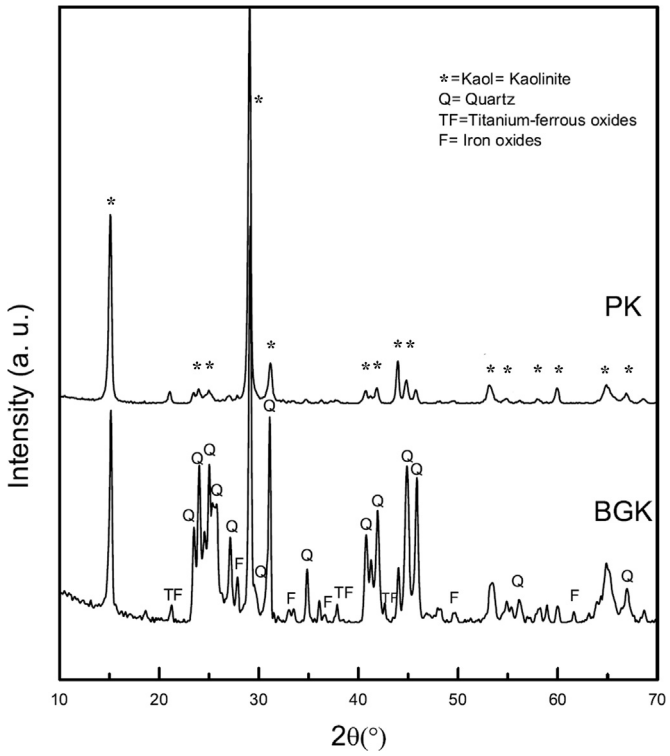

Fig. 1. Diffractograms of the BGK and PK samples.

Table 1
Chemical composition of kaolin samples: food-grade (PK) and mined (BGK inlet and BGK outlet).

	Al_2O_3 (% wt)	SiO_2 (% wt)	Fe_2O_3 (% wt)	TiO_2 (% wt)
PK	40.38	43.91	0.92	0.1
BGK inlet	35.17	47.71	1.89	1.1
BGK outlet	34.92	42.84	1.08	1.03

titanium oxide. Similarly, in the PK sample was observed the presence of iron. This can be found in some species that do not provide color to the clay since this sample was white. In the PK sample, we confirmed the presence of titanium and that the SiO_2 content was lower than in the BGK sample.

The study of Z potential for both kaolin samples, displaying negative potentials in almost all the pH scale (Fig. 2). These results show that the surfaces of the kaolin particles, similarly to other types of clays, were mainly negatively charged (Vaccari, 1998; Méndez et al., 2014; Uddin, 2017). On the other hand, since iron and titanium are hydroxo complexes for pH values lower than 3, they could modify the net charge causing the isoelectric point to be at higher pH values. This behavior is typical of this type of clays (Au and Leong, 2013). This was confirmed finding the isoelectric point of the BGK sample at pH 2.38, while that of the PK sample was located at pH 1.53.

Fig. 3 shows the FTIR spectra of BGK and PK samples. These spectra show the characteristic bands of kaolinite. In the region between 3800 and 3600 cm^{-1}, corresponding to OH stretch, were four bands at 3695, 3670, 3653, 3620 cm^{-1} (Liu et al., 2014; Cheng et al., 2016). Moreover, in the region corresponding to Si—O, between 1000 and 1120, there were sent bands at 1115, 1033 and 1004 cm^{-1} in the PK sample. However, in the BGK sample we found another band at 1088 cm^{-1}, this can be attributed to the presence of a different Silicon compound in this sample. Finally, in the region corresponding to the Al-OH vibration were two bands at 938 and 912 cm^{-1} (Rahier et al., 2000). The obtained values were similar those reported by Franco et al. (2004). Therefore, ensuring that the BGK sample showed a spectrum which