Successive Methods for the Separation of Titanium Oxide from the Black Sands of Ecuador

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ABSTRACT

The black sands found on certain Ecuadorian beaches present a high ilmenite contents up to 50%. In this work, TiO_2 was obtained from the black sands of Muisne beaches – Ecuador by combining the thermal, chemical and ion exchange treatments. For the thermal treatment, the raw material was smelted at temperature of 1100 °C using a basic flux. Subsequently, the chemical treatment was initiated in the presence of Fe^0 metal using chemical digestion with HCl, and the sample was purified by separating the precipitates from a series of reactions developed at different pHs with NH_4OH, Na_2S and HCl. The final effluent resulting from the last HCl digestion was purified by ion exchange using Amberlite IRA 400 resin of strongly anionic character. The effluent is then treated in basic medium and the resulting precipitate is calcined. The recovery yield of the TiO_2 pigment was 46% with 92% purity.

Keywords: ion exchange resin, muisne, Eesmeraldas – Ecuador, black sands, titanium dioxide

INTRODUCTION

Currently, the natural resources of titanium oxide in the form of Rutile, Anatase, Leucoxine, Perovskit, Sphene and Brookite are insufficient to cover the requirements of titanium oxide in different industrial applications, ranging from the elaboration of pigments, voltaic cells, food additives, in the pharmaceutical and cosmetic industry, as an antiseptic agent, etc. or as a constituent of the raw material for the recovery of metallic titanium (Valderrama et al. 2005, Perez and Sharadqah 2017).

The main ilmenite producers are: South Africa, Australia, Canada, China, India, Vietnam, Norway and Ukraine. These countries combined produced 5.3 million metric tons of ilmenite in 2009 (Gasques et al., 2014). This quantity is still insufficient to meet the growing demand for TiO_2, especially for the pigment industry.

Several studies have shown that the Pacific coast has large amounts of titaniferous sand (black sands), among them Ecuadorian coasts, from which ilmenite could be obtained for the recovery of TiO_2 (Martijena 1970, Trujillo and Managon 2016, Soledispa and Villacreses 1990). These sands contain variable concentrations of iron and titanium oxides, which might be bonded with other metals such as Mn, Mg, Al, V, Ca, Zr, and monazite (Dewan et al., 2010). However, in spite of the potential sources of existing in Ecuador, almost all of the TiO_2 consumed is imported. Thus, the Central Bank statistics reflect that in 2015 Ecuador spent USD 1,992,350 on the imports of TiO_2 (Trujillo and Managon 2016).

Generally, TiO_2 recovery methods involve thermal treatments, chemical extractions, or a combination of these two methods. In some cases, the ilmenite of the black sands is concentrated beforehand by magnetic separation (Valderrama et al. 2005, Valderrama 2008, Cruz-Crespo et al. 2001, Perez and Sharadqah 2017). However, previous studies have corroborated that the magnetic treatment prior to other processes does not significantly influence the concentration of the TiO_2 in the final product (Perez and Sharadqah 2017). For this reason the objectives of this work are:

- Present a modified method of TiO_2 recovery omitting the stage of magnetic concentration, applying the thermal and chemical treatments in combination with ion exchange.
- Investigate the use of this modified method using metal iron as a reducing agent in the chemical treatment, with the background that in quite high levels of yield and purity (yield 40% and 90% purity) have been obtained in the presence of metallic iron in the authors' previous work (Perez and Sharadqah 2017) and to analyze if it is possible to improve these levels by applying this modified method.

MATERIALS AND METHODS

The Esmeraldas coast presents large deposits of black sand, a raw material which could be used to obtain the TiO_2. The beaches of the canton Muisne, south of the province Esmeraldas were chosen to obtain the raw material for the present study (Fig. 1).

The treatments used for the recovery of TiO_2 are thermal, chemical and finally ion exchange; each of them will be explained as follows:

1. Thermal treatment. A basic flux for the melting of the sample at 1100°C was applied. NaOH is the most commercially used compound and was applied in proportion 1:2 in relation to the amount of raw material and flux. The sample resulting from the thermal treatment has been dif-ferentiated to two distinct bands: the pale gray color nucleus and the dark outer crust. The treatments were continued using the pale gray part in which the TiO_2 content is higher.

2. Chemical treatment (acid digestion). Acid digestion is performed in order to separate the iron contaminants. Concentrated HCl was used in the pale gray fraction of the sample product of the melting because it is richer in Na_2TiO_3 and poor in iron impurities like Fe_2O_3. Figure 3 of Perez and Sharadqah 2017 work summarizes the details of the method; with the consideration that at this stage it was only experimented in the presence of metallic iron.

3. Ion exchange and calcination. An effluent which contains the iron contaminants in the form of $FeCl^{-4}$ anionic complex was obtained from the acid digestion. For this reason, it was decided to choose the AMBERLITE IRA-400, which is a strongly anionic resin, to remove this complex. The AMBERLITE was activated with 9N HCl. The optimum flow conditions were determined by analyzing the iron content of the effluent, finally adopting a system of 2 columns and flow of 1.5 ml/min. After iron impurities were removed by ion exchange, 4% $NH_4(OH)$ was added to precipitate the amorphous titanium. This precipitate was then calcined at 900°C, thus obtaining the purified TiO_2 of rutile structures. Figure 2 shows the sequence of the combined methods employed and the principal mechanisms of chemical reactions.

Fig. 1. Location of samples in Muisne coasts – Ecuador
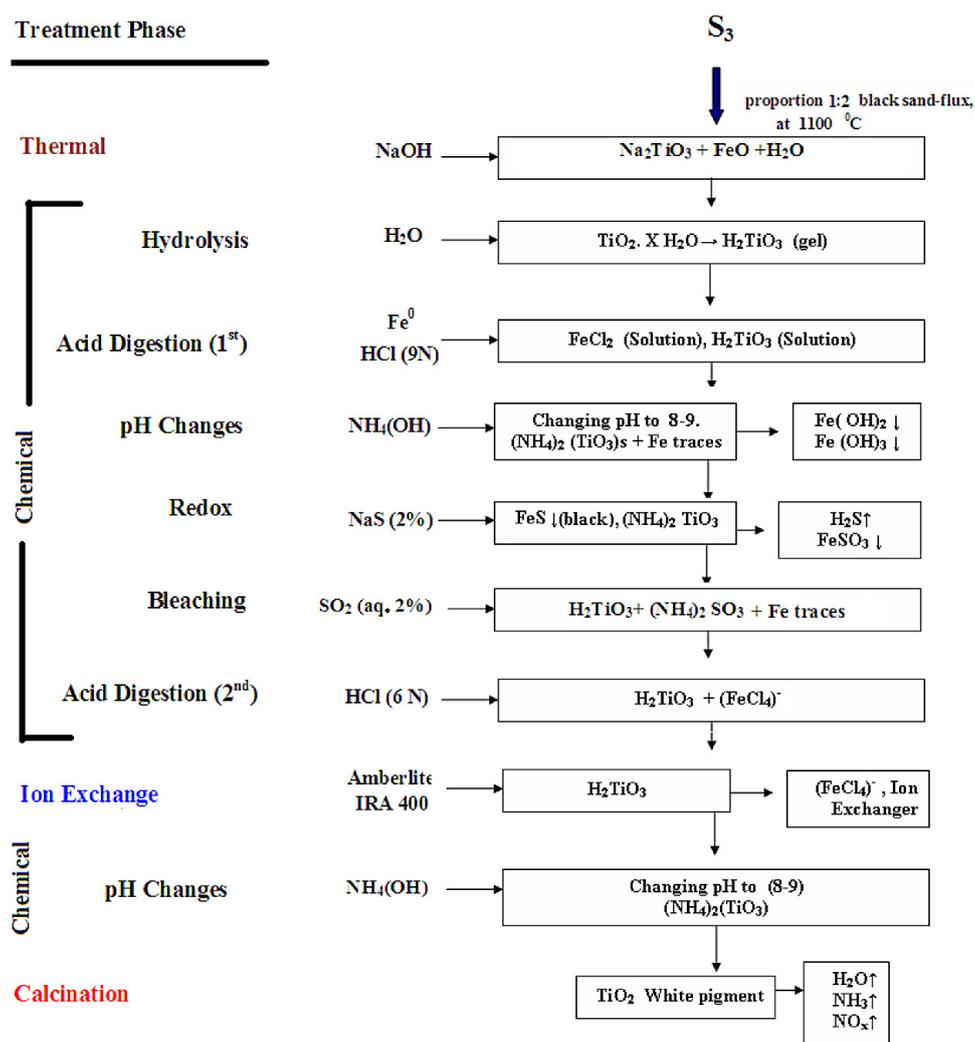
Fig. 2. The principal chemical reactions mechanisms and the experimental design sequence of the combined methods employed to TiO_2 recovery

RESULTS AND DISCUSSION

Row material

The chemical analysis of different samples of black sand from Muisne beaches is presented in Figure 3. In general, it was found that the content of TiO_2 in the raw material (black sands) ranges from 25 to 28%. By stoichiometry, the percentage of ilmenite ($FeO.TiO_2$) corresponding to the raw material for each sample is calculated, assuming that the total TiO_2 content is of the ilmenite, the average percentage of which is around 51%. Other studies in black sands in the province of Esmeraldas-Ecuador are in agreement with the data obtained in this work, (Perez and Sharadqah 2017) (Martijena 1970, Trujillo and Managon 2016). This concentration of ilmenite is quite high, but even so, it does not reach the characteristics of a concen-

trate, which should reach a percentage higher than 75% (Xiong et al., 2011). The presence of ilmenite and other iron minerals such as magnetite (Fe_3O_4) and hematite (Fe_2O_3) are confirmed by the high iron content quantified as Fe_2O_3.

The physicochemical analyses performed in 4 samples determined an average real density of 4.79 g/cm³, and an apparent density of 3.03 g/cm³, as well as the particle size of 186 μm. The average mineralogical content calculated from the results of Figure 2 shows that 26.7%, 52.24%, and 18.74% is TiO_2, iron quantified as Fe_2O_3 and SiO_2 respectively. These results are in a good agreement with the studies carried on black sand in different coasts of Esmeralda province (Trujilllo and Managon 2016, Perez and Sharadqah 2017). The sample S3 was chosen to continue the chemical treatment considering that it presents the highest percentage of ilmenite (54.1%).
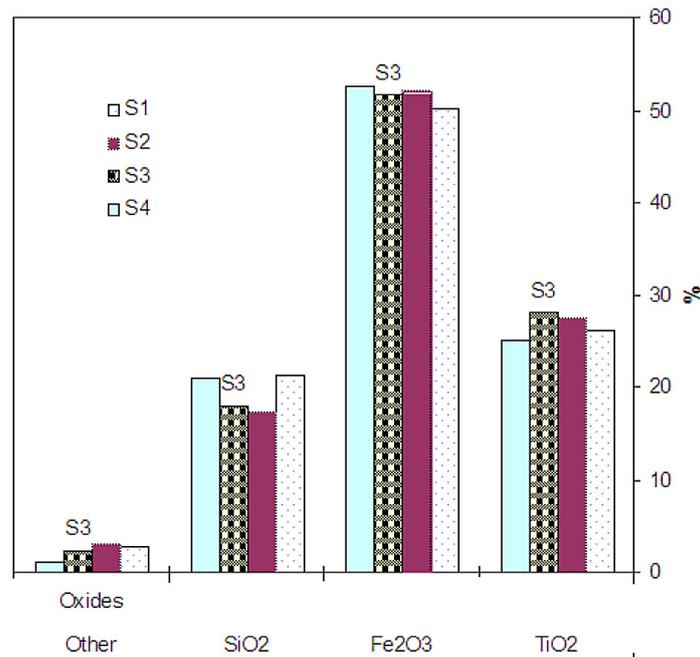
Fig. 3. Chemical analysis of four different samples (S) of black sands

Thermal treatment

The gray fraction resulting from the thermal treatment of the S3 sample was analyzed and presented a composition of 37% Iron, 30% TiO_2, 28% SiO_2 and about 5% of other compounds. Thermal treatment is recommended to remove impurities that can not be removed by conventional physical or mechanical treatments. The other black fraction also resulting from the thermal treatment had the following composition: 70% Iron, 22% TiO_2 and 8% SiO_2. Reaction (1a) and (1b) (Perez and Sharadqah 2017) synthesizes the possible components resulting from this step.

$$FeO.TiO_2 + 2NaOH \xrightarrow{1100^oC} Na_2TiO_3 + FeO + H_2O \quad (1a)$$

$$2FeO.TiO_2 + 4NaOH + 1/2O_2 \xrightarrow{1100^oC} 2Na_2TiO_3 + Fe_2O_3 + 2H_2O \quad (1b)$$
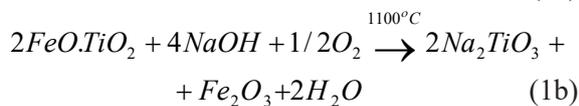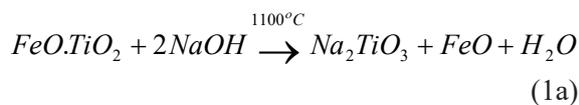
Chemical treatment and ion exchange

The gray fraction resulting from the smelting process is hydrolyzed with water to obtain the hydrated titanium dioxide ($TiO_2.XH_2O$), which has a gelatinous aspect and a chemical structure similar to the silicon compounds, because it belongs to the same family (Ayres 2017). The major reactions of this stage are the following:

$$Na_2.TiO_3 + H_2O \rightarrow TiO_2(aq.) + 2NaOH \quad (2)$$

$$TiO_2(aq.) \xrightarrow{H2O} TiO_2.xH_2O \rightarrow xH_2TiO_3(gel) \quad (3)$$
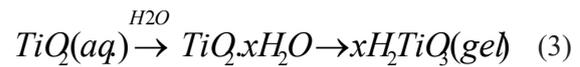
Subsequently, the acid digestion was performed in the presence of iron as the reducing agent of the titanate obtained in the previous phase with the antecedent in the presence of which better yield levels of this metal are obtained (Martijena 1970).

The above-mentioned product is treated in a basic medium and bleached with sodium sulfide as indicated by the procedure detailed in Perez and Sharadqah 2017.

The last step of the chemical treatment is a second acid digestion with HCl in which the iron traces participate in a series of reactions in contact with the chloride ions (Cl^-). The formation of the anionic $FeCl^{4-}$ complex occurs due to the following consecutive chemical reaction mechanisms (Ponn 2006):

$$FeCl_3 + H_2O \rightarrow Fe^{3+} + 3Cl^- \quad (4)$$

$$Fe^{3+} + 6H_2O \rightarrow [Fe(H_2O)_6]^{3+}(aq.) \quad (5)$$

$$[Fe(H_2O)_6]^{3+}(aq.) + 4HCl \rightarrow Fe(H_2O)_2Cl_4^- + 4H_3O^+ \quad (6)$$

$$Fe(H_2O)_2Cl_4^- + 2H^{2+} \rightarrow FeCl_4^-(aq.) + 2H_3O^+ \quad (7)$$
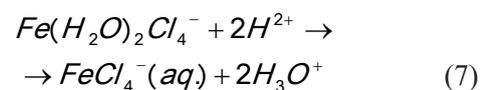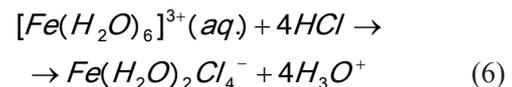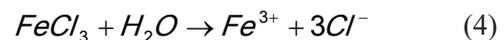
The $FeCl^{4-}$ anionic complex is retained in the Amberlite Ira-400 resin, which is evidenced with a clear yellow to transparent color change of the exchange column effluent. The degree of iron reten-

tion in the column was quite high, since the chemical analysis of the effluent before and after the ion exchange was 3522 ppm and 41 ppm Fe_2O_3, respectively. This result is in a good agreement with previous works (Perez and Sharadqah 2017).

From the ion exchange, an iron-free solution is obtained, which is brought to the pH between 8 and 9 in order to precipitate $TiO_2.XH_2O$ in this medium. The precipitate is a white solid that is subsequently subjected to calcination at a temperature of 900°C to reach rutile structures. The purity of TiO_2 after this calcination stage is 92%. The obtained yield is 46% of all the titanium content in the raw material. This recovery level is higher than what was achieved in other studies (Perez and Sharadqah 2017, Trujillo and Managon 2016). Taking into the account that this methodology just considers one portion of the complex resulted from the smelting process, the results become more satisfactory.

The percentage of the recovered titanium in this study is slightly higher than what achieved by Perez and Sharadqah (2017); however, in that study, the authors applied more treatments and longer procedure. This was essentially due to poor efficiency of magnetic separation in that study.

CONCLUSIONS

1. The composition of the black sands of Muisne were basically ilmenite, iron oxide, quartz and various types of silicates, such as pyroxene, olivine, leucoxene, amphiboles, epidote, zircon and cinnabar.

2. The presence of the basic NaOH flux in a 2:1 ratio in the sample melted at 1100°C actually plays an important role in the first stage of separation of the iron impurities from the ilmenite.

3. The combination of the thermal treatment with acid digestion in the presence of metallic iron and subsequent ionic exchange, reflects a remarkable improvement in relation to the previous methods that additionally carry magnetic concentration. This means that the magnetic separation is not really relevant to the recovery of titanium and the application of this combined method achieves better levels of purity and yield of TiO_2 (92% purity and 46% TiO_2).

4. The high retention capacity of the iron complex by Amberlite Ira 400 resin is 99%. This facilitates achieving high purity levels of 92% of the TiO_2 pigment.

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