Industrial Use of Brazilian Bentonite Modified by Mild Acid Attack

C.G. Bastos Andrade, D.M. Fermino, M.G. Fernandes and F.R. Valenzuela-Diaz

Abstract Treatments with high concentration solution of inorganic acid at temperatures under boiling point are a usual method for clay minerals structure modification. For many industrial uses bentonites must be cleared of impurities. In the present paper, a sample of Brazilian bentonite from Vitoria da Conquista, Bahia was modified by mild acid attack using hydrochloric acid under moderate conditions (90 °C, reaction times of 1, 6, 12, 18 and 24 h in close reactor, concentration of the aqueous solution of hydrochloric acid 1.5 M, acid solution/clay ratio of 1 g/10 mL). The attacked samples were characterized by CEC, XRF, SEM, EDS and Stereomicroscopy. The purpose of these attacks is to reduce the concentration of impurities with minimal damage in clay minerals structure. The modified bentonite presented good results and tends to be a good economic and environmental alternative to manufacturing products with high added value such as polymer/clay nanocomposites, cosmetics and medicines.

Keywords Bentonite · Clay · Industrial use · Mild acid attack

Introduction

The Brazilian bentonite from Vitoria da Conquista, Bahia´s State, is a smectite clay naturally calcic, containing low iron concentration and presenting a green color [1–3].

The classification of bentonites is determinate according the geologic origin of clay, but if the smectite clays presents the same properties of traditional bentonites and/or is commercialized to the same use, those clays, by a common agreement, can be classified as bentonites, which presents similar properties such as colloidal material, absolving capacity and activation capacity with high grades [2–5].

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The bentonite products are vast, mostly with medium added value. For example, mineral binders and foundry molds, drilling fluids and adsorbents. In last case is used an activated clay with strong acid. To industrial application, bentonites must be cleaned of mineral impurities. Strong acid attack is a common method that provides a good cleaning of mineral impurities. Other benefit of acid attack is improving of acid sites with more porosity, excellent properties when apply in catalysis [6–11].

Several groups have been studying treatments to modified clays using organic acid with highly concentrations and temperatures, aiming clays bleaching e purifying, for posterior use mostly in food industry to bleaching process. The industrial use for clays is also based on exchangeable cations and clay minerals properties [12–14].

Calcic bentonites are wide used in modification process since, in essence, are montmorillonite clays were the predominate cation is calcium. Otherwise, exist an another type of montmorillonite with a negative response to acid attack, that is the case of sodic bentonite [15–17].

Studies of brazilian bentonite modified by mild acid attack demonstrated that could be a good alternative to material raw with economic advantages over imported clays used in processes to obtain products with high value as cosmetics and nanocomposites.

Materials and Methods

Start Materials

The calcic bentonite, from Vitoria da Conquista, Bahia´s State, Brazil in its natural form, was submitted to mild acid attack using a concentration of the aqueous solution of hydrochloric acid 1.5 M, clay/acid solution ratio of 1 g/10 mL, at 90 °C under bellow boiling temperature and at short times of reaction 1, 6, 12, 18 and 24 h in close reactor.

The attacked clay was washed, by filtration, with distilled water until pH 7–8, and then subjected to drying at 60 °C for 24 h.

After drying, the clay was grounded using a manual mortar and vibratory ball mill until completely pass through #200 mesh sieve.

Materials Characterization

The modified samples were characterized by X-ray fluorescence (XRF) and Energy Dispersive X-ray Detector (EDS) to observe the chemical composition after treatment. Another important clay property was verified by Cation Exchange Capacity

(CEC) which is indicative of the crystalline structure preservation. The images were obtained by Stereomicroscopy and Scanning Electron Microscopy (SEM) to observe impurities reduction, decolorizing, particles size and distribution.

The scanning electron microscopy (SEM) and energy dispersive X-ray detector (EDS) were performed on scanning electron microscopy, Philips - EDAX INSPECT 50 with energy dispersive X-ray detector (EDS).

To observe the clay was used a stereomicroscopy Zeiss, model Stemi 2000C.

CEC was performed using the ammonium acetate method.

The XRF was performed, using TBL Rock standard tablets as a parameter, on X-ray fluorescence spectrometer Panalytical model Axios Advanced with loss on ignition.

Results and Discussion

Figure 1 present the EDS specter of sample treated with water for 24 h at 90 °C. It is possible to observe the presence of Si, O, Al, Fe and Mg. For this test was used a thin layer of gold over the sample.

Figure 2 present the EDS specter of sample submitted to mild acid attack for 24 h at 90 °C. It is possible to observe the peak reduction of metals, remaining a minor peak of Al. This indicates a good result of bentonite purification.

Table 1 presents the XRF results of bentonite submitted to treatment, a quantitative analysis where the values are expressed in percentage of oxides. The presence of aluminum and iron predominates among other elements, and after treatment, presenting a significant reduction. It is possible to observe the oxides reduction due to the increase of the attack time.

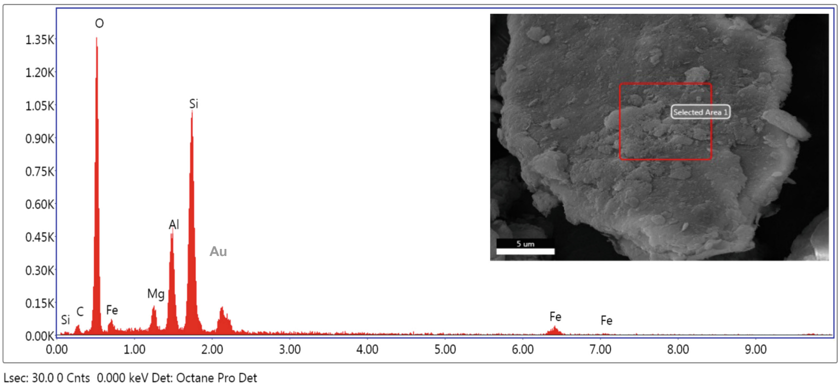

Fig. 1 EDS specter of bentonite sample treated with H_2O for 24 h

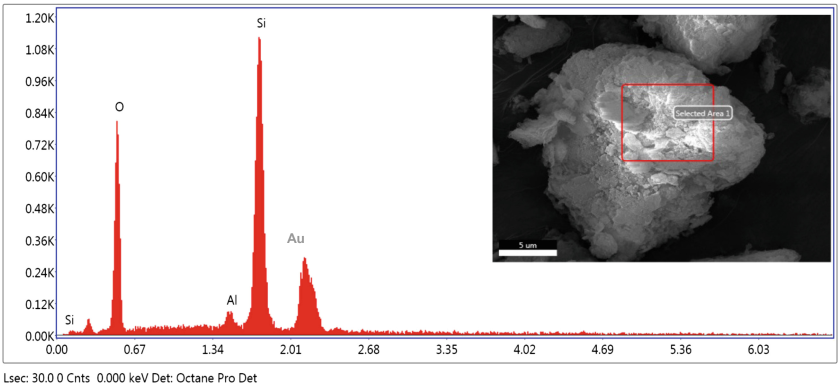

Fig. 2 EDS specter of bentonite sample treated with HCl for 24 h

Table 1 XRF results of bentonite submitted to treatment, quantitative analysis, values in percentage of oxides

Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	Li
H_2O 24 h	54.7	19.8	8.06	<0.10	3.73	0.20	0.10	<0.10	0.36	<0.10	13.5
HCl 1 h	57.7	20.6	7.82	<0.10	3.01	<0.10	<0.10	<0.10	0.39	<0.10	11.0
HCl 6 h	60.1	19.0	6.97	<0.10	2.71	<0.10	<0.10	<0.10	0.39	<0.10	11.2
HCl 12 h	64.1	15.9	5.08	<0.10	2.11	0.18	<0.10	<0.10	0.43	<0.10	13.0
HCl 18 h	65.9	15.0	4.65	<0.10	1.93	0.10	<0.10	<0.10	0.43	<0.10	12.6
HCl 24 h	63.2	16.1	5.31	<0.10	2.22	0.12	<0.10	<0.10	0.42	<0.10	13.3

In Fig. 3, it is possible observe a good reduction in the concentration of iron oxides and aluminum concentration. For aluminum a reduction of 18% and to 34% iron. This indicates an estimate of the destruction of the octahedral layer where aluminum and iron, hypothetically are located.

Table 2 presents the CEC values of bentonite samples submitted to mild acid attack. The results are indicative of low destruction of the crystalline clay mineral structure. A reduction of 40% compared with sample treated only with purified water was observed after 24 h of treatment.

The Fig. 4 shows the stereomicrography of bentonite sample treated with water for 24 h where it is possible observe several impurity particles.

In Fig. 5, it is possible to observe a good bleaching and cleaning of impurity particles at bentonite sample treated with HCl for 24 h.

Figures 6, 7, 8 and 9 shows the SEM images of bentonite sample treated with purified water and with HCl, both for 24 h. It is possible observe the lamellar structure agglomerated in layers, mostly presenting same size and irregular forms. This could indicate a good preservation of smectite crystal structures after acid attack.

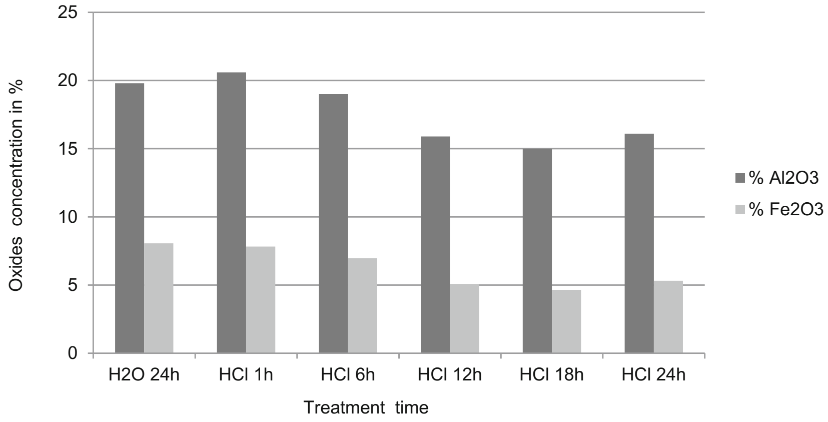

Fig. 3 Percentages of aluminum and iron oxides obtained by X-ray fluorescence of bentonite sample submitted to mild acid attack with treatment time

Table 2 CEC results of bentonite treated

Sample	CEC (meq/100 g)
H_2O 24 h	92
HCl 1 h	79
HCl 6 h	77
HCl 12 h	74
HCl 18 h	72
HCl 24 h	52

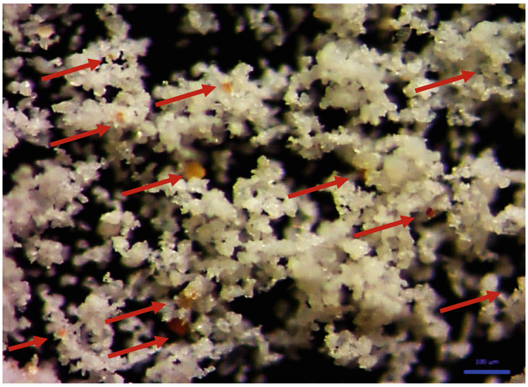

Fig. 4 Stereomicrography of sample treated with water for 24 h

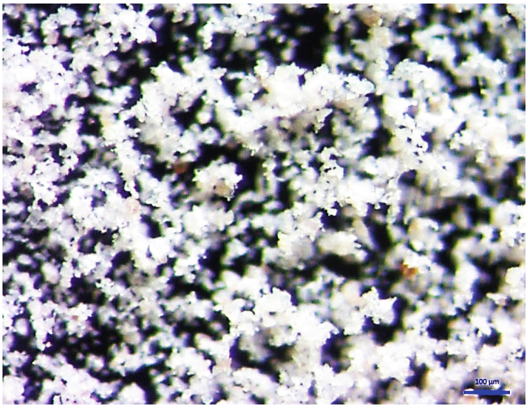

Fig. 5 Stereomicrography of bentonite sample treated with HCl for 24 h

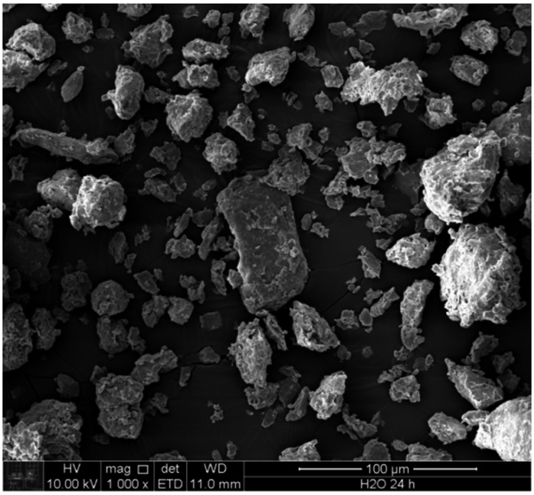

Fig. 6 SEM image of sample treated with water for 24 h (crystals dispersion)

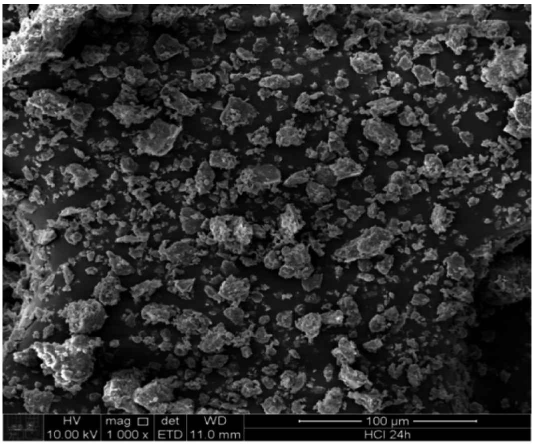

Fig. 7 SEM image of sample treated with HCl for 24 h (crystals dispersion)

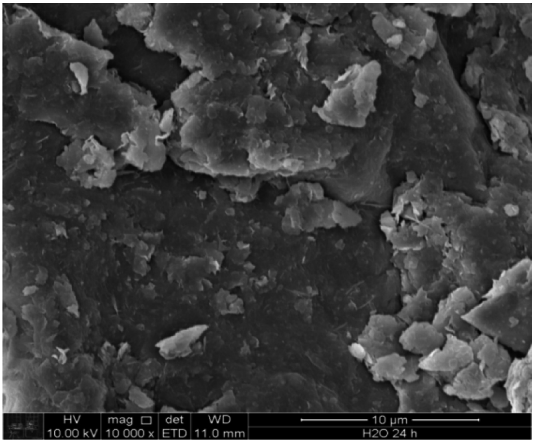

Fig. 8 SEM image of sample treated with water for 24 h (crystal detail)

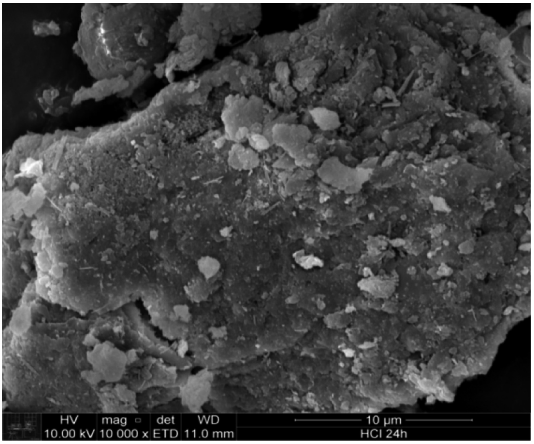

Fig. 9 SEM image of sample treated with HCl for 24 h (crystal detail)

Conclusions

The brazilian bentonite sample from Vitoria da Conquista submitted to mild attack acid under moderated conditions demonstrated a good response to proposed process.

The bleaching and purification were obtained with a good preservation of crystalline structure which was observed in Stereomicroscopy and SEM images.

A good purification of metallic oxides and other elements was observed in XRF.

The most evident modifications in decolorizing and CEC occurred in the first 12 h of acid treatment.

The results acquired presented a good concentration reduction of impurities with no significant change in crystalline clay mineral structure.

According the methodology presented, the proposed process permits new possibilities to industrial use of bentonite, in products of high value such as cosmetics and polymer/clay nanocomposites and could be an efficient alternative to economy and environment.

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