Characterization of Sardinian Bentonite

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Abstract

The employment of clays in industry and on laboratory scale is still of interest, despite their long history. The chemical-physical characteristics of such material are strongly related to their geographical origin and the availability of proper characterization techniques is of great importance in order to gain as more information about their behavior when utilized as filling materials. In the present contribute a physical characterization by meaning of Thermogravimetry, N_2 physisorption, , XRD and SEM analyses of samples of commercial bentonite collected from the north of Sardinia (Italy) is reported.

Keywords: bentonite, N_2 physisorption, BET, thermogravimetry, clay

Introduction

Clay earths were employed in the last 50 years as clarification agents, including applications in vegetal and mineral oil discoloration and deodorization [1], as well as in the field of wine clarification [2]. With the terms "*clay minerals*" we usually label a large family of natural alumina-silicates with a wide range of structures and properties. In particular, the bentonite is mainly constituted from montmorillonite (MMT), a member of the family of smectites, originated from the decomposition of volcanic ashes.

Bentonite is organized in alternated layers with a tetrahedral symmetry separated by an octahedral intermediate layer (TOT) [3]. The tetrahedral layer contains Silicium atoms bonded to four oxygen atoms which form six terms rings where every tetrahedron shares three oxygens. As consequence of this structural motif, the characteristic element of bentonite is the anion $Si_2O_5^{2-}$, which determines a negative overall charge. In the octahedral layer, neutral magnesium or aluminum oxides are presented [4]. Usually in bentonite structure an overall negative charge is observed as result of the replacement of octahedral Al or Mg atoms by lower oxidation number atoms. Inorganic cations located in the interlayer spaces, such as Na^+ and Ca^{2+} balance this negative charge. The interlayer space surfaces generally show a hydrophilic character due to the presence of H_2O clusters surrounding the inorganic cations. The structure of the interlayer spaces is also characterized by the presence of cavities or micro-pores [5].

Specific applications of bentonite are usually related to its characteristic composition. In the case of wine clarification, the negative charge of bentonite layers is usually exploited for protein sequestering [6]. In the case of edible oils, filtration on a pad of activated bentonite allows to remove cations, wax and pigments.**Error! Bookmark not defined.** Additionally, waste cooking oils can be treated with bentonite for decoloring procedure [7]. Bentonite has also been employed for water treatment, as resulted efficient in adsorbing organic matter and in retaining Fe [8] or copper [9]

Especially, montmorillonite has been largely employed in foundries, cosmetic, enology, and catalysis industries main for its easy availability, and for the possibility to tune its swelling behavior, adsorption and cation exchange capacity and surface area by modifying the kind of cation and the dimension of the pores [10]. These intrinsic characteristics of clay materials are strongly related to the geographic area of origin [11]. In this contest a proper exploiting of bentonite can be done only on the basis of the characteristics of the crude material.

In the present contribution, a physical chemical characterization of commercial bentonite originated from the north of Sardinia (Italy), by meaning of BET and XRD analysis will be presented, including its thermal stability evaluation by thermogravimetric analysis.

Experimental

Samples of bentonite originated from a cave sited in the north part of Sardinia (Italy) were considered for the present study.

Thermogravimetric analysis

Thermal stability of bentonite A1 was further evaluated using a thermogravimetric apparatus (TGA) coupled with a differential scanning calorimeter (DSC) (Labsys Setaram). The experiment was carried out on 20 mg of sample under an Ar flow of 120 ml min^{-1} between 25 °C and 800 °C with heating and cooling rates of 30 °C min^{-1}. A ceramic crucible was used for the analysis in order to avoid undesired reaction with the powders during the annealing.

N_2 Physisorption

N_2 sorption isotherms were collected with a Sorptomatic 1990 instrument (Fisons Instruments, Milan, Italy). For a standard measure, 200 mg of sample were collocated in a quartz tube and degassed under high vacuum (1×10^{-3} bar) at 250 °C for 24 h. The dead volume was evaluated through helium measurements.

Results and Discussion

The distribution of the superficial area, as well as the size and the volume of the pores are within the most important parameters in clay´s characterization.

N_2 physisorption technique was employed for the measurement of the external surface area according to the BET method [12], while BJH method was used for calculate the distribution of the porous [13].

In figure 1 the adsorption and desorption curves for samples of bentonite A1 are reported and respectively indicated with blue and red color.
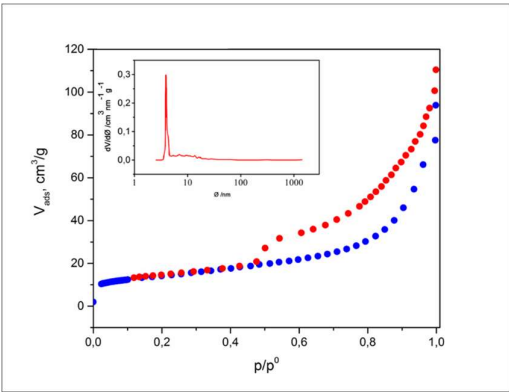
Figure 1: N_2 physisorption isotherm for bentonite A1.

The experimental curve obtained was classified as a type IV adsorption isotherm (BDDT classification) [14], in agreement to the observations reported by Hayati-Ashtiani for a bentonite originated from the Isfahan Province of Iran [15]. The classification of the hysteresis is consistent with a type H3, referred to *aggregates of platelike particles forming slit-like pores* [10b].

The sample presents a value of superficial area of 49.09 m^2/g, a porous volume of 0.094 cm^3/g and maximum porous size of 3.949 nm at -196 °C. The distribution of the porous is monomodal as showed in figure 1 (inbox).

Thus, bentonite A1 results composed mainly from montmorillonite and does not present the classical defects associated to the crude material, reflecting the commercial quality of the mineral.

In order to evaluate the thermal stability of the specific bentonite considered, the superficial area, as well as the porous size and volume of bentonite A1 were measured after three subsequent thermic treatments in order to monitor the thermal stability of the material (from 25 °C to 120 °C, at 200 °C and 300 °C) as reported in Table 1.

Table 1: structural parameters of bentonite A1 samples at different temperatures.

Entry		Nitrogen absorption		
		$S_{BET} \pm 5$ m^2/g	Porous volume ±0.002 cm^3/g	Porous size ±0.5 nm
1	25 °C	49	0.094	3.9
2	120 °C	46	0.089	3.9
3	200 °C	45	0.087[1]	3.9
4	300 °C	44	0.086	3.9

BET and BJH analysis do not show any significant difference pointing to a high thermal stability of the material in the rage 25-300 °C.

In order to evaluate the thermal stability of the bentonite, a thermogravimetric profile was registered through TGA analysis.

The results reported in figure 2 (blue line), show two endothermic peaks corresponding to two distinct steps where a part of the mass of the sample is lost. The first step, between 60 °C and 120 °C, is associated to the physically adsorbed water, which is lost in an amount of 0.5 mg, corresponding to the 2.5% of the total initial mass. The second step, between 600 °C e 800 °C, is related to the condensation of the oxidryl structure, expulsed in form of water [16]. Similar results were observed in the case of Brazilian [17] and Turkish bentonites [18].

The DSC profile (green line) does not show any significant thermal events.
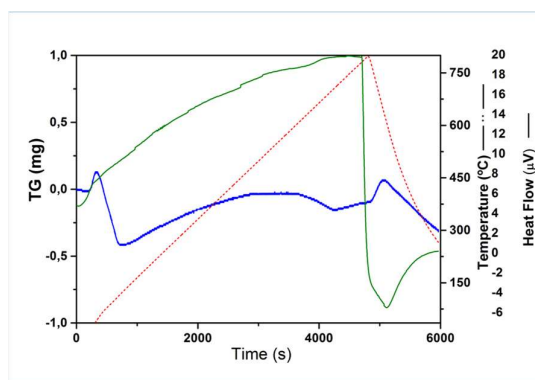
Figure 2: TG-DSC plot of bentonite A1. Blue colour indicates the TG profile, the red one the heating ramp and the green one the DSC profile.

Conclusions

Commercial bentonite originated from a cave in the north of Sardinia has been characterized by N2 physisorption and by thermogravimetric analysis, including the evaluation of its thermal stability. BET and BJH data are in agreement with the typical structural characteristics of montmorillonite and clearly indicate a pre-treatment characteristic of commercial bentonites.

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Bibliography

[1] a) H. H. Murray, *Applied Clay Science, 5-6*, 379 (**1991**); b) V. F. R. Diaz, P. S. De Souza, *Quím. Nova*, *24*, 345, (**2001**); c) L. L. Richardson, *J. Am. Oil Chem. Soc. 55*, 777, (**1978**).

[2] R. Chagas, S. Monteiro, R. Boavida Ferreira, *American Journal of Enology and Viticulture*, *63*, 574 (**2012**).

[3] a) R.E. Grim, Clay Mineralogy, second ed., McGraw-Hill, New York (**1968**); b) F. Bergaya, B.K.G. Theng, G. Lagaly, Handbook of Clay Science, Elsevier, Oxford UK (**2006**).

[4] M. Kotal, A. K. Bhowmick, *Progress in Polymer Science*, *51*, 127 (**2015**).

[5] R. S. Varma, *Tetrahedron*, *58*, 1235 (**2002**).

[6] a) R. Dordoni, R. Galasi, D. Colangelo, D. M. De Faveri, M. Lambri, *Institute of Food Science and Technology*, *50*, 2246 (**2015**); b) E.J. Waters, G. Alexander, R. Muhlack, K.F. Pocock, C. Colby, B.K. O'Neill, P.B. Høj, P. Jones, *Australian Journal of Grape and Wine Research*, *11*, 215 (**2005**).

[7] A. Mannu, G. Vlahopoulou, V. Sireus, G. L. Petretto, G. Mulas, S. Garroni, *Natural Product Communications*, 13, 4 (**2018**).

[8] a) M. Naswir, S. Arita, Salni, Journal of Clen Technologies, 1(4), 313 (**2013**); b) C. A. P. Almeida, N. A. Debacher, A. J. Downs, L. Cottet, C. A. D. Mello, *Journal of Colloid and Interface Science*, 46, 332 (**2009**); c) A. N. Fernandes, C. A. P. Almeida, N. A. Debacher, M. M. S. Sierra, *Journal of Molecular Structure* 982, 62 (**2010**); d) G. P. Gillman, *Applied Clay Science*; 53; 361 (**2011**).

[9] C. Bertagnolli, S. J: Kleinübing, M. G. C. da Silva, *Applied Clay Science*; 53(1); 73 (**2011**).

[10] A. Itadani, M. Tanaka, T. Abe, H. Taguchi, M. Nagao, *Journal of Colloid and Interface Science*, *313*, 747 (**2007**).

[11] N: Stanković, M. Logar, J. Luković, J. Pantić, M. Miljević, B. Babić, A. Radosavljević-Mihajlović, *Processing and Application of Ceramics* 5 (2), 97 (**2011**).

[12] K. Song, G. Sandi, *Clays Clay Miner. 49*, 119 (**2001**).

[13] E. P. Barrett, L. G. Joyner, P. H. Halenda, *J. Am. Chem. Soc. 73*, 373 (**1951**).

[14] a) S. Brunauer, L. Deming, W. Deming, E. Teller, *J. Am. Chem. Soc. 62*, 1723 (**1940**); b) K. S. W.Sing, D. H. Everett, R. A. W. Haul, L. Moscou, L. A. Pierotti, J. Rouquérol, T. Siemieniewska, *Pure & Appl. Chem. 57*, 603 (**1985**); c) IUPAC Recommendations, *Pure & Appl. Chem. 66*, 1739 (**1994**).

[15] M. Hayati-Ashtiani, *Part. Part. Syst. Charact. 28*, 71 (**2011**).

[16] P.S. Suchithra, Linsha Vazhayal, A. Peer Mohamed, S. Ananthakumar, *Chemical Engineering Journal, 200-202*, 589 (**2012**).

[17] C. I. R. de Oliveira, M. C. G. Rocha, A. L. N. da Silva, L. C. Bertolino**,** Cerâmica 62**,** 272 (**2016**).

[18] B. Caglar, B. Afsin*, A. Tabak, E. Eren, *Chemical Engineering Journal,* 149, 242 (**2009**).