

CHARACTERIZATION OF NATURAL CLAYS FROM ITALIAN DEPOSITS WITH FOCUS ON ELEMENTAL COMPOSITION AND EXCHANGE ESTIMATED BY EDX ANALYSIS: POTENTIAL PHARMACEUTICAL AND COSMETIC USES

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Abstract—Purification processes performed on natural clays to select specific clay minerals are complex and expensive and can lead to over-exploitation of some deposits. The present study aimed to examine physicochemical (mineralogy, morphology, size, surface charge, chemical composition, cation exchange capacity [CEC], and pH) and hydration (swelling, wettability, water sorption, and rheological behavior) properties of three native clays from Italian deposits for potential pharmaceutical and cosmetic uses due to the presence of phyllosilicate minerals. Particular emphasis was placed on energy dispersive X-ray (EDX) microanalysis coupled with the ‘cesium method’ to assay clay elemental composition and CEC. One bentonite of volcanic origin (BNT) and two kaolins, one of hydrothermal origin (K-H) and another of lacustrine-fluvial origin (K-L), were evaluated in comparison with a commercial, purified bentonite. The CEC assay revealed the complete substitution of exchangeable cations (Na^+ and Ca^{2+}) by Cs^+ in BNT samples and CEC values consistent with those of typical smectites (100.64 ± 7.33 meq/100 g). For kaolins, partial substitution of Na^+ cations occurred only in the K-L samples because of the interstratified mineral component which has small CEC values (11.13 ± 5.46 meq/100 g for the K-H sample and 14.75 ± 6.58 meq/100 g for the K-L sample). The degree of isomorphous substitution of Al^{3+} by Mg^{2+} affected the hydration properties of BNT in terms of swelling, water sorption, and rheology, whereas both of the poorly expandable kaolins exhibited significant water-adsorption properties. The EDX microanalysis has proved to be of considerable interest in terms of providing more information about clay properties in comparison with other commonly used methods and to identify the role played by both chemical and mineralogical composition of natural clays for their appropriate use in pharmaceutical and cosmetic fields.

Key Words—Bentonite, Cation Exchange Capacity, Energy Dispersive X-ray Analysis, Kaolin, Rheology, Water Sorption.

INTRODUCTION

Phyllosilicate minerals are the most important and abundant class of soil minerals mined worldwide and they have unique physicochemical features, due to their layered structure, which explain the wide range of their applications (in ceramics, oil, and animal-waste absorption, as a bonding agent in animal feeds, in the purification of wastewater, in the clarification of wine, in decoloration agents, metal, and paints, in the paper industry, and in pharmaceuticals and cosmetics) (Murray, 1991; Lopez-Galindo *et al.*, 2007). Bentonite, a rock term used to describe a smectite-rich material for industrial mineral commodities where the most common smectite is montmorillonite (which has a 2:1 Si:Al ratio), and kaolin, a rock term used to describe a soil rich in kaolinite (which has a 1:1 Si:Al ratio) for industrial mineral commodities, are both used extensively in

various applications according to their structural and chemical characteristics (Velde, 1992). Monographs about bentonite and kaolin are included in the current editions of both the US and European Pharmacopeias, and both have also received special mention by the World Health Organization in the ‘Environmental Health Criteria 231’ (World Health Organization, 2005). Bentonite and kaolin are common ingredients in pharmaceutical formulations used as excipients (adsorbents, binders, anticaking agents, disintegrants for solid dosage forms, dispersion stabilizers in semisolid dosage forms) or as active compounds for oral administration (antacid, antitoxic, antidiarrheal, and gastric protectant), and for topical applications in the field of cosmetics (rheology-control agents, adsorbents of skin exudates or bacterial toxins, peloid thermal muds) (Lopez-Galindo *et al.*, 2007; Veniale *et al.*, 2007; Viseras *et al.*, 2010). Recently, bentonite has been proposed for use in organo-clay development due to its interaction with several drugs and how it affects their release or bioavailability (White and Hem, 1983; Aguzzi *et al.*, 2007; de Paiva *et al.*, 2008; Katti *et al.*, 2010; Iannuccelli *et al.*, 2015), and in nanocomposites, consisting of nano-scale dispersions

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of clays into polymers which exhibited increased strength and heat resistance (Tran *et al.*, 2006; Katti *et al.*, 2010; Jin *et al.*, 2010; Sharma and Thakur, 2010; Rajkumar *et al.*, 2011; Rodrigues *et al.*, 2013).

The special properties of bentonite are derived from montmorillonite crystal imperfections, *i.e.* isomorphous Si and Al atom substitutions in tetrahedral and octahedral sheets, respectively, with atoms of lower valence leading to excess negative charge in the lattice which is balanced by cations (mainly Na⁺ and Ca²⁺) in the interlayer space of smectite. These cations are exchangeable with inorganic or organic cationic compounds due to their loose electrostatic interactions typically giving them a large CEC value (~100 meq/100 g) (World Health Organization, 2005; Pusch, 2015). Moreover, interruption of the montmorillonite periodic structure confers on the edge surface an amphoteric character and also the capacity to react at the level of these sites with inorganic or organic cations or anions. The structural characteristics of montmorillonite lead to an ability to form thixotropic gels with water, to adsorb rapidly large quantities of water and expand, and to create large CEC values for both inorganic and organic cationic compounds (World Health Organization, 2005).

Unlike montmorillonite, kaolinite is a poorly or non-expandable clay mineral in aqueous solution because of the very poor isomorphous substitution in the lattice and, consequently, a CEC value (~2–10 meq/100 g) considerably smaller than that of montmorillonite. Nevertheless, kaolinite is able to adsorb lipids, proteins, bacteria, and viruses on the external planes or edges of particle surfaces, owing to broken bonds and exposed hydroxyl groups (Grim, 1968; Van Olphen, 1997; Huertas *et al.*, 1998), and this property is exploited for use in medicine.

The specific function for each particular formulation depends on both the mineralogical and chemical composition: these influence several physicochemical properties (particle size and shape, surface area, surface chemistry and charge, CEC, water sorption, swelling, and rheological properties) (Grim, 1968; Hosterman and Patterson, 1992; Lopez-Galindo *et al.*, 2007; Patterson and Murray, 1983; Tateo and Summa, 2007). Clay properties can be modified significantly by industrial processes performed on raw materials to remove impurities, to meet regulatory requirements, or to modify the type of exchangeable ions in the clay's crystal lattice. For large-scale industrial applications, however, purification processes performed on natural clays to select specific clay minerals are complex and expensive and can lead more rapidly to deposit depletion by over-exploitation (Bergaya *et al.*, 2012; Bergaya and Lagaly, 2013; Alves *et al.*, 2016).

Three native clays (one bentonite and two kaolins from Italian deposits) were investigated here to assess physicochemical properties, namely mineralogy, particle size, zeta potential, elemental composition, CEC value,

wettability, swelling, water sorption, and rheology, in order to establish their potential applications in pharmaceutical and cosmetic fields without modification of their mineralogical compositions. In addition, a novel application of EDX microanalysis is proposed to determine cesium CEC values and acquire more information about the elements involved in the exchange process than that achievable by means of the commonly used methods.

METHODS

Materials

Bentonite (BNT) of volcanic origin from the Iglesias (Sardinia, Italy) deposit (average mineralogical composition from the producer's datasheet: montmorillonite 80%, quartz 13%, illite-kaolinite 5%, plagioclase 2%), kaolin of hydrothermal origin (K-H, average mineralogical composition from the producer's datasheet: kaolinite 56%, K-feldspar 18%, quartz 16%, illite 8%, plagioclase 2%), and kaolin of lacustrine-fluvial origin (K-L, average mineralogical composition from the producer's datasheet: kaolinite 15%, interstratified clay mineral 30%, K-feldspar 11%, quartz 42%, plagioclase 2%) from the Piloni di Torniella deposits (Roccastrada, Tuscany, Italy) were kindly donated by Eurit (Colorobbia Group, Porto Azzurro, Italy). The terms 'bentonite' and 'kaolin,' both used as rock terms and as pharmacopeial names throughout the text, indicate soils rich in montmorillonite and kaolinite, respectively. For comparison, a purified bentonite (MM) (Veegum R, USP/NF Magnesium Aluminum Silicate Type IA, mineralogical composition from the producer's datasheet: montmorillonite >90%) supplied by Vanderbilt Minerals, LLC (Norwalk, Connecticut, USA) was used. All clay materials comply with the requirements of the European and United States Pharmacopoeias for chemical limitations, alkalinity, loss on drying, and microbial contaminations (total viable aerobic count and absence of *Escherichia coli*) as reported on the material datasheets. For CEC determination, cesium chloride (CsCl) was purchased from Sigma-Aldrich (Milan, Italy). All of the other chemicals were of analytical grade (Carlo Erba, Milan, Italy).

X-ray powder diffraction

Identification of clay minerals in the BNT, K-H, and K-L samples was by means of powder XRD at the Department of Engineering Enzo Ferrari (University of Modena and Reggio Emilia). The samples were analyzed using a conventional Bragg-Brentano diffractometer (Philips-Panalytical, PW3710) with Ni-filtered CuK α radiation. All XRD data were collected under the same experimental conditions, in the angular range 5°<2 θ <60° (step size 0.02°2 θ and 1 s counting time for each step). The phases were identified from peak positions and intensities using the reference JC-PDF database.

Morphology, size, and surface charge

Clay morphology was evaluated by means of Environmental Scanning Electron Microscopy (ESEM, Quanta 200, FEI, The Netherlands). Particle size, expressed as the diameter of the most represented dimensional class (main class), was determined both before and after the milling process which used a vibrating ball mill (FRITSCH GmbH, Idar-Oberstein, Germany) for 10 h. The analysis was carried out on 10 mg/mL clay-water suspensions by laser granulometer (Mastersizer 2000, Malvern Instruments Ltd, Worcestershire, UK). Clay surface charge values were determined on 10 mg/mL clay suspensions in pH 6.8 deionized water using Photon Correlation Spectroscopy (PCS) (Zetasizer version 6.12, Malvern Instruments, Ltd) equipped with a 4 mW He-Ne laser (633 nm) and DTS software (Version 5.0). The determinations were carried out in triplicate from three different batches. All of the analyses described below were performed on the milled samples.

Elemental composition by EDX analysis

The clay elemental composition was determined by EDX analysis (INCA 350, Oxford Instruments, Abingdon, UK) coupled with ESEM at the Interdepartmental Large Instruments Center (University of Modena and Reggio Emilia, Modena, Italy). Elements can be identified qualitatively and semi-quantitatively as a function of the X-ray energy emitted by their electrons transferring from a higher-energy shell to a lower-energy one. X-ray emission from $K\alpha$ or $K\beta$ levels of the atoms Ca, K, O, Na, Mg, Al, Si, and other elements with atomic numbers from 4 upward were recorded by the selected area method related to whole clay particles from samples mounted without a conductive coating on carbon stubs with the following experimental settings: low vacuum (0.70 Torr), accelerating voltage 12 kV, spot size setting of 3, element detection limit ~ 0.05 wt.%, spatial resolution 0.1 μm , total spectrum counts $>250,000$, and accuracy within $\pm 5\%$ relative errors by reference to standards. The EDX spectra representing the plots of X-ray counts vs. element and semi-quantitative results, expressed as relative weight percentage of the elements present in the specimen, were recorded. The reported data were averaged over three determinations for each sample.

Cation exchange capacity by EDX analysis

The CEC value of each clay sample was measured by placing 100 mg of clay in a 0.1 M solution of CsCl (125 mL) under magnetic stirring for 24 h. After centrifugation (model 4235, ALC International, Milan, Italy) at $1189 \times g$ for 15 min, the clay was rinsed with deionized water, vacuum dried, compressed in a hydraulic press (Perkin-Elmer, Norwalk, Connecticut, USA) at 200 kg/cm^2 for 1 min using 12.5 mm-diameter punches, mounted on

carbon stubs without conductive coating, and assayed by EDX analysis coupled with ESEM. In the present case, determination of the CEC of the clay and the peculiar affinity of phyllosilicate minerals for some elements, among which was Cs, was done by EDX. X-ray emission of Cs atoms was evaluated at the intensity characteristic of this element ($L\alpha = 4.2865 \text{ keV}$) and under the same working conditions as described above. The CEC was determined through the weight percentage of Cs_2O , applying the following equation (Hillier, 1992):

$$\text{CEC (meq/100 g of clay)} = (1000 \times \text{wt. \% Cs}_2\text{O}) / (282/2)$$

The value reported was averaged over three determinations from three different batches.

Cation exchange capacity by the ammonium acetate method

The CEC of the BNT sample was determined by the slightly modified ammonium acetate method (Thomas, 1982). In practice, 500 mg of BNT was shaken with 50 mL of 1 M ammonium acetate solution for 12 h. The suspension was centrifuged at $2115 \times g$ for 20 min. The sediment, dispersed in 50 mL of water under mechanical stirring for 12 h and recovered by centrifugation, was subjected to two further rounds of exchange washing under the same conditions mentioned above using 40 mL of the ammonium acetate solution. The excess ammonium ions were removed in 50 mL of water under stirring for 12 h. The sediment recovered was subjected to four washes with 95% ethanol and dried in an oven at 65°C for 2 h. Then, BNT water suspension (100 mg/25 mL) was loaded into the bulb of the Kjeldahl apparatus with 50 mL of 30% w/w sodium hydroxide solution and distillation was run. The distillate was collected in 25 mL of 0.1 M nitric acid solution and titrated with 0.1 M sodium hydroxide. The CEC was calculated by applying the following equation (Hillier, 1992):

$$\text{CEC (meq/100 g of clay)} = (1000 \times \text{wt. \% NH}_4^+) / 18$$

The reported values were averaged over three determinations from three different batches.

pH

The pH of 2% clay water suspension, according to the U.S. Pharmacopeia monograph for bentonite, was determined by potentiometry both just after the preparation of the suspension and again 1 h later. The reported values were averaged over three determinations from three different batches.

Wettability

Clay wettability was determined on 500 mg clay samples compressed in a hydraulic press (Perkin-Elmer) at 200 kg/cm^2 for 1 min using 12.5 mm-diameter punches by direct measurement of the contact angle, *i.e.* the tangent angle at the contact point between a deionized water drop and the tablets, at room

temperature. The determinations were carried out in triplicate from three different batches.

Swelling extent and water sorption

The clay expansion extent was determined by monitoring the size of clay particles upon contact with deionized water at $25 \pm 1^\circ\text{C}$ through an optical microscope (N-400FL, Optika Microscopes, MAD Apparecchiature Scientifiche, Bergamo, Italy) by measuring the diameter change of at least 200 particles on recorded computerized images. Water uptake was evaluated at room temperature on 100 mg of clay sample by means of the Enslin apparatus (Enslin, 1933) up to 24 h. These analyses were carried out in triplicate from three different batches.

Rheological behavior

The rheological behavior of each clay water suspension was analyzed by a coaxial cylinder rheometer (Rotovisco HAAKE RV12, Karlsruhe, Germany) on 10% and 25% w/v solid content. After 24 h, flow curves were obtained using a defined program of gradient flow (from 48 to 1536 s^{-1}) generating ascending and descending rheograms at a temperature of $25 \pm 1^\circ\text{C}$. The reported values were averaged over three determinations from three different batches.

Statistical analysis

Data obtained were evaluated statistically using one-way analysis of variance (ANOVA). Differences at p values (calculated probability) <0.05 were considered significant.

RESULTS AND DISCUSSION

The pharmaceutical and cosmetics industry sectors make extensive use of clays and clay minerals, especially phyllosilicate minerals. For these purposes, phyllosilicate minerals should possess, in addition to the pharmacopeial requirements, other properties based on interlayer reactions, swelling, water sorption, and rheological behavior that justify their use either as excipients in both conventional dosage forms and controlled release formulations, or as active biological agents in combination with water (geotherapy) or

mineral-medicinal waters (Carretero, 2002; Lopez-Galindo *et al.*, 2007). Clay properties, related to their mineralogical and chemical compositions, which, in turn, depend on the geological background of the different deposits, usually dictate the type of use. Hence, a bentonite of volcanic origin (BNT) as well as two kaolins of different geological origins, a kaolin of hydrothermal origin (K-H), and a kaolin of lacustrine and fluvial origin (K-L), were investigated for physico-chemical properties (mineralogy, particle size, surface charge, elemental composition, CEC, pH value) and hydration properties (wettability, swelling, water sorption, rheology) in order to assess their possible applications in pharmaceutical or cosmetic fields. The name kaolin was also conferred on sample K-L in spite of the small kaolinite content (Bloodworth *et al.*, 1993). The characterization results were compared with those obtained from a pharmaceutical-grade bentonite (MM).

Physicochemical properties

The original, unmilled clay particles had irregular shapes (Figure 1) and a broad size distribution in the fine-grained range of $\sim 1\text{--}100 \mu\text{m}$, irrespective of the sample. Although these dimensions are considered proper for several pharmaceutical and cosmetic applications, the particle size is known to affect the CEC values, water sorption, swelling, and rheological behavior (Lloyd and Conley, 1970; Stul and van Leemput, 1982; Stepkowska *et al.*, 2001; Adeyinka *et al.*, 2009; Chemani, 2015). For these reasons, all clays, including MM, used for comparison, were subjected to a milling process which provided uniform particle dimensions among the samples in the range of $\sim 1\text{--}3 \mu\text{m}$ (Table 1).

Identification of the clay minerals which make up the clayey materials was performed by XRD (Figure 2). The diffraction peaks of the BNT sample indicated the following composition: montmorillonite, a mineral of the smectite group with chemical formula $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (Mnt) (Anthony *et al.*, 1995); quartz, a tectosilicate with formula SiO_2 , present in different polymorphic phases of cristobalite (Crs) (Anthony *et al.*, 1995) and α -quartz (Qz) (Anthony *et al.*, 1995); albite, a plagioclase feldspar mineral with formula $\text{NaAlSi}_3\text{O}_8$ (Ab) (Anthony *et al.*, 1995); illite, a non-expanding

Table 1. Particle size, swelling extent, and water-sorption capacity of bentonite (BNT), hydrothermal kaolin (K-H), and lacustrine kaolin (K-L), in comparison with a pharmaceutical-grade bentonite (MM). Mean values \pm SD.

	Size after milling ($\mu\text{m} \pm \text{SD}$)	Swelling size ($\mu\text{m} \pm \text{SD}$)	Swelling ratio	Water sorption (mL/100 mg)
BNT	1.26 ± 0.38	16.00 ± 3.03	1:13	0.21 ± 0.02
K-H	2.76 ± 1.14	7.40 ± 1.15	1:2.5	0.60 ± 0.05
K-L	1.91 ± 0.66	8.10 ± 1.32	1:4	0.66 ± 0.03
MM	1.06 ± 0.31	18.65 ± 3.22	1:18	0.78 ± 0.05

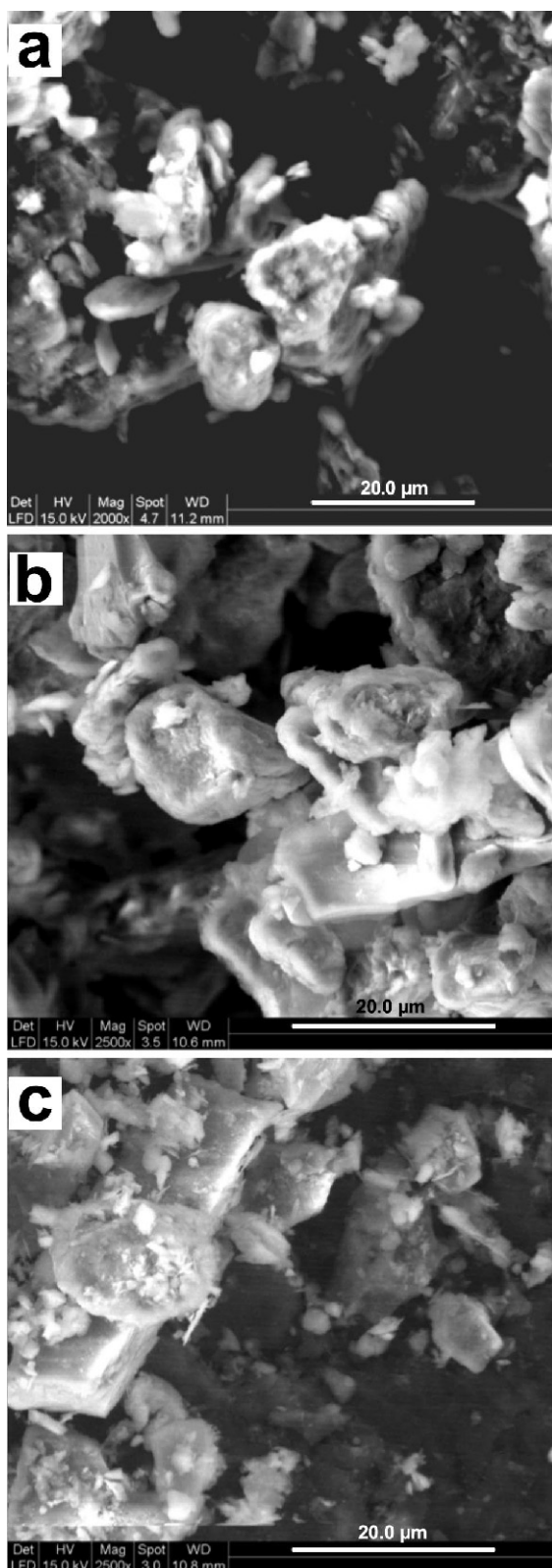


Figure 1. ESEM images of clay samples before milling: bentonite (BNT) (a), hydrothermal kaolin (K-H) (b), and lacustrine kaolin (K-L) (c).

crystalline clay mineral with chemical formula $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)](Ilt.)$ (Rieder *et al.*, 1998); and kaolinite, another crystalline clay mineral with composition $Al_2Si_2O_5(OH)_4$ (Kln). The mineralogical composition of BNT corresponds with a sodium bentonite, an Al phyllosilicate consisting mostly of montmorillonite with quartz, feldspar, illite, and other minerals as minor components (Nones *et al.*, 2015). The K-H sample is kaolin, and contains mainly: kaolinite (Kln); sanidine, a potassium feldspar with formula $K(AlSi_3O_8)$ (Sa) (Anthony *et al.*, 1995); quartz (Qz); intermediate Albite (Ab); illite (Ilt); and montmorillonite (Mnt). The K-L sample consisted mainly of quartz (Qz), kaolinite (Kln), sanidine (Sa), illite (Ilt), and montmorillonite (Mnt). These results were consistent with the mineralogical analysis from the supplier's datasheet.

The clay elemental composition was identified by EDX analysis obtaining the relative quantitative abundance of each element present in the samples (Figure 3, Table 2). For all of the clays the results showed characteristic Si^{4+} and Al^{3+} ions in the tetrahedral and octahedral sheets, respectively. As expected, BNT exhibited partial substitution of Al^{3+} by Mg^{2+} ($2.07 \pm 0.03\%$) in the octahedral sheet, even if less than that of substitution in MM ($9.59 \pm 0.15\%$), which is used here for comparison purposes. Such substitution was absent or $<1\%$ in the K-H or K-L samples. Given that isomorphous Al^{3+} substitution is seldom found in Kln (Grim, 1968), Mg^{2+} in the K-L sample could have originated as a component of interstratified clay minerals containing Mnt.

Isomorphous substitutions in the octahedral sheets lead to excess negative structural charge within the lattice that is balanced by inorganic cations (mainly Na^+ and Ca^{2+}). Additional negative polar sites available for inorganic cation adsorption consist of octahedral Al-OH and tetrahedral Si-OH groups located at the broken edges as well as of exposed hydroxyl end-groups on the terminated planes. The abundances of Na^+ and Ca^{2+} in the clays studied were as follows: $MM > BNT > K-L > K-H$. For smectites (MM and BNT) the broken-edge surface contributed only 20% of the total surface area involved in cation adsorption; hence, cation concentration may be related mainly to the degree of isomorphous substitution indicated by the abundance of Mg^{2+} ions. In between the two exchangeable cations, both kaolins contained only Na^+ ions which are reasonably ascribable to one or more of the following three components: compensating cations adsorbed on the crystal edges or the external surfaces where terminal hydroxyl groups are present; interstratified clay minerals containing Mnt; and a Na-feldspar mineral (Ab) as a mineralogical component of the K-H sample.

In addition, all the samples contained iron, ranging from ~ 1.2 to 2.9%, which is often present in soils as free iron oxide at low concentrations (Singh and Gilkes,

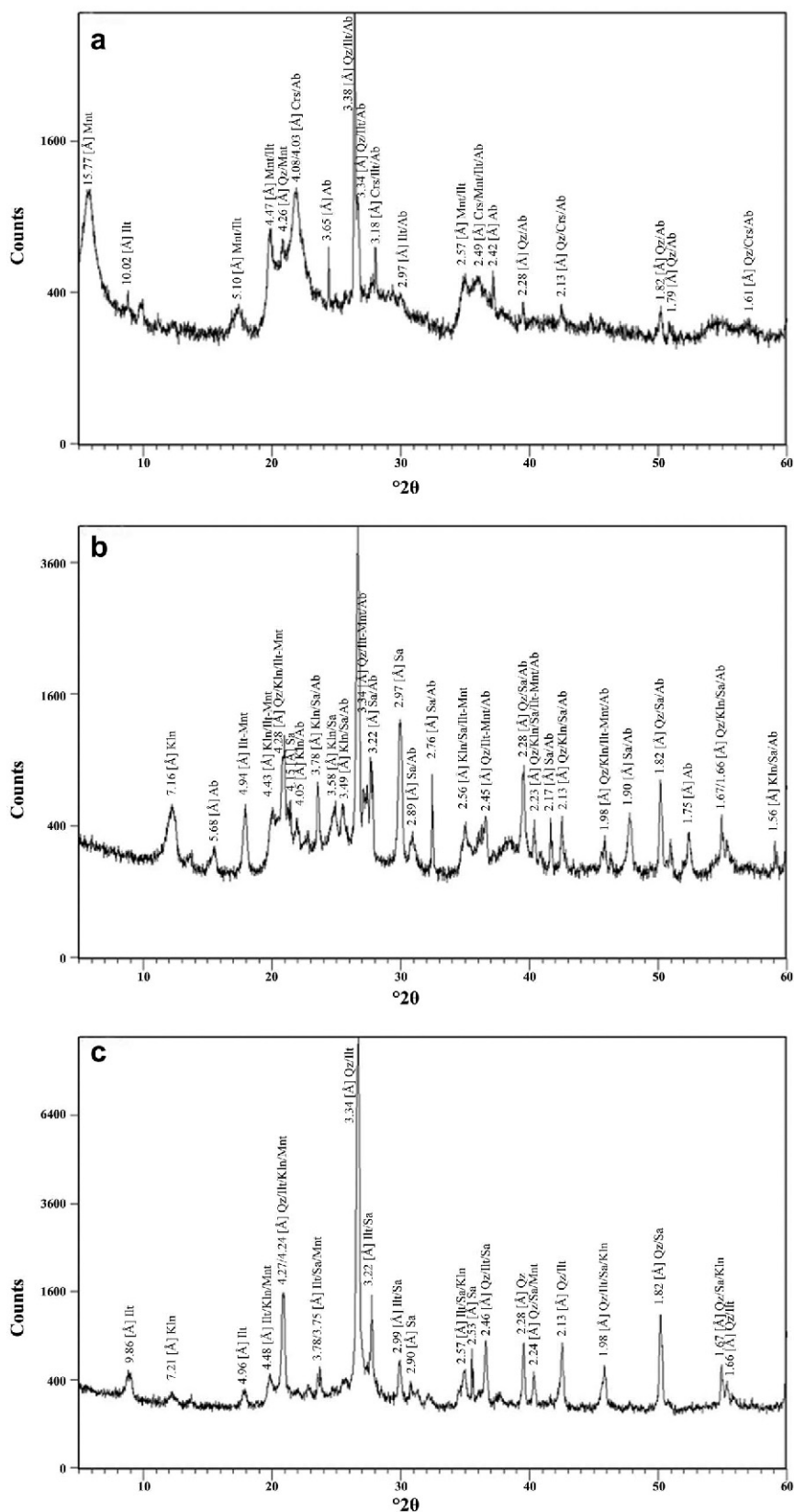


Figure 2. XRD patterns of bentonite (BNT) (a), hydrothermal kaolin (K-H) (b), and lacustrine kaolin (K-L) (c) samples.

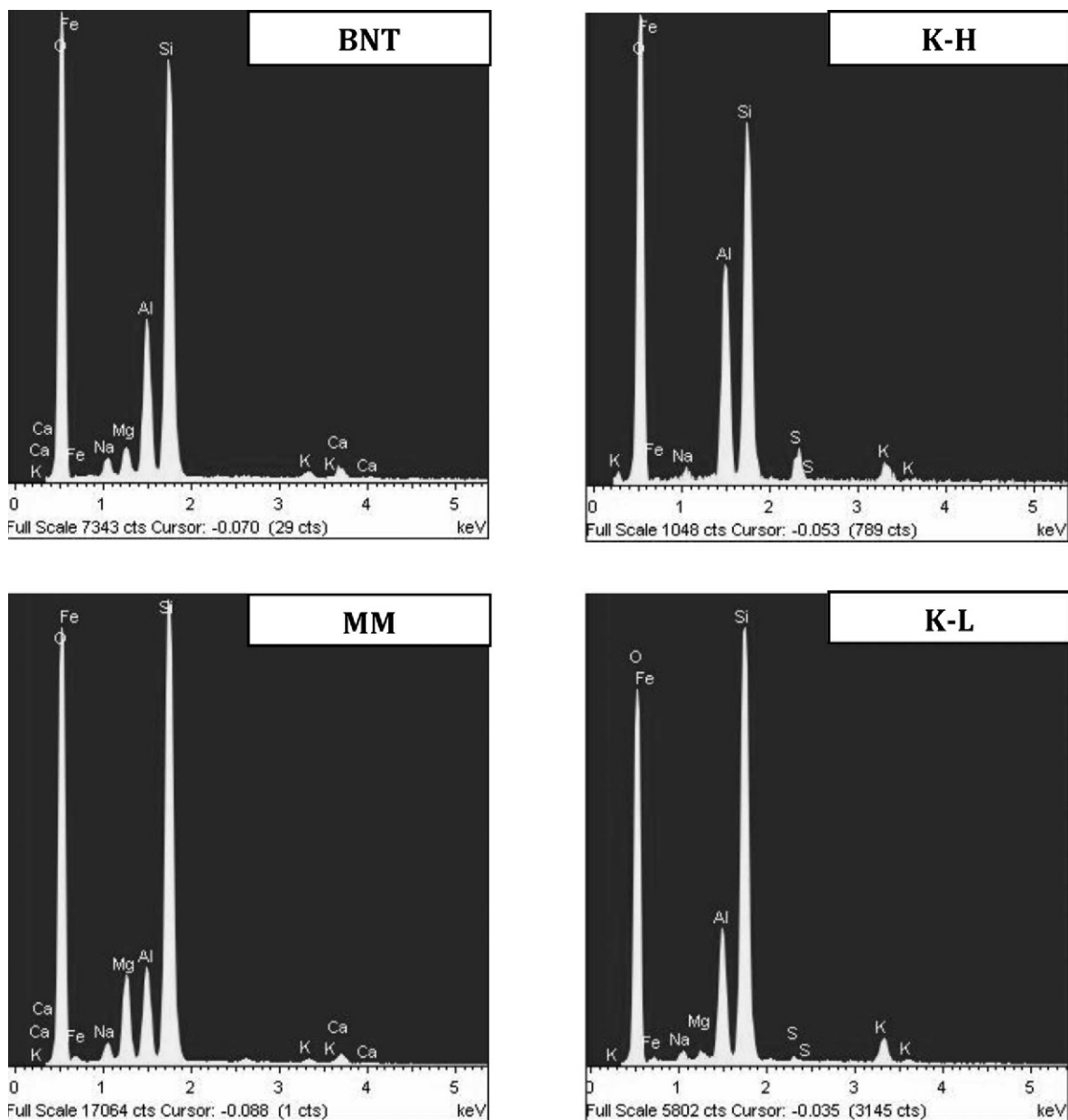


Figure 3. EDX spectra from the elements contained in bentonite (BNT), hydrothermal kaolin (K-H), and lacustrine kaolin (K-L), in comparison with a pharmaceutical-grade bentonite (MM).

1991), and non-exchangeable K^+ ions. K^+ ion percentages were greater in kaolins (~3.5%, regardless of the sample, $p > 0.05$) than those in both bentonites ($p < 0.05$), reasonably owing to greater 1:1 phases, a 2:1 clay mineral with K^+ as the main cation in the interlayer, and to the presence of K-feldspar (Sa) phases in both kaolins. The clay elemental composition was consistent with the average chemical analysis from the supplier's datasheet.

The tendency of clays to exchange the inorganic cations located in the interlayer space with chemical moieties with which they come in contact is quantified by

the CEC, which varied from one original clay deposit to another (He *et al.*, 2010). A small fraction of the CEC may also arise from cations dissociating from hydroxyl end-groups located at the external surfaces and at the edge surfaces or to cations originating from broken bonds around the crystal edges. The clay CEC was assayed by using Cs^+ as the exchanged cation and by evaluating the modification of the elements with respect to those exhibited by the untreated clays through EDX analysis. Cesium interacts strongly and semi-permanently with phyllosilicate minerals, removing the exchangeable

Table 2. EDX semi-quantitative analysis of the elements present in bentonite (BNT), hydrothermal kaolin (K-H), and lacustrine kaolin (K-L), in comparison with a pharmaceutical-grade bentonite (MM). All data are expressed as oxide relative percentage of the elements >0.5%. Mean values \pm SD.

	BNT	K-H	K-L	MM
SiO ₂	75.06 \pm 0.03	59.42 \pm 1.63	74.60 \pm 1.23	70.89 \pm 0.47
Al ₂ O ₃	15.89 \pm 0.20	26.67 \pm 1.90	15.09 \pm 0.59	10.71 \pm 0.04
FeO	2.94 \pm 0.14	2.44 \pm 0.10	2.48 \pm 1.12	1.26 \pm 0.03
TiO ₂	0.00	0.00	0.65 \pm 0.28	0.00
CaO	1.67 \pm 0.04	0.00	0.00	2.15 \pm 0.16
MgO	2.07 \pm 0.03	0.00	0.83 \pm 0.09	9.59 \pm 0.15
K ₂ O	1.62 \pm 0.12	3.38 \pm 0.40	3.53 \pm 0.68	0.66 \pm 0.04
Na ₂ O	0.47 \pm 0.14	0.72 \pm 0.67	1.14 \pm 0.22	1.86 \pm 0.02
SO ₃	0.00	7.36 \pm 0.74	0.81 \pm 0.14	0.00

cations and binding to the interlayer spaces, probably owing to its low hydration energy (Motokawa *et al.*, 2014). The element identification and quantification (Figure 4, Table 3) revealed the complete replacement of Na⁺ and Ca²⁺ cations by Cs⁺ in BNT, as well as the complete and almost complete replacement of Na⁺ and Ca²⁺ cations, respectively, in MM clay. Contrary to this, substitution of Na⁺ cations did not occur in K-H kaolin and it was only partial in K-L kaolin. Considering that separating Kln aluminosilicate units is almost impossible, the partial exchange in K-L kaolin is attributable to the greater Mnt phase present in the K-L sample. Accordingly, the CEC values were high for bentonites (100.64 \pm 7.33 meq/100 g for BNT, 84.81 \pm 3.45 meq/100 g for MM), in good agreement with typical montmorillonite CEC values (Donahue *et al.*, 1977), and low for kaolins (11.13 \pm 5.46 meq/100 g for K-H, 14.75 \pm 6.58 meq/100 g for K-L) without significant difference ($p > 0.05$) between them. The CEC determinations obtained using the cesium exchange method combined with EDX analysis were validated on BNT samples by means of the standard ammonium acetate method giving a comparable CEC value of 95.90 \pm 4.70 ($p < 0.05$).

Upon contact with water, both BNT and MM provided alkaline suspensions (pH of \sim 10), in accor-

dance with the values required by both U.S. and European Pharmacopeias, whereas both kaolins provided almost neutral suspensions (pH of \sim 7.5) (Table 4). All clay pH values remained unchanged after 1 h of dispersion in water. Unlike kaolins, bentonite alkalinity is generated by Mnt-exchangeable Na⁺ ions that are retained by electrostatic attraction onto the interlayer surfaces and can be exchanged quickly by the H ions in water (Alkan *et al.*, 2005; Kaufhold *et al.*, 2008).

The net surface charge of the clay samples was investigated by determining the zeta potential, which was confirmed to be negative for all samples (Table 3) with a slightly greater magnitude in kaolins (\sim -42 mV, without a significant difference between the two samples, $p > 0.05$) compared with bentonites (\sim -28 mV in BNT and -35 mV in MM, $p < 0.05$). The net surface charge of kaolins is related to their mineralogical composition, with the contribution from Kln, Qz, and interstratified minerals containing Mnt. The main effect on the net surface charge of Kln and Qz arises from the exposed basal hydroxyls in Kln and Qz at their basal surfaces, contributing 20% and 100% of the total surface, respectively (World Health Organization, 2005), always negative at a natural neutral pH whereas Kln structural substitution generating permanent pH-

Table 3. EDX semi-quantitative analysis of the elements present in bentonite (BNT), hydrothermal kaolin (K-H), and lacustrine kaolin (K-L), in comparison with a pharmaceutical-grade bentonite (MM) following cation exchange by cesium. All data are expressed as oxide relative percentage of the elements >0.5%. Mean values \pm SD

	BNT	K-H	K-L	MM
Cs ₂ O	14.19 \pm 1.27	1.57 \pm 0.08	2.08 \pm 0.17	11.28 \pm 0.40
SiO ₂	64.87 \pm 2.19	56.72 \pm 0.43	73.81 \pm 0.48	65.68 \pm 0.10
Al ₂ O ₃	13.65 \pm 0.29	27.66 \pm 0.18	14.42 \pm 0.49	10.01 \pm 0.20
FeO	3.68 \pm 0.83	2.13 \pm 0.09	3.44 \pm 0.12	1.48 \pm 0.34
TiO ₂	0.00	0.00	0.00	0.00
CaO	0.00	0.00	0.00	0.78 \pm 0.12
MgO	1.34 \pm 0.04	0.00	0.77 \pm 0.09	8.53 \pm 0.25
K ₂ O	1.34 \pm 0.09	3.04 \pm 0.20	3.72 \pm 0.19	0.50 \pm 0.03
Na ₂ O	0.00	0.58 \pm 0.07	0.55 \pm 0.02	0.00
SO ₃	0.00	7.25 \pm 0.14	0.70 \pm 0.09	0.00

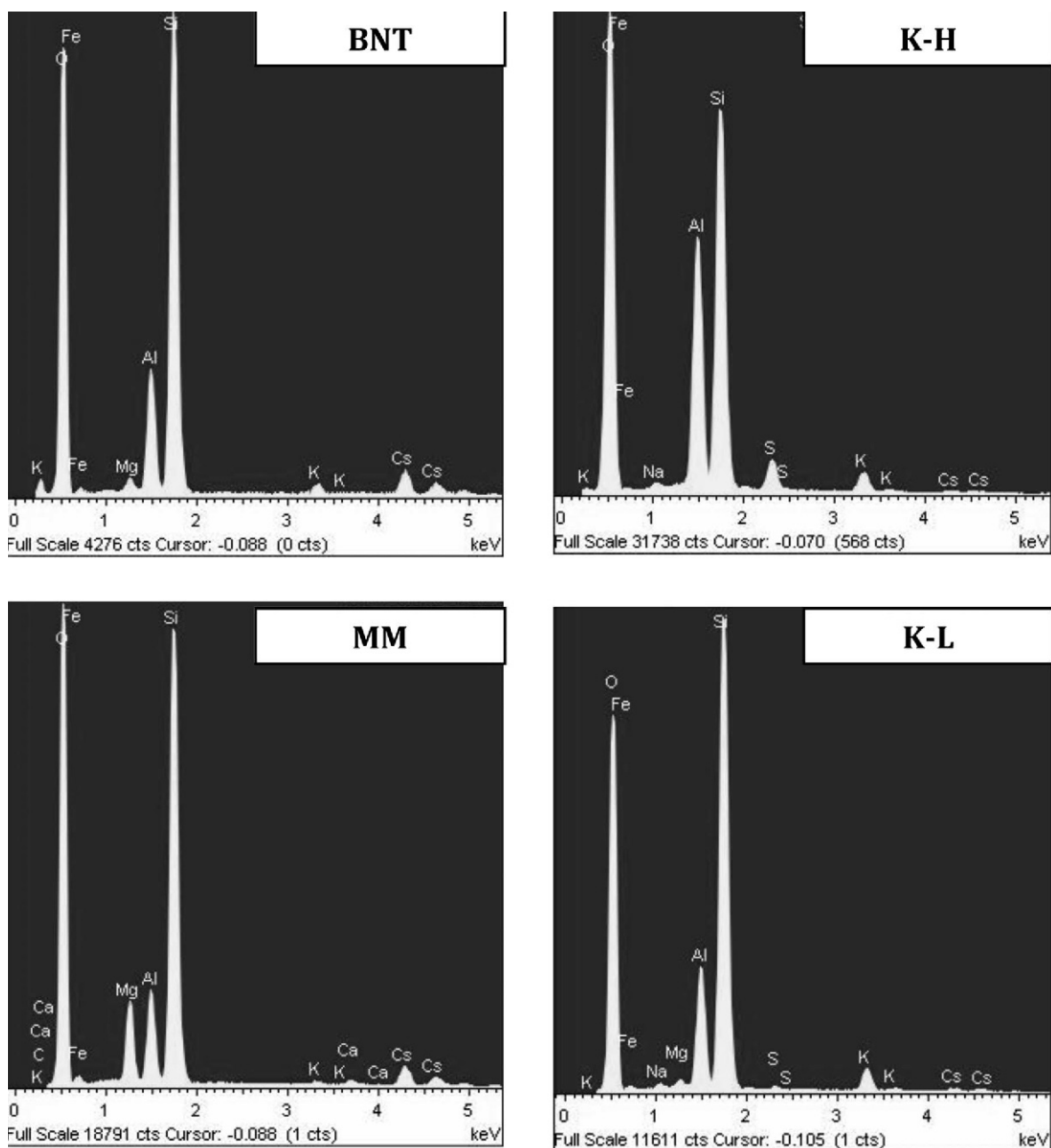


Figure 4. EDX spectra from the elements contained in bentonite (BNT), hydrothermal kaolin (K-H), and lacustrine kaolin (K-L), in comparison with a pharmaceutical-grade bentonite (MM), following cation exchange with cesium.

independent charge is minor, generally contributing <5% (Delgado *et al.*, 1986; Ma and Eggleton, 1999; Alkan *et al.*, 2005; Dohnalova *et al.*, 2008). For bentonite, the net surface charge is mainly due to Mnt pH-independent structural charges accounting for 90–95% of the total charge (Au and Leong, 2013; Pecini and Avena, 2013). After all, the edge surface charges of both Kln and Mnt have been estimated to be very close to zero in a natural, neutral pH medium (Delgado *et al.*, 1986; Furukawa *et al.*, 2009) and the degree of dissociation in aqueous

solution of exchangeable cations at Mnt interlayers makes a relatively small contribution (Low, 1981).

Hydration properties

Clay hydration properties, in terms of water-sorption capacity and swelling extent, are strictly related to clay chemical composition, degree of isomorphous substitution, and to the amounts and nature of exchangeable cations (Foster, 1954; World Health Organization, 2005; Segad *et al.*, 2010; Salles *et al.*, 2010). Clay

Table 4. pH values and zeta potential of bentonite (BNT), hydrothermal kaolin (K-H), and lacustrine kaolin (K-L), in comparison with a pharmaceutical-grade bentonite (MM).

	pH value (mean \pm SD)	pH value after 1 h (mean \pm SD)	Z potential (mV \pm SD)
BNT	9.43 \pm 0.48	9.30 \pm 0.23	-28.40 \pm 0.98
K-H	7.63 \pm 0.43	7.41 \pm 0.18	-41.17 \pm 1.29
K-L	7.82 \pm 0.26	7.35 \pm 0.25	-42.50 \pm 0.17
MM	10.24 \pm 0.30	10.00 \pm 0.30	-34.47 \pm 0.49

samples were evaluated for wettability, swelling extent, and water sorption. Upon contact with water, all the clay samples expanded, reaching a plateau value within just a few minutes (Figure 5). Because of the hydrophilicity conferred by hydroxyl groups present on the broken edges or terminated surfaces, water spread quickly on all sample surfaces giving contact angles of zero degrees. The BNT and MM swelled significantly in water achieving particle dimensions from 13 to 18 times the original, respectively, (Table 1) owing to water adsorption in the interlayer space and in the voids between particles (Salles *et al.*, 2010). Conversely, kaolins increased their diameter to only 2.5 (K-H) or 4 (K-L) times the original. The greater swelling extent of the K-L than of the K-H sample may reasonably be related to its greater Mnt phase. The swelling extent was found to be in agreement with the clay structural characteristics and consistent with the definition of “expandable” for smectites and “non-expandable” or “low-expandable” for kaolinite-rich clays (Holtz and Kovac, 1981; Taylor and Smith, 1986; Miranda-Trevino and Coles, 2003). Despite the poor level of crystal expansion, both kaolins were able to adsorb a larger volume of water (~ 0.65 mL, regardless of the sample, $p > 0.05$) than BNT (0.21 ± 0.02 mL) ($p < 0.05$) (Table 1, Figure 6), but slightly lower than that adsorbed by MM ($0.78 \pm$

0.05 mL) ($p < 0.05$). Kaolinite has strong adsorption properties provided by the highly ionizable cations placed at the level of the terminated planes and edges (Foster, 1954). The smaller degree of water adsorption along with the smaller swelling extent of BNT compared with MM may be attributed to the lesser abundance of Mg^{2+} , *i.e.* isomorphous substitution of Al^{3+} by Mg^{2+} in the BNT octahedral sheet, producing fewer exchangeable cations considered to be the main factor influencing water sorption. Influences may arise from the larger amount of impurities in BNT such as Qz (Dontsova *et al.*, 2004).

Relevant differences in rheological properties among the clays analyzed were also recorded. The flow behavior of a clay suspension has a significant impact upon its processability, applications, and storage for several areas of application (Abu-Jdayil, 2011). The shear-stress *vs.* shear-rate curves for clay suspensions with 10 or 25% solid content were recorded (Figure 7). All the samples exhibited non-Newtonian pseudoplastic patterns with a decrease in apparent viscosity with increasing shear rate. Flow curves of BNT, K-H, and K-L suspensions with 10% solid content were not significantly different from each other ($p > 0.05$). The rheology of these clays was weak with viscosity values ranging from ~ 6 to 3 mPa·s at low shear rate (43.28 s $^{-1}$), and decreasing to ~ 1 mPa·s at high shear rate (1384.96 s $^{-1}$), without displaying thixotropic properties (overlapped ascending and descending rheograms). Conversely, MM suspensions exhibited greater viscosities, ranging from ~ 140 mPa·s at low shear rate (43.28 s $^{-1}$) to 36 mPa·s at high shear rate (1384.96 s $^{-1}$) with a yield stress of ~ 9 Pa and a hysteresis loop formed by the descending curve which was higher than that of the ascending loop, indicating negative thixotropic behavior, *i.e.* a rapid increase in recovery of the original viscosity. The rheological properties of clay suspensions are known to be related to the association between clay particles (Galindo-Rosales and Rubio-Hernandez, 2006).

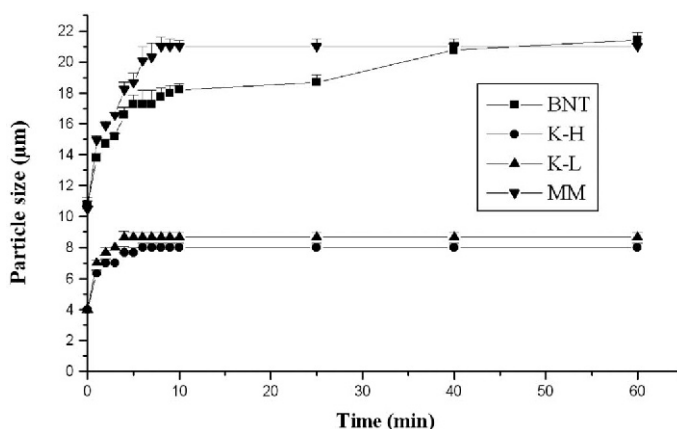


Figure 5. Particle swelling of bentonite (BNT), hydrothermal kaolin (K-H), and lacustrine kaolin (K-L), in comparison with a pharmaceutical-grade bentonite (MM), upon contact with water (determined by optical microscopy).

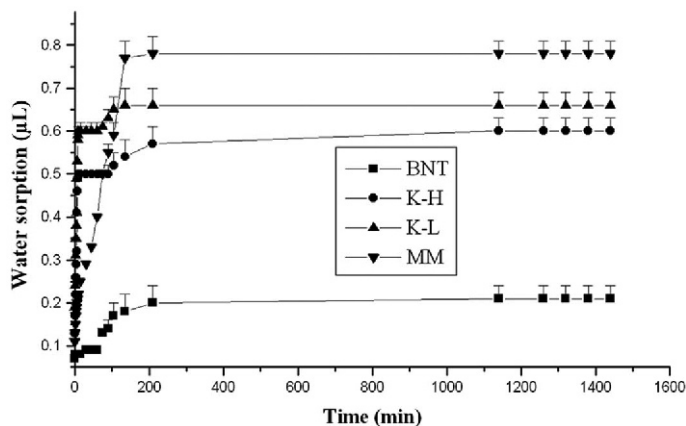


Figure 6. Water sorption of bentonite (BNT), hydrothermal kaolin (K-H), and lacustrine kaolin (K-L), in comparison with a pharmaceutical-grade bentonite (MM), upon contact with water (determined by means of an Enslin apparatus).

When 2:1 clay minerals are dispersed in polar media, a highly structured system is formed as a consequence of face-to-face and edge-to-face repulsive forces (Luckham and Rossi, 1999; Kennedy and Kennedy, 2007) causing platelets to exfoliate and delaminate. This leads to high viscosity, yield stress, and thixotropy which characterize suspensions of bentonites consisting of 70–90% Mnt, from a 3% solids content (Luckham and Rossi, 1999). The reduction in viscosity with increase in shear rate can be attributed to the progressive orientation of the individual platelets in the flow direction as well as to the breaking of the bonds between clay-mineral platelets (Heller and Keren, 2001). The BNT, however, showed rheological behavior which was significantly weaker, with lower viscosity values than MM. Because the rheological properties of bentonites are determined by the swelling components (Au and Leong, 2013), this finding can be attributed to the lower water adsorption along with the lesser swelling extent of BNT in comparison with MM, as described above. The BNT

contains minerals in addition to Mnt, *e.g.* Qz, and has a $\text{Na}^+/\text{Ca}^{2+}$ ratio less than that of MM which could mitigate the rheological properties (Packter, 1956; Bena and Gorea, 2004). With regard to 1:1 clay minerals, no water can penetrate between the layers in Kln due to the strong hydrogen bonds, no charge deficiency is present in their structures, and the surface area is much smaller than that of bentonites. Consequently, kaolins display low viscosity except at high solids contents (>40%) (Au and Leong, 2013). The increase determined in solids content, to 25%, increased viscosities for BNT suspensions only with values ranging from ~ 12 mPa·s at low shear rate (43.28 s $^{-1}$) to 5 mPa·s at a higher shear rate (from 346.24 to 1384.96 s $^{-1}$), without yield stress or thixotropy (overlapped ascending and descending rheograms), whereas rheograms of both kaolins showed no changes in the function of the solid content. At 25% solid percentage, the handling of MM suspensions was impracticable due to the extreme viscosity.

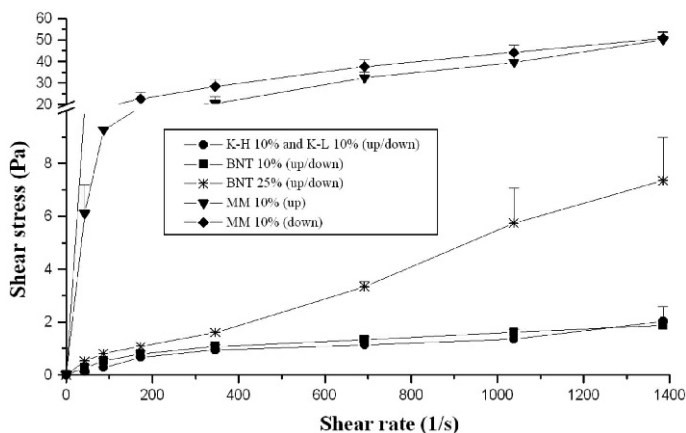


Figure 7. Flow behavior (shear stress vs. shear rate) of bentonite (BNT), hydrothermal kaolin (K-H), and lacustrine kaolin (K-L), in comparison with a pharmaceutical-grade bentonite (MM), determined by coaxial cylinder rheometer on a 10% or 25% clay water suspension

CONCLUSIONS

The characterization of three native Italian clays, one bentonite and two kaolins, with the aim of establishing their possible uses in pharmaceutical and cosmetic formulations, has revealed different properties according to the mineralogical and elemental composition of each clay. In this regard, EDX analysis has proved of considerable interest in identifying and quantifying the elements within the clay-lattice structures. Bentonite from the Iglesias deposit exhibited hydration properties such as swelling, water sorption, and viscosity, which were less than those typical of clays with Mnt as the main component. The CEC, however, was comparatively large and appropriate for drug interactions in modified drug-delivery systems or thermal muds following clay maturation in contact with thermal and/or mineral waters. Both kaolins from the Roccastrada deposit proved to be good adsorbents and useful, therefore, in pharmaceuticals as dermatological protectors, or in cosmetics as deodorants, protectants, bath powders, and face masks, for their capacity to increase the adherence of the preparation as well as the adsorption of undesirable substances such as skin exudates. Despite the weak rheological properties, all of the samples are suitable for use in the stabilization of pharmaceutical and cosmetic dispersions because of their presence at the interface boundaries between the formulation phases. Nevertheless, for topical application, samples could require some treatments to reduce the amount of abrasive materials such as quartz or feldspar.

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