Characterization and adsorption capacity of Brazilian kaolin

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Abstract

This study has evaluated chemical, radiological composition and determined the cation exchange capacity (CEC) for three commercially available Brazilians raw kaolins. The mineralogical characterization indicated the presence of kaolinite, kaolinite and quartz and pirophylliteas the mains mineral constitution of the samples. The results of the adsorption study indicated that the three samples did not show a significant increase in CEC due to acid or thermal treatments. However, the sample that presented the highest kaolinite content and CEC showed an effective cost benefit for water treatment application with low energy and chemical reagents spending.

Keywords Kaolinite adsorption · Clay adsorption · Cation exchange capacity · Blue methylene titration

Introduction

Clays are natural, earthy, fine-grained materials which usually acquire certain plasticity when moistened. Chemically, they are mainly composed of extremely small crystalline particles with a diameter below 2 μm, of a restricted number of minerals known as "clay minerals". The clays may be composed of particles of a single or mixture of various clay minerals generally formed by hydrated aluminum and iron silicates and may contain different levels of alkali and alkaline earth elements. Other materials and minerals, such as "organic matter", soluble salts and quartz particles, pyrite, mica, calcite, dolomite and non-crystalline or amorphous minerals may also be found [1].

Due to its properties, abundance and ease in handling, clays are employed both as raw materials as well as finished products in various industry types, e. g., agriculture, soil mechanics, paper, metallurgical and petroleum [2–4]. Due to its adsorbent capacity, they also have been employed as molecular sieves, as filtration agents, oil adsorbents and for ions removal from aqueous solution. This last application

has been noticed in a growing number of studies [5–10]. As ions adsorbent several clay types has been successfully applied for removal of different elements from solution, such as rare earth elements [11, 12], actinides [13, 14] and heavy metals [15–17] among others.

For clay characterization, mainly for its technological use, it is worth to know the variability of its properties. The objective of this work was to characterize three types of Brazilian kaolin commercially available by means of X-ray Diffraction, X-ray fluorescence, Neutron Activation Analysis and Gamma Spectrometry in order to verify its mineral, chemical and radiological composition and to determine the Cation Exchange Capacity of the raw clay and its chemical and thermal activated forms, by means of methylene blue titration with the aim of it's application as an ion adsorbent.

Material and methods

Sampling

Three commercialized types of Brazilin kaolin were acquired from different vendors in the regular market, and no information about the mining region where the raw material came from was available in the product labels. Here they are identified as CA, CB and CC.

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Sample Pre-treatment

Before starting any of the tests, all three samples were dried at 90 °C for 3 h and the procedure was repeated until constant weight and then samples were pulverized with a mortar and pestle, and sieved to at least 75 μm.

Physical–chemical characterization

The thermal characteristics of the kaolin samples were analyzed by the lost of mass method at 105 °C for moisture determination and loss of ignition (LOI) at 550 and 1000 °C, sequentially, in an oven furnace and muffle, respectively [18]. Also, a thermogravimetric analyis was done by using a Thermogravimetric Analyzer (TGA) model STD 660 from TA instrumets [19].

X-Ray diffraction

The X-ray diffraction (XRD) technique is of great mineralogical importance because it is the most suitable method for the determination of crystalline phases present in clays, as they can be defined as a set of randomly oriented small crystals. In the crystalline or semi-crystalline solids, the atoms or molecules arrange themselves into three-dimensional shapes that are periodically separated by layers in the same order of magnitude as the X-rays wavelength. Therefore, it is possible to identify the clay minerals main groups based on the basal interplanar spacing, i.e. the distance between the layers that define the crystalline structure of the lamellar clay mineral [20]. The clay minerals in each sample were identified by X-ray powder diffraction using a Siemens automated powder diffractometer equipped with a graphite monochromator, and Cu Kα radiation at 40 kV and 40 mA. All samples were scanned in the 2θ range of 2°–60° with a step size of 0.020°, using Cu Kα radiation at 40 kV and 40 mA. Three X-ray patterns were recorded at air-dried condition, after solvation with ethyleneglycol during 24 h and after heating at 550 °C for 3 h.

X-Ray fluorescence

Due to its simplicity, speed and accuracy, the technique of X-ray fluorescence (XRF) is being increasingly used for the chemical analysis of clays and clay minerals. The method is based on the measurement of a characteristic X-ray emitted by an electron occupying a vacancy left in the inner orbital shell for another ejected electron. Because the energy difference between two specific orbital shells is always the same, the X-ray emitted when an electron moves between these two levels the energy is always the same and therefore by determining the wavelength of the emitted X-ray for a particular element, it is possible to determine the identity of this element [21]. The chemical characterization was carried out using a WDXRF spectrometer RIGAKU Co., model RIX 3000 with X ray tube, an Rh anode, a 75 μm Be window, a 60 kV maximum acceleration voltage, scintillation detector NaI(Tl) and flow-proportional counter. The samples were prepared in pressed pellets, where in 1.8 g of the sample, 0.2 g powder wax (analytical grade, HOECHST) was added, mixed and homogenized in Mixer/Mill and then, all of them were pressed using a hydraulic press. The Fundamental Parameters method was applied for correction of the absorption/excitation effects. The methodology was evaluated, using standard reference material SRM 2709—San Joaquin Soil and SRM 2711—Montana Soil, from NIST (National Institute of Standards & Technology).

Instrumental neutron activation analysis

The technique of Instrumental Neutron Activation Analysis (INAA) involves the bombardment of a given material with neutrons, followed by the measurement of its induced radioactivity. The method is based on a nuclear reaction resulting from the interaction of a neutron with a target producing a nucleus in an excited state, which will decay in accordance with the half-life of the formed nuclide through a variety of forms. The induced activities are determined by means of semiconductor detectors [22].

For the elemental determination in the analyzed clays, approximately 100 mg of each sample and reference materials (STM-2 from United State Geological Survey and HISS-1 from the National Research Council Canada) were accurately weighed and sealed in pre-cleaned double polyethylene bags and irradiated for 8 h in a thermal neutron flux of 10^{12} cm^{-2} s^{-1} in the IEA-R1 nuclear research reactor at IPEN (Nuclear and Energetic Research Institute, São Paulo, Brazil). After irradiation, two series of countings were made, one after one week of decay and the second after 15–20 days [23]. The counting time was 1.5 h for each sample and reference materials. Gamma spectrometry was performed using an EG & G Ortec Ge-Hiperpure detector and associated electronics, with resolution of 1.9 keV and 2.04 keV for ^{57}Co and ^{60}Co, respectively. The concentrations were obtained by comparing the photopeak area of the interest element in the spectrum of the sample with that of the standard reference materials.

Gamma spectrometry

Gamma spectrometry is based on the counting of the gamma photons emitted by natural nuclides for a hipper pure Ge detector [24]. The activity concentrations of ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{40}K were determined by a HPGe detector with

25% relative efficiency, model GEM20190 from EG & G Ortec Industries and associated electronics.

Prior to the measurements, homogenized samples were sealed and left apart for a 30-day minimum delay to ensure that radioactive equilibrium between ^{226}Ra and its short-lived decay products was obtained. The activity concentrations were obtained by comparing the photopeak area of the interest nuclide in the spectrum of the sample, with that of the IAEA 327 Standard Reference Material (radionuclides in soil) counted in the same geometry.

The activity concentration of ^{226}Ra was taken as the mean activities measured for the ^{214}Pb (351 keV) and ^{214}Bi (609 and 1120 keV) photopeaks, for ^{228}Ra determination it was used as the mean activities of the ^{228}Ac (328 and 911 keV), ^{212}Pb (328 keV) and ^{212}Bi (727 keV). The activity concentration of ^{210}Pb was determined by its own photopeak of 46.5 keV as well as, ^{40}K was determined by its own 1460.8 keV photopeak.

Self-attenuation by the samples for the ^{210}Pb gamma radiation can occur, due to its low energy. The correction for this effect was performed for each sample according to the procedure described by Cutshall et al. [25].
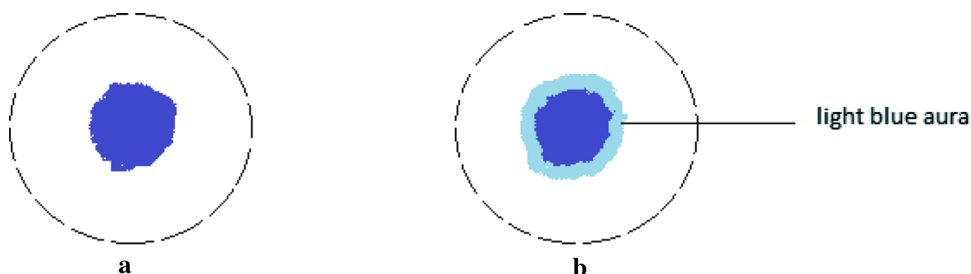
Thermal and chemical clay activation

The clay adsorption capacity can vary according to various parameters such as contact time, pH, concentration of metal ions, etc. However, this adsorption capacity can be increased if they undergo an activation process that consists of the application of chemical or physical treatment in order to change its properties [26–28].

For the thermal treatment carried out in a furnace oven, the three white clay samples were heated at temperatures of 150, 200, 250 and 300 °C for periods of 1, 2 and 3 h.

In the chemical treatment, the samples were treated with hydrochloric acid or sulfuric acid in concentrations of 1, 2, 3, 4 and 6 mol L^{-1}, for 1 h at 90 °C heating under constant agitation. After the acid treatment the samples were vacuum filtered, washed with ultrapure water until neutral pH and subsequently oven-dried at 100 °C for a period of 24 h. After that the samples were pulverized and sieved to 75 μm and again taken into the furnace oven at a temperature of 200 °C for a period of 1 h.

Cation exchange capacity determination

To determine the cation exchange capacity (CEC) the method of methylene blue adsorption was employed for its speed, simplicity and good reproducibility. This method, described by Moreira et al. [29], constitutes a suspension of 0.5 g of clay (sieved at 0.074 mm) in 300 mL of water titration with a 0.01 mol L^{-1} Methylene Blue solution under constant stirring. After each 1 mL of the dye solution addition and 5 min stirring, one drop of the suspension (water + clay + dye) was removed with the aid of a Pasteur pipette and then dropped on a filter paper (Whatman No. 41). The turning point was registered when the spot formed by the diffusion of the drop on the paper presented a clear blue aura, meaning that the dye was in excess in the suspension, according to what is shown in Fig. 1.

The CEC was calculated by using the following Eq. 1:

$$CEC = \frac{V.C.100}{w} \qquad (1)$$

Being CEC the Cation Exchange Capacity in meq/100 g; V: the volume (ml) of methylene blue solution used in the titration; C, the Methylene Blue concentration (mol L^{-1}) and w, the mass (g) of the clay used in the titration.

Results

Adsorbent characterization

Physical–chemical characterization

In general, clay minerals have characteristics of similar thermal behavior, such as water loss and phase transition. Around 100 °C the moisture water evaporates, between 550 °C and 600 °C the crystal internal water is eliminated and only above this temperature can the effective start of sintering be identified. Between 850 °C and 1000 °C, carbonates decompose, forming calcium oxides that do not react with silicates. Above 900 ºC the fluxes (oxides of

Fig. 1 Identification of the methylene blue titration end point. **a** all of methylene blue is adsorbed and **b** light blue aura, indicating that there is an excess of methylene blue in the suspension (adapted from Moreira et al. [20])

light blue aura

potassium, sodium and iron, among others) form a liquid phase. After 1000 °C, clay minerals are reorganized into new crystalline structures.

According to the results presented in Table 1, there is a small loss of moisture for the three samples at 100 °C. Figure 2a, b and c show the thermogram for the analyzed kaolin samples. It can be seen from the result obtained for CA sample (Fig. 2a) an exothermic peak below 100 ºC, that may have been caused by crystallization, curing, oxidation or adsorption, which may indicate that the CA clay may had

Table 1 Percentage of moisture, LOI at 550 °C and 1000 °C for samples of kaolins

	CA	CB	CC
Moisture (%)	0.20	0.30	0.62
LOI 550 °C (%)	3.40	4.16	12.71
LOI 1000 °C (%)	4.00	5.27	14.32

undergone some previous thermal treatment before being marketed. The endothermic peak found at 545 °C to 550 °C (Fig. 2a, b and c) are related to the dehydroxylation of the water bounded to the crystalline phases. The theoretical mass loss in this process was 3.15%, 4.80% and 13.39% (thermogravimetric method), respectively, for samples CA, CB and CC; and 3.40%, 4.16% and 12.71% obtained in the lost of mass method. Zatta [30] found 13.96% of theoretical mass loss, a close value when compared with the results of the CC sample found by both methods. At 1000 °C, the event of the crystallization of mullite is attributed, that is, to a phase transition of the constituent oxides of kaolinite [31].

X-Ray diffraction

The X-ray diffraction of CA, CB and CC samples are represented in Figs. 3, 4 and 5, respectively.

CA sample showed the predominance of quartz and a small amount of kaolinite, CB sample proved to be
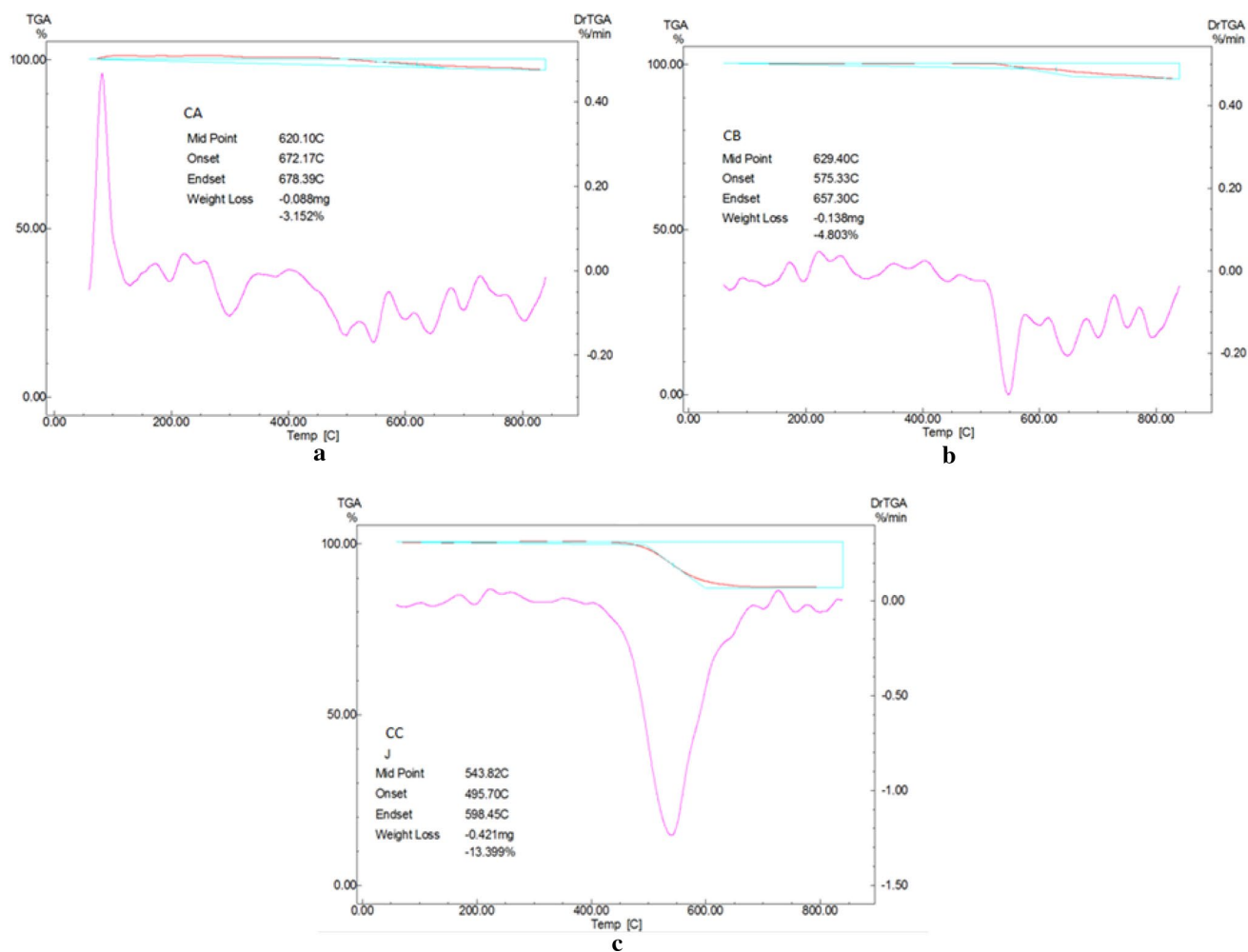

Fig. 2 TGA curves of CA **a**, CB **b** and CC **c**

Fig. 3 Diffractogram referring
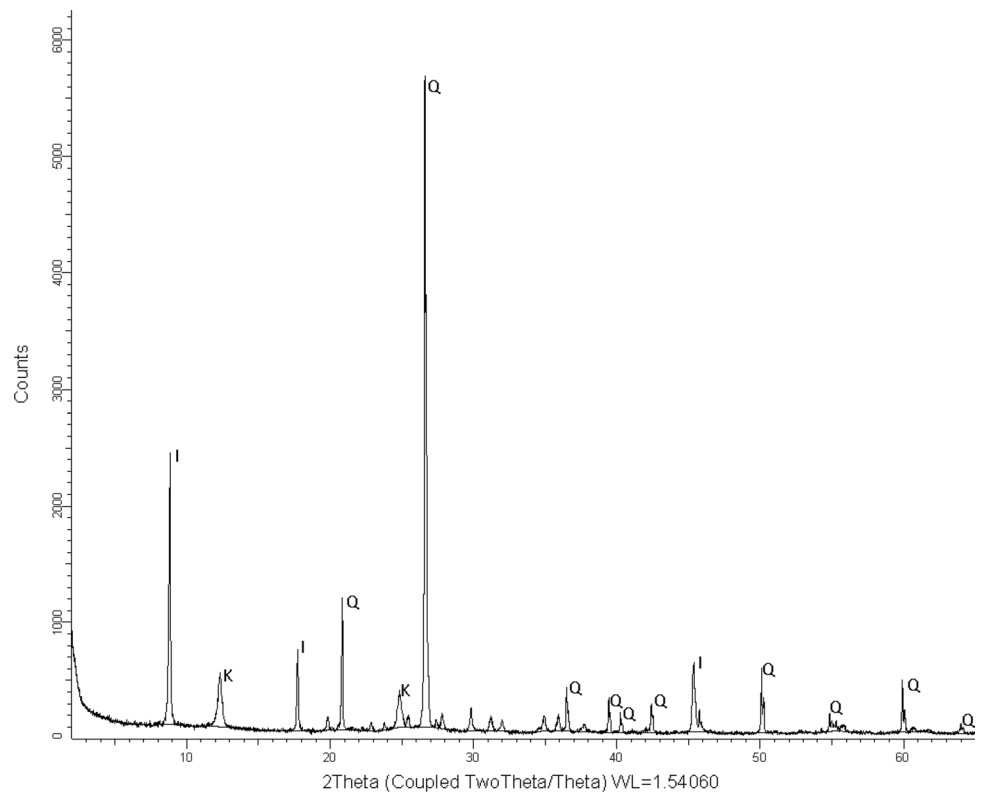to the sample AC. K = kaolinite,
Q = quartz and I = illite

Fig. 4 Diffractogram referring
to the sample CB. P = pyrophyl-
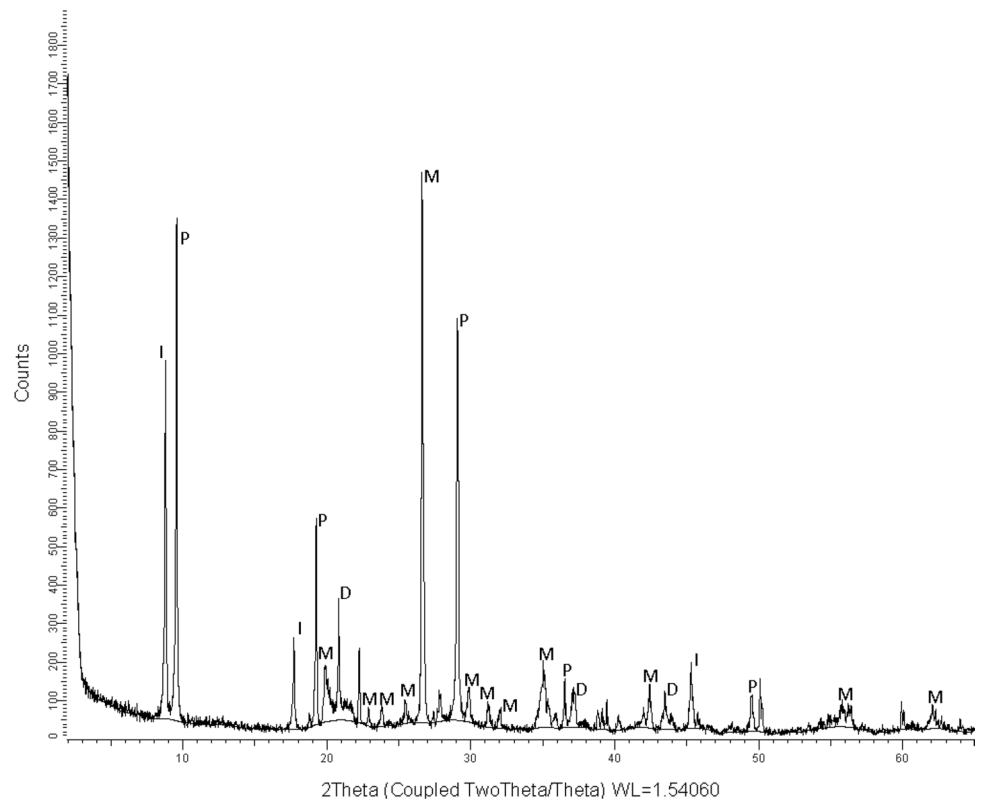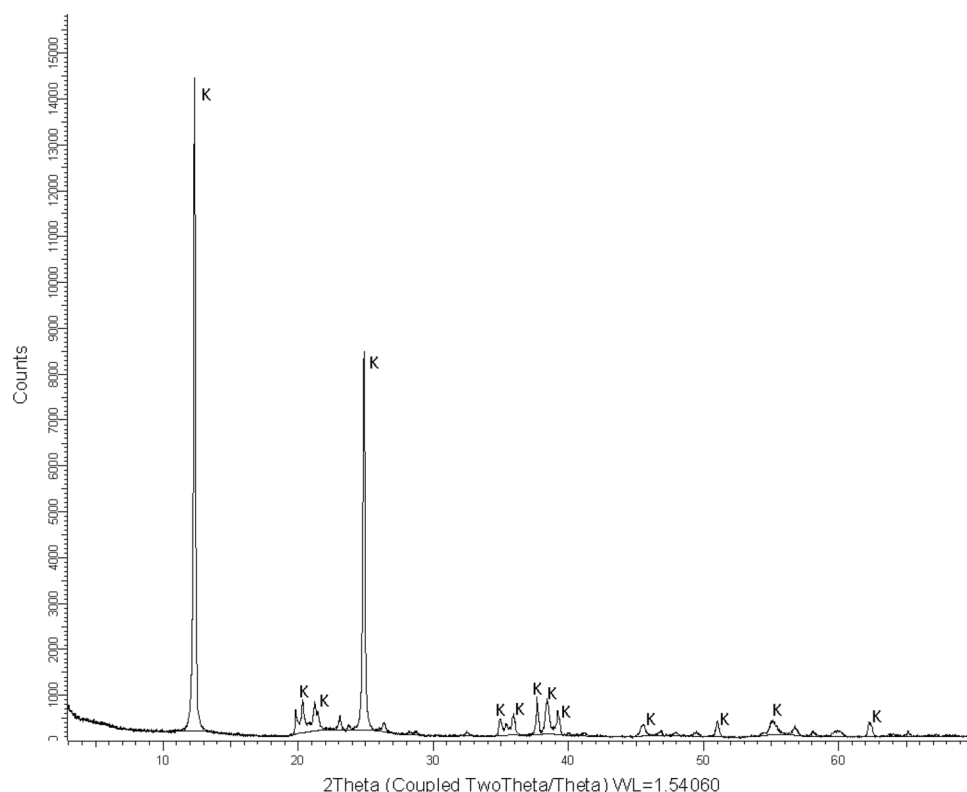lite, M = muscovite, I = illite and
D = diaspore

Fig. 5 Diffractogram referring to the sample CC (pure kaolinite, K)

composed of pyrophylitte with considerable amounts of muscovite, illite and diaspore, while the CC sample resulted in pure kaolinite.

Pyrophyllite is a hydrous aluminium silicate, relatively rare, found in metamorphic rocks, often intimately associated with other minerals, not so easy to characterize, but the X-ray pattern showed in Fig. 3 is in well agreement with the cell parameters found in [32].

Chemical composition

In Table 2 the results obtained through the X-Ray Fluorescence analysis are shown together with studies found in literature for comparative purposes.

It can be observed by the results that there is considerable variation in the oxide content of the samples, not only due to the fact that the chemical composition of minerals are peculiar to the regions they were formed in, but also because these commercial clays are not composed by pure kaolinite except for sample CC. As expected by the X-Ray Diffraction

Table 2 Major elements content (% in oxide) of the analyzed samples with studies found in literature according to Zatta [30], Aragão et al. [33] and Sales et al. [34]

Element (%)	CA	CB	CC	Zatta [30]	Aragão et al. [33]	Sales et al. [34]
SiO_2	65.00	61	53	50.30	74.30	52.75
Al_2O_3	19.90	34	46	25.50	19.70	43.13
Fe_2O_3	2.40	0.3	0.40	5.00	1.02	3.05
K_2O	6.90	3.4	0.025	–	2.01	0.52
TiO_2	1.00	0.3	0.40	–	0.096	–
Na_2O	0.18	0.35	0.34	–	0.18	0.09
MnO_2	<0.01	<0.01	–	–	–	–
MgO	0.17	0.07	–	–	0.59	0.46
H2O	–	–	–	–	–	–
CaO	0.01	0.07	0.006	–	0.05	0.00
TiO_2/CaO	100	–	–	–	–	–
P_2O_5	–	–	0.067	1.3		

results only sample CC presents the molar ratio SiO_2/Al_2O_3 similar to the theoretical kaolinite 2.0. This value for sample CA 5.54 indicates a high amount of free silica and the relatively high amounts of Fe, K and Ti indicates the presence of impurity of Fe- and Ti- oxides and mica [35]. According to Brindley et al. [36] higher amounts of cation substitution are related to the disordered structure, indicating that the sample CC is better crystalized than samples CA and CB. For sample CB the molar ratio SiO_2/Al_2O_3 equal to 3.06 is smaller than the theoretical value 3.96 [37]. The higher value of Al_2O_3 must be accounted for by the muscovite and illite presence consistent with the K_2O content found.

The composition of minor and trace elements for the three analyzed kaolin, obtained by neutron activation analysis (Table 3) show a wide variation as shown by the X-Ray fluorescence results.

The sample CA showed higher concentrations for the elements Ca, Cr, Cs, Fe, K, Rb, Sb and Sc. Samples CC showed high concentrations only for the light rare earth elements Ce, La, Nd and for the element Br. All the other elements were present in higher concentrations in the sample CB. Rare earth enrichment in kaolinite phase has been documented by

Aja [38], Marques et al. [39] and Yanfei et al. [40] since diagenetic processes causing remobilizations on rare earth that are adsorbed by clay minerals mainly those formed under low-temperature conditions such as kaolinite. The higher concentrations of K, Rb and Cs in samples CA and CB can be explained by the presence of k-rich mica minerals, illite and muscovite as well as the relatively higher amount of the other trace elements, which can be explained by the presence of these same minerals because they are well known to have many sites available for substitution due to its layered structure [41]. Only sample CA showed an amount of iron around 1% and as shown in the diffractograms no Fe-bearing mineral was identified which can also explain the relatively low concentration of Co, another siderophile element.

Radionuclide content

Based on the results shown in Table 4 it can be concluded that the samples of the three CA, CB and CC clays do not present any radiological risk since they are in the same order of magnitude normally found in soils [42].

The fact that ^{228}Ra is in a higher activity concentration than ^{226}Ra is in accordance with the results for the parents of their respective radioactive series ^{232}Th and ^{238}U. According to Ramasamy et al. [43] ^{232}Th and ^{40}K in clayey fractions are more associated with light minerals than ^{238}U being the principal element responsible for the dose rate for gamma radiation exposure in this case. It also has been noted that a high ^{232}Th/^{40}K ratio indicates the presence of heavy minerals and low values of ^{232}Th/^{40}K indicates the presence of light minerals [44, 45]. This ratio observed for samples CA and CC are in agreement with this statement as well as with the X-ray diffraction results and the low amount of Fe and Ti in the samples that did not indicate the heavy mineral presence.

Cation exchange capacity

Cation Exchange Capacity (CEC) is the main characteristic of a clay being employed as an adsorbent [46] and is dependent on a series of factors, mainly the pH. The results obtained for the CEC of the three kaolin samples analyzed in this study, are shown in Tables 5 and 6.

Table 3 Trace elements concent (in mg kg^{-1}) obtained by instrumental neutron activation analysis

Element (mg kg^{-1})	CA	CB	CC
As	1.1 ± 0.2	2.4 ± 0.3	0.4 ± 0.1
Ba	561 ± 82	623 ± 83	–
Br	–	0.5 ± 0.2	0.7 ± 0.2
Ce	102 ± 7	139 ± 10	202 ± 14
Co	1.3 ± 0.1	0.73 ± 0.09	0.6 ± 0.1
Cr	98 ± 14	16 ± 3	25 ± 4
Cs	8.0 ± 0.8	4.3 ± 0.4	0.20 ± 0.06
Eu	1.13 ± 0.05	1.70 ± 0.08	1.22 ± 0.06
Hf	7.5 ± 0.2	12.5 ± 0.2	4.3 ± 0.1
La	70 ± 21	110 ± 5	200 ± 8
Lu	0.68 ± 0.04	1.58 ± 0.07	0.20 ± 0.03
Nd	51 ± 17	87 ± 7	173 ± 20
Rb	252 ± 16	125 ± 8	–
Sb	3.7 ± 0.6	0.8 ± 0.1	0.6 ± 0.1
Sc	21.8 ± 0.2	10.6 ± 0.1	5.73 ± 0.06
Se	–	8 ± 1	3.3 ± 0.9
Sm	8.8 ± 0.5	20 ± 1	8.2 ± 0.5
Ta	1.3 ± 0.1	5.3 ± 0.2	1.0 ± 0.1
Tb	4.1 ± 0.4	7.8 ± 0.4	1.4 ± 0.3
Th	24 ± 2	91 ± 9	44 ± 4
U	3.8 ± 0.5	10.5 ± 0.9	1.3 ± 0.3
Yb	2.8 ± 0.3	8.1 ± 0.7	1.0 ± 0.1
Zn	84 ± 5	99 ± 6	73 ± 5
Zr	314 ± 53	510 ± 52	178 ± 35

Table 4 Activity concentration of the radionuclides in the three white clay samples

Radionuclides (Bq kg^{-1})	CA	CB	CC	IAEA 327
^{226}Ra	42 ± 5	77 ± 3	14 ± 2	35 ± 0.05
^{210}Pb	–	388 ± 172	105 ± 18	56 ± 7
^{228}Ra	127 ± 18	266 ± 32	55 ± 10	39 ± 3
^{40}K	–	711 ± 46	1009 ± 66	668 ± 44

Table 5 Results of the cation exchange capacity of the three samples after thermal treatment

Time (hour)		Temperature (°C)				
		Without treatment	150 °C	200 °C	250 °C	300 °C
	Clay	CEC (meq/100 g) ($n=3$)				
1	CA	7.94	6.62	7.94	5.96	7.94
	CB	5.95	5.94	6.57	5.96	5.98
	CC	9.00	7.92	3.98	5.96	7.96
2	CA	–	5.98	5.9	5.91	5.98
	CB	–	5.98	5.9	5.94	6.63
	CC	–	5.97	3.97	5.97	5.95
3	CA	–	5.32	4.59	5.99	5.98
	CB	–	5.32	6.58	5.99	5.98
	CC	–	6.96	3.98	5.96	6.96

Table 6 Results of the cation exchange capacity of the three samples after the acid treatment

		Acids concentration (mol L^{-1})				
		1.0	2.0	3.0	4.0	6.0
	Clay	CEC (meq/100 g) ($n=3$)				
H_2SO_4	CA	5.92	6.95	5.94	5.91	6.95
	CB	6.93	6.61	6.62	6.61	5.98
	CC	7.95	5.97	–	5.97	–
HCl	CA	5.96	6.94	7.27	5.98	6.62
	CB	5.30	5.97	5.97	6.92	5.94
	CC	5.96	6.96	–	6.00	–

Measurements were done at neutral pH both for the raw material and the activated samples and the reported results are the mean of three replicates. The non-treated kaolinite samples presented CEC of 7.94 and 9.00 meq/100 g while the pyrophyllite sample showed the smaller CEC value 5.95 meq/100 g. The values for samples are in well agreement as that reported by Unuabonah et al. [47] and Jiang et al. [48] for naturally occurring kaolinite.

From Tables 2 and 3 it can be observed that thermal and chemical treatments did not cause substantial changes in the cation exchange capacity of the samples.

The fact that the values for thermally and acid treated samples do not show an increase in the CEC, is probably related to the temperature in which the activation was done. An increase in the CEC has been reported for kaolinite heated over 600 °C [10] and in this work the maximum temperature of activation was 300 °C. Also, the observed decrease in CEC is indicative of the reduced number of exchangeable sites caused during the dehydroxylation process [49]. Acid treated kaolinite heated in relatively low temperatures, under 300 °C, also does not show a significant increase in the CEC [50]. On the other hand the cost benefit of spending energy and reagents just to raise the kaolinite CEC in few meq/100 g has not been considered. In this case,

according to our results the use of non-treated kaolin can be justified.

Conclusion

Three commercialized types of kaolin were characterized. X-ray diffraction has indicated that among the samples only the CC sample possesses a high content of kaolinite. The CA sample possesses a small amount of kaolinite and quartz, while the CB sample is formed by pirophyllite associated with other clay minerals. Chemical composition of the samples determined by x-ray fluorescence and neutron activation analysis proved to be in wide variation due to their mineralogical differences. Gamma spectrometry results also reflected the mineralogical differences in the origin of the samples, indicating that they presented no radiological risk since they are in the same order of magnitude normally found in soils. The results of the adsorption study indicated that the three samples CA, CB and CC did not show a significant increase in CEC due to acid and thermal treatments. However, the use of the *in natura* sample CC that presented the highest CEC can be the best cost benefit application of kaolinite for water treatment, since the research has shown

low improvement when spending energy and chemical reagents to barely raise the capacity for the removal of ions from solutions.

Declarations

Conflicts of interest The authors declare that they have no conflict of interest.

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