SOME PHYSICOCHEMICAL PROPERTIES OF PERLITE AS AN ADSORBENT

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SUMMARY

Perlite is a glassy volcanic rock, which will, upon rapid controlled heating, expand into a frothy material of bulk density. Considering the fact that the uses of perlite are based primarily upon its physical and chemical properties, it is aimed to investigate some physical and chemical properties of unexpanded and expanded perlite. Structural changes occurring during the expansion of perlite are discussed.

During the expansion a transition from amorphous structure to a crystalline form has been found to occur, and also some part of water has been removed, but there has still been some water in crystal lattice. Acid activation has caused a little increase in cation exchange capacity of perlite, while the density has remained almost unchanged.

KEYWORDS: Perlite, acid activation, surface area, cation exchange capacity.

INTRODUCTION

Perlite, a glassy volcanic rock, has the unusual characteristic of expanding to about 20 times its original volume when heated to an appropriate temperature within its softening range [1]. The name "perlite" is a derivation from "perlstein" originally given "to certain glassy rocks (hyaloliparites, hyalo-rhyolites) with numerous concentric cracks, from the fancied resemblance of broken fragments to pearls [2]. Petrographically, perlite can be described as a glassy, volcanic, rhyolitic rock having a pearl-like luster and usually exhibiting numerous concentric cracks resembling an onionskin in appearance. Chemically, crude perlite is essentially a metastable amorphous aluminum silicate. Commercially, the term "perlite" also includes the expanded product [1].

Along the Aegean Coast, Turkey possesses about 70 percent ($70x10^9$ tons) of the world's known perlite reserves [3]. The uses of expanded perlite are many and varied and are based primarily upon its physical and chemical properties. Because of i.) its low bulk density; ii.) low thermal conductivity; iii.) high resistance to fire; and iv.) low sound transmission, expanded perlite is used to a great advantage as aggregate and insulating material in the construction industry [4]. The more important applications include the following: abrasives, acoustical plaster and tile, charcoal barbecue base, cleanser base, concrete construction aggregates, filter aid, fertilizer extender, foundry ladle covering and sand additive, inert carrier, insulation board filler, loosefill insulation, molding filler medium, packaging medium, paint texturizer, pipe insulator, plaster aggregate and texturizer, propagating cuttings for plants, refractory products, soil conditioner, tile mortar aggregate and lightweight insulating concrete for roof-decks, and wallboard core filler [1]. As most perlites have a high silica content, usually greater than 70 % and are adsorptive, they are chemically inert in many environments and hence are excellent filter aids and fillers in various processes and materials [4].

In our previous works, we investigated the electrokinetic properties [5] and surface titrations [6] of perlite suspensions; the adsorptions of methylene blue [7], methyl violet [8], victoria blue [9] from aqueous solutions onto perlite samples; and also adsorption kinetics of methyl violet [10] and victoria blue [11] from aqueous solutions onto perlit samples. In the present study, the acid-activated perlite samples have been prepared from expanded and unexpanded perlite samples, and then the cation exchange capacities, densities and specific surface areas of these samples have been determined. Knowledge of these properties is necessary for a better understanding of reactions occurring onto perlite surface in aqueous solution. We did not find such a work in literature, which investigated some of the physicochemical properties of perlite.

MATERIAL AND METHODS

The unexpanded and expanded perlite samples were obtained from Cumaovası Perlite Processing Plants of Etibank (İzmir, Turkey). The chemical composition and some physical properties of the perlite found in Turkey are given in Table 1 and 2 [3]. The unexpanded and ex-

panded perlite samples were treated before using in the experiments as follows: a suspension containing 10 g/L perlite was mechanically stirred for 24 h, after waiting for a couple of minutes, the supernatant of suspension was filtered. The solid sample was dried at 110°C for 24 h, and then sieved by 100-mesh sieve [7].

TABLE 1
Chemical composition of perlite.

Constituent	Percentage Present
SiO_2	71-75
Al_2O_3	12.5-18
Na_2O	2.9-4.0
K_2O	4.0-5.0
CaO	0.5-2.0
Fe_2O_3	0.1-1.5
MgO	0.03-0.5
TiO_2	0.03-0.2
MnO_2	0.0-0.1
SO_3	0.0-0.1
FeO	0.0-0.1
Ba	0.0-0.1
PbO	0.0-0.5
Cr	0.0-0.1

TABLE 2
Some physical properties of perlite

Parameter	Data
Color	Gray, white, black
Softening point	800 - 1000 °C
Melting point	1.315 - 1.390 °C
pH	6.6 - 8.0
Specific heat	0.2 kcal/kg°C
Maximum free moisture	0.5 percent

In order to obtain the acid-activated perlite samples H_2SO_4 solutions were used. The aqueous suspensions of both the unexpanded and expanded perlite samples in 0.2, 0.4 and 0.6 M H_2SO_4 solutions (so that acid/solid ratios were 1/5, 2/5 and 3/5) were refluxed with a reflux apparatus, then filtered and dried at 110°C for 24 h [12].

The cation exchange capacity (CEC) of the samples obtained as described above was determined by the ammonium acetate method, density by piknometer method [12]. The specific surface area of the samples of expanded (EP), acid-activated expanded perlite (EHP(0.6)), unexpanded (UP), and acid-activated unexpanded perlite (UHP(0.6)) were measured by BET N_2 adsorption.

The IR spectra of perlite samples, sized < 150 μm, were investigated using a Mattson 1000 FTIR spectrometer. The perlite samples were dried at 120 ºC for twelve hours. Approximately, 0.0015 g perlite samples were mixed with 100 mg KBr, ground in an agate mortar, and then pelletted under vacuum with an applied pressure of 10 tons/m^2.

A computer controlled-automatic Huber-GuinierG600 powder diffractometer was used for taking X-Ray diffraction of the powders with CuK_α (λ=1.54178 Å) radiation obtained by using a voltage of 30-40 kV and a current of 12-20 mA. The X-Ray diffractograms were corrected with silicon as a standard.

A JEO-JSM840 Scaning Electron Microscopy was used to obtain SEM pictures.

All chemicals were made by Merck.

RESULTS AND DISCUSSION

The cation exchange capacities of the samples were shown in Figure 1 as a function of acid concentration. As seen in this figure, cation exchange capacity of expanded perlite is higher than that of unexpanded perlite. This increase in cation exchange capacity is thought as a result of increasing the broken edges during the expanded perlite production. When perlite is used to improve the quality of the soil, its CEC becomes an important property to be taken into consideration. The soil mineral fraction, as well as being an important source of soil nutrients, also serves as a nutrient sink. The cations may become adsorbed cations held in this way and readily released back into the soil solution by a process known as ion exchange. The CEC of the whole soil is a measure of the exchange capacity or negative charges of the soil, as milligram equivalents per 1000 grams of soil i.e. meg.kg^{-1}. When the total content of exchangeable cations is expressed as meg.kg^{-1}, the amount may seem small, but when recalculated on the basis of the amount of cations available to a growing crop there are usually several thousand kg of cations per hectare. The cation exchange capacities of kaolinite, vermiculite and montmorillonite are 30-150, 1000-1500 and 800-1500 meg kg^{-1}, respectively [13].

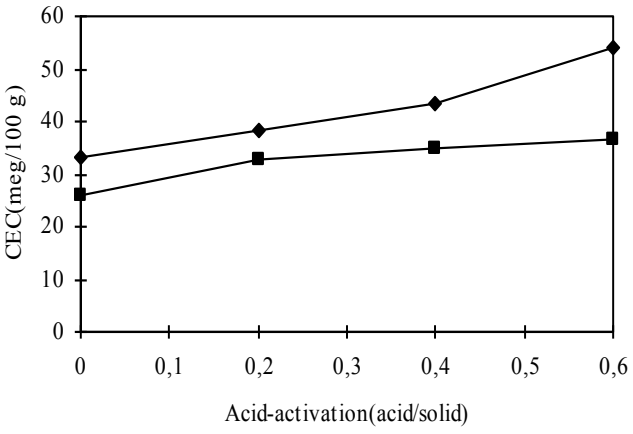
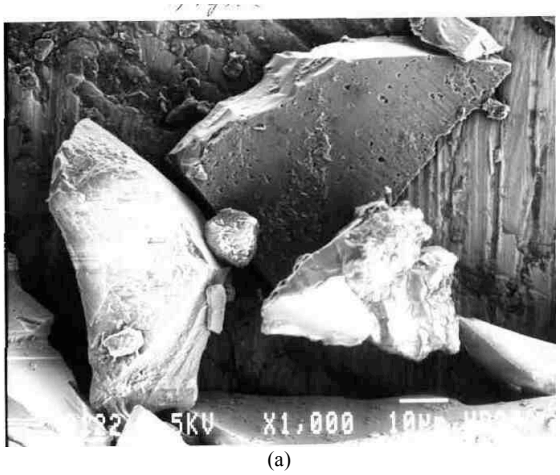


FIGURE 1 - The effect of acid-activation on the cation exchange capacity of perlite (♦: expanded, ■: unexpanded).

Cation exchange capacity of the expanded and unexpanded perlite samples increased with acid-activation, because of formation of new charged sites resulting from surface reactions occurring during the treatment with acid solution [6].

TABLE 3 - Some physicochemical properties of perlite samples used in the study.

Sample	Nomenclature	Density (g/mL)	Specific Surface Area (m^2/g)
Expanded, purified in water	EP	2.2	2.30
Expanded, 0.2-M acid-activated	EHP(0.2)	2.1	----
Expanded, 0.4-M acid-activated	EHP(0.4)	2.0	----
Expanded, 0.6-M acid-activated	EHP(0.6)	1.9	2.33
Unexpanded, purified in water	UP	2.3	1.22
Unexpanded, 0.2-M acid-activated	UHP(0.2)	2.3	----
Unexpanded, 0.4-M acid-activated	UHP(0.4)	2.4	----
Unexpanded, 0.6-M acid-activated	UHP(0.6)	2.5	1.99



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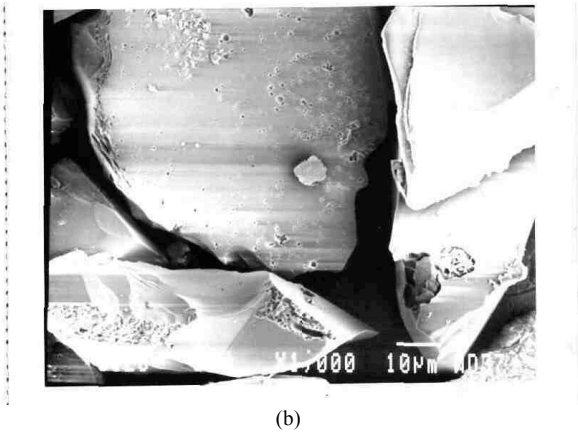

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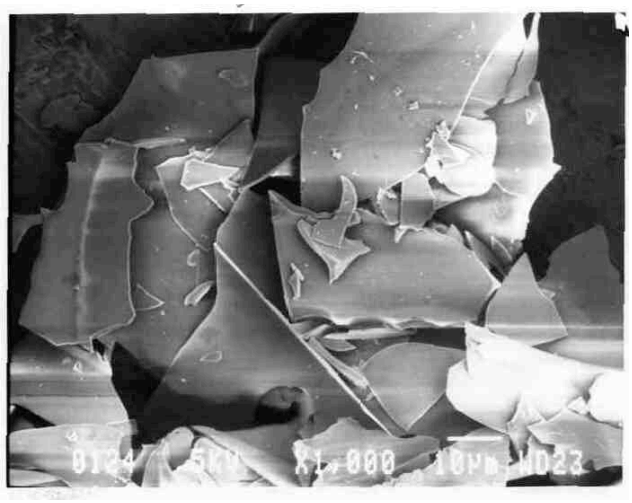
FIGURE 2
SEM pictures of unexpanded perlite samples: a) UP, b) UHP(0.6)



(a)

(b)

FIGURE 3
SEM pictures of expanded perlite samples: a) EP, b) EHP(0.6)

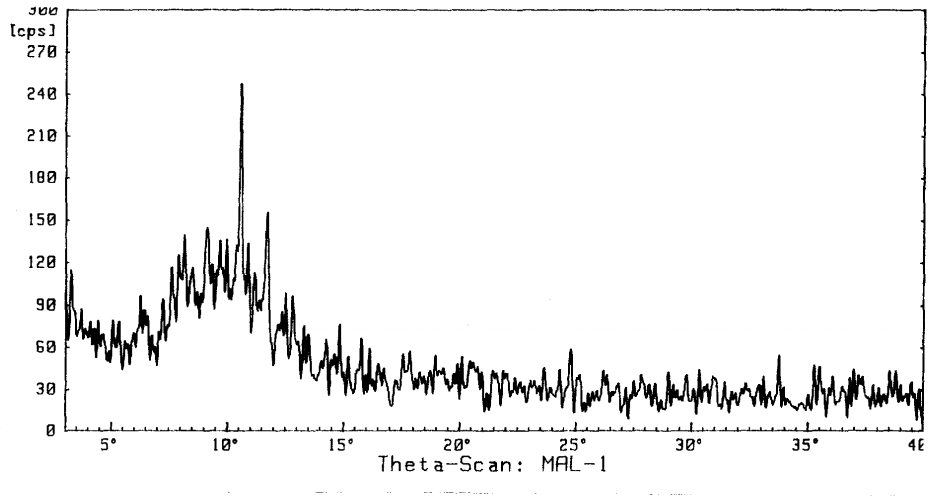
The densities of all samples and the specific surface area of expanded perlite, 0.6 M H-expanded perlite, unexpanded perlite and 0.6 M H-unexpanded perlite are given in Table 3. The densities of expanded perlite and unexpanded perlite are 2.24 and 2.30 g/cm^3, respectively. The scanning electron microscopic (SEM) pictures in Figure 2 and 3 show that the shape of the perlite particles is converted into the form of thin plates, and they do not form a structure which can prevent the penetration of the liquid, and also that the porosity of both of them is very low. Therefore, while the bulk density of the perlite decreases 4-20 times, the true density almost remains unchanged.

As seen in the same figures, the porosity of the samples does not change by acid activation, so the densities and specifice surface areas do not change significantly during the acid activation.

The X-ray powder diffraction pattern of unexpanded perlite given in Figure 4 shows that the sample has an

amorphous structure, so a qualitative analysis is impossible. A transition from amorphous structure to crystalline form occurs during the thermal treatment of perlite. This is also supported by higher count per second values of expanded perlite. The peak at 4.19 A^0 is not a result of only one phase, but also of more than one phase, which are silicates and oxides. By comparing the d values obtained in this study and taken from ICPDS charts the crystal structures given in Table 4 were estimated to be formed.

Infrared spectroscopy is a universal method, which has been developed for silica surface studies. The Infrared spectra of the samples are given in Figure 5 and 6. The broad band between 3750 and 3000 cm^{-1} is attributed to the vibration of hydrogen-bonded hydroxyl groups at the surface. The band at 3720 ± 20 cm^{-1} is attributed to the fundamental streching vibration of free or isolated hydroxyl groups. The band at 3660 ± 90 cm^{-1} arises from hydroxyl groups involved in hydrogen bonding called before vicinal. The band at 3520 ± 200 cm^{-1} is assigned to hydroxyl group, hydrogen bonded to adsorbed water.



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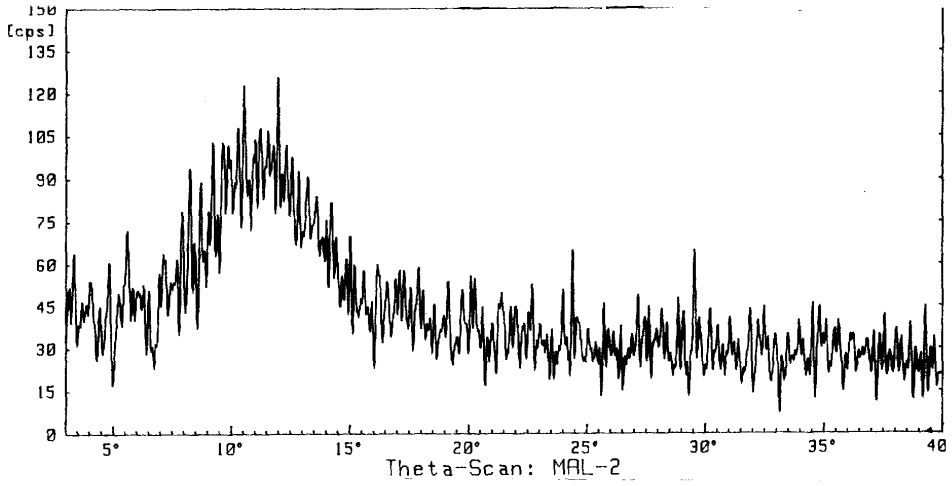

(b)

FIGURE 4
X-ray powder diffraction patterns of perlite samples: a) expanded, b) unexpanded.

TABLE 4
The crystal structures formed during the expansion.

Name	Formula	ICPDS No
Vuagnatite	$CaAl(SiO_4)(OH)$	29-289
Gismondine	$Ca(Al_2Si_2O_8).4H_2O$	20-452
Hibonite	$CaAl_{12}O_9$	25-121
Stishovite	SiO_2	15-26
Fassaite	$Ca(Mg,Fe,Al)(Si,Al)_2O_6$	25-1217
Chrysotile-2orel	$Mg_3Si_2O_5(OH)_4$	25-646
Analcime	$NaAlSi_2O_6.H_2O$	18-1180

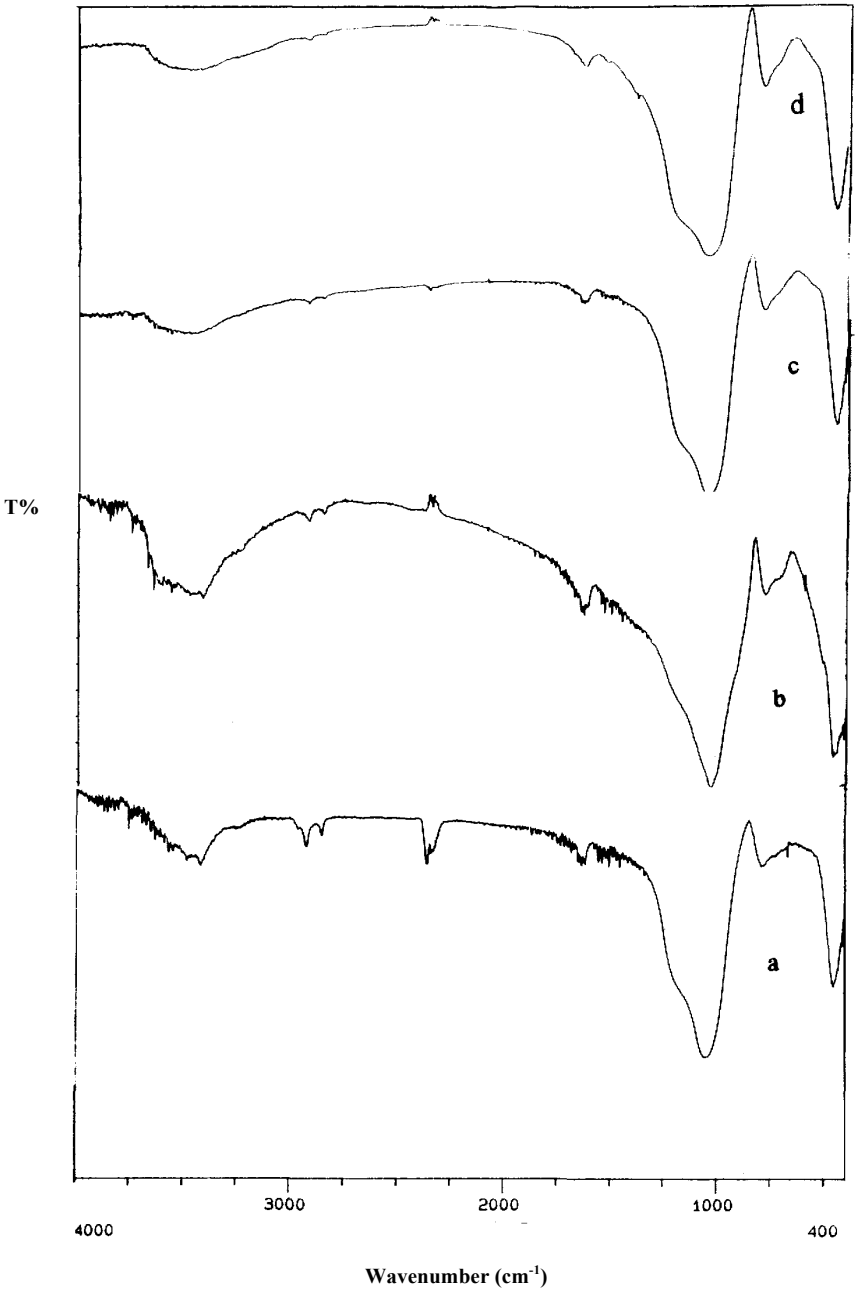

FIGURE 5 - Infrared spectrums of perlite samples: a) expanded, b) 0.2 M H-expanded, c) 0.4 M H-expanded, and D) 0.6 M H-expanded.

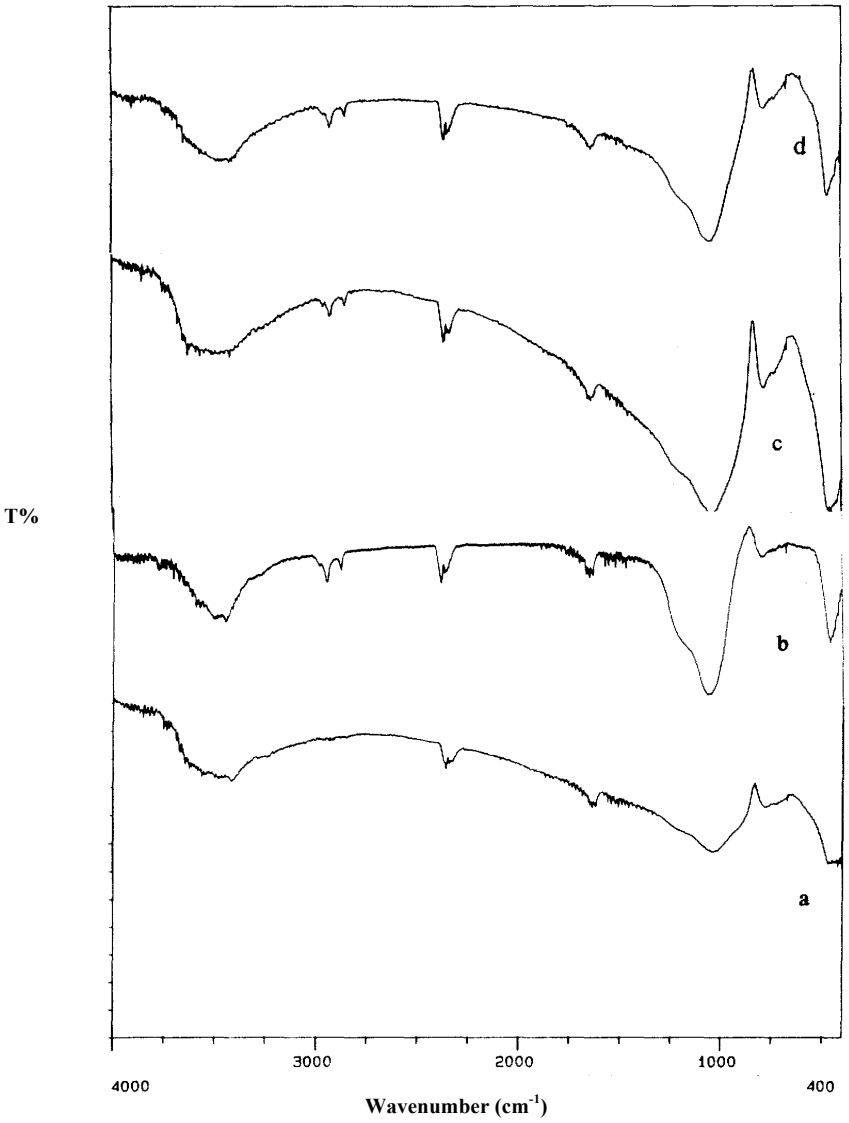

FIGURE 6 - Infrared spectrums of perlite samples: a) unexpanded, b) 0.2 M H-unexpanded, c) 0.4 M H-unexpanded, d) 0.6 M H-unexpanded.

The investigation of the infrared spectra of expanded and unexpanded perlite samples show that there is a difference in the intensities of bonds in the region between 3750 and 3000 cm^{-1}, resulting from the population of hydroxyl groups of the surface of the expanded perlite.

The bonds observed at 800-1250 cm^{-1} are attributed to the fundamental Si-O vibrations. In comparison of the transmission spectra of all samples, a very small difference may be seen in the region between 1100 and 1250 cm^{-1}. It can be concluded that the surface of expanded perlite is more polar that of unexpanded perlite, because the level of Si-O-Si vibration in this region for unexpanded perlite is greater than that of expanded perlite [14].

The peak observed at 1650 cm^{-1} is attributed to the physical-sorbed water [15] and hydroxyl bonding frequency. The intensity of this peak for expanded perlite is somewhat greater than that of unexpanded perlite, because of having more hydroxyl groups, which result in more chemi-sorbed and physical-sorbed water [14].

The absorptions at about 850-900 cm^{-1} correspond to the vibrational modes of Al-OH-Al and Al-OH-Mg groups, respectively. The absorption at 795 cm^{-1} corresponds to Si-O-Al vibrations and the peak at about 630 cm^{-1}, to Al-O vibrations; that at about 525 cm^{-1}, to Al-O and Si-O vibrations [16]; and that at about 540-420 cm^{-1}, to Si-O-Al skeletal vibrations [17].

CONCLUSIONS

The results obtained from this study may be summarized as follows:

1. During the thermal treatment, the true density of perlite does not change significantly, while the bulk density changes about 4-20 times.
2. Cation exchange capacity of perlite increases during the expansion. Cation exchange capacity of unexpanded and expanded perlite samples slightly increases with acid-activation, because of forming new charged sites, resulting from surface reactions occurring during the treatment with acid solution.
3. During the expansion a transition from amorphous structure to a crystaline form and some crystaline structures have been found to form.
4. Some part of water in the structure has been removed during the expansion, but there has still been some water in crystal lattice.

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