



*Dedicated to Professor Zeno Simon
on the occasion of his 80th anniversary*

SORPTION OF VITAMIN C ON ACID MODIFIED CLINOPTILOLITE

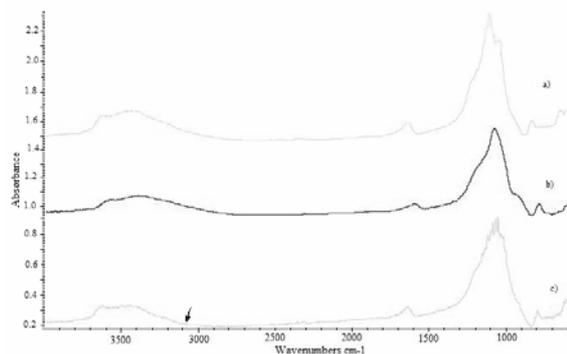
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The use of acid treated clinoptilolite as a carrier of vitamin C that can be applied in various fields was investigated. Vitamin C was adsorbed on acid modified clinoptilolite from aqueous solutions at room temperature and pH 10. The powder X-Ray diffraction (XRD), Infrared (IR) spectroscopy and thermal analysis techniques were used for characterization of analyzed samples. The XRD results showed that molecules of vitamin C were bounded to the cation from the tetrahedron cluster and L-ascorbic acid is embedded into the crystalline structure. Also, results of FT-IR indicated that vitamin C molecules can be fixed to the tetrahedron Si-O bonds from acid treated clinoptilolite, leading to the decreased peaks due to formation of ascorbate anion.



INTRODUCTION

The natural zeolites are a category of materials of particular interest due to their applications as adsorbents and acid solid catalysts.¹⁻⁹ Among them, the clinoptilolite is the best known and could be found in concentrations up to 70% in volcanic tuff. Beside clinoptilolite, the volcanic tuffs contain also volcanic glass, quartz, feldspar, etc.¹⁰

From chemical point of view, clinoptilolite is an abundant component of volcanogenic sedimentary rocks,¹¹ which belongs to the heulandite family with the following general chemical formula: $(\text{Na,K,Ca})_4\text{Al}_6\text{Si}_{30}\text{O}_{72}\cdot 24\text{H}_2\text{O}$.¹² Its crystal habits include blocky or tabular crystals with good monoclinic crystal form and the framework forms

oblate channels confined by ten-membered ($7.5 \times 3.1 \text{ \AA}$) and eight-membered tetrahedral cluster ($4.6 \times 3.6 \text{ \AA}$) parallel to the C-axis.¹³ Its secondary porosity, consisting of mesopores and macropores, is connected with voids between zeolite crystals and other mineral grains in the rock.

A variety of biologically active substances, such as amino acids, vitamins and minerals can be adsorbed on this zeolite due its ability for sorption. Thus, the availability and low cost of natural zeolites has stimulated further research for new applications in medicine, cosmetics or pharmacology.¹⁴⁻²¹

Zeolites can be modified by various treatments in order to improve their activity and selectivity and to be used in various fields. Thus, the potential application of this mineral was described in our

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previous papers, where the performances were shown to depend strongly on the zeolite chemical and structural properties (composition, porosity, etc) as well as on the treatment conditions of the zeolites.²²⁻²⁷

Vitamin C also known as ascorbic acid is a water soluble vitamin found widely in raw fruits, vegetables and juices. Also, vitamin C has received a great attention due its antioxidant properties. According to the literature data, a new method with practical value is insertion and stabilization of vitamin C into montmorillonite.²⁸

These reasons explain the opportunity of our study where we propose to obtained a new material for various areas, in special medicinal field, through the adsorption vitamin C on acid treated clinoptilolite. The present data will provide information about the vitamin C adsorbed on acid treated clinoptilolite.

MATERIALS AND METHODS

1. The acid treatment of clinoptilolite

In this study was used a clinoptilolite-rich volcanic tuff (70%) mined from the Mirsid deposits in Roumania. Its average chemical composition was the following: 84.45% SiO₂; 7.60% Al₂O₃; 0.42% Na₂O; 1.94% K₂O; 3.88% CaO; 1.35% MgO; 0.36% Fe₂O₃.²⁶ Initially the rocks were grounded for a particle size of approximately 0.25-0.50 mm and washed with distilled water to remove impurities. After filtration and drying, the crude native tuff (NT) was modified by acid treatment. In order to obtain the acid modified tuff (ANT), the crude native tuff was suspended in a 5 M HNO₃ solution (solid to liquid phase ratio 1:20), under stirring, at room temperature for 10 h. The acid-treated solid was filtered, washed several times with distilled water and dried at 100°C for 3 h.

2. Characterization of samples

The elemental chemical analysis was performed in National Institute for Cryogenics and Isotopic Technologies Laboratory (Rm.Valcea – Roumania).

The specific surface areas of the samples were determined using the Brunauer-Emmett-Teller (BET) method by performing nitrogen sorption measurements using a Micrometrics ASAP 2010 instrument. The adsorption and desorption experiments were done at 77 K after initial pretreatment of the samples by degassing at 120°C for 2 h. X-ray powder diffraction patterns of the samples were obtained using a Rigaku Ultima IV diffractometer. The wavelength of Cu-K α : X-ray radiation used was 1.5418 Å while the beam voltage and current were 45 kV and 40 mA, respectively.

FT-IR spectra were recorded using BRUKER IFS 66 model FT-IR spectrometer in the region 4000–400 cm⁻¹ by employing standard KBr pellet technique. Thermal gravimetric analysis (TGA) of the samples was conducted using Labsys TM SETARAM type of instrument. Approximately 10 mg sample was heated at a heating rate of 100°C/min under nitrogen purge stream with the pressure 1.5 bar up to 1000°C.

3. Adsorption of vitamin C on acid treated clinoptilolite

For adsorption process of vitamin C on acid treated clinoptilolite was used a 2% solution of commercially available vitamin C (from drugstore). Initially the sample of acid treated clinoptilolite (ANT) was suspended in a 2% vitamin C solution (solid to liquid phase ratio 1:20), under stirring, at room temperature for 72 h and pH 10 obtaining the sample with vitamin C (CANT). After this process, the CANT sample was filtered, washed several times with distilled water and dried at room temperature.

RESULTS AND DISCUSSION

The chemical analysis of the acid treated sample indicates substantial modifications of the composition. In Table 1 the chemical compositions of the analyzed samples are comparatively shown.

Table 1

Chemical compositions of the analyzed samples (%)

Samples	BET, (m ² /g)	Si/Al	Si,%	Al,%	Mg,%	Ca,%	Fe,%	K, %	Na,%
NT	30.7334	5.76	33.54	5.82	0.46	2.62	0.58	2.14	0.27
ANT	257.1204	13.02	39.74	3.04	0.16	0.24	0.14	0.30	0.17

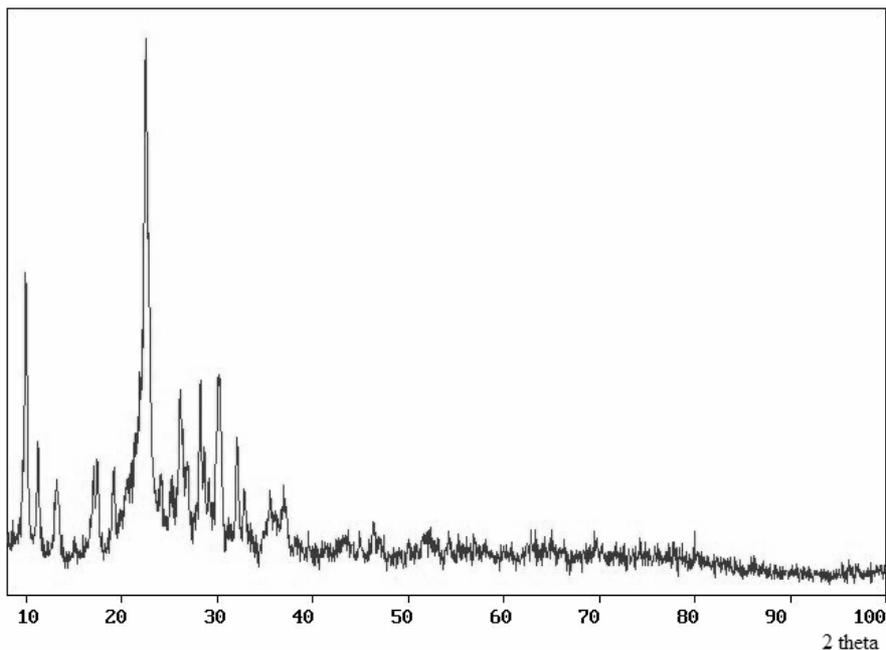


Fig. 1 – The X-ray diffractogram of the native volcanic tuff (NT).

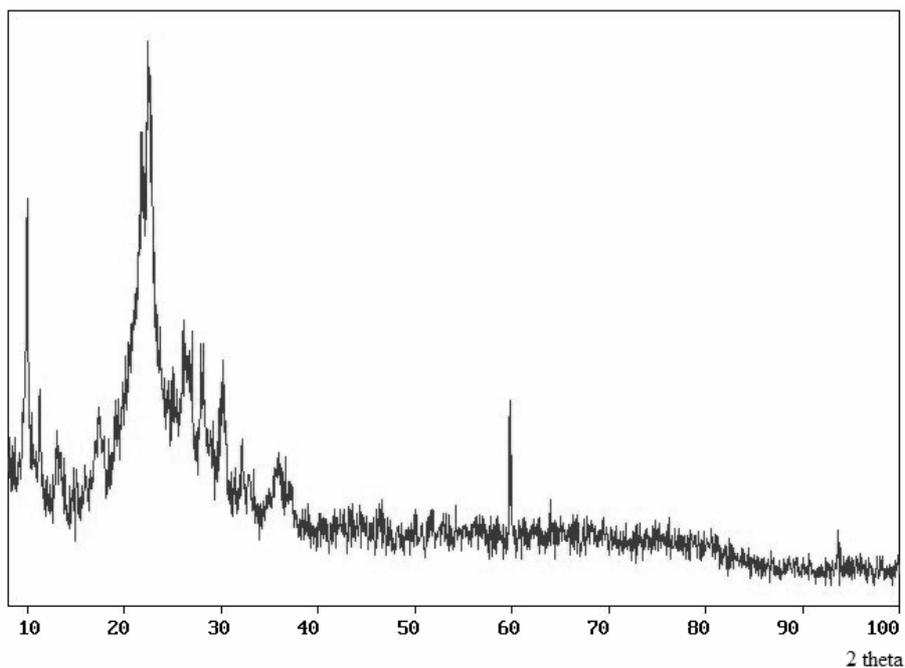


Fig. 2 – The X-ray diffractogram of the acid treated volcanic tuff (ANT).

As can be seen in Table 1, the acid treatment influences the chemical composition of a zeolite. Thus, a significant dealumination is noticed for the Si/Al ratio in the dealuminated sample comparing to the native volcanic tuff. In CANT sample, the Si/Al ratio is much lower than in the native volcanic tuff. Also, it can be seen that the weight of the metals present in ANT is low. In this case we can conclude that through acid treatment the metals present as both ions of compensatory charge were removed greatly from the initial tuff

structure and the metal cations were replaced by H^+ cations from the HNO_3 solution.

The sample structural characteristics were estimated by X-ray diffraction measurements (DRX). In Fig. 1 is presented the X-ray diffractogram of the native volcanic tuff.

According to the X-ray diffraction data depicted in the Fig. 1, the clinoptilolite is identified by its characteristic peaks at $2\theta=9.85^\circ$, 22.4° and 30° .²⁹ In Fig. 2 is presented the X-ray diffractogram of the acid treated clinoptilolite.

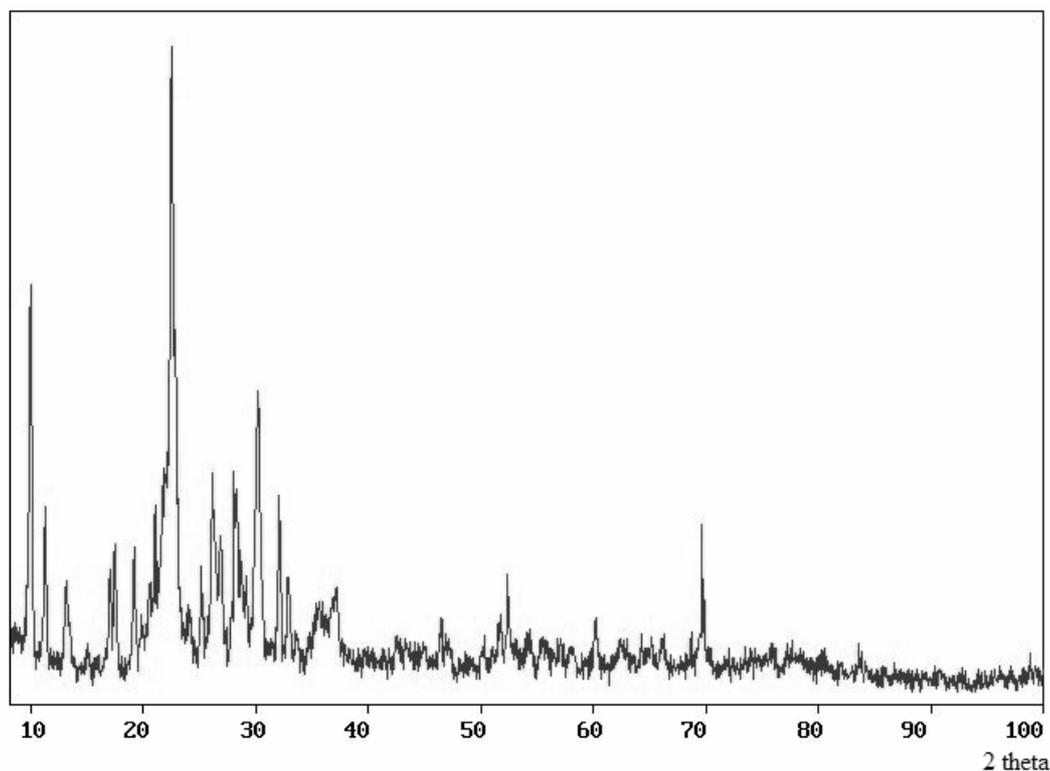


Fig. 3 – The X-ray diffractogram of the CANT sample.

As can be seen in Fig. 2, by acid treatment the crystallinity of sample is much affected. Taking into account the intensities of the peaks from this figure and those from the native tuff diffractogram,³⁰ it was estimated the crystallinity degree of the acid treated clinoptilolite sample. Although the mentioned peaks are observed for the acid treated samples, however both their intensities and the ratio of reflection intensities are diminished. Also, a series of the diffraction planes (illustrated as peaks in diffractogram) were diminished or even disappeared. Therefore, it can be seen that the acid treatment leads to the increasing of the pore size and channels that translate into an increasing of the adsorption ability.

In Fig. 3 is presented the X-ray diffractogram of the CANT sample.

As can be seen in Fig. 3 the X-ray diffractogram of the CANT sample is much different from the diffractograms of the NT respectively ANT samples. In this case, the intensity of the characteristics peaks is less lower than for the native volcanic tuff (NT) sample. Also, on the diffractogram could be distinguished more peaks that are most likely due to the excipients included into the vitamin C pills.

The FT-IR spectra of the natural and acid activated clinoptilolite samples reflect the structural modification which takes place due to acid activation. The values of the wave number and vibration type that cause them for natural clinoptilolite are given in Table 2.³¹

The IR spectra of the samples are shown in Fig. 4.

Table 2

IR vibrations of natural clinoptilolite

Wavenumber (cm ⁻¹)	Vibration type
~ 3600	O–H stretching (Si, Al)–OH
~ 3400	O–H stretching H–OH
~ 1650	H–O–H deformation
~ 1150	Si–O stretching
~ 1050	Si–O–Si stretching
~ 520	Si–O–Si deformation

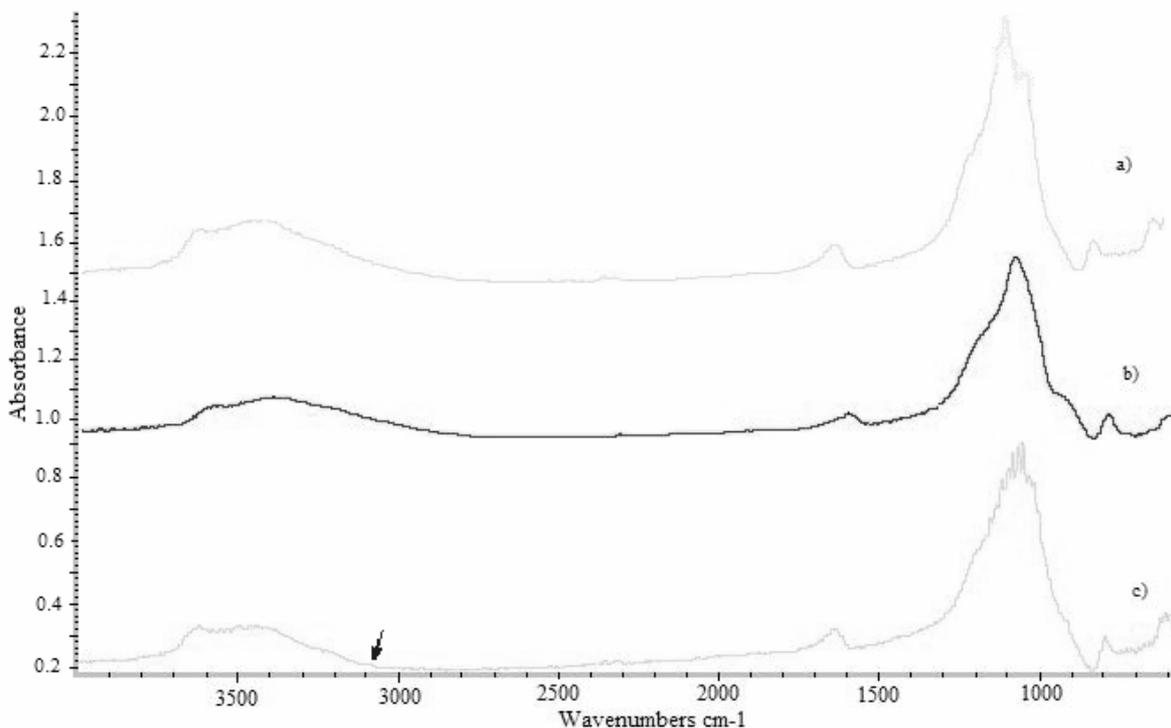


Fig. 4 – The IR spectra of the samples: a). NT; b). ANT; c). CANT.

By analyzing our FT-IR spectra for the native volcanic tuff, Fig. 4-(a), we observe the corresponding peaks at the same wavelengths as in literature: 1050, 1150, 1650, 3400 and 3600 cm^{-1} . Literature data show that the peak at 1010-1100 cm^{-1} is assigned to complex Si-O stretching vibrations in the tetrahedral sheets.³²

Thus, the Si-O band for amorphous SiO_4 ³³ is at 1150 cm^{-1} and the peak at 1600-1700 cm^{-1} is generated by H-O-H deformation.

In case of the ANT sample, Fig. 4-(b), the FT-IR spectra reflect the structural degradation of the tuff components and the formation of an amorphous silica phase during acid treatment. The acid treatment causes the decreasing of the intensity of the absorption bands at 1050, 1150 and 1650 cm^{-1} . These results suggest the partial depletion of Al, Mg and Ca from the clinoptilolite structure, in accordance with the changes in chemical composition. The bands at 3400-3500 and 1600-1700 cm^{-1} for water of hydration and the hydroxyl stretching show significant decreases after acid activation. It is due to the removal of cations, causing the loss of water and hydroxyl groups coordinated bonded to them. However, the persistence of a weak peak at 1650 cm^{-1} indicates that the zeolite structure is not fully destroyed. Also, the Si-O stretching bands at 1150 cm^{-1} become dominant due to the formation of three-dimensional networks of amorphous Si-O-Si units.

The presence of a band at about 800 cm^{-1} is usually taken as evidence for a three-dimensional amorphous silica phase.^{34,35} The intensity increased in this region may suggest that depletion of the cations is followed by the formation of silica with a three-dimensional cross-linked structure. One interesting feature of the acid treated sample is the absence of the Si-OH band at 1050 cm^{-1} found in natural clinoptilolite.

The spectra of the CANT sample, Fig. 4-(c) shows the basic peaks, some of them being even more intense. The literature data indicate that the C-H stretching bands most occurred in the 3020-2800 cm^{-1} region,³⁶ thus the increase in the bands (ca. 3100 cm^{-1} , pointed by arrow in the figure) intensity indicated the existence of more protons and ascorbate ions released from the solution in order to interact with C-H bond due to deprotonation of clinoptilolite at pH.³⁷

Also, the results might suggest that the L-ascorbate molecules were bounded to the cation in tetrahedron cluster, and L-ascorbic acid was intercalated into the layers. The L-ascorbic acid spectrum is presented in Fig. 5.

As shown in Fig. 5 for the typical L-ascorbic acid spectrum, the spectra of C-H bond stretching vibrations appeared at ca. 2915 cm^{-1} .

The TGA curves of the ANT and CANT samples are shown in Fig. 6.

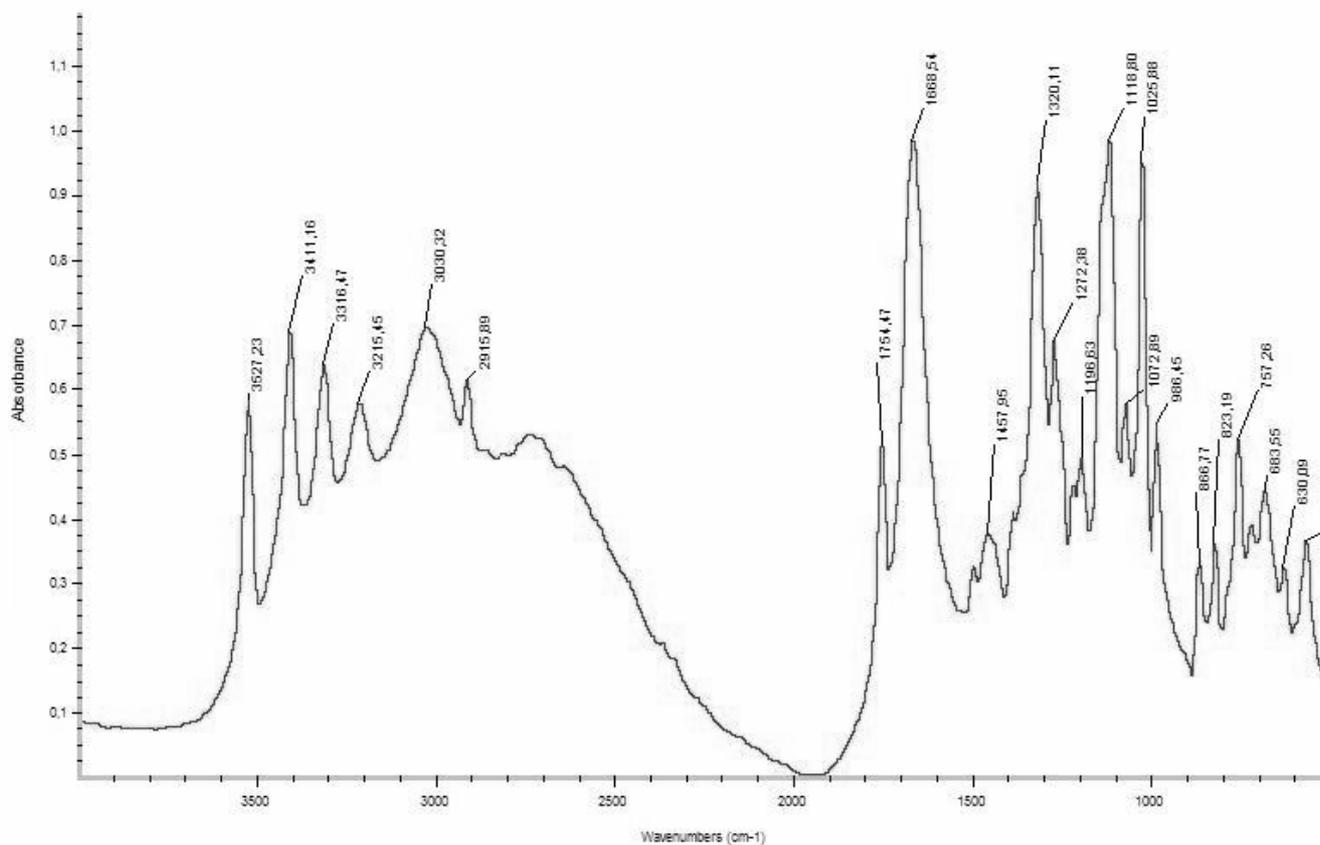


Fig. 5 – The IR spectra of the vitamin C.

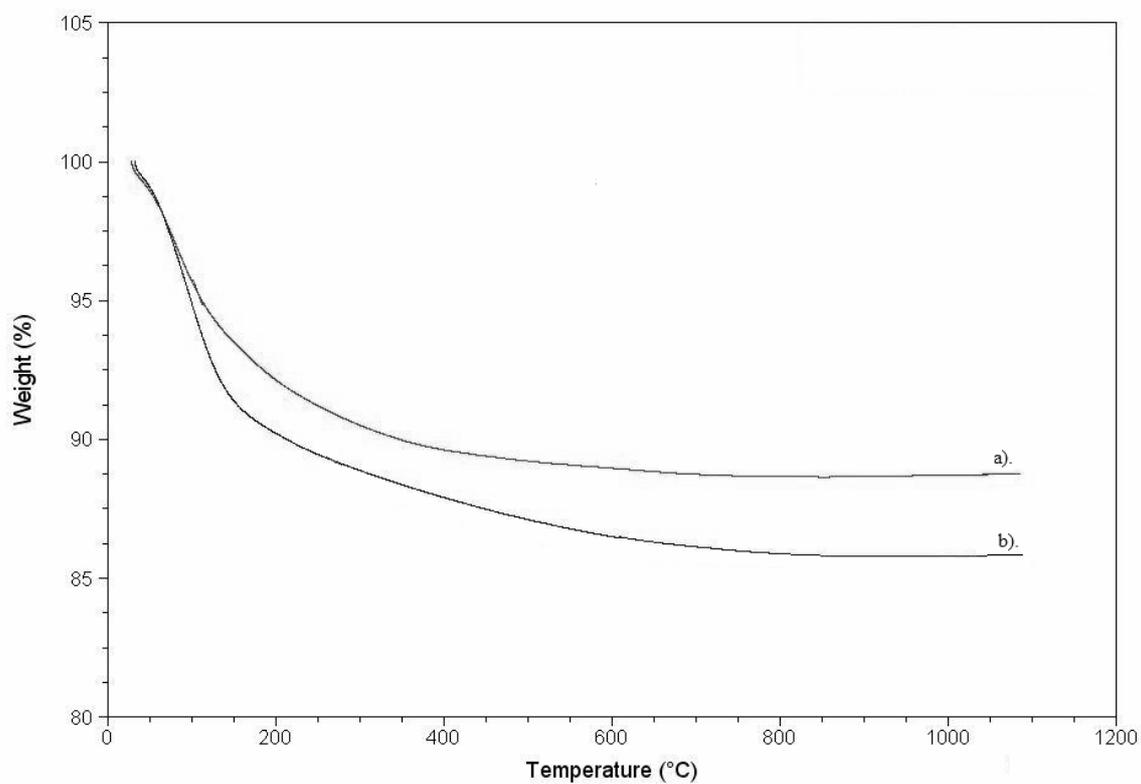


Fig. 6. The TGA curves of analysed samples. a). ANT and b). CANT.

For the ANT sample the thermal analysis curve shows that dealumination treatment causes a dehydration process at about 100°C. Also, the same effect was observed in case of the CANT sample. A new loss occurs at about 400°C, associated with a small weight loss but no change in the XRD pattern (Fig. 3). The thermal effect can be associated with the amorphous precipitate postulated above on the basis of changes in the chemical and mineralogical composition.

CONCLUSIONS

In this paper we studied applications for a new material in various fields, such as absorption of vitamins. The XRD results showed that molecules of vitamin C were bounded to the cation in tetrahedron and L-ascorbic acid is intercalated into the crystalline structure. Also, results of FT-IR indicated that vitamin C molecules can be fixed to the tetrahedron Si-O bonds, leading to the decreased peaks due to formation of ascorbate anion.

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