

Experimental Studies for the Cinnamaldehyde Adsorption on Dealuminated Clinoptilolite Using as Carrier

CLAUDIA COBZARU¹, ADRIANA MARINOIU^{2*}, CORINA CERNATESCU¹, ADRIAN CATALIN PUTTEL¹, AMALIA SOARE²

¹ Gheorghe Asachi Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 73 D. Mangeron Blvd., 700050, Iasi, Romania.

² National R D Institute for Cryogenics and Isotopic Technologies- ICIT, 4 Uzinei Str., 240401, Rm Valcea, Romania.

In this study the adsorption of cinnamaldehyde on the dealuminated clinoptilolite has been studied in order to investigate the possibility of using this mineral as carrier for organic compound. The characterization of dealuminated clinoptilolite and adsorption of cinnamaldehyde on the material surface has been investigated by BET, SEM and FTIR methods. These analyses show that by dealumination, significant modifications are produced in chemical composition, pore volume and surface area of the clinoptilolite and the cinnamaldehyde was adsorbed in the structure of dealuminated zeolite. Due to properties of the cinnamaldehyde, the obtained product can be used as an agrichemical.

Keywords: adsorption of cinnamaldehyde, dealuminated clinoptilolite, agrichemical

The literature data show that the most common natural zeolite for both chemical and agricultural applications is the clinoptilolite due to its relatively high adsorption rate, cation exchange, catalysis and dehydration capacities [1-3]. This material is found in volcanic rocks in concentration of 60-90%, beside the volcanic glass, quartz, feldspar, etc [4]. In Romania there are many important deposits of the volcanic tuff with 70% clinoptilolite content [5]. From the chemical point of view the clinoptilolite has the general chemical formula: $(\text{Na,K,Ca})_4\text{Al}_6\text{Si}_{30}\text{O}_{72}\cdot 24\text{H}_2\text{O}$ and the framework is formed by two parallel channels of 10-member rings ($7.5 \times 3.1 \text{ \AA}$) and two channels of eight-member rings ($4.6 \times 3.6 \text{ \AA}$, $4.7 \times 2.8 \text{ \AA}$) [6]. Its secondary porosity, consisting of meso- and macropores is connected with the size of zeolite and other minerals grains in the rock. The potential of this natural material in different applications (which made the object of several previous papers) has demonstrated that the performances obtained depend very much on both the chemical and the structural properties of the zeolite (composition, porosity, etc) and the treatments conditions which they have subjected [7-19]. The literature data show that the clinoptilolite is largely applied especially as adsorbent in removing heavy metal cations from wastewaters [20-26]. But this natural material can be used as carrier for different pharmaceutical products. For example, Rivera et al.(2003) have studied the adsorption of three drugs on the purified clinoptilolite in order to investigate the possibility of using this mineral as carrier in slow-release dosage forms. From these studies [20-26] was observed that the key in the adsorption process is the use of an adsorbent with a high selectivity, obtained by modification of its surface area and the pore structure. The one of the methods used for modification of surface and structure of zeolites is the dealumination who leads to materials with improved special properties comparing to the initial product [28-30].

It is well known that the cinnamon is a popular spices used worldwide not only for cooking but also in traditional and modern medicines [31-36]. The cinnamaldehyde is one of the most important constituent of the cinnamon, which gives its flavor and odor and could be found in cinnamon essential oil at concentrations about 50% [37, 38]. From the chemical point of view, the cinnamaldehyde

is an organic compound with a lot of uses such as insecticide, flavor in food products or in some perfumes, corrosion inhibitor for steel and other ferrous alloys in corrosive fluids, in combination with dispersing agents, solvents and other surfactants and in medicine due its antimicrobial properties [39-46]. The literature data show that due its low toxicity and well-known properties the cinnamaldehyde can be used as fungicide making it ideal for agriculture application [44].

Our current objective is to study the adsorption of cinnamaldehyde on the dealuminated clinoptilolite in order to investigate the possibility of using the mineral as carrier for this organic compound. Furthermore, due its properties, the obtained product can be used as an agrichemical.

Experimental part

Cinnamon extract

For this study, the cinnamon from *Cinnamomum Verum* specie has been used without further additions, in powder form and commercially available. In order to obtain the cinnamon extract, about 13 g cinnamon powder was put in 130 mL ethanol solution 80%. After shaking for 8 hours, the mixture was placed aside until the two phases separated. Finally, the solution was decanted and used for further analysis.

Preparation of dealuminated clinoptilolite

The volcanic tuff (from Marsid deposit, Romania) used as a raw material contains about 70% clinoptilolite with the following composition: 68.54% SiO_2 , 11.95% Al_2O_3 , 0.40% Na_2O , 2.8% K_2O , 3.35% CaO , 0.70% MgO and 0.86 wt. % Fe_2O_3 [5].

The native volcanic tuff (noted with T1) was washed with distilled water and dried afterwards at 333K. Then, the natural tuff was grounded and sieved, obtaining particles of about 0.25-0.50 mm in size. The dealuminated volcanic tuff was obtained through a procedure involving the acidic treatment of the starting material. First, the material was treated with 6M HNO_3 aqueous solution (1:20 ratio) at 353 K for 10 h. Second, the washing of the treated material with distilled water and the drying allowed obtaining the dealuminated sample noted as T2.

* email: adriana.marinoiu@icsi.ro

Adsorption of the cinnamaldehyde on the dealuminated clinoptilolite

In order to achieve the adsorption procedure, about 25 ml of the cinnamon ethanolic extract were mixed with 5 g zeolite and subjected to adsorption for 24 h at the room temperature by shaking the solution with a revolution speed of 100 rpm. After about 24 h the mixture was filtered and the solid material was washed with distilled water and dried. The obtained sample was noted as T3.

Characterisation of catalysts

The obtained samples were analysed in order to estimate the effect of the acid treatment and adsorption process on the properties of the solid materials.

The specific surface areas of the samples were determined using the BET method by performing nitrogen sorption measurements using a Quantachrome Autosorb IQ equipment. The adsorption and desorption experiments were done at 77 K after initial pre-treatment of the samples by degassing at 115°C for 4 hours.

A Sigma VP FEG Carl Zeiss SEM was used for the characterization of the scanning electron microscopy (SEM) and EDS analyses. Samples were non-conductive therefore we used the Variable Pressure (VP) mode. They were mounted as-received on a carbon tape and then analyzed. Spot EDS elemental analysis was performed at different points on the surface in order to minimize any possible anomalies arising from the heterogeneous nature of the analyzed surface.

FT-IR spectra were recorded by a Perkin Elmer FT-IR spectrometer in the region of 400-4000 cm⁻¹. A mixture consisting of 1 mg analyzed sample and 200 mg KBr was compressed under pressure of 7 tons cm⁻² for 30 s.

Results and discussions

Characterisation of catalysts

The chemical compositions of catalytic materials, expressed in term of oxide species, are provided in table 1.

Sample	Composition, % mol						
	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	MgO	FeO	Other
T1	69.4	5.44	0,11	0.35	0.44	0.79	23.08
T2	75	4.8	0,5	0.18	0.23	0.4	19.28
T3	74.74	6.17	0,05	0.11	0.23	0.42	18.28

Table 1
CHEMICAL COMPOSITIONS OF ANALYZED CATALYTIC MATERIALS

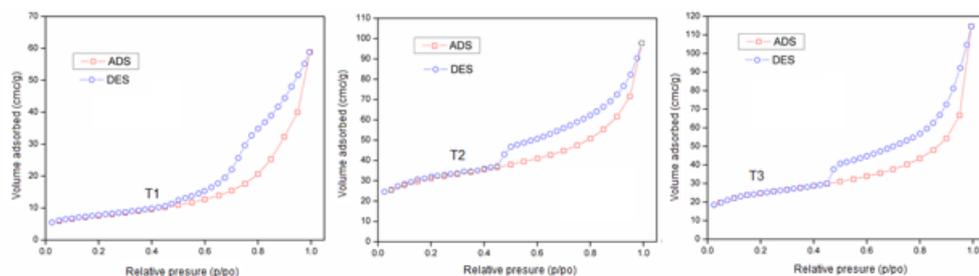


Fig 1. N₂ adsorption-desorption isotherm of T1, T2 and T3 samples

Samples	Specific area (m ² /g)	Porous volume (cm ³ /g)
T1	26	0.0875
T2	100	0.1062
T3	79	0.1375

Table 2
THE VALUES OF THE BET SPECIFIC AREAS AND PORE VOLUME OF THE ANALYSED SAMPLES

As expected, the acid treatment has produced significant modifications in clinoptilolite chemical composition. These modifications are due to Al ions leaching during the acid treatment, fact observed by the increasing concentration of Si ions in dealuminated sample (T2). Also, in this sample (T2) the concentration of Na, Ca, Mg and Fe ions are considerably diminished because they were replaced by protons. In the case of T3 sample, the ratio between different cations strongly changed after the adsorption process.

The textural characteristics were evaluated using nitrogen adsorption-desorption procedure (fig. 1).

As it can be seen in table 1, the T1 sample displayed an isotherm type IV with a distinct hysteresis loop. On the contrary, the accessible pore volume and surface area of T2 sample significantly improved by acid treatment (table 2).

It can be assumed that the increasing of the micropore volumes in the T2 sample is caused by unblocking the channels of the aluminosilicate framework structure of the zeolite during acid treatment. Furthermore, during the acid treatment the Al atoms were extracted from the natural material lattice, resulting in a number of structural changes and formation of new micropores and mesopores [47]. Therefore, the contribution of mesopores to the total volume increases from 0.0875 cm³·g⁻¹ (for T1 sample) to 0.1062 cm³·g⁻¹ for the acid treated sample (T2). This fact was important for adsorption of cinnamaldehyde molecules. Thus, the S_{BET} of T3 sample was about 79 m² g⁻¹ (table 2), which means that the adsorption process has been achieved. The nitrogen molecules cannot penetrate in clinoptilolite micropore channels which are occupied by organic species.

Scanning Electron Microscopy (SEM) was used to investigate the surface morphology of the analyzed samples (fig. 2). The SEM images demonstrate that the native clinoptilolite (T1 sample) is a lamellar texture material (fig. 2, a). The surface of zeolite treated with acid

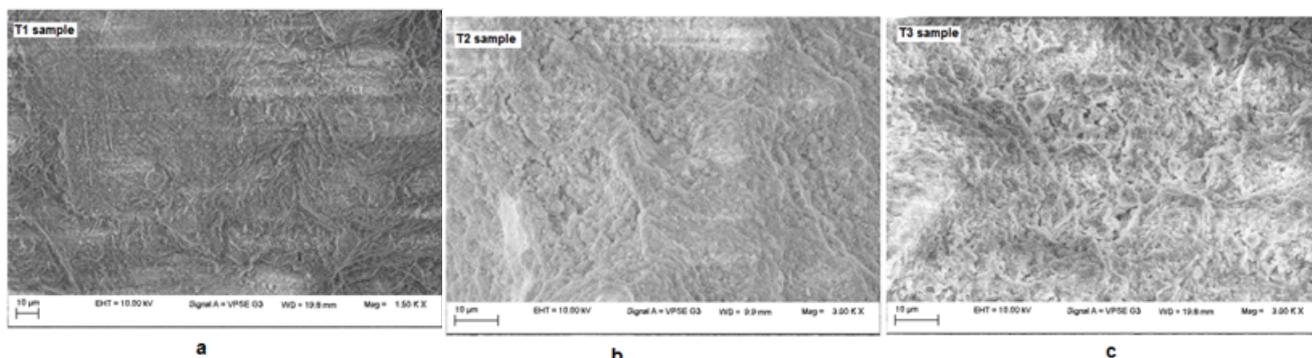


Fig. 2. The SEM images for the three analyzed samples: a. T1; b.T2; c.T3.

(T2 sample) is represented by white spots that indicate the formation of new micropores and mesopores (Figure 2, b). After adsorption, cinnamaldehyde on the surface of the zeolite was clearly observed (fig. 2, c). The SEM analysis confirms that the cinnamaldehyde had been adsorbed on the zeolite surface.

The FT-IR spectra recorded for the analyzed samples are shown in figure 3.

In the case of T1 sample, the bands in the wavenumber region $3440-3468\text{ cm}^{-1}$ which correspond to symmetric and asymmetric stretching vibration of the OH groups have been observed (fig. 3). These bands, characteristic for stretching vibrations of OH groups from the associated water molecules, are asymmetrical and its high frequency component has a clearly detectable shoulder at 3628 cm^{-1}

1 remainder after the acid treatment and caused by a bridge SiO(H)Al group (T2 sample). A band at 1635 cm^{-1} characterizing the deformation vibrations of water molecules for T1 sample demonstrates a slight high frequency shift at acid treatment (T2 sample) and adsorption process (T3 sample). A very intense and wide complex-shaped band in the region of $1250-980\text{ cm}^{-1}$ is a superposition of several bands attributed to vibrations of Si-O-Si and Si-O-Al fragments [48]. In the FT-IR spectrum of T1 sample, it is situated at 1240 cm^{-1} and has a shoulder at 975 cm^{-1} . In the FT-IR spectra of the T2 and T3 samples, these bands disappear.

The data obtained indicate that, significant changes in the Si-O-Al structural fragment take place by acid treatment.

The IR characteristic peaks for the T3 sample are mostly in the range of $1640-600\text{ cm}^{-1}$. Thus, the peak at 1626 cm^{-1} corresponds to the stretching vibration of an aldehyde carbonyl $>C=O$. This peak corresponds to high levels of aldehydes in the cinnamon extract. The peak at 1450 cm^{-1} is very characteristic for an alcohol C-OH within the bending vibration absorption. The peak at 1072 cm^{-1} is attributed to the stretching vibrations of C-OH. The peak at 792 cm^{-1} is assigned to benzene rings CH vibration absorption.

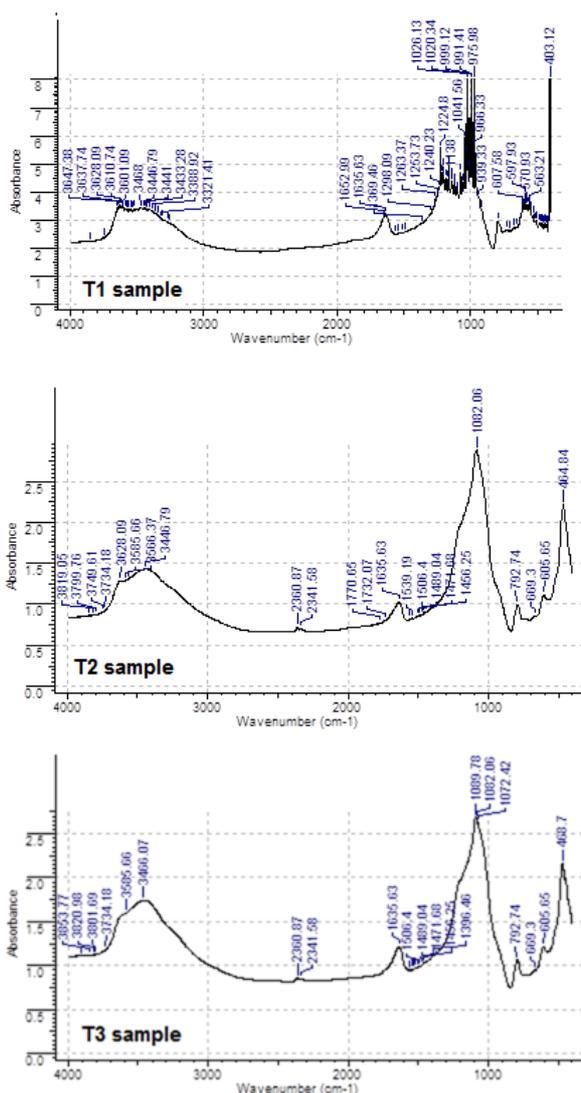


Fig. 3. The FT-IR spectra recorded for the analyzed samples

Conclusions

In this paper the adsorption of cinnamaldehyde on the dealuminated clinoptilolite has been studied in order to investigate the possibility of using this mineral as carrier for this organic compound.

After the acid treatment, a material with important properties for the adsorption of cinnamaldehyde was obtained.

The characterization and porous structure of modified clinoptilolite as a sorbent for the cinnamaldehyde has been investigated by the means BET, SEM and FTIR methods.

The FT-IR analysis shows that by adsorption process the cinnamaldehyde was incorporated in the structure of dealuminated clinoptilolite.

Due to properties of the cinnamaldehyde, the obtained product can be used as an agrichemical.

References

1. TORII, K., in *Natural Zeolites: Occurrence, Properties, Use*, eds. SAND, L.B. & MUMPTON, F.A., Pergamon, Elmsford, NY, 1978, p. 441-450.
2. BURRIESCI, N., VALENTE, S., OTTANA, R., CIMINO, G., ZIPELLI, C., *Zeolites*, **4**, 1984, p. 58-60
3. FLANIGEN, M., MUMPTON, F.A. *Mineralogy. Miner. Soc. Amer.*, **4**, 1981, p. 165-175.
4. TSITSISHVILI, G., ANDRONIKASHVILI, T., KIROV, G., FILZOVA, L., *Natural Zeolites*, Ellis Horwood, New York, 1992, p. 133-145.

5. BARBAT, A., MARTON, A., ZEOLITICAL VOLCANIC TUFFS, ED. DACIA, CLUJ-NAPOCA, 1989, p. 39-45.
6. BAERLOCHER, CH., MEIER, W.M., OLSON, D.H., Atlas of Zeolite Framework types, Elsevier, 2001, p.204-210.
7. ALTIN, A., DEGIRMENCI, M., Sci. Total Environ., **337**, 2005, p.1-10.
8. LEGGO, P.J., LEDESERT, B., CHRISTIE, G., Sci. Total Environ., **363**, 2006, p.1-9.
9. REHAKOVA, M., CUVANOVA, S., DZIVAK, M., RIMAR, J., GAVALOVA, Z., Current Opinion in Solid State Mater. Sci., **8**, 2004, p. 397-403.
10. POLT, E., KARACA, M., DEMIR, H., J. Fruit Ornament. Plant Res., **12**, 2004, p.56-59.
11. PAPAIOANNOU, D., KATSOULOS, P.D., PANOUSIS, N., KARATZIAS, H., Micropor. Mesopor. Mater., **84**, 2005, p. 161-167.
12. GRCE, M., PAVELIC, K., Micropor. Mesopor. Mater., **79**, 2005, p.165-170.
13. TEIXEIRA, M.F.S., BERGAMINI, M. F., BOCCHI, N., Talanta, **63**, 2004, p.1083-1087.
14. STOCKER, M., Micropor. Mesopor. Mater., **82**, 2005, p. 257-292.
15. ACKLEY, M.W., REGE, S.U., SAXENA, H., Micropor. Mesopor. Mater., **61**, 2003, p. 25-42.
16. MICHALKIEWICZ, B., Appl. Catal. A: Gen., **307**, 2006, p.270-274.
17. ONYESTYAK, G., KALLO, D., Micropor. Mesopor. Mater., **61**, 2003, p. 199-204.
18. COBZARU, C., OPREA, S., HULEA, T., HULEA, V., DUMITRIU, E., Rev. Chim.(Bucharest), **53**, 2002, p. 674-680.
19. DUMITRIU, E., HULEA, V., COBZARU, C., OPREA, S., Rev. Chim.(Bucharest), **54**, 2003, p.14-20
20. INGLEZAKIS, V.J., LOIZIDOU, M.M., GRIGOROPOULOU, H., J. Colloid Interf. Sci., **275**, 2004, 570-576.
21. ERDEM, E., KARAPINAR, N., DONAT, R., J. Colloid Interf. Sci., **280**, 2004, p. 309-314.
22. PETRUS, R., WARCHOL J.K., Wat Res., **39**, 2005, p. 819-830.
23. DOULA, M.K., IOANNOU, A., Microp. Mezop. Mat., **58**, 2003, p. 115-130.
24. PERIC J., TRGO M., VUKOJEVIC MEDVIDOVIC N., Wat Res., **38**, 2004, p. 1893-1899.
25. IVANOVA, E., KARSHEVA, M., KOUMANOVA, B., J. Chem. Technol. Metal., **45**, 2010, p. 295-302.
26. WANG, SH., PENG, Y., Chem. Eng. J., **156**, 2010, p. 11-24.
27. RIVERA, A., FARIAS, T., RUIZ-SALVADOR, A.R., DE MENORVAL, L.C., **61**, 2003, p. 249-259.
28. ROZIC, M., CERJAN-STEFANOVIC, S., KURAJICA, S., MAEEFAT, M. R., MARGETA, K., FARKAS, A., J. Colloid. Inter. Sci., **284**, 2005, p.48-53.
29. HUTCHINGS, G. J., BURROWS, A., RHODES, C., KIELY, C. J., MCCLUNG, R., J. Chem. Soc., Faraday Trans., **93**, 1997, p. 3593-3600.
30. TSYBULEVSKII, A.M., KLYACHKO, A.L., BEREZHNYAYA, V.I., PLUZHNIKOVA, M.F., BRUEVA, T.R., KAPUSTIN, G.I, Catal. Today., **97**, 2004, p. 283-288.
31. SANGAL, A., Appl. Sci. Res., **2**, 2011, p. 440-450.
32. VANGALAPATI, M., SREE SATYA, N., SURYA PRAKASH, D., AVANIGADDA, S., Res. J. Pharm., Biolog. Chem. Sci., **3**, 2012, p. 653-663.
33. SUBASH BABU, P., PRABUSEENIVASAN, S., IGNACIMUTHU, S., Phytomedicine, **14**, 2007, p.15-22.
34. JAKHETIA, V., PATEL, R., KHATRI, P., J. Advanced Sci. Res., **1**, 2010, p. 19-12.
35. MATHEW, S. ABRAHAM, T. E., Food Chemistry, **94**, 2006, p. 520-528.
36. KIM, S. H., HYUN, S. H., CHOUNG, S. Y., J. Ethnopharmacology, **104**, 2006, pp. 119-123.
37. GUTZET, H., Plant Natural Products: Synthesis, Biological Functions and Practical Applications. Wiley, 2014, p. 19-21.
38. SINGH, G., MAURYA, S., DE LAMPASONA, M.P., CATALAN, C.A.N., Food and Chemical Toxicology, **45**, 2007, p. 1650-1661.
39. GROWCOCK, F. B., Corrosion, **45**, 1989, p.1003-1007.
40. GROWCOCK, F. B., FRENIER, W. W., ANDREOZZI, P. A., Corrosion, **45**, 1989, p. 1007-1015.
41. KA, H., PARK, H-J., JUNG, H-J., CHOI, J-W., CHO, K-S., HA, J., LEE, K-T., Cancer Lett., **196**, 2003, p. 143-152.
42. LOPEZ, P., SANCHEZ, C., BATLLE, R., NERÍN, C., J. Agric. Food Chem. **55**, 2007, p. 4348-4356.
43. BANDELL, M., STORY, G.M., HWANG, S.W., VISWANATH, V., EID, S.R., PETRUS, M.J., EARLEY, T.J., PATAPOUTIAN, A., Neuron, **41**, 2004, p. 849-857.
44. Cinnamaldehyde Use. PAN Pesticides Database. Retrieved, 2007, p. 10-23.
45. CHENG, S-S., LIU, J-Y, TSAI, K-H., CHEN, W-J., CHANG, S-T., J. Agric. Food Chem., **52**, 2004, p. 4395-4400.
46. MA, W.B, FENG, J.T, JIANG, Z.L, ZHANG, X., J. Amer. Mosquito Control Assoc., **30**, 2014, p. 199-203.
47. COBZARU, C., OPREA, S., DUMITRIU, E., HULEA, V., Appl. Catal. Gen., **351**, 2008, p. 253-258.
48. LAZAREVIC, S., JANKOVIC-CASTVAN, I., JOVANOVIC, D., MILONJIC, S., JANACKOVIC, D., PETROVIC, R., Appl. Clay. Sci., **37**, 2007, p. 47-57.

Manuscript received: 23.05.2017