"AUREL VLAICU" UNIVERSITY OF ARAD
FACULTY OF FOOD ENGINEERING, TOURISM AND ENVIRONMENTAL PROTECTION
CHEMICAL AND TECHNOLOGICAL RESEARCH CENTER

Scientific and Technical Bulletin

Series CHEMISTRY, FOOD SCIENCE & ENGINEERING

Chemical analysis of essential oils from plants by gas chromatography coupled with mass spectrometry technique (pages 20-23)

Year XVI, Vol. 15, 2018
ISSN 1582-1021

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E-mail: dana.copolovici@uav.ro

EDITORIAL

SCIENTIFIC AND TECHNICAL BULLETIN, SERIES: CHEMISTRY, FOOD SCIENCE AND ENGINEERING IN THE ROMANIAN CENTENARY YEAR

Dana Maria COPOLOVICI

Faculty of Food Engineering, Tourism and Environmental Protection, "Aurel Vlaicu" University, Romania, 2 Elena Dragoi St., Arad 310330, Romania
Corresponding author email: dana.copolovici@uav.ro

Scientific and Technical Bulletin, Series: Chemistry, Food Science and Engineering (Scien. Tech. Bull-Chem. Food Sci. Eng.), an annual peer-reviewed, open access journal edited by Faculty of Food Engineering, Tourism and Environmental Protection, "Aurel Vlaicu" University from Arad, Romania, is now publishing its fifteenth volume, marked by the important event, the *Romanian Centenary* (1918 – 2018).

As our main interest is to publish research results in interdisciplinary fields, we focus to address both ***research and education*** areas in chemistry, biology, physics, food science and engineering, environmental science and engineering, materials science and medicine, engineering management, agribuiseness, suatainability, for a wide audience: academic staff, students and teachers, and people from economic sector.

We thank our editors and our reviewers, which are well recognized academic staff from wide areas of scientific researches, for their work and professional achievements.

In the present volume we present results obtained in (i) environmental research area: synthesis and characterization of new polycatenar compounds with potential application in water treatment, analysis of some properties of air, wastewater management; and (ii) obtaining techniques and analysis of plant-based products.

We hope that you will enjoy this volume and you will propose us new results from your research area, even in informal settings, to enhance the success of the journal.

Author information
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Web of Science Researcher ID: C-5207-2012
ORCID: 0000-0002-1491-0473

Scien. Tech. Bull-Chem. Food Sci. Eng., Vol. 15(XVI), 2018, 4-7

THE SEARCH STRUCTURE OF TERPINEN-4-OL USING ITS FRAGMENTATION ENERGY PROFILE: CASE STUDY FOR A GC-MS ANALYSIS OF THE LAVENDER OIL

Lucian COPOLOVICI, Dumitru CONDRAT, Nicolae DINCA*

Faculty of Food Engineering, Tourism and Environmental Protection, "Aurel Vlaicu" University, Romania, 2 Elena Dragoi, Arad 310330, Romania
**Corresponding author email: nicolae.dinca@uav.ro*

Abstract: *The automated elucidation by GC-MS of isomeric structures by using mass spectral libraries and retention indexes databases often offers contradictory results in the case of the high similarity of the structures and the spectra. Under these circumstances, a certification of the unknown structures by using additional orthogonal filtering of candidate structures would increase the confidence in the analysis. For such additional filtering we propose here a correlation algorithm between the profile of some primary ionic currents and that of corresponding fragmentation energies obtained through quantum chemical calculation (QCC). In our paper we present the application of this algorithm in the case of terpinen-4-ol, a biologically active compound from essential oils. The fragmentation energy profile of the terpinen-4-ol has been identified with the maximum correlation (94.2%) among the fifteen components revealed in GC-MS analysis of lavender oil. An additional validation was done by applying the algorithm for another fourteen candidate structures, isomeric with terpinen-4-ol. The result is consistent with the library-based assignments and chromatographic alignment. One of the advantages of this approach is that the use of these three analytical variants can provide high accuracy of analysis without the direct use of chemical standards.*

Keywords: differential mass spectrometry, structure identification, fragmentation energy, lavender oil, terpinen-4-ol

INTRODUCTION

The limitations of mass spectrometry regarding the automated identification of isomeric structures with similar mass spectra are well known. In these cases, the discrimination between isomers through the interpretation of fragmentation patterns is not feasible, because the mass spectra of these isomeric analytes contain the same signals (Kind et al. 2007). The spectral similarity of a great number of essential oils causes difficulty in obtaining positive identification of individual components. The mass spectrum library-search inevitably offers a range of false positive responses. A post-search filter using experimental or calculated retention index (RI) rejects candidate structures whose retention index is not consistent with the retention index of the unknown component (Shellie et al. 2002). However, it should be taken into account that the agglomeration of RI flavour and fragrance compounds (FFC), its confidence interval (E.g., ±5 index units) and the measurement and calculation errors of RI can force a false positive result, especially when there are several similar candidate structures. In this case, a certification of the unknown structure by an additional orthogonal filtering would increase the confidence in the analysis. For this purpose, we used an algorithm based on differential mass spectrometry (ΔMS) quantitative and structure-fragmentation relationship (QSFR) strategy (Dinca et al. 2012). This uses the inverted linear correlation (LCOR) of the intensities' series of the main isobaric ions with the corresponding calculated enthalpies' series (Dinca et al. 2014). Because no unified enthalpies databases exist, these were calculated using quantum chemical methods, usually semi-empirical methods, which give reliable values and which can be quickly implemented on ordinary computers (Rocha et al. 2006). In this paper we propose to validate this algorithm for the identification of terpinen-4-ol, a biologically active compound from lavender oils.

MATERIALS AND METHODS

The preparation of the lavender essential oil and its GC-MS analysis were presented in previous papers (Copolovici et al. 2017). The ionization energy was 20 and 70 eV. The GC-MS chromatogram of lavender oil at 20 eV is shown in Figure 1.

The strategy of $\Delta_f H$ database calculation. The heats of formation ($\Delta_f H$) were calculated with the semi-empirical method RM1 using the HyperChem 8.0.10 software. The geometries of the molecules and radicals were optimized with the MM+ force field and re-optimized, using the RHF operators for molecules or ions and UHF for radicals (Rocha et al. 2006), the molecule being considered in vacuum. The fragmentation enthalpies ($\Delta_f H$(frag)) were calculated according to eqn.1:

$$\Delta_f H(\text{frag}) = \Delta_f H(\text{ion}) + \Sigma\Delta_f H(\text{F}) - \Delta_f H(\text{M}) \quad (1)$$

where $\Delta_f H$(ion) is the formation enthalpy of the main ion, $\Sigma\Delta_f H$(F) is the sum of the formation enthalpies of secondary fragments (radicals and molecules) and $\Delta_f H$(M) the formation enthalpy of the molecule (Dinca et al. 2014).

RESULTS AND DISCUSSIONS

The chromatographic integration revealed fifteen chemical entities in lavender oil (Figure 1). The chromatographic alignment and library-based assignments indicates the terpinen-4-ol as the ninth compound of the chromatogram with a retention time of 17.91 minutes.

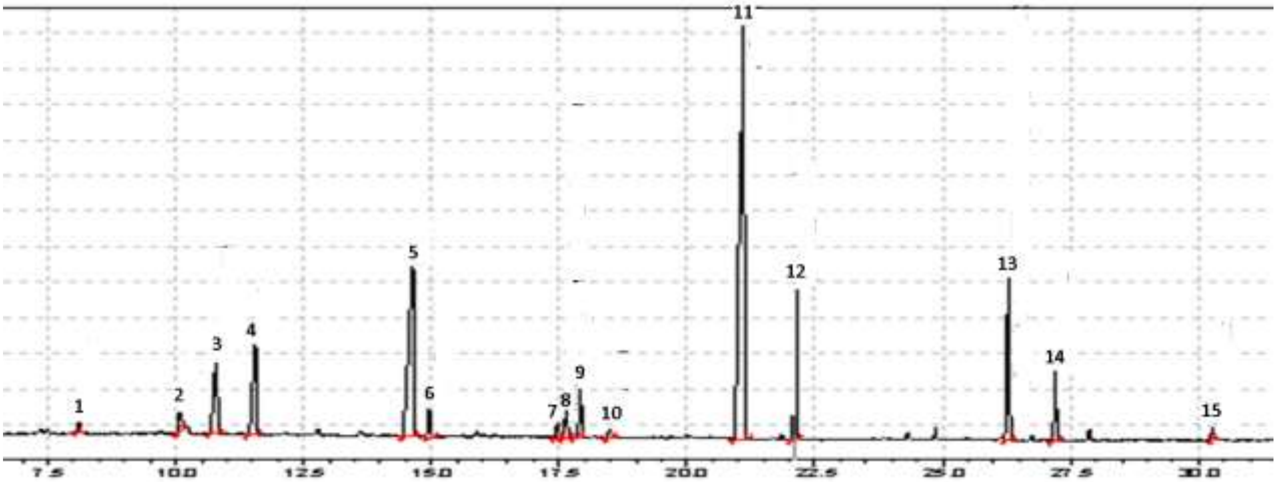

Figure 1. The GC-MS chromatogram of the lavender oil.

To increase the confidence of the analysis, terpinen-4-ol was also searched for among the fifteen components using a QSFR strategy based on its energy profile. It contains the molecular ionization / fragmentation energies for five principal ions: $M^{+\cdot}$ at m/z 154, $M\text{-}CH_3]^+$ at m/z 139, $M\text{-}OH]^+$ at m/z 137, $M\text{-}H_2O]^{+\cdot}$ at m/z 136 and $M\text{-}H_2O\text{-}CH_3]^+$ at m/z 121 (Table 1).

Table 1 The fragmentation energies of terpinen-4-ol

	m/z 154	m/z 139	m/z 137	m/z 136	m/z 121
	$\Delta_f H$ frag (kcal/mol)				
Terpinen-4-ol	189.3	244.0	244.4	184.2	224.3

The corresponding ionic currents (ICs) were collected at the maximum of each chromatographic peak (Table 2). The linear correlation of calculated energy profile of terpinen-4-ol with each of the fifteen ICs series leads to coefficients *R* that are converted into probabilities using eqn. 2:

$$P_{\mathrm{LCOR}(\%)} = 100(1 - R)/2 \qquad (2)$$

The resulted probabilities are presented in the last column of Table 2. The maximum probability (94.2%) corresponds to the ninth GC peak. In this way, the presence of terpinen-4-ol has also been confirmed in the lavender oil.

Table 2. The series of ICs (arbitrary units) for the five principal ions used for energetic profile. The correlation probability (*P*%) with energy profile of terpinen-4-ol is maximal for the ninth GC peak.

GC peak	**Ionic currents**					*P*(%)
	m/z 154	m/z 139	m/z 137	m/z 136	m/z 121	
1	501	522	752	3004	3899	64
2	14844	25410	1989	6309	7173	42
3	524	494	653	2255	26097	45
4	494	486	844	6079	48681	47
5	1436	7519	4742	22077	126705	46
6	486	592	500	484	544	16
7	90	3566	428	3037	6765	42
8	31	413	313	1200	7921	45
9	**11604**	**4604**	**2538**	**23814**	**7276**	**94.2**
10	10	295	657	8944	14403	61
11	15890	13644	12528	70634	452033	47
12	2916	1156	5232	47895	161007	52
13	514	496	3116	8879	72012	46
14	486	499	1496	1548	14850	43
15	506	575	1850	1496	5589	41

The accuracy of the algorithm was verified in the case of some stereoisomers and positional isomers of terpinen-4-ol with similar mass spectra and close RI. Their structures are shown in Figure 2: borneol (**1**), iso-borneol (**2**), terpinen-4-ol (**3**), α-terpineol (**4**), 1-myrcenol (**5**), bicyclo[2.2.1]heptan-1-ol, 4,7,7-trimethyl- (**6**), bicyclo[2.2.1]heptan-2-ol, 4,7,7-trimethyl-, (1*S*-*exo*)- (**7**), bicyclo[2.2.1]heptan-2-ol, 4,7,7-trimethyl-, (1*S*-*endo*)- (**8**), linalool (**9**), nerol (**10**), geraniol (**11**), terpinen-1-ol (**12**), β-terpineol (**13**), δ-terpineol (**14**), γ-terpineol (**15**). The filtration based on energy profile establishes that none of this candidate structures get a higher probability than terpinen-4-ol (Table 3).

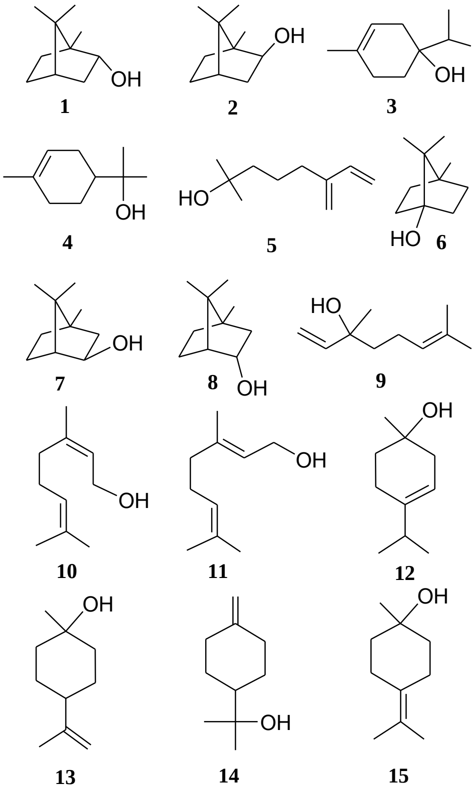

Figure 2. Stereoisomers and positional isomers of terpinen-4-ol, possible candidate structures for the ninth GC peak.

Table 3. The $\Delta_f H$ frag profiles of the fifteen candidate structures. The correlation probability ($P_{(\%)}$) of this profiles with ICs series of the ninth GC peak is maximum for structure **3** (terpinen-4-ol).

Structure	$\Delta_f H$ frag (kcal/mol)					$P_{(\%)}$
	m/z 154	m/z 139	m/z 137	m/z 136	m/z 121	
1	198.5	239.9	255.3	216.1	232.2	83
2	205.6	234.9	255.0	215.8	231.9	85
3	**189.3**	**244.0**	**244.4**	**184.2**	**224.3**	**94.2**
4	190.0	221.7	248.1	196.6	265.3	83
5	193.1	223.7	247.6	203.9	271.0	79
6	206.2	239.5	280.2	247.3	287.9	67
7	204.9	235.5	256.2	216.6	232.7	85
8	203.8	239.3	255.9	216.3	232.4	85
9	191.3	216.8	239.1	192.6	262.5	82

10	194.3	252.0	240.5	212.8	262.7	80
11	191.6	257.9	242.8	215.3	265.2	79
12	187.5	218.8	243.9	183.2	222.4	93
13	203.6	219.5	244.1	197.5	263.9	84
14	198.7	221.7	248.1	202.6	263.1	82
15	189.6	219.5	245.6	199.4	267.5	80

The algorithm offers good sensitivity and selectivity by distributing structures **1-15** in a probability range of nearly 30 units. The proportionality between structural and probability differences is due to the ability of QCC to provide unitary formation enthalpies which can includes the finest structural details. E.g., the position isomers **3** and **12** are separated in the list by ΔP=1.2%, while structure **3** compared to the chain isomers **9**, **10** and **11**, by $\Delta P \approx 15\%$. The calculated energy profiles places the terpinen-4-ol structure on the first place in the list of probabilities, just like library-based assignments and chromatographic alignment.

CONCLUSIONS

At least for the primary ions of terpinen-4-ol isomers, the inverse proportionality between ionic currents and fragmentation energies can be evaluated by GC-MS and QCC and used in analytic purpose. There are wide prospects for generalizing, optimizing and automating this technique because it has important advantages: do not require chemical standards, uses common PC equipment and software, is orthogonal with the currently applied analytical methods and can establish integral *de novo* structures.

ACKNOWLEDGEMENTS

Part of this work was supported by the POSCCE project nr. 621/2014.

REFERENCES

Copolovici, L., Condrat, D., Dinca, N., 2017. Quantitative structure-fragmentation relationship technique applied for discrimination of *cis*-β-ocimene and *trans*-β-ocimene from lavender oil. Scien. Tech. Bull-Chem. Food Sci. Eng., Vol. 14(XV), 28-32.

Dinca, N., Covaci, A., 2012. Structural identification by differential mass spectrometry as a criterion for selecting the best quantum chemical calculation of formation enthalpy for tetrachlorinated biphenyls. Rapid Commun. Mass Spectrom. 26, 2033-2040.

Dinca, N., Dragan, S., Dinca, M., Sisu, E., Covaci, A., 2014. New Quantitative Structure-Fragmentation Relationship Strategy for Chemical Structure Identification Using the Calculated Enthalpy of Formation as a Descriptor for the Fragments Produced in Electron Ionization Mass Spectrometry: A Case Study with Tetrachlorinated Biphenyls. Anal. Chem. (Washington, DC, U. S.) 86, 4949-4955.

Kind, T., Fiehn, O., 2007. Seven Golden Rules for heuristic filtering of molecular formulas obtained by accurate mass spectrometry. BMC Bioinformatics 8, 105.

Rocha, G.B., Freire, R.O., Simas, A.M., Stewart, J.J.P., 2006. RM1: A reparameterization of AM1 for H, C, N, O, P, S, F, Cl, Br, and I. J. Comput. Chem. 27, 1101-1111.

Shellie, R., Mondello, L., Marriott, P., Dugo, G., 2002. Characterization of lavender essential oils by using gas chromatography-mass spectrometry with correlation of linear retention indices and comparison with comprehensive two-dimensional gas chromatography. J. Chromatogr. A. 970(1-2), 225-234.

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POLYCATENAR COMPOUNDS AS ADSORBENTS FOR CONGO RED DYE

Maria Angela SPIRACHE[1], Elisabeta I. SZERB[1] and Lavinia LUPA[2]*

[1]Institute of Chemistry Timisoara of Romanian Academy, 24 Mihai Viteazu Bvd., 300223-Timisoara, ROMANIA
[2]Politehnica University Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Parvan Bvd., 300223, Timisoara, ROMANIA
Corresponding author email: lavinia.lupa@upt.ro

Abstract: *The adsorption capacities for two polycatenar compounds, a benzoic acid and its silver salt were determined. Both compounds showed relatively good adsorption in the removal of Congo Red dye from aqueous solutions. The adsorption capacity of the silver salt was found to be slightly lower than its acid precursor.*

Keywords: Adsorption. Congo Red. Polycatenar compounds.

INTRODUCTION

Water pollution caused by industrial activities gives rise to severe environmental issues, especially in developing countries. Dye pollutants are considered as highly problematic for several reasons: i) high quantity of coloured wastewaters produced by different industries (textile, cosmetics, paper, rubber, leather, food); ii) even a trace of dye can remain highly visible; iii) are carcinogenic and mutagenic; iv) are inert and non-biodegradable (Pereira *et al.*, 2012). Therefore, efficient dye removal is highly required.

Lately, adsorption and photocatalysis were proposed as advantageous strategies of removing dyes from wastewaters, in alternative to the conventional methods of precipitation, ion exchange, filtration or electrochemical treatment (Guo *et al.*, 2013; Khaniabadi *et al.*, 2017; Iryani *et al.*, 2017).

Moreover, the design of adsorbents that may have other actions like water treatment, disinfection, etc. can be a winning strategy to obtain highly pure water by recycling wastewater. Recently, organogels based on polycatenar compounds were reported to remove pollutants from water (Cheng *et al.*, 2018). Moreover, silver is known from ancient times to have antimicrobial properties, being used to store and disinfect water (Melaiye *et al.*, 2005).

Herein, two polycatenar compounds, a benzoic acid (**BzOH**) and its ionic Ag salt (**BzOAg**) whose chemical structures are presented in Figure 1, were tested as adsorbents for Congo Red (CR) dye in water.

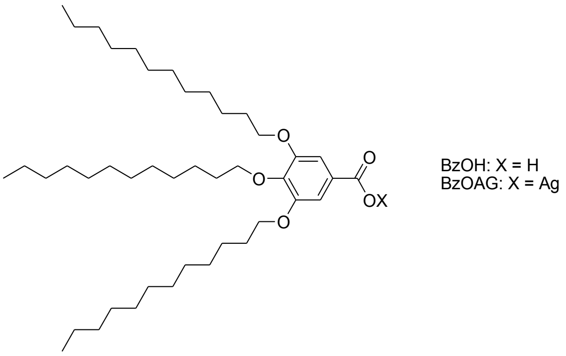


Figure 1. Chemical structure of the polycatenar compounds tested as adsorbents for CR.

MATERIALS AND METHODS

The synthesis and characterisation of the compounds were reported previously (Rowe *et al.*, 1998; Szerb *et al.*, 2013).

The adsorption studies of CR were carried out discontinuously, at constant temperature (25±2°C) and speed rates (200 rpm), using a Julabo SW23 shacking water bath. A stock solution of 1 g/L of RC was prepared. The lower concentrations were obtained by dilution from the stock solution with distilled water. The concentration of CR was determined by absorption using a UV-VIS Varian Cary spectrofotometer. The calibration curve and the equation used to determine the residual CR concentration of the solutions which have undergone absorption, at 498 nm wavelenght are presented in Figure 2.

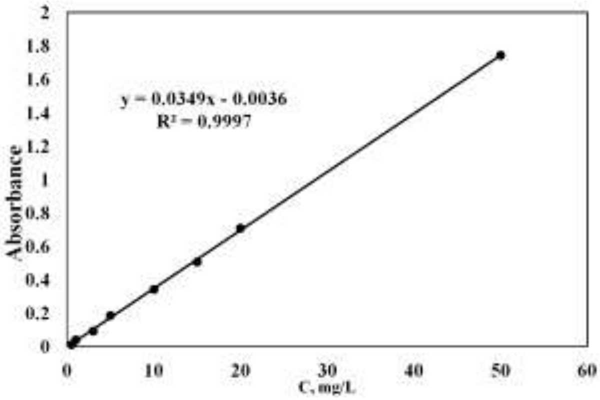


Figure 2. Calibration curve for CR.

The adsorption capacity of compounds **BzOH** and **BzOAg** for CR removal from water was calculated using Equation 1.

$$q = \frac{\left(C_0 - C_e\right)\cdot V}{m} \qquad (1)$$

where: q - quantity of CR adsorbed (mg/g); C_0 and C_e - initial and respectively the equilibrium concentration of CR in solutions (mg/L); V – volume of the solution (L); m – mass of adsorbent (g).

The time necessary to obtain equilibrium time between the adsorbent and adsorbate was determined using a solution of 10 mg/L CR at a ratio of S:L = 1 g/L (Solid: Liquid ratio). The two species were kept in contact in a time range between 18-180 min. Consequently, the solutions were filtrated and the residual concentration of CR was determined from the solution.

The equilibrium studies were determined using different CR concentrations (10-700 mg/L), keeping the other parameters constant (S:L = 1 g/L), pH = 8.75, shacking time 45 minutes).

RESULTS AND DISCUSSIONS

The absorption spectra of the solutions used for determining the equilibrium time for the two compounds under discussion (**BzOH** and **BzOAg**) are presented in Figure 3.

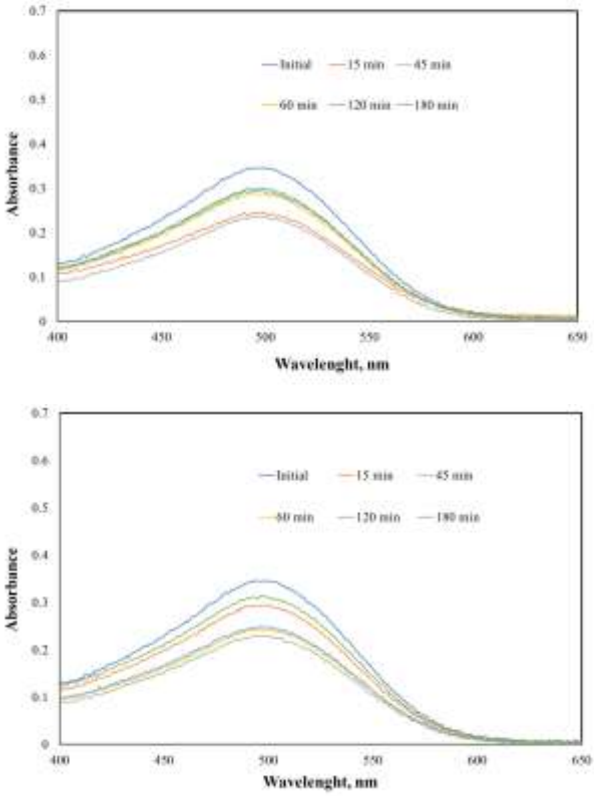


Figure 3. Variation of the absorption spectra of the adsorbed CR over contact time for: up – **BzOH** and down: **BzOAg**.

The experimental data show for both systems a decrease of the absorption maxima with increasing contact time until 45 minutes, following an increase of the absorption maxima in time, probably because of the desorption process of the CR from the adsorbent surface.

The adsorption capacity of both materials (**BzOH** and **BzOAg**) for the removal of CR from water as a function of time is presented in Figure 4.

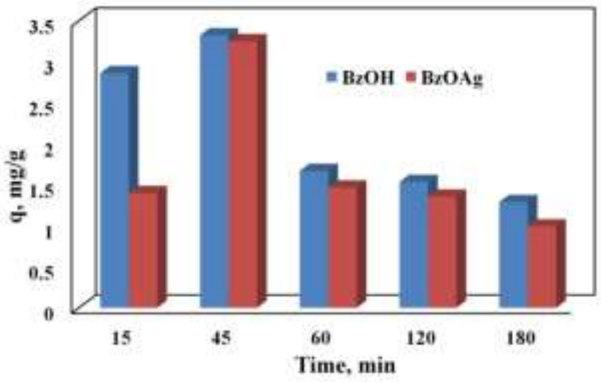


Figure 4. Adsorption capacities of the two adsorbents under consideration.

The best adsorption time resulted to be 45 minutes. It is not reccomended an increased contact time to avoid de consequently desorption of the dye. At this optimum contact time equilibrium studies were performed. The equilibrium isotherms are presented in Figure 5.

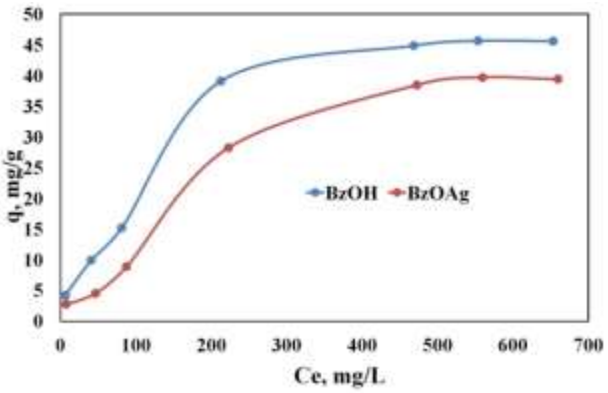


Figure 5. Variation of the amount of the adsorbed CR over optimum contact time.

The equilibrium isotherms show that the adsorption capacities of both compounds under study increase with concentration until a constant value is reached. The maximum adsorption capacities are 45.6 mg/g for **BzOH** and respectively 40.0 mg/L for **BzOAg**. The values found are lower than the ones reported in literature for some zeolites (97.08 mg/g, Iryani *et al*., 2017) or chitosan (94.39 mg/g, Rouf *et al*., 2015), but with lower contact times (100 min. and respectively 240 min.).

CONCLUSIONS

The adsorption capacities of two polycatenar compounds, a benzoic acid (**BzOH**) and its Ag(I) salt (**BzOAg**) were determined. The adsorption capacities for **BzOAg** resulted slightly lower than of its acid precursor. However, being a silver salt, further studies will be performed in order to determine other actions of the **BzOAg** like photocatalysis or antimicrobian activities for wastewaters.

ACKNOWLEDGEMENTS

Authors Spirache M. A. and Szerb E. I. acknowledge the Ministery of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-20160720, within PNCDI III and Romanian Academy, Program 4.

REFERENCES

Cheng, H.-F., Xing, W., Zhang, B., Yu, J., Cheng, X.-H., 2018. Bisphenylsulfone-based polycatenar mesogens via CuAAC click reaction: Self-assembly and their applications in water purification. Tetrahedron 74, 2735-2742.

Guo, H., Ke, Y., Wang, D., Lin, K., Shen, R., Chen, J., Weng, W., 2013. Efficient adsorption and photocatalytic degradation of Congo red onto hydrothermally synthesized NiS nanoparticles. J. Nanopart. Res. 15: 1475.

Iryani, A., Ilmi, M. M., Hartanto, D., 2017. Adsorption study of congo red dye with ZSM-5 directly synthesized from Bangka kaolin without organic template. Mal. J. Fund. Appl. Sci. 13, 832-839.

Khaniabadi, Y. O., Mohammadi, M. J., Shegerd, M., Sadeghi, S., Saeedi, S., Basiri, H., 2017. Removal of Congo red dye from aqueous solution by a low-cost adsorbent: activated carbon prepared from Aloe vera leaves shell. Environ. Eng. Manag. J. 4(1), pp. 29-35.

Melaiye, A., Youngs, W. J., 2005. Silver and its application as an antimicrobial agent: Expert Opinion on Therapeutic Patents, 15:2, pp. 125-130.

Pereira, L., Alves, M., 2012. Dyes-Environmental Impact and Remediation: Environmental Protection Strategies for Sustainable Development, Strategies for Sustainability, Malik, A., Grohmann, E., (eds.), Springer Science+Business Media B.V., pp. 111-162.

Rouf, R., Nagapadma, M., Ramakoteswara, R. R., 2015. Removal of Harmful Textile Dye Congo Red from Aqueous Solution Using Chitosan and Chitosan Beads Modified with CTAB. Int. J. Eng. Res. Appl. 5(3), 75-82.

Rowe, K. E., Bruce, D. W., 1998. The synthesis and mesomorphism of di-, tetra- and hexa-catenar liquid crystals based on 2,2’-bipyridine. J. Mater. Chem. 8, 331-341.

Szerb, E. I., Pucci, D., Crispini, A., La Deda, M., 2013. Soft Luminescent Materials Based on Ag(I) Coordination Complexes. Mol. Cryst. Liq. Cryst. 573, 34-45.

MUNICIPAL SOLID WASTE MANAGEMENT

Dan DANCIU[1], Florentina-Daniela MUNTEANU[2*]

[1]*Faculty of Engineering, „Vasile Alecsandri” University of Bacău, Calea Mărăşeşti, nr. 157, 600115, Bacău, România*
[2]*Faculty of Food Engineering, Tourism and Environmental Protection, “Aurel Vlaicu” University, Romania, 2 Elena Dragoi, Arad 310330, Romania*
Corresponding author email: florentina.munteanu@uav.ro

Abstract: *The present paper has in attention the alleviation of the environmental issues when a proper management of the solid waste is considered by the authorities. Moreover, the most used waste management activities are screened in order to evaluate which one is providing sustainable social and economic benefits.*

Keywords: solid waste, management, sustainability, environmental impact.

INTRODUCTION

The accelerated population growth in the urban areas has led to an increase in the amount of waste, resulting in a major impact on the environment, health and the socio-economic climate. The human activity leads to different by-products known as municipal solid waste (MSW). MSW consists of different solid wastes that may include biodegradable wastes, but also hazardous, medical, electrical and electronic and composite wastes.

Nowadays a big concern is raised in connection to the municipal solid waste management, as the activities associated with this process might lead to an inappropriate impact on human health, environmental quality and economic benefits. A simple search in Web of Science, Clarivate Analytics, on the topic „municipal solid waste” leads to almost 18000 search results, most of which are considering different options for a sustainable municipal waste management (Haupt et al., 2018; Heidari et al., 2019; Soni et al., 2016; Yadav and Samadder, 2018). In general, for environmental good practices is necessary to apply a systematic management of the solid waste, independent of the origin, composition or the hazardous potential of the waste. Therefore, a rigorous environmental planning will critically contribute to the hygiene of the environment (Mohammadi et al., 2019; Simatele et al., 2017).

For the evaluation of the environmental burden and of the benefits that are brought by a product or of an industrial process one can use computer-based tools referred as Life Cycle Assessment (LCA) (Klopffer, 1997). In the case of waste management, this tool can be used to study the life cycle of the wastes and their impact on the environment as it is presented by several published papers on this subject (Bartolozzi et al., 2018; Haupt et al., 2018; Liu et al., 2017).

In the present study, we will present different procedures for the treatment of the solid waste having in attention the European Commission Circular Economy Package (EC, 2015) that should be seen as be primarily seen as a starting point for any research initiative in this field.

DISCUSSION

The least friendly option for the management of the solid waste is the landfilling, which, unfortunately is still the most used method. Even though, there are some results (Babu et al., 2014) that show that landfilling might be a better option than open burning or open dumping. However, according to the Final Circular Economy Action Plan, adopted by the European Commission in 2015 (EC, 2015), there are certain restriction on regard to the landfilling. In this document it is specified that the municipal waste landfilled must be below 10% of the total amount of the generated municipal waste.

The thermal treatment of the solid waste is another common method for the solid waste removal. The pyrolysis and gasification are not very attractive because of their costs constraints, while incineration is much more applied (Boesch et al., 2014), but in this case a strict control of the emissions from the waste treatment plants should be controlled.

Soni et al. proposed in their studies a method to obtain energy from waste (Soni et al., 2016). Firstly, they were looking to the composition of the solid waste (Figure 1) that can be processed and valorised.

In their studies they concluded that waste should not be considered just as simple waste, but rather as a source of energy.

Moreover, with proper treatments the biodegradable part of the solid waste can be successfully used for the obtaining of the biodiesel, Bio-CNG, Fuel ethanol and liquid manure. The non-biodegradable part, after recycling can be further used for incineration or landfilling.

Figure 1. Composition of municipal solid waste that can be treated as a source for production of the necessary energy. From (Soni et al., 2016)

During the entire process of the solid waste management, it has to be taken the best decision in terms of the most appropriate option for the treatment techniques. In Figure 2 are shown the techniques that can be used.

Figure 2. Techniques used for waste management. Adapted from (Khandelwal et al., 2019)

During the composting process the organic fraction is partially degraded by the microorganisms, and carbon dioxide and water is obtained, while the other fraction is continuously humidified in order to obtain a stable compost material that can be used as biological fertilizer (Milinković et al., 2019). It has to be mentioned that the quality of the compost is depending of the air supply, temperature control, homogeneous mixing. If all these parameters are monitored then the processing and capital costs can be controlled (Baeta-Hall et al., 2005).

However, the acceptance of the composting as an option for the solid waste management is dependent on how well-developed are the exploitation strategies used for the obtained products as well as for the environmental protection. As a consequence, it is necessary to have an appropriate evaluation of the systems in terms of the products acceptability and maximized efficacy (Khandelwal et al., 2019; Muscolo et al., 2018).

CONCLUSIONS

Based on the impressive number of studies present in the Clarivate Analytics database, and that are treating the options for an optimal management of the municipal solid waste, it has to emphasize the fact that the regional conditions play an important role. The site-specific composition of the waste should be placed on a higher position in the hierarchy of the decisions, followed by the treatment efficiency, energy yield, etc. Moreover, a special attention should be paid to the action plan that is contained in the Annex 1 of the EC Circular Economy Package. Last, but not least is commendable to use life cycle assessment as a tool of evaluation in the municipal solid waste management.

REFERENCES

Babu, G.L.S., Lakshmikanthan, P., Santhosh, L.G., 2014. Life cycle analysis of municipal solid waste (MSW) land disposal options in Bangalore city, ICSI 2014: Creating Infrastructure for a Sustainable World. .

Baeta-Hall, L., Ceu Saagua, M., Lourdes Bartolomeu, M., Anselmo, A.M., Fernanda Rosa, M., 2005. Bio-degradation of olive oil husks in composting aerated piles. Bioresour Technol 96, 69-78.

Bartolozzi, I., Baldereschi, E., Daddi, T., Iraldo, F., 2018. The application of life cycle assessment (LCA) in municipal solid waste management: A comparative study on street sweeping services. Journal of Cleaner Production 182, 455-465.

Boesch, M.E., Vadenbo, C., Saner, D., Huter, C., Hellweg, S., 2014. An LCA model for waste incineration enhanced with new technologies for metal recovery and application to the case of Switzerland. Waste Manag. 34, 378-389.

EC, 2015. http://ec.europa.eu/environment/circular-economy/index_en.htm.

Haupt, M., Kagi, T., Hellweg, S., 2018. Modular life cycle assessment of municipal solid waste management. Waste Manag 79, 815-827.

Heidari, R., Yazdanparast, R., Jabbarzadeh, A., 2019. Sustainable design of a municipal solid waste management system considering waste separators: A real-world application. Sustainable Cities and Society 47, 101457.

Khandelwal, H., Dhar, H., Thalla, A.K., Kumar, S., 2019. Application of life cycle assessment in municipal solid waste management: A worldwide critical review. Journal of Cleaner Production 209, 630-654.

Klopffer, W., 1997. Life cycle assessment. From its beginning to the current state. Environ. Sci. Pollut. Res 4, 223-228.

Liu, G., Hao, Y., Dong, L., Yang, Z., Zhang, Y., Ulgiati, S., 2017. An emergy-LCA analysis of municipal solid waste management. Resources, Conservation and Recycling 120, 131-143.

Milinković, M., Lalević, B., Jovičić-Petrović, J., Golubović-Ćurguz, V., Kljujev, I., Raičević, V., 2019. Biopotential of compost and compost products derived from horticultural waste—Effect on plant growth and plant pathogens' suppression. Process Safety and Environmental Protection 121, 299-306.

Mohammadi, M., Jämsä-Jounela, S.-L., Harjunkoski, I., 2019. Optimal planning of municipal solid waste management systems in an integrated supply chain network. Computers & Chemical Engineering 123, 155-169.

Muscolo, A., Papalia, T., Settineri, G., Mallamaci, C., Jeske-Kaczanowska, A., 2018. Are raw materials or composting conditions and time that most influence the maturity and/or quality of composts? Comparison of obtained composts on soil properties. Journal of Cleaner Production 195, 93-101.

Simatele, D.M., Dlamini, S., Kubanza, N.S., 2017. From informality to formality: Perspectives on the challenges of integrating solid waste management into the urban development and planning policy in Johannesburg, South Africa. Habitat International 63, 122-130.

Soni, A., Patil, D., Argade, K., 2016. Municipal Solid Waste Management. Procedia Environmental Sciences 35, 119-126.

Yadav, P., Samadder, S.R., 2018. A critical review of the life cycle assessment studies on solid waste management in Asian countries. Journal of Cleaner Production 185, 492-515.

Scien. Tech. Bull-Chem. Food Sci. Eng., Vol. 15(XVI), 2018, 14-17

THE TREND OF PARTICULATE MATTER (PM10) CONCENTRATIONS IN THE WESTERN PART OF ROMANIA

Adina BODESCU, Lucian COPOLOVICI*

Faculty of Food Engineering, Tourism and Environmental Protection, "Aurel Vlaicu" University, Romania, 2 Elena Dragoi, Arad 310330, Romania
**Corresponding author email: lucian.copolovici@uav.ro*

Abstract:*Particulate matter (PM) is one of the most known air pollutant and is formed as a mixture of solid particles and liquid droplets. From them, PM10 are the inhalable particles with diameters smaller than 10 micrometers. Such particles could create seriously health problems for the population as increases the risk of lung cancer and heart diseases. Due to those effects on the human health, the concentrations of PM10 are monitored as a daily routine by National Environmental Agency. The present study compare the concentration of PM10 (as has been reported by National Environmental Agency) during the last three years in the West part of Romania (Timisoara, Arad, Satu Mare and Bihor County). For all county the medium concentrations are under their legal limits (40 µg/m^3) with very few exceptions. The highest concentrations have been found in winter due to heating and higher transport fluxes. The maximum concentrations are higher than the daily legal limits (50 µg/m^3) mainly in Arad probably due to the high traffic. Anyway, compare with the European trend, the daily concentration limit have been overtaken very few times (less than ten).*

Keywords: particulate matter, air pollution, human health

INTRODUCTION

Particulate matter (also called particle pollution) are a complex mixture of liquid droplets and solid particles with different composition and sources. The size of those particles vary between approximately 0.002 and 100 µm aerodynamic diameters. The classification of particulate matter are function of their diameters. Usually, could be distinguish coarse, fine and ultrafine particles as their diameter is less than 10 µm (PM10), 2.5 µm (PM2.5) and 0.1 µm respectively (PM 0.1) (Muhlfeld, et al., 2008). The main sources for those pollutants are divided in two main classes: primary (as incomplete combustion, automobile emission, dust or domestic fuel burning) and secondary (particles are formed in the atmospheric reactions) (Kelly and Fussell, 2016, Naidja, et al., 2018). Furthermore, the sources could be anthropogenic as industrial or households and natural as dust, soil, sea salt. In the case of PM10 the main contribution of globally world emission has traffic (25%) followed by natural dust and sea salt (22%), industrial activity(18%), and from domestic fuel burning (15%) (Karagulian, et al., 2015). In Central and Eastern Europe, the main contributor of PM10 emission is domestic fuel burning (45%) while in Middle East and Southwestern Europe the main source are natural (mainly dust and seasalt) with represent 44% and 39% form total, respectively (Karagulian, et al., 2015). In Romania it has been found that in urban area the main source of PM10 is traffic and fuel burning while in rural zones the natural sources are predominated (Roba, et al., 2014).

Regarding to human health it well known that exposure to PM on short-term or long-term determine negative effects. The influence of PM to human health include lung cancer (Wang, et al., 2018), cardiac and respiratory disease (Lipfert, 2018, Pan, et al., 2018, Wang, Zhang, et al., 2018) even diabetes and pregnancy-birth endpoints (Lipfert, 2018). The main transport mechanism of those particles in the lung is diffusion with only minimal contributions of gravitation or inertia. Therefore, PM10 reach the alveolar region and are not retained in the trachea bronchiolar region (Muhlfeld, Rothen-Rutishauser, et al., 2008). Cellular responses to particle exposure include the generation of reactive oxygen (ROS) and nitrogen species (RNS), the release of proinflammatory, inflammation-associated proteins, and injury of nuclear DNA (Muhlfeld, et al., 2008). Recently, it has been found a link between PM exposure and metabolic syndrome (Matthiessen, et al.,

2018) and the fact that a medium-term PM exposures were positively associated with glucose increases in nondiabetic adults (Lucht, et al., 2018).

The goal of our study has been to show the PM10 trend in four county in Northwest Romania over the last three years.

MATERIALS AND METHODS

The data have been provided by National Agency for Environmental Protection. All data regarding to PM10 for Arad (AR), Bihor (BH), Satu Mare (SM) and Timis (TM) for 3 years (2015-2017) have been downloaded from (http://www.anpm.ro/raport-de-mediu) and processing using Origin 8.0 (OriginLab Corporation, USA). The monitoring station for every county have been situated in the city centre of the town.

RESULTS AND DISCUSSIONS

Arad (AR), Bihor (BH), Satu Mare (SM) and Timis (TM) counties are located in the west part of Romania at the border with Hungary and Serbia. The air quality in this region is consider good. The trends for PM10 concentration are presented in Figure 1.

For all counties, the emission of PM10 have been shown the same trend with high values in the winter months and lower ones in the summer. Anyway, the emission of such particles exceed the approved level (40 μg/m^3) only punctually in winter 2017 for Arad and in winter 2015 for Bihor. The source for such high emissions in winter are the heating of houses and road transportation. Such trend of PM 10 emissions are compare with the ones found in Stockholm, Gothenburg, and Malmoover 2005-2017 (Olstrup et al., 2018). The total emission of particulate in suspension are decreasing in Romania from 16000 tones/year in 2002 at 5300 tones/year in 2015 which are collaborated with the fact that all emission of pollutants as SO_2, NOx, CO_2 are decreasing. PM10 concentration decrease with 78 % in 2015 compare with 2002 while over the period of 2009-20015 the values are almost constant.

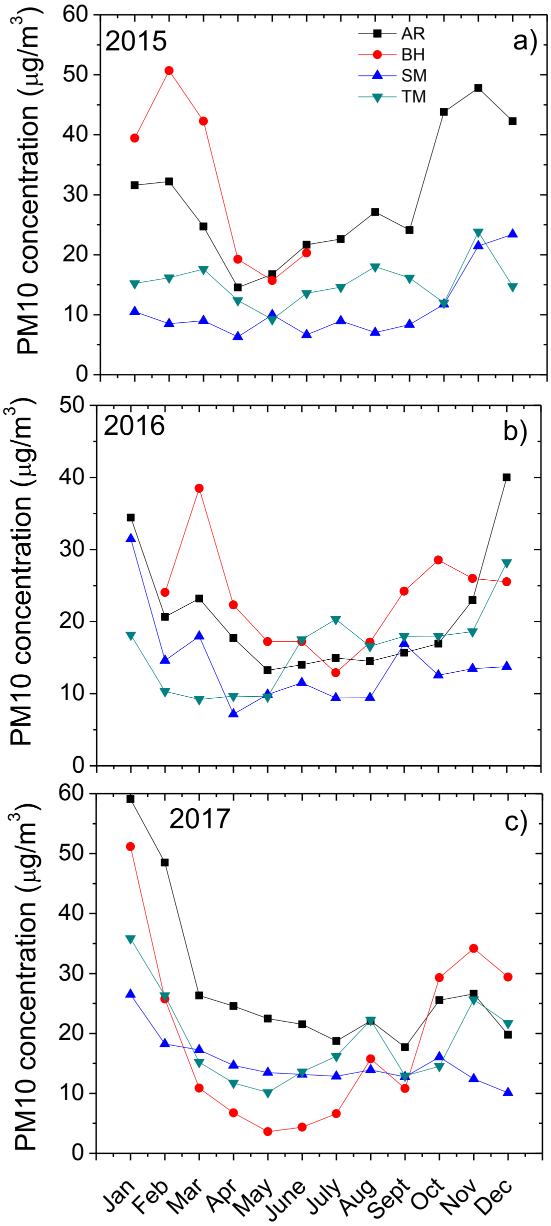
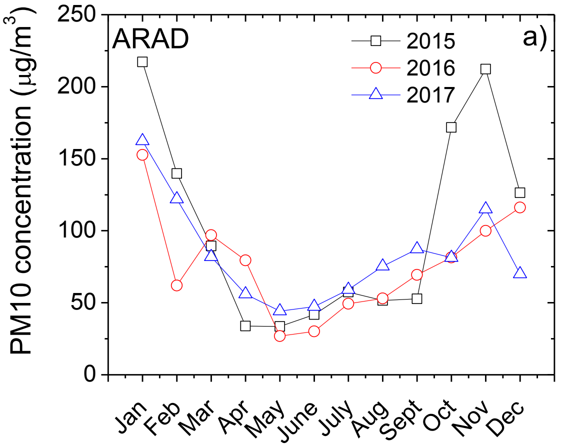


Figure 1. The evolution of the average PM10 concentration over the year for 2015 (a), 2016 (b) and 2017 (c)



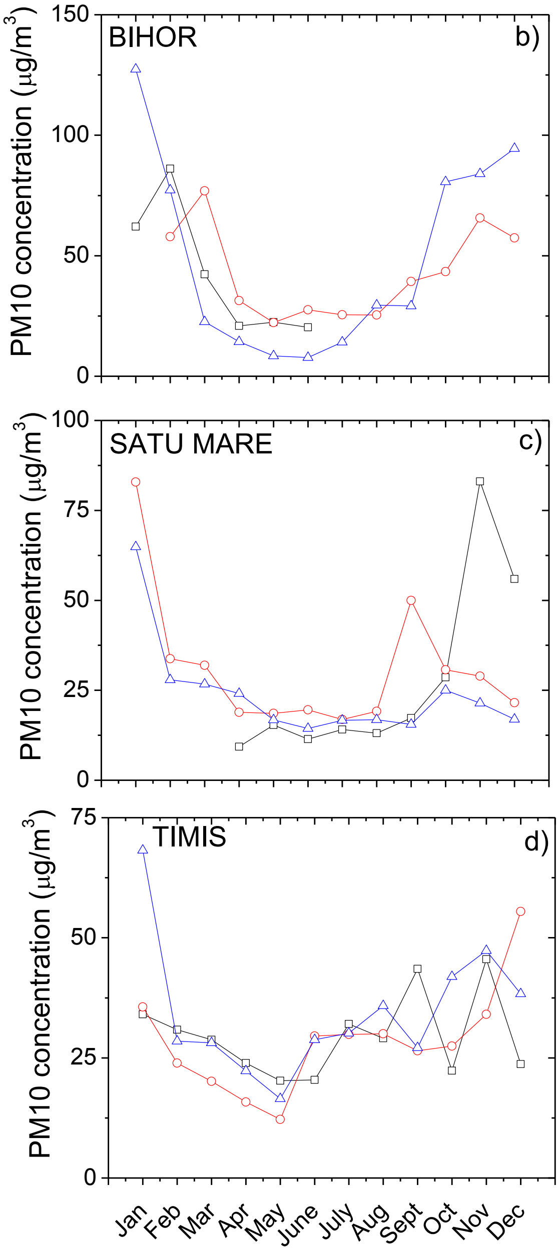


Figure 2. The evolution of maximum concentration over 3 years for counties in the west part of Romania

Regarding to the highest values of PM10 over every months there are many values which are over the approved limits. In Arad for example the PM10 concentrations exceed 150 μg/m^3 every year in January. The presence of PM10 particles in the air at such high concentration could determine important health concerns as respiratory problems or cardiological diseases.

In contrast, in Timis county the PM10 concentrations the approved limits only ones in January. Such difference could be due to the fact that in Timis the monitoring station is situated in the city centre (a pedestrian zone) while in Arad is in the most circulated intersection. Anyway, such behaviour could underline that the traffic is the most important sources of particles in the atmosphere.

CONCLUSIONS

In the present study it has been shown the trend of particles matter PM 10 over the year in four counties. The average values are mostly under the legal limits. On the other hand, the maximum values exceed in Arad 200 μg/m^3 which is over the attention limits regarding to human health.

REFERENCES

Karagulian, F., Belis, C.A., Dora, C.F.C., Pruss-Ustun, A.M., Bonjour, S., Adair-Rohani, H., 2015. Contributions to cities' ambient particulate matter (PM): A systematic review of local source contributions at global level. Atmos. Environ. 120, 475-483.

Kelly, F.J., Fussell, J.C. 2016. Health Effects of Airborne Particles in Relation to Composition, Size and Source. In: R. E. Hester, R. M. Harrison and X. Querol, editors, Airborne Particulate Matter: Sources, Atmospheric Processes and Health, pp. 344-382.

Lipfert, F.W. 2018. Long-term associations of morbidity with air pollution: A catalog and synthesis. Journal of the Air & Waste Management Association 68, 12-28.

Lucht, S.A., Hennig, F., Matthiessen, C., Ohlwein, S., Icks, A., S. Moebus, 2018. Air Pollution and Glucose Metabolism: An Analysis in Non-Diabetic Participants of the Heinz Nixdorf Recall Study. Environmental Health Perspectives 126.

Matthiessen, C., S. Lucht, F. Hennig, S. Ohlwein, H. Jakobs, Jockel, K.H., 2018. Long-term exposure to airborne particulate matter and NO2 and prevalent and incident metabolic syndrome - Results from the Heinz Nixdorf Recall Study. Environment International 116, 74-82.

Muhlfeld, C., Rothen-Rutishauser, B., Blank, F., Vanhecke, D., Ochs, M., Gehr, P., 2008. Interactions of nanoparticles with pulmonary structures and cellular responses. American Journal of Physiology-Lung Cellular and Molecular Physiology 294, L817-L829.

Naidja, L., Ali-Khodja H., Khardi, S., 2018. Sources and levels of particulate matter in North African and Sub-Saharan cities: a literature review. Environmental Science and Pollution Research 25, 12303-12328.

Olstrup, H., Forsberg, B., Orru, H., Spanne, M., Nguyen, H., Molnár, P., Johansson, C., 2018.

Atmos. Chem. Phys. Discuss., under review. https://doi.org/10.5194/acp-2018-7.

Pan, L., Wu, S.W., Li, H.Y., Xu, J.H., Dong, W., Shan, J., 2018. The short-term effects of indoor size-fractioned particulate matter and black carbon on cardiac autonomic function in COPD patients. Environment International 112, 261-268.

Roba, C., Stefanie, H., Torok, Z., Kovacs, M., Rosu, C., Ozunu, A., 2014. Determination of volatile organic compounds and particulate matter levels in an urban area from Romania. Environmental Engineering and Management Journal 13, 2261-2268.

Wang, N., Mengersen, K., Kimlin, M., Zhou, M.G., Tong, S.L., Fang, L.W., 2018. Lung cancer and particulate pollution: A critical review of spatial and temporal analysis evidence. Environmental Research 164, 585-596.

Wang, X.J., Zhang, L.L., Yao, Z.J., Ai, S.Q., Qian, Z.M., Wang, H., 2018. Ambient coarse particulate pollution and mortality in three Chinese cities: Association and attributable mortality burden. Science of the Total Environment 628-629, 1037-1042.

Scien. Tech. Bull-Chem. Food Sci. Eng., Vol. 15(XVI), 2018, 18-22

CHARACTERIZATION OF ALKALINE AND ENZIMATICALLY TREATED HEMP FIBRES BY FT-IR ATR SPECTROSCOPY

Dorina Rodica CHAMBRE[1], Mihaela DOCHIA[2*]

[1]Faculty of Food Engineering, Tourism and Environmental Protection, "Aurel Vlaicu" University, Romania, 2 Elena Dragoi, Arad 310330, Romania
[2] Research Development Innovation in Natural and Technical Sciences Institute, "Aurel Vlaicu" University, Romania, 2 Elena Dragoi, Arad 310330, Romania
Corresponding author email: dochiamihaela@yahoo.com

Abstract: *The FT-IR ATR spectra of the alkaline and enzymatically treated hemp fibres (1%, 2%, 3% o.w.f. enzyme, 15, 35, 55 minute enzyme action time) were recorded aiming to evaluate the pectin elimination. The relative absorbance values of the 1732 cm^{-1} band which might be attributed to the presence of the carboxylic groups (C=O) in pectin were evaluated. The results showed a diminishing of the pectin amount with increasing concentration (% o.w.f.) and action time (minutes) of the enzyme mixture. So that, the absorbance recorded at 1732 cm^{-1} with FT-IR ATR spectroscopy can quantify removed pectin from the material, thus enabling characterization of proposed biotechnology and monitoring the process.*

Keywords: hemp fibres, alkaline treatment, enzyme treatments, pectin elimination, FT-IR ATR

INTRODUCTION

Biocomposites are becoming strategic materials with various applicative purposes such as: building materials, automotive components, etc. Bast fibres such hemp, flax, or jute are the most used of plant fibres as bio based fillers or reinforcements constituents in polymer – based composites due to the fact that are biodegradable and have good mechanical, thermal and acoustic properties (Väisänen et al. 2018, Iucolano et al. 2018). Due to its strength and stiffness, hemp fibre has good potential as a composite reinforcement. The main constituent of hemp fibre is cellulose (~74 %). In addition to cellulose, other constituents like pectins (~1%), hemicellulose (~14 %), lignin (~5%), waxes, extractable substances, minerals, etc. (~6%) are present in the fibres structure (Väisänen et al. 2018, Shahzad, 2012). The homogeneity, fineness and effectiveness of fibres can be improved by removing the pectin and hemicellulose that bond the fibres bundle together (Kozlowski et al. 2006). For this purpose, chemical, physical or enzymatic treatments can be used. Recently, the use of enzymes is an ecological alternative to classical treatments, with a lower environmental impact. Enzymatic treatments provide numerous benefits over chemical and physical methods due to their high selectivity. Many studies have shown that the use of pectinases is very efficient for the removing of pectins which leads to the improvement of hydrophilicity without affecting the mechanical properties of the material (Iucolano et al. 2018, Thygesen et. al. 2013, Li et al. 2008).

The FT-IR ATR spectroscopy has proven to be a simple and rapid technique for obtaining information on the structure of the fibres constituents and chemical changes taking place in hemp fibres after different treatments (Dochia et al. 2018a, Wang et al. 2006, Terpáková et al. 2012, Choe et al. 2018, Ouajai et al. 2005).

Continuing our previous studies (Dochia et al. 2018a, 2018b), in this paper are presented the results obtained by FT-IR ATR investigation in order to quantify pectin elimination from hemp fibres after alkaline treatment and enzymatic treatments (conducted under different experimental conditions). For this purpose, the 1732 cm^{-1} intensity band, which might be attributed to the presence of the carboxylic groups (C=O) in pectin was evaluated.

MATERIALS AND METHODS

Materials

The following samples were analysed: raw hemp fibres denoted as RWH sample; alkaline treated hemp fibres denoted as ATH sample (raw sample treated at 95 ^{0}C with 10 g.L^{-1} sodium hydroxide for 60 minutes); enzymatically treated hemp fibres denoted as ETHx-y (were x is the concentration of enzyme, % over weight fibre - o.w.f, and y- minutes of the enzyme action time) –ETH1-35, ETH2-15, ETH2-35, ETH2-55, ETH3-35.

Enzymatic treatments were performed as follows: distilled water reaction media; 1:20 fibres to liquid ratio; commercial enzyme Beisol PRO from CHT Bezema Company (a mixture of Polygalacturonases - which act on pectin polygalacturonic chains and Pectinesterases enzymes - which act on pectin ester groups); pH 8.5 (assured by buffer CAS:7732-18-5); 55^{0}C treatment temperatures; 2 g.L^{-1} (~10 mmol.L^{-1}) sodium citrate (monosodium citrate, CAS: 18996-35-5) as complexing agent from Sigma-Aldrich; 0.5% surfactant Denimcol Wash-RGN detergent (from CHT Bezema Company).

Method

The FT-IR ATR experiments were performed on samples taken from conditioned raw and treated hemp fibres (up to 105 0C on Sartorius MA 100 system). The spectra were acquired using the Bruker Vertex 70 spectrophotometer equipped with the ATR cell, on the 600-3000cm^{-1} wavelength range with a resolution of 4cm^{-1} and 36 scans. The OPUS software was used for the acquisition and processing of experimental data (spectra normalization and baseline correction). The background calibration was made before each measurement.

RESULTS AND DISCUSSIONS

Lignocellulosic fibres are usually characterized by several absorption bands as can be notice in Scheme 1 which shows the FT-IR ATR spectra of the RWH, ATH and ETH3-35 samples recorded on 600 – 4000 cm^{-1}.

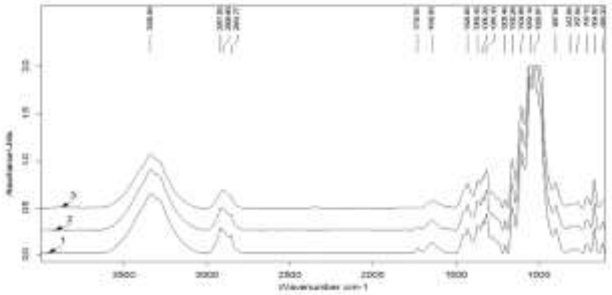


Figure 1. FT-IR ATR spectra of: 1- RWH, 2 - ETH3-35 and 3 – ATH samples

The peak recorded at 3000cm^{-1}-3600cm^{-1} can be assign to the free -OH stretching vibration and to the intra- and intermolecular hydrogen bond related to cellulose structure (Wang et al. 2006, Perincek et. al. 2016, Le Troedec et al. 2008). The peak located at 2800-3000cm^{-1} is due by CH symmetrical stretching of cellulose and the two extra bands at 2917cm^{-1} and 2851 cm^{-1}, can be related to the CH2 and CH groups stretching vibration from pectin and waxes (Wang et al. 2006, Choe et al. 2018, Subramanian et al. 2005). The bands observed at around 1732cm^{-1} and 1642cm^{-1} are specifics for pectin and can be attributed to the COOH and COOCH3 groups of polygalacturonic acid and to symmetrical/asymmetrical oscillations of ionized carboxyl groups COO-, respectively (Wang et al. 2006, Dai et al. 2010) Due to the superposition of the OH bending of absorbed water (1642 cm^{-1}) with the carboxyl ion band recorded around 1550cm^{-1}-1700cm^{-1}, the quantification of the pectin elimination in this area is quite difficult. (Dai et al. 2010, Ouajai et al. 2005).

The fingerprint area of the cellulose located between 600cm^{-1}-1400cm^{-1} contains specific and common bands (Dai et al. 2010). The 1428 cm^{-1} band was attributed to HCH and OCH in-plane bending vibration of cellulose and is known as “crystalline” band (Ouajai et al. 2005, Ciolacu et al. 2011).

The band from 1368cm^{-1} is given by in-the-plane CH bending of cellulose and hemicellulose. Band due to the deformation of OH group of cellulose was recorded at 1335cm^{-1}. CH2 rocking vibration from cellulose was observed at 1315 cm^{-1} (Dai et al. 2010).

The bands to 1160cm^{-1} and 1203cm^{-1} are for C-O-C symmetric and asymmetric stretching from cellulose and hemicellulose (Dai et al. 2010). The bands at 1029cm^{-1}, 1053 cm^{-1} and 1104 cm^{-1} indicate the C-OH, C-C, C-H ring and side group vibrations in cellulose and hemicellulose (Dai et al. 2010).

The observed band at 897cm^{-1} can be attributed to COC, CCO and CCH deformation and stretching from cellulose being known as “*amorphous*” band (Ciolacu et al. 2011, Ouajai et al. 2005).

The band at 812 cm^{-1} is specific for lignin (Ouajai et al. 2005) and that to 661 cm^{-1} to the OH out-of-plane bending (Le Troedec et al. 2008, Dai et al. 2010).

In order to analyse the influence of the enzymatically treatments, which aims the elimination of a large amount of pectin from cellulosic and lignocellulosic materials, different authors recommend the investigation of the changes occurring in the absorbance intensity of the bands located at 2900cm^{-1}- 2919cm^{-1}, 2850cm^{-1}- 2860cm^{-1} and around 1630-1640cm^{-1} but especially of those at 1730cm^{-1}- 1734cm^{-1}, which is specific for the carboxylic group of polygalacturonic acid and COOCH3 (Wang et al. 2006, Abdel-Halim et al. 2008, Ouajai et al. 2005, Le Troedec et al. 2008).

From Figure 1 it can be seen that the intensity of the two extra bands located at 2917cm^{-1} and 2851cm^{-1} decrease from RWH to enzymatically treated sample due to the elimination of waxes and of a pectin fraction by breaking of the 1-4 carbohydrate bonds from D-galacturonic acid under Polygalacturonases action, and disappear for ATH sample.

In the alkaline treatment the CH and CH2 stretching vibration of cellulose was recorded at 2899 cm^{-1}.

The intensity of the specific band at 1732 cm^{-1} which indicate the existence of pectin it's diminishing for ETH3-35 sample and is not found in the FT-IR spectrum of the ATH sample. This behaviour suggests that enzymatically treatment eliminates hemp fibre pectin only partially comparing to alkaline conditions.

As pectin is eliminated the band located at 812 cm^{-1}, assign to lignin, becomes more intense compared to the RWH sample. This band disappears totally for ATH sample, suggesting that alkaline treatment removes all non-cellulosic attendants.

The changes occurring in the FT-IR spectra of the ATH sample observed at 3000-3500 cm^{-1}, 2851-2917 cm^{-1}, 1428 cm^{-1} and 897 cm^{-1} suggest that NaOH affected the crystalline cellulose structure and diminished the number of OH bonds present in cellulose chains with the formation of $-O^{-}Na^{+}$ groups.

In Figure 2 are presented the FT-IR spectra recorded around 1732 cm^{-1} (band specific for pectin) for raw hemp fibres and enzymatically treated samples at different enzyme concentrations.

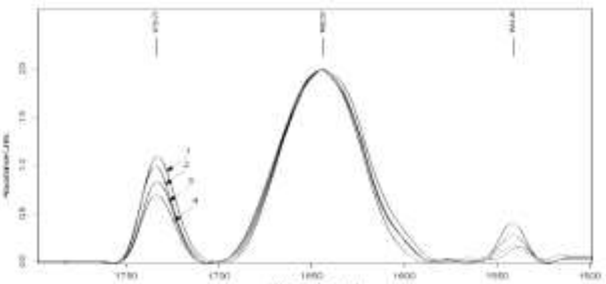


Figure 2. FT-IR ATR spectra of: 1- RWH, 2 – ETH1 -35, 3 – ETH2 -35, 4 – ETH3 -35 samples on 1500 – 1800 cm^{-1} range

With the increasing of the enzymes concentration, the absorbance intensity values of the 1732 cm^{-1} band (A_{1732}) presented in Table 1 decreases.

Table 1. The relative absorbance values, A_{1732} (a.u.) of hemp samples for the same enzyme action time at different concentration

Samples	A_{1732} (a.u.)
RWH	1.22
ETH1 -35	1.05
ETH2 -35	0.75
ETH3 -35	0.60

At the same enzyme action time, a more noticeable decrease in relative absorbance values can be observed by increasing the concentration from 1% to 2% than from 2% to 3%.

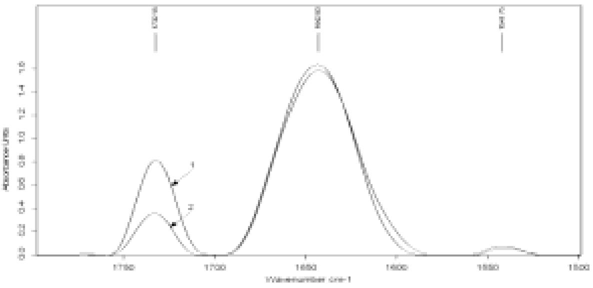


Figure 3. FT-IR ATR spectra of: 1- ETH2 - 15, 2 – ETH2 - 55 samples on 1500 – 1800 cm^{-1} range

Table 2 shows the influence of enzyme action time on the absorbance intensity values of the 1732 cm^{-1} band (A_{1732}).

Table 2. The relative absorbance values, A_{1732} (a.u.) of hemp samples for the same enzyme concentration at different action time

Samples	A_{1732} (a.u.)
ETH2 -15	0.83
ETH2 -55	0.37

Prolonging the enzyme action time from 15 to 55 minutes leads to an advanced decrease of the absorbance intensity value suggesting that a larger amount of pectin was removed. Similar behaviour was reported in the literature by Wang Q. et al. for the characterization of bioscoured cotton fabrics using FT-IR ATR spectroscopy (Wang et al. 2006).

Even that a long enzyme action time favours a more advanced elimination of pectin from the lignocellulosic substrate, the results reported in the literature do not recommend uses of prolonged treatments because this can lead to the degradation of the crystalline cellulose structure with negative effects on the mechanical properties of the fibres.

CONCLUSIONS

The influence of the alkaline and enzymatic treatments on the pectin elimination from hemp fibres were investigated by FT-IR ATR spectroscopy. For enzymatically treated samples, the relative absorbance values of the pectin specific band located at 1732 cm^{-1} showed a diminishing of the amount of pectin with increasing concentration (% o.w.f.) and action time (minutes) of the enzyme mixture. The obtained results suggest that, the input variables (concentration of enzyme and action time) are factors that consistently influence dependent variable of interest (% of eliminated pectin). So that, the absorbance recorded at 1732 cm^{-1} with FT-IR ATR spectroscopy can quantify removed pectin from the material, thus enabling characterization of proposed biotechnology and monitoring the process.

Even that the alkaline treatment has led to a complete removal of non-cellulosic components, enzyme treatment is recommended because it has the advantage of being eco-friendly with good results in pectin removal without affecting the properties of hemp fibres.

ACKNOWLEDGEMENTS

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, project number PN-II-RU-TE-2014-4-1370, and „Centru de Cercetare în Științe Tehnice și Naturale-CESTN" co-funded by European Union through European Regional Development Fund Structural Operational Program "Increasing of Economic Competitiveness" Priority axis 2. Operation 2.2.1. POSCCE Nr. 621/2014 POS-CCE.

REFERENCES

Abdel-Halim, E.S., Fahmy, H.M., Fouda Moustafa, M.G., 2008. Bioscouring of linen fabric in comparison with conventional chemical treatment. Carbohydrate Polymers 74, 707–711.

Choe, E. K., Lee, M., Park, K. S., Chung, C., 2018. Characterization of cotton fabric scouring by Fourier transform-infrared attenuated total reflectance spectroscopy, gas chromatography mass spectrometry and water absorption measurements. Textile Research Journal 0(00), I - II. DOI:10.1177/0040517518790976journals.sagepub.com/home/trj.

Ciolacu, D., Ciolacu, F., Popa, V.I., 2011. Amorphous cellulose – structure and characterization. Cellulose Chemistry and Technology 45, 13-21.

Dai, D., Fan, M., 2010. Characteristic and Performance of Elementary Hemp Fibre. Materials Sciences and Applications 1, 336-342.

Dochia, M., Chambre, D., Gavrilaș, S., Moisă, C., 2018a. Characterization of the complexing agents' influence on bioscouring cotton fabrics by FT-IR and TG/DTG/DTA analysis. Journal of Thermal Analysis and Calorimetry 132, 1489–1498.

Dochia, M., Pustianu, M.·Moisă, C.,·Chambre, D.,·Gavrilaş, S., 2018b. Sodium citrate as an eco -friendly complexing agent for the bioscouring treatment of the cellulosic/lignocellulosic fabrics. Chemical Papers 72, 1881–1888.

Iucolano, F., Liguori, B., Aprea, P., Caputo, D., 2018. Evaluation of bio-degummed hemp fibers as reinforcement in gypsum plaster. Composites Part B 138, 149–156.

Kozlowski, R., Batog, J., Konczewicz, W., Mackiewicz-Talarczyk, M., Muzyczek, M., Sedelnik, N., 2006. Enzymes in bast fibrous plant processing. Biotechnology Letters 28, 761–765.

Le Troedec, M., Sedan, D., Peyratout, C., Bonnet, J. P., Smith, A.,.Guinebretiere, R.,. Gloaguen, V, Krausz, P., 2008. Influence of various chemical treatments on the composition
and structure of hemp fibres. Composites: Part A 39, 514–522.

Li, Y., Pickering, K.L., 2008. Hemp fiber reinforced composites using chelator and enzyme treatments. Composites Science and Technology 68:3, 293–298.

Ouajai, S., Shanks, R.A., 2005. Composition, structure and thermal degradation of hemp cellulose after chemical treatments. Polymer Degradation and Stability 89, 327-335.

Perincek, S. Duran, K., 2016. Optimization of enzymatic and ultrasonic bio-scouring of linen fabrics by aid of Box-Behnken experimental design. Journal of Cleaner Production 135, 1179–1188.

Shahzad, A., 2012. Hemp fiber and its composites–a review. Journal of Composite Materials 46, 973–986.

Subramanian, K., Senthil Kumar, P., Jeyapal, P., et al. Characterization of ligno-cellulosic seed fiber from Wrightia Tinctoria plant for textile applications—an exploratory investigation. European Polymer Journal 41, 853–61.

Terpáková, E., Kidalová, L., Eštoková, A.,. Čigášová, J., Števulová, N., 2012. Chemical modification of hemp shives and their characterization. Procedia Engineering 42, 931 – 941.

Thygesen, A., Liu, M., Meyer, AS., Daniel, G., 2013. Hemp fibres: enzymatic effect of microbial processing on fiber bundle structure. Risø international symposium on materials science Proceedings 34, 373–380.

Väisänen, T., Batello, P., Lappalainen, R., Tomppo, L., 2018. Modification of hemp fibers (*Cannabis Sativa* L.) for composite applications. Industrial Crops & Products 111, 422-429.

Wang, Q., Fan, X., Gao, W., Chen, J., 2006. Characterization of bioscoured cotton fabrics using FTIR ATR spectroscopy and microscopy techniques. Carbohydrate Research 341, 2170–2175.

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CHEMICAL POLYMORPHISM OF *SATUREJA HORTENSIS* L. ESSENTIAL OILS DURING DIFFERENT PHENOLOGICAL STAGES AND VEGETATION CYCLES

Cristian MOISA[1,2]*, Lucian COPOLOVICI[1], Georgeta POP[2], Zina MOISA[3]
Andreea LUPITU[1,2], Dana COPOLOVICI[1]

[1]Aurel Vlaicu University, Faculty of Food Engineering, Tourism and Environmental Protection; Institute for Research, Development, and Innovation in Technical, and Natural Sciences, Romania, 2 Elena Dragoi St., Arad, 310330, Romania
[2]Banat University of Agricultural Sciences and Veterinary Medicine King Michael 1st of Romania from Timisoara, 119 Calea Aradului St., Timisoara, Romania
[3]Adam Müller Guttenbrunn Theoretical High School Arad, Calea Timișorii 29-31, Arad, Romania
**Corresponding author email: moisa.cristian@yahoo.com*

Abstract:

Chemical polymorphism is common in the Lamiaceae family, where one or more compounds differ quantitatively within the phenological phases, thus modifying the chemotype according to the major component determined in the essential oil. Thymol and carvacrol are the most common chemotypes present in thyme plants, they have the same molecular weight (M = 150 g.mol^{-1}), but with a different position of the OH group on the phenolic ring (meta and ortho). Usually, thymol and carvacrol are accompanied by two precursors: p-cymene and γ-terpinene. Depending on the end purpose of the essential oil and the desired chemical composition, there is a need for specific analysis of the chemical variations according to the phenological stages. For this purpose, essential oils were obtained and analyzed by GC-MS, in two phenological phases, before and after flowering over two years, and their chemical composition was compared.

The main chemical compounds of the four essential oils analyzed were: γ-terpinene, carvacrol, p-cymene, α-terpinolene, β-pinene, etc.. The chemical composition and chemotype of the essential oils, can vary and depends on many factors like variety, cultivation area and the phenological phase when harvesting is taking place.

Keywords: essential oils, phenological stages, *Lamiaceae,* summer savory, GC-MS

INTRODUCTION

The *Lamiaceae* or *Labiatae* family comprises a large group of herbaceous, shrubs or subshrub perennial or annual plants. They are strongly aromatic and produce a wide variety of secondary compounds, being mostly recognised for essential oils secreted by glandular trichomes on the surface of leaves and inflorescences (Avram, 1974; Harley et al., 2004; Moisă et al., 2018a, 2018b; Rhnid, 2012; V. Heywood et al., 2007).

This family includes 236 genres and numbers about 7,173 species and is divided into several subfamilies (Harley et al., 2004). Essential oil production is not a general feature of the whole family, but is specific to the subfamily of *Nepetoideae,* consisting mainly of monoterpenoid - menthone in *Mentha*, thymol in *Thymus*, carvacrol in *Satureja*, linalool in *Origanum*; sesquiterpenoids - caryophyllene and eugenol in *Ocimum* (Harley et al., 2004).

Volatile oils obtained from members of the *Lamiaceae* family (lavender, thyme, oregano, mint, sage, etc.) have a high pharmacological potential in the control of bacterial infections (Aguiar et al., 2016; Gustavo, 2016; Tripathi et al., 2011).

However, chemical polymorphism is common in the *Lamiaceae* family, when one or more compounds differ quantitatively within the phenological phases, thus modifying the chemotype according to the major component determined in the essential oil (Clarke, 2009; Thompson et al., 1998). Also, there are many differences in the essential oils chemical composition of specific plant organs: leaves, stems, flowers, roots, and bark (Moisa et al., 2018).

For this purpose, essential oils were obtained and analyzed by GC-MS, in two phenological stages, before and after flowering, and their chemical composition was compared.

MATERIALS AND METHODS

Plant material

Aerial plant parts (leaves and inflorescences) of *Satureja hortensis* L. were gathered in two different phenological phases: in late June before flowering and in July after flowering throughout two different vegetation cycles (2017 and 2018) from a local producer in Arad.

Harvested plant material was dried in a ventilated room, avoiding direct sunlight, for two weeks. Dried herba was stored in brown paper bags until further processes were applied. Essential oil extraction and GC-MS analysis were performed. For each phenological phase, voucher specimens were numbered and cataloged.

Essential oil extraction

Leaves and flowers were separated from the aerial plant parts and were subjected to classical hydro-distillation using a 0.5 L Clevenger installation.

The essential oil and aromatic water mixture were separated using a separating funnel, and the collected essential oils were stored at 4 ºC in dark glass vials until further GC-MS analysis. Extraction yields have been calculated.

GC-MS analysis

The chemical constituents for all the obtained essential oils were determined by gas chromatography (GC-MS) (Shimadzu 2010, Kyoto, Japan) coupled with a mass spectrometer (TQ 8040, Shimadzu, Kyoto, Japan). The analysis method and parameters were as previously presented by (Moisa et al., 2019).

All significant compounds have been identified by their mass spectra using NIST 14 library and Wiley 09 library.

RESULTS AND DISCUSSIONS

Essential oil composition

The essential oil extraction yields, before and after flowering stages, were calculated and better results were recorded after the flowering stage. In 2017 before flowering the yield was ~0.9% and after flowering, it was ~1.9%, in 2018 the situation was similar with 1.3% before and 2.3% after flowering. The essential oils chemical compositions are presented in table 1.

Table 1. *Satureja hortensis* L. essential oils chemical composition in different phenological stages and vegetation cycles

Nr. Crt.	Compound	2017		2018	
		BF %	AF %	BF %	AF %
1	α-Thujene	1.17	1.51	0.96	1.53
2	α-Pinene	0.47	0.95	0.58	1.1
3	Camphene	0.13	0.22	0.16	0.22
4	Sabinene	0.27	0.43	0.42	0.54
5	1-Octen-3-ol	-	0.14	-	-
6	β-Pinene	1.49	1.98	2.01	1.83
7	α-Phellandrene	0.3	0.42	0.45	0.53
8	3-Carene	0.1	0.17	-	-
9	α-Terpinolene	4.16	4.49	4.41	3.68
10	*p*-Cymene	3.59	5.55	6.22	7.08
11	D-Limonene	0.49	0.73	0.65	0.13
12	*trans*-beta-Ocimene	0.15	0.10	0.35	0.15
13	γ -terpinene	40.14	44.9	50.45	37.31
14	*cis*-Sabinene hydrate	0.27	0.69	0.41	0.66
15	α-Terpinolen	0.07	0.19	-	-
16	*trans*-Sabinene hydrate	0.07	0.39	-	-
17	Terpinen-4-ol	0.14	0.34	0.42	0.33
18	α-terpineol	0.08	0.08	-	-
19	Carvacrol methyl ether	0.18	0.47	0.15	0.12
20	Dihydroedulan	-	-	0.21	-
21	Thymol	0.17	0.07	0.16	-
22	Carvacrol	43.03	31.02	24.14	41.34
23	β-Bourbonene	-	-	0.15	-
24	Caryophyllene	1.87	3.47	1.77	2.16
25	α-Humulene	0.06	0.20	0.17	0.15
26	Germacrene D	0.27	0.26	2.7	-
27	γ-Elemene	-	-	0.5	0.26
28	β-Bisabolene	1.15	1.10	0.94	-
29	α-Farnesene	-	-	0.36	0.6
30	δ-Cadinene	-	-	0.24	-
31	α-Bisabolene	0.18	0.13	0.18	0.02
32	Isogermacrene D	-	-	0.19	0.26
33	*cis*-Carveol	-	-	0.12	-

BF – before flowering, AF – after flowering

Between all four essential oils, a number of 33 compounds were identified, with 18 being present in all phenological phases. Two major compounds make around 70-80% of the total composition, γ-terpinene, and carvacrol, exchanging the oils chemotype between phenological phases.

As depicted in figure 1, in 2017, carvacrol is the primary compound found in the essential oil before flowering with 43.03% and decreases to 31.02% after flowering. In contrast, most compounds increased percentage after flowering: γ-terpinene (40.14% to 44.9%) becoming the dominant compound after flowering, *p*-cymene (3.59% to 5.55%), α-

terpinolen (4.16% to 4.49%) among many others with different percentages.

In 2018 (figure 2), γ-terpinene, before flowering, is the major compound, accounting for 50.45% of all constituents. Immediately after blooming, its content drops to 37.31%, leaving carvacrol to become the new major compound, increasing from 24.14% to 41.34%. The quantitative differences of the other compounds are minor, some increasing or decreasing with small percentages, such as α-Terpinolene who dropped from 4.41% to 3.68% and Germacrene D from 1.77% before flowering to completely disappearing during flowering. The compounds that grew during the flowering stage were: α-Thujene, α-Pinene, p-Cymene, Caryophyllene.

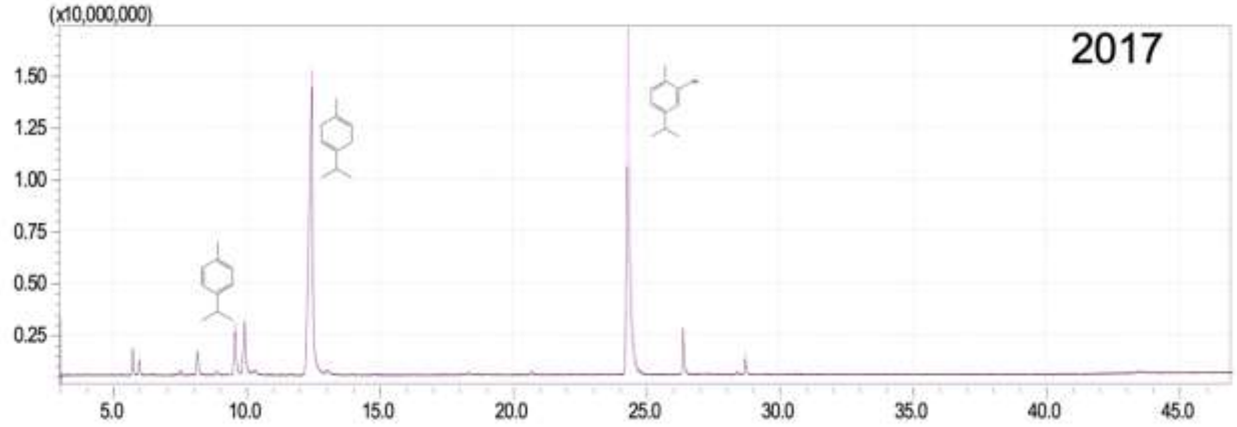

Figure 1. Overlapped chromatogram of *Satureja hortensis* L. essential oil from 2017 (pink - before flowering, black - after flowering)

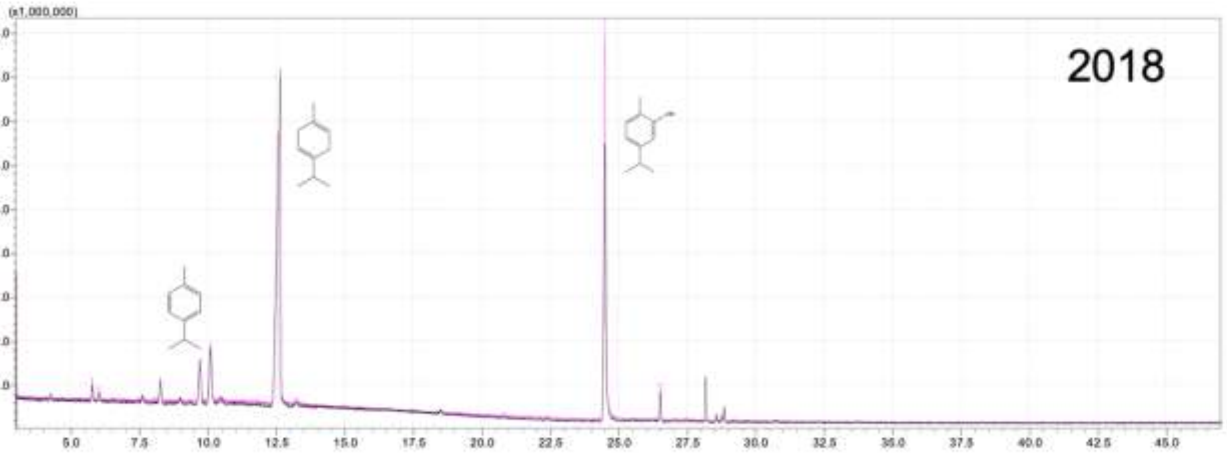

Figure 2. Overlapped chromatogram of *Satureja hortensis* L. essential oil from 2018 (pink - after flowering, black - before flowering).

The major compounds found in *Satureja hortensis* L. essential oils were: γ-terpinene 37.31 - 50.45%, carvacrol 24.14 - 43.03%, and p-cymene 3.59 - 7.08%.

For both vegetation cycles (2017 and 2018) and phenological stages (before and after flowering), the chemotype for *Satureja hortensis* L. oscillates between carvacrol and γ-terpinene.

Table 2. The chemotypes of essential oils studied for two years (2017 and 2018) and two phenological phases (before and after flowering).

Essential oil	Phenological stage	Chemotype
Satureja hortensis L. 2017	before flowering	carvacrol
	after flowering	γ-terpinene
Satureja hortensis L. 2018	before flowering	γ-terpinene
	after flowering	carvacrol

CONCLUSIONS

The main chemical compounds of the four essential oils analyzed were: γ-terpinene, carvacrol, *p*-cymene, α - terpinolene, β-pinene, etc.

The chemical composition and chemotype of the essential oils, can vary and depends on many factors like variety, cultivation area and the phenological phase when harvesting is taking place. Thus, for both vegetation cycles (2017 and 2018) and phenological stages (before and after flowering), the chemotype for *Satureja hortensis* L. oscillates between carvacrol and γ-terpinene.

ACKNOWLEDGMENTS

Funding for some of the equipment used in the study has been provided by the European Commission and the Romanian Government (project POSCCE 621/2014).

REFERENCES

Aguiar, J.J.S., Sousa, C.P.B., Figueredo, F.G., Bitu, V.C.N., Santos, F.A.V., Ferreira, M.I., Silva, M.A.d., Peixoto, F.S.N., Coutinho, H.D.M., Matias, E.F.F., 2016. Evaluation of essential oil of ocimum gratissimum L. for antibacterial activity and potential to modify aminoglycoside toxicity, in: Peters, M. (Ed.), Essential oils - Historical significance, chemical composition and medicinal uses and benefits. Nova Science Publishers Inc. , New York, pp 81-88.

Avram, R., 1974. Botanica Farmaceutica. Editura Didactica si Pedagogica, Bucuresti.

Clarke, S., 2009. Essential Chemistry for Aromatherapy, Second Edition, Second ed. Churchill Livingstone - Elsevier.

Gustavo, H.d.C.V.B., Barbosa Dias; Denise, Caren Ozório Leonel, 2016. Essential Oils: Properties, Applications, Extraction Methods,

and Perspectives, in: Peters, M. (Ed.), Essential oils: historical significance, chemical composition and medicinal uses and benefits. Nova Science, New York - USA, pp 1 - 19.

Harley, R.M., Atkins, S., Budantsev, A.L., Cantino, P.D., Conn, B.J., Grayer, R., Harley, M.M., de Kok, R., Krestovskaja, T., Morales, R., Paton, A.J., Ryding, O., Upson, T., 2004. Labiatae, in: Kadereit, J.W. (Ed.), Flowering Plants · Dicotyledons: Lamiales (except Acanthaceae including Avicenniaceae). Springer Berlin Heidelberg, Berlin, Heidelberg, pp 167-275.

(a) Moisă, C., Copolovici, L., Bungau, S., Pop, G., Imbrea, I., Lupitu, A.-I., Nemeth, S., Copolovici, D., 2018. Wastes resulting from aromatic plants distillation - bio-sources of antioxidants and phenolic compounds with biological active principles. Revista Farmacia 66, 289-295.

(b) Moisă, C., Copolovici, L., Pop, G., Lupitu, A., Ciutina, V., Copolovici, D., 2018. Essential Oil Composition, Total Phenolic Content, and Antioxidant Activity - Determined from Leaves, Flowers and Stems of Origanum Vulgare L. Var. Aureum. Sciendo 1, 555 - 561.

Moisă, C., Lupitu, A., Pop, G., Chambre, D.R., Copolovici, L., Cioca, G., Bungau, S., Copolovici, D.M., 2019. Variation of the Chemical Composition of Thymus Vulgaris Essential Oils by Phenological Stages. Rev. Chim. 70, 633 - 637.

Rhnid, J.P., 2012. Essential oils - a handbook for aromatheray practice 2nd edition. Singing Dragon, London - UK.

Thompson, J.D., Manicacci, D., Tarayre, M., 1998. Thirty-Five Years of Thyme: A Tale of Two Polymorphisms: Why so many females? Why so many chemotypes? Bioscience Journal 48, 805 - 815.

Tripathi, N.N., Mishra, A.K., Tripathi, S., 2011. Antibacterial potential of plant volatile oils: A review. Proc. Nat. Acad. Sci. India Sect. B-Biol. Sci. 81, 23-68.

V. Heywood, R. Brummitt, A. Culham, Brummit, R.K., 2007. Flowering Plant Families of the World. Firefly Books, Limited.