1st CRC. KS

202

1st Chemical Research Conference Kavala Students

BOOK OF ABSTRACTS

GRID LAB, KAVALA CAMPUS JUNE 8

ORGANIZERS

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Published and made openly accessible by: The Department of Chemistry, Kavala Campus 65404 St. Lucas, Kavala, Greece *First published in 2023



2023 Department of Chemistry

ABSTRACTS

1st Chemical Research Conference of Kavala Students



CHEMICAL RESEARCH CONFERENCE OKAVALA STUDENTS

GRID LAB, KAVALA CAMPUS ● JUNE 8 2023

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FORWARD

Dear Colleagues,

1st Chemical Research Conference of Kavala Students (1CRS-KS) is an endeavor of the Department of Chemistry of the International Hellenic University to introduce research driven education to undergraduate students.

The event was conducted in the frame of the Research Seminar Lab at the spring Semester of the 3rd year. It is the first time in Greece that such an educational method is included to a chemistry curriculum and the results are very encouraging to be continued.

The Conference was taken place in the Grid Lab of our University at the Kavala Campus, June 8th 2023. There were 15 participant groups with a total of 82 students. There were 6 oral and 9 poster presentations in a time span of 3 hours. The students work was at very high standards; some of them very new and surpassingly very interesting. The topics were from all areas of Chemistry: Physical, Organic, Inorganic, Analytical, Biochemistry, Chemical Technology and Material Science.

Both the supervisors and the students enjoyed a Conference of high standards, exchange ideas with their colleagues and strengthened their desire to include research in their future plans. The works were reviewed by two referees, major and minor corrections were suggested and the articles were included into the Conference Proceeding Book of Abstracts that is available at the site of the Chemistry Department (www.chem.ihu.gr).

The Conference Organizing Committee would like to congratulate and thank all the participants for contributing to the 1CRC-KS.

On behalf of the Organizing Committee

Prof. A. Ch. Mitropoulos

Dpt. of Chemistry, International Hellenic University

Director of Hephaestus Advanced Lab



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APPLICATIONS OF NANOBUBBLES ON FORWARD OSMOSIS

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The need for seawater desalination is growing due to the increasing demand for fresh water worldwide [1]. Forward osmosis (FO), is a spontaneous process based on the difference in chemical potentials between two solutions in contact with a semipermeable membrane. Specifically, the membrane allows only solvent molecules to pass through it. If the chemical potential of pure solvent is μ^* and the chemical potential of the solvent in a solution is μ then: $\mu = \mu^* + RT \ln x$, where x is the mole fraction of the solvent, R is the gas constant, and T is the temperature. It follows the van't Hoff's equation, V = 0. The equation shows that the osmotic pressure Π is proportional to the quantity of the dissolved substance in the solution The FO process is marked by low energy consumption and almost zero liquid discharge.

In this work, the effect of air nanobubbles (NBs) on the FO process using an Aquaporin HFFO2 membrane is studied [2]. This is a biomimetic membrane that allows high flux of water from feed to draw solution. Biologically, Aquaporins (AQP) are a set of proteins that located in the lipid bilayer of the cell [4]. They formed tetramers and each subunit has a central pore. The pore consists of two motifs of asparagine, proline and alanine, which allows the high flux of water [3]. Aquaporin HFFO2 is a biomimetic membrane of this kind. Figure 1 shows both the natural and the technological aquaporins.

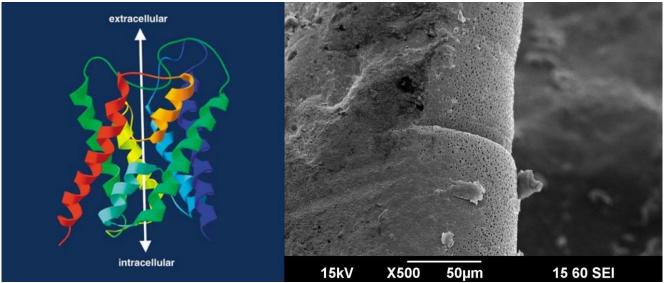


Figure 1: Aquaporins: Left natural AQP; right artificial Aquaporin (SEM microgram).

A NB generator described elsewhere [4] is used to produce NBs of average size 200nm and concentration $150x10^6\text{NB/mL}$. Four different cases are examined: 1) feed solution (FS) of deionized water (DIW) and draw solution (DS) of deionized water with NaCl; 2) FS/DIW and DS/DIW/NBs/NaCl, 3) FS/DIW/NBs and DS/DIW/NaCl; and 4) FS/DIW/NBs and DS/DIW/NBs/NaCl. All measurements are conducted at ambient temperature and the results were normalized to 25°C. The time to collect 100mL from the FS to DS is recorded; after each transfer about 0.5g of NaCl salt is added to the DS. Figure 2 illustrates the FO process.

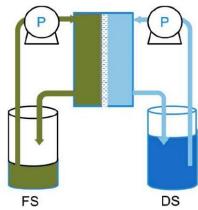


Figure 2: The FO process: Water is transferred from feed to draw solution via the semipermeable membrane (Aquaporin).

Figure 3 shows the results. When both solutions contained NBs, the procedure is the fastest one compared to the others. When NBs added only in the FS, surprisingly, it is found that the process speeds up more than in the case of adding NBs to the DS only. In specific, from A to B the process is faster by 8%, from A to C by 24%, and from A to D by 46%. It assumed that NBs work as "buses" for the water molecules in the side of FS, bringing them closer to the membrane front, and as carriers of NaCl ions from the side of DS. In this way the exchange of water molecules accelerates.

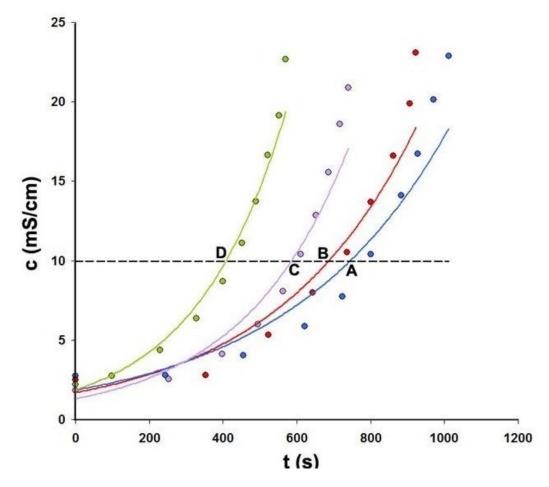


Figure 2: Conductivity measurements of DS for different cases. Case-1: blue points; case-2: red points; case-3 violet points; case-4: green points (for details see the text). In all the cases NaCl was added when of 100ml of DI.W transferred from FS to DS. Conductivity measurements are converted at 25°C. Fit lines are exponential. At B the time to collect 100mL of water is 8% faster than A; at C 24%; and at D 44%.

In this paper the potential of NBs in the field of water desalination using a biomimetic membrane is examined. The use of NBs appeared to significantly accelerate the process, primarily when contained in both solutions and secondarily when contained in FS alone. It was concluded that NBs may help FO process.

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ΕΦΑΡΜΟΓΕΣ ΤΩΝ ΝΑΝΟΦΥΣΑΛΙΔΩΝ ΣΤΗΝ ΕΜΠΡΟΣΘΙΑ ΩΣΜΩΣΗ

Η αφαλάτωση θαλασσινού νερού αποκτά ολοένα και μεγαλύτερη σημασία λόγω της παγκόσμιας ζήτησης για πόσιμο νερό. Η εμπρόσθια όσμωση (FO) είναι μια αυθόρμητη διεργασία που βασίζεται στη διαφορά του χημικου δυναμικού δύο διαλυμάτων δια μέσου μιας ημιπερατής μεμβράνης. Πλεονέκτημα της μεθόδου, είναι η χαμηλή ενεργειακή κατανάλωση και η σχεδόν μηδενική απόρριψη αλμόλοιπου. Στην παρούσα εργασία χρησιμοποιήθηκε η εμπορική μεμβράνη "Aquaporin HFFO2".. και εξετάστηκε η επίδραση των νανοφυσαλίδων (NBs) στην ταχύτητα της αφαλάτωσης. Οι NBs αέρα παρασκευάσθηκαν από ειδική γεννήτρια, που λειτουργεί με την πίεση του δικτύου (δηλ. χωρίς ενεργειακό κόστος) και έχουν κατά μέσο όρο 200 nm και συγκέντρωση 150x10⁶ NB/mL. Τα αποτελέσματα, υποδεικνύουν ότι όταν εισάγονται NBs και στο διάλυμα τροφοδοσίας και στο διάλυμα έλξης η ταχύτητα αυξάνεται κατά 44%.

THE EFFECT OF ROTATION ON CO2 ADSORPTION

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Adsorption of gases on activated carbon (AC) is a common method for reducing greenhouse effect in order to mitigate climate change [1]. In specific, adsorption of CO_2 emissions by AC is a standard practice for eliminating excess CO_2 in industry and other anthropogenic activities. To this end, the amount adsorbed as well as the surface area of the AC plays an important role to the capturing process.

In this study we have examined the effect of rotation as to whether or not it increases the adsorption capacity of activated carbon. Two sets of experiments have been conducted: a) measurements of CO_2 adsorption isotherms on AC at 25°C with and without rotation and b) process kinetics. A specially designed sample cell that allows adsorption in conjunction with rotation is used; more details are given elsewhere [2]. A fine powder of Aldrich AC is used, having a BET area of about 1,000 m²/g and an average pore size of 2 nm. Rotation, whenever applied, was under an angular velocity $\omega = 5,000$ rpm. In the adsorption isotherm rotation at the same ω is conducted for every pressure step.

Figure 1 shows the adsorption isotherms with and without rotation. In both cases, the isotherms are of type-I according to IUPAC [3] classification. The isotherms are fitting very well to the Langmuir model [4]. In the case of non-rotation, the equilibrium amount is calculated at $q_e = 0.016$ kg/kg and the Langmuir constant at $K_L = 0.213$. In the case of rotation $q_e = 0.035$ kg/kg and $K_L = 0.082$, respectively. Rotation increases the amount adsorbed by 54%; however, K_L decreases. According to the Langmuir model [4]:

$$K_1 P S_1 = K_2 S_2 \tag{1}$$

where K_1 is the rate of adsorption and K_2 is the rate of desorption at a given pressure P, S_1 is the number of empty sites and S_2 is the number of occupied sites; $S_1 + S_2 = S_{Total}$, where S_{Total} is the total number of sites:

$$\begin{array}{ccc}
K & \overline{K} \\
L & \frac{1}{K} & \underline{\mathbf{s}}_{\underline{2}} & - \\
K & \underline{P}S & \underline{P}S
\end{array} \tag{2}$$

Rotation introduces an angular momentum governed by a factor ϕ [5]:

$$\varphi = \frac{m \omega^2}{2RT} r^2 \tag{3}$$

where m is equal to 44 g/mol CO_2 , r is the maximum radius of the rotating cell r = 5 cm, R is the gas constant and T = 25°C ; $\phi = 0.006$. Under the influence of a rotating field the strikes of the adsorptive molecules on the solid surface are increased. As a result, previously inaccessible sites become accessible in a specific way such that, although the number of occupied sites S_2 increases and the number of free sites, S_1 increases too, the ratio is less than the original one:

$$\underset{F}{\overset{\S^{f}}{PS_{1}}} \quad \frac{S_{2}}{PS} \tag{4}$$

This inequality suggests that rotation introduces a different mechanism than fragmentation of the adsorbent; for the latter K_L would be expected to increase, whereas the former is characterized by a lower Langmuir constant due to the fact that previously inaccessible sites become accessible as aforementioned.

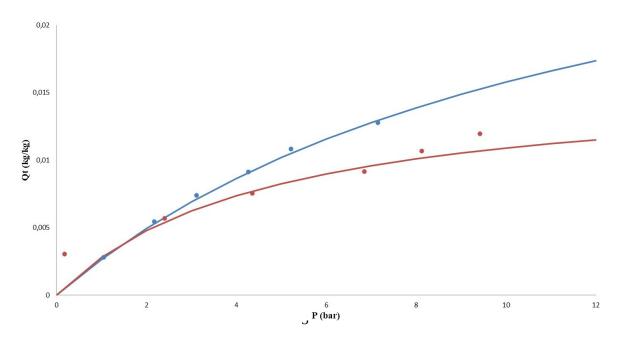


Figure 1 Adsorption isotherms with (blue) and without (red) rotation

We have also examined the kinetics with and without rotation. Kinetic experiments are recorded for 90 minutes. Figure 2 illustrates the result. Both curves are showing good fits on the pseudo-second-order (PSO) kinetic model [6]. During rotation there is a desorption process which corresponds to the nose of the curve, soon after followed by an increase in the amount adsorbed - more than it does in the case without rotation.

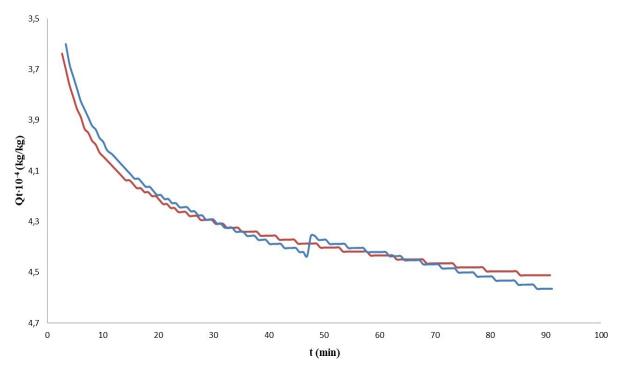


Figure 2 Adsorption kinetics with (blue) and without (red) rotation

Acknowledgements: The authors would like to thank Dr. A. C. Mitropoulos and R. I. Kosheleva for their supervision.

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Η ΕΠΙΔΡΑΣΗ ΤΗΣ ΠΕΡΙΣΤΡΟΦΗΣ ΣΤΗΝ ΠΡΟΣΡΟΦΗΣΗ ΤΟΥ CO₂

Η συσσώρευση τεράστιων ποσοτήτων αερίων του θερμοκηπίου στην ατμόσφαιρα συνιστά σημαντικό ζήτημα τις τελευταίες δεκαετίες. Η εκπομπή του διοξειδίου του άνθρακα ως απόρροια τόσο βιομηχανικών όσο και άλλων ανθρωπογενών δραστηριοτήτων, αναμφίβολα εντείνει την επίδραση της κλιματική αλλαγής, δημιουργώντας την ανάγκη για περαιτέρω έρευνα και ανάπτυξη σε τεχνικές διοχέτευσης και εναπόθεσης του. Στην παρούσα εργασία μελετήθηκε η επίδραση της περιστροφής σε μία εγκαθιδρυμένη τεχνική, την προσρόφηση διοξειδίου του άνθρακα σε ενεργό άνθρακα. Για το σκοπό αυτόν υλοποιήθηκε μεθοδολογία που αφορούσε τη χρήση μίας καινοτόμου συσκευής, που επιτρέπει την περιστροφή με πλάνο αφενός την μελέτη των ισόθερμων προσρόφησης, με και χωρίς περιστροφή μετά από κάθε βήμα προσρόφησης – και σύγκριση των σταθερών K_L σύμφωνα με το μοντέλο Langmuir - αφετέρου τη μελέτη των κινητικών τους, χρησιμοποιώντας το pseudo-second-order (PSO) μοντέλο - για εξαγωγή συμπερασμάτων, μεταξύ μίας προσρόφησης με και χωρίς περιστροφή. Η περιστροφή αυξάνει την προσρόφηση κατά 54% ενώ η μείωση της σταθεράς προσρόφησης Langmuir (K_L) υποδεικνύει ότι η συγκεκριμένη επαύξηση δεν οφείλεται σε θρυμματισμό.

EFFECT OF NANOBUBBLES ON STRATUM CORNEUM

A. Vlachou, K. Drosopoulou, A. Karaligas, N. Kasviki, O. Kechaidou, A. Koritsidis Division of, physical chemistry and Chemical Technology, Department of Chemistry International Hellenic University, St. Lucas 65404, Kavala Campus, Greece

Epidermis is the largest organ in human body. The outermost layer of epidermis is the Stratum Corneum (SC) that serves as a barrier between the body and the outside environment. There is a paradox for this layer since it consistent from dead cells and the same provides a potential protection to the vital part of epidermis. Understanding the stratum corneum is of critical importance in the development of pharmaceuticals, slow-release drugs, and skincare products that can hydrate, exfoliate, and improve the appearance of the skin. The SC prevents excessive water loss, defends against toxic substances, and guards against microbial invasion for both people and animals, making its integrity crucial for overall health. For many years SC is considered impermeable. However, there are path for penetrating SC. Figure 1 show two of these paths; the intercellular route and the transcellular route [1]. In this work we have studied the effect of nanobubbles (NB) on Stratum Corneum in conjunction with a glycerin solution.

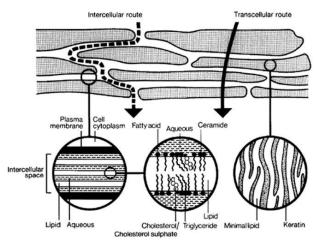


Figure 1 The SC brick and mortar model

A NB generator described elsewhere [2] is used to produce NBs with size of 200nm and concentration of 150x106 NB/mL. First, we have used an artificial membrane, Strat-M of Merck and then the skin of porcine ear obtained from the local slaughterhouse according to the authorized protocol [3]. In both cases the effect of glycerin 15% v/v with and without NBs aquatic solution is examined. The measurements are taken by the PerkinElmer FT-IR/NIR Spectrometer Frontier. Transmission spectra for both samples have been measured and the chemical groups have been identified according to the literature [4]. Concerning the IR Spectrum of porcine skin, the 3200 cm⁻¹ band is characteristic of water, while the 1650 and 1540 cm⁻¹ peaks represent amide I and II respectively, clearly corresponding to proteins. Several peaks also appear in the lower wavenumber range. The 1080 cm⁻¹ peak is quite prominent, revealing the protein nature of the sample. Triglycerides are predominantly located in the lower layers of the dermis, as proved by the integration area of the 1750 cm⁻¹ C=O stretch band, while lipids are generally present in all layers, as shown as in the 2800 cm⁻¹ C-H peak. Strat-M presents a similar structure with –OH and –CH peaks, though in a lower range of transmittance. Figure 2 shows the transmission FTIR spectra of Strat-M and porcine skin without any treatment.

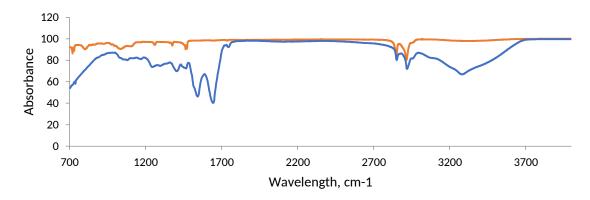


Figure 2 IR Spectra of Strat-M (orange line) and porcine skin (blue line)

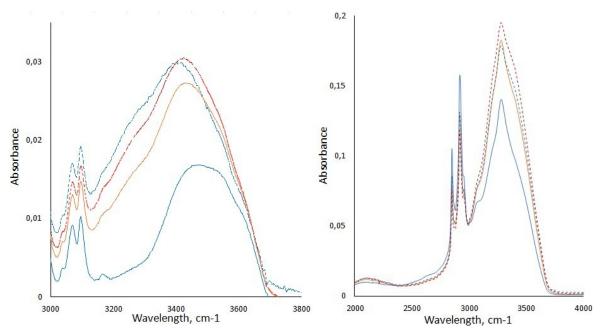


Figure 3 IR Spectra of Strat-M (Left) and porcine skin (Right) with various solutions: Orange line: Water with NBs, Blue line: Water without NBs, Dashed Orange line: 15% glycerin solution with NBs, Dashed Blue line: 15% glycerin solution without NBs

Figure 3 shows the result for the case of Strat-M and porcine skin. Water without NBs shows a lower absorbance than water with NBs. However, as glycerin is added to the solutions the absorbance increases equally for both cases; i.e. with and without NBs. A similar behavior is observed in the case of porcine skin. The result indicates that NBs may achieve a similar effect of glycerin. The latter is also indicated by pendant drop measurement where 15% glycerin with NBs results to have a surface tension of 65.22 mN/m which is very close to that of pure glycerin (63.4 mN/m). Since NBs have been generated by using the pressure of the water network and air it comes that it may substitute in much economical way glycerin additives. Moreover Strat-M seems to have a similar behavior with porcine skin. The latter is considered as a best match of human SC. Therefore Strat-M may overtake animal abuse especially in the cosmetic industry.

Aknowledgements: The authors would like to thank Prof. A.C. Mitropoulos and Mrs R. Kosheleva for their supervision.

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ΕΠΊΔΡΑΣΗ ΤΩΝ ΝΑΝΟΦΥΣΑΛΙΔΩΝ ΣΤΗΝ ΚΕΡΆΤΙΝΗ ΣΤΙΒΆΔΑ

Το δέρμα αποτελεί βασικό παράγοντα προστασίας του οργανισμού από το περιβάλλον, ωστόσο δεν αποτελεί απόλυτα αδιαπέραστο μέσο και για τον λόγο αυτό παρουσιάζει μεγάλο ενδιαφέρον. Στην παρούσα έρευνα μελετήθηκε η κεράτινη στιβάδα του δέρματος και η διαπερατότητα που παρατηρείται σε ορισμένες ουσίες. Συγκεκριμένα πραγματοποιήθηκαν δύο πειράματα. Το πρώτο σε αυτί χοίρου και το δεύτερο σε τεχνητό δέρμα ανθρώπινης προσομοίωσης έτσι ώστε να υπάρχει ένα μέτρο σύγκρισης. Στο πρώτο πείραμα έγινε εμβάπτιση δύο δειγμάτων αυτιού για πέντε λεπτά. Το ένα σε διάλυμα απιονισμένου νερού και το δεύτερο σε διάλυμα απιονισμένου νερού εμπλουτισμένο με νανοφυσαλίδες. Στο δεύτερο πείραμα τοποθετήσαμε, σε διαφορετική κάθε φορά επιφάνεια της τεχνητής μεμβράνης, μια σταγόνα απιονισμένο νερό, μία σταγόνα απιονισμένο νερό με 15% ν/ν γλυκερίνη, μια σταγόνα απιονισμέο νερό-νανοφυσαλίδες και μία σταγόνα απιονισμένο νερό-νανοφυσαλίδες με 15% ν/ν γλυκερίνη. Και στα δύο πειράματα πραγματοποιήθηκαν μετρήσεις FTIR και συγκρίθηκαν τα αποτελέσματα από τα οποία ήταν φανερό ότι το νερό με τις νανοφυσαλίδες είχε μεγαλύτερη επίδραση στην κερατοειδή στιβάδα απ΄ οτι το απλό νερό και η γλυκερίνη.

GRAPHENE OXIDE COATED MEMBRANES: SYNTHESIS AND CHARACTERIZATION

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The rise of human population results in a growing need for clean water and a successful treatment of waste, in a more environmentally- friendly way. This fact leads to the development of some advanced separation techniques such as membrane nanofiltration (NF). Membranes show an abundance of benefits at wastewater treatment, like low energy consumption, efficient ion capture, minimum carbon footprint and low function cost. However, they have some disadvantages, for instance membrane fouling, and low monovalent ion retention rate. To overcome this problem, one method that is commonly used is the addition of an extra layer on the membrane surface, and it has been found that grapheme oxide (GO) is the most efficient material [1][2].

Graphene oxide can be described as a single 2D carbon sheet, and has multiple functional groups, such as hydroxyl (-OH), carbonyl (-C=O), epoxy and carboxyl groups (-COOH). GO can be an innovative material for separation processes, because it is an indestructible barrier for wastewater, and with its addition on a polymeric mixed matrix membrane (MMM), can improve the membrane's performance. Graphene oxide appears to have many unique properties, like high conductivity, chemical stability, hydrophilicity, because of the oxygenated functional groups, and can potentially provide high ion selectivity [3][4].

In this study, the main object was the synthesis of membranes based with GO, and their characterization, to obtain a various amount of information for these modified membrane samples, and to verify the successful coating of GO. For the characterization section, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM) and X- Rays Diffraction (XRD) were used. The current experiment involves the utilization of graphene oxide in the form of a membrane coating material for the purpose of nanofiltration of aqueous solutions. The GO sample employed in this study was obtained from the Hephaestus Advanced Laboratory at the International Hellenic University [5]. The sample was synthesized using the modified Hummers oxidation method and subsequently subjected to further analysis. To determine the necessary quantity of graphene oxide, samples of membranes that have been circularly trimmed are subjected to weighing. The membrane samples have an estimated weight of 0.2 g. Consequently, to obtain each colloidal solution, 2 mg (0.002 g) of GO are meticulously weighed using an analytical balance (OHAUS Pioneer). The quantity in question is subject to evaluation based on its economic feasibility, taking into consideration both the minimum concentration percentage of one percent and the cost effectiveness of the experiment. Weighting of these factors is deemed necessary. Firstly, the mass of 0.002 g is placed into a vial, and subsequently, the vial is filled with deionized water. Subsequently, the solution is transformed into its colloid form through sonication, accompanied by datum citation. It is imperative that the diameter of the vial exceeds that of the ultrasonic processor tip, which has been manufactured by Hielscher, to ensure optimal performance. Moreover, it is recommended that the tip be inserted within the vial without making any contact with the glass, as friction could potentially impair its functionality. Following the repositioning of the support, the apparatus is activated, and the entirety of the progression endures an estimated span of 10-15 minutes. Upon completion of the colloid production process, the membrane sample is meticulously positioned within a laboratory apparatus that has been expressly devised for this experiment, in order to preclude any seepage. Subsequently, the solution is cautiously poured onto the membrane surface, with careful attention paid to ensuring that the precipitate remains confined within the original vial. Finally, the specimens are subjected to desiccation via a furnace maintained at a temperature range of 40-50° C, until complete removal of the solvent by means of evaporation.

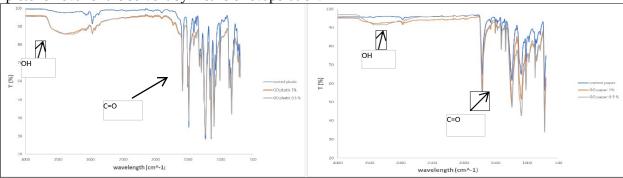


Figure 1 On the left side; FTIR for plastic side of membrane (control, 0.5% and 1% GO); On the right side; FTIR for paper side of membrane (control, 0.5% and 1% GO)

After the completion of the characterization process, it is realized that the coating of the polymeric films with GO happened successfully, however, although an attempt was made to coat the membrane uniformly, it was not achieved because graphene oxide is to a certain extent hydrophobic and tends to aggregate. Therefore, the issue of uniform distribution should be further investigated. Regarding the part of characterization, FTIR, XRD and SEM were used to analyze the samples. FTIR is a qualitive characterization process, which gives information for the functional groups that appear on the samples' surface. By evaluating the FTIR spectra (Figure 1), a broad peak of high intensity is observed from 3,100 to 3,600 cm⁻¹, which indicates the presence of the hydroxyl groups of GO, making the

membrane hydrophilic. Then, with XRD analysis, the crystallinity of a material can be observed, and conclusions from the comparison of the control and the coated samples can be drawn. From the obtained XRD spectra (Figure 2), the characteristic peak appears at approximately 2θ =10°, which corresponds to GO. The GO peak after coating is now of lower intensity, which indicates the incomplete crystalline structure of the film, and moreover, due to the honeycomb-like structure of GO, the crystallinity of the polymeric membrane is enhanced. Finally, SEM is used for getting images of the samples and from them, it can be observed how the extra layer of GO modifies the membrane's surface. From interpreting the SEM images (Figure 3), the conclusion that is extracted is the following; the plastic side seems to be an amorphous-smooth surface without micropores, in contrast to the paper side, which presents fibers of various sizes and waviness.

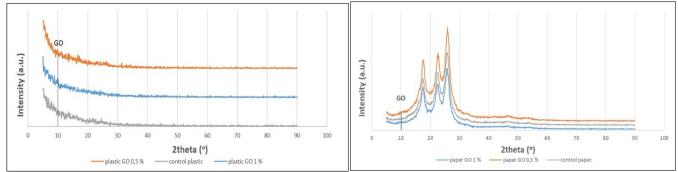


Figure 2 On the left side; XRD for plastic side of membrane (control, 0.5% and 1% GO); On the right side; XRD for paper side of membrane (control, 0.5% and 1% GO)

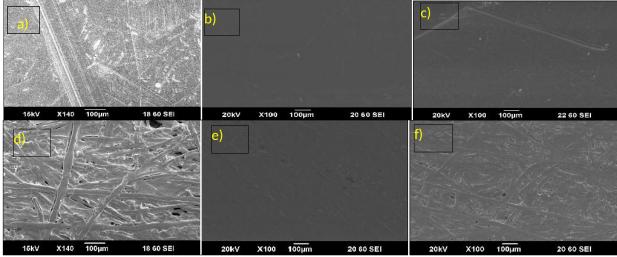


Figure 3 SEM images; a) plastic control, b) plastic 0.5% GO, c) plastic 1% GO, d) paper control, e) paper 0.5% GO, f) paper 1% GO.

Aknowledgements: The authors would like to thank Prof. G.Z. Kyzas for his supervision and PhD student D. Trikkaliotis for the suuport.

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ΜΕΜΒΡΑΝΕΣ ΜΕ ΕΠΙΚΑΛΎΨΗ ΟΞΕΙΔΙΌ ΤΟΥ ΓΡΑΦΕΝΙΟΎ: ΣΎΝΘΕΣΗ ΚΑΙ ΧΑΡΑΚΤΗΡΙΣΜΌΣ

Η πρόσβαση σε καθαρό και πόσιμο νερό αποτελεί σημαντικό ζήτημα τις τελευταίες δεκαετίες. Η εκροή των βιομηχανικών αποβλήτων σε ποταμούς και θάλασσες, ρυπαίνει τόσο τα ίδια τα νερά όσο και τα γύρω οικοσυστήματα με αποτέλεσμα να μειώνονται τα αποθέματα νερού. Αυτό έχει οδηγήσει την έρευνα να στραφεί στην αποφυγή περαιτέρω μόλυνσης μέσω κατάλληλης επεξεργασίας των αποβλήτων, με στόχο τον καθαρισμό ήδη υπαρχόντων. Η χρήση των μεμβρανών ξεκίνησε με σκοπό τον καθαρισμό του νερού. Ειδικότερα, τα τελευταία χρόνια με την ανακάλυψη του οξειδίου του γραφενίου (GO), που φαίνεται πολλά υποσχόμενο λόγω των επιφανειακών ιδιοτήτων του και των μηχανισμών διαχωρισμού. Η συνύπαρξη της μεμβράνης με αυτό το υλικό αναμένεται να προσδώσει μεγαλύτερη επιλεκτικότητα και αντοχή στην πολυμερική μήτρα. Στην παρούσα εργασία θα γίνει σύνθεση αυτού του τύπου των μεμβρανών και χαρακτηρισμός των μεμβρανών ως προς την δομή και τις ιδιότητες τους με τις τεχνικές SEM, XRD και ΑΤR-FTIR.

SYNTHESIS AND STUDY OF ZINC PORPHYRIN COMPLEXES WITH NITROGEN-DOPED CARBON DOTS FOR PHOTOCATALYTIC APPLICATIONS

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Currently, water contamination due to improper waste disposal from industries is one of the major challenges that affects the whole world. Organic dyes are one of the most significant pollutants in wastewater due to their high toxicity and nonbiodegradability in the environment [1]. Therefore, recently various methods of pollutant removal such as flocculation, adsorption and photocatalysis have been studied. In particular, photocatalysis is one of the most widely known and effective methods of pollutant degradation, exploiting the properties of various materials. Even though there is a great progress in high efficiency of the photocatalysts there are still issues that need to be improved, such as widelyuse of visible solar light, charge recombination, stability of the photocatalysts and control of product selectivity. Many compounds have been used as photocatalysts including titanium dioxide and other metal oxides able to operate only under UV light irradiation. In order to take advantage of the whole spectrum it is essential to synthesize photocatalysts that are able to degrade dyes in visible light. Metal porphyrins are compounds that were found in biological systems such as heme in blood and chlorophyll in plants and are able to absorb light in the visible region. Therefore, porphyrins can be used as photocatalysts for the degradation of organic pollutants, since under light irradiation and in the presenceof oxygen can excite triple oxygen into singlet oxygen [2]. On the other hand, carbon dots, among other nanomaterials exhibit several advantages for their use as photocatalysts such as photostability, electron transfer properties and low-costpreparation [3].

The aim of this project was the combination of a porphyrin metal complex with carbon dots in order to synthesize a novel material able to act as an efficient photocatalyst for dye degradation in water. This approach presents the advantage of easy preparation of the compounds and combination of their advance photocatalytic properties towards the degradation of dyes.

Initially, free-base tetraphenyl porphyrin (**TPP**) was synthesized by reaction of 4 equivalents of pyrrole with 4 equivalents of benzaldehyde, in the presence of propionic acid under reflux for 1 h. After cooling down the reaction mixture to room temperature, purple crystals were afforded. Then, the purple solid was isolated by filtration under vacuum in order to obtain 1.796 g of **TPP** in 14.4 % yield. Then, the zinc metalated porphyrin (**ZnTPP**) was synthesized by reaction of zinc acetate in CH₂Cl₂:MeOH in a ratio of 10:1.5 under reflux overnight. The reaction mixture was washed three times with water, dried with anhydrous sodium sulfate, filtered and the organic solvents were removed via a rotary evaporator. The purple solid of **ZnTPP** was recrystallized with MeOH/CH₂Cl₂ (2:1) and was isolated by filtration under vacuum. The yield of the metalation reaction was 58.9 %. The identification and analysis of both compounds **TPP** and **ZnTPP** was done with TLC (the R_f values were calculated and compared to the ones present in the literature), UV-Vis (the molecular absorbance (ε) was calculated) and FT-IR (characteristic vibration peaks wereobserved). Nitrogen-Doped Carbon dots were synthesized and combined with **ZnTPP** in one pot. The reaction wasperformed in an autoclave where one equivalent of both ethylediamine and citric acid were dissolved in ultra-pure waterand then 15 milliequivalents of **ZnTPP** were added. The autoclave was heated at 180 °C for 8 h in an oven and left toreach room temperature overnight. Then the mixture was centrifuged twice for 20 min, at 4000 rpm in order to removeinsoluble particles. The composite was added in the freeze dryer for the removal of water and the product **NCDot@ZnTPP** was isolated as a red powder. The material was characterized with UV-Vis, FT-IR and SEM techniques. After the successful synthesis and characterization, nanocomposite NCDot@ZnTPP was used as a photocatalyst for dye degradation. A series of experiments were performed with two different dyes, methylene blue (MB) and reactive black 5 (RB5). During the photocatalytic experiments the catalyst was diluted in a reactor vial with ultra- pure water in the presence of the dye and was irradiated with a white led light of 100 W. The reaction sample was placed at around 14 cm away from the lamp and the reaction was followed by UV-Vis spectroscopy. Samples were obtained every 15-minute until the complete degradation of the dye. In all experiments the λ_{max} of each dye was tracked and the

data obtained were used for the preparation of appropriate graphs showing the photocatalytic activity of the composite. Overall, during this work an efficient photocatalyst NCDot@ZnTPP was prepared with a simple hydrothermal reaction route in water. All synthesized molecules and final composite were characterized with UV-Vis, FT-IR and SEM methods. The results during the photocatalytic experiments of two different dyes showed sufficient dye degradation especially in the case of MB. All measurements were run with a control containing just the dye under the same reaction conditions. Therefore, a quite promising photocatalyst was efficiently prepared with facile and low-cost synthetic procedure. The material could be recycled and reused in additional dye degradation reactions. Further optimization of the photocatalytic experiments must be performed in future work, concerning the amount of catalyst

used and the pH of the reaction mixture.



Scheme 1. Synthetic procedure for the preparation of **TPP** and **ZnTPP**.

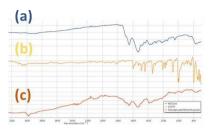


Figure 1. FT-IR spectra of (a)NCDot, (b)ZnTPP and (c)NCDot@ZnTPP.

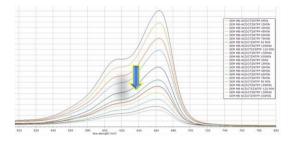


Figure 2. Absorption spectra obtained upon photodegradation of MB.

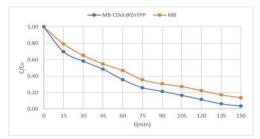
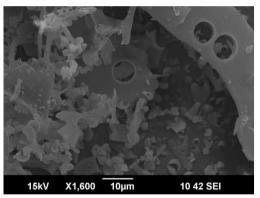


Figure 3. Photodegradation under visible led light irradiation.



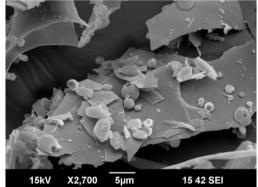


Figure 4. SEM images of NCDot@ZnTPP.

Key-words: Porphyrins, carbon dots, photocatalytic reaction, dye degradation.

Acknowledgements: The authors would like to thank Dr. K. Ladomenou for her supervision.

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ΣΥΝΘΕΣΗ ΚΑΙ ΜΕΛΕΤΗ ΜΕΤΑΛΛΙΚΩΝ ΠΟΡΦΥΡΙΝΙΚΩΝ ΣΥΜΠΛΟΚΩΝ ΜΕ ΑΖΩΤΟΥΧΕΣ ΝΑΝΟΤΕΛΕΙΕΣ ΑΝΘΡΑΚΑ ΓΙΑ ΦΩΤΟΚΑΤΑΛΥΤΙΚΕΣ ΕΦΑΡΜΟΓΕΣ

Η μόλυνση των υδάτων λόγω της ακατάλληλης απόρριψης αποβλήτων από τις βιομηχανίες είναι μια από τις μεγαλύτερες προκλήσεις που επηρεάζει ολόκληρο τον κόσμο. Οι οργανικές χρωστικές είναι ένας από τους πιο σημαντικούς ρύπους στα λύματα λόγω της υψηλής τοξικότητάς τους και της μη βιοαποδόμησης τους στο περιβάλλον. Στην παρούσα εργασία συντέθηκαν σύμπλοκα πορφυρινών με ψευδάργυρο, συνδυασμένα με αζωτούχες νανοτελείες άνθρακα (nitrogen-doped carbon dots), NCDot@ZnTPP και εξετάστηκε η φωτοκαταλυτική ικανότητα τους ως προς την διάσπαση ρύπων. Το υλικό που παρασκευάστηκε χαρακτηρίστηκε με αναλυτικές τεχνικές και μελετήθηκε η διάσπαση των χρωστικών methylene blue και reactive black5 με απόλυτη επιτυχία.

COMPARATIVE STUDY ON VARIOUS PARAMETERS AFFECTING CHEMICAL PROFILE OF ROSEMARY PLANT EXTRACTS

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Medicinal and aromatic plants (MAPs) are globally defined as promising sources of biologically active aromatic compounds capable of producing a variety of extractable biochemical products, such as essential oils. In recent years, there has been a constant demand to improve the quality of essential oils as they possess food preservation, natural antioxidant, remedial and pharmacological properties [1,2]. One of the most important MAPs is Rosmarinus Officinalis, commonly "Rosemary", a member of the *Lamiaceae* family, which flowers mainly in the Mediterranean region, including Greece. Rosemary has been known since ancient time for its superior health benefits [3]. In general, essential oil composition has been reported to vary depending on genetic and environmental conditions, seasonal harvesting, plant part or growth stage [4]. The present study aims to investigate the factors which may affect the composition of rosemary extracts and therefore their quality and uses. The specific objectives include the study of the effect of: a) the plant drying time and temperature, b) extraction method, c) solvent, temperature and time on solvent extraction, and d) UV radiation on the essential oil.

The rosemary plants that were used in this study, were collected between late March and early April 2023 in Northern Greece, Kavala. Three samples were collected from two nearby home gardens near the sea (two cultivated and one wild-growing, the latter had reached two meters in height) and one sample was collected from our university area. Moreover, one sample of dried rosemary leaves was procured from local market.

Chemical composition of the extracts and essential oils was extensively analyzed via Gas Chromatography-Mass Spectrometry (GC-MS) method, using an "Agilent 6890N" gas chromatograph coupled with an "MSD 5973B" mass spectrometer. All concentrations were based on relative area percentages. Identification of organic compounds present was determined by comparison of their mass spectra with available NIST 2.0 MS data and with published data. Chromatographic separation occurred by using an Agilent DB-XLB column (low polarity, 30 m x 0.25 mm I.D., and 0.25 μ m film thickness) with following conditions: initial temperature 40°C for 2 min, ramp rate 2°C/min to 270°C, hold 5 min and post run 320 °C for 5 min; inlet: split ratio 1:100, initial temperature 250°C, Helium with flow rate 1mL/min. MS: EI method at 70 eV. An "Agilent 7683B" automatic liquid sampler was used for the injection of 1 μ L per sample.

In total, 32 extracted compounds were identified by GC-MS analysis, including monoterpenes, oxygenated monoterpenes, flavonoids, polyphenols and triterpenic acids. The percentage composition of the main oxygenated monoterpenes (1,8-Cineole, Linalool, Camphor, Borneol, *a*-Terpineol, Verbenone and Bornyl acetate) and the presence of highly oxygenated compounds were used for comparing analyzed samples.

Extraction of Plant Constituents. Five different techniques of extraction were applied to extract the constituents of the rosemary aerial plant samples. a) Clevenger Hydrodistillation (15g sample and 150 mL deionized water, heating 3 h), b) Cold solvent extraction (2g sample and 20 mL solvent, 2 h stirring). Solvents of different polarity used were hexane, acetone, ethyl acetate and ethanol, c) Hot solvent extraction (2g sample, 60-65 °C for 30 min, twice with 40 mL of Ethanol), d) Reflux (15g sample, 150 mL ethanol, reflux 2 h), e) Ultrasonication (solvents used: hexane and ethanol, time, and temperature: 30 min, room temperature and 15 min, heating at 40 °C).

The results indicated that there are significant differences both qualitative and quantitative between the different extraction techniques and the published results [5,6]. It is interesting to note the presence of high verbenone content in three of the four essential oils examined and the absence (or very low amount) of α -pinene in the samples obtained by hydrodistillation. Chromatographic analysis of the hexane and ethyl acetate extracts revealed qualitative similarities in chemical composition to the hydrodistillation samples. Extracts with organic solvents were characterized by a comparatively increased amount of monoterpene compounds (α -pinene, camphene, myrcene, β pinene, α-phellandrene, lemonene). Ethyl acetate and ethanol extracted comparatively higher amounts of oxygenated monoterpenes (1,8-cineole, borneol, verbenone). In addition, the ethanolic extract at room temperature was characterized by a high percent of flavonoids. In contrast, the temperature-short time ethanol extraction gave the main oxygenated monoterpenes (1,8-cineole, camphor, borneol, verbenone) in a higher amount than flavonoids. The reflux method had significant impact on the camphor amount, which was selectively increased. Moreover, caryophyllene that was present only in trace amounts in the other extracts, appeared in significant relative percentage in this method. Ultrasound-assisted extraction with hexane obtained a comparatively reduced proportion of monoterpenes and an increased amount of borneol and cineole. In the corresponding sonication and heating extraction process, the percentage of 1,8-cineole and borneol compared to the verbenone decreased significantly. Ethanol ultrasonication, recovered a large number of phenolic acids, diterpenes and flavonoids compared to conventional extraction at room temperature or after heating.

Study of influence of drying time and temperature. The drying methods investigated were shade drying in air and room temperature conditions, for a period of 1 week and 5 weeks and after heating in an oven (45°C) for 3 h. Fresh and dried rosemary leaves were utilized to extract essential oil using the hydrodistillation method. According to

the results, all drying methods had a significant effect on the relative ratio of the main components in agreement to literature data [4]. The dried samples showed a higher content of verbenone, borneol acetate and of sesquiterpenes (caryophyllene, caryophyllene oxide), compared to the fresh plant material, in contrast to literature reports [7]. The oven drying method additionally, led to a significant loss of camphor and borneol, while the presence of a-pinene and other monoterpenes was in notable concentrations. (Figure 1)

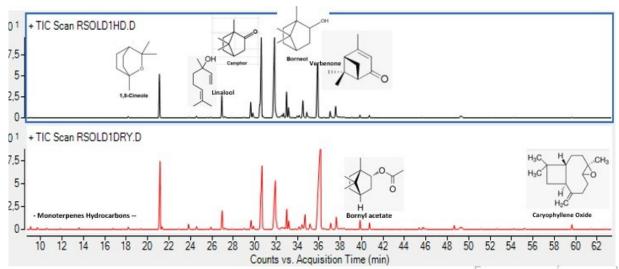


Figure 1 Comparison of the Total Ion Chromatogram (TIC) between samples of fresh and dried plant

Study of the effect of UV radiation. Photodegradation can cause changes in the chemical composition of an essential oil and form new compounds with different activity [8]. Solutions of essential oil in three solvents (hexane, dichloromethane, and ethanol) at concentrations of $100~\mu L/mL$ were exposed for 15 min under UV light at 254 nm, 365 nm, and both at 254 and 365 nm. Contrary to literature data, the results showed zero significant difference in the qualitative and quantitative composition due to radiation.

Conclusions. The present study provides experimental confirmation that different drying methods and extraction techniques can be used to influence the chemical composition and properties of rosemary essential oil and extracts. Each solvent has a different extraction selectivity concerning the main components. Ultrasonic extraction with hexane gives similar chemical profile to the conventional hexane extraction and hydrodistilled products, while ethanol can help the extraction of polyphenolic contents. Generally, results showed that shade drying favors the amount of verbenone. Finally, it is remarkable that Rosemary essential oil showed short-term UV stability. However, further research on this topic is still needed to clarify the key factors influencing rosemary essential oil's chemical composition.

Acknowledgements: The authors would like to thank S. Mitkidou and E. Dimitrakoudi for their supervision **References:**

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ΣΥΓΚΡΙΤΙΚΗ ΜΕΛΕΤΉ ΤΩΝ ΠΑΡΑΜΕΤΡΩΝ ΠΟΥ ΕΠΗΡΕΑΖΟΥΝ ΤΗ ΧΗΜΙΚΉ ΣΥΝΘΕΣΉ ΤΩΝ ΕΚΧΥΛΙΣΜΑΤΩΝ ΤΟΥ ΦΥΤΟΥ ROSEMARY

Αντικείμενο της παρούσας μελέτης αποτελεί η σύγκριση και αξιολόγηση των παραμέτρων που επιδρούν στην ανάκτηση των βιοδραστικών συστατικών του αρωματικού φυτού Rosemary Officinalis, πολύτιμου για τη διατροφική και φαρμακευτική αξία του και τη φυσική αντιοξειδωτική του δράση. Μελετήθηκαν οι τεχνικές της υδροαπόσταξης, διαβροχής και εκχύλισης με διαλύτη και υποβοηθούμενης με υπερήχους εκχύλισης και προσδιορίστηκε η δυνατότητα απομόνωσης εκχυλισμάτων πλούσιων σε συγκεκριμένα βιοδραστικά συστατικά. Εξετάστηκαν οι παράμετροι: μέσο εκχύλισης, θερμοκρασία και χρόνος εκχύλισης. Επιπλέον, αξιολογήθηκε η τεχνική της υδροαπόσταξης σε χλωρό και ξηρό φυτικό υλικό και εξετάστηκε η επίδραση του χρόνου και της θερμοκρασίας ξήρανσης, καθώς και η επίδραση UV ακτινοβολίας στη χημική σύσταση του αιθέριου ελαίου. Τα πειράματα πραγματοποιήθηκαν σε πέντε δείγματα φυτικού υλικού, από την περιοχή της Καβάλας, στη Βόρεια-Ανατολική Ελλάδα. Η ανάλυση με GC-MS επιβεβαίωσε ότι η χρήση διαφορετικών μεθόδων και συνθηκών ξήρανσης και εκχύλισης επιφέρει σημαντικές αλλαγές στην ανάκτηση των κύριων συστατικών και την ποιότητα των εκχυλισμάτων.

e-PRESENTATION

THE EFFECT OF NANOBUBBLES ON THE WETTABILITY OF STRATUM CORNEUM

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The term Stratum Corneum (SC), refers to the outermost layer of the epidermis, serving as a physical barrier of the body, regulating the entering or excretion of foreign or endogenous substances respectively [1]. It consists of 15-20 flattened dead cells (corneocytes), surrounded by a lipid phase. The corneocytes work as blocks being held together by a binder-mixture consisting of cholesterol, fatty acids, triglycerides, ceramides, and sterols, creating a net of dead tissue which is essential for the function of SC [2]. Even though its biological function is essentially that of a physicochemical barrier, there are penetration pathways through the SC that allow the passage of substances and their penetration into the skin. The recorded pathways of absorption are through sweat pores, hair follicles and SC itself, as seen in figure 1, with the penetration through SC being the most significant [3],[4]. In this study, the effect of nanobubbles (NBs) on stratum corneum (SC) is examined by using water-isopropanol solutions at different concentrations, both with and without nanobubbles.

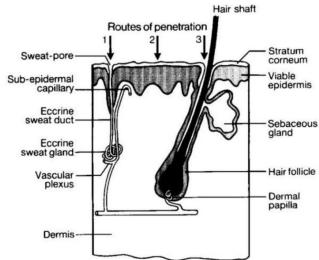


Figure 1 Absorption roots in human skin.

A NBs generator is employed to produce NBs having sizes around 200 nm and concentration 150x106 NB/mL. The NBs were later measured using nanosight. Two sets of experiments have been conducted: a) with the artificial membrane of Merc, Strat-M and b) with skin from porcine ears. The latter is obtained from the local slaughterhouse. The ears have been washed with tap water and shaved with a standard razor blade. Three different solutions of isopropanol|water of 10%, 13%, 15% v/v are prepared and used in both sets of experiments. The contact angle of both samples have been recorded using a Biolin contact angle meter. Moreover, the porcine ears have been immersed in deionized water and deionized water with NBs for an hour. The resulting samples have been examined with a Bruker microCT.

Table 1 summarizes the contact angle measurements. As the concentration of isopropanol increases, the contact angle decreases. However, this trend is not very well demonstrated in the case of the porcine ear; one reason being the rugosity of the skin. The NBs seem to decrease the contact angle of the droplets which may indicate an increased absorption from the SC. Moreover, it seems that the artificial skin membrane is more hydrophobic than the porcine ear, as the contact angle in the latter is greater.

Table 1 Contact angle of water/isopropanol

	Porcine Ear		Strat-M	
Isopropanol v/v	Water	Water NB	Water	Water NB
0%	68	-	84,9	78
10%	58	63	80,2	73,7
13%	-	62	73,7	45
15%	47	43	49,1	-

In order to gain a better insight on the effect of water with and without NBs on the SC, two samples treated as aforementioned introduced to the micro-CT. Figure 3 shows the result. From the coronal image it comes obvious that the water with NBs is absorbed more uniformly from the skin, than the water alone. Similar results are also witnessed from the transverse sagittal planes. The lipid phase, which is visible in the case of water without NBs, diminishes when NBs are present. Moreover, the physical condition of the skin was contracted when immersed in water with NBs; a similar behaviour is not observed in the case of water without NBs. The result indicates that NBs may help in stretching the skin, which is very important for many skincare and cosmetic applications.

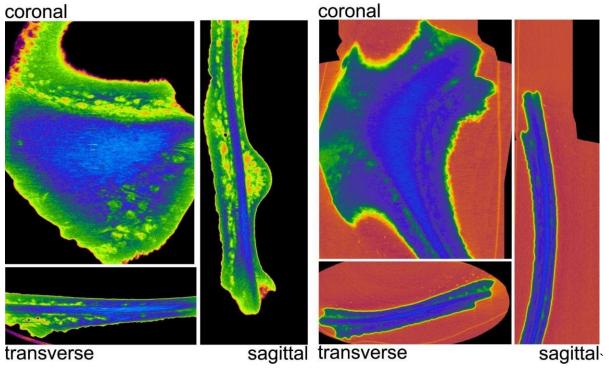


Figure 2 MicroCT scans; water (left); water with NBs (right).

Acknowledgements: The authors would like to thank Mrs Ramonna Kosheleva for her supervision

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Η ΕΠΙΔΡΑΣΗ ΤΩΝ ΝΑΝΟΦΥΣΑΛΙΔΩΝ ΣΤΗ ΔΙΑΒΡΟΧΗ ΤΗΣ ΚΕΡΑΤΙΝΗΣ ΣΤΙΒΑΔΑΣ

Η κεράτινη στιβάδα (Stratum Corneum SC), αναφέρεται στην εξωτερική επιφάνεια της επιδερμίδας, λειτουργώντας σαν φυσικός φραγμός για τον ανθρώπινο οργανισμό. Αποτελεί στρώμα νεκρών απύρηνων, πεπλατισμένων κυττάρων (corneocytes), τα οποία συνενόνται ισχυρά, δημιουργωντας μια κεραμωτή αλληλουχία. Παρά το γεγονός ότι παλαιότερα θεωρούταν μη διαπερατή, πλέον το SC, έχει καταγραφηθεί ως το κύριο μονοπάτι εισόδου του δέρματος.Η απορροφητικότητα της κεράτινης στιβάδας έχει απασχολήσει σημαντικά την επιστήμη τα τελευταία χρόνια καθώς αποτελεί θέμα της κοσμητολογίας, της φαρμακευτικής χημείας κ.ά. Οι νανοφυσαλιδες παρουσιάζουν σημαντικό ενδιαφέρον λόγω των ιδιαίτερων ιδιοτήτων τους. Η εφαρμογή τους στο δέρμα ενδέχεται να αποτελέσει μια ακόμη ευεργετική εφαρμογή τους. Στην παρούσα εργασία πραγματοποιήθηκε μελέτη για την επίδραση των νανοφυσαλιδων στην απορρόφηση από το δέρμα. Για το σκοπό αυτό αξιοποιήθηκαν δύο επιφάνειες: α) μια τεχνητή μεμβράνη δέρματος της Merk, Strat-M, β) αυτιά χοίρου καθώς χρησιμοποιούνται ευρέως ως μοντέλα για την εξέταση της δερματικής διείσδυσης χημικών ενώσεων λόγω της ομοιότητάς τους με το ανθρώπινο SC. Η γωνία επαφής διαλυμάτων ισοπροπανόλης|νερού, με και χωρίς νανοφυσαλιδες, μετρήθηκε με οπτικό γωνιόμετρο. Επιπλέον, διεξήχθη ex νίνο μικρο-CT ανάλυση δύο δειγμάτων αυτιών χοίρου, αφού πρώτα εμβαπτίστηκαν σε νερό και σε νερό NBs αντίστοιχα.

e-POSTER

ELECTROCHEMICAL TREATMENT OF EFFLUENT FROM AN ANAEROBIC DIGESTION UNIT OF AGRO-LIVESTOCK WASTE

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Anaerobic digesters are used internationally for the biological treatment of organic waste produced by various agro-industrial and livestock enterprises [1]. In these digesters, the treatment of complex organic substrates, which are characterized by high concentrations of suspended solids and moderate or low biodegradability (e.g. lignocellulosic, manure) is carried out [2]. These plants achieve the production of significant amounts of energy (biogas). At the same time, however, we also have the generation of wastewater with high concentrations of persistent organic substances and ammonia. The purpose of this study was to evaluate the effectiveness of electro-flocculation and electro-oxidation to achieve the removal of soluble and particulate organics [3].

Electrocoagulation is an environmentally friendly electrochemical method with many advantages. It is a technique with many applications, which uses the principles of electrochemistry and flocculation to treat wastewater and remove hazardous pollutants from it by electrolysis. During flocculation the particles aggregate and settle out of colloidal suspensions. Generation of hydrogen gas bubbles at the cathode resulted in digestate particulate matter flotation, while the amount of solids transferred to the foam increased with increasing current density. The most common electrodes for electroflocculation are aluminum and iron.

Electrooxidation is also widely applied for waste treatment. In general, for electrochemical oxidation to occur in an electrolyte there must be sufficient flow of ions between the electrodes through the solution. If the conductivity of the medium is low, it should be increased by adding a suitable electrolyte, which will increase the conductivity and help produce free radicals that will oxidize the organic contaminants. In this process organic compounds are efficiently oxidized, with little consumption of additional chemicals and little or no sludge production.

The experimental apparatus consists of a DC power supply, the multimeter, the magnetic stirrer, the electrochemical cell containing the sample of liquid animal waste and the electrodes.

electrocoagulation, iron electrodes with applied current intensity (600 mA) and treatment time of 3 hours were used in the anode and cathode. The process resulted in high COD removal from 3300 mg/L to 983 mg/L (> 70%). Also, respectively in electro-oxidation, electrodes with boron-doped diamond (BDD) anode and Ti/Pt cathode and applied current density (1500 mA) and treatment time of 3 h were used. The process resulted in high COD removal from 3300 mg/L to 862 mg/L (>73%).

The remaining liquid after 3 h electroprocessing time was characterized by low COD and negligible color and solids concentration [4]. Also COD was below the standards set by the Hellenic legislation for digestate reuse in agriculture.



Picture 1: Experimental setup

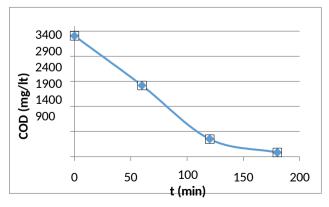


Figure 1: COD variation versus time in electrocoagulation treatment

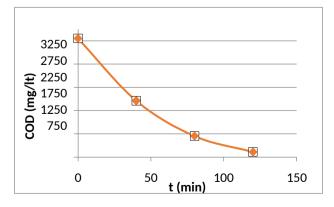


Figure 2: COD variation versus time in electro-oxidation treatment

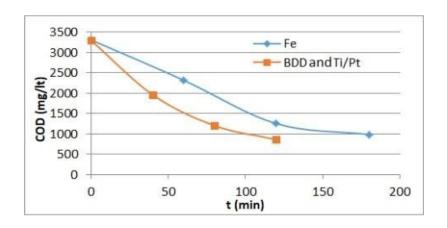


Figure 3: Comparison between two methods



Picture 2: Comparison of original sample (left), with iron electrodes (in the middle) in 3 hours electrocution and with BDD and Ti/Pt electrodes in 2 hours electro-oxidation (right)

In conclusion, it can be argued that the purification of waste from an anaerobic digestion plant by electrochemical method is an economically and environmentally advantageous solution. In particular, the results showed that both electrodes and time are the two main factors in reducing COD levels in waste. On both sides, COD reduction was the desired (<1200) although it was achieved at different times. Typically, the electrode with BDD anode and Ti/Pt cathode gave faster results and remained unchanged compared to the Fe electrode, which although effective took a longer time to act sufficiently and deteriorated, as shown in figure and picture 2.

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ΗΛΕΚΤΡΟΧΗΜΙΚΗ ΕΠΕΞΕΡΓΑΣΙΑ ΥΓΡΩΝ ΑΠΟΒΛΗΤΩΝ ΑΠΟ ΜΟΝΑΔΑ ΑΝΑΕΡΟΒΙΑΣ ΧΩΝΕΥΣΗΣ ΑΓΡΟΚΤΗΝΟΤΡΟΦΙΚΩΝ ΑΠΟΒΛΗΤΩΝ

Η μελέτη που πραγματοποιήθηκε στηρίζεται στην ηλεκτροχημική επεξεργασία υγρών αποβλήτων από μονάδα αναερόβιας χώνευσης. Τις τελευταίες δεκαετίες, όλο και αυξάνεται η παραγωγή σημαντικών ποσοτήτων ενέργειας (βιοαερίου) από απόβλητα που παράγονται από διάφορες αγροτοβιομηχανικές και κτηνοτροφικές επιχειρήσεις. Αυτό έχει ως αποτέλεσμα την δημιουργία υγρών αποβλήτων που διαθέτουν μεγάλες συγκεντρώσεις ανθεκτικών οργανικών ουσιών και αμμωνίας. Συγκεκριμένα, εξετάζεται η αποτελεσματικότητα της ηλεκτροκροκίδωσης και της ηλεκτρο-οξείδωσης, για την επίτευξη της απομάκρυνσης των διαλυτών και σωματιδιακών οργανικών ουσιών. Επιπλέον, ύστερα από την ολοκλήρωση της πειραματικής διαδικασίας, αξιολογήθηκε ο τρόπος με τον οποίο ο χρόνος και τα ηλεκτρόδια επηρεάζουν τη μείωση των επιπέδων COD από τα απόβλητα. Ειδικότερα, σύμφωνα με τα πειραματικά αποτελέσματα, αποδείχτηκε ότι η διαδικασία της ηλεκτρο-οξείδωσης, στην οποία χρησιμοποιήθηκαν ηλεκτρόδια με άνοδο BDD και κάθοδο Ti/Pt έδωσε πιο γρήγορα αποτελέσματα σε σχέση με την ηλεκτροκροκίδωση με ηλεκτρόδια σιδήρου.

INVESTIGATION OF FACTORS AFFECTING THE EFFICIENCY OF PHOTOVOLTAIC CELLS

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Renewable Energy Sources (RES) are these that exist in abundance in the natural environment and are renewed annually at rates higher than their consumption by humans. Specifically, there is energy derived from heat recovery in the short-term, such as solar energy (solar heat). An example of RES is the photovoltaic panel, the device in which electricity is produced as effect of exposure to light. The "panel" refers to the industrial arrangement of several individual photovoltaic cells in connection. In essence, these are artificial semi-conductors, usually, made of silicon. Photovoltaic technology involves the use of solar cells, which convert sunlight directly into electricity through the photovoltaic effect and has a critical role in the renewable energy field.

Various research efforts that focus on the investigation of factors affecting the efficiency, (n), of PV cells, have been noted. On this regard, PV panels have life expectancy approximately between 25 to 30 years. During this time frame PV panels are exposed to weather conditions, while the natural wear and tear causes a reduction of their efficiency [1]. *Solar Radiation* (SR) is a major factor that affects the energy production and the intensity of it changes throughout the dayimpacting on the efficiency of PV panels. Around midday, increased power output can be produced by PVs because they can transform more solar energy to electricity at this time [2]. In addition, PV aging is a severe concern, while, several factors may lead to the degradation of the solar cells with a progressive reduction in their efficiency over the years. More specifically, PV aging heavily depends on the type of photovoltaic technology and on the environment where the modules are installed. Taking all that into account, experimental tests were performed, using mono-Si and organic cells so that I-V characteristics curves can be plotted and their efficiency be evaluated and compared to that of previous years. Furthermore, each type of solar cells has an efficiency rate. Monocrystallic panels have almost 20% and their efficiency is higher than organic solar cells, which are more prone to recombination[3,4].

Due to the abovementioned considerations, the main motivation behind the current study is the investigation of factors affecting the efficiency of PV panels. To meet our objectives, we designed an experimental study that involved the evaluation of SR, and maximum Power, resulting, in turn, to the calculation of the performance of two specific PV types that are monocrystallic, (Mono-Si) and organic, (Organic). The operation of the cells was measured at two experimental conditions (Outdoors/Chamber), placed at 0-degree tilt in relation to the ground level and were connected to a load a voltmeter and an ammeter. Before each measurement, both the Open Circuit Voltage, (Voc) and SR were estimated. The same procedure was carried out in a simulation chamber. The data collection phase covered a three-month period (March-April 2023), while the database was further augmented with measurements from previous experimental runs conducted at several past years (2014, 2018, 2021, 2022).

After the fusion of several heterogenous datasets into a unified database, appropriate pre-processing steps (encoding of categorical features, identification and removal of missing and inconsistent values), were carried out in order to ensure that the results meet certain quality standards, while univariate and exploratory analytics were conducted for gaining insights concerning the characteristics of the dataset. For the continuous variables of the dataset (VoltageU (Volt), CurrentI (mA), PowerP (W), AreaS (m²), Solar RadiationSR (W/m²), Efficiency (n)), appropriate measures of central tendency (mean, median) and measures of dispersion (standard deviation, minimum and maximum) were computed, whereas the distributions were graphically inspected via histograms in order to assess, whether the variables satisfied the normality assumption. Regarding the categorical variables (Year, Month, Time of the Day, Experimental Condition and PV Type), the frequency distribution of each experimental factor was graphically evaluated through bar-plots. Moreover, exploratory analytics approaches (boxplots with violin plots) were leveraged in order to investigate the potential effect of the examined factors on the response variable (*n*). Finally, inferential statistics were used in order to study the effect of these factors on the parameter of interest (*n*). Due to the fact that the Kolmogorov-Smirnov test of normality indicated that the variable of interest did not follow a normal distribution, (p < 0.001), non-parametric statistical hypothesis testing procedures were used for the examination of the effect of factors on the dependent variable. In specific, the non-parametric Wilcoxon Signed Rank test was conducted for the comparison of two independent populations (experimental factors with two levels), whereas the Kruskal-Wallis test was used for the examination of the overall effect of an experimental factor with more than two levels followed by a post-hoc analysis via the *Dunn's* test and *Bonferroni* correction in order to adjust the *family-wise error rate* (or *Type I* error). The statistical analysis was conducted using the programming language R, while, in all tests a difference was considered statistically significant when the p-value (significance) was less than the alpha level of 0.05 (a =0.05).

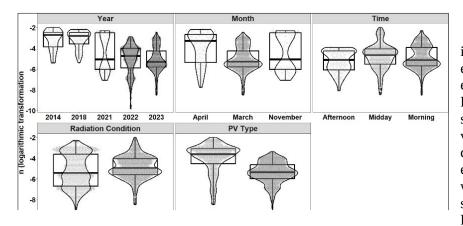


Figure 1. Boxplots with violin plots of n (in logarithmic transformation) across levels of catebighar afficiency values compared to the

Due to space limitations, we, indicatively, present the main findings extracted from the conduction exploratory and inferential analytics. Regarding the former axis, Figure 1 showcases the boxplots accompanied by violin plots concerning the efficiency distributions (in logarithmic scale) for each level of the examined factors from which, it is evident that they seem to significantly affect the response variable. For example, mono-Si cells tend to have organic ones, whereas the month and the time of the sampling seem to influence

the efficiency of PV cells, due to different weather and climatic conditions (temperature, atmospheric conditions, solar radiation, etc.). Generally, the efficiency of PV panels is related to the time of the day, since higher values of efficiency appear during the midday, in comparison to morning or afternoon, while April days offer more energy generation than shorter days of March and November. In addition, the efficiency of the PV cells measured outside was higher than that measured in the chamber. Last but not least, the aging indicated by the year of the sampling seems to be a critical factor deteriorating the performance of PV cells. Indeed, a Mann-Whitney test showed that *Radiation Condition* (W(1) = 729118, p < 0.001) and *PV Type* (W(1) = 1478861, p < 0.001) presented a statistically significant main effect on the distributions of the efficiency. Additionally, the conduction of a Kruskal-Wallis test indicated statistically significant main effects for *Year* (aging) (3²(4) = 173.8, p < 0.001), *Month* (3²(2) = 42.9, p < 0.001) and *Time of the Day* (3²(2) = 16.7, p < 0.001) on the distributions of the response variable.

In conclusion, it is evident that the efficiency of photovoltaic panels is influenced by the above-mentioned factors. Recognizing these factors is crucial for optimizing the utilization of photovoltaic systems, allowing for better planning, maintenance, and replacement strategies to ensure maximum efficiency and take advantage of the full potential of solar energy.

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ΔΙΕΡΕΥΝΗΣΗΠΑΡΑΓΟΝΤΩΝΠΟΥΕΠΗΡΕΑΖΟΥΝ ΤΗΝΑΠΟΔΟΣΗΦΩΤΟΒΟΛΤΑΙΚΩΝΚΥΨΕΛΩΝ

Η παρούσα έρευνα πραγματεύεται τους παράγοντες που επηρεάζουν την απόδοση των φωτοβολταϊκών (Φ/Β)κυψελών, μιας μορφής ανανεώσιμων πηγών ενέργειας. Στα πλαίσια του πειράματος, χρησιμοποιήθηκαν δυο είδη κυψελών, το μόνο κρυσταλλικό και το οργανικό, το οποίο εμφανίζει χαμηλότερες τιμές απόδοσης σύμφωνα με ευρήματα που εξάγονται από την υπάρχουσα βιβλιογραφία, κάτω από δυο πειραματικές συνθήκες, τον εξωτερικό χώρο και τον θάλαμο προσομοίωσης. Τα πειραματικά δεδομένα αναλύθηκαν με στατιστικές μεθόδους και συγκρίθηκαν με μετρήσεις προηγούμενων πειραματικών δοκιμών. Πιο συγκεκριμένα, έγινε χρήση μεθόδων περιγραφικής και διερευνητικής ανάλυσης για τη συνοπτική παρουσίαση των υπό-εξέταση παραγόντων ενώ για τη μελέτη της επίδρασης των παραγόντων στην απόδοση των κυψελών και την εξαγωγή συμπερασμάτων για τους πληθυσμούς χρησιμοποιήθηκαν κατάλληλες μέθοδοι μη-παραμετρικής επαγωγικής στατιστικής. Τα αποτελέσματα της έρευνας φανέρωσαν στατιστικά σημαντική επίδραση των υπό-εξέταση παραγόντων (Έτος, Μήνας, Ώρα, Πειραματικές Συνθήκες, Τύπος Φ/Β)στην απόδοση των κυψελών παρέχοντας σημαντικές πληροφορίες που μπορούν να καθοδηγήσουν την ορθή χρήση των φωτοβολταϊκών πάνελ.

e-POSTER

THERMAL OXIDATION STABILITY OF SUNFLOWER OIL ENRICHED WITH NANOBUBBLES

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Sunflower oil is one of the basic edible oils used in the food industry in many applications. One of the most important uses of sunflower oil in food production is as a basic ingredient for frying, a process that accelerates the deterioration of the quality of the oil. In general, the quality of sunflower oil deteriorates more when exposed to high temperatures, oxygen, and light. These factors lead to various reactions such as oxidation and polymerization, which results in the degradation of essential fatty acids and the formation of compounds undesirable to the end user [1]. Thermal oxidation leads to undesirable by-products more rapidly than autoxidation. Deep frying is a drying method and is used for foods with relatively high-water concentration. The presence of water during frying greatly accelerates various reactions, such as the formation of free fatty acids, glycerol, and mono/biglycerides. Finding a method to improve the properties of sunflower oil and reduce its perishability is one of the main objectives of the food industry to save supplies, energy and reduce waste. Due to this problem a method of enriching sunflower oil with nanobubbles (NBs) was developed for first time according to the literature sources.

Nanobubbles (NBs), are tiny gas cavities up to 200 nm in size that are characterized by special physical properties such as longevity in water, high internal pressure, low ascent velocity, and enhanced transport activity [2]. They are also particles with high temperature stability, even at 100 °C, where water boils, the nanobubbles remain completely unaffected. Due to their unique properties, they can change the physicochemical properties of the water media to which they are added. It is worth to be emphasized that no attempt has yet been made to enrich a kind of vegetable oil with nanofluids. The applications of nanobubbles are numerous, especially in the pharmaceutical industry, chemistry, and materials manufacturing.

The aim of this experiment is to study the behavior of NBs in sunflower oil in a thermal environment, the effect of oxygen on the colloids of the sunflower oil-NBs and the interaction of NBs with the main quality characteristics of sunflower oil during heating and in the presence or absence of oxygen [3].

The application of nanobubbles into sunflower oil was accomplished by the nanobubble generator arrangement. The gas that was introduced into the sunflower oil was nitrogen, as an inert element for edible oil. The oil was mixed with nitrogen under pressure to generate bubbles in the liquid. The bubbles generated at this stage were gradually broken down into microbubbles in the first generator. Then, the liquid was passed through a second generator with a porous plug head to produce NBs.

Eight different samples were prepared, each containing 30g of sunflower oil. Four of them contained commercial sunflower oil and the rest of them, contained sunflower oil with NBs. All samples were placed in an oven at a temperature of 105 °C. The first two samples of each sunflower oil, the reference (commercial) and the one with the NBs, were tested in the presence of atmospheric air -open system- for 48 and 72 hours, respectively, while the other two samples were tested for the same time but without atmospheric air- closed system. The samples were given code names according to the process they were subjected to and their environment (Table 1¹).

To evaluate the quality characteristics of the sunflower oils, an analysis of acidity and peroxide value was carried out for all the treated samples and the reference samples. The methods recommended in the legislation were used for evaluation. In particular, the following chemical reagents were used for the measurement of acidity: Ethanol with 95% purity, diethyl ether, phenolphthalein, NaOH 0.0943 M. For the measurement of peroxide value, the following reagents were used: Chloroform, starch (liquid), KI (liquid), acetic acid, sodium thiosulfate 0.01 M.

Measurements of nanobubbles after heat treatment of sunflower oil samples containing nitrogen nanobubbles and reference sunflower oil samples with nanobubbles were performed. Their initial concentration and size were measured using the Nanosight instrument.

From the results of acidity and peroxide value, the important conclusion is that the process of adding nanobubbles caused an increase in peroxide value in sunflower oil. At the sample that contained nanobubbles and was heated without oxygen - a closed system - a particular point of scientific interest arose. In this sample, no change in the peroxide value was observed for 48 h, while the acidity remained at a similar level. The sample was the only one that showed similar turbidity to the reference sample after 48 h of heat treatment. It should be mentioned that in the corresponding 72-h sample, the peroxide value increased sharply, and no turbidity appeared. The evolution of the concentration of nanobubbles as well as their size in the same sample was completely different than in samples that were in an open system. The concentration of nanobubbles decreases similarly in the first 48 h, while after 72 h a slight increase is observed in the open-lid sample, while the concentration decreases rapidly in the closed-lid sample. Inhomogeneity is also observed in the size of the nanobubbles, with a shrinkage of the average size in the open system, while the size in the closed system doubles in the first 48 h.

Regarding the two samples that showed differences (Table 2), it was observed that the open system after the heat treatment follows the same pattern of nanobubble stability as the pattern observed in aqueous solution, according

¹ For all Tables and Figures: O₂ means the presence of Oxygen and WO₂ means the absence of Oxygen

to previous studies [4]. It is assumed that the external electrostatic pressure generated by the charged interface of the nanobubbles balances the internal Laplace pressure and, therefore, no net diffusion of the gas is expected in equilibrium [5]. In contrast, in the closed system the pattern observed is different. In the first 48 h there is no differentiation between the closed and open system and this is probably because the closed system achieves equilibrium but is at an early stage of nanobubble concentration change. After this point, due to the fact that the pressure increases sufficiently at the margin between oil and cap the nanobubble-oil system differentiated nanobubble aggregates are formed and therefore the size increases. Consequently, this increase in size causes the nanobubbles to rise to the surface and break down, so the pressure on the outside increases even more and the disintegration of the nanobubbles will continue until equilibrium between the pressures in the triple system is reached. In this way, a rapid decrease in the concentration of nanobubbles in the closed system is justified.

These results demonstrate that the introduction of nanobubbles into oil is of great interest and of course in terms of their behaviour during thermoxidation. The resistance to the increase of peroxide value in the two days of heating, by finding another potential way of introducing the nanobubbles into the oil and limiting their subsequent rapid increase can be an important innovation in the transport and storage of oils.

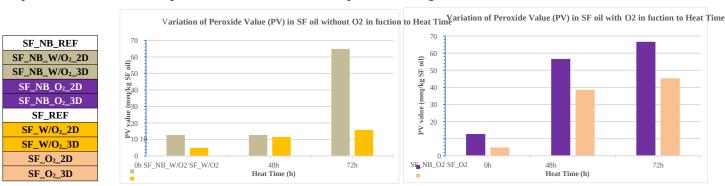


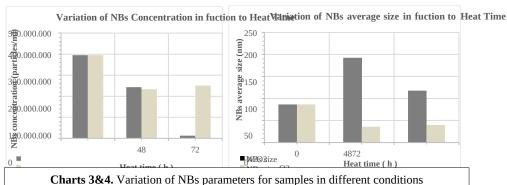
Table 1. of the

Code names samples

	SF_NB _s _W/O2		SF_NB _s _O2	
Heat time (hours)	NBs concentration (particles/ml)	NBs average size (nm)	NBs concentration (particles/ml)	NBs average size (nm)
0	395.000.000,00	86,4	395.000.000,00	86,4
48	243.000.000	192,6	233.000.000	36,2
72	12 900 000	117.8	251 000 000	40.1

Table 2. NBs parameters during heat time

Charts 1&2. Variation of peroxides in different samples and conditions



Acknowledgements: The authors would like to thank professor Th. Markopoulos, V. Prokopiou and R. Kosheleva for their supervision.

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ΘΕΡΜΙΚΗ ΟΞΕΙΔΩΣΗ ΗΛΙΕΛΑΙΟΥ ΜΕ ΝΑΝΟΦΥΣΑΛΙΔΕΣ (NBs)

Το ηλιέλαιο είναι ένα από τα πλέον χρησιμοποιούμενα είδη τροφίμων, με πλήθος εφαρμογών και χρήσεων στην καθημερινή ζωή. Είναι ευπαθές στην οξείδωση, στην θέρμανση και στην επίδραση της ακτινοβολίας. Ένας σημαντικός δείκτης ποιότητας του εκάστοτε βρωσίμου ελαίου, είναι ο αριθμός υπεροξειδίων, ο οποίος συμβάλει στην διερεύνηση της ποιότητας του ηλιελαίου, με σκοπό τον περιορισμό της υποβάθμισης του. Για τον σκοπό αυτό, το ηλιέλαιο στα πλαίσια του παρόντος πειράματος εμπλουτίστηκε με νανοφυσαλίδες αζώτου, ακολούθως υπέστη θερμοοξείδωση, υπό διαφορετικές συνθήκες. Οι νανοφυσαλίδες, θεωρητικά, μεταβάλλουν τα φυσικοχημικά χαρακτηριστικά των ρευστών στα οποία επιβιώνουν. Στόχος της παρούσας εργασίας είναι η παρατήρηση και η αξιολόγηση της επίδρασης τους στην θερμοοξείδωση του ηλιελαίου, ο χρόνος ζωής τους καθώς και η μεταβολή του μεγέθους τους. Τα αποτελέσματα έδειξαν ότι η συμπεριφορά τους διαφέρει σε κλειστό και ανοιχτό σύστημα, καθώς παρουσιάζουν διαφορετική συγκέντρωση και μέγεθος λόγω των διαφορετικών συνθηκών (πίεσης – συγκέντρωσης) και οδηγούν σε διακριτή συμπεριφορά των νανοφυσαλίδων.

COMPARISON OF ULTRASOUND AND MICROWAVE DIGESTION TECHNIQUES IN SEDIMENT PRETREATMENT AND HEAVY METAL DETERMINATION BY USING ICP-MS

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The study reports on the measurement of heavy metals in sediment samples taken from two sites in the coastal zone of the estuary of the Nestos River and classified as numbers 8 and 4. Heavy metals are one of the main causes of environmental pollution due to their persistence of degradation and toxicity, with anthropogenic activities being the main source [1, 2, 3]. Heavy metals are transported into the aquatic environment, and as a result, through transport processes, they pass from plants to animals and eventually end up in humans [4]. For this reason, heavy metal monitoring is essential in ecosystem. In recent years, many techniques have been developed to determine the concentration of heavy metals in water, air, soils, sediments etc. When samples are in solid form, they must be treated by acid digestion, so that heavy metals are carried over into the liquid phase. Digestion is achieved by methodologies such as microwaves, ultrasound, and open vessel, in which high concentration and high purity acid solutions are used combined with heating [1, 3, 5]. Although microwave digestion is the most used process, it has been observed that ultrasonic digestion has shown satisfactory results [3]. The present research work aims to compare the results of acid digestion of sediment by ultrasound and microwave. Then the quantification of the concentration of 4 heavy metals: (cadmium-Cd, lead-Pb, chromium-Cr, arsenic-As) was measured by ICP-MS technique.

Samples of pretreated sediments approximately 200 mg and 400 mg were weighed, from two different areas (No. 8 and 4). They were digested with ultrasound and microwave techniques. For ultrasonic digestion, HNO₃ was used for a series of samples from sampling points No. 8 and 4, as follows: to the 200 mg samples, 2 mL was added, while to the 400 mg samples 5 mL of HNO₃ was added. In another series of samples No. 8 and 4, aqua regia was used, adding 2 and 5 mL respectively. The digestion of all samples was carried out in two stages. In the first, the samples were heated at 70–75 °C for 40 min, while in the second, the same amount of acids (as at the beginning) was added back to each sample and the same digestion procedure was followed [3, 4]. After completion of the procedure, the samples were centrifuged for 10 min at 3000 rpm and filtered, while the filtrates were diluted to a final volume of 25 mL with 3% v/v HNO₃. For microwave digestion, 5 mL of HNO₃ was added to the 200 mg samples, and 7 mL to the 400 mg samples from No. 8 and 4. The samples were then digested using microwave, according to EPA 3051 A for 20 min at 175 °C. The samples were then cooled, filtered, and diluted to a final volume of 25 mL with 3% v/v HNO₃. The determination of the concentration of heavy metals in all the solutions obtained from the digestions, was carried out by the ICP-MS technique.

Table 1 Samples' heavy metal concentrations

Sample	Didestion	Solvent	Sample mass	Cr	As (mg	Cd	Pb
site	method		(g)	(mg Kg ⁻¹)	Kg ⁻¹)	(mg Kg ⁻¹)	(mg Kg ⁻¹)
8	Microwave	HNO_3	0,200	69.91	9.61	0.24	31.54
8	Microwave	HNO_3	0,399	68.60	11.01	0.12	32.96
4	Microwave	HNO_3	0,200	85.86	12.19	0.12	38.49
4	Microwave	HNO_3	0,400	85.96	11.96	0.12	39.93
8	Ultrasonic	HNO_3	0,200	64.17	8.22	0.10	30.23
8	Ultrasonic	HNO_3	0,401	57.37	7.74	0.08	28.13
4	Ultrasonic	HNO_3	0,200	36.02	8.11	0.09	29.69
4	Ultrasonic	HNO_3	0,405	35.74	8.19	0.09	29.45
8	Ultrasonic	aqua regia	0,204	36.09	21.30	1.27	30.96
8	Ultrasonic	aqua regia	0,400	32.99	22.65	0.58	23.27
4	Ultrasonic	aqua regia	0,201	42.74	19.99	0.57	24.97
4	Ultrasonic	aqua regia	0,403	35.47	26.44	0.20	24.93

From the ICP-MS analysis it was found that the measurements of the samples processed by microwave digestion gave better results than those which were processed by ultrasonic digestion. Furthermore, HNO₃ digestion for both techniques gave similar results for the 4 metals because satisfactory recovery was achieved from 200 and 400 mg samples (Table 1). As for aqua regia which was used only in the ultrasonic technique, it gave different the results from the samples digested with HNO₃. From all the above we conclude that the optimal method of digestion of sediments for the determination of the specific heavy metals is microwave digestion using HNO₃ as solvent. [3].

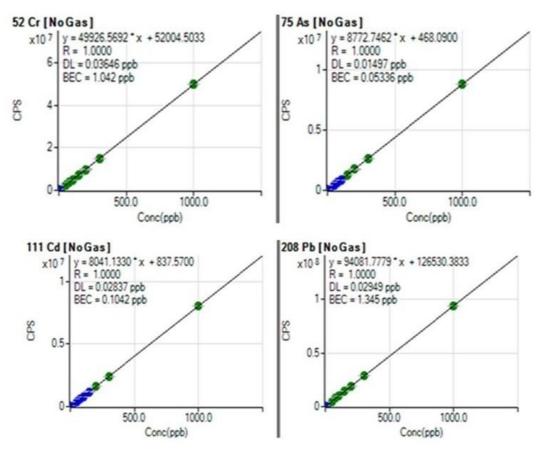


Figure 1 Calibration curve for each metal

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ΣΥΓΚΡΙΣΗ ΤΕΧΝΙΚΩΝ ΥΠΕΡΗΧΩΝ ΚΑΙ ΜΙΚΡΟΚΥΜΜΑΤΩΝ ΣΤΗΝ ΠΡΟΕΠΕΞΕΡΓΑΣΙΑ ΙΖΗΜΑΤΩΝ ΚΑΙ ΤΟΝ ΠΡΟΣΔΙΟΡΙΣΜΟ ΒΑΡΕΩΝ ΜΕΤΑΛΛΩΝ ΜΕ ICP-MS

Τα βαρέα μέταλλα είναι ανθεκτικά στην αποδόμηση και τοξικά. Τα χαρακτηριστικά αυτά τα καθιστούν μια από τις κύριες αιτίες της ρύπανσης του περιβάλλοντος, κύρια πηγή τους είναι οι ανθρώπινες δραστηριότητες. Τα βαρέα μέταλλα μεταφέρονται στο υδάτινο περιβάλλον με αποτέλεσμα μέσω διαδικασιών μεταφοράς να μεταφέρονται από τα φυτά στα ζώα και τελικά στον άνθρωπο. Έχουν αναπτυχθεί διάφορες τεχνικές επεξεργασίας των δειγμάτων για τον προσδιορισμό της συγκέντρωσης των βαρέων μετάλλων στα ιζήματα. Κρίσιμο στάδιο όλων των τεχνικών είναι η προκατεργασία των δειγμάτων με όξινη χώνευση. Η παρούσα εργασία συγκρίνει τα αποτελέσματα της χώνευσης ιζημάτων διαφορετικών περιοχών με υπερήχους και με μικροκύματα, με σκοπό την ανάδειξη της καταλληλότερης μεθόδου για την εξαγωγή.

<u>e-POSTER</u>

EXPERIMENTAL COMPARATIVE STUDY OF CRUDE OILS FROM GREEK REFINERIES WITH THE USE OF EURO-DIST

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In Greece there are 4 refineries and 2 refining enterprises. Motor Oil Hellas, which owns the Corinth refinery, and the Hellenic Petroleum S.A. that operates those of Thessaloniki, of Aspropyrgos and of Elefsinas. The refinery plant of Hellenic Petroleum has a high degree of adaptability. Its facilities account for around 65% of the nation's total refining capacity and contain crude oil and product storage tanks with a combined capacity of 6.65 million m³. Since 2014, it has been able to vary the yield of middle distillates between 50% - 58% and the yield of gasoline between 20% - 24%. Fuel oil yields are only about 5%, and there are currently no plans to build any more substantial units for the industry. In an effort to compare the capacity between the Greek refineries with those of Europe, it has been found that the Hellenic Petroleum which consists of a total of only 3 refineries has a capacity of 344,000 bpd, while BP's number of facilities is 15 with a total capacity of 1,640,000 bpd. As for the Shell company, its 22 plants have a strength of 1,700,000 bpd.

The refinery complex of Motor Oil Hellas (MOH) consists of two independent refining units, the A and B with total capacity for crude oil distillation of 185,000 bsd (barrels per stream day). It produces a variety of oil products with a highly automated manufacturing process and cutting-edge technologies to ensure the high quality of them. Its storage capacity is accounted to be 2,600,000 m³ (1,000,000 m³ for crude oil, 1,600,000 m³ for intermediate and finished products).

ASTM develops several standard methods that a researcher can follow to arrive at commonly accepted conclusions [1]. The ASTM D-2892 method is a standard method for the processing and study of crude oil and in fact, it is a single and reliable tool for any researcher who wants to characterize mixtures of a crude oil. The method is essentially a crude oil distillation process at a final temperature of about 400 °C. Following the steps of this process, the TBP curve is constructed, which is a graphical representation of the boiling temperature of the fractions resulting from the crude oil distillation process [1].

This standard method is a controlled distillation, where the crude oil is separated into 15 different theoretical plates, hence it is also called (15-Theoretical plate column), with a relative reflux of 5:1. This distillation is usually carried out in a special instrument, such as the EuroDist [2], which is a fully designed instrument to strictly follow the requirements of the method and has the ability to control and determine the pressure values according to the boiling point of each specific fraction according to the method. According to the ASTM D-2892 method for each boiling point range a specific pressure is applied (i.e. for IBP (Initial Boiling Point) – 180 °C the pressure is set by the instrument to 760 mm Hg). For the range 180 - 260 °C the pressure drops to 100 mm Hg, for the range 260 - 320 °C the pressure stabilizes at 10 mm Hg while finally at 320 - 360 °C the pressure stops at 2 mm, where it is the last boiling point according to the method [2].

The ASTM-D2892 method is continuously and widely used because of the automation provided by Eurodist, the monitoring and control of the distillation process through control systems, and the recording and analysis of data through Eurodist Control software. It is also used because of its ability to estimate, determine value, of the fractional yields of various crude oil boiling ranges and therefore provides us with valuable information for technical discussions of a commercial nature.

There are also other than ASTM D-2892 methods for the distillation of many types of crude oils, such as ASTM D-86, D-7169 (HTSD), D-1160 and ASTM D-5236. However, there are differences between these methods, which make a method suitable or unsuitable depending on the process in which it will be used (Table 1). These differences can be minor or major. For example, the difference in temperatures affects the choice of the sample the researcher wishes to study, based on how well the method can provide the appropriate temperature grades for it. On the other hand, the differences in the subclasses of method devices (TBP-L, MPS) do not significantly affect sample selection, because their differences range between the amount of sample and the different configuration of the device.

Table 1 Differences among the ASTM methods

Features	Volume	Pressure	Temperature	
Devices				
ASTM D-5236	Requires small volume (2-22 L)	Low (up to 0.1 mmHg)	High (above 565 °C)	
ASTM D-2892	ASTM D-2892 Requires larger volume (2-100 L)		Low (up to 450 °C)	
ASTM D-1160	Very small volume	High	Low	

Samples were taken from Greek refineries and distilled through the Eurodist following the ASTM D-2892 method, in order to analyze and compare the characteristics of crude oils (Table 2) from two different countries of origin (Kazakhstan, Libya). The TBP distillation curves of the two crude oils were developed to illustrate the distillation profile of the different feedstocks (Figure 1).

Table 2 Crude oil characteristics from two different countries of origin before distillation

Measurements Sample	API GRAVITY @ 60 °F	Viscosity @ 20°C (mm²/s)	Sulphur (%m/m)
Crude oil (LIBYA)	36.4	7.74	0.46
Crude oil (KAZAKHSTAN)	43.9	2.99	0.60

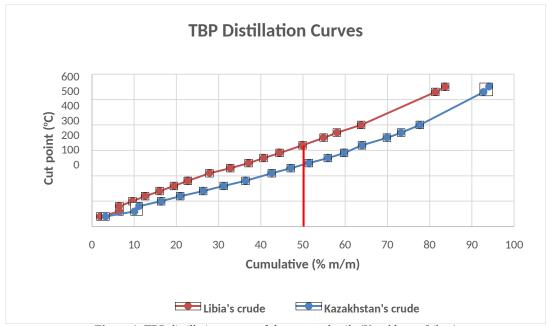


Figure 1: TBP distillation curves of the two crude oils (Kazakhstan, Libya)

From the Figure 1, it can be seen that the 50% of the distilled cuts from Lybia's crude oil requires higher temperatures than those of Kazakhstan's oil. Thus, it was led to the conclusion that the oil of Kazakhstan is more volatile. As it is observed from Table 2, the crude oil of Kazakhstan has a higher API gravity than that of Libya. Moreover, the viscosity of Libya's crude oil appears in higher values, which leads to a thicker raw material and proportionately less volatile. Taking everything into consideration, the distillation of the crude oil coming from Kazakhstan will run in the Greek refineries at lower temperatures than the Libyan one.

Acknowledgements: The authors would like to thank Dr N. C. Kokkinos and A. Lazaridou for their supervision.

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ΠΕΙΡΑΜΑΤΙΚΗ ΣΥΓΚΡΙΤΙΚΗ ΜΕΛΕΤΗ ΑΡΓΩΝ ΠΕΤΡΕΛΑΙΩΝ ΕΛΛΗΝΙΚΩΝ ΔΙΥΛΙΣΤΗΡΙΩΝ ΜΕ ΤΗ ΧΡΗΣΗ ΤΗΣ EURODIST

Το αργό πετρέλαιο θεωρείται σημαντικό ενεργειακό οργανικό υπόστρωμα καθώς αποτελεί την πρώτη ύλη στη διύλιση. Η Ελλάδα συμμετέχει στη βιομηχανία αυτή μέσω τεσσάρων διυλιστηρίων των επιχειρήσεων Motor Oil και Ελληνικά Πετρέλαια Α.Ε.. Ωστόσο οι διαθέσιμες βιβλιογραφικές πληροφορίες σχετικά με τον χαρακτηρισμό των αργών στα ελληνικά διυλιστήρια είναι ελάχιστες. Για τον λόγο αυτό, χρησιμοποιήθηκε στο εργαστήριο η πλήρης αυτοματοποιημένη στήλη Eurodist εφαρμόζοντας την ASTM D-2892 σε δυο αργά πετρέλαια προερχόμενα από το Καζακστάν και από τη Λιβύη. Αναλυτικότερα, πραγματοποιήθηκε ελεγχόμενη απόσταξη σε στήλη 15 θεωρητικών πλακών. Με βάση τις πρότυπες καμπύλες TBP που σχηματίστηκαν, η απόσταξη του αργού πετρελαίου προερχόμενο από το Καζακστάν θα πραγματοποιηθεί στα ελληνικά διυλιστήρια σε χαμηλότερες θερμοκρασίες από το αντίστοιχο της Λιβύης.

QUALITY CONTROL OF CRUDE OIL DISTILLATION'S STRAIGHT RUN FRACTIONS

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Crude oil, known since ancient times, is a mixture of gas, liquid or/and solid hydrocarbons, that mainly consists of carbon (84-87%), hydrogen (12-14%), sulfur (1-2%), nitrogen and oxygen compounds. Straight run cuts are mixtures of hydrocarbons and the result of the atmospheric pressure distillation. Gasoline is a mixture of hydrocarbons that contains four to twelve atoms of carbons. Kerosene -a light distillate of crude oil- is an oily yellow liquid with a characteristic smell. Naphtha -aliphatic or aromatic- contains low boiling hydrocarbons with six to sixteen carbons that include quantities of benzene, toluene and xylene. Gas oil, is a heavier portion, while petroleum residues are the remaining most complicated fraction after crude oil distillation and can contain trace metals and impurities. The physical parameters such as density, boiling point (Table 1), as well as sulfur, nitrogen and aromatics' concentration were examined.

Table 1 Boiling point range for all the straight run fractions of crude oil using ASTM-D2892.

Fractions of crude oil	Boiling point range (°C)	References
Butane (and lighter compounds)	32-50 or <32.2	[1], [2], [4]
Gas	<15,5 and -1611	[1]
Gasoline	15,5-149, -1-180, 67-119	[1], [2], [3], [4]
Kerosene	149-232, 205-260, 168-241	[1], [3], [4]
Light gas oil	260-315, 241-265	[1], [2], [4]
Heavy gas oil	315-425	[1], [2], [4]
Light vacuum gas oil	343-371	[1]
Heavy vacuum gas oil	371-566	[1], [2]
Light naptha	-1 to 50, 90	[2]
Medium naptha	149-139	[1], [2], [3], [4]
Heavy naptha	150-205	[1], [2], [3], [4]
Lubricating oil	>400, >343	[2]
Residues	>425, >510-566	[1], [3], [4]

Blending from straight run fractions of crude oil requires careful quality control to ensure that the final product meets the desired specifications and regulatory standards. Quality control is an important aspect of blending. It involves testing the different fractions of crude oil before blending to determine their physical properties, the compatibility of different fractions and their suitability for blending. Referring to heavy crude oils, they contain high percentages of sulfur, nitrogen and condensed polyaromatic compounds. Such unwanted characteristics can be eradicated through different methods of processing in refineries. As for gasoline, one of the most carefully monitored quality environmental indicators is the sulfur content. The sulfur content can be determined using the method described in ASTM D4294-16 and is calculated in percent of weight or mg/ kg. Gasoline's octane number is also a sign of its quality. Gasoline with a higher octane rating is more desirable and high priced than gasoline with a lower octane number. The experimental results from the refining process of crude oil samples from Kazakhstan and Libia are illustrated at Figure 1.

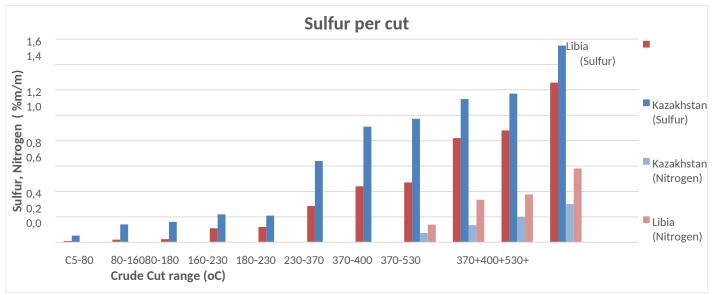
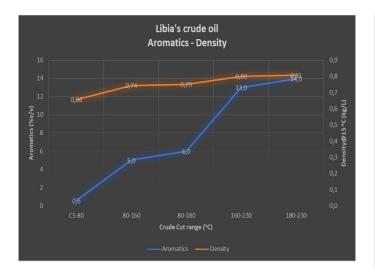


Figure 1 Sulphur and nitrogen content per cut.

The figure above shows the sulfur and nitrogen content (%m/m) per cut of two crude oils from two different countries, Kazakhstan and Libia. Sulfur compounds have an impact on the quality of crude oil and are particularly significant as they increase as oil density does. Comparing the contents of the two crude oils, it is noticed that the Kazakhstan oil cuts have a higher sulfur content. In addition, there is a significant increase in sulfur content in the heavier fractions. On the other hand, nitrogen compounds appear in heavier fractions (>300°C), mainly in residues. In contrast to the sulfur content, it is noticed that Libian crude oil cuts have a higher nitrogen content, the value of which increases the heavier the cut is.

Comparing Figures 2a and 2b, it is observed that in both crude oils (Libia and Kazakhastan) the increase in the concentration of aromatics leads to an increase in density. In figure 2a, the straight run cut with boiling point between $80-160^{\circ}$ C, has 5% v/w aromatics and density equal to 0.74 kg/L, while in figure 2b the same straight run cut has 9.8% v/w and density equal to 0.75 kg/L. Additionally moving towards heavier fractions, a sharp increase of both the aromatics' concentration and density is observed. Indicatively, in both samples an increase in aromaticity by approximately 7 v/w leads to an increase in density by 0.5 kg/L.



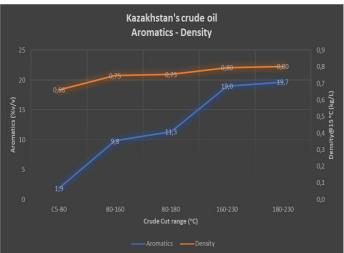


Figure 2a Density and aromatic distribution of Libia's crude oil cuts.

Figure 2b Density and aromatic distribution of Kazakhstan's crude oil cuts.

Aknowledgements: The authors would like to thank Dr N. C. Kokkinos and A. Lazaridou for their supervision.

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ΠΟΙΟΤΙΚΟΣ ΕΛΕΓΧΟΣ ΑΠΕΥΘΕΙΑΣ ΚΛΑΣΜΑΤΩΝ ΑΠΟΣΤΑΞΗΣ ΑΡΓΩΝ ΠΕΤΡΕΛΑΙΩΝ

Το αργό πετρέλαιο, αποτελεί ανομοιογενές μίγμα άνθρακα, υδρογόνου, θείου, αζώτου, ενώσεων οξυγόνου κ.ά. Η κλασματική απόσταξη προσφέρει σειρά απευθείας κλασμάτων με κυριότερα τη βενζίνη, τη κηροζίνη, τη νάφθα, το πετρέλαιο εσωτερικής καύσης και τα υπολείμματα, κάθε ένα από τα οποία εξετάζεται ως προς τις φυσικοχημικές του ιδιότητες. Στη παρούσα εργασία πραγματοποιήθηκε επισκόπηση των χαρακτηριστικών ιδιοτήτων των κλασμάτων αργών πετρελαίων προερχόμενων από το Καζακστάν και τη Λιβύη, με σκοπό τον ποιοτικό έλεγχο. Παρατηρήθηκε ότι η αύξηση της περιεκτικότητας σε θείο και αρωματικές ενώσεις οδηγεί σε υψηλότερη πυκνότητα όλων των απευθείας κλασμάτων, ενώ η αύξηση της περιεκτικότητας σε άζωτο αυξάνει τη πυκνότητα των βαρύτερων μόνο κλασμάτων.

COMPARISON OF CHROMATOGRAPHIC FINGERPRINT AND CHEMOTYPE CHARACTERISTIC OF ESSENTIAL OIL OF ROSEMARY GROWING WILD OR CULTIVATED IN-HOME GARDEN IN KAVALA, GREECE

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Rosmarinus Officinalis is a dense, evergreen, and perennial plant, belonging to the most important medicinal and aromatic plants, due to its antibacterial, antioxidant, and chemo-preventive properties [1]. Rosemary, a member of the most common Greece family *Lamiaceae*, is grown mainly in Mediterranean environments. In Greece, there is a particular interest in the production of the rosemary plant, due to its growing demand and use in a variety of industries [2]. Several reports indicate the correlation between geographical origin and the chemical composition of essential oils [3]. To the best of our knowledge, the only report on the essential oil composition of rosemary plants grown in Northern Greece refers to an experimental farm in the region of Thessaloniki [4]. In the present study, we investigated the chromatographic "signature" of rosemary essential oil from a site in Northeastern Greece and subsequently, the chemotypes and the possible geographic differentiation. Specific objectives include evaluating (i) the effect of different plant ages on chemical composition and (ii) the relationship between essential oils obtained from wild and cultivated populations of rosemary species grown in the same region.

A total of six samples were analyzed for the purpose of this study. The samples of rosemary plants were collected between late March and early April 2023 in Kavala in Northern Greece. Three samples were collected from two nearby home gardens near the sea to minimize environmental covariates. Sample RSNEW refers to a cultivated in-home garden plant 1-year-old. Sample RSOLD1 refers to a 2m tall plant, over 10 years old, characterized as native to the same home garden. Sample RSOLD2 is 8 years old, cultivated in a second short-distance home garden. In addition, a fourth native rosemary plant from our university area in Kavala (RSUNIV), one sample of dried leaves from the local market (RSCOM), and one reference essential oil of Rosmarinus officinalis, cineole type (RSEOREF) was analyzed.

The samples were collected from the aerial part of the plants and were subjected to air/shade drying for a week before the extraction. For the extraction process, 15g of dried samples with 150 ml distilled water were subjected to hydro-distillation for 2,5 hours using Clevenger apparatus.

All samples were then identified by gas chromatography-mass spectrometry (GC-MS) method, using an Agilent 6890N gas chromatograph coupled with an MSD 5973B mass spectrometer. Best separation achieved under the following chromatographic conditions. Capillary column Agilent DB-XLB (low polarity, 30 m x 0.25 mm I.D., and 0.25 μ m film thickness), initial temperature 40°C for 2 min, ramp rate 2°C/min to 270°C, hold 5 min and post run 320°C for 5 min, inlet: split ratio 1:100, Helium flow rate 1mL/min. MS: EI method at 70eV. All concentrations were based on relative area percentages. Identification of organic compounds present was determined by comparison of their mass spectra with available NIST 2.0 MS data and with published data.

The most abundant group of components identified in all samples was oxygenated monoterpenes, namely 1,8-cineole (eucalyptol), linalool, camphor, borneol, 3-pinanone, terpinene-4-ol, α -terpineol, verbenone, and bornyl acetate. Monoterpene hydrocarbons (α -pinene, camphene, myrcene, β -pinene), which are mentioned as a major group in many reports, were not detected in any sample. To our surprise, the results of the analysis revealed significant variability in the chemotypes patterns of the samples examined. The plant Rosmarinus Officinalis is characterized by several essential oils chemotypes varying accordingly to genetic and environmental conditions, seasonality, and geographical origin [5]. The three most common chemotypes of rosemary essential oil are ct. cineol, ct. camphor and ct. verbenone. The main components of the samples analyzed from the farm in the region of Thessaloniki are α -Pinene, 1,8-Cineol, Camphor, Camphene, and Borneol [4]. On the contrary, samples analyzed from Crete Island are characterized by a high amount of a-terpineol (>5%) and the absence of monoterpenes hydrocarbons [6].

Samples RSNEW and RSOLD1 belong to chemotype dominated by verbenone (>25%), and relative high camphor and borneol concentration. 1,8-cineole is the fourth component in concentration in both samples, while borneol acetate is present only in low quantity. Other dominant components are linalool, 3-pinanone, and a-terpineol. The sesquiterpene caryophyllene oxide in present only in sample RSNEW. Similar chemical profile has sample RSUNIV, which belongs also to chemotype verbenone and camphor and borneol are present in equal quantities. In contrast, sample RSOLD2 belongs to chemotype dominated by camphor (36,1%) and only low amount of verbenone (3,5%). The next most abundant components are 1,8-cineole (21,8%), borneol (15,1%) and α -terpineol (4,3%). Moreover, the sample from the local market is camphor type. The other major components are 1.8-cineole and verbenone, while borneol identified in lower concentration. (Figure 1)

According to literature data, high percentages of 1,8-cineole and verbenone are referred to help with allergic disorders. Additionally, cineole and camphor have been shown to have antimicrobial activities against different strains of yeast and bacteria. Furthermore, borneol has been reported to have antibacterial, antispasmodic, and choleretic

effects. Camphor has a positive effect on circulation and respiratory function. Verbenone is also known for its beneficial effect on the liver, high blood sugar, and arteriosclerosis [7].

However, high doses of verbenone and camphor have been contraindicated in pregnancy, small children, and epileptics due to the possible risk of overstimulation, irritation, and various allergic reactions. Camphor, specifically, has been reported to lead to poisoning if ingested orally and there have been reports of toxic absorption through the skin and by inhalation. Considering the beneficial properties of the plant and the results of the analysis of the commercially available rosemary sample, it's possible to guarantee the beneficial properties of the plant and to significantly reduce the adverse reactions caused by some of the plant's components [1, 8].

The samples examined showed two different chemotypes: (1) verbenone/camphor/borneol, and (2) camphor/1,8-cineole/borneol. The percentage of the main components of essential oils are comparatively a little higher in wild populations than cultivated ones. These preliminary results indicated that chemotype and variability in rosemary essential oils are mainly dependent on genetic conditions, rather than where the plants grow and environmental conditions. Further studies are necessary to evaluate the correlation between chemical composition and the population location or plant age and between wild and cultivated plants.

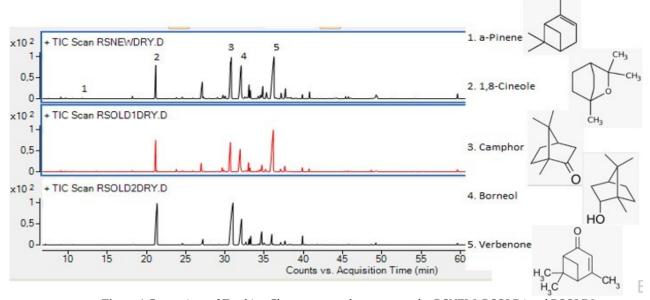


Figure 1 Comparison of Total ion Chromatograms between samples RSNEW, RSOLD1 and RSOLD2

Aknowledgements: The authors would like to thank S. Mitkidou and E. Dimitrakoudi for their supervision.

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ΜΕΛΕΤΉ ΤΟΥ ΧΡΩΜΑΤΟΓΡΑΦΙΚΟΎ ΑΠΟΤΥΠΩΜΑΤΟΣ ΚΑΙ ΤΟΥ ΧΗΜΕΙΟΤΥΠΟΎ ΤΟΥ ΑΙΘΕΡΙΟΎ ΕΛΑΙΟΎ ΤΟΥ ΔΕΝΔΡΟΛΙΒΑΝΟΎ ΠΟΥ ΑΝΑΠΤΎΣΣΕΤΑΙ ΑΓΡΙΟΉ ΚΑΛΛΙΕΡΓΕΙΤΑΙ ΣΕ ΚΗΠΟΎΣ ΣΤΗΝ ΠΕΡΙΟΧΉ ΤΗΣ ΚΑΒΑΛΑΣ

Το αιθέριο έλαιο του δενδρολίβανου παρουσιάζει πολύτιμες αντιοξειδωτικές ιδιότητες και εντυπωσιακές θεραπευτικές δράσεις. Ανήκει στα φυτά που εμφανίζουν διαφορετικούς χημειότυπους και ως εκ τούτου διαφορετική βιολογική δράση ανάλογα με τα συστατικά που βρίσκονται σε μεγαλύτερη αναλογία. Η παρούσα μελέτη στοχεύει στη μελέτη της χημικής σύστασης αιθερίων ελαίων δενδρολίβανου που φύονται άγρια ή καλλιεργούνται σε κήπους σε παραθαλάσσια περιοχή της Καβάλας, στο νοτιοανατολικό τμήμα της Μακεδονίας. Τα αποτελέσματα της GC-MS ανάλυσης έδειξαν ότι τα δείγματα, αν και προέρχονται από την ίδια περιοχή, ανήκουν σε δύο διαφορετικούς χημειότυπους: (1) βερμπενόνη/καμφορά/βορνεόλη και (2) καμφορά/1,8-κινεόλη/βορνεόλη. Το ποσοστό των κύριων συστατικών των αιθερίων ελαίων ήταν συγκριτικά λίγο υψηλότερο στα αυτοφυή φυτά. Η ηλικία των φυτών δεν αποδείχθηκε ότι επηρεάζει το χημικό προφίλ. Τα αποτελέσματα έδειξαν ότι ο χημειότυπος και η μεταβλητότητα στη χημική σύσταση του αιθερίου ελαίου εξαρτώνται κυρίως από τις γενετικές συνθήκες, παρά από την τοποθεσία ανάπτυξης του φυτού και τις περιβαλλοντικές συνθήκες.

TARGET ANALYSIS OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN SOIL USING ULTRASOUND-ASSISTED EXTRACTION (UAE) AND LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY (LC–MS/MS)

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Pharmaceuticals and personal care products (PPCPs) are constantly released into the environment, mainly through wastewater discharge. As a result, these products are extremely likely to end up in soil [1]. In the last decades, PPCPs have raised concerns as pollutants, given the long-term effects they may pose on human health. Some of them have been included in the "Water Framework Directive of the European Union" to be monitored systematically [1,2]. Thus, more and more findings are needed to provide updates [2].

The ultrasound-assisted extraction (UAE) has been largely applied as an extraction method for the isolation of target PPCPs from soil samples [3,4]. In parallel, liquid chromatography-tandem mass spectrometry (LC–MS/MS) combines excellent separation with high sensitivity and selectivity provided by the triple quadrupole (QQQ) mass analyzer, which is ideal for identification and quantification in complex matrices, such as soils. The isolation of the analytes is the first step, prior to MS/MS fragmentation of the analyte using quadrupoles and collision energy. This technique is broadly applied when quantification at trace levels is desirable. The method appears to be particularly valuable for target analysis [6].

Herein, a previously developed and validated protocol for the determination of PPCPs in soil was verified and applied in real samples [1]. Spiked blank soil (50 ng/g) was used for verification purposes, while real samples collected from different cities in Greece were used to test method applicability. Once collected, the samples were dried, homogenized and sieved, prior to be stored in the freezer (-18 °C). Briefly, 2 g of soil were weighed and placed into centrifuge tubes. Subsequently, the samples were extracted by sonication with 5 mL MeOH (0.5% v/v, formic acid) in an ultrasonic bath for 15 min. After the extraction, the tubes were centrifuged at 3500 rpm for 10 min. The supernatant was then transferred to a clean tube and the extraction procedure was repeated in triplicate. A small volume of the final extract (approximately 1.5 mL) was transferred into vials, filtered with PTFE filters (0.22 μ m), and injected into an LC–MS/MS system.

The applied method was verified and evaluated in terms of linearity, accuracy (% recoveries), method detection limits (MDL) and method quantification limits (MQL), as well as precision expressed as repeatability (n=5) (Table 1). The % recoveries ranged from 50 to 106%, MDLs and MQLs ranged from 0.9 to 5 ng g⁻¹ and 2.9 to 16.5 ng g⁻¹, respectively, while the average repeatability expressed as RSD_r was 9.5% (Figure 1). The linear correlation coefficient was excellent, exhibiting an average of 0.9988. The method applicability was tested over real soil samples collected in Lamia, Ioannina, Thessaloniki, and Crete, close to sources of anthropogenic pollution, demonstrating very few positive findings (<MQL in all cases).

Table 1. Method verification and application results (MQL and real sample's concentration are expressed in ng g⁻¹)

	%Rec	RSDr%	MQL (ng g ⁻¹)	\mathbb{R}^2	Sample 1 (Crete)	Sample 2 (Lamia)	Sample 3 (Ioannina)	Sample 4 (Thessaloniki)
Paracetamol	70	9.7	3.3	0.9980	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Diclofenac	70	9.7	5.0	0.9987	<mdl< td=""><td><mql< td=""><td><mql< td=""><td><mdl< td=""></mdl<></td></mql<></td></mql<></td></mdl<>	<mql< td=""><td><mql< td=""><td><mdl< td=""></mdl<></td></mql<></td></mql<>	<mql< td=""><td><mdl< td=""></mdl<></td></mql<>	<mdl< td=""></mdl<>
Ciprofloxacin	50	14.6	5.5	0.9990	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Sulfamethoxazole	60	8.4	4.5	0.9991	<mql< td=""><td><mql< td=""><td><mql< td=""><td><mdl< td=""></mdl<></td></mql<></td></mql<></td></mql<>	<mql< td=""><td><mql< td=""><td><mdl< td=""></mdl<></td></mql<></td></mql<>	<mql< td=""><td><mdl< td=""></mdl<></td></mql<>	<mdl< td=""></mdl<>
Caffeine	97	13.4	3.1	0.9990	<mql< td=""><td><mql< td=""><td><mql< td=""><td><mql< td=""></mql<></td></mql<></td></mql<></td></mql<>	<mql< td=""><td><mql< td=""><td><mql< td=""></mql<></td></mql<></td></mql<>	<mql< td=""><td><mql< td=""></mql<></td></mql<>	<mql< td=""></mql<>
Gemfibrozil	70	8.2	5.5	0.9991	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Atenolol	67	8.8	3.8	0.9994	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Cimetidine	68	16.2	6.2	0.9980	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Phenazone	99	8.7	9.9	0.9990	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Risperidone	93	7.6	2.9	0.9990	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Citalopram	106	7.4	3.1	0.9991	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Carbamazepine	100	6.8	5.5	0.9990	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Fluoxetine	76	7.6	12.4	0.9987	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Ketoprofen	71	12.4	4.5	0.9987	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Bezafibrate	103	4.8	6.2	0.9984	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
Fenofibrate	71	7.4	16.5	0.9987	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>

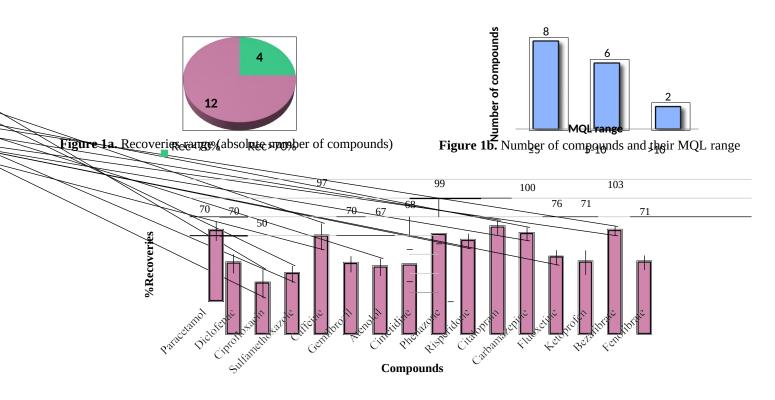


Figure 1c. Average recoveries (n=5) for the studied compounds along with their calculated RSD_r%

Considering that 56% of the studied PPCPs showed recoveries > 70% and low enough MQLs, it is concluded that the verified process is sufficient to trace the occurrence of PPCPs. Apart from caffeine, which is a common anthropogenic pollution marker, diclofenac (non-steroidal anti-inflammatory drug) and sulfamethoxazole (antibiotic and veterinary medicine) were detected, implying the successful applicability of the method in areas with moderate to intensive anthropogenic activities.

Acknowledgment: The authors would like to thank Dr. C. Nannou for her supervision.

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ΑΝΑΛΎΣΗ ΦΑΡΜΑΚΕΥΤΙΚΏΝ ΚΑΙ ΠΡΟΙΌΝΤΏΝ ΠΡΟΣΩΠΙΚΉΣ ΦΡΟΝΤΊΔΑΣ ΣΕ ΕΔΑΦΟΣ ΜΕ ΧΡΉΣΗ ΕΚΧΥΛΊΣΗΣ ΜΕ ΥΠΕΡΗΧΟΎΣ ΚΑΙ ΥΓΡΉΣ ΧΡΏΜΑΤΟΓΡΑΦΊΑΣ ΣΥΖΕΥΓΜΕΝΉΣ ΜΕ ΦΑΣΜΑΤΟΜΕΤΡΊΑ ΜΑΖΑΣ

Η παρουσία φαρμακευτικών στο περιβάλλον αποτελεί μείζον ζήτημα τις τελευταίες δεκαετίες. Τα φάρμακα εισέρχονται στο περιβάλλον μέσω της απέκκρισης από τον άνθρωπο ή της απευθείας διάθεσης των ληγμένων/αχρησιμοποίητων σκευασμάτων, έχοντας ως αποτέλεσμα οι εκροές των Μονάδων Επεξεργασίας Υγρών Αποβλήτων (ΜΕΥΑ), μεταξύ άλλων, να αποτελούν την κύρια οδό για την είσοδό τους στο περιβάλλον και κατ' επέκταση στα εδάφη. Στην παρούσα εργασία, πραγματοποιήθηκε επαλήθευση μιας επικυρωμένης μεθόδου για τον προσδιορισμό φαρμακευτικών ενώσεων σε έδαφος, με τη χρήση εκχύλισης με υπερήχους σε συνδυασμό με υγρή χρωματογραφία συζευγμένη με φασματομετρία μάζας (LC–MS/MS). Η μέθοδος παρουσίασε εξαιρετική ακρίβεια (ανακτήσεις 50-106%, μέση επαναληψιμότητα 9,5%) και γραμμικότητα καθώς και χαμηλά όρια ανίχνευσης και ποσοτικοποίησης (0,9-5 ng g⁻¹ και 2,9-16,5 ng g⁻¹, αντίστοιχα). Για την εξέταση της εφαρμοσιμότητάς της σε πραγματικά δείγματα αναλύθηκαν άγνωστα δείγματα από διαφορετικές περιοχές με μέτρια έως έντονη ανθρωπογενή ρύπανση και ταυτοποιήθηκαν τρεις από τις επιλεγμένες ενώσεις (καφεΐνη, δικλοφενάκη και σουλφαμεθοξαζόλη).

e-POSTER

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