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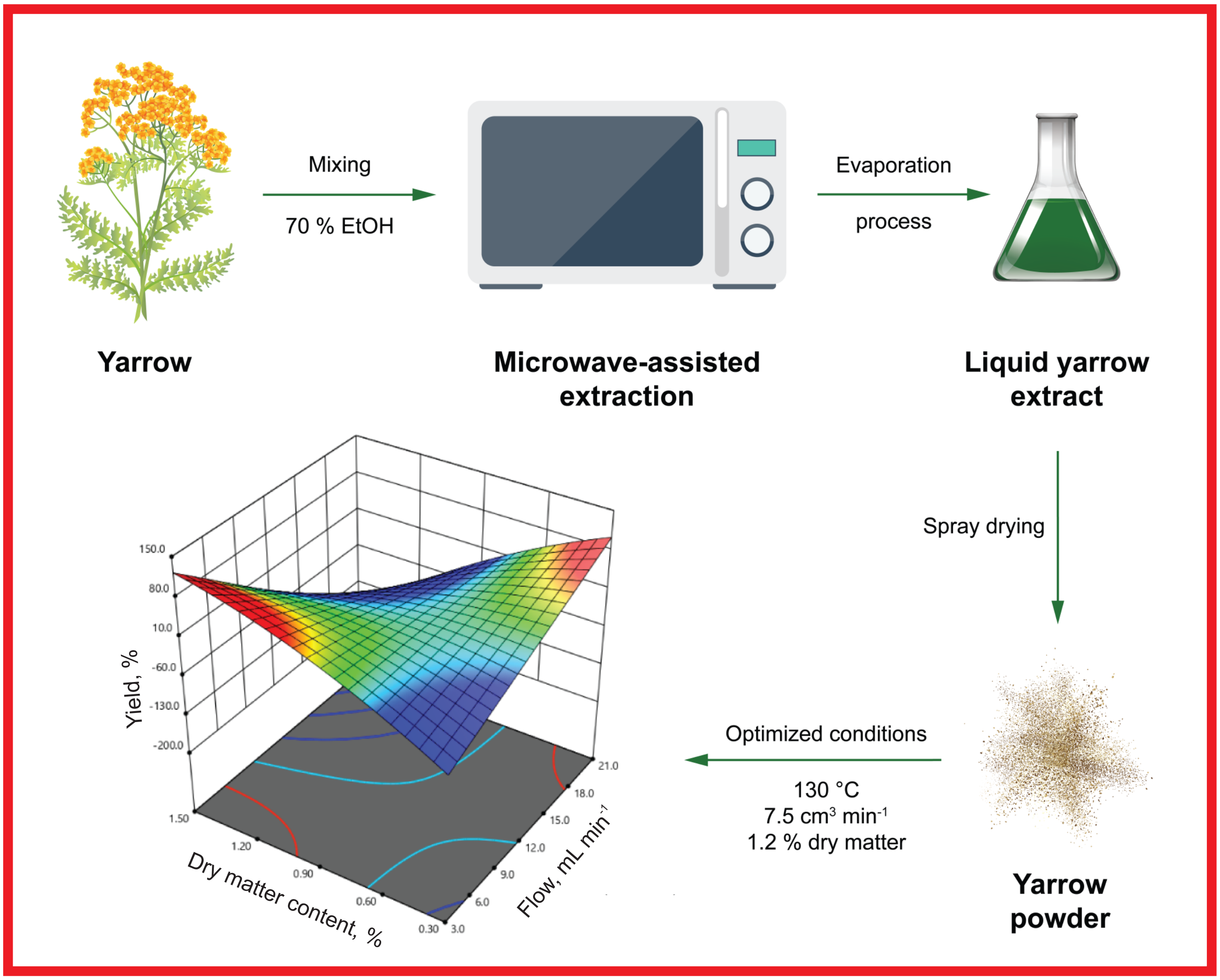
Vol. 75

# Hemijska industrija

Časopis Saveza hemijskih inženjera Srbije

# Chemical Industry

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## SADRŽAJ/CONTENTS

# Removal of diesel pollution by biochar – support in water remediation

**Zorica Lopičić[1], Jelena Avdalović[2], Jelena Milojković[1], Anja Antanasković[1], Marija Lješević[2], Nikoleta Lugonja[2] and Tatjana Šoštarić[1]**

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*Abstract*

Water contaminated with diesel oil represents one of the greatest challenges in waste water management. Water soluble fraction (WSF) is of particular interest because of its toxicity to aquatic organisms and discharge regulations set by environmental authorities. Biochar sorbents have attracted great attention, due to their low cost origin and advantageous properties as well as high sorption capacities in sorption processes. In this study, we have reported the synthesis and characteristics of novel biochar sorbent made from waste lignocellulosic biomass (peach stones (PS)) and evaluated its possible application in removal of diesel WSF from synthetic water. Physiochemical characteristics of the biochar sample were analysed by scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) method, and Fourier-transform infrared spectroscopy (FTIR), along with the elemental analysis. Characterisation of PS biochar (PS-B) indicated high multi porous surface area (159.1 $m^2$ $g^{-1}$) with the average pore diameter 2.7 nm. FTIR results indicated higher presence of aromatic compounds in PS-B as compared to PS. The sorption experiments performed in a batch system using PS-B resulted in more than 95 % removal of diesel WSF, reaching equilibrium after 5 h. Equilibrium data were well fitted by Freundlich isotherm, while the pseudo-second order equation fitted well the kinetic data, indicating chemisorption involving valency forces through the sharing/exchange of electrons between the sorbent and PS-B. Applications of ecotoxicology tests based on a microbial biosensor (*Aliivibrio fischeri*) have shown a significant toxicity reduction of water sample after the treatment with biochar.

*Keywords:* petroleum hydrocarbons; food processing waste; pyrolysed biomass; sorption; ecotoxicology.

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## 1. INTRODUCTION

Development of technology and industry, population growth, and urbanization had led to the inevitable generation of waste which amounts have exceeded the self-purification capacity of ecosystems. Wastes that cannot be decomposed by biological processes degrade the environment, with negative consequences for the ecosystem and human health. Crude oil at its origin is not considered as a pollutant, but with further exploitation, processing, storage, transport, it becomes a serious environmental issue. During the processing of crude oil into derivatives (gasoline, diesel fuel, asphalt bases, heating oil, kerosene and liquefied petroleum gas), various pollutants are emitted into the atmosphere, while harmful liquid and solid wastes are generated on a daily basis. Most of them are toxic, especially polycyclic and aromatic hydrocarbons, which have been classified as carcinogenic.

According to reference [1], world oil consumption in the period from 1994 to 2019 had increased by approximately 0.9 million barrels per day (b/d), while the demand for all liquid fuels (including biofuels) increased by 1.1 million b/d and reached, for the first time in 2019, value of 100 million b/d. In 2020, as a consequence of global lockdowns and

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other coronavirus restrictions, world oil consumption as well as oil production, dropped for the first time since 2009 by 9.1 million b/d and 6.6 million b/d, respectively.

Petroleum and its derivatives consist of a mixture of hydrocarbons of diverse chemical configurations [2]. They are one of the most common sources of environmental pollution and it is therefore necessary to take appropriate measures to mitigate the negative effects they induce. It is very important to say that there are numerous techniques developed for removal of insoluble (floating) diesel oil fractions, but the fraction that dissolves into water is the fraction that intimately contacts aquatic organisms, posing serious environmental hazard. The term "water soluble fraction" (WSF) is commonly used to describe the aqueous solution, which is formed when diesel oil and water are brought into contact, containing several toxic constituents like hydrocarbons (polycyclic aromatic hydrocarbons (PAHs), mono aromatic hydrocarbons as BTEX (benzene, toluene, ethylbenzene and xylenes), phenols and heterocyclic compounds, containing nitrogen and sulphur) and heavy metals, among which copper and nickel are the most common [3]. The composition and concentration of the WSF depends upon several factors such as: composition of the oil, properties of the water, temperature and the method of preparation. Wastewaters loaded with WSF can neither be directly discharged into the environment nor collected by the municipal system, imposing the urgent need for alternative treatment strategies. For this purpose, different techniques are used, but sorption and biological remediation techniques are often considered as the ones with the most ecological and economic benefits. Both techniques are inexpensive, relatively easy to perform, having high removal efficiencies with minimal energy/chemical consumption and secondary contamination.

Recently, sorbents of biological origin (biosorbents) have been drawing a lot of attention, due to their low price and advantageous physicochemical properties, which made these materials good hydrocarbons sorbents. By-products and/or lignocellulosic biomass waste from the food industry or agriculture are of particular interest, because their application leads to a decrease of waste generation onto landfills, reduces greenhouse gas emissions, and provides a new value to the wasted products. Lignocellulosic biomasses are widespread, available, and cheap, with characteristics suitable for sorbents development. Some of them have proven to be good sorbents for oil removal: walnut shell [4], chipboard, rice husk and coconut shell [2], sugar cane processing waste [5], etc. Excellent physicochemical properties and diversified functionalities of biochar provide the great potential in wastewater treatment fields [6]. Biochar (a renewable material generated from waste) can be a cost-effective substitute for activated carbon (AC) in selected pollutant adsorption processes because AC is commonly generated from non-renewable sources and requires energy-intensive thermal activation to develop appropriate sorption properties [7]. Compared with the AC production price ($1,100− $1,700 per ton), production of biochar costs from 350 to 1,200 $ per ton, on a mass basis [7]. Biochar production might have other important environmental benefits including energy coproduction, carbon sequestration, and bio-waste valorisation. Implementation of the food industry waste biomass in this manner would help in minimizing waste disposal and resource depletion at the same time [8]. Abdullah et al. [9] further pointed out that natural organic sorbents are easier to dispose after use and can be co-applied with other techniques such as bioremediation.

To the best of our knowledge, purification of waste waters contaminated by diesel using biochar produced of peach stones was not investigated yet. To produce a valuable low-cost adsorbent with excellent surface structure, and high absorption performance of diesel pollution, we have chosen peach stones (waste from the fruit processing industry), since most of the by-products from biomass in Serbia are still treated as waste. So, the new approach, described in this paper will integrate the waste management and environment/economy principles in order to support waste utilization in Serbia and possibly other countries. The obtained results might serve other researchers who are investigating similar material types in attaining effective sorbents for water purification.

In this paper, the possibility of unmodified peach stone biochar prepared at suitable pyrolysis temperatures as a novel sorbent in the removal of diesel WSF polluted wastewater was investigated. Specifically, physiochemical characteristics of the samples were analysed by scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) method, and Fourier-transform infrared spectroscopy (FTIR), along with elemental analysis. The sorption kinetics and isotherms were studied as the assessment guides for removal of these organic pollutants from contaminated water. After the sorption process was completed, ecotoxicology tests were conducted using initial and treated water samples, in order to evaluate the effect of biochar on the toxicity of chemical compounds found in water samples.

## 2. EXPERIMENTAL

### 2. 1. Materials

Peach stones (*Prunus persica* L.) were obtained from the Juice Factory Vino Župa Aleksandrovac, Serbia. They were washed with tap water in order to remove dirt from the surface, and dried at room temperature. Dried stones were further grinded using the vibrating disk mill Siebtechnik – TS250 (Siebtechnik GmbH, Germany), and sieved into different particle sizes. For the purposes of these investigations, the class between 0.1 to 0.5 mm was used. The ground peach samples (PS) were further pyrolysed at 500 °C under oxygen-limited conditions in a Nabertherm 1300 muffle furnace (Nabertherm, Germany) at the heating rate of 10 °C min$^{-1}$, for 1 h. Finally, the obtained biochar (PS-B) was stored in closed vials with polypropylene caps in the dark until the sorption experiments started.

Diesel oil used in sorption experiments was purchased from the local commercial gas station (NIS Petrol, Serbia).

Bacterial strain of *Aliivibrio fischeri* NRRL B-11177 (Macherey-Nagel GmbH & Co. KG, and Duren, Germany) was used for the evaluation of acute eco-toxicity of water contaminated with diesel fuel before/after treatment with biochar.

### 2. 2. Sorbent characterisation

Vario-EL III; CHNS-O Elementar Analyzer (Hanau, Germany) has been used for elemental analysis (C, H, N and S). Operating ranges varied between the elements: 0.03–20 mg for C; 0.03–3.0 mg for H; 0.03–2.0 mg for N and 0.03–6.0 mg for S. Oxygen content was obtained by subtracting the sum of the obtained elemental values from 100 %.

Contact pH, also known as the pH of the suspension ($pH_{sus}$) was determined according to the procedure described in the ASTM D6851-02 standard. The pH of the suspension solution was determined by suspending 0.2 g of sorbent material in 30 cm$^3$ of distilled water, left in a closed container and stirred occasionally for 72 h after which pH was measured by using a pH meter SensION3 (Hach, USA).

Scanning Electron Microscopy− Energy Dispersive X-Ray Spectroscopy (SEM− EDX) analysis was performed on dried samples under vacuum coated with thin layer of gold and observed using a JEOL JSM-6610 LV model (JEOL Ltd., Japan).

The specific surface area (SSA) and the porosity of the PS and PS-B were determined by nitrogen adsorption–desorption isotherm at −195.8 °C on ASAP 2020 (Micromeritics Instrument Corporation, Norcross, GA, USA). The SSA was calculated according to the Brunauer–Emmett–Teller (BET) method [10].

Surface functional groups in samples were determined by Fourier Transform Infrared Spectroscopy (ATR mode) using a Thermo Nicolet 6700 FTIR device (International Equipment Trading Ltd., USA). The spectra were recorded by averaging 32 scans from 4000 to 400 cm$^{-1}$.

### 2. 3. Batch sorption experiments

A saturated solution of diesel oil was prepared as follows: distilled water and diesel oil in excess were poured into a glass separator funnel, mixed vigorously by shaking, and left 24 h for phases to settle down. The saturated solution of WSFs was collected from the bottom of the bottle and used for further experiments. For kinetic experiments, initial saturated diesel solutions at the concentration of 20 mg dm$^{-3}$ were shaken for different time intervals (0.25, 0.5, 1, 2, 3, 4, 6, 12 and 24 h). Experiments were conducted by adding 0.15 g biochars to 100 cm$^3$ diesel solution in 250 cm$^3$ Erlenmeyer flasks at 25 °C, and placed at orbital shaker (Heidolph Unimax 1010, USA) at the agitation speed of 200 rpm. The pH value of the initial solutions was 6.

Adsorption isotherm experiments were conducted under a constant agitation rate (200 rpm), initial pH 6, and an initial WSF concentration varying from 2 to 20 mg dm$^{-3}$ at equilibrium time of 24 h. The solid and liquid phases in all experiments were separated in a centrifuge at 4000 rpm after a specific period. Finally, diesel concentration in the liquid phase was detected according to SRPS EN method [11], by gas chromatographic analyses conducted on an Agilent 7890A gas chromatograph (Agilent Technologies, USA) with a flame ionization detector (FID). The gas chromatograph was equipped with a 30 m × 0.32 mm i.d. × 0.25 µm film chromatographic column HP-5. The chromatographic conditions were set as follows: injection at 60 °C oven temperature (injector temperature 250 °C, detector temperature 300 °C), 1 min hold, with the temperature increase programmed at 4 °C·min$^{-1}$ to 300 °C. Velocity of hydrogen, that was used as a gas carrier, was 30 cm·s$^{-1}$. Data were processed using the ChemStation software from Agilent Technologies. All experiments were carried out two times, and the average values are presented.

The sorption capacity *q* and the removal efficiency of diesel WSF were calculated according to the following equations:

$$q_e = (C_o - C_e) / mV \quad (1)$$

$$R = (C_o - C_e) / C_o\ 100 \quad (2)$$

where $C_e$ and $C_o$ are the equilibrium and the initial concentrations, respectively; *V* is the volume of the solution and *m* is the weight of the sorbent.

### 2. 4. Eco-toxicity test

Bacterial strain *Aliivibrio fischeri* NRRL B-11177 (Macherey-Nagel GmbH & Co. KG, and Duren, Germany) was used for evaluation of acute eco-toxicity of water contaminated with diesel fuel before/after treatment with biochar. The test was performed according to [12], using freeze-dried bacteria and BioFix® Lumi-10 (Macherey-Nagel GmbH & Co. KG, Duren, Germany). Tested samples were prepared so that the pH was between 6.5-7.5 and NaCl concentration was 20 g dm$^{-3}$. Freeze-dried bacteria were suspended in the reconstitution solution according to the manufacturer's instructions. Bacteria were incubated at 15 °C at several dilutions of the initial sample with 20 mg dm$^{-3}$ WSF (50, 25, 12.5, 6.25 and 3.125 %) for 15 min. The results were expressed as percent of inhibition and the effective concentrations causing 50 % luminescence inhibition ($EC_{50}$ values) were calculated. All tests were performed in triplicates.

## 3. RESULTS AND DISCUSSION

### 3. 1. Sorbent characterisation

The results of PS-B characterisation along with characterisation of the initial material (PS) which was performed previously [13] are presented in Table 1.

*Table 1. Elemental compositions of the peach stone feedstock (PS) and derived biochar (PS-B)*

| | N | C | H | S | O** | H/C | O/C |
|---|---|---|---|---|---|---|---|
| | Content, % | | | | | | |
| PS* | 0.27 | 47.42 | 6.06 | 0.21 | 46.04 | 0.13 | 0.97 |
| PS-B | 0.30 | 69.37 | 2.74 | <0.10 | 27.49 | 0.04 | 0.40 |

*data reported in [13]; **calculated as difference from 100 %

PS-B was prepared by pyrolysis, which has a great effect on the properties of biochar. Pyrolysis favours the removal of H and O over C, because the volatile components, which form a significant fraction of the surface functional group elements, are progressively lost during this process, thus leading to biochars with higher C concentration [14].

Ratios H/C and O/C are used to determine the degree of aromaticity and hydrophilicity in biochar [15]. The H/C ratios of PS and PS-B are 0.13 and 0.04, respectively. Lower H/C ratio indicates the stronger aromatic and stable structure of biochar. Also, the PS-B sample has a lower O/C ratio than PS, which is caused by the lower number of polar functional groups on the surface of PS-B. Onorevoli *et al.* [16] also obtained lower H/C and O/C ratios for lignin biochar, compared to the native sample.

The $pH_{sus}$ of biochar suspended in water was found to be 5.76, which is higher compared to the $pH_{sus}$ of the raw material (4.10). This increase in pH might be a consequence of the increased concentration of inorganic elements, which are not pyrolized, already present in the original feedstocks, such as alkali ions and carbonates formed by $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ ions [17].

The SEM micrograph (Fig. 1) showed that the pyrolysed sample mostly retains its original structure similar to the raw PS biomass [8], presented in Figure D-1 (Supplementary material). As can be seen from Fig. 1a, the SEM micrograph indicated that PS-B contains large (20-30 μm) and small (1-3 μm) diameter pores where the smaller ones are located inside the larger pores. Amounts of detected elements are presented in Figure 1b. Gold was observed because of the sample preparation. EDX analysis results are consistent with the elemental composition of the derived biochar (PS-B) (Table 1).

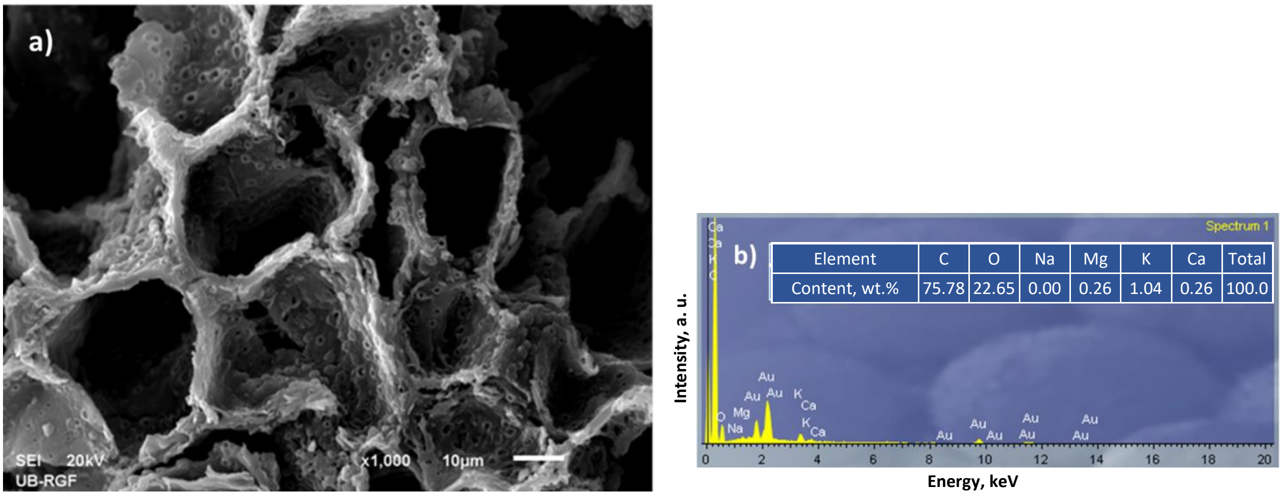


*Figure 1. SEM-EDX analysis of the biochar sample (PS-B): a) SEM micrograph; b) EDX analysis results*

According to the BET analysis the specific surface area (SSA) increased from 0.545 $m^2\ g^{-1}$ (PS) to 159.1 $m^2\ g^{-1}$ (PS-B) after the thermal treatment, which is highly beneficial for sorption processes by biochar. The increase in SSA occurs due to the destruction of organic groups and formation of micropores in biochar after high temperature treatment [15]. BET analysis results also showed that the average pore diameter drastically decreased from 28.5 nm for PS to much lower pore diameter for PS-B which is 2.7 nm, both falling in mesopores range (2-50 nm). It is evident that the obtained material PS-B has highly developed micro- and meso- pore structures in comparison to PS. According to the literature [18] biomass rich with lignin develops macro- porous biochar, while biomass rich in cellulose develops a predominantly microporous biochar after pyrolysis. Since raw PS has 58.0 % cellulose and 16.5 % lignin, such structure can be expected after the thermal treatment at 500 °C [19].

FTIR spectra (Fig. 2) of raw peach stones (PS) showed absorption bands at 3340, 2920, 1422 and 1230 $cm^{-1}$ which disappeared after pyrolysis.

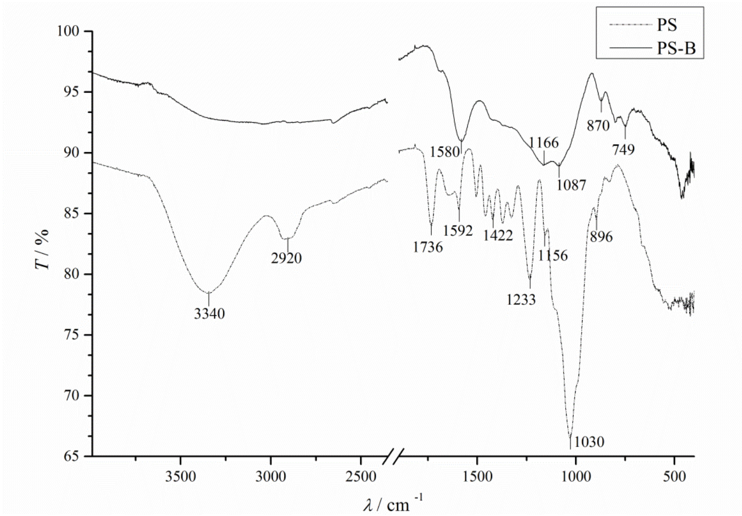


*Figure 2. FTIR spectra of the raw material (PS) and biochar (PS-B)*

These peaks can be attributed to the hydroxyl (–OH) stretching, alkane $–CH_2$ symmetric stretching, in-plane bending of carbonyl (–COH) and alkane $–CH_2$ symmetric stretching, respectively [20]. As a result of hemicellulose degradation after pyrolysis the prominent peak at 1736 $cm^{-1}$ assigned to aromatic carbonyl or carboxyl C=O stretching of carboxylic acids or their esters has disappeared too [21, 22]. There are clear shifts which correspond to –COO− from 1592 to 1580 $cm^{-1}$ and asymmetric C–OC bridge stretching from 1156 $cm^{-1}$ in PS to 1166 $cm^{-1}$ for PS-B. Lessening of peaks in the fingerprint region is the result of lignin depolymerisation. When the pyrolysis reaction temperature is within the range

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of 150-400 °C lignin depolymerisation starts with the cleavage of weak linkages (most of the ether linkages are destroyed including β-O-4, which is one of the most abundant linkages within the lignin molecule [23]). Disappearance of the peak at 1233 cm$^{-1}$ confirms this process because this peak is attributed to C-O-C stretching from aryl-alkyl ether linkage (*i.e.* α and β-O-4 linkages) [24]. Peaks recognized in the region of 700 and 900 cm$^{-1}$ originated from aromatic compounds. FTIR spectra presented in Figure 2 reveal the evolution of aromatic functional groups replacing aliphatic groups of raw biomass; they show an increase in aromatic carbon in the biochar sample. At a temperature of 500 °C, aliphatic radicals rich in oxygen from lignin and hemicellulose are nearly entirely volatilized; carbon chains that remain reorganized are creating polycondensed aromatic structures [25].

### 3. 2. Sorption kinetics results

Adsorption kinetics profiles of diesel WSF to the biochar over time are shown in Figure 3. As it can be seen (Fig.3.a), the sorption is initially fast, the WSF concentration dropping from the initial 20 mg dm$^{-3}$ down to 4.2 mg dm$^{-3}$ after only 30 min of contact time, where more than 79% of the initial pollution is removed. The WSF removal was initially fast and then decreased towards accomplishing the equilibrium. The adsorption rate was higher during the first hour because of the presence of active sites on the biochar surface. The equilibrium is attained after 5 h with the maximum removal percentage of approximately 95 % at the investigated experimental conditions. Experimental kinetic data were further modeled by using nonlinear forms, as recommended in [26], of the three most common models: pseudo-first order [27], pseudo-second order [28] and Elovich [29], which is shown in Figure 3b.

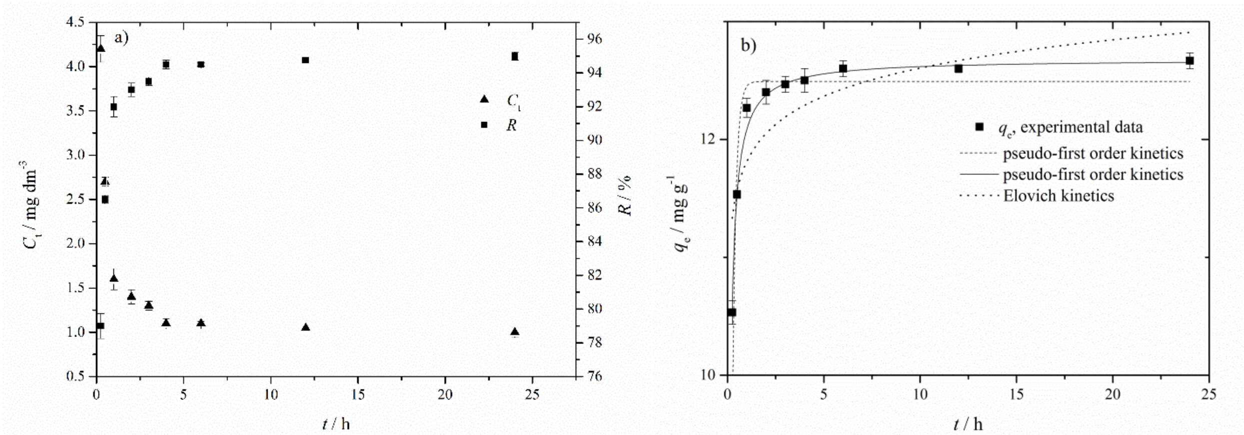


*Figure 3. Sorption kinetics: a) experimentally determined diesel WSF concentration ($C_t$) and removal percentage (R) over time; b) sorbed WSF per mass of PS-B ($q_t$) as a function of time: experimental data (symbols) and the best fit predictions of the pseudo-first and pseudo second order kinetics and Elovich's equation (lines)*

As it can be seen, the best fit was obtained by using the pseudo second order kinetic model, with the correlation coefficient ($R^2$) equal to 0.989 and low chi-factor ($\chi^2$) of 0.006, indicating the sorption mechanism that is limited by bonding forces through electrons sharing between the sorbate (diesel WSF) and the sorbent (PS-B), and implying that chemical process might be the limiting step in diesel sorption [30]. Application of the Elovich model does not fit any experimental data, over-estimating the equilibrium stage at the same time.

Previous reports on sorption kinetics by biochars of other origins suggest that pseudo second order kinetics govern most of the sorption processes in which the cellulose containing porous adsorbents are involved. For example, Cai *et al.* [31] have investigated the potential of crab shell biochar in sorption of diesel oil and reported that the adsorption process by the KOH modified biochar was well described by the pseudo-second-order model, indicating similar mechanism as that in the present work. Barman *et al.* [32] have shown that pseudo second order kinetics best described the PAH sorption process onto alkali modified biochar made from Indian almond nut shells, indicating that the limiting factor is chemical interaction such as electron sharing or exchange amongst the adsorbate and adsorbent species. They have also optimised sorption conditions based on the Derringer's desirability factor and reported that the initial PAH concentration should be 5.43 mg dm$^{-3}$ for the highest removal efficiency at the experimental conditions applied. This concentration falls in the range of investigated concentrations performed in the present study.

### 3. 3. Isotherm determination results

The relation between the equilibrium activity or concentration of the sorbent and the quantity of sorbate on its surface (at the constant temperature) is usually employed to describe adsorption behaviour. According to literature [33], there are five types of adsorption isotherms, each attained under unique conditions. The experimental adsorption isotherm determination results were modeled by using different isotherm types, but the shape of the obtained data (Fig. 4) indicated the Freundlich model as the only appropriate. This model is widely applied in heterogeneous systems especially for adsorption of organic compounds or highly interactive species on activated carbon and molecular sieves. The Freundlich isotherm equation [34] is given by:

$$q_e = K_f C_e^{1/n} \quad (3)$$

where $q_e$ is the sorption capacity at equilibrium, $K_f$ is the Freundlich constant, $C_e$ is the equilibrium concentration of the sorbate in the solution, and $1/n$ is the Freundlich heterogeneity factor.

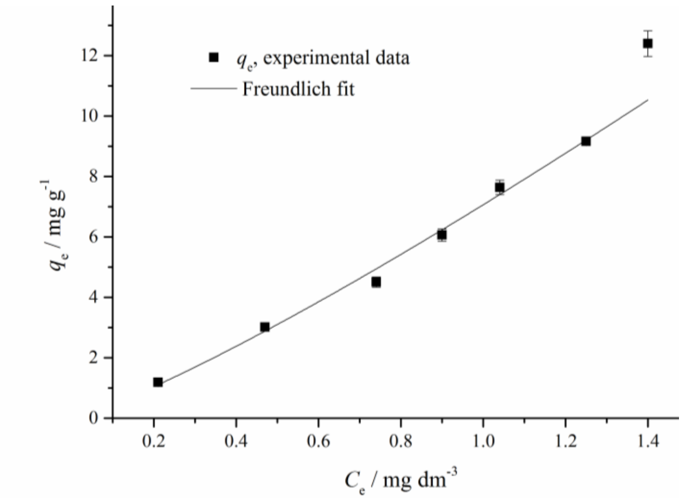


*Figure 4. Experimental isotherm data and nonlinear Freundlich model fit of diesel WSF sorption onto PS-B*

Sorption of diesel WSF onto PS-B follows the pattern of type III isotherm, which reflects no saturation limit, and indicates a multi-layer formation after completion of the monolayer, where the adsorbate interaction with the adsorbed layer is greater than the interaction with the adsorbent surface. Such behavior is most often found in sorbents with a wide distribution of pore sizes, where after the first point of inflexion when a monolayer is completed, the subsequent sorption process occurs in successive layers.

The isotherm shape shown at Figure 4, may also be referenced as the H-type (high-affinity) isotherm which is indication of strong sorbate–sorbent interactions such as formation of inner-sphere complexes [35]. The value of 1/n, the Freundlich heterogeneity factor, might range from 0 to 1, in the case of chemisorption [36], while the values higher than 1 imply cooperative adsorption. In the case of diesel WSF sorption onto PS-B, the value of $1/n$ was determined as 0.705, which indicates the chemisorption nature of this sorption process. This may well be reasonable, since the thermal conversion of biomass involves fracturing of most of the chemical bonds initially present in the biomass and many of these bonds are left “dangling”, giving rise to chemisorption properties of the pyrolysed product [37].

The isotherm data were also fitted by the Langmuir isotherm model, which resulted in a lower coefficient of determination, $R^2$, and a higher $\chi^2$ value (Table D-1, Supplementary material, S.2), but the obtained maximal capacity, $q_m$, was used to compare sorption performance of PS-B toward diesel oil fractions with other sorbents found in literature. As it can be seen (Table D-2), the obtained maximum sorption capacity ($q_m$ = 64.97 mg g$^{-1}$) falls in the range of published values, indicating that peach stone biochar can be efficiently used as a sorbent for diesel oil WSFs.

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### 3. 4. Eco-toxicity tests

The increased use of diesel fuel raises the likelihood of aquatic contamination due to accidents in the production and transportation of these fuels [38]. It was shown that diesel fuel has a negative impact on living organisms [38,39], which is why the biological monitoring is of particular interest when assessing the effectiveness of remediation methods. *Aliivibrio fischeri* bioluminescence inhibition bioassay is a rapid, sensitive and cost effective method for the toxicity monitoring [40].

Results of the acute ecotoxicity test on the bacteria *Aliivibrio fischeri* are shown in Figure 5. Untreated water contaminated with diesel (control-C) causes 80 % of bioluminescence inhibition with the $EC_{50}$ value of 11.7 ± 1.5 %. The inhibition level is concentration dependent, where higher concentrations cause higher inhibition. After the treatment with biochar (BT), bioluminescence inhibition dropped to around 30-40 %, regardless of the concentration. These results indicate a decrease in toxicity of diesel WSF on *Aliivibrio fischeri* after water treatment by biochar PS-B.

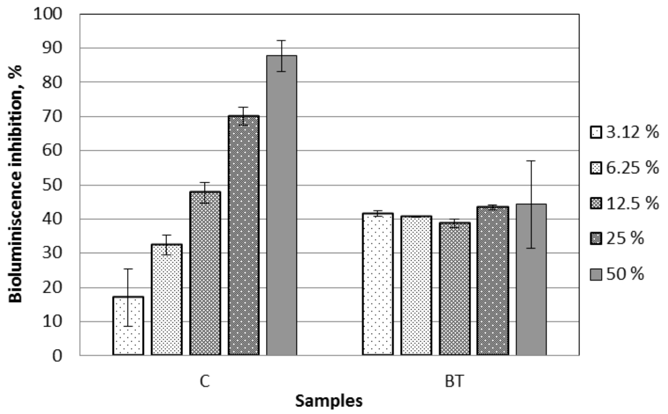


*Figure 5.* Ecotoxicity of water contaminated with diesel WSF before (C) and after treatment with biochar (BT); results are expressed as the percent of bioluminescence inhibition and are the average of n=3. Different bars represent different dilutions of the initial sample with 20 mg dm$^{-3}$ WSF

## 4. CONCLUSION

Environmental challenges have rapidly grown over the last decade. This is a clear indication that both scientists and natural resource managers should put efforts to investigate the potential of renewable, waste materials, which should be considered as valuable sources. Biochar and its proper applications have potentials in solving these pollution problems. An especially attractive aspect of biochar application is its potential to reduce pollution caused by diesel oil, facilitating efforts in achieving a more circular economy. In this concept, waste streams, such as peach stones, are reutilized from landfills to produce efficient sorbents. In this paper, pyrolysed waste peach stone feedstock was efficiently used as a sorbent for removal of WSF of diesel oil. This fraction most often represents a serious risk for aquatic organisms and for human health as well. Results presented in this paper show that the pyrolysed sample contains a large multi porous surface area, rich in surface functional groups, with increased aromaticity compared to the native sample. Sorption kinetics followed the pseudo second order model, suggesting that chemisorption mechanism occurs; this was also confirmed by isotherm studies, which indicated a high-affinity multilayer chemisorption process without reaching the maximum sorption capacity. This study also demonstrates that the application of peach stones biochar sorbent in contaminated water polluted by diesel WSF decreases its toxicity on *Aliivibrio fischeri* and opens the door for further investigation of its potential application. The obtained results support the concept of using biochar to reduce diesel oil pollution from contaminated water streams, which in the same time reduces the amount of landfill wastes and decreases greenhouse gas emissions (by carbon sequestering).

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## REFERENCES


[1] Oil. https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy/oil.html. Accessed August 10, 2021.

[2] Pintor A, Vilar VJP, Botelho CMS, Boaventura RAR. Oil and grease removal from wastewaters: Sorption treatment as an alternative to state-of-the-art technologies. A critical review. *Chem Eng J*. 2016; 297: 229-255 https://doi.org/10.1016/j.cej.2016.03.121.

[3] Santos CA, Lenz D, Brandão GP, Chippari-Gomes AR, Gomes LC. Acute toxicity of the water-soluble fraction of diesel in *Prochilodus vimboides* Kner (Characiformes: Prochilodontidae). *Neotropical Ichthyology*. 2013; 11(1): 193-198 https://doi.org/10.1590/S1679-62252013000100022.

[4] Srinivasan A, Viraraghavan T. Oil removal from water using biomaterials. *Bioresour Technol*. 2010; 101(17): 6594-6600 https://doi.org/10.1016/j.biortech.2010.03.079.

[5] Khan E, Virojnagud W, Ratpukdi T. Use of biomass sorbents for oil removal from gas station runoff. *Chemosphere*. 2004; 57(7): 681–689 https://doi.org/10.1016/j.chemosphere.2004.06.028.

[6] Huang Q, Song S, Chen Z, Hu B, Chen J, Wang X. Biochar-based materials and their applications in removal of organic contaminants from wastewater: state-of-the-art review. *Biochar*. 2019; 1: 45-73 https://doi.org/10.1007/s42773-019-00006-5.

[7] Thompson KA, Shimabuku KK, Kearns JP, Knappe DRU, Summers RS, Cook SM. Environmental Comparison of Biochar and Activated Carbon for Tertiary Wastewater Treatment. *Environ Sci Technol*. 2016; 50(20): 11253-11262 https://doi.org/10.1021/acs.est.6b03239.

[8] Lopičić Z, Stojanović M, Kaluđerović-Radoičić T, Milojković J, Petrović M, Mihajlović M, Kijevčanin M. Optimization of the process of Cu (II) sorption by mechanically treated *Prunus persica* L. - Contribution to sustainability in food processing industry. *J Clean Prod*. 2017; 156: 95-105 https://doi.org/10.1016/j.jclepro.2017.04.041.

[9] Abdullah MA, Rahmah AU, Man Z. Physicochemical and sorption characteristics of Malaysian *Ceiba pentandra* (L.) Gaertn. as a natural oil sorbent. *J Hazard Mater*. 2010; 177(1-3): 683-691 https://doi.org/10.1016/j.jhazmat.2009.12.085.

[10] Rouquerol F, Rouquerol J, Sing K. Adsorption by Powders and Porous Solids. 1975; London: *Academic press*.

[11] EN ISO 9377: Water quality — Determination of hydrocarbon oil index — Part 2: Method using solvent extraction and gas chromatography. 2000

[12] EN ISO 11348-3: Water quality-Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (luminescent bacteria test) - Part 3: Method using freeze-dried bacteria. 2007

[13] Lopičić Z, Stojanović M, Marković S, Milojković J, Mihajlović, M, Kaluđerović-Radoičić T, Kijevčanin M. Effects of different mechanical treatments on structural changes of lignocellulosic waste biomass and subsequent Cu(II) removal kinetics. *Arab J Chem*. 2019; 12(8): 4091-4103 https://doi.org/10.1016/j.arabjc.2016.04.005.

[14] Crombie K, Masek O, Sohi SP, Brownsort P, Cross A. The effect of pyrolysis conditions on biochar stability as determined by three methods. *GCB Bioenergy*. 2012; 5(2): 122-131 https://doi.org/10.1111/gcbb.12030.

[15] Zhang L, Ren Y, Xue Y, Cui Z, Wei Q, Han C, He J. Preparation of biochar by mango peel and its adsorption characteristics of Cd(II) in solution. *RSC Adv*. 2020; 10(59): 35878-35888 https://doi.org/10.1039/d0ra06586b.

[16] Onorevoli B, Maciel G, Machado ME, Corbelini VA, Caramão EB, Jacques, R. Characterization of feedstock and biochar from energetic tobacco seed waste pyrolysis and potential application of biochar as an adsorbent. *J Environ Chem Eng*. 2018; 6(1): 1279-1287 https://doi.org/10.1016/j.jece.2018.01.039.

[17] Chan KY, Van Zwieten L, Meszaros I, Downie A, Joseph SD. Agronomic values of greenwaste biochar as a soil amendment. *Aust J Soil Res*. 2007; 45(8): 629-634 https://doi.org/10.1071/SR07109.

[18] Joseph SD, Downie A, Munroe P, Crosky A, Lehmann J. Biochar for carbon sequestration, reduction of greenhouse gas emissions and enhancement of soil fertility: a review of the materials science. In: Proceedings of the *Australian Combustion Symposium*. Australia, 2007, pp 130–133.

[19] Lopičić Z, Milojković J, Šoštarić T, Petrović M, Mihajlović M, Lačnjevac Č, Stojanović M. Influence of pH value on Cu (II) biosorption by lignocellulose peach shell waste material. *Hem Ind*. 2013; 67(6): 1007–1015 https://doi.org/10.2298/HEMIND121225018L.

[20] Özçimen D, Ersoy-Meriçboyu A. Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. *Renew Energ*. 2010; 35(6): 1319-1324 https://doi.org/10.1016/j.renene.2009.11.042.

[21] Pehlivan E, Altun T, Cetin S, Iqbal BM. Lead sorption by waste biomass of hazelnut and almond shell. *J Hazard Mater*. 2009; 167(1-3): 1203–1208 https://doi.org/10.1016/j.jhazmat.2009.01.126.

[22] Šoštarić T, Petrović M, Milojković J, Lačnjevac Č, Ćosović A, Stanojević M, Stojanović M. Application of apricot stone waste from fruit processing industry in environmental cleanup: copper biosorption study. *Fruits*. 2015; 70(5): 271-280 https://doi.org/10.1051/fruits/2015028.

[23] Chonlong C, Mohini S, Wensheng Q. Lignin utilization: A review of lignin depolymerization from various aspects. *Renew Sust Energ Rev*. 2019; 107: 232-249 https://doi.org/10.1016/j.rser.2019.03.008.

[24] Haiping Y, Rong Y, Hanping C, Dong HL, Chuguang Z. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*. 2007; 86(12-13): 1781-1788 https://doi.org/10.1016/j.fuel.2006.12.013.

[25] Lehmann J, Rillig MC, Thies J, Masiello CA, Hockaday WC, Crowley D. Biochar effects on soil biota – A review. *Soil Biol Biochem*. 2011; 43(9): 1812-1836 https://doi.org/10.1016/j.soilbio.2011.04.022.

[26] Obradović B. Guidelines for general adsorption kinetics modeling. *Hem Ind*. 2020; 74(1): 65-70 https://doi.org/10.2298/HEMIND200201006O.

[27] Lagergren S, Svenska K. About the theory of so called adsorption of soluble substances. *Veternskapskad Handl*. 1898; 24(4): 1-39.

[28] Ho YS, McKay G. Pseudo-second order model for sorption processes. *Process Biochem*. 1999; 34: 451-465.

[29] Low MJD. Kinetics of chemisorption of gases on solids. *Chem Rev*. 1960; 60: 267-312.

[30] Wang RZ, Huang DL, Liu YG, Zhang C, Lai C, Zeng GM, Cheng M, Gong XM, Wan J, Luo H. Investigating the adsorption behaviour and the relative distribution of $Cd^{2+}$ sorption mechanisms on biochars by different feedstock. *Bioresour Technol*. 2018; 261: 265–271 https://doi.org/10.1016/j.biortech.2018.04.032.

[31] Cai L, Zhang Y, Zhou Y, Zhang X, Ji L, Song W, Zhang H, Liu J. Effective Adsorption of Diesel Oil by Crab-Shell-Derived Biochar Nanomaterials. Mater. 2019; 12(2): 236 https://doi.org/10.3390/ma12020236.

[32] Barman SR, Das P, Mukhopadhayay A. Biochar from waste *Sterculia foetida* and its application as adsorbent for the treatment of PAH compounds: Batch and optimization. Fuel. 2021; 306: 121623 https://doi.org/10.1016/j.fuel.2021.121623.

[33] Lowell S, Shields JE. Adsorption isotherms. In: Powder Surface Area and Porosity. Dordrecht, Germany, 1984, Springer.

[34] Freundlich HMF. Over the adsorption in solution. *J Phys Chem*. 1906; 57: 385–470.

[35] Sparks DL. Sorption Phenomena on Soils. In: Environmental Soil Chemistry, 2nd ed. Burlington: Academic Press; 2003: 133-186.

[36] Foo KY, Hameed BH. Insights into the modelling of adsorption isotherm systems. *Chem Eng J*. 2010; 156(1): 2-10 https://doi.org/10.1016/j.cej.2009.09.013.

[37] Antal MJ, Grønli M. The Art, Science, and Technology of Charcoal Production. *Ind Eng Chem Res*. 2003; 42(8): 1619−1640 https://doi.org/10.1021/ie0207919.

[38] Muller JB, Melegari SP, Perreault F, Matias WG. Comparative assessment of acute and chronic ecotoxicity of water soluble fractions of diesel and biodiesel on *Daphnia magna* and *Aliivibrio fischeri*. *Chemosphere*. 2019; 221: 640-646 https://doi.org/10.1016/j.chemosphere.2019.01.069.

[39] Hawrot-Paw M, Koniuszy A, Zając G, Szyszlak-Bargłowicz J. Ecotoxicity of soil contaminated with diesel fuel and biodiesel. *Sci Rep*. 2020; 10: 16436 https://doi.org/10.1038/s41598-020-73469-3.

[40] Abbas M, Adil M, Ehtisham-ul-Haque S, Munir B, Yameen M, Ghaffar A, Shar GA, Tahir MA, Iqbal M. *Vibrio fischeri* bioluminescence inhibition assay for ecotoxicity assessment: A review. *Sci Total Environ*. 2018; 626: 1295–1309 https://doi.org/10.1016/j.scitotenv.2018.01.066.

## SAŽETAK

### Uklanjanje zagađenja dizela sorpcijom na biočađi – podrška remedijaciji kontaminiranih voda

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(Naučni rad)

Prečišćavanje voda zagađenih dizelom predstavlja jedan od glavnih izazova u tretmanu otpadnih voda. Frakcija rastvorna u vodi (engl. water soluble fraction, WSF) je naročito važna, obzirom na njenu direktnu toksičnost po vodene organizme, kao i na granične vrednosti postavljene zakonskom regulativom. Sorbenti na bazi biočađi privlače značajnu pažnju istraživača, zbog na njihove ekonomske isplativosti i svojstva koja doprinose velikim sorpcionim kapacitetima. U ovom radu prikazane su sinteza i karakterizacija biočađi dobijene od otpadnog lignoceluloznoog materijala koštice breskve, i ispitana je moguća primena ovog materijala kao sorbenta u uklanjanju rastvorne frakcije dizela iz kontaminiranih voda. Fizičko-hemijske karakteristike biočađi analizirane su primenom skenirajuće elektronske mikroskopije (SEM) i infracrvene spektroskopije sa Furijeovom (Fourier) transformacijom (FTIR) zajedno sa elementarnom organskom analizom dok je specifična površina određena primenom BET (Brunauer – Emmett – Teller) metode. Karakterizacija biočađi koštice breskve pokazala je multiporoznu strukturu velike specifične površine (159.1 $m^2 g^{-1}$) sa prosečnom veličinom pora 2.7 nm. Rezultati FTIR analize su ukazali na veće prisustvo aromatičnih jedinjenja u biočađi u odnosu na nativni uzorak. Sorpcioni eksperimenti izvedeni u šaržnom sistemu pokazali su da je procenat uklanjanja rastvorene frakcije dizela veći od 95 % pri inicijalnoj koncentraciji od 20 mg $dm^{-3}$ i sadržaju biočađi od 1.5 g $dm^{-3}$, uz postizanje ravnoteže nakon 5 h. Ravnotežni podaci su najbolje opisani Frojndlihovom izotermom, dok je jednačina kinetike pseudo-drugog reda najbolje opisala kinetičke podatke, ukazujući na proces hemisorpcije koji uključuje valentne sile kroz izmenu/delenje elektrona između sorbata i biočađi. Ekotoksikološki testovi su pokazali smanjenje ekotoksičnosti na *Aliivibrio fischeri* nakon tretmana voda uzorkom biočađi.

*Ključne reči*: naftni ugljovodonici; otpad iz prehrambene industrije; pirolizovana biomasa; sorpcija; ekotoksikologija

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# Thermal conductivity analysis of $Al_2O_3$/water-ethylene glycol nanofluid by using factorial design of experiments in a natural convection heat transfer apparatus

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*Abstract*

Thermal conductivity of a heat transfer fluid plays a significant role in improving the heat transfer performance of a heat exchanger. In this work, experiments were performed in a natural convection heat transfer apparatus by mixing homogenized $Al_2O_3$ nanoparticles in a base fluid of water-ethylene glycol mixtures. The effects of heat input, nanoparticle volume content in the base fluid, and ethylene-glycol volume content in the base fluid on thermal conductivity of the nanofluid were analyzed. Based on results obtained by MINITAB® design software (factorial design matrix), 16 experimental runs were performed with the lower and higher levels of input factors. The levels for heat input were 10 and 100 W; for nanoparticle volume content in the base fluid 0.1 and 1 vol.% and for the base fluid composition 30 and 50 vol.% of ethylene glycol in water. From the obtained experimental results, a Pareto chart, normal probability plot, contour plot and surface plot were drawn. Based on the results, a new correlation was proposed, and predictions were compared with the experimental results. From the study, the maximum thermal conductivity value 0.49 W $m^{-1}$ $K^{-1}$ was observed at a nanoparticle volume content in the base fluid of 1.0 vol.%, ethylene glycol volume content in the base fluid of 30 vol.% and heat input of 100 W.

*Keywords:* heat exchanger; base fluid; Minitab; nanoparticle; contour and surface plots.

*Available on-line at the Journal web address:* http://www.ache.org.rs/HI/

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**UDC: 52-334.6:661.183.8+
661.725.822:519.242.7**

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## 1. INTRODUCTION

Transfer of heat to and from the process fluid is an essential part of most chemical processes [1]. The initial idea on using solid nanosized particle suspensions in a liquid fluid for enhancing the thermo-physical properties of conventional heat transfer fluid was coined by Choi *et al.* [2]. They proposed both metals and metal oxides nano-suspensions in their invention. This idea gives a pathway to engineers to explore nanofluid applications in heat transfer processes. It was shown in the literature [3,4] that $Al_2O_3$ nanoparticle addition provides suitable thermal conductivity enhancement of a base fluid (water- ethylene glycol mixture) at minimal amounts of the nanoparticle additive. In another experimental work [5] with synthesized $Al_2O_3$ nanoparticles it was concluded that the nanoparticle material properties, nanoparticle volume content in the base fluid, bulk temperature, and nanoparticle size, all played a significant role in the improvement in thermal conductivity of base fluids. Also, in the experimental study in a horizontal tube with alumina nanofluid [6] it was reported that the Nusselt number of the nanofluid under turbulent flow increased with the nanoparticle concentration as well as the Reynolds number. Addition of nanoparticles was shown to enhance the overall heat transfer (*e.g*. addition of $Al_2O_3$ nanoparticles (0.01 vol.%) to therminol 55 [7], addition of copper nanoparticles (0.1 wt. %) to water [8] as well as the thermal conductivity of the base fluid (*e.g.* addition of graphene nanoparticles [9], $TiO_2$ and ZnO nanoparticles [10-12], $Al_2O_3$, ZnO, and $TiO_2$ nanoparticles in ethylene glycol-water mixtures as well as addition of $Al_2O_3$,CuO to water [13,14]). Furthermore, it was reported that in order to increase the thermal conductivity

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particle size should be smaller [15]. Also, the overall heat transfer coefficient in a plate heat exchanger improved up to 30% at 6 vol.% $Al_2O_3$ nanofluid [16]. Thermal conductivity was enhanced by addition of copper oxide nanoparticles to water and ethylene glycol base fluids as compared to addition of microparticles [17], which was attributed to the smaller particle size and uniform dispersion of nanoparticles in the base liquid.

Higher nanoparticle concentrations were reported to increase the heat transfer coefficient [18,19] as well as the thermal conductivity [20] but decreases the specific heat capacity [21]. On the contrary, in the study by Pandey *et al.* [22] of $Al_2O_3$/water nanofluid in a plate heat exchanger, it was found that the heat transfer behaviour improved with a decrease in the nanoparticle concentration. Heat transfer in experimental $Al_2O_3$ nanoparticle-water systems was also studied regarding determination of the Nusselt number [23,24]. The base fluid also has an influence on the overall heat properties of a nanofluid [25]. Hence, it was shown that the heat transfer enhancement was higher for $Al_2O_3$/ethylene glycol nanofluid compared with $Al_2O_3$/water nanofluid [26]. Factorial design is a useful tool for studying the effects of several individual independent variables simultaneously and it was used to analyse a $TiO_2$-ZnO hybrid nanofluid and the effects of nanoparticle content, operating temperature, and channel height on heat transfer performance in a micro channel heat exchanger [27]. All the investigated input factors were found to significantly affect the thermo-physical properties of the prepared nanofluid. The summary of literature review is presented in Table. 1

*Table 1 Summary of selected literature review*

| Ref. | Nanofluid, base fluid and concentration | Equipment used | Results of the study |
|---|---|---|---|
| [3] | $Al_2O_3$, CuO/water, EG* and 1-5 vol.% of CuO and $Al_2O_3$ in water. | Heat exchanger | Thermal conductivity ratios increase almost linearly with the content tested up to 0.05 vol.%, but at different rates of increase for each system |
| [4] | $Al_2O_3$, ZnO, $TiO_2$, CuO, $Fe_2O_3$, and $CeO_2$/EG and 0.5, 1.5, 3.0 and 4.0 vol.% of nanoparticles in the base fluid | Steady state parallel plate | The highest thermal conductivity enhancement at 4 % volume content |
| [27] | Copper-water, 0.1 wt.% of copper nanoparticle in water | Micro heat exchanger | 42.1 % enhancement in the heat transfer coefficient |
| [5] | CuO/water, $Al_2O_3$/water and 2–10 vol.% of $Al_2O_3$ in water | Heat exchanger | A linear regression equation was proposed for estimation of the thermal conductivity ratio based on temperature and volume content |
| [6] | $Al_2O_3$/water | Horizontal tube | Nusselt number of the nanofluid under turbulent flow increased with nanoparticle concentration |
| [7] | $Al_2O_3$-Therminaol 55, 0.01 vol.% of $Al_2O_3$ in the base fluid. | Reactor | Heat transfer rate from the main vessel to the safety vessel was increased significantly by the addition of nanoparticles |
| [9-11] | graphene, $TiO_2$ and ZnO / EG-water | Plate heat exchanger | Thermal conductivity and heat transfer coefficient were directly enhanced with addition of the prepared nanoparticles |
| [13] | $Al_2O_3$ (particle size 36 and 47 nm) | Plate heat exchanger | Linear equations were proposed to determine the heat transfer coefficient |
| [16] | $Al_2O_3$/water 6 vol.% of $Al_2O_3$ in water | Plate heat exchanger | Overall heat transfer coefficient improved up to 30% |
| [14] | Copper/water | Moving wedge | Observed an improvement in thermal radiation |
| [18] | $Al_2O_3$/water | Heat exchanger | Increase in Reynolds number and nanoparticle concentration, led to increase in the heat transfer coefficient particularly at the entrance region |
| [23] | $Al_2O_3$/water | Natural convection heat transfer apparatus | Correlation was provided in order to determine the Nusselt number |

| Ref. | Nanofluid, base fluid and concentration | Equipment used | Results of the study |
|---|---|---|---|
| [19] | γ- $Al_2O_3$ in water | Corrugated cavity | Heat transfer coefficient enhanced significantly with the nanoparticle addition |
| [25] | $SnO_2$, $Al_2O_3$, Cu2O, ZnO, $TiO_2$, $SiO_2$, CuO, Cu, $Fe_2O_3$, SiC, and MWCNT** | Solar stills | Observed significant improvement in heat transfer performance of solar stills |
| [26] | $Al_2O_3$- water, $Al_2O_3$ EG | Inside circular tubes | Heat transfer enhancement was higher for $Al_2O_3$/EG nanofluid compared to $Al_2O_3$/water nanofluid |
| [22] | $Al_2O_3$/water | Corrugated plate heat exchanger | Heat transfer behaviour improved with a decrease in the nanoparticle concentration |
| [24] | $Al_2O_3$/water | U-tube heat exchanger | Maximum increment in the Nusselt number occurs at the maximal Reynolds number and nanoparticle volume content |
| [13] | $Al_2O_3$/water | Plate heat exchanger | At a constant Reynolds number, the heat transfer was better than that of the base fluid due to the increase in the thermal conductivity |
| [20] | $Al_2O_3$, CuO, $SiO_2$, ZnO/PG***, water and 6 vol.% of nanoparticle in water | Heat exchanger | Thermal conductivity of nanofluids mainly depended on the particle size, nanoparticle volume content, temperature, and properties of particles and the base fluid |
| [27] | $TiO_2$-ZnO hybrid nanofluid water | Micro channel heat exchanger | All input factors significantly affected the thermo- physical properties of the prepared nanofluid |

*EG – ethylene glycol; **MWCNT – Multi Walled Carbon NanoTube; ***PG – Propylene Glycol

From the introduction of the concept “nanofluid”, many research studies explored the unique properties and capabilities exhibited by these new engineered fluids. Literature search shows that many studies concentrated on size reduction of heat exchangers and utilization of lower volumes of heat transfer fluids based on beneficial heat transfer properties of these energy efficient fluids. Although nanofluids exhibit many advantages, there are certain weaknesses found in applications. Some of the common problems associated with the application of nanofluids in heat exchangers in real time situations are fouling and surface erosion. The other weaknesses are high costs of energy and materials. From the literature review, it was noted that miniature heat exchangers are more efficient with better performance of nanofluids.

Several studies in literature were conducted to determine the effects of nanoparticle addition on thermal conductivity and heat transfer enhancement of the base fluid in different heat exchanger geometries. However, application of full factorial designs to analyze the influence of various input factors on the thermal conductivity is not often found in literature. In the present work, an experimental study was performed in a natural convection heat transfer apparatus with $Al_2O_3$/water-ethylene glycol mixture. The effects of input factors such as heat input ($Q$), nanoparticle volume content, and base fluid composition on the thermal conductivity as the output response were analyzed by using a Pareto chart, normal probability plot, contour plot and a surface plot. The optimized results obtained from the developed model are validated with the experimental results.

## 2. EXPERIMENTAL

### 2. 1. Nanofluid and base fluid preparation

$Al_2O_3$/water-ethylene glycol nanofluid used in the present study was prepared by using a two step method. Distilled water was used while EG was of technical grade and purchased from Global Scientific Company (India) and the $Al_2O_3$ nanoparticles (80 nm in size, 99 % purity) purchased from Sigma Aldrich (India) were suspended in two EG-water mixtures with different volumetric ratios of EG : water *i.e.* 30 : 70 and 50 : 50 %. The nanoparticles were added to the base fluid (water-EG) mixture to yield two volume content ($\phi$ = 0.1 and 1 vol.%) that are calculated by the equation (1):

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$$\varphi = \frac{(m/\rho)_{Al_2O_3}}{(m/\rho)_{Al_2O_3} + (m/\rho)_{W:EG}} \quad (1)$$

where $(m/\rho)_{Al_2O_3}$ represents the nanoparticle volume (*i.e*. ratio of the nanoparticle mass and density (3500 kg $m^{-3}$, [23]) while $(m/\rho)_{W:EG}$ represents the base fluid volume (calculated as the ratio of the water-EG mixture mass and density where density was determined using specific gravity bottle.

In order to prepare a stable nanofluid, in the second step a high-pressure homogenizer (VS-500 Ltrs, Vino Technical Services, India) was used in our study for 180 min.

This prepared nanofluid was found to be stable in the operating temperature range (45 to 60 °C), evident from visual observation in the range of concentrations, as particle settling was not observed. It was also noted that the particles were homogeneously dispersed throughout the base fluid in an acceptable manner and ensured a good nanofluid suspension because of the use of the high-pressure homogenizer.

### 2. 2. Experimental procedure

The mechanism involved in natural convection heat transfer is the motion of fluid caused only due to a density difference resulting from temperature gradients without the use of external agents. The experimental set up of natural convection heat transfer apparatus is shown in Figure 1. The experimental setup consisted of a vertical stainless-steel tube of diameter (*d*) 45 mm and length (*L*) 500 mm with an electrical heater coil along the axis of the tube enclosed in a duct. Temperature was measured along the length of the plate by thermocouples embedded beneath the heated surface. Control panel instrumentation consisted of a multi channel digital display with a temperature indicator displaying surface temperatures $T_1$ to $T_7$ and ambient temperature $T_8$ and a digital ammeter and voltmeter (Legion, India). Heat input is provided by an electrical heating element. For measuring the surface temperature along the tube, thermocouples were inserted at different heights. In order to minimize radiation loss, the tube surface was polished. Temperature and voltage measurements associated with the electrical voltage and current supplied for heating were recorded. By increasing the power level, the system was allowed to stabilize, and temperature was recorded. The experiment was performed at various combinations of input parameters determined by the MINITAB factorial design of experiments. Thermal conductivity of the nanofluid was measured with the use of a thermal conductivity meter (Scientico, India).

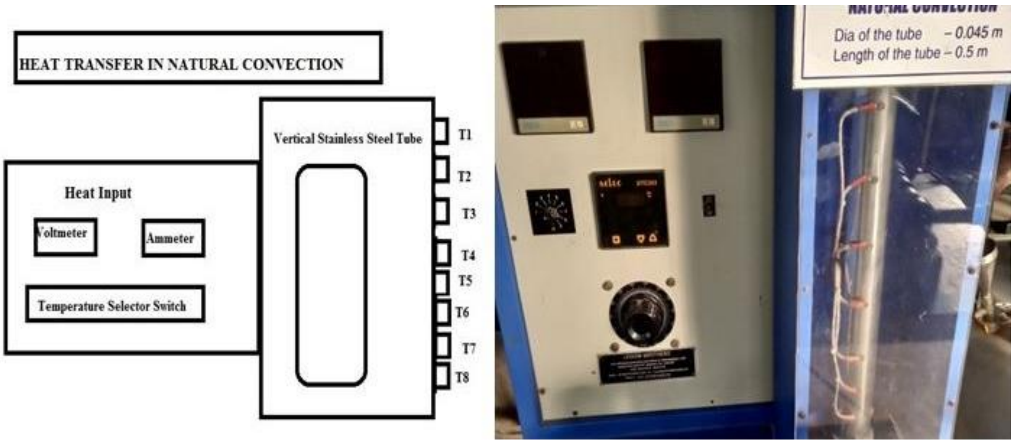


*Figure 1. Experimental natural convection heat transfer apparatus*

### 2. 3. Factorial design and analysis

2. 3. 1. Input parameters and their levels

Each experimental operating condition is a “Run", the output response is an “Observation” and the entire set of runs is the "Design" [28,29]. Two-level full factorial design was employed with two replications, which provides 16 experimental combinations. The response factor “thermal conductivity” is measured at all combinations of the experimental factor levels as provided by the design software. Table 2 shows the design summary and factors and levels for the full factorial design applied in the present study.

*Table 2. Design summary and factors and levels for the full factorial design*

| | | | |
|---|---|---|---|
| Factors | | 3 | |
| Base design | | 3, 8 | |
| Number of experimental runs | | 16 | |
| Replicates | | 2 | |
| Blocks | | 2 | |
| | | Level | |
| Input factors | Code | Low | High |
| Heat input, W | *A* | 10 | 100 |
| Nanoparticle content in the base fluid, vol.% | *B* | 0.1 | 1.0 |
| EG content in the base fluid, vol.% | *C* | 30 | 50 |

Statistical analysis is used to investigate the significance of the input factors (*A*, *B*, *C*) and their interactions on the output response (thermal conductivity - $K_{nf}$).

### 3. RESULTS AND DISCUSSION

In order to measure nanoparticle size, size distribution and its morphology, Transmission Electron Microscopy (TEM) technique was used. Table 3 provides the experimental results of the full factorial design for 16 experiments with 3 input factors (*A*: heat input, *B*: nanoparticle volume content in the base fluid, *C*: EG volume content in the base fluid) and one output variable (thermal conductivity of the nanofluid) at the approximate temperature of 50 °C.

*Table 3. Experimental results of the full factorial design*

| | | Factorial input variable | | | | |
|---|---|---|---|---|---|---|
| Standard order | Run order | *A* $Q$ / W | *B* Nanoparticle content in the base fluid, vol. % | *C* EG content in the base fluid, vol.% | Response variable, $K_{nf}$ / W m$^{-1}$ K$^{-1}$ | $T_{avg}$ / °C |
| 1 | 4 | 10 | 0.1 | 30 | 0.4850 | 49.2 |
| 2 | 1 | 100 | 0.1 | 30 | 0.4890 | 52.9 |
| 3 | 3 | 10 | 1.0 | 30 | 0.4750 | 49.4 |
| 4 | 5 | 100 | 1.0 | 30 | 0.4930 | 52.6 |
| 5 | 7 | 10 | 0.1 | 50 | 0.4390 | 51.2 |
| 6 | 6 | 100 | 0.1 | 50 | 0.4450 | 53.2 |
| 7 | 8 | 10 | 1.0 | 50 | 0.4660 | 51.4 |
| 8 | 2 | 100 | 1.0 | 50 | 0.4780 | 52.4 |
| 9 | 15 | 10 | 0.1 | 30 | 0.4860 | 51.6 |
| 10 | 14 | 100 | 0.1 | 30 | 0.4895 | 54.1 |
| 11 | 12 | 10 | 1.0 | 30 | 0.4760 | 49.5 |
| 12 | 9 | 100 | 1.0 | 30 | 0.4935 | 52.0 |
| 13 | 11 | 10 | 0.1 | 50 | 0.4395 | 49.7 |
| 14 | 10 | 100 | 0.1 | 50 | 0.4455 | 53.9 |
| 15 | 16 | 10 | 1.0 | 50 | 0.4670 | 49.6 |
| 16 | 13 | 100 | 1.0 | 50 | 0.4788 | 49.3 |

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The measured thermal conductivity for 30 % EG : 70 % water is 0.45 W $m^{-1}$ $K^{-1}$ and for 50 % EG : 50 % water is 0.4295 W $m^{-1}$ $K^{-1}$. The thermal conductivity obtained for the 0.1 vol.% of nanoparticle volume content in the base fluid, 10 W heat input and 30 % EG : 70 % water is 0.439 W $m^{-1}$ $K^{-1}$, whereas the value is 0.493 W $m^{-1}$ $K^{-1}$ for 30 % EG and 70 % water with 1 vol.% of nanoparticle volume content in the base fluid and 100 W heat input. $K_{nf}$ of pure water is 0.598 W $m^{-1}$ $K^{-1}$ and for Ethylene Glycol is 0.258 W $m^{-1}$ $K^{-1}$. Hence it was noted from the study that 9.55 % improvement in the thermal conductivity of 30 % EG : 70 % water base fluid, by the addition of nanoparticle content of 1.0 vol.%. The observed thermal conductivities of $Al_2O_3$ nanofluids were analysed by using the factorial fit and ANOVA results for thermal conductivity values versus input variables *A*, *B*, and *C* as shown in Table 3. The ANOVA analysis is used to test the significance of main effects and interaction effects on the output response (thermal conductivity, $K_{nf}$).

A second order polynomial equation was derived from the observed data by MINITAB® statistical software (Minitab llc, US), by using a multiple regression analysis. The objective of the equation is to articulate the relationship between factors and the response. The second order polynomial equation in its coded form is:

$$K_{nf} = 0.00981A + 0.01356B - 0.02856C + 0.00494AB - 0.00094AC + 0.01656BC - 0.0021ABC \quad (2)$$

The maximum thermal conductivity of 0.493 W $m^{-1}$ $K^{-1}$ was observed at the operating conditions (30 % EG : 70 % water, 1 vol.% of nanoparticle volume content in the base fluid and 100 W heat input) and it is consistent with the thermal conductivity determined by the Eq.(2).

### 3. 1. Pareto chart for thermal conductivity of $Al_2O_3$/water-EG nanofluid

A Pareto chart is drawn for identifying the significant input factors and differentiating these factors from the insignificant ones in experiments performed. Figure. 2 shows the Pareto chart drawn for thermal conductivity as the output response for three input factors *A*, *B* and *C.* Pareto charts show the absolute values of the standardized effects. The standardized effects are t-statistics that test the null hypothesis that the effect is 0. If the error term has one or more degrees of freedom, the red line on the Pareto chart is drawn at *t*, where *t* is the $(1 - \alpha / 2)$ quantile of a *t*-distribution with degrees of freedom equal to the degrees of freedom for the error term. Minitab labels this graph Pareto Chart of the Standardized Effects. Minitab identifies important effects using Lenth's pseudo standard error (PSE). The red line of the Pareto chart is drawn at the margin of error (ME = *t* PSE). In Minitab Pareto chart, the factors crossing the margin of error (reference line) indicates significant factor. Hence it is revealed from the chart that the bars representing all the factors and their interactions cross the reference line (*i.e.*, 2.4) indicating these factors as significant with respect to thermal conductivity. These factors show statistical significance of the present model at the 0.05 level of significance.

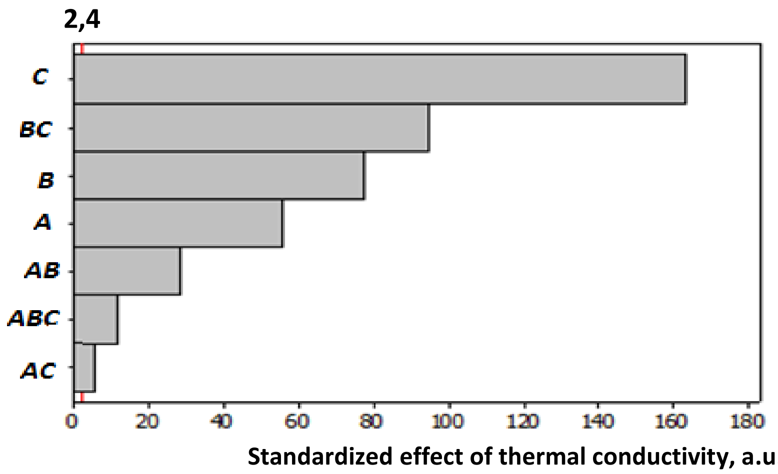


*Figure 2. Pareto Chart for thermal conductivity of $Al_2O_3$/water-EG nanofluid at the significance level of 0.05*



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### 3. 2. Normal probability plot for thermal conductivity of $Al_2O_3$/water-EG nanofluid

A normal probability plot indicates the relationship among the input-output variables involved in an experiment. Figure 3 shows the normal probability plot of the standardized effects for the thermal conductivity as the response. In normal probability plot, the factors far from 0 (red line) are statistically significant. Positive effects increase the output response (thermal conductivity), whereas negative effects decrease the response when the settings change from the low-level value of the input factor to the high-level value.

Hence the factors *A*, *B*, *AB* and *BC* have a positive standardized effect and factor *C* has negative standardized effect on the response. According to the Figure 3, the factors *AC* and *ABC* are slightly significant.

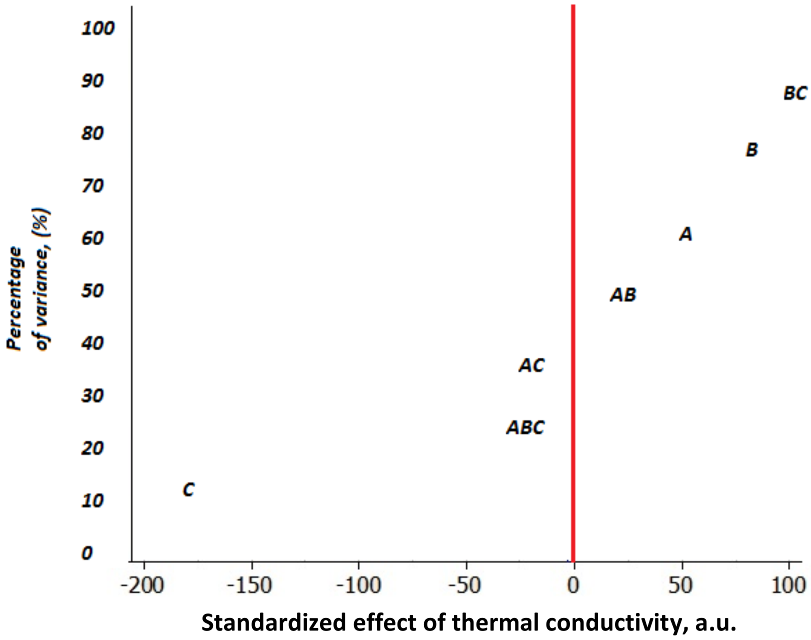


*Figure 3. Normal probability plot of the standardized effect for thermal conductivity of $Al_2O_3$/water-EG nanofluid*

### 3. 3. Main effect, interaction and cube plots for thermal conductivity of $Al_2O_3$/water-EG nanofluid

Main and interaction effects of various input factors are analysed by corresponding plots as shown in Figure 4.

The main effect is obtained when the mean response changes across the levels of an input factor. Interaction and cube plots are used to compare the relative strength of each effect across factors. Figure 4(a) shows the difference between the level means for the factors *A*, *B* and *C*. Based on the results it can be deduced that the order of significant factors are *B*, *C* and *A*. Figure 4(b) shows the interaction effects of $Al_2O_3$ nanoparticle addition on thermal conductivity of water-EG base fluids. It can be observed that factor B (nanoparticle volume content in the base fluid) shows a significant effect on thermal conductivity. A similar trend was observed in the cube plot for thermal conductivity of the nanofluid as shown in Figure 4(c). This positive effect is due to the fact that solids have higher thermal conductivities than liquids, hence the thermal conductivity of a base fluid increased significantly.

### 3. 5. Contour and surface plots for thermal conductivity of $Al_2O_3$/water-EG nanofluid

Figure 5 shows the two-dimensional contour plot with input variables heat input, nanoparticle volume content in the base fluid and base fluid composition. For drawing the contour plot, significant factors identified from ANOVA results were taken (*i.e.,* factors *B* and *A* are significant). Thermal conductivity (output response) varied between 0.476 and 0.492 kW $m^{-1}$ $K^{-1}$ based on variations of *B* (nanoparticle volume content in the base fluid) and *A* (heat input). With increasing the nanoparticle concentration and heat input, thermal conductivity also gradually increased.

Figure 6 provides the surface plot for thermal conductivity with respect to input factors *B* and *A*. A similar pattern as in the contour plot can be observed that is, thermal conductivity gradually increased with respect to both the

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nanoparticle volume content in the base fluid and heat input. The reason for the enhancement is due to the mixing of high conductive solid nanoparticles with the liquid.

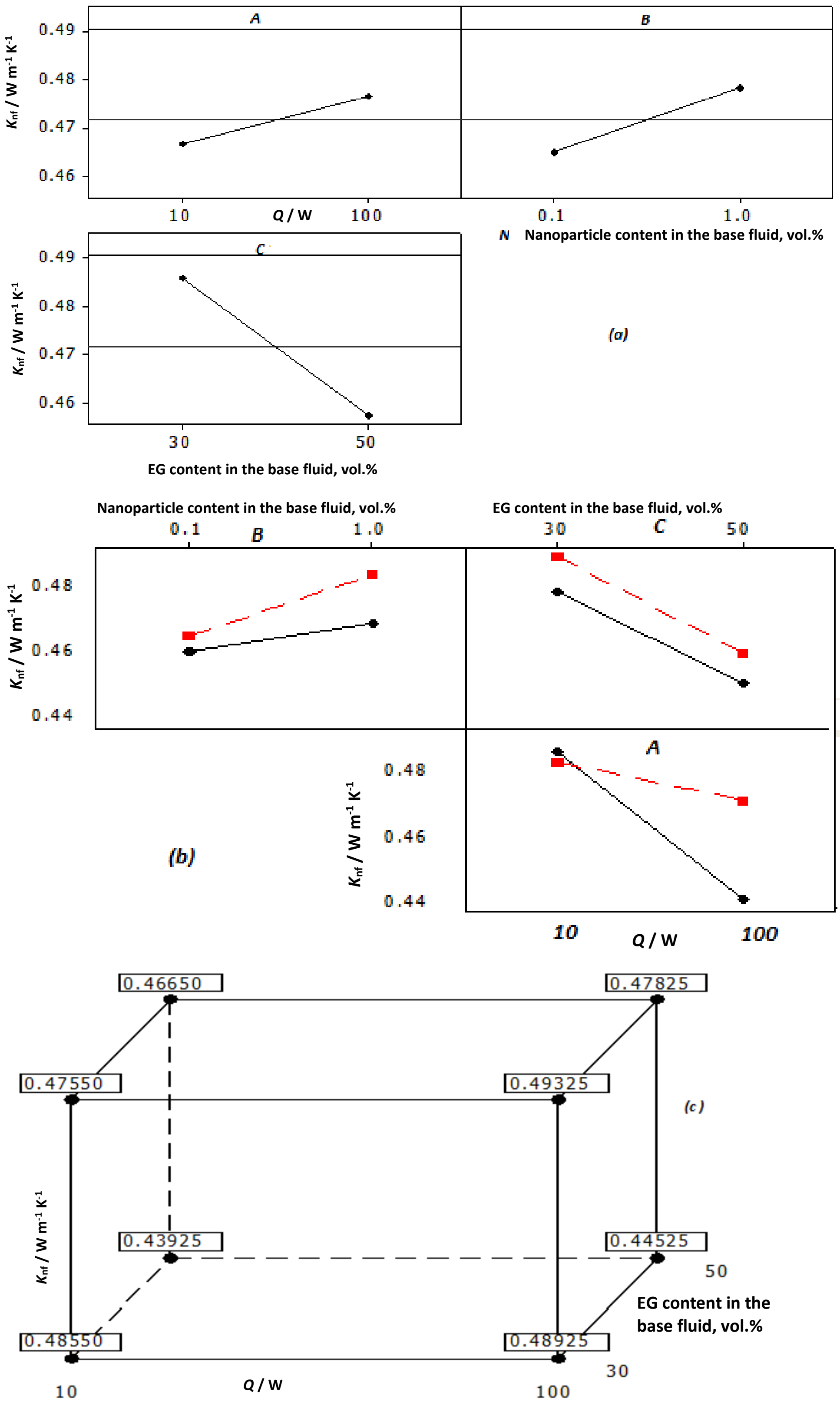


*Figure 4. Plots showing relationships between factors and the response (thermal conductivity of $Al_2O_3$/water-EG nanofluid): a - main effects plot; b - interaction plots; c - cube plot*



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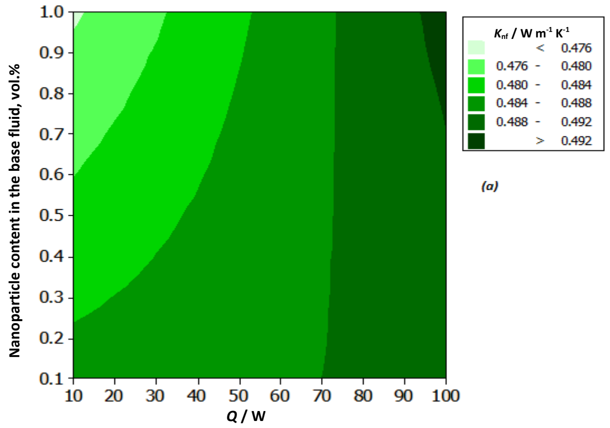
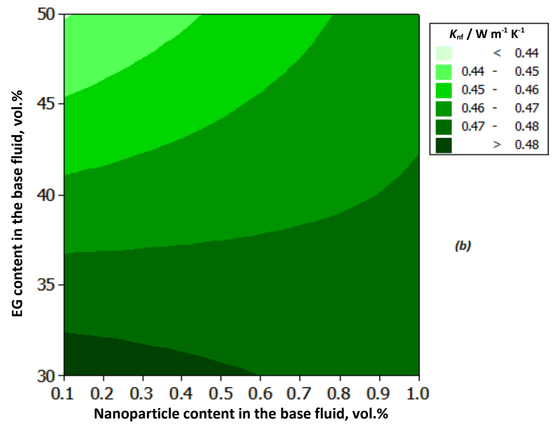


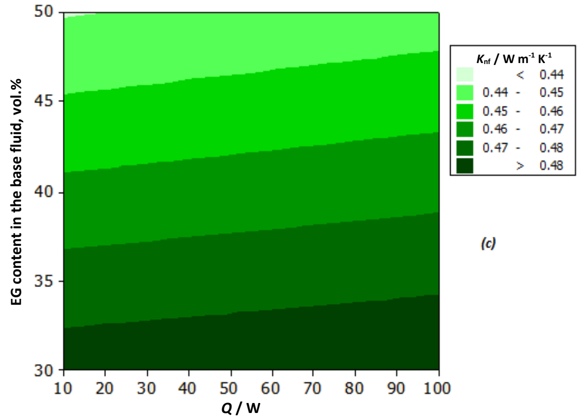
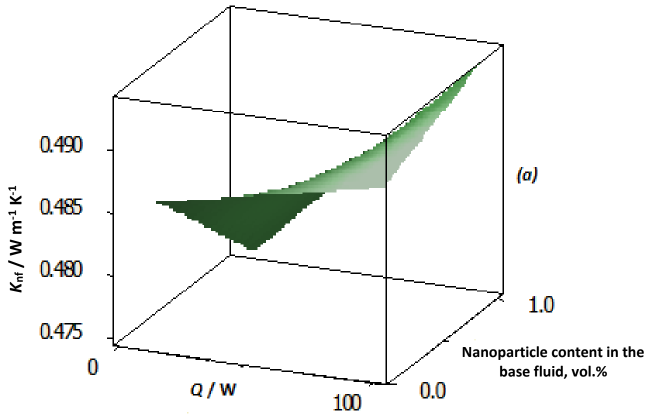
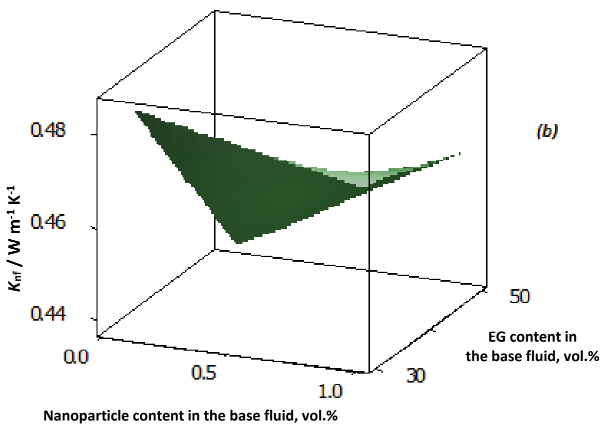




*Figure 5. Contour plots for thermal conductivity of $Al_2O_3$/water-EG nanofluid: (a) function of nanoparticle volume content in the base fluid and heat input; (b) function of nanoparticle volume content in the base fluid and EG content in the base fluid; (c) function of heat input and EG content in the base fluid*



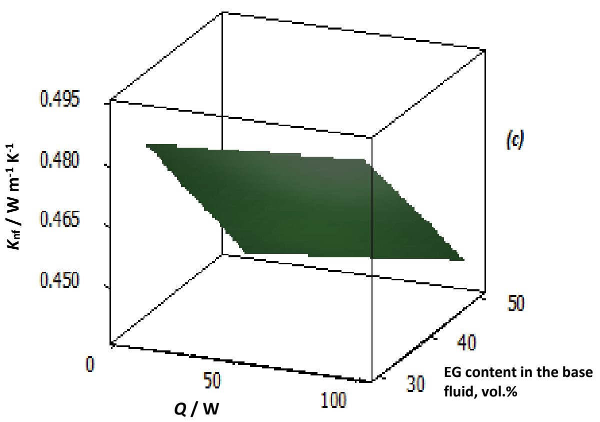




*Figure 6. Surface plot for thermal conductivity of $Al_2O_3$/water-EG nanofluid: a - function of nanoparticle volume content in the base fluid and heat input; b - function of nanoparticle volume content in the base fluid and EG content in the base fluid; c - function of heat input and EG content in the base fluid*

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## 4. CONCLUSION

Variations of thermal conductivity of nanofluids based on a suspension of $Al_2O_3$ nanoparticles in mixtures of ethylene glycol and water as a base fluid were analyzed by the application of a full factorial design of experiments ($2^3$ full factorial design matrix), and the influences of heat input (*A*), nanoparticle volume content in the base fluid (*B*) and ethylene glycol volume content in the base fluid (*C*) were studied in a natural convection heat transfer apparatus. The obtained results were graphically presented and analysed by Pareto, normal probability, main effect, interaction, cube, contour, and surface plots. Based on the plots, all the investigated factors and their interactions are significant factors with respect to thermal conductivity enhancement. It may be concluded from the results of contour and surface plots that by increasing the nanoparticle concentration and heat input, the thermal conductivity increases gradually as also reported in literature [9,15,17]. A new correlation was proposed, and the predictions were compared with the results obtained from the experimental study showing that the thermal conductivity prediction was consistent with the experimental result. The maximal thermal conductivity value of 0.493 W $m^{-1}$ $K^{-1}$ was observed at the higher investigated nanoparticle volume content in the base fluid of 1.0 vol.%, lower EG content in the base fluid of 30 vol.% and the higher heat input of 100 W. Significance of this study lies in the possibility for scaling up the presented concept to utilize potential benefits of the investigated nanofluid in industries handling heat exchangers.

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## REFERENCES

[1] Zlatković NR, Majstorović DM, Kijevčanin ML, Živković EM. Plate heat exchanger design software for industrial and educational applications. *Hem. Ind.*2017;71:439-449.https://doi.org/10.2298/HEMIND161021007Z

[2] Choi SUS. Enhancing Thermal Conductivity of Fluids with Nanoparticles. In: D. A. Siginer and H. P. Wang, eds. *Developments and Applications of Non-Newtonian Flows*, FED-Vol. 231/MD-Vol. 66, ASME, New York, 1995, pp. 99–105.

[3] Lee S, Choi SUS, Li S, Eastman JA. Measuring thermal conductivity of fluids containing oxide nanoparticles. *J Heat Transfer.* 1999;121:280-289. https://doi.org/10.1115/1.2825978

[4] Wang X, Xu X, Choi SUS. Thermal Conductivity of Nanoparticle - Fluid Mixture. *J Thermophys Heat Transfer.* 1999;13:474–480. https://doi.org/10.2514/2.6486

[5] Li CH, Peterson GP. The effect of particle size on the effective thermal conductivity of $Al_2O_3$ water nanofluid. *J Appl Phys.* 2007;101:044312. https://doi.org/10.1063/1.2436472

[6] Pak BC, Cho YI. Hydrodynamic and heat transfer study of dispersed fluids with submicron metallic oxide particles. *Exp Heat Transfer.* 1998;11:151–170. https://doi.org/10.1080/08916159808946559

[7] Anisha M, Kanimozhi B, Beemkumarb N, Jayaprapakar J. Experimental and numerical analysis of heat transfer from main vessel to safety vessel using $H_2O/Al_2O_3$ nanofluid in a nuclear reactor vault. *Desalin Water Treat.* 2018;114:135-145. https://doi.org/10.5004/dwt.2018.22384

[8] AbdEihafez SE, El-Shazly AH, El- Maghraby A. Improving the rate of solar from nanofluid using micro heat exchanger. *Desalin Water Treat.* 2016;57: 23066-23073. https://doi.org/10.1080/19443994.2016.1157987

[9] Manikandan SP, Baskar R. Assessment of the Influence of Graphene Nanoparticles on Thermal Conductivity of Graphene/Water Nanofluid Using Factorial Design of Experiments. *Period Polytech Chem Eng.* 2018;62:317-322. https://doi.org/10.3311/PPch.11676

[10] Manikandan SP, Baskar R. Experimental heat transfer studies on copper nanofluid in a plate heat exchanger. *Chem Ind Chem Eng Q.* 2021;27:15-20. https://doi.org/10.2298/CICEQ191220020P

[11] Manikandan SP, Baskar R. Heat transfer studies in compact heat exchanger using ZnO and $TiO_2$ Nanofluid in Ethylene Glycol/Water. *Chem Ind Chem Eng Q.* 2018;24:309-318. https://doi.org/10.2298/CICEQ170720003M

[12] Manikandan SP, Baskar R. Studies on thermo physical property variations of graphene nanoparticle suspended ethylene glycol/water. *Chem Ind Chem Eng Q.* 2021;27:177-187. https://doi.org/10.2298/CICEQ200504036P

[13] Huang D, Wu Z, Sunden B. Pressure drop and convective heat transfer of $Al_2O_3$/water and MWCNT/water nanofluid in a chevron plate heat exchanger. *Int J Heat Mass Transfer.* 2015;89:620–626. https://doi.org/10.1016/j.ijheatmasstransfer.2015.05.082

[14] Shanmugapriya M, Sangeetha P. Entropy generation analysis of Cu-water nanofluid flow over a moving wedge. *Desalin Water Treat.* 2018;121:14-21. https://doi.org/10.5004/dwt.2018.22189

[15] Kim SH, Choi SR, Kim D. Thermal conductivity of metal-oxide nanofluids: Particle size dependence and effect of laser irradiation. *J Heat Transfer.* 2007:129:298-307. https://doi.org/10.1115/1.2427071

[16] Kwon YH, Kim D, Li CG, Lee JK, Hong DS, Lee JG, Kim SH. Heat Transfer and Pressure Drop Characteristics of Nanofluid in a Plate Heat Exchanger. *J Nanosci Nanotechnol.* 2011;11:5769–5774. https://doi.org/10.1166/jnn.2011.4399

[17] Patel HE, Sundararajan T, Das SK. An experimental investigation into the thermal conductivity enhancement in oxide and metallic nanofluids. *J Nanopart Res.* 2010; 12:1015–1031. https://doi.org/10.1007/s11051-009-9658-2

[18] Wen D, Ding Y. Experimental investigation into convective heat transfer of nanofluid at the entrance region under laminar flow conditions. *Int J Heat Mass Transfer*. 2004;47: 5181–5188. https://doi.org/10.1016/j.ijheatmasstransfer.2004.07.012

[19] Mohebbi R, Khalilabad SH, Ma Y. Effect of -$Al_2O_3$/Water nanofluid on natural convection heat transfer of corrugated shaped cavity: study the different aspect ratio of grooves. *J Appl Fluid Mech.* 2019;12:1151-1160. https://doi.org/10.29252/JAFM.12.04.29455

[20] Satti JR, Das DK, Ray D. Investigation of the thermal conductivity of propylene glycol nanofluid and comparison with correlations*. Int J Heat Mass Transfer.* 2017:107: 871–881. https://doi.org/10.1016/j.ijheatmasstransfer.2016.10.121

[21] Barbés B, Páramo R, Blanco E, Pastoriza-Gallego MJ, Piñeiro MM, Legido JL. Thermal conductivity and specific heat capacity measurements of $Al_2O_3$ nanofluids. *J Therm Anal Calorim.* 2013; 111:1615–1625. https://doi.org/10.1007/s10973-012-2534-9

[22] Pandey SD, Nema VK. Experimental analysis of heat transfer and friction factor of nanofluidas a coolant in a corrugated plate heat exchanger*. Exp Therm Fluid Sci.*2012;38:248–256. https://doi.org/10.1016/j.expthermflusci.2011.12.013

[23] Rashidi I, Mahian O, Lorenzini G, Biserni C, Wongwises S. Natural convection of Al2O3/water nanofluid in a square cavity: effects of heterogeneous heating. *Int J Heat Mass Transfer.* 2014;74: 391–402. https://doi.org/10.1016/j.ijheatmasstransfer.2014.03.030

[24] Durga Prasad PV, Gupta S, Sreeramulu M, Sundar LS, Singh MK, Sousa ACM. Experimental study of heat transfer and friction factor of $Al_2O_3$ nanofluid in U-tube heat exchanger with helical tape inserts. *Exp Therm Fluid Sci.* 2015; 62:141–150. https://doi.org/10.1016/j.expthermflusci.2014.12.006

[25] Arunkumar T, Kaiwalya Raja, Denkenberger D, Velraja R. Heat carrier nanofluid in solar still-A review. Desalin Water Treat. 2018; 130:1-16. https://doi.org/10.5004/dwt.2018.22972

[26] Maiga SEB, Nguyen CT, Galanis N, Roy G. Heat transfer behaviours of nanofluid in a uniformly heated tube. *Superlattices Microstruct.* 2004; 35:543–557. https://doi.org/10.1016/j.spmi.2003.09.012

[27] Nesakumar D, Baskar R. Analysis of $TiO_2$-ZnO/EG Hybrid Nanofluid Effect on Heat Transfer Enhancement. *Appl Math Inf Sci.* 2019:13: 965-972. https://doi.org/10.18576/amis/130609

[28] Lenth RV. Quick and easy analysis of unreplicated factorials. *Technometrics*. 1989;31:469-473. https://doi.org/10.2307/1269997

[29] Plackett RL, Burman JP. The Design of Optimum Multifactorial Experiments. *Biometrika*. 1946;33:305-325. https://doi.org/10.2307/2332195

**SAŽETAK**

## Analiza toplotne provodljivosti nanofluida $Al_2O_3$/voda-etilen glikol korišćenjem faktorskog dizajna eksperimenata u aparatu za prenos toplote sa prirodnom konvekcijom

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(Naučni rad)

Toplotna provodljivost fluida za prenos toplote ima značajnu ulogu u poboljšanju performansi razmenjivača toplote. U ovom radu eksperimenti su izvedeni u aparatu za prenos toplote sa prirodnom konvekcijom mešanjem homogenizovanih nanočestica $Al_2O_3$ u osnovnom fluidu koji predstavlja smešu voda-etilenglikol. Analizirani su efekti unosa toplote, zapreminskog sadržaja nanočestica u osnovnom fluidu i zapreminskog udela etilenglikola u osnovnom fluidu na toplotnu provodljivost nanofluida. Na osnovu rezultata dobijenih pomoću programskog paketa MINITAB® (matrica faktorskog dizajna), izvedeno je 16 eksperimentalnih ciklusa sa nižim I višim nivoima ulaznih faktora. Nivoi za unos toplote bili su 10 i 100 W; za zapreminski sadržaj nanočestica u osnovnom fluidu 0,1 i 1,0 vol.% i za sastav osnovnog fluida 30 i 50 vol.% etilenglikola u vodi. Iz dobijenih eksperimentalnih rezultata kostruisani su Pareto dijagram, dijagram normalne verovatnoće, konturni grafikon i površinski grafikon. Na osnovu rezultata predložena je nova korelacija, a predviđanja su upoređena sa eksperimentalnim rezultatima. Iz studije je uočena maksimalna vrednost toplotne provodljivosti od 0,49 W $m^{-1}K^{-1}$ pri zapreminskom sadržaju nanočestica u osnovnom fluidu i od 1,0 vol.%, zapreminskom udelu etilenglikola u osnovnom fluidu od 30 vol.% i unosu toplote od 100 W.


*Ključne reči:* izmenjivač toplote; osnovni fluid; MINITAB; nanočestica; konturni i površinski dijagrami

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# Optimization of spray drying conditions for production of *Achillea millefolium* extract powder

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ORIGINAL SCIENTIFIC PAPER

**UDC: 66.047.47 048.34: 633.88**

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*Abstract*

In this study, a spray drying process of yarrow (*Achillea millefolium* L.) liquid extracts was optimized by using the response surface methodology. The study aimed to determine the influence of temperature (120-195 °C), liquid flow rate (3-16.5 cm$^3$ min$^{-1}$) and dry matter content in the liquid extract (0.3-1.5 %) on the yield of the drying process, the total polyphenols content and the antioxidant activity of the dry powder. Under the tested conditions the yield varied dramatically and ranged from 8 to 75 %, while the effects on the polyphenol content and antioxidant activity were lower. The optimized conditions for the maximum antioxidant activity and maximal yield of the dried extract were as follows: temperature of 130 °C, liquid flow rate of 7.5 cm$^3$ min$^{-1}$ and dry matter content of 1.2 %. Under the optimal conditions, the yield was 66 %, while there was a slight decrease in the polyphenol content in the dried extract as compared to that in the liquid extract (145 mg of gallic acid equivalents [GAE] per g of the total dry matter *vs*. 152 mg GAE g$^{-1}$, respectively). Consequently, antioxidant activity of the dry powder was only slightly reduced as compared to that of the liquid extract (DPPH neutralization was 58 *vs*. 64 %, respectively). The dried yarrow powder preserved its antimicrobial activity against pathogenic bacteria *Staphylococcus aureus* (MIC value of 10 mg cm$^{-3}$) and *Pseudomonas aeruginosa* (MIC value of 20 mg cm$^{-3}$).

*Keywords:* yarrow; polyphenols; antioxidant activity; antimicrobial activity.

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## 1. INTRODUCTION

Medicinal plants are widely used in medicine, cosmetics and human nutrition. The *World Health Organization* (WHO) estimates that 65 to 80 % of the world population uses medicinal plants as a primary form of health care [1]. The positive effect of medicinal herbs is explained by the presence of bioactive compounds, secondary metabolites, which can exhibit various biological activities, such as antimicrobial, antioxidant, anti-inflammatory, cytotoxic, diuretic, spasmolytic and many other effects [2]. Plant organisms contain pharmacologically active compounds, while the efficacy of the produced plant preparations depends on the preparation method, which can dramatically influence the quality of the final product. It is well established that different extraction methods, different solvents and drying conditions are investigated for maintaining the quality of herbal products [3-5].

*Achillea millefolium* L. (yarrow) is among the most widely used medicinal plants belonging to the family of *Asteraceae*. Yarrow is commonly found in Europe, North Africa, North America, and Asia [6]. The plant is used in the folk medicine to treat respiratory tract infections, diabetes, kidney disorders, to improve digestion and as an appetite-enhancing drug [6,7]. Yarrow has proven antimicrobial, antitumor, antioxidant and anti-inflammatory properties due to the presence of bioactive compounds that primarily belong to the group of polyphenols [8-10], which are mostly phenolic acids and flavonoids [8,11].

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In order to prepare herbal products, medicinal herbs are subjected to various processes including drying, mechanical processing (grinding, sieving and separation), distillation and extraction in various solvents. Extraction of the pharmacologically and biologically active ingredients from the plant material yields liquid extracts, which upon drying produce semi-solid or solid-consistency preparations [5,12]. Dried plant extract powder is the most common and widely used form of medicinal plant products because the solid form offers higher physicochemical and microbiological stability than the corresponding liquid form, while transport and storage become easier [13-16]. Several techniques including spray drying, freeze-drying, spouted bed and fluidized bed drying can be used to obtain powder extracts [17,18]. Spray drying is a commonly used technique that may be employed to produce powders of fine particles with higher concentrations and stability of active substances [19,20]. This technology offers high production rates and lower operating costs in comparison to alternatives, and it is a single step drying process [21,22]. Spray drying consists of atomization of feed, droplet-air contact, drying, and separation of the dried product from the gas phase [23]. The feed solution is dispersed into droplets that are rapidly dried due to the high surface area and intimate contact with the drying gas. The obtained dried powder is protected from overheating by rapid removal from the drying zone and the final product can be removed from the gas stream by cyclones and/or filters [19].

In order to improve the spray drying process and avoid problems such as low yields, sticking and high moisture content in the obtained particles, operating variables (inlet air temperature, the flow rate of the drying gas and liquid feeds, and atomizing conditions) should be optimized [21,24,25]. In addition, during the drying process degradation of bioactive compounds should be prevented by selecting appropriate conditions.

The aim of this study was to optimize spray drying conditions to produce *A. millefolium* L. dry extract with preserved bioactive components belonging to the group of polyphenols. Influence of spray drying parameters (temperature, liquid flow rate and dry matter content in the dried liquid extract) on the yield, polyphenol content and antioxidant activity of the dry powder were modeled by using the response surface methodology (RSM). Upon optimization, antimicrobial activity of the dry powder produced under optimal condition was tested against *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

## 2. MATERIALS AND METHODS

### 2. 1. Materials

For this study, waste yarrow was used as a raw material, which was obtained from the Institute of Medicinal Plant Research "Dr Josif Pančić", Belgrade, Serbia. The experimental material was a dust waste discarded after production of tea, for which yarrow was grind and fractionated and the plant material with particle sizes lower than 0.3 mm was discarded as dust. The yarrow dust was stored in the dark, at room temperature in paper bags. Ethanol (96 %) supplied by Zorka Pharma, Serbia was used as a solvent for the extraction process. Folin-Ciocalteu reagent, methanol, gallic acid and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were obtained from Sigma Aldrich, while sodium carbonate was purchased from Lach-Ner, Czech Republic. Resazurin was purchased from Acros Organics, Geel, Belgium. All chemicals were the highest commercial grades and were used as received without any further purification.

### 2. 2. Microwave-assisted extraction (MAE) of waste yarrow

Liquid yarrow extracts were prepared by microwave-assisted extraction (MAE) at conditions previously optimized to maximize the yield of total polyphenols and biological activity in a scaled-up process [11]. In short, the waste yarrow was mixed with 70 % ethanol at a liquid/solid ratio of 40 $cm^3 g^{-1}$ in total volume of 420 $cm^3$. Extraction was performed in a microwave oven (Samsung Electronics Euro QA Lab, United Kingdom) for 30 s at the microwave power of 600 W. The obtained liquid extract was separated from solids by filtration by using a vacuum pump (V-700, Buchilabortechnik AG, Fanil, Switzerland) and concentrated in a rotary evaporator (Buchilabortechnik AG, Fanil, Switzerland) at a vacuum pressure of 150 mbar and temperature of 60 °C. After the evaporation process, dry matter content in the extracts was determined by using a moisture analyser (Kern MLS-A, Balingen, Germany).

## 2. 3. Experimental design of spray drying

In order to determine the optimal conditions for spray drying resulting in the maximum yield, total polyphenol content and antioxidant activity, RSM and central composite design (CCD) were used. RSM is the most commonly used mathematical and statistical method for modeling and analyzing a process (when the response of interest is affected by various variables and the objective of the method is to optimize the response) [26]. According to the experimental design, the effect of process factors was analyzed within following range: inlet air temperatures (95-195 °C), liquid flow rates (3 – 21 $cm^3$ $min^{-1}$) and dry matter content in the liquid extracts (0.3 - 1.5 %). A statistical package, Design-Expert (Version 8, Stat-Ease, Inc., Minneapolis, United States) was used for experimental design and the experimental data analysis. Yarrow liquid extracts (200 $cm^3$) were fed into a drying chamber by a peristaltic pump connected to a two-fluid atomizer linked to an air compressor (Büchi Mini Spray Dryer B-290, Switzerland). The compressor forces air into the outer tube of the nozzle which causes the liquid to emerge as a fine, atomized spray. The feed system of drying gas constituted of a blower and an air filter. Dried product was collected in a cyclone. After performing 23 predicted experiments of spray drying, 8 series of experiments yielded products of poor quality (insufficiently dried material was obtained). These experimental points were eliminated from the calculations in the model, and the historical data design with 15 experimental runs was selected for modeling and analysis of the relationships between the inlet parameters and the responses. As a result, the process variables were reduced to the following ranges: temperature, 120-195 °C (*A*); liquid flow rate, 3-16.5 $cm^3$ $min^{-1}$ (*B*) and dry matter content, 0.3-1.5 % (*C*). The influence of these variables on three system responses (yield ($Y_1$), total polyphenol content ($Y_2$) and antioxidant activity of the dried extract powders ($Y_3$)) was evaluated (Table 1). The experimental data were fitted to a cubic polynomial model, and by applying the analysis of variance (ANOVA) adequacy and statistical significance of the proposed mathematical models were assessed.

*Table 1. Design matrix and corresponding responses (A is the temperature, B is the liquid flow rate, C is the dry matter content, $Y_1$ is the yield, $Y_2$ is the total polyphenol content, $Y_3$ is the antioxidant activity of the dried extract powders)*

| Run | Independent variable | | | Responses | | |
|---|---|---|---|---|---|---|
| | *A* / °C | *B* / $cm^3$ $min^{-1}$ | *C* / % | $Y_1$ / % | $Y_2$ / mgGAE $g^{-1}$ | $Y_3$ / % |
| 1 | 120 | 7.5 | 0.6 | 62 | 145 | 41.5 |
| 2 | 120 | 7.5 | 1.2 | 65 | 137 | 53 |
| 3 | 145 | 3 | 0.9 | 41 | 148 | 47 |
| 4 | 145 | 3 | 0.9 | 27 | 141 | 54 |
| 5 | 145 | 12 | 0.3 | 20 | 140 | 61 |
| 6 | 145 | 12 | 0.3 | 25 | 137 | 59 |
| 7 | 145 | 12 | 0.9 | 38 | 155 | 57 |
| 8 | 145 | 12 | 0.9 | 40 | 157 | 58 |
| 9 | 145 | 12 | 0.9 | 37 | 149 | 59 |
| 10 | 145 | 12 | 1.5 | 8 | 131 | 47 |
| 11 | 145 | 12 | 1.5 | 11 | 137 | 49 |
| 12 | 170 | 7.5 | 0.6 | 39 | 145 | 64 |
| 13 | 170 | 7.5 | 1.2 | 75 | 135 | 41 |
| 14 | 170 | 16.5 | 0.6 | 45 | 141 | 42 |
| 15 | 195 | 12 | 0.9 | 65 | 154 | 62 |

By using backward elimination, terms in the models that had a non-significant effect on a response ($p > 0.1$) were removed from the equations and the experimental data were refitted. The models were validated by performing additional experiment using the optimal conditions predicted by the RSM. The fitted polynomial equations were presented as surface plots in order to visualize the relationship between the independent variables and the response variables.

## 2. 4. Yield

The drying yield was calculated as the ratio of the powder dry weight and the dry weight of the liquid extract and expressed as %.

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### 2. 5. Determination of the total polyphenol content

The total polyphenol content was quantified colorimetrically by using a modified Folin-Ciocalteu method and gallic acid (GAE) as a reference standard [27]. For determination of phenolic content, 0.1 $cm^3$ of the liquid yarrow extract or dissolved dry extract at the final concentration of 10 mg $cm^{-3}$ was combined with 0.5 $cm^3$ of the Folin-Ciocalteu reagent and 6 $cm^3$ of distilled water. The mixture was shaken for 60 s and subsequently, 2 $cm^3$ of 15 % $Na_2CO_3$ was added, and the mixture was additionally shaken for 30 s. Finally, distilled water was added to reach the final volume of 10 $cm^3$. After 2 h of incubation in the dark at room temperature, the absorbance was read at 750 nm by using a UV/visible spectrophotometer (Ultrospec 3300 pro, Amersham Bioscience, Sweden). The blank was prepared by using 70 % ethanol instead of a sample. Results were reported as mass of GAE per mass of the total dry matter. Three series of experiments were performed, and the results are presented as mean values.

### 2. 6. Determination of antioxidant activity

Antioxidant activity of the liquid and dried extracts was measured by using the DPPH radical-scavenging assay [28]. DPPH solution (0.2 mM) was prepared by dissolving the adequate amount of DPPH in methanol. To measure the DPPH neutralization capacity the total of 0.05 $cm^3$ of the liquid yarrow extract or dissolved dry extract in 70 % ethanol, at the final concentration of 1 mg $cm^{-3}$, was mixed with 3.95 $cm^{-3}$ of methanol and 1 $cm^{-3}$ of 0.2 mM DPPH methanol solution. The obtained solutions were vigorously shaken and kept in the dark at room temperature for 30 min. The absorbance was read against a blank (methanol) at 517 nm. A control sample was prepared by using 70 % ethanol solution instead of an extract. Results were expressed as inhibition percentages of free DPPH radicals relative to the control sample and calculated according to the equation:

$$\text{Inhibition} = \frac{A_c - A_s}{A_c} 100 \qquad (1)$$

where $A_c$ is the absorbance of the control and $A_s$ is the absorbance of the sample. Three series of experiments were performed, and the results are presented as mean values.

### 2. 7. Determination of the minimum inhibitory concentration

The microdilution method was used to determine the minimum inhibitory concentration (MIC) of *A. millefolium* L. dry extract obtained under optimal drying conditions with resazurin as an indicator of cell growth. The dry yarrow extract was dissolved at the final concentration of 40 mg $cm^{-3}$ in 20 % ethanol. Resazurin solution (6.75 g $dm^{-3}$) was prepared by dissolving the appropriate amount in distilled water, vortexed and filter sterilized (0.45 µm filter). The Gram-positive bacterium *Staphylococcus aureus* ATCC 25923 and Gram-negative bacterium *Pseudomonas aeruginosa* PAO1 were grown in Trypton soy broth (TSB, Torlak, Serbia). TSB was prepared by dissolving 30 g of the commercially available TSB powder and 6 g of yeast extract in 1 $dm^3$ of distilled water. The medium was boiled for 15 min and then sterilized in an autoclave for 30 min at 120 °C.

The nutrient medium (TSB 0.1 $cm^3$) was poured into all wells of a 96 well microtiter plate, followed by addition of 0.1 $cm^3$ of yarrow extracts in the first column (therefore the concentration of the extract in the first column was 20 mg of total dry matter per $cm^3$). A series of double dilutions was achieved by transferring 0.1 $cm^3$ of the mixture of medium and yarrow extracts to the next column so that the final volume in each well was 0.1 $cm^3$. Eight series of dilutions were made so that the yarrow concentration varied in the range from 0.16 to 20 mg of the total dry matter per $cm^3$. Next, 0.01 $cm^3$ of the resazurin solution and 0.01 $cm^3$ of bacterial suspension were added to each well so that the final concentration was $5 \times 10^6$ CFU $cm^{-3}$. Controls were prepared in parallel with the samples. The positive control contained 0.1 $cm^3$ of TSB medium, 0.01 $cm^3$ of resazurin and 0.01 $cm^3$ of bacterial suspension, and the negative control contained 0.05 $cm^3$ of TSB medium, 0.05 $cm^3$ of yarrow extract and 0.01 $cm^3$ of resazurin. Microtiter plates were incubated for 24 h at 37 °C. After the incubation, the minimum inhibitory concentration was determined visually based on the colour. Any change in colour from purple to pink or colourless was considered as positive (indicative of microbial growth). The lowest concentration at which colour change not was observed was adopted as the MIC value [29]. The tests for both strains were performed twice, and the results are presented as mean values.

## 3. RESULTS AND DISCUSSION

### 3. 1. Model determination

Multiple regression analysis was applied to the experimental data resulting in correlations between the spray drying parameters (temperature, liquid flow rate and dry matter content) and the yield, polyphenol content and antioxidant activity of the powders. By application of the analysis of variance (ANOVA) the adequacy and statistical significance of all models was assessed. Two measured responses, *i.e*. the yield and the antioxidant activity of the dry powders fitted the third order polynomial equation. The total polyphenol content in dry powders was not significantly influenced by the drying conditions, and only a mean value for this response was obtained.

Values of the coefficient of determination for the yield and antioxidant activity between the response function and the experimentally obtained results were high amounting to 0.98 and 0.90, respectively. “Adequate Precision” measures the signal to noise ratio, and a ratio greater than 4 is desirable. The ratio of 16.4 and 12.2 for the yield and antioxidant activity, respectively, indicated an adequate signal. The lack of fit of both models was not significant, and after removing the effect of non-significant factors by using backward reduction, the relationship between the two responses and tested variables could be explained by the following equations:

$$Y_1 = 22.75 - 24.50A - 38.42B - 28.83C - 128.25AB - 67.00AC - 113.17BC + 66.75A^2 - 22.33C^2 - 183.50ABC \quad (2)$$

$$Y_3 = 56.54 + 4.38A + 6.37B + 18.72AC + 30.20BC + 90.64ABC \quad (3)$$

where $Y_1$ (the yield) and $Y_3$ (the antioxidant activity) are the responses, and the independent variables are $A$ (temperature), $B$ (liquid flow rate) and $C$ (dry matter content).

### 3. 2. Influence of drying parameters on the dried extract yield

High yield is one of the objectives of spray drying processes. Under the tested drying conditions, the yield varied from 8 to 75 % (Table 1). The highest product yield was 75 % at an inlet air temperature of 170 °C, liquid flow rate of 7.5 $cm^3 min^{-1}$ and dry matter content of 1.2 % (run 13). According to the analysis of the experimental data three linear terms ($A$, $B$ and $C$), three interaction parameters ($AB$, $AC$ and $BC$), two quadratic terms ($A^2$ and $C^2$) and one cubic interaction parameter ($ABC$) had significant effects on the dried extract yield. Positive sign of the quadratic term of temperature (Eq (2) $A^2$) indicated presence of a function minimum, while the negative sign of the quadratic term in relation to dry matter content ($C^2$) indicated existence of a function maximum. Interactions between the temperature and the liquid flow rate, between the temperature and the dry matter content, and between the liquid flow rate and the dry matter content had an antagonistic effect on the dried extract yield. In order to visualize influence of the interacting variables ($AB$, $AC$ and $BC$) on the dried extract yield, response surface plots were created (Fig. 1).

The dried extract yield increased when the dry matter content was in the range 0.9-1.2 % and achieved the highest value at 1.2 % of dry matter content (Table 1, run 13). It is well documented in the literature that when feed concentration increases, the amount of moisture is decreasing together with the energy needed to evaporate water [30]. With the higher feed concentration, more complete drying prevents sticking of the product resulting in better separation [31,32]. Furthermore, more concentrated solutions provide larger particles with better cyclone separation [33,34]. However, further increase in the feed concentration (in this study up to 1.5 % of the dry matter content) can produce even larger particles, which are drying more slowly than the smaller ones, obtained at lower solid contents in the final product. This phenomenon increases deposition in the drying chamber and hence reduces the yield [35].

The maximum dried extract yield was obtained at the liquid flow rate of 7.5 $cm^3 min^{-1}$ (Table 1, run 13). Existence of the function maximum could be explained by the liquid residence time. In specific, as the liquid flow rate is decreased, the liquid residence time is increasing providing droplets the chance for drying. Correspondingly, as the flow rate is increased, the residence time is decreased resulting in incomplete drying and poorer yield. The same trend as observed in our study was reported by others [36,37]. Both research groups favored lower flow rates that allowed more complete water evaporation and decreased the probability of dispersion and condensation on the chamber walls, which consequently resulted in better process yields. Moreover, in another study it was concluded that the pump rotation speed could induce a negative effect on the yield since higher flow rates can cause clogging of the atomization nozzle,

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resulting in lower drying mass yields [38]. Negative influence of higher flow rates on the yield, could be also explained by reduction of the outlet air temperature, and consequent lower thermal energy supply that was probably insufficient for complete drying. In this case, sticking occurred in the drying chamber, lowering the yield and increasing the moisture content, in line with previous reports [39].

Temperature had a different influence on the drying yield within the tested temperature range (up to 170 °C). Figure 1 shows that high yields are obtained in the drying process under two scenarios: 1) at low temperature, lower liquid flow rate and high dry matter content, or 2) at high temperature, low liquid flow rate and high dry matter content. In general, at a temperature of 170 °C the yield reached the maximum, while a slightly lower yield was observed at a temperature of 120 °C with the same dry matter content in the liquid extract. In our study, at lower temperatures and very high liquid flow rates, the particles were sticking together, which is in line with the observation of others [39,40]. When higher inlet air temperatures are used, heat and mass transfers are enhanced so that the probability of moist particles to stick to the drying chamber wall is decreasing [41-45].

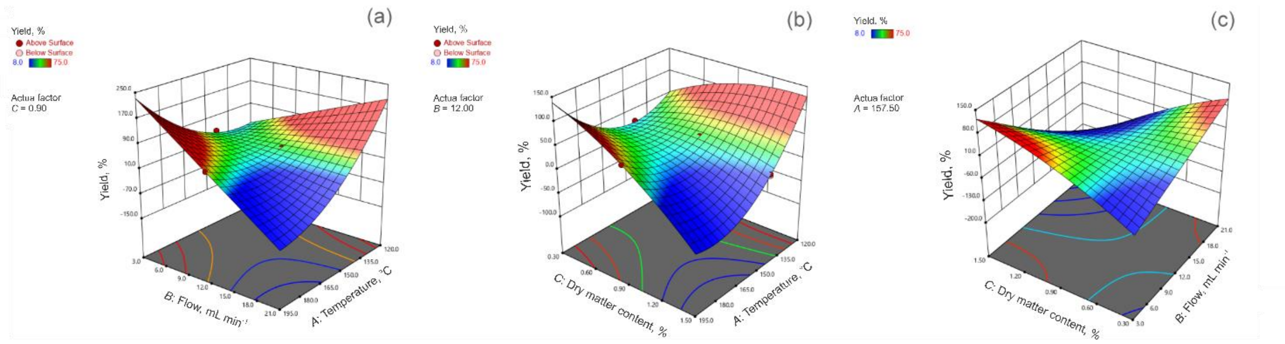


*Figure 1. Surface plots of interactive effects on the dried extract yield of drying parameters: a) temperature and liquid flow rate (AB), b) temperature and the dry matter content (AC) and c) liquid flow rate and the dry matter content (BC)*

### 3. 3. Influence of drying parameters on the total polyphenol content

Total polyphenol contents in the dried extracts obtained under the tested spray drying conditions were in the range of 131-157 mg GAE $g^{-1}$ dry matter, which was comparable to the total polyphenol content in the starting liquid extract (feed) amounting to 152 mg GAE $g^{-1}$ dry matter. Although it is typical to observe a slight decrease in the polyphenol content in the powder extracts as a result of the exposure to high temperatures [46,47], selection of relatively mild drying conditions in this study apparently prevented significant polyphenol degradation.

### 3. 4. Influence of drying parameters on antioxidant activity

Antioxidant activity of dry extracts was significantly influenced by two linear (*A*, *B*), two interaction parameters (*AC*, *BC*), and one cubic interaction parameter (*ABC*). The Eq. (3) shows that both linear parameters (temperature and liquid flow rate) had positive effects on antioxidant capacity, indicating that the higher antioxidant activity of the dried extract was achieved with the increase in these factors. Interactions between the temperature and the dry matter content, between the liquid flow rate and the dry matter content, and between all tested parameters (*ABC*) had synergetic and positive effects on the antioxidant activity. In order to visualize the influence of the interacting variables on the antioxidant activity, response surface plot was created (Fig. 2).

Although there was significant influence of the drying parameters on the antioxidant activity of the dried extracts, it should be stressed that compared to the antioxidant activity of the liquid extract (64 % DPPH scavenging activity), only a slight change in the antioxidant activity after the drying process was observed.

Antioxidant activities of the obtained powders correlate with the total polyphenol content. Souza et al. reported that high temperatures generate higher water evaporation; therefore, drying is more rapid, and the loss of labile compounds is lower [48]. There are also examples of increased total polyphenol content after heat treatment of various food products: green pepper, green beans, spinach [49], or onion powder [50]. This increase is attributed to the liberation of phenolic compounds by the cleavage of esterified and glycosylated bonds [50]. While in this study negligible effects of the drying conditions on the total polyphenol content were observed, the observed relative decrease in the DPPH scavenging activity could be attributed to some subtle changes in the chemical nature of the polyphenols. Similar results of slight decrease of antioxidant activity upon drying were noted by others [51,52].

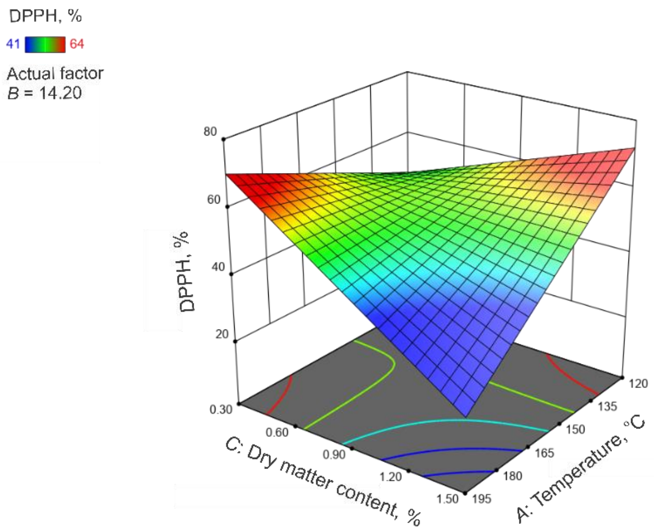


*Figure 2. Surface plot of interactive effects of temperature and the dry matter content (AC) on the total antioxidant activity*

### 3. 5. Validation of the models

The objective of this study was to optimize spray drying conditions for obtaining the maximal yield of yarrow powder extracts with the maximal antioxidant activity. The optimal conditions were determined by using the desirability function approach yielding: 130 °C; 7.5 cm$^3$ min$^{-1}$ the liquid flow rate and 1.2 % of dry matter content in the feed. Predicted values for the two outcomes were the following: the antioxidant activity of 57 %, and maximal yield of 61 %. Measured values for dry extracts obtained under the optimal conditions fitted within the 95 % Pis for all parameters and were close to the most probable predicated values: the antioxidant activity (58 %) and dried extract yield (66 %). The DPPH radical scavenging activity of the dry extract obtained under the optimal conditions was 58 %, which marked a slight decrease in the radical scavenging activity as compared to that of the liquid extract that valued 64 %. Compared to the polyphenol content in the liquid extract (152 mg GAE g$^{-1}$), there was a slight decrease in the polyphenols content after drying of extract (145 mg GAE g$^{-1}$). This result indicated a more significant reduction in antioxidant capacity then that in the total polyphenol content. About 91 % of antioxidant capacity was retained after the drying process, while 95 % of total polyphenols were preserved in the dried extract.

### 3. 6. Antimicrobial activity of liquid and dried extracts

Antimicrobial activity of medicinal plants results from the combined effect of compounds, mostly polyphenols. In this study we evaluated the antimicrobial activity of the dry powder obtained under optimal conditions against two pathogens. The results showed that the antimicrobial activity of yarrow extract against *S. aureus* and *P. aeruginosa* was preserved after the drying process. Sensitivity of *P. aeruginosa* was similar to the liquid and dry extracts (MIC value of 20 mg cm$^{-3}$), while, in line with the slight decrease in the antioxidant activity, the dry powder was slightly less potent when suppressing the growth of *S. aureus* (MIC value of the liquid extract was 5 mg cm$^{-3}$, and 10 mg cm$^{-3}$ for the dry extract).

It is well established that yarrow extracts exhibit antibacterial activity against Gram-positive bacterial species, while the results against Gram-negative species are less evident, which is in line with our findings [53]. The resilience of Gram-negative bacteria can be ascribed to the structure of their cell wall, which contains lipopolysaccharide, which is relatively impermeable to polyphenols [54,55]. The observation that Gram-negative bacteria are less sensitive to the *A. millefolium* antibacterial activity than Gram-positive was also shown by the research of Tajiket al. [56]. *A. millefolium* L. in addition to flavonoids that are typical for the genus *Achillea*, contains sesquiterpene lactones as active compounds [57]. It is believed

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that the α-methylene lactone moiety of the molecule is responsible for the activity, because the activity disappears when the double bond is reduced, as shown in the case of α-methyl lactones from *Achillea atrata* [58].

## 4. CONCLUSION

The results reported in this study indicate the significant impact of spray drying conditions on properties of the obtained *Achillea millefolium* L. dry extract. RSM was successfully applied to model the effects of temperature, liquid flow rate and the dry matter content in the feed on the yield and antioxidant activity of the dry yarrow extract. The obtained mathematical models were applied to optimize drying conditions, which yielded production of a dry extract in which 91 % of the antioxidant potential was preserved. In addition to these properties, powder obtained under the optimal drying conditions, showed a preserved antimicrobial activity against *S. aureus* and *P. aeruginosa*. Therefore, it can be concluded that drying conditions predominantly influence the yield of the product with a moderate effect on the biological activity of the dry extract, under tested conditions. The obtained spray dried yarrow powder was green/brown in color with evident bioactive properties suitable for various medical or pharmaceutical applications. This research is useful as it identifies the most appropriate operating conditions for spray drying of liquid yarrow extracts, and it can be used as a reference for further research.

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## REFERENCES

[1] Palhares RM, Gonçalves Drummond M, dos Santos Alves Figueiredo Brasil B, Pereira Cosenza G, das Graças Lins Brandao M, Oliveira G. Medicinal plants recommended by the world health organization: DNA barcode identification associated with chemical analyses guarantees their quality. *PloS one*. 2015;10:e0127866. https://doi.org/10.1371/journal.pone.0127866

[2] Popovic V, Tatic M, Sikora V, Ikanovic J, Drazic G, Djukic V, Mihailovic B, Filipovic V, Dozet G, Jovanovic Lj, Stevanovic P. Variability of yield and chemical composition in soybean genotypes grown under different agro-ecological conditions of Serbia. *Rom Agric Res*. 2016;33:29-39.

[3] Pham HNT, Nguyen VT, Vuong QV, Bowyer MC, Scarlett CJ. Effect of extraction solvents and drying methods on the physicochemical and antioxidant properties of *Helicteres hirsuta* Lour. leaves. *Technol*. 2015;3:285-301. https://doi.org/10.3390/technologies3040285

[4] Azmin SNHM, Manan ZA, Alwi SRW, Chua LS, Mustaffa AA, Yunus NA. Herbal processing and extraction technologies. *Sep Purif Rev*. 2016;45:305-320. https://doi.org/10.1080/15422119.2016.1145395

[5] Zhang QW, Lin LG, Ye WC. Techniques for extraction and isolation of natural products:a comprehensive review. *Chin Med-UK*. 2018;13:2-26. https://doi.org/10.1186/s13020-018-0177-x

[6] Lakshmi T, Geetha RV, Roy A, Kumar SA. Yarrow (*Achillea Millefolium Linn*.) a herbal medicinal plant with broad therapeutic use-A review. *Int J Pharm Sci Rev Res*. 2011;9:136-141.

[7] Cavalcanti AM, Baggio CH, Freitas CS, Rieck L, de Sousa RS, Da Silva-Santos JE, Mesia-Vela S, Marques MC. Safety and antiulcer efficacy studies of *Achillea millefolium* L. after chronic treatment in Wistar rats. *J Ethnopharmacol*. 2006;107:277-284. https://doi.org/10.1016/j.jep.2006.03.011

[8] Benedek B, Kopp B. *Achillea millefolium* L. s.l. revisited:Recent findings confirm the traditional use. *Wien Med Wochenschr*. 2007;157:312-314. https://doi.org/10.1007/s10354-007-0431-9

[9] Saeidnia S, Gohari AR, Mokhber-Dezfuli N, Kiuchi F. A review on phytochemistry and medicinal properties of the genus *Achillea*. *DARU*. 2011;19:173-86.

[10] Othman L, Sleiman A, Abdel-Massih RM. Antimicrobial activity of polyphenols and alkaloids in Middle Eastern plants. *Front Microbiol*. 2019;10:911. https://doi.org/10.3389/fmicb.2019.00911

[11] Milutinovic M, Radovanovic N, Corovic M, Siler-Marinkovic S, Rajilic-Stojanovic M, Dimitrijevic-Brankovic S. Optimisation of microwave-assisted extraction parameters for antioxidants from waste *Achillea millefolium* dust. *Ind Crop Prod*. 2015;77:333-341. https://doi.org/ 10.1016/j.indcrop.2015.09.007

[12] Sasidharan S, Chen Y, Saravanan D, Sundram KM, Yoga Latha L. Extraction, isolation and characterization of bioactive compounds from plants' extracts. *Afr J TraditComplem*. 2011;8:1-10. https://doi.org/10.4314/ajtcam.v8i1.60483

[13] Oliveira WP, Bott RB, Souza CRF. Manufacture of standardized dried extracts from medicinal Brazilian plants. *Dry Technol*. 2006;24:523-533. https://doi.org/10.1080/07373930600612073

[14] Bakowska-Barczak AM, Kolodziejczyk PP. Black currant polyphenols:their storage stability and microencapsulation. *Ind Crop Prod*. 2011;34:1301-1309. https://doi.org/10.1016/j.indcrop.2010.10.002
[15] Rocha GA, Favaro-Trindade CS, Grosso CRF. Microencapsulation of lycopene by spray drying:Characterization, stability and application of microcapsules. *Food Bioprod Process*. 2012;90:1-6. https://doi.org/10.1016/j.fbp.2011.01.001
[16] Yatsu FKJ, Borghetti GS, Bassani VL. Technological characterization and stability of *Ilex paraguariensis* St. Hil. Aquifoliaceae (Mate) spray-dried powder. *J Med Food*. 2011;14:413-419. https://doi.org/10.1089/jmf.2010.0044
[17] Souza CRF, Oliveira WP. Powder properties and system behaviour during spray drying of *Bauhinia forficata* link extract. *Dry Technol*. 2006;24:735-749. https://doi.org/10.1080/07373930600685905
[18] Cortes-Rojas DF, Oliveira WP. Physicochemical properties of phytopharmaceutical preparations as affected by drying methods and carriers. *Dry Technol*. 2012;30:921-934. https://doi.org/10.1080/07373937.2012.666608
[19] Amaro MI, Tajber L, Corrigan OI, Healy AM. Optimisation of spray drying process conditions for sugar nanoporousmicroparticles (NPMPs) intended for inhalation. *Int J Pharm*. 2011;421:99-109. https://doi.org/10.1016/j.ijpharm.2011.09.021
[20] Nedovic V, Kalusevic A, Manojlovic V, Petrovic T, Bugarski B. Encapsulation Systems in the Food Industry. In:Advances in Food Process Engineering Research and Applications, Boston, MA:Springer Nature America, Inc;2013:229-253. https://doi.org/10.1007/978-1-4614-7906-2_13
[21] Chegini GR, Ghobadian B. Spray dryer parameters for fruit juice drying. *World J Agric Sci*. 2007;3:230-236.
[22] Patel RP, Patel MP, Suthar AM. Spray drying technology:an overview. *Indian J Sci Technol*. 2009;2:44-47. https://doi.org/10.17485/ijst/2009/v2i10.3
[23] Andrea T, Marcela F, Lucia C, Esther F, Elena M, Simona M. Microencapsulation of lipase and savinase enzymes by spray drying using Arabic gum as wall material. *JEAS*. 2016;6:161-173. https://doi.org/10.1007/978-1-4614-7906-2_1310.4236/jeas.2016.64012
[24] Ozmen L, Langrish TAG. An experimental investigation of the wall deposition of milk powder in a pilot-scale spray dryer. *Dry Technol*. 2003;21:1253-1272. https://doi.org/10.1081/DRT-120023179
[25] Kudra T. Sticky region in drying:Definition and identification. *Dry Technol*. 2003;21:1457-1469. https://doi.org/10.1081/DRT-120024678
[26] Montgomery DC. Response Surface Methods and Designs. In:Design and analysis of experiments, Eighth Edition John Wiley and Sons, Inc, New Jersey;2005:478.
[27] Singleton V, Rossi JA. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *Am J Enol Vitic*. 1965;16:144-158.
[28] Lee SK, Mbwambo Z, Chung H, Luyengi L, Gamez E, Mehta R, Kinghorn A, Pezzuto J. Evaluation of the antioxidant potential of natural products. *Comb Chem High Throughput Screen.*1998;1:35.
[29] Sarker SD, Nahar L, Kumarasamy Y. Microtitre plate-based antibacterial assay incorporating resazurin as an indicator of cell growth, and its application in the in vitro antibacterial screening of phytochemicals. *Methods*. 2007;42:321-324. https://doi.org/10.1016/j.ymeth.2007.01.006
[30] Tontul I, Topuz A. Spray-drying of fruit and vegetable juices:Effect of drying conditions on the product yield and physical properties. *Trends Food Sci Tech*. 2017;63:91-102. https://doi.org/10.1016/j.tifs.2017.03.009
[31] Billon A, Bataille B, Cassanas G, Jacob M. Development of spray-dried acetaminophen microparticles using experimental designs. *Int J Pharm.* 2000;203:159-168. https://doi.org/10.1016/s0378-5173(00)00448-8
[32] Nguyen DQ, Nguyen TH, Mounir S, Allaf K. Effect of feed concentration and inlet air temperature on the properties of soymilk powder obtained by spray drying. *Dry Technol*. 2017;36(7):817-829. https://doi.org/10.1080/07373937.2017.1357040
[33] Prinn KB, Costantino HR, Tracy M. Statistical modeling of protein spray drying at the lab scale. *AAPS Pharm Sci Tech*. 2002;3:E4. https://doi.org/10.1208/pt030104
[34] Poozesh S, Jafari SM, Akafuah NK. Interrogation of a new inline multi-bin cyclone for sorting of produced powders of a lab-scale spray dryer. *Powder Technol*. 2020;373:590-598. https://doi.org/10.1016/j.powtec.2020.07.012
[35] Maurya M, Murphyb K, Kumarb S, Shib L, Leea G. Effects of process variables on the powder yield of spray-dried trehalose on a laboratory spray-dryer. *Eur J Pharm Biopharm*. 2005;59:565-573. https://doi.org/10.1016/j.ejpb.2004.10.002
[36] Gallo L, Llabot Juan M, Allemandi D, Bucala V, Pina J. Influence of spray-drying operating conditions on *Rhamnus purshiana* (Cascara sagrada) extract powder physical properties. *Powder Technol*. 2011;208:205-214. https://doi.org/10.1016/j.powtec.2010.12.021
[37] Telang AM, Thorat BN. Optimization of process parameters for spray drying of fermented soy milk. *Dry Technol*. 2010;28:1445-1456. https://doi.org/10.1080/07373937.2010.482694
[38] Toneli J, Park K, Negreiros A, Murr F. Spray-drying process optimization of chicory root inulin. *Dry Technol*. 2010;28:369-379. https://doi.org/10.1080/07373931003645017

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[39] Mihajlovic T, Ibric S, Mladenovic A. Application of design of experiments and multilayer perceptron neural network in optimization of the spray-drying process. *Dry Technol*. 2011;29:1638-1647. https://doi.org/10.1080/07373937.2011.592960

[40] Tee LH, Chuah L, Pin KY, Abdull Rashih A, Yusof YA. Optimization of spray drying process parameters of *Piper betle*L. (Sirih) leaves extract coated with maltodextrin. *J Chem Pharm Res*. 2012;4:1833-1841.

[41] Goula AM, Adamopoulos KG. Spray drying of tomato pulp in dehumidified air:I. The effect on product recovery. *J Food Eng*. 2005;66:25-34. https://doi.org/10.1016/j.jfoodeng.2004.02.029

[42] Tonon RV, Brabet C, Hubinger MD. Influence of process conditions on the physicochemical properties of acai *(Euterpe oleraceae* Mart) powder produced by spray drying. *J Food Eng*. 2008;88:411-418. https://doi.org/10.1016/j.jfoodeng.2008.02.029

[43] Ramos FdeM, Oliveira CCMde, Soares ASP, Silveira Junior V. Assessment of differences between products obtained in conventional and vacuum spray dryer. *Food Sci Technol*. 2016;36 (4):724-729. https://doi.org/10.1590/1678-457X.09216

[44] Jafari SM, Ghalenoei MG, Dehnad D. Influence of spray drying on water solubility index, apparent density, and anthocyanin content of pomegranate juice powder. *Powder Technol*. 2017;311:59-65. https://doi.org/10.1016/j.powtec.2017.01.070

[45] Pinon-Balderrama CI, Leyva-Porras C, Teran-Figueroa Y, Espinosa-Solis V, Alvarez-Salas C, Saavedra-Leos MZ. Encapsulation of Active Ingredients in Food Industry by Spray-Drying and Nano Spray-Drying Technologies. *Processes.* 2020;8 (8):889. https://doi.org/10.3390/pr8080889

[46] Eldridge JA, Repko D, Mumper RJ. Retention of polyphenolic species in spray-dried blackberry extract using mannitol as a thermoprotectant. *J Med Food*. 2014;17:1064-1069. https://doi.org/10.1089/jmf.2013.0177

[47] Bastias-Montes JM, Choque-Chavez MC, Alarcon-Enos J, Quevedo-Leon R, Munoz-Farina O, Vidal-San-Martin C. Effect of spray drying at 150, 160, and 170 °C on the physical and chemical properties of maqui extract (Aristotelia chilensis (Molina) Stuntz). *Chil J Agric Res*. 2019;79 (1):144-152. https://doi.org/10.4067/S0718-58392019000100144

[48] Souza V, Thomazini M, Balieiro J, Trindade C. Effect of spray drying on the physicochemical properties and color stability of the powdered pigment obtained from vinification byproducts of the Bordo grape (*Vitis labrusca*). *Food Bioprod Process*. 2015;93:39-50. https://doi.org/10.1016/j.fbp.2013.11.001

[49] Turkmen N, Sari F, Velioglu YS. The effect of cooking methods on total phenolics and antioxidant activity of selected green vegetables. *Food Chem*. 2005;93:713-718. https://doi.org/10.1016/j.foodchem.2004.12.038

[50] Sharma K, Ko EY, Assefa AD, Ha S, Nile SH, Lee ET, Park SW. Temperature-dependent studies on the total phenolics, flavonoids, antioxidant activities, and sugar content in six onion varieties. *J Food Drug Anal*. 2015;23:243-252. https://doi.org/10.1016/j.jfda.2014.10.005

[51] Fang Z, Bhandari B. Effect of spray drying and storage on the stability of bayberry polyphenols. *Food Chem*. 2011;129:1139-1147. https://doi.org/10.1016/j.foodchem.2011.05.093

[52] Edrisi M, Langrish TAG. Spray drying bioactive orange-peel extracts produced by Soxhlet extraction:Use of WPI, antioxidant activity and moisture sorption isotherms. *LWT - Food Sci. Technol*. 2016;72:1-8. https://doi.org/10.1016/j.lwt.2016.04.033

[53] Frey FM. and Meyers R. Antibacterial activity of traditional medicinal plants used by Haudenosaunee peoples of New York State. *BMC Complement Altern Med.* 2010;10:64. https://doi.org/10.1186/1472-6882-10-64

[54] Nostro A, Germano MP, D´Angelo V, Marino A, Cannatelli MA. Extraction methods and bioautography for evaluation of medicinal plant antimicrobial activity. *Lett Appl Microbiol*. 2000;30:379-384. https://doi.org/1046/j.1472-765x.2000.00731.x

[55] Li Z-H, Cai M, Liu Y-S, Sun P-L, Luo S-L. Antibacterial activity and mechanisms of essential oil from *Citrus medica* L. *var. sarcodactylis*. *Molecules*. 2019;24:1577. https://doi.org/10.3390/molecules24081577

[56] Tajik H, Jalali FSS, Sobhani A, Shahbazi Y, Zadeh MS. *In vitro* assessment of antimicrobial efficacy of alcoholic extract of *Achillea millefolium* in comparison with penicillin derivates. *J Anim Vet Adv*. 2008;7:508-511.

[57] Lyss G, Glasl S, Jurenitsch J, Pahl HL, Merfort I. A sesquiterpene and sesquiterpene lactones from the *Achillea millefolium* group possess antiinflammatory properties but do not inhibit the transcription factor NF-γB. *Pharm Pharmacol Lett*. 2000;10:13-15.

[58] Aljancic I, Vajs V, Menkovic N, Karadzic I, Juranic N, Milosavljevic S, Macura S. Flavones and sesquiterpene lactones from *Achillea atrata* subsp. *multifida*:antimicrobial activity. *J Nat Prod*. 1999;62:909-911. https://doi.org/10.1021/np980536m

**SAŽETAK**

## Optimizacija uslova sušenja raspršivanjem za proizvodnju praha ekstrakta *Achillea millefolium*

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(Naučni rad)

U radu je optimizovan postupak sušenja raspršivanjem tečnog ekstrakta hajdučke trave (*Achillea millefolium L.*) primenom metode odzivnih površina. Ispitan je uticaj temperature (120-195 °C), protoka tečnosti (3-16,5 $cm^3\ min^{-1}$) i sadržaja suve materije u tečnom ekstraktu (0,3-1,5 %) na prinos sušenja, sadržaj polifenola i antioksidativnu aktivnost suvog ekstrakta. Pod ispitivanim uslovima prinos je drastično varirao (od 8 do 75%), dok je uticaj sušenja na sadržaj polifenola i antioksidativnu aktivnost dobijenog praha bio manji. Optimizovani uslovi za maksimalnu antioksidativnu aktivnost i maksimalan prinos suvog ekstrakta bili su sledeći:130 °C pri protoku od 7,5 $cm^3\ min^{-1}$ tečnog ekstrakta sa 1,2 % suve materije. Pri optimalnim uslovima prinos sušenja je iznosio 66 %, dok je zabeležen blagi pad sadržaja polifenola u suvom ekstraktu u poređenju sa tečnim ekstraktom (145 mg ekvivalenta galne kiseline [GAE] po g suve materije naspram 152 mg GAE $g^{-1}$, redom). Antioksidativna aktivnost suvog praha neznatno je smanjena u poređenju sa tečnim ekstraktom (neutralizacija DPPH (di(fenil)-(2,4,6-trinitrofenil)iminoazanijum) je bila 58 % naspram 64 %). U osušenom prahu hajdučke trave očuvana je antimikrobna aktivnost prema patogenim bakterijama *Staphylococcus aureus* (vrednost minimalne inhibitorne koncentracije (MIK) je bila 10 mg $cm^{-3}$) i *Pseudomonas aeruginosa* (MIK vrednost je bila 20 mg $cm^{-3}$).

*Ključne reči*:hajdučka trava;polifenoli;antioksidativna aktivnost;antimikrobna aktivnost

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# New directions of biology and biotechnology in urban environmental sciences

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*Abstract*

Living organisms and biological methods are widely used in recycling urban waste and improving the quality of the urban environment. Urban biology is a branch of biology that studies organisms living in cities. We propose using the new term "urban biotechnology". Urban biotechnology is the use of biotechnological methods to protect the urban environment and in urban energy. Urban biotechnology in the future may be included in the curriculum of the Master's degree programs "Biotechnology", "Ecology " (profile "Applied Ecology"), "Chemistry" (profile " Chemistry of the urban environment "), and Chemical Engineering (profile "Chemical and Biochemical Engineering "). We consider it important to train specialists in the fields of urban biology and urban biotechnology. We hope that urban biotechnology and urban biology will become independent disciplines in the future.

*Keywords:* urban biotechnology; urban biology; ecology; chemical and biochemical engineering; de-icing agents.

*Available on-line at the Journal web address: http://www.ache.org.rs/HI/*

LETTER TO THE EDITOR

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Biological sciences are important in the study and solution of urban environmental problems. New directions of urban environmental sciences are of great importance - such as urban biology and urban biotechnology.

## Urban biology

The term "urban biology" is rarely used [1,2]. Urban biology is a branch of biology that studies organisms living in cities. We suggest considering urban biology as an academic discipline.

## Urban biotechnology

Applied biotechnology includes environmental biotechnology, medical biotechnology, industrial biotechnology, agricultural biotechnology, food biotechnology, bioenergy, and other directions. We propose using the new term "urban biotechnology", which is a recent direction in biotechnology and bioengineering. Urban biotechnology is the use of biotechnological methods to protect the urban environment and in urban energy. Energy urban biotechnology (urban bioenergy) could be an important area in the future. Establishing the microbial fuel technology as an alternative source for the generation of renewable energy sources can be a state of art technology owing to its high efficiency, cleanliness [3].

Living organisms and biological methods are widely used in recycling urban waste and improving the quality of the urban environment.

Biotechnological methods can increase the resilience of plants to urban environments. As an example, consider plants and de-icing agents. De-icing agents are a major cause of soil salinisation in urban ecosystems. The application of de-icing salts maintenance is recognized as a major environmental factor to the decline of urban plants [4,5]. Sodium chloride (NaCl) is one of the most used de-icing agents [6,7].

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**How can you reduce the negative effects of de-icing agents on plants?**

We suggest using urban biotechnology in greening. We have obtained plants that are resistant to de-icing agents [8,9,10]**.** We used cell selection to obtain salt-tolerant plants. This biotechnology has been used to obtain lawn grasses that are resistant to de-icing agents.

Urban biology studies aspects of life of organisms living in cities. Urban biotechnology uses biotechnological methods to protect the urban environment.

We consider it important to train specialists in the fields of urban biology and urban biotechnology.

Urban biotechnology in the future may be included in the curriculum of the Master's degree programs "Biotechnology", "Ecology " (profile "Applied Ecology"), "Chemistry" (profile "Chemistry of the urban environment"), and Chemical Engineering (profile "Chemical and Biochemical Engineering ").

**Education bachelor's degree program "Urban Biological and Environmental Sciences"**

We propose the creation of an educational programme in the future on "Urban Biological and Environmental Sciences".

We offer an education bachelor's degree program "Urban Biological and Environmental Sciences", direction "Urban Sciences" (Table 1).

*Table 1. Disciplines in the education bachelor's degree program "Urban Biological and Environmental Sciences" (direction "Urban Sciences")*

| Academic discipline (specialist discipline) |
|---|
| Urban biotechnology |
| Urban ecology |
| Urban biology |
| Urban botany and phytotechnology |
| Basics of biotechnology, bioenergy, and bioengineering |
| Ecology |
| Chemistry of the urban environment |
| Protection of the urban environment |

Academic disciplines " Ecology" and "Biology" provide fundamental biological and ecological training of students. The main specialist disciplines are Urban Biology, Urban ecology, Urban biotechnology, Chemistry of the urban environment, and Urban botany and phytotechnology.

We hope that urban biological sciences will become independent scientific disciplines in the future.

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**REFERENCES**

[1] Schultz B. Urban Biology: An Ecological Approach. *The American Biology Teacher*. 1960; 22(3): 147–152 https://doi.org/10.2307/4439282
[2] Szulkin M, Munshi-South J, Charmantier A, eds. *Urban Evolutionary Biology,* Oxford and New York: Oxford University Press. 2020; 320. ISBN: 978-0-19-883684-1
[3] Ramamurthy PC, Singh S, Kapoor D, Parihar P, Samuel J, Prasad R., Kumar A, Singh J. Microbial biotechnological approaches: renewable bioprocessing for the future energy systems. *Microb Cell Fact*. 2021; 20: 55. https://doi.org/10.1186/s12934-021-01547-w

[4] Equiza MA, Calvo-Polanco M, Cirelli D, Señorans J, Wartenbe M, Saunders C, Zwiazek JJ. Long-term impact of road salt (NaCl) on soil and urban trees in Edmonton, Canada. *Urban Forestry & Urban Greening.* 2017; 21: 16-28. https://doi.org/10.1016/j.ufug.2016.11.003

[5] Łuczak K, Czerniawska-Kusza I, Rosik-Dulewska C, Kusza G. Effect of NaCl road salt on the ionic composition of soils and *Aesculus hippocastanum* L. foliage and leaf damage intensity. *Scientific Reports* 2021; 11: 5309. https://doi.org/10.1038/s41598-021-84541-x

[6] Tone Merete M, Jan-Willem K, Sanne B, van der Veen I, van Tol j. A review of applications of de-icing chemicals, representative for European countries. Deliverable 1.1 & 1.2. Tauw BV and the Norwegian University of Science and Technology. 2019;3.

[7] Durickovic I. NaCl Material for Winter Maintenance and Its Environmental Effect. *Salt in the Earth*. Çinku MC, Karabulut S, eds., IntechOpen, 2019. https://doi.org/10.5772/intechopen.86907

[8] Gladkov Evgeny A, Gladkova Olga V. *Ecology and ecological - biotechnological aspects of the use of phytotechnologies*. Moscow, Internauka. 2018. 102 p. ISBN 978-5-9500175-9-9

[9] Gladkov Evgeny A, Gladkova Olga V. Cell Selection to Increase Deicing Reagents Resistance. Plant posters (P-2024). *In Vitro Cell.Dev.Biol.-Animal* 2021; 57: 48-61. https://doi.org/10.1007/s11626-021-00567-5

[10] Gladkov Evgeny A, Gladkova Olga V. Ornamental plants adapted to urban ecosystem pollution: lawn grasses tolerating deicing reagents. *Environmental Science and Pollution Research*. 2021. https://doi.org/10.1007/s11356-021-16355-3

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## SAŽETAK

### Novi pravci biologije i biotehnologije u naukama o zaštiti urbane životne sredine

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(Pismo uredniku)

Živi organizmi i biološke metode imaju široku primenu u reciklaži gradskog otpada i poboljšanju kvaliteta urbane sredine. Urbana biologija je grana biologije koja proučava organizme koji žive u gradovima. Predlažemo korišćenje novog termina „urbana biotehnologija“. Urbana biotehnologija je upotreba biotehnoloških metoda za zaštitu urbane životne sredine i za primenu u urbanoj energiji. Urbana biotehnologija u budućnosti može biti uključena u nastavne planove i programe studijskih programa "Biotehnologija", "Ekologija" (profil "Primenjena ekologija"), "Hemija" (profil "Hemija urbane sredine"), i Hemijsko inženjerstvo (profil "Hemijsko i biohemijsko inženjerstvo“). Smatramo da je važno osposobljavanje stručnjaka u oblastima urbane biologije i urbane biotehnologije i nadamo se da će urbana biotehnologija i urbana biologija u budućnosti postati samostalne discipline.

*Ključne reči*: urbana biotehnologija; urbana biologija; zaštita životne sredine; hemijsko i biohemijsko inženjerstvo; agensi za odmrzavanje

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# Horizon 2020 projects, PREMUROSA, PANBioRA and ExcellMater, successfully organised a session at the TERMIS2021 World Congress

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*Abstract*

Three Horizon 2020 projects: "PANBioRA: Personalised and generalised integrated biomaterial risk assessment", MSCA ITN project "PREMUROSA - Precision medicine for musculoskeletal regeneration, prosthetics, and active ageing", and "ExcellMater: Twinning to excel materials engineering for medical devices" jointly organised a very successful session entitled: "Strategies to enhance musculoskeletal regeneration: from bench to bedside" at the 6th world congress of the Tissue Engineering and Regenerative Medicine International Society (TERMIS2021). The session provided a comprehensive insight into the strategies for musculoskeletal regeneration, and it was a source of information on the latest achievements in the area thanks to the renowned speakers. Besides participants in the projects organising the session, many other researchers were attracted to the session, which is a key benchmark that the topic was interesting and relevant. In general, this session was a successful outcome of the collaboration among Horizon 2020 projects and at the same time, encouragement for similar activities to be organised in the future. Here, a short overview of the session is presented.

*Keywords:* Horizon 2020 projects collaboration; session review; tissue engineering; regenerative medicine; musculoskeletal regeneration.

*Available on-line at the Journal web address: http://www.ache.org.rs/HI/*

BOOK AND EVENT REVIEW

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Three Horizon 2020 projects: "PANBioRA: Personalised and generalised integrated biomaterial risk assessment", MSCA ITN project "PREMUROSA - Precision medicine for musculoskeletal regeneration, prosthetics, and active ageing", and "ExcellMater: Twinning to excel materials engineering for medical devices" jointly organised a very successful session entitled: "Strategies to enhance musculoskeletal regeneration: from bench to bedside" on the last day of the 6th world congress of the Tissue Engineering and Regenerative Medicine International Society (TERMIS2021), prior to the closing ceremony. TERMIS 2021 conference with the overarching topic "Biologically inspired technology driven regenerative medicine" was held online November 15-19, 2021. It comprised 9 parallel thematic sessions that tackled tissue engineering and regenerative medicine of the whole tissue palette, as well as a number of special sessions, including national societies sessions, Student and Young Investigator Section (SYIS) sessions, industrial sessions, clinical sessions, European Project sessions, lunch workshops, and business plan competition. The Congress gathered numerous scientists, researchers, industry representatives, and students. Even though the conference was forced to be held remotely due to the COVID-19 pandemic, the physical distance of the attendees did not jeopardize the main objective of this world event: communicating science and generating knowledge. On the contrary, the virtual event platform was a lively venue that allowed an intensive flow of scientific thoughts, exchange of ideas, and staying on track with ever-faster advances in the fields.

The session "Strategies to enhance musculoskeletal regeneration: from bench to bedside" offered a thorough insight into musculoskeletal tissue regeneration: answers were given to the questions concerning what has been done so far, current efforts, and future perspectives in the field. Besides participants in the projects organising the session, many other researchers were attracted to the session, which is a key benchmark that the topic was interesting and relevant. Thus, the

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session was a source of information on the latest achievements in the area thanks to the renowned speakers presenting ongoing studies that are breaking the boundaries between state-of-the-art science and issues yet to be resolved.


*Figure 1. Overview of the session "Strategies to enhance musculoskeletal regeneration: from bench to bedside" at the TERMIS2021 World Congress organised by Horizon 2020 projects PREMUROSA, PANBioRA and ExcellMater*

Chairs of the session – Prof. Lia Rimondini from the University of Eastern Piedmont, Italy, and Prof. Michael Gasik from the Aalto University Foundation, Finland, welcomed session attendees and introduced two keynote speakers: Prof. Mauro Alini from the AO Research Institute, Switzerland, and Prof. Sophia Antimisiaris, from the University of Patras, Greece. Prof. Alini presented the talk "Organ culture and bioreactors for assessing biomaterials (and more) for tissue


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regeneration“ in which he stressed the necessity for development and utilization of *in vitro* models for biomaterials evaluation and presented bioreactors for engineering of intervertebral discs created in his laboratory as well as cultured tissue models. The 3rd generation of intervertebral disc bioreactors with a uniaxial loading device and an advanced model with added hexapod for 6 degrees of freedom aim to recapitulate complex motions existing *in vivo* to a greater extent. In his opinion, *in vitro* models for biomaterial testing would significantly increase the prospects for clinical translation, while advancements in design and utilization of bioreactors will allow the 3R principle (replacement, reduction, refinement) in animal experimentation to come into force. Prof. Antimisiaris, the second keynote speaker, gave a different perspective on musculoskeletal tissue regeneration in her talk: ”Novel liposomal drug delivery and targeting approaches for tissue regeneration“. She introduced challenges in tissue regeneration and provided an overview of current knowledge and the future potential of delivery of growth factors to the site of regeneration. Prof. Antimisiaris pointed out that issues in drug administration such as low stability and inadequate physicochemical drug properties can be overcome by utilization of liposomal nanomedicines.

Other speakers who equally contributed to the high-quality program of the session were:

- Prof. Alicia El Haj, Healthcare Technology Institute; University of Birmingham, UK – “Engineering orthopaedic cell therapies: translation to the clinic“
- Dr Anh Vu Truong, Department of Chemical Engineering, National Tsinghua University, China - “Crispr-mediated epigenetic modification rescues osteoporotic ASC chondrogenic deficiency and promotes calvarial bone healing in osteoporotic rat“
- Dr Jonathan Dawson, University of Southampton, UK - “Regenerative nanoclays - translating a novel biomaterial“
- Prof. Michael Gasik, Aalto University Foundation, Finland – “Model-free assessment of biomechanical properties for personalized medical devices“
- Dr Michael Pujari Palmer, Department of Materials Science and Engineering, Uppsala University, Sweden – “Development, and preclinical evaluation, of a novel, bioinspired biomaterial, for use as a calcified tissue adhesive “

In conclusion, this session originated as the result of the fruitful collaboration of PANBioRA, PREMUROSA, and ExcellMater projects, which are funded within the European Union’s Horizon 2020 research and innovation programme. This event was a proper opportunity to increase the participants’ awareness of common aspirations of the projects reflected in the session theme. Generally, the session accomplished its goal by providing a comprehensive understanding of the strategies for musculoskeletal regeneration as well as addressing the challenges to be overcome in the future. According to the questions speakers received from the audience, the presentations were thought-provoking, to the mutual pleasure of both organisers and the audience. This session was a successful outcome of the collaboration among these projects and at the same time, encouragement for similar activities to be organised in the future.

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**SAŽETAK**

## Horizon 2020 projekti PREMUROSA, PANBioRA i ExcellMater uspešno su organizovali sesiju na Svetskom kongresu TERMIS2021

Ivana Banićević[1] i Lia Rimondini[2]

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(Prikaz knjiga i događaja)

Tri Horizont 2020 projekta: "PANBioRA: Personalised and generalised integrated biomaterial risk assessment", MSCA ITN projekat "PREMUROSA - Precision medicine for musculoskeletal regeneration, prosthetics, and active ageing", i "ExcellMater: Twinning to excel materials engineering for medical devices" su zajedno organizovali veoma uspješnu sesiju pod nazivom: "Strategije za unapređenje mišićno-skeletne regeneracije: od klupe do kreveta" na Šestom svjetskom kongresu Međunarodnog društva za inženjerstvo tkiva i regenerativnu medicinu (TERMIS2021). Sesija je pružila opširan uvid u strategije regeneracije mišićno-skeletnog tkiva i bila je izvor informacija o najnovijim dostignućima u ovoj oblasti zahvaljujući renomiranim predavačima. Pored učesnika projekata koji su organizovali sesiju, ovaj događaj je privukao mnoge druge istraživače, što je ključni pokazatelj da je tema bila zanimljiva i interesantna. Uglavnom, ova sesija je ishod uspješne saradnje Horizont 2020 projekata i istovremeno je ohrabrenje za organizovanje sličnih aktivnosti u budućnosti. Ovaj rad predstavlja kratak pregled sesije.

*Ključne reči*: Saradnja Horizont 2020 projekata; pregled sesije; inženjerstvo tkiva; regenerativna medicina; regeneracija mišićno-skeletnog tkiva

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# 2nd SFUS scientific symposium
# Pharmacy and the Nature - Complex Relations and Mutual Impacts

**Nada Kovačević[1], Branislava Miljković[1,2] and Jelena Parojčić[1,2]**

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*Abstract*

From the idea of a pharmaceutical product, through the development of materials and technologies for their production, analysis, and control, application in different patient populations, to the proper disposal and destroying of pharmaceutical waste, everything is connected and has an impact on the soil, water, and air, as well as to all living beings on this planet. Intending to invite the colleagues to consider how their pharmacy practice, science, and education can impact nature and global environmental trends, Pharmaceutical Association of Serbia has organized the 2nd SFUS scientific symposium, entitled **Pharmacy and the Nature - Complex Relations and Mutual Impacts** on 28th October 2021, in the conference center of the Science and Technology Park Belgrade, with the presence of more than 60 participants. Within the Symposium, the introductory lecture was held by Prof. Dr. Nada Kovačević, along with eight invited lectures, three oral presentations, and thirty-two poster presentations.

*Keywords:* sustainable pharmacy practice and research; green pharmacy; environmental protection.

*Available on-line at the Journal web address: http://www.ache.org.rs/HI/*

BOOK AND EVENT REVIEW

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Nature represents the unity of the earth, water, air, and all living beings. Mankind affects life on our planet differently, often through gross violations of natural laws and delicate, subtle connections and mutual influences between the environment and different sorts and forms of the living world. Numerous initiatives over the last decades indicate that every human activity and "world of people" should be observed and evaluated from the aspect of environmental impact. The development of the economy and society must be based on technologies in harmony with nature. The use of natural resources has to be organized and controlled without the devastation of natural habitats, violation of natural laws, and environmental disasters.

The International Pharmaceutical Federation (FIP) [1] has been involved in these kinds of initiatives by publishing appropriate strategic documents and policies on environmentally sustainable pharmacy practice. This indicates that pharmacists in various fields of pharmaceutical activities must take responsibility for reducing the environmental consequences of drug production, distribution, and usage (FIP Green pharmacy practice: Taking responsibility for the environmental impact of medicines [2]).

In the field of health, preservation, and improvement of the health of individuals and society, nature is essential not only as a source of pharmaceutically active and auxiliary substances but also as a source of ideas, different problems, and solutions which are hidden somewhere, and are usually simple, but should be discovered and well understood. From the idea of a pharmaceutical product, through the development of materials and technologies for their production, analysis, and control, application in different patient populations, to the proper disposal and destroying of pharmaceutical waste, everything is connected and has an impact on the soil, water, and air, as well as to all living beings on this planet.

Intending to invite the colleagues to consider how their pharmacy practice, science and education can impact nature and global environmental trends, Pharmaceutical Association of Serbia has organized the 2nd SFUS scientific symposium with international participation, entitled **Pharmacy and the Nature - Complex Relations and Mutual Impacts** in October 2021. This event was an opportunity to share the results, thoughts, and experiences and consider how scientific discoveries and solutions affect the world we live in.

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*The introductory lecture held by Prof. Dr. Nada Kovačević at the 2nd SFUS scientific symposium* ***Pharmacy and the Nature - Complex Relations and Mutual Impacts***

The second scientific symposium of the Pharmaceutical Association of Serbia was held on October 28, 2021 in the conference center of the Science and Technology Park Belgrade, with the presence of more than 60 participants. Within the Symposium, the introductory lecture **Pharmacy and nature - plenty of diversity** was held by Prof. Dr. Nada Kovačević, along with eight invited lectures, three oral presentations and thirty-two poster presentations. Invited speakers who equally contributed to the high-quality program of the Symposium were:

- Christophe Marčić, Faculté de Pharmacie, Université de Strasbourg, France: **Natural deep eutectic solvent – a green alternative for extraction and separation science.**
- Ivana Aleksić, University of Belgrade, Faculty of Pharmacy, Belgrade, Serbia: **Green pharmaceutical manufacturing: approaches and perspectives.**
- Nikola Stefanović, University of Niš-Faculty of Medicine, Niš, Serbia: **Significance of pharmacogenetics in modern medicine and pharmacy.**
- Aleksandra Buha Đorđević, University of Belgrade, Faculty of Pharmacy, Belgrade, Serbia: **Endocrine-disrupting pharmaceuticals in the environment-threat to the health and safety of humans and aquatic species?**
- Marina Odalović, University of Belgrade, Faculty of Pharmacy, Belgrade, Serbia: **Green pharmacy - recomendations for pharmacy practice improvement**
- Bojana Obradović, University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia: **Multifunctional composites based on alginate hydrogels for potential use in wound dressings**
- Biljana Otašević, University of Belgrade, Faculty of Pharmacy, Belgrade, Serbia: **New strategies in the development of ecologically friendly RP-HPLC methods based on the charged aerosol detector.**
- Dragana Vasiljević, University of Belgrade, Faculty of Pharmacy, Belgrade, Serbia: **Organic and natural cosmetic products - who benefits the most?**

Abstracts were published in the Supplement edition of the Archives of Pharmacy Vol. 5, 2021 [3].

*Poster session at the 2nd SFUS scientific simposium* ***Pharmacy and the Nature - Complex Relations and Mutual Impacts***

Awards for the best poster presentations were given to: Nevena Đajić, University of Belgrade, Faculty of Pharmacy (PP30 Poster entitled: **Chemometrically supported UHPLC method development: a strategy for achieving eco-friendliness**), Ana Gledović, University of Belgrade, Faculty of Pharmacy (PP19 Poster entitled: **Low energy nanoemulsions as potential carriers for essential oils in formulations for antioxidant skin protection**) and Darija Sazdanić, University of Novi Sad, Faculty of Medicine (PP10 Poster entitled **Daily intake of anthocyanins and polyphenols provided by the consumption of bilberry-based juices**).


*Best poster awards announcement at the 2nd SFUS scientific simposium* ***Pharmacy and the Nature - Complex Relations and Mutual Impacts***

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*Closing ceremony and the group photo of the 2nd SFUS scientific symposium* ***Pharmacy and the Nature - Complex Relations and Mutual Impacts***

Through gathering academics and professionals from the different fields of pharmaceutical sciences at this meeting, we aimed to raise the awareness about different aspects of environmental preservation and protection. Even more importantly, we hope that such events would initiate that each participant start to contemplate his/her own research work and its impact on the nature, to think about our everyday life, work, and behavior and the ways we can contribute to protecting the environment and save our planet.

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**REFERENCES**

[1] FIP - International Pharmaceutical Federation Home , https://www.fip.org/about, Accessed December 30th 2021
[2] International Pharmaceutical Federation (FIP). Green pharmacy practice: Taking ersponsability for the environmental impact of medicines. The Hague: International Pharmaceutical Federation; 2015 https://www.fip.org/files/fip/publications/2015-12-Green-Pharmacy-Practice.pdf, Accessed December 29th 2021
[3] Archives of Pharmacy - 2nd SFUS scientific symposium , Vol. 71 No. Suppl. 5 (2021), https://aseestant.ceon.rs/index.php/arhfarm/issue/view/1306, Accessed 29th 2021

## SAŽETAK

### Drugi naučni simpozijum Saveza farmaceutskih udruženja Srbije: Farmacija i priroda - kompleksne relacije i međusobni uticaji

Nada Kovačević[1], Branislava Miljković[1,2] i Jelena Parojčić[1,2]

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(Prikaz knjiga i događaja)

Od ideje za farmaceutski proizvod, preko razvoja materijala i tehnologija za njihovu proizvodnju, analizu i kontrolu, primene kod različitih populacija pacijenata, do pravilnog odlaganja i uništavanja iskorišćenog i neiskorišćenog materijala i proizvoda, sve je povezano i ima uticaj na zemlju, vodu i vazduh, kao i na sva živa bića na ovoj planeti. Sa ciljem da se bolje razmotri na koji način aktivnosti u okviru farmaceutske struke, nauke i obrazovanja mogu da utiču na prirodu i glabalna ekološka kretanja, održan je 2. naučni simpozijum pod naslovom **Farmacija i priroda – kompleksne relacije i međusobni uticaji**. Simpozijum je organizovao Savez farmaceutskih udruženja Srbije i održan je 28. oktobra 2021. godine u konferencijskom centru Naučno-tehnološkog parka Beograd, uz prisutvo više od 60 učesnika. U okviru Simpozijuma je održano jedno uvodno predavanje, osam predavanja po pozivu, tri usmena saopštenja i prikazane su trideset i dve poster prezentacije.

*Ključne reči*: održiva farmaceutska praksa i istraživanja, zelena farmacija, zaštita životne sredine

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# CORRIGENDUM
## IN THE ARTICLE

# Extraction of ammonium nickel sulfate hexahydrate by hydrometallurgical process from the hyperaccumulating plant *Odontarrhena muralis* – case study from Serbia

**Branislav Marković[1], Dragana Ranđelović[1], Gvozden Jovanović[1], Gordana Tomović[2], Ksenija Jakovljević[2], Tomica Mišljenović[2] and Miroslav Sokić[1]**

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CORRIGENDUM

*Hem. Ind.* **75 (6)** 379 (2021)

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| 289 | Figure 3b, inserted upper table, first row, fourth column | P | Mg |
| 289 | Figure 3b, inserted lower table, second row, third column | 9.39 | 9.29 |

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# ERRATA
## IN THE ARTICLE
# Upgrading fuel potentials of waste biomass via hydrothermal carbonization

**Jelena Petrović[1], Marija Simić[1], Marija Mihajlović[1], Marija Koprivica[1], Marija Kojić[2] and Ivona Nuić[3]**

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ERRATA

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This article has been published under the category Technical paper instead of Original scientific paper by mistake made by the Editorial Office of the journal Hemijska industrija during the proofreading process. Apologies are offered to authors and readers of the journal Hemijska industrija.

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