

Removal of diesel pollution by biochar – support in water remediation

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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. Physicochemical 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 ($159.1 \text{ m}^2 \text{ g}^{-1}$) 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, physicochemical 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 cm³ 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 cm³ diesel solution in 250 cm³ 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:

$$q_e = (C_0 - C_e) / mV \quad (1)$$

$$R = (C_0 - C_e) / C_0 \cdot 100 \quad (2)$$

where C_e and C_0 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 (EC₅₀ 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 pyrolyzed, already present in the original feedstocks, such as alkali ions and carbonates formed by Na⁺, K⁺, Mg²⁺ and Ca²⁺ 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).

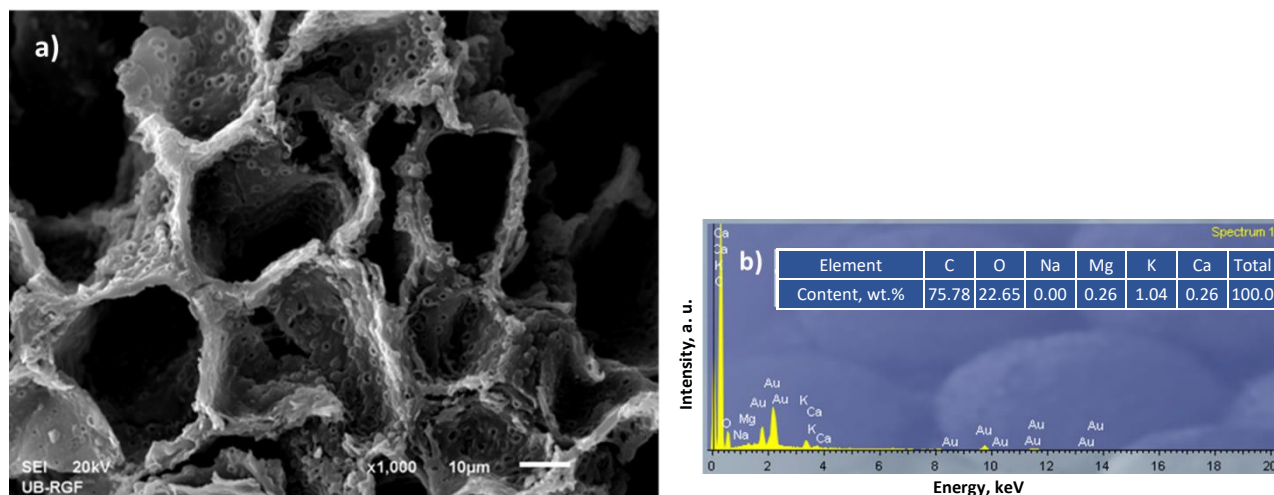


Figure 1. SEM-EDX analysis of the biochar sample (PS-B): a) SEM micrograph; b) EDX analysis results

According to the BET analysis the specific surface area (SSA) increased from $0.545 \text{ m}^2 \text{ g}^{-1}$ (PS) to $159.1 \text{ m}^2 \text{ g}^{-1}$ (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 $500 \text{ }^\circ\text{C}$ [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.

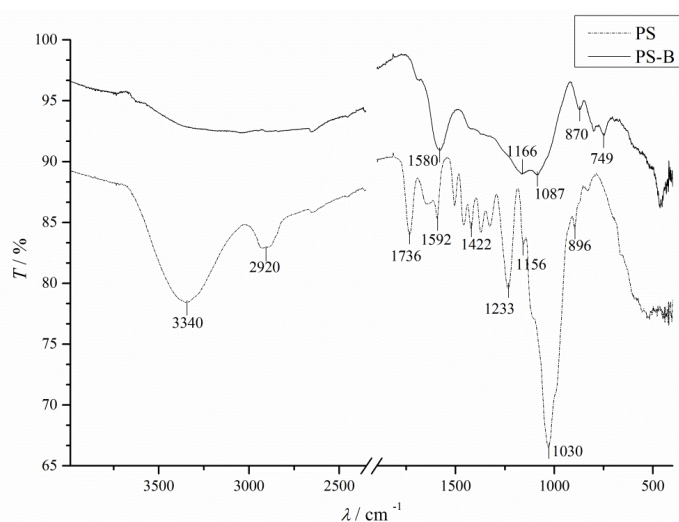


Figure 2. FTIR spectra of the raw material (PS) and biochar (PS-B)

These peaks can be attributed to the hydroxyl ($-\text{OH}$) stretching, alkane $-\text{CH}_2$ symmetric stretching, in-plane bending of carbonyl ($-\text{COH}$) and alkane $-\text{CH}_2$ 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 $\text{C}=\text{O}$ stretching of carboxylic acids or their esters has disappeared too [21, 22]. There are clear shifts which correspond to $-\text{COO}-$ from 1592 to 1580 cm^{-1} and asymmetric $\text{C}-\text{OC}$ 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

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.

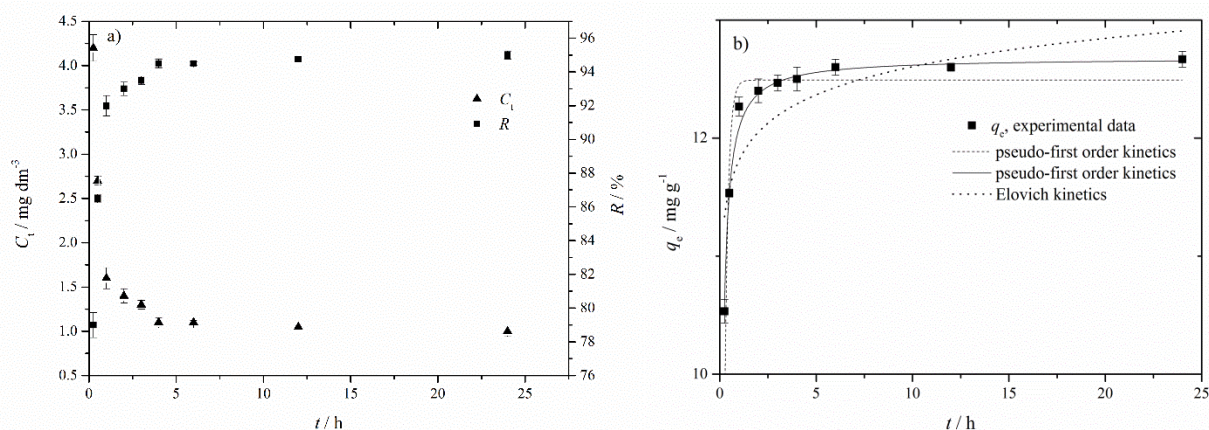


Figure 3. Sorption kinetics: a) experimentally determined diesel WSF concentration (C_t) and removal percentage (R) over time; b) sorbed WSF per mass of PS-B (q_t) as a function of time: experimental data (symbols) and the best fit predictions of the pseudo-first and pseudo second order kinetics and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

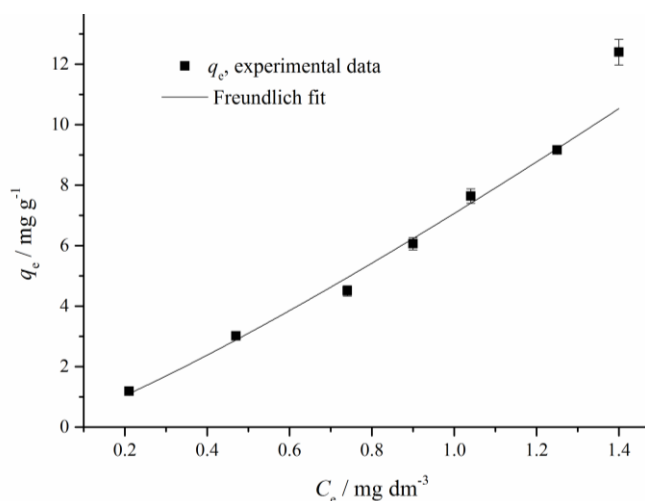


Figure 4. Experimental isotherm data and nonlinear Freundlich model fit of diesel WSF sorption onto PS-B

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 χ^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 ($q_m = 64.97 \text{ mg g}^{-1}$) falls in the range of published values, indicating that peach stone biochar can be efficiently used as a sorbent for diesel oil WSFs.

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.

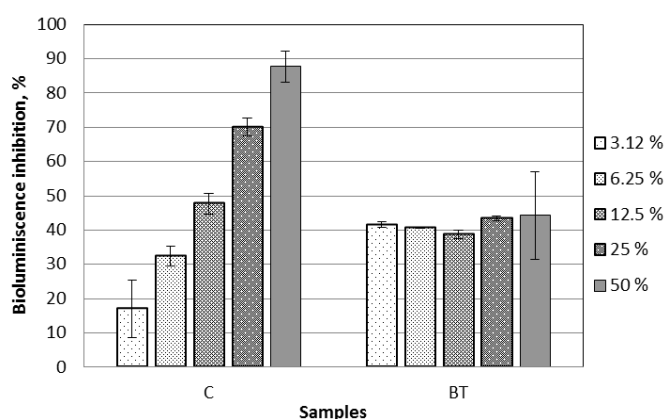


Figure 5. Ecotoxicity of water contaminated with diesel WSF before (C) and after treatment with biochar (BT); results are expressed as the percent of bioluminescence inhibition and are the average of $n=3$. Different bars represent different dilutions of the initial sample with 20 mg dm^{-3} WSF

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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SAŽETAK**Uklanjanje zagađenja dizela sorpcijom na biočađi – podrška remedijaciji kontaminiranih voda**

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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 lignoceluloznog 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 ($159.1 \text{ m}^2 \text{ g}^{-1}$) 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

