Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 87 (2) 205–217 (2022)
JSCS–5516

Original scientific paper
Published 2 February 2022

Beech sawdust based adsorbents for solid-phase extraction of pesticides and pharmaceuticals

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(Received 14 June, revised 14 July, accepted 15 July 2021)

Abstract: Carbonaceous solid-phase extraction (SPE) sorbent, efficient in isolation and enrichment of multiclass pesticides and pharmaceuticals from water, was synthesized starting from cheap waste beech sawdust and using KOH as the activated agent. The first step in carbon material preparation was hydrothermal carbonization of the waste beech sawdust. Following hydrothermal treatment, the obtained material was activated, using different amounts of KOH. It was found that applied activation leads to changes in material structure, an increase in specific surface area, and a decrease in the number of surface oxygen groups compared to carbonized sample. SPE procedure of multiclass pesticides and pharmaceuticals from water using activated carbonized beech sawdust (AcSD) was optimized by selecting the appropriate elution solvents, the sample pH, and the sample volume to obtain the highest enrichment efficiency. The optimized SPE procedure was applied for water analysis using different AcSD samples as a sorbent for analyte preconcentration. Activated carbon sorbent, obtained with the highest amount of KOH, showed the highest recoveries regarding the most analytes, which were comparable with the recoveries obtained by commercial cartridges.

Keywords: waste sawdust; hydrothermal synthesis; surface properties; method optimization; organic pollutants analysis.

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https://doi.org/10.2298/JSC210614051V

INTRODUCTION

Over the last few decades, due to their increased use and application, pharmaceuticals and pesticides have been frequently detected in the aquatic environment. Intensive application of pesticides in agriculture brings significant pollution of surface water and groundwater and become an increasing environmental problem.[1–4] Pharmaceuticals used in human and veterinary medicine also contribute to pollution of the aquatic environment, due to their occurrence in the water system as a consequence of frequent use, improper disposal, as well as the inability of wastewater treatment plants to eliminate them. The presence of pesticides and pharmaceuticals in water may have a huge negative impact on human health, as well as the aquatic ecosystem and therefore it is necessary to develop appropriate methods for their constant monitoring.[5–9]

Residues of pesticides and pharmaceuticals are usually present at low concentrations in surface water and groundwater, and therefore the methods for their determination must include an enrichment step, before analysis. For this purpose, a commonly used sample preparation technique is solid-phase extraction (SPE), since it provides analytes isolation, concentration, and the extract clean-up in a single step. The choice of the sorbent is critically important in SPE because it controls parameters such as selectivity, affinity, and extraction capacity.[10] In addition to the commonly used commercially available polymeric or silica-based SPE cartridges, such as poly(styrene-divinylbenzene), C18, and zeolite, various tailor-made carbon materials are increasingly used as SPE sorbents.[8,11–13] Since the type of carbon sorbent, its structure, and the nature of the interaction between the carbon surface and the analyte greatly influence the preconcentration efficiency, the selection of suitable carbon sorbent is a crucial step in order to achieve high recoveries of the SPE method. However, sometimes, in addition to the good analytical performance of the carbon sorbent, it is also necessary to consider its cost, and the potential way to reduce the cost is using waste biomass as a starting material for obtaining cheap SPE sorbents.[14] The usage of different types of biomass waste represents an environmentally sound conversion process, and a current trend in the field of material production. In addition, as an alternative to dry pyrolysis which is carried out in an inert atmosphere at high temperatures, the wet pyrolysis process (hydrothermal carbonization) allows obtaining the carbonaceous solids with relatively high yields at mild temperatures (120–180 °C). The obtained carbon materials are suitable for further modification by different methods of activation or functionalization, and in this way, it is possible to tailor the desired characteristics depending on the potential application.[15–17]

In this work, beech sawdust, obtained as a waste from the wood industry, was used as a starting material for the production of SPE carbon sorbents. Carbon sorbents were obtained starting from sawdust and using hydrothermal carbonization, followed by activation in the presence of KOH as an activating agent. By varying the activation parameters, activated carbonized beech sawdust (AcSD) samples with different characteristics were obtained. To achieve the highest possible recoveries, the SPE method was optimized in terms of selecting the appropriate type of organic extraction solvent, as well as the volume and pH of the water sample. The possibility of using activated carbonized beech sawdust samples as an adsorbent in the solid phase extraction method was tested using an aqueous solution of pharmaceuticals and pesticide mixtures. Additionally, recoveries obtained by AcSD samples were compared with the recoveries obtained by commercial cartridges. Four pharmaceuticals: carbamazepine, lorazepam, diazepam (sedatives), clopidogrel (cardiovascular) and two metabolites of metamizole (4-acetylaminoantipyrine, 4-AAA, and 4-formylaminoantipyrine, 4-FAA), as well as seven pesticides: atrazine, propazine (triazine), imidacloprid, acetamiprid (neonicotinoid), dimethoate, malathion (organophosphate) and tebufenozide (diacylhydrazine) were selected for this study.

EXPERIMENTAL

Sample preparation

Beech sawdust obtained as waste from the wood industry was used as the starting material for the preparation of hydrothermal carbon (HTC). Hydrothermal carbonization of sawdust was carried out into Teflon lined stainless steel autoclave at a temperature of 180 °C and self-generated pressure for 24 h. The carbonization reaction mixture consisted of 6 g of sawdust, 40 cm^3 of distilled water, and 0.015 g of citric acid, which was used as a catalyst. After hydrothermal carbonization, the solid product was filtered and washed with methanol and distilled water. In order to improve the sorption characteristics of the material, HTC was activated using KOH as an activating agent. Activation was carried out in an electric furnace under the constant nitrogen flow (150 cm^3 min^{-1}), up to a temperature of 900 °C, with a heating rate of 5 °C min^{-1}. By varying the mass ratios of KOH and HTC, different carbon sorbent samples were obtained and denoted as: AcSD$_0$ (KOH/HTC = 0/1), AcSD$_{0.5}$ (KOH/HTC = 0.5/1) and AcSD$_1$ (KOH/HTC = 1/1).

Sample characterization

The surface morphology on examined samples and the influence of activating agent on surface morphology was examined by scanning electron microscopy (Mira Tescan 3X, Tescan Orsay Holding, Czech Republic).

Nitrogen adsorption and desorption isotherms were measured on activated carbonized beech sawdust samples at –196 °C. The specific surface area and the pore size distribution (PSD) of AcSDs samples were analyzed using the Surfer (Thermo Fisher Scientific, USA). PSD was estimated by applying the BJH method[18] to the desorption branch of isotherms and mesopore surface and micropore volume were estimated using the t-plot method.[19]

The type of functional groups present on the activated carbonized beech sawdust surface was examined by Fourier transform infrared spectroscopy (FTIR). FT-IR spectra were recorded in the range from 400 to 4000 cm^{-1} (Bomem MB-Series, Hartmann Braun, Germany).

The nature and thermal stability of activated carbonized beech sawdust surface oxygen groups were examined by temperature-programmed desorption (TPD) in combination with mass spectrometry. The TPD profiles were obtained using a custom-built set-up, consisting of a quartz tube placed inside an electrical furnace, as it is described in the literature.[20] The sample was outgassed in the quartz tube and subjected to TPD at a constant heating rate of 10 °C min^{-1} up to 900 °C, under a high vacuum. The amounts of CO and CO_2 released from the carbon sample (0.1 g) were monitored using an Extorr 300 quadrupole mass spectrometer (Extorr Inc., USA).

Solid-phase extraction procedure

SPE cartridges were prepared by filling empty SPE columns with 0.05 g of activated carbonized beech sawdust, and two polyethylene frits were used to hold the adsorbent packing in the cartridge. The aqueous solution of selected pharmaceuticals and pesticides was prepared by spiking deionized water to the concentration of 1 ng cm^{-3} per each analyte. The following parameters that may affect the SPE procedure efficiency were optimized: volume and pH of the water sample and type of elution solvents. The optimal volume of the aqueous solution of the analyte mixture was selected based on the SPE method recoveries using 50, 100 and 200 cm^3 of the aqueous solution, without pH adjustment. To select the optimal pH of the aqueous solution, pH values were adjusted on 4, 5, 6, 7 and 8, prior to extraction. An appropriate elution solvent was selected based on the method recoveries obtained using: methanol, dichloromethane–methanol (1:1) and acetonitrile. For SPE optimization experiments, the SPE cartridges were preconditioned with 5 cm^3 of selected elution solvent followed by 5 cm^3 of deionized water. Spiked water samples were loaded at a flow rate of 1 cm^3 min^{-1}. The cartridges were then dried under vacuum for 10 min and analytes were eluted with selected elution solvent to extract a volume of 15 cm^3. Extracts were evaporated to dryness under N_2 and reconstituted with 1 cm^3 of methanol. The final extracts in methanol were filtered through 0.45 μm polyvinylidene fluoride (PVDF) filters, into the autosampler vials and analyzed using high performance liquid chromatography–tandem mass spectrometry (LC–MS/MS, Thermo Scientific). Recoveries (*R* / %) were calculated as ratio between peak area of analyte in methanol extract (PAext), and peak area of analyte in standard solution (PAstd):

$$R = 100\frac{\mathrm{PAext}}{\mathrm{PAstd}} \tag{1}$$

Relative standard deviation (*RSD* / %) was calculated as ratio between recovery standard deviation std(*R*), and average recovery (average(*R*)):

$$RSD = 100\frac{\mathrm{std}(R)}{\mathrm{average}(R)} \tag{2}$$

LC–MS/MS method conditions are given in Supplementary material to this paper. The optimized SPE procedure was applied to test the possibility of using different activated carbonized beech sawdust samples as SPE adsorbents for the extraction of selected pesticides and pharmaceuticals from water. Additionally, recovery values obtained using the $AcSD_1$ sample were compared with the recoveries obtained by commercial cartridges: Supelclean Envi-Carb, Supelclean Envi-18, Supelclean LC-SCX, Supelclean LC-18 (Sigma–Aldrich) and Oasis HLB (Waters, USA).

RESULTS AND DISCUSSION

Surface characteristics of activated carbonized beech sawdust samples

Morphology of hydrothermally treated and activated carbonized beech sawdust samples were analyzed by scanning electron microscopy (Fig. 1). Morphologies of AcSD samples are more or less featured by the presence of clearly defined carbon spheres with a smooth surface, which is characteristic of hydrothermal carbons.[15–17,21] It can be noted that the surface of the AcSD$_0$ sample is completely covered with spherical particles of different diameters, ranging from 50 up to 700 nm. The differences in surface structure caused by activation in the presence of KOH are reflected in the decrease of the carbon spheres diameters, or, in the case of more aggressive treatment, their disappearance. In that way, sample AcSD$_{0.5}$ is characterized by the presence of carbon spheres with diameters lower than 200 nm, while the AcSD$_1$ surface contains spheres with diameters lower than 50 nm, and only a few with diameters up to 200 nm. Additionally, activation in the presence of KOH leads to the smoothing of the surface of hydrothermally treated beech sawdust, along with the formation of large pores.

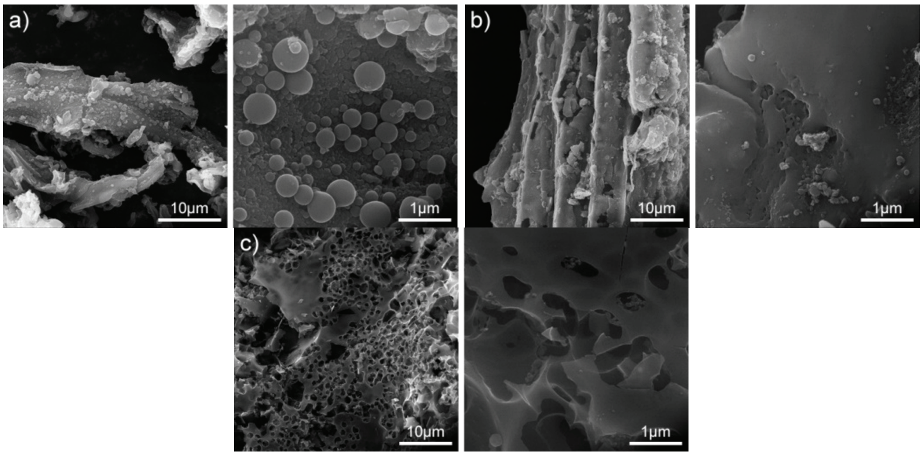

Fig. 1. FESEM photographs of activated carbonized beech sawdust samples: a) AcSD$_0$, b) AcSD$_{0.5}$ and c) AcSD$_1$.

Calculated porosity parameters of AcSD samples are given in Table I.

TABLE I. Porous properties and amount of CO (Q_{CO}) and CO$_2$ (Q_{CO_2}) evolving surface groups of activated carbonized beech sawdust samples

Sample	AcSD$_0$	AcSD$_{0.5}$	AcSD$_1$
S_{BET} / m^2 g^{-1}	213	514	729
S_{meso} / m^2 g^{-1}	3	3	6
S_{mic} / m^2 g^{-1}	210	511	723
V_{mic} / cm^3 g^{-1}	0.187	0.255	0.375
r_{med} / nm	1.5	1.6	1.9
Q_{CO} / mmol g^{-1}	68.15	26.25	10.39
Q_{CO_2} / mmol g^{-1}	585.78	545.94	338.25
Q_{CO} + Q_{CO_2} / mmol g^{-1}	653.93	572.19	338.64

Specific surface areas (S_{BET}) ranged from 213 (AcSD$_0$) to 729 (AcSD$_1$) m^2 g^{-1}, while the mean pore diameters (r_{med}) were below 2 nm for all samples and increases with increasing the amount of activating agent. Hydrothermal carbonization of sawdust followed by activation in the presence of KOH yielded microporous materials with a low proportion of mesoporosity. The increased amount of KOH opens up the porous surface structure, increasing the volume of micropores and strongly increasing the specific surface area of the activated carbonized beech sawdust.

Fourier transform infrared spectroscopy and temperature-programmed desorption were used to determine the nature and amount of AcSD surface oxygen groups and to evaluate the influence of the activation process on AcSD surface chemistry. The FTIR spectra displayed in Fig. 2. give qualitative information about functional groups present on the surface of the AcSD samples.

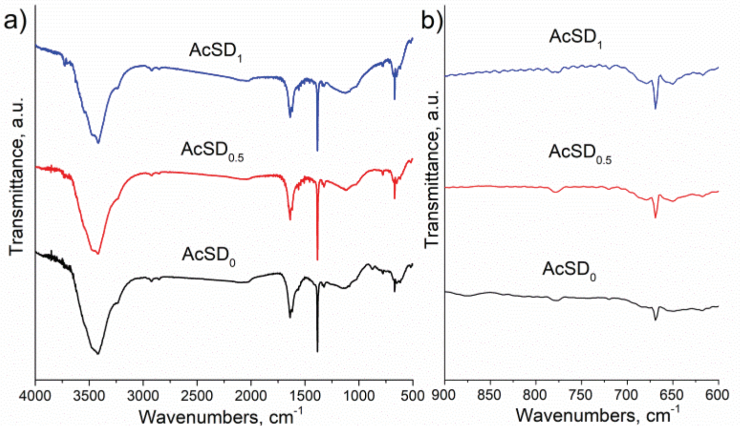

Fig. 2. FTIR spectra of AcSD samples (a) and enlarged section from 600 to 900 cm^{-1} (b).

All tested samples showed very similar FTIR spectra with slight differences in peak intensity, indicating that activation in the presence of KOH had no significant effect on the nature of the surface functional groups. The intense broad band, in the 3600–3300 cm$^{–1}$ region, is characteristic of stretching vibrations of the O–H bond in hydroxyl or carboxyl groups. Two low-intensity bands with maxima at 2850 and 2920 cm$^{–1}$, observed for all tested samples, are attributed to the symmetrical and asymmetrical deformation vibrations of C–H groups in methyl and methylene groups (CH_3, CH_2, CH_2–OH).[22] The moderate-intensity band at 1640 cm$^{–1}$ may originate from the bending vibration of the O–H bond, or the stretching vibration of the aliphatic C=C bond, while the shoulder at 1620 cm$^{–1}$ originates from the vibrations of the aromatic C=C bond.[15,23–25] The intense peak at 1384 cm$^{–1}$ corresponds to the deformation vibration of the C–O bond in the carboxyl group.26 A low-intensity band in the range of 1300–1000 cm$^{–1}$ may derive from the stretching vibrations of the C–OH, or bending vibrations of the O–H bond, indicating the presence of hydroxyl groups.[27] The low-intensity peak at 875 cm^{-1} originates from the vibration of the aromatic C–H bond twist, while the peak at 669 cm^{-1} originates from deformation vibrations of the aromatic ring. These two peaks are affected by KOH activation: peak at 875 cm^{-1} observed for AcSD$_0$ sample disappears upon KOH activation, while the intensity of the peak at 669 cm^{-1} increase with the increase in the amount of KOH.

The TPD profiles of CO and CO$_2$, released during thermal decomposition of the surface oxygen groups, were recorded and shown in Fig 3. TPD analysis of sample AcSD$_0$ showed pronounced evolution of CO at a relatively low temperature of 465 K, which may originate from thermal decomposition of carbonyl groups in α-substituted ketones and aldehydes,[15,28] as well as slightly weaker CO release up to a temperature of 1000 K, which can be assigned to phenols, ethers, carbonyls and quinones.[28,29] TPD profile of CO$_2$ for sample AcSD$_0$ showed a peak at 580 K, along with the shoulders at 420 and 520 K, which can originate from thermal decomposition of carboxylic and lactone groups,[30,31] while the peak displayed around 820 K may originate from lactones or carboxylic anhydride groups.[32] CO decomposition profiles showed maxima around 541 K, for sample AcSD$_{0.5}$, and maxima around 640 and 1000 K, for sample AcSD$_1$, while CO$_2$ decomposition profiles showed maxima around 625 K for sample AcSD$_{0.5}$, and 580 K, for sample AcSD$_1$. TPD profiles of CO showed that the increase in activating agent amount, shifts temperature maxima to higher values, while temperature, at which CO$_2$-releasing oxygen groups decompose, remains the same or increases with increase in KOH amount. This temperature increase indicates the stabilization the oxygen groups on materials surface. Additionally, an increased amount of KOH decreases the peak intensity of TPD profiles, which indicates a decrease in the number of surface groups.

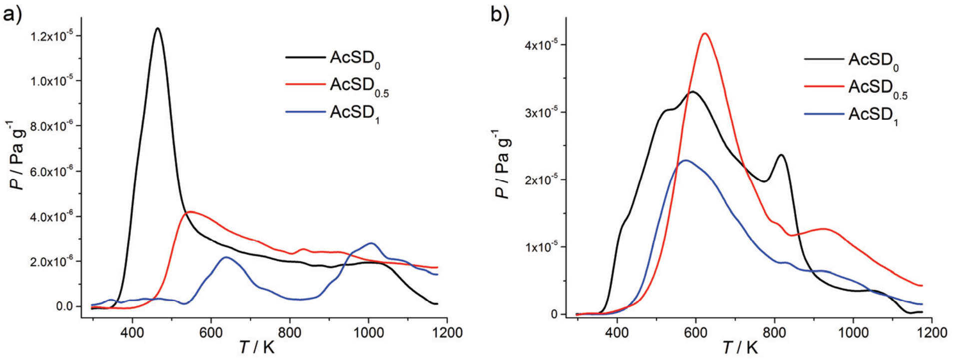

Fig. 3. TPD spectra of AcSD samples: a) CO and b) CO$_2$ desorption profiles.

The amounts of CO and CO$_2$ evolving groups (Table I) were obtained by the integration of the appropriate TPD profile. Obtained results indicate that AcSD samples contain a significant amount of CO$_2$ evolving groups and carboxyl, lactone, and anhydride groups are mainly present on the surface of the material. Changes in the amounts of CO and CO_2 evolving groups along with the temperature maxima shifts, both induced by different amount of KOH used for activation, indicate that during the activation process the reduction of oxygen groups already existing on the carbon material surface occurs, with the simultaneous formation of the more stable oxygen groups.[20]

Activated carbonized beech sawdust samples as an adsorbent in solid-phase extraction

The parameters that determine the recoveries of the SPE method have to be optimized to achieve the highest efficiency of the method. Optimization of the SPE method was performed using a sample with the largest specific surface area, $AcSD_1$, as an SPE adsorbent. The SPE recoveries obtained by optimization of water sample volume, initial pH value and elution solvent are presented in Fig. 4. The SPE method is considered to be efficient if the obtained recovery values fall within 70–120 %, with relative standard deviation (*RSD*) $\leq$ 20 %.[14,33–36] The most suitable recoveries of selected analytes were obtained for 100 cm^3 of water samples, and for all analytes, except dimethoate, diazepam, and atrazine, obtained recoveries ranged from 70 to 119 % (Fig. 4a).

The following step in SPE optimization was to select the most appropriate pH value of the water sample of selected analytes. Therefore, initial pH values were adjusted to 4, 5, 6, 7 and 8. The best recoveries (71–111 %) were obtained at the pH value of 6 (Fig. 4b), and this pH value was chosen as the optimal for extraction of selected analytes from water samples. The optimization of elution solvents (Fig. 4c) led to the selection of a mixture of dichloromethane-methanol (1:1) as an optimal solvent, since obtained recoveries were better than those obtained using methanol and acetonitrile.

After the optimization, the SPE procedure for the enrichment of selected pesticides and pharmaceuticals in water samples implies the usage of 100 cm^3 of the water sample, with the pH value adjusted to 6, along with the usage of dichloromethane–methanol (1:1) mixture for elution of analytes. This procedure was applied to examine the possibility of using different samples of activated carbonized beech sawdust as SPE adsorbents. Recoveries obtained in this way (Fig. 5) showed that sample $AcSD_0$ can be used for the enrichment of only six of thirteen tested analytes, including imidacloprid, diazepam, clopidogrel, atrazine, malathion and tebufenozide, with recoveries ranging from 72 to 88 %. Sample $AcSD_{0.5}$ showed high performance for eleven tested analytes, with recoveries ranging from 72 to 100 %, while recoveries obtained for dimethoate and carbamazepine were insufficient. Additionally, good recoveries (71–111 %) for all tested analytes, except atrazine (65 %) were obtained using sample $AcSD_1$.

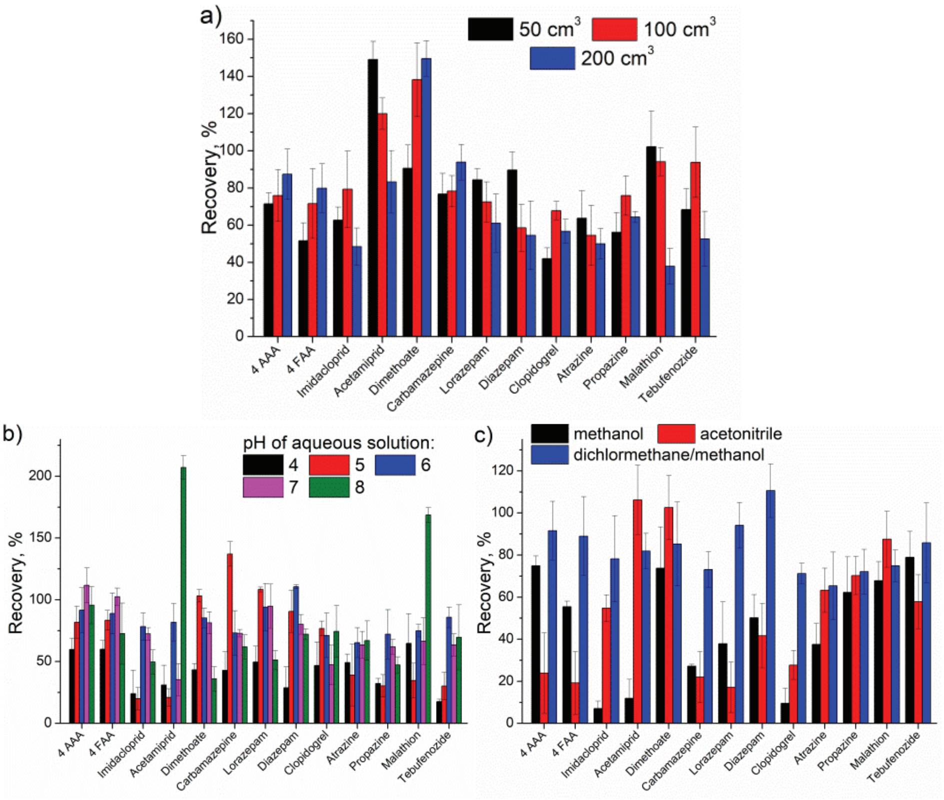

Fig. 4. Recoveries of selected analytes on AcSD$_1$ for different: a) sample volumes, b) initial pH values, c) elution solvents obtained for the water samples spiked at 1 ng cm^{-3} per each analyte.

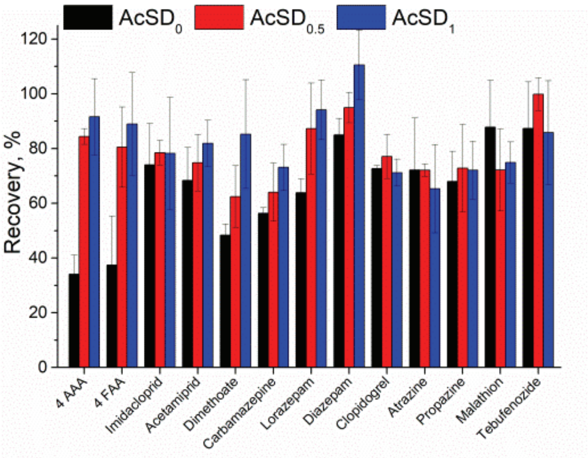

Fig 5. Recoveries of selected pesticides and pharmaceuticals obtained using different AcSD samples as SPE cartridges.

These results imply that the extraction efficiency of activated carbonized beech sawdust is highly affected by the surface characteristics of the material. An increase in specific surface area and mean pore diameter enhance extraction efficiency of activated carbonized beech sawdust. The lowest recoveries obtained for sample AcSD$_0$ can be the consequence of low specific surface area, along with the negative influence that surface oxygen groups may have on SPE efficiency. It was noted that presence of surface oxygen groups has detrimental effect on extraction efficiency of activated carbonized beech sawdust. Carboxyl groups present on the surface of activated carbonized beech sawdust, as electron acceptor groups, may withdraw π-electrons from the graphene layers, decreasing in that way dispersive interactions between adsorbate (aromatic organic compounds) and adsorbent (carbon surface) and leading to reduced adsorption.[8,29] Also, hydrophilic carboxyl groups intensify adsorption of water onto carbon surface, along with the formation of water clusters that reduce the availability of carbon surface for adsorption of organic compounds.[37]

Comparing the recovery values obtained for commercial cartridges and AcSD$_1$ (Table II), it was shown that the AcSD$_1$ sample could be successfully applied as a solid-phase adsorbent for the analysis of selected pharmaceuticals and pesticides in water samples. Additionally, for 4 AAA and lorazepam, recoveries obtained by tested material were higher than the ones obtained by commercial cartridges.

TABLE II. Recoveries of selected analytes obtained using commercial cartridges and SPE cartridges filled with AcSD$_1$ as a sorbent

Analyte	Recovery (*RSD*), %					
	AcSD$_1$	Envi-18	Envi Carb	LC-18	LC-SCX	Oasis HLB
4 AAA	92 (14)	44 (6)	86 (2)	91 (7)	19 (4)	90 (9)
4 FAA	89 (19)	64 (7)	76 (15)	100 (9)	13 (26)	86 (6)
Imidacloprid	78 (20)	97 (9)	99 (9)	105 (18)	50 (7)	83 (6)
Acetamiprid	82 (8)	96 (7)	95 (11)	100 (7)	60 (3)	82 (5)
Dimethoate	85 (20)	70 (6)	90 (6)	87 (4)	12 (19)	71 (10)
Carbamazepine	73 (8)	93 (5)	91 (11)	95 (5)	90 (4)	78 (6)
Atrazine	65 (16)	77 (6)	88 (13)	85 (16)	82 (7)	78 (9)
Lorazepam	94 (11)	91 (9)	80 (7)	90 (11)	90 (6)	73 (7)
Propazine	72 (11)	75 (2)	78 (9)	75 (22)	78 (7)	75 (17)
Diazepam	111 (13)	100 (2)	91 (2)	97 (6)	39 (10)	80 (9)
Malathion	75 (8)	62 (11)	86 (9)	85 (10)	76 (2)	77 (2)
Tebufenozide	86 (19)	97 (16)	97 (12)	103 (18)	98 (12)	85 (11)
Clopidogrel	71 (5)	70 (20)	77 (18)	69 (18)	-	77 (19)

CONCLUSION

Activation of hydrothermally treated beech sawdust using potassium hydroxide induced changes in material morphology and surface chemistry and porosity. The increase in KOH amount led to the increase in specific surface area, while maintaining the high microporosity of the surface. The clearly defined carbon spheres, characteristic for hydrothermally treated material, disappeared upon KOH activation, along with the decrease in the number of surface oxygen groups. In this way, the efficient carbon sorbent for isolation and enrichment of multiclass pesticides and pharmaceuticals was obtained. The results showed that it is possible to synthesize solid-phase extraction sorbents, starting from cheap waste beech sawdust material and using KOH as the activated agent. Furthermore, cartridges obtained with a larger amount of KOH showed the highest efficiency in analyte preconcentration, comparable to the efficiency of much more expensive commercial cartridges.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/10859, or from the corresponding author on request.

Acknowledgement. The research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No. 451-03-9/2021--14/200135, Contract No. 451-03-9/2021-14/200287 and Contract No. 451-03-9/2021--14/200017).

ИЗВОД

УГЉЕНИЧНИ АДСОРБЕНТИ НА БАЗИ БУКОВЕ ПИЉЕВИНЕ ЗА ПРЕДКОНЦЕНТРИСАЊЕ ПЕСТИЦИДА И ЛЕКОВА У МЕТОДИ ЕКСТРАКЦИЈЕ НА ЧВРСТОЈ ФАЗИ

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Предмет овог рада био је испитивање могућности примене активног угља на бази хидротермално третиране пиљевине као адсорбента у методи екстракције на чврстој фази (енгл. solid phase extraction, SPE) при анализи остатака лекова и пестицида из површинских и подземних вода. У циљу добијања нових SPE адсорбената, отпадна пиљевина је најпре хидротермално карбонизована, а затим је активирана коришћењем KOH као активирајућег агенса. Варирањем количине активирајућег агенса добијени су различити узорци активираног хидротермалног угљеника (AcSD). Површина добијених материјала окарактерисана је одређивањем специфичне површине, пречника и запремине пора, као и врсте и количине површинских група. У циљу постизања максималних приноса лекова и пестицида, извршена је оптимизација SPE методе одабиром одговарајуће запремине и pH вредности узорка воде, као и органског растварача за елуирање. Оптимизована SPE метода примењена је за анализу воде коришћењем различитих узорака AcSD као SPE адсорбената, а добијени приноси су упоређени са приносима ове методе на комерцијалним кертрицима. Добијени резултати су показали да се активи-

рани хидротермални угљеник на бази пиљевине може успешно користити за предконцентрисање лекова и пестицида из воде.

(Примљено 14. јуна, ревидирано 14. јула, прихваћено 15. јула 2021)

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