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Influence of the precursor chemical composition on heavy metal adsorption properties of hemp (*Cannabis Sativa*) fibers based biocarbon

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Abstract: Waste hemp (*Cannabis sativa*) fibers were used as sustainable and renewable raw materials for production of low-cost biocarbon sorbent for heavy metals removal. Carbon precursors of different chemical composition were obtained by oxidative and alkaline treatments of hemp fibers. Influence of lignocellulosic precursor chemical composition on hemp fibers-based biocarbon (HFB) characteristics was examined by BET surface area measurement, scanning electron microscopy and mass titration. It was found that lignin content and polymorphic transformation of cellulose increase the S_{BET} of microporous HFBs, while hemicelluloses induce more homogeneous distribution of adsorption active sites. Heavy metal ions adsorption onto HFBs is primarily influenced by the amount of surface oxygen groups, while specific surface area plays a secondary role. Equilibrium data obtained for lead ions adsorption were analyzed by different nonlinear adsorption isotherms, and the best fitting model was chosen using standard deviation and Akaike information criterion (AIC_c). The maximum adsorption capacities of HFBs ranged from 103.1 to 116.3 mg Pb/g. Thermodynamic parameters showed that Pb^{2+} adsorption onto HFBs is a spontaneous and complex endothermic process, suggesting the coexistence of physisorption and chemisorption mechanisms.

Keywords: hemp fibers; chemical composition; biocarbon; heavy metal ions; adsorption mechanism.

INTRODUCTION

Hemp (*Cannabis sativa*), an old and controversial plant, has been planted agriculturally for many centuries to get its bast fibers and hempseed oil. Now-

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adays, due to increased demand for comfortable, biodegradable and ecological fibers, production of hemp fiber is experiencing a renaissance again. Hemp fibers are an inexhaustible, sustainable source of annually renewable industrial raw materials, which can be combined with man-made or natural polymers to provide a wide range of useful products such as composites,¹ construction,² automotive industry,³ etc. Following the general trend of finding low-cost and easily available adsorbent, short and entangled bast fibers, waste from textile industry, were used as biosorbents for water purification.⁴⁻⁶ Despite the satisfactory performance of hemp fibers biosorbent in water purification, activated carbons are known to be more efficient in adsorbing a greater amount of pollutants, although its large-scale application is limited by the high cost. Therefore, utilization of inexpensive and renewable materials as carbon precursors could make the adsorption process cost effective. Being lignocellulosic material, hemp fiber contains cellulose, hemicelluloses and lignin, which are rich in carbon, and therefore it can be utilized as a low-cost precursor for biocarbon sorbents production.⁷⁻¹³

It is widely agreed that surface characteristics of carbon materials is largely influenced by the nature of the starting material. The hemp fibers are characterized by cross section complexity and specific surface morphology. It can be considered as composites of hollow cellulose fibrils held together by a lignin and hemicelluloses matrix. The primary fibrils are assembled into microfibrils with the hemicelluloses decorating the outside. Hemicelluloses act as the connection between the microfibrils, creating the primary structural network. Lignin can be deposited within this network in two ways: either as isolated lumps (when it acts to limit the movement of the microfibrils, thus increasing stiffness by steric hindrance) or as a continuous matrix, which then supplements and presumably replaces the hemicelluloses in importance as a linker of the cellulose microfibrils. The hydrophobic lignin network affects the properties of other networks in a way that it acts as a coupling agent and increases the stiffness of the cellulose/hemicelluloses composite.^{14,15} It was suggested that this complex structure and heterogeneous chemical composition of hemp fibers are one of the crucial factors that affect the specific surface area, amount of surface oxygen groups and morphology of carbonized hemp fibers.¹¹

The aim of this investigation was to attain the appropriate specific structure of hemp fibers based carbon precursor that promotes the formation of the required porosity and surface chemistry of the biocarbon, to facilitate adsorption of heavy metal ions. For that reason, different biocarbons were obtained by chemical modification of pristine short hemp fibers followed by carbonization. The possibility of using obtained biocarbons for the removal of heavy metals from polluted water was tested through the adsorption of lead, zinc and cadmium ions. Equilibrium studies of heavy metals adsorption on carbon materials, based on unmodified and modified hemp fibers, were performed using lead ions as a

model of divalent heavy metal ions. Adsorption data were modeled and evaluated by different nonlinear adsorption isotherms (Langmuir, Freundlich, Redlich–Peterson and multilayer), standard deviation (STD) and corrected Akaike information criterion (AIC_C) as a statistical estimating and ranking tool. Defining the correlation between hemp fibers-based biocarbon (HFB) structural parameters and determined isothermal and thermodynamic parameters, will enable a better understanding of lead ions adsorption mechanism.

EXPERIMENTAL

Materials

Biocarbon samples were obtained by carbonization of short and entangled hemp fibers, obtained as a waste in textile industry. Prior to carbonization, hemp fibers were alkali and oxidatively treated, in order to obtain carbon precursors of different chemical composition. Selective removal of hemicelluloses and lignin was brought by treating the fibers with 17.5 % NaOH and 0.7 % NaClO₂ solution, respectively,¹⁶ at the solid to liquid ratio of 1/50. Carbon precursors pChL5 and pChH5 were obtained after 5 min of oxidative and alkali treatment, respectively, while precursors pChL60 and pChH45 were obtained using prolonged oxidative and alkali treatments (60 and 45 min), respectively. Chemical composition of pristine (pCh1) and modified hemp fibers was determined according to the scheme of Soutar and Bryden¹⁶ by successive removal of water solubles, fats and waxes, pectins, lignin and hemicelluloses. The samples obtained by chemical modification, along with the pristine short hemp fibers, were carbonized in electrical furnace at 1000 °C under constant nitrogen flow, with the heating rate of 5 °C/min, followed by a “heat soak” time of 30 min at end temperature. Finally, five HFB samples mark as, Ch1, ChL5, ChL60, ChH5 and ChH45, were obtained.

Materials characterization

Textural characteristics of HFB samples were obtained from the N₂ adsorption and desorption isotherms measured at the temperature of liquid nitrogen using Micromeritics ASAP 2020, surface and porosity analyzer (Micromeritics Instrument Corporation, U.S.). The total pore volume (V_{total}), micropore volume (V_{micro}) and mesopore including external surface area (S_{meso}), were obtained from the adsorption data, using the manufacturer’s software ASAP 2020 V3.05 H. Pore size distribution was estimated by applying BJH method¹⁷ to the desorption branch of isotherms and mesopore surface and micropore volume were estimated using the high resolution α_s plot method.¹⁸ The surface area corresponding to the micropores was obtained from the difference between S_{BET} and S_{meso} .

Surface structure and morphology were studied by scanning electron microscopy (SEM JEOL JSM 5800 operated at 20 keV).

Amount of HFB surface oxygen groups, that have acidic or basic properties, was determined by acid–base titration method.^{19,20} The amounts of acidic and basic sites were determined by mixing 0.1 g of biocarbon with 25 cm³ of 0.1 M NaOH or 0.1 M HCl, in 50 cm³ beakers. The beakers were sealed and shaken for 24 h. Solutions were then filtered and titrated with 0.1 M HCl or 0.1 M NaOH.

The point of zero charge (PZC) of the tested biocarbons was determined by mass titration^{21,22} by placing various amounts (0.05, 0.1, 0.5, 1 and 10% by weight) of biocarbon in 10 cm³ of 0.1 M KCl solution (prepared using preboiled water to eliminate CO₂). The beakers were shaken overnight in N₂ atmosphere, to eliminate any contact with air. The limiting pH value was taken as the PZC.

Adsorption experiments

Adsorption of heavy metal ions from ternary mixture (Pb^{2+} , Cd^{2+} and Zn^{2+}) by different HFB samples was performed from aqueous solutions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in the batch system at 25 °C. Initial concentration per each ion was 50 mg/dm^3 . 0.1 g of biocarbon samples were immersed in 50 cm^3 of heavy metal ions solution and constantly shaken. Based on previous investigation¹² and experimental data for adsorption kinetics, shown in Supplementary material to this paper, all adsorption experiments were performed for a period of two hours. In order to determine the optimal pH value of heavy metals aqueous solution, the effect of pH on biocarbon adsorption capacities was studied. For this, the initial pH values of metal ions aqueous solution was adjusted by stepwise addition of HNO_3 or NH_4OH . Heavy metal ions concentration in the solution was measured by atomic absorption spectrometry (PYE UNICAM SP9, Pye Unicam, Ltd., UK).

In order to assess the maximal adsorption capacity of the HFBs, adsorption of lead ions was performed in the batch system at 25 °C, with constant shaking for two hours, from water solution (pH 5.5) at various initial ion concentrations (25, 50, 100, 200, 300 and 400 mg/dm^3). The adsorption behavior of lead ions on HFB samples was modeled by Langmuir, Freundlich, Redlich–Peterson and multilayer isotherm equation (Table S-I of the Supplementary material). Nonlinear regression analysis was performed in order to determine the values of isotherm model parameters. Standard deviation and corrected Akaike information criterion,²³ presented in Table S-I, were used to evaluate the applicability of each model isotherm equation to the experimental data.

The influence of the temperature on the adsorption capacity of HFBs was assessed by performing the adsorption experiments, in temperature-controlled water bath, at three different temperatures 25, 35 and 45 °C: 0.1 g of biocarbon was equilibrated with 50 cm^3 of lead ions aqueous solution (50 mg/dm^3), and constantly shaken for two hours. The thermodynamics of adsorption process were estimated according to Liu²⁴ (details are given in Supplementary material).

RESULTS AND DISCUSSION

Materials characterization

Chemical composition of pristine (pCh1) and modified hemp fibers, which was used as precursors for biocarbon production, is shown in Fig. 1. After the

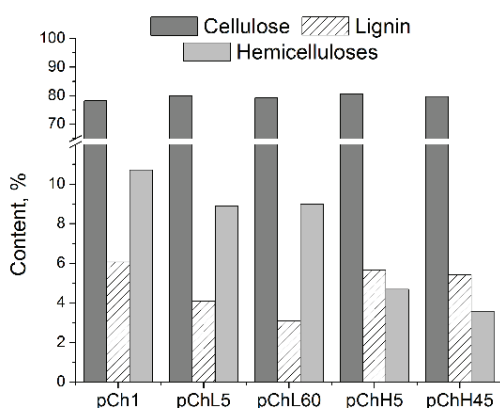


Fig. 1. Chemical composition of origin and modified hemp fibers used as carbon material precursors.

alkaline treatment, the level of hemicelluloses content was lower than in the unmodified fibers, while lignin content was almost unchanged. On the other hand, the sodium chlorite treatment of hemp fibers progressively removed lignin and slightly changed hemicelluloses content.

Biocarbon samples morphology, revealed by scanning electron microscopy, is shown in Fig. 2. It can be observed that all HFB samples retained fibrous structure of precursor, with the more or less pronounced fibrillation, depending on chemical treatment used prior to carbonization. Prolonged modification of carbon precursor increases the fibrillation rate, which is especially noticeable for ChH45 (Fig. 2e). Additionally, in case of sample ChL60 (Fig. 2c), the presence of a few completely liberated nanofibrils (with the diameter less than 100 nm) is observed.

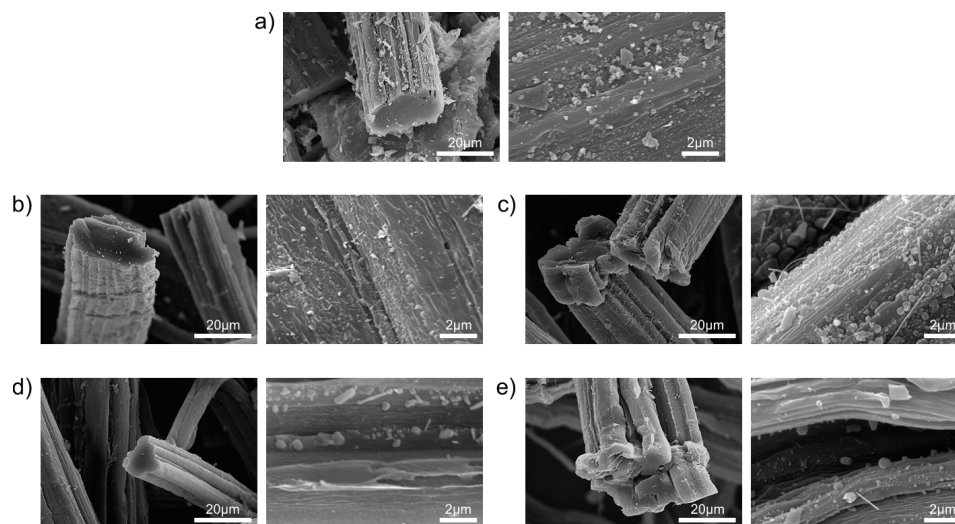


Fig. 2. SEM photographs of hemp fibers-based biocarbon samples: a) Ch1, b) ChL5, c) ChL60, d) ChH5 and e) ChH45.

Textural characteristics of HFB samples are summarized in the Table I. All tested HFB samples poses relatively high specific surface area (S_{BET}). The values of V_{total} and V_{micro} , as well as S_{micro} , indicate that all samples are predominantly microporous, with the similar ratio of mesoporosity. The chemical composition of the lignocellulosic precursor affects the textural characteristics of the HFBs. It can be observed that lower lignin content (Fig. 1), obtained for oxidative treated precursors (pChL5 and pChL60), leads to the lower specific surface area of resulting biocarbons (ChL5 and ChL60). However, this trend is not observed for biocarbons obtained from alkali treated precursors. Despite the similar content of lignin in precursor, specific surface area of these samples differs.

TABLE I. Surface properties of hemp fibers-based biocarbon samples^{11,12}; Ac and Bc – amount of acidic and basic surface groups, respectively

Surface property	Sample				
	Ch1	ChL5	ChL60	ChH5	ChH45
$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	519	429	389	426	573
$S_{\text{meso}} / \text{m}^2 \text{g}^{-1}$	132	94	86	89	137
$S_{\text{micro}} / \text{m}^2 \text{g}^{-1}$	387	335	303	337	436
$V_{\text{total}} / \text{cm}^3 \text{g}^{-1}$	0.291	0.208	0.194	0.207	0.290
$V_{\text{micro}} / \text{cm}^3 \text{g}^{-1}$	0.180	0.156	0.140	0.157	0.203
Ac* / mmol g ⁻¹	0.230	0.097	0.387	0.220	0.190
Bc* / mmol g ⁻¹	0.580	0.758	1.072	0.825	0.870
Ac+Bc/ mmol g ⁻¹	0.810	0.854	1.459	1.045	1.060
pH _{PZC}	10.58	11.05	10.87	10.72	10.95

High specific surface area of sample ChH45 may be the consequence of polymorphic transformation of cellulose I to more reactive cellulose II,^{25,26} which was induced by experimental conditions used during the alkali treatment of carbon precursor.

In order to obtain quantitative information about the oxygen groups present on the surface of biocarbons, acid/base titration method was used. The results obtained by acid/base titration (Table I) show that modification of carbon precursor increases the amount of surface oxygen groups. Also extension of oxidation and alkali treatment time, leads to the increased amount of the surface oxygen groups. According to the amounts of acidic and basic groups, all tested samples show basic character, which is in accordance to pH_{PZC} values (Table I).

Adsorption studies

pH of aqueous solution plays an important role in adsorption of heavy metal ions since it affects the solubility of metal ions and the ionization state of the functional groups of the biocarbon surface. Fig. 3 illustrates the influence of the solution pH on the Cd²⁺, Pb²⁺ and Zn²⁺ adsorption on sample Ch1.

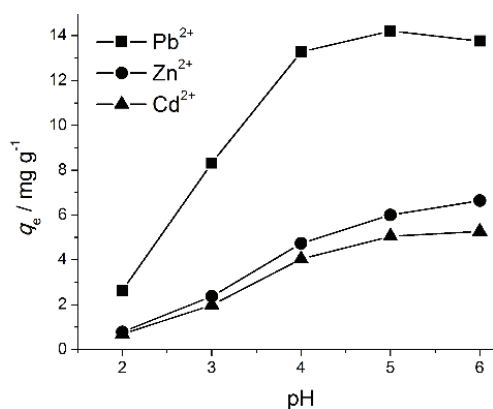


Fig. 3. Effect of initial pH on the Cd²⁺, Pb²⁺ and Zn²⁺ adsorption on Ch1 (initial concentration of solution 50 mg/dm³ per each metal ion).

It can be noted that adsorbed amount of Cd^{2+} , Pb^{2+} and Zn^{2+} increase in the pH range of 2–6. At low pH, the amount of the adsorbed metal ions is very low due to high proton concentration and protonation of the biocarbon surface groups, *i.e.*, lack of the free binding sites for metal ions adsorption. With increasing pH, proton concentration decreases and metal ions compete more effectively for available binding sites, which increase adsorption, especially between pH 4.0 and 6.0. Therefore, in order to decrease competition between protons and heavy metal ions for surface adsorption sites, and at the same time to prevent ions precipitation, adsorption of heavy metal ions on the HFBs were performed from the aqueous solution at pH 5.5.

Adsorption properties of biocarbon samples tested through the heavy metal ions adsorption from the ternary mixture are presented in Fig. 4.

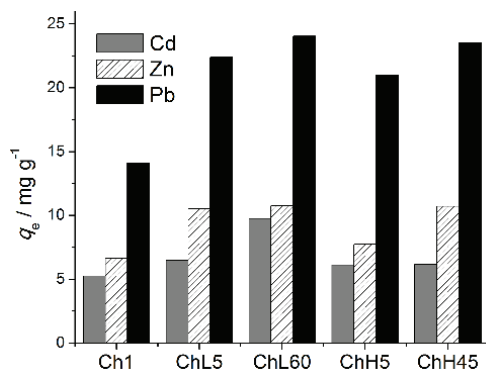


Fig. 4. Total uptake capacity of heavy metal ions by HFB samples from ternary ion mixture of initial concentration 50 mg/dm^3 per each metal ion.

It is notable that modification of hemp fibers prior to carbonization increases the total uptake capacities, especially for oxidatively treated samples. Also, longer treatment duration increases adsorption capacity, since the highest heavy metals uptake was observed for the samples ChL60 and ChH45 (Fig. 4). This capacity improvement is especially notable for lead ions adsorption. Additionally, lead ions adsorption onto HFBs is most competitive due to much higher total uptake capacity for Pb^{2+} than for Cd^{2+} and Zn^{2+} . Generally, adsorption of heavy metal ions can be affected by specific surface area, material structure and amount of surface oxygen groups that may act as active sites for adsorption. Taking into account the results obtained by surface characterization (Table I), it can be observed that specific surface area has no decisive influence on the adsorption capacity, since sample Ch1, despite its high specific surface area, shows the lowest adsorption capacity. On the other hand, the clear dependence between the amount of surface oxygen groups and the adsorption can be noted: the highest adsorption capacity is obtained for sample ChL60 which contain the highest amount of surface oxygen groups. Also, the correlation between the adsorption (Fig. 4) and material structure (Fig. 2) shows that enhanced fibrillation increases

the ability of hemp fiber biocarbons to remove lead ions, due to facilitated penetration of lead ions into biocarbon structure. In the aqueous solution metal ions are surrounded by solvation layer, whose thickness affects the ion transport through the solution. Ions with smaller radius (Cd^{2+} and Zn^{2+}) have thicker solvation layer,²⁷ therefore their transport toward the sorbent surface is slower. Lead ions that have larger radius compared to cadmium and zinc, and thinner solvation layer, need the shorter time to reach the biocarbon surface.⁵ Consequently, lead ions have a priority of deposition in porous biocarbon structure which make lead ions adsorption onto HFBs most competitive. Therefore, adsorption of lead ions was used for further examination of HFBs adsorption properties.

In an attempt to reveal the adsorption behavior of the system lead ions – HFBs at the equilibrium, as well as specific relation of pollutant concentration and its uptake degree by the solid phase, four isotherm models were used (Fig. 5).

The values of the model parameters and the error deviation between experimental and equilibrium adsorption data, predicted by studied isotherm models, as well as the best fitting model, were determined by standard deviation and corrected Akaike information criterion (Tables II and III).

The experimental isotherm data for HFBs obtained from modified precursors (Fig. 5b–e) show a rapid increase in q_e values, especially for sample ChH45, due to facilitated lead ions diffusion into highly fibrillated structure. Consequently, higher extent of adsorption during the initial stages of the process could be expected.

The lack of the plateau at higher concentration, noticeable for all tested samples, may indicate a slower adsorption induced by hindered lead ions diffusion to the remaining vacant active sites. These observations were consistent with the higher values of the equilibrium constant for the first layer adsorption (K_1) than for the multilayer sorption (K_2), calculated by the multilayer model (Table II). The experimentally obtained maximum equilibrium capacity of tested samples ranged from 84 mg/g, for Ch1, to 114.6 mg/g, for ChH45, while the monolayer capacity according to the Langmuir model ranged from 103.1 mg/g, for ChL5, to 116.3 mg/g, for ChH5. Obtained adsorption capacities of HFBs are comparable, or even higher than the adsorption capacities of activated carbons derived from different biomass, despite their much higher specific surface area.^{28–30}

As it can be noticed from the Fig. 5, experimental data obtained for Ch1, ChL5 and ChL60 are well fitted with Langmuir isotherm model, while samples ChH5 and ChH45 are in good correlation with Freundlich model. These observations are in agreement with the results obtained by error analysis and corrected Akaike criterion (Table III).

According to the Akaike criterion, equilibrium data for samples Ch1 and ChL5 are better correlated with Langmuir equation, while standard deviation have shown that the Redlich and Peterson model, which is reduced to Langmuir model, for $b = 1$, are the best fitting model. Values of Akaike criterion, along

with the standard deviation, showed that equilibrium experimental data obtained for sample ChL60 are correlated well with Langmuir model, while data obtained for alkali treated and carbonized samples obey Freundlich model. These observations suggest that the Langmuir and Freundlich model are sufficient enough for description of adsorption behavior of the system lead ions – HFBS at the equilibrium.

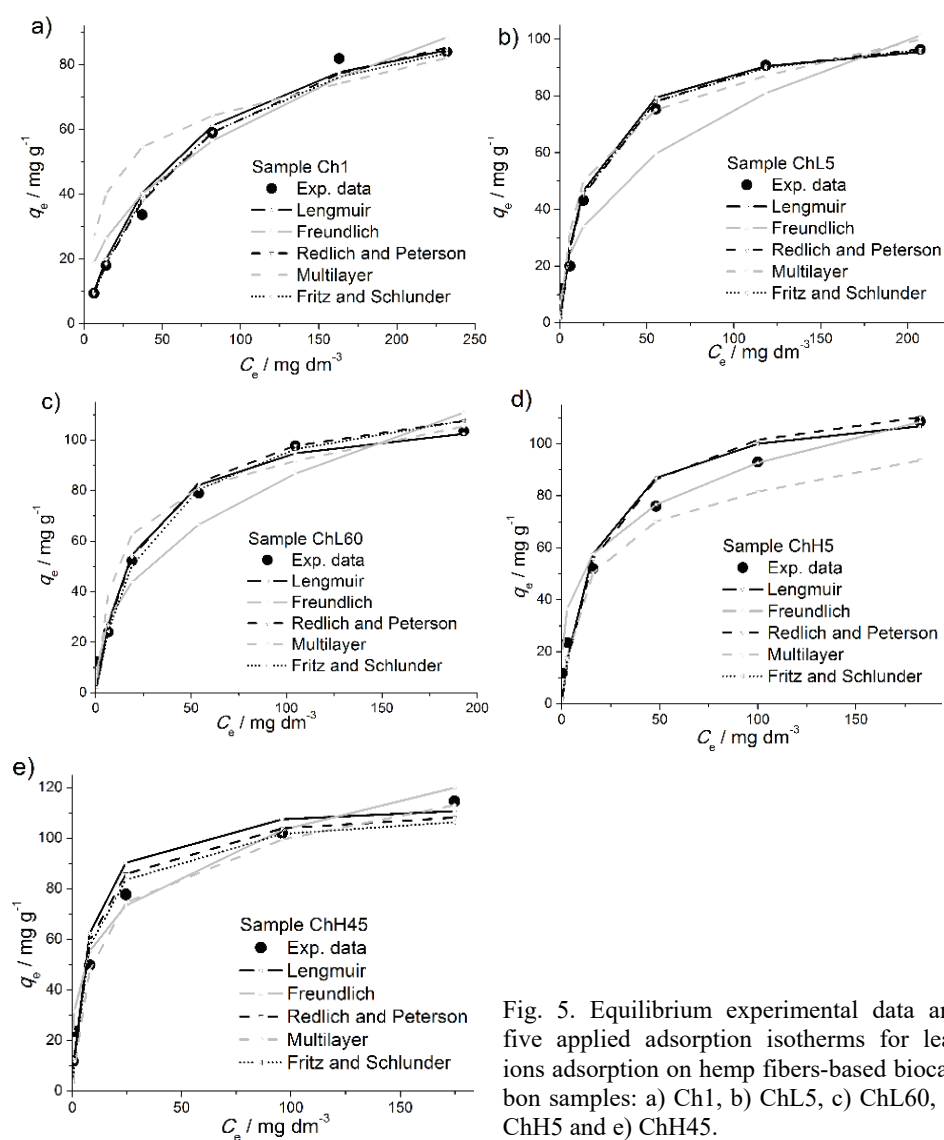


Fig. 5. Equilibrium experimental data and five applied adsorption isotherms for lead ions adsorption on hemp fibers-based biocarbon samples: a) Ch1, b) ChL5, c) ChL60, d) ChH5 and e) ChH45.

TABLE II. Model parameters for the system lead ions – HFBs obtained through nonlinear regression analysis of applied isotherms

Model	Parameter	Sample				
		Ch1	ChL5	ChL60	ChH5	ChH45
Langmuir	$K_A / \text{dm}^3 \text{mg}^{-1}$	0.0164	0.0606	0.0490	0.0614	0.15
	$Q_0 / \text{mg g}^{-1}$	106.7	103.1	113.3	116.3	114.9
Freundlich	$K_F / \text{mg}^{(1-n_F)} \text{dm}^{3n_F} \text{g}^{-1}$	8.5	12	13	28	33
	n_F	0.040	0.43	0.43	0.26	0.25
Redlich and Peterson	$K_R / \text{dm}^3 \text{g}^{-1}$	1.61	6.10	5.30	6.70	17.20
	$\alpha_R / \text{dm}^3 \text{mg}^{-1}$	0.0171	0.0651	0.0490	0.0614	0.17
Multilayer	B	0.97	0.98	0.98	0.98	0.98
	$Q_m / \text{mg g}^{-1}$	65	82	88	80	89
	$K_1 / \text{dm}^3 \text{mg}^{-1}$	0.11	0.11	0.12	0.10	0.12
	$K_2 / \text{dm}^3 \text{mg}^{-1}$	0.001	0.001	0.001	0.001	0.001

TABLE III. Error deviation data determined by standard deviation and corrected Akaike information criterion

Sample	Error function	Model			
		Langmuir	Freundlich	Redlich and Peterson	Multilayer
Ch1	STD	3.520	6.220	2.890	12.63
	AIC _C	25.32	33.09	33.84	54.55
ChL5	STD	6.510	7.490	6.000	7.750
	AIC _C	31.95	35.73	42.61	46.09
ChL60	STD	5.529	8.269	5.686	9.457
	AIC _C	30.07	36.19	41.93	48.46
ChH5	STD	8.208	5.424	8.285	5.701
	AIC _C	34.68	33.26	46.56	48.91
ChH45	STD	10.12	5.724	8.586	7.225
	AIC _C	37.25	33.77	46.94	45.91

The highest values of Freundlich parameter, n_F , obtained for the oxidative treated and carbonized samples, suggests that these samples have the most homogeneous distribution of surface active sites. This can be the consequence of the altered precursor's structure and chemical composition induced by oxidative treatment. Changes in fiber surface and structure can be ascribed not only to the decrease of lignin or hemicelluloses content, but also to the location of these components in the hemp fiber. Lignin is located in the middle lamellae and secondary wall of hemp fibers and it can be more or less strongly associated with the cellulose microfibrils. During the oxidation treatment lignin is selectively removed, resulting in more homogenous middle lamella, due to the homogeneous distribution of hemicelluloses in fiber structure.^{6,31} It can be assumed that homogeneous distribution of active sites on the surface of carbonized materials is affected by this homogenous distribution of hemicelluloses in the precursor structure. For all tested samples values of n_F were less than unite, indicating that lead

ions adsorption on hemp fibers-based biocarbons is chemical process which occurs through the ion exchange reaction on the surface functional groups.

In order to obtain some additional information concerning the adsorption mechanism, the thermodynamic studies of lead ions adsorption on HFB samples were performed at three temperatures 25, 35 and 45 °C (Fig. 6).

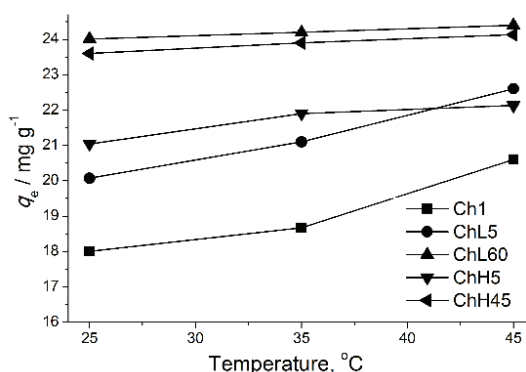


Fig. 6. Effect of temperature on hemp fibers-based biocarbon lead ions adsorption capacities.

Noticeable increase in adsorption capacity at the higher temperatures is observed for samples Ch1 and ChL5, while adsorption capacity of samples ChH5, ChH45 and ChL60 is only slightly increased. Nevertheless, for all tested samples lead ions adsorption capacity increases with the increase in temperature, due to the faster diffusion of lead ions through porous matrices of adsorbent and consequently more favorable adsorption. Significant increase in adsorption capacity of samples Ch1 and ChL5 at the higher temperatures is probably the consequence of increased diffusion which enables easier penetration of lead ions through less fibrillated morphology of these samples.

The thermodynamic parameters, the values of enthalpy, ΔH , entropy, ΔS and Gibbs energy change, ΔG , of lead ions adsorption on HFBs are given in the Table IV.

Obtained positive values of ΔH show that lead ions adsorption onto the HFBs is endothermic process, which is confirmed by the effect of temperature on lead ions removal. Negative values of ΔG obtained for all tested samples indicate that lead ions adsorption is spontaneous process, favorable at the higher temperatures.

The values of ΔG and ΔH can give information whether the adsorption process is of chemical or physical nature. It is generally accepted that physical adsorption involves an enthalpy change between 2 and 21 kJ/mol and Gibbs energy change between -20 to 0 kJ/mol, while for chemical adsorption enthalpy change values fall within the range 80–200 kJ/mol and Gibbs energy change range from -400 to -80 kJ/mol.^{32,33} The values of Gibbs energy change, presented in the Table IV, suggests that lead ions adsorption on HFBs can be considered as phys-

Table IV. Thermodynamic parameters for Pb²⁺ adsorption onto HFBs

Sample	Temperature, K	Thermodynamic parameter		
		$\Delta G / \text{kJ mol}^{-1}$	$\Delta H / \text{kJ mol}^{-1}$	$\Delta S / \text{kJ mol}^{-1} \text{K}^{-1}$
Ch1	298.15	-8.15	44.62	0.18
	308.15	-9.92		
	318.15	-11.69		
ChL5	298.15	-7.27	44.31	0.17
	308.15	-9.00		
	318.15	-10.73		
ChL60	298.15	-6.92	39.89	0.16
	308.15	-8.49		
	318.15	-10.06		
ChH5	298.15	-6.84	38.48	0.15
	308.15	-8.36		
	318.15	-9.88		
ChH45	298.15	-9.99	37.12	0.16
	308.15	-11.57		
	318.15	-13.15		

isorption, while the enthalpy change values, falling in the range from 37 to 45 kJ/mol, does not favor either physisorption or chemisorptions. Adsorption studies have shown that adsorption was affected by the number of surface functional groups, rather than the specific surface area. Carboxylic anhydride groups, present on the surface of HFB samples, can be hydrolyzed in aqueous solution rendering two carboxylic groups,³⁴ which might behave as ion-exchange sites for the retention of lead ions. Since samples containing high amount of surface oxygen groups, ChL60 and ChH45, showed high adsorption efficiency, it is assumed that lead ions can be adsorbed through the mechanism of ion-exchange, which is corroborated by the positive values of entropy change (Table IV). It was shown that pH_{PZC} values of HFBs lie in the alkaline range, and therefore the surface examined biocarbons is positively charged in solutions having $\text{pH} < \text{pH}_{\text{PZC}}$. This indicates that adsorption of metal ions takes place against the repulsive electrostatic forces, which is a strong argument in favor of chemisorption. Accordingly, chemisorption can contribute to the overall adsorption of lead ions onto HFBs. Since oxygen in the surface functional groups possess a pair of lone electrons (Lewis base) that can act as a center capable for coordination with electron deficient lead ions (Lewis acid),³⁵ surface complexation between lead ions and oxygen containing groups may contribute to the overall adsorption mechanism. Obtained results indicate that lead ions adsorption onto HFBs is a complex process, with the various contribution of physisorption and chemisorptions, and cannot be resolved without further, more sophisticated analysis.

CONCLUSIONS

Distribution of the celluloses, lignin and hemicelluloses in the hemp fiber structure, as well as the changes in their amount induced by chemical modification, affects the surface properties, morphology and consequently, adsorption properties of the resulting hemp fibers-based biocarbons. Progressive removal of both hemicelluloses and lignin from the precursor structure lead to liberation of elementary fibers, and that fibrous structure is preserved after carbonization. Lignin content and polymorphic transformation of cellulose I to more reactive cellulose II primarily affects the porosity of hemp fibers-based biocarbon, while homogenous distribution of hemicelluloses in the precursor structure induce more homogeneous distribution of adsorption active sites on the surface of hemp fibers-based biocarbons. Prolonged chemical modification of carbon precursor greatly improved adsorption capacity of hemp fibers-based biocarbons, by increasing the amount of surface oxygen groups and the level of material fibrillation. Adsorption and thermodynamic studies showed that Pb^{2+} adsorption onto HFBS is a spontaneous and complex endothermic process, suggesting the coexistence of physisorption and chemisorption mechanisms. High adsorption capacities at increased temperatures, enables the utilization of hemp fibers-based biocarbons as filter materials for removal of heavy metals from wastewater.

NOMENCLATURE

α_R :	Redlich-Peterson isotherm constant, $\text{dm}^3 \text{mg}^{-1}$
A :	Constant that depends on temperature, $\text{dm}^{3/2} \text{mol}^{-1/2}$
AIC:	Akaike information criterion
AIC _C :	Corrected Akaike information criterion
b :	Redlich-Peterson isotherm constant
γ_e :	Activity coefficient at the adsorption equilibrium
C_e :	Equilibrium adsorbate concentration in the liquid phase, mg dm^{-3}
θ_e :	Fraction of the surface covered at equilibrium
ΔG :	The Gibbs energy change, kJ mol^{-1}
ΔH :	The enthalpy change, kJ mol^{-1}
I_e :	The ionic strength of the solute at adsorption equilibrium, mol dm^{-3}
K_a :	Thermodynamic equilibrium constant
K_A :	Langmuir sorption equilibrium constant, $\text{dm}^3 \text{mg}^{-1}$
K_L :	Langmuir isotherm constant, $\text{dm}^3 \text{mol}^{-1}$
K_F :	Freundlich isotherm constant, $\text{mg}^{(1-nf)} \text{dm}^{3nf} \text{g}^{-1}$
K_R :	Redlich-Peterson isotherm constant, $\text{dm}^3 \text{g}^{-1}$
K_1 :	Equilibrium constant for the first layer adsorption in the multilayer isotherm model, $\text{dm}^3 \text{mg}^{-1}$
K_2 :	Equilibrium constant for multilayer adsorption in the multilayer isotherm model, $\text{dm}^3 \text{mg}^{-1}$
n :	number of isotherm parameters
n_F :	The heterogeneity factor in the Freundlich model
p :	Number of experimental data points

Q_m :	Maximum monolayer adsorption capacity in the multilayer isotherm model, mg g ⁻¹
Q_0 :	Maximum adsorption capacity in the Langmuir isotherm model, mg g ⁻¹
q_e :	The equilibrium sorbate concentration in the solid phase, mg g ⁻¹
q_e^{exp} :	Experimental equilibrium solid phase concentration, mg g ⁻¹
q_e^{mod} :	Model calculated equilibrium solid phase concentration, mg g ⁻¹
q_{max} :	Adsorption capacity of adsorbent at its maximum value, mg g ⁻¹
R :	Gas constant 8.314, J mol ⁻¹ K ⁻¹
ΔS^0 :	The entropy change, kJ mol ⁻¹ K ⁻¹
T :	Experimental temperature, K
z :	Charge of ions in solution

SUPPLEMENTARY MATERIAL

Adsorption kinetics data are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

УТИЦАЈ ХЕМИЈСКОГ САСТАВА ПРЕКУРСОРА НА АДСОРПЦИЈУ ТЕШКИХ МЕТАЛА БИОКАРБОНОМ НА БАЗИ ВЛАКАНА КОНОПЉЕ (*Cannabis sativa*)

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Биокарбон на бази кратких и замршених влакна конопље (*Cannabis sativa*), коришћен је као ефикасан и јефтин адсорбент за уклањање јона тешких метала из воде. Оксидациони и алкални третмани влакана конопље коришћени су за добијање угљеничних прекурсора различитог хемијског састава. Испитан је утицај хемијског састава прекурсора на специфичну површину биокарбона, његову морфологију, као и хемију површине. Показано је да садржај лигнина и полиморфна трансформација целулозе утичу на вредности специфичне површине микропорозних биокарбона. Са друге стране, садржај хемицелулоза и њихов положај у структури прекурсора утичу на хомогену расподелу функционалних група на површини карбона. Утврђено је да на адсорпцију тешких метала већи утицај има садржај површинских група него специфична површина биокарбона. Равнотежни адсорпциони подаци анализирани су различитим адсорпционим изотермама. У циљу утврђивања најбољег слагања експерименталних и моделних вредности коришћени су стандардна девијација и Акаике критеријум (Akaike information criterion). Максимални адсорпциони капацитети биокарбона кретали су се у опсегу од 103,1 до 116,3 mg Pb/g. Термодинамички параметри показују да је адсорпција Pb²⁺ на различитим биокарбонима, спонтани ендотермни процес који се одвија комбинованим механизмима физисорпције и хемисорпције.

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