Marija Mihajlović[1], Jelena Petrović[1], Mirjana Stojanović[1],
Jelena Milojković[1], Zorica Lopičić[1], Marija Koprivica[1],
Časlav Lačnjevac[2]*

[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia, [2]University of Belgrade, Faculty of Agriculture, Belgrade, Serbia

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Hydrochars, perspective adsorbents of heavy metals: - A review of the current state of studies

ABSTRACT

As an alternative to dry pyrolysis, hydrothermal carbonization has been proposed as a promising route for conversion of different wastes into biofuels, adsorbents and specific chemicals. Herein, the application of a wide range of waste biomasses as precursors to obtain hydrochars - efficient adsorbents of heavy metals from wastewaters, using hydrothermal conversion, was reviewed. The efficiency of biosorbents has been discussed with respect to the structural characteristics, reaction parameters, sorption capacities and mechanisms, as well as proposed methods of improving hydrochar´s surface reactivity. Altogether, biosorption with hydrochars has been identified as a proper alternative to the existing technologies applied for the removal of toxic metal ions from wastewater streams.

***Keywords**: hydrochar, heavy metals, adsorption, activation*

1. INTRODUCTION

Large-scale technological activities, primarily mining and metal processing, generate significant quantities of industrial effluents. The increased release of heavy metals into watercourses has damaging effects to biota worldwide [1]. Lead, cadmium, cobalt, nickel, etc., can affect the formation of blood cells, cause malfunctions in the liver, kidneys, the circulatory system, and the movement of nerve signals. Some heavy metals are highly cancerogenic. However, the environmental contamination and human exposure to toxic metals have dramatically increased during the past century [2]. Along with the persistence against chemical and biological degradation, heavy metals have high environmental mobility and ability for bioaccumulation in the food chain [3].

Therefore, nowadays, more attention is directed towards discovery of more efficient wastewaters treatments. Conventional wastewater treatments have proved to be more inimical than beneficial [4]. Hence, in the past two decades raise of the environmental awareness led to the development of new, eco-friendly technologies for wastewater purification. This period can be considered as the beginning of biosorption [1-8].

Utilization of different biological materials for removing pollutants from aqueous solutions has been suggested to have numerous advantages in relation to the conventional methods like selectivity, effectiveness at low concentration of pollutants, low-price, and sustainability [4]. Expended biomass sometimes can be regenerated, reused, or its effectiveness can be increased using different physical and/or chemical treatments [8-12]. Therefore, a number of raw industrial and agricultural residues have been tested as low cost sorbents of heavy metals from wastewaters [1-15]. However, a major drawback for almost all raw biosorbents is the release of organic components that may cause secondary pollution and oxygen reduction in water [16]. One of the proposed pathways of overcoming this issue is the use of different carbonization techniques of raw biomass [17].

The renaissance of research on conversion processes and their products has been driven by current world initiative of development “green” technologies to reduce global warming [17, 18]. One of such technologies is hydrothermal carbonization (HTC) also known as wet pyrolysis. Proposed back in the early 20th Century [19], this process, described as a simulation of the natural formation of coal, after recent studies on chemistry of the resulting products suddenly revived interest. During HTC, biomass heated between 180°C and 300°C in the closed system at autogenic pressure, undergoes a thermochemical transformation into carbonaceous solid, hydrochar (HC) [20]. The major advantage of HTC over the other two most commonly used biomass conversion technologies,

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*Corresponding author: Marija Mihajlović
Email: m.mihajlovic@itnms.ac.rs
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dry pyrolysis and gasification, is that HTC does not require pre-drying of raw material, which significantly facilitates its implementation and opens up a wider field of potential feedstock. Unlike conversion by dry pyrolysis, which is limited to usage of biomass with low water content such as woods and some agricultural residues, HTC feedstock except lignocellulosic residues can be unconventional biomasses such as animal manures, sewage sludge, municipal solid waste, as well as different aquacultures [17, 20-22]. This is very important since these continuously generated wastes require proper treatment and management anyway. Furthermore, the HTC process converts record high content of carbon from biomass to the coal, with no methane or CO_2 release into the atmosphere [20].

So far, HTC has been utilized on various feedstocks [10, 21-44]. The resulting HC, created via reactions between subcritical water and biomass, is coal like solid material with specific physiochemical properties which affected its potential applications, including carbon sequestration, soil amelioration, bioenergy production, and wastewater pollution remediation [18, 20]. Aside from the solid, this process generates larger quantities process water and smaller amount of the gaseous phase.

Although literature suggests that HCs are valuable resources superior to biochar [18], characterization of these materials is relatively at its beginnings. Therefore, effective utilization of HCs requires further investigations of the structure and underlying action mechanisms, especially when it comes to biosorption studies that are still in developing phase.

This review focuses on to date present knowledge regarding the application of HCs as adsorbents of heavy metals from aqueous solution with an emphasis on relevant physical and structural characteristics of the solid, biosorption potential, mechanisms of metal binding, and tailoring the structure of HCs in order to improve its adsorption abilities.

2. PHYSICAL AND STRUCTURAL CHARACTERISTICS OF HYDROCHARS

Feedstock types and reaction conditions (process temperature and reaction time) are main determinants affecting the HC resulting composition. Potential biomasses used for production of HC, and following HCs characteristics are given in Table 1.

Similar to other thermochemical conversion processes, hydrothermal reconstruction of the biomass is driven by different chemical mechanisms, decarboxylation, dehydration, condensation, aromatization, etc., except that during HTC hydrolysis of biomacromolecules is determining first step [29, 30]. Free-radical mechanisms, characteristic for dry pyrolysis, are overcomed in subcritical hot water in favor of ionic reactions. Therefore, HC is largely formed by recondensation reactions and exhibits distinct characteristics from dry pyrolysis biochar [17].

Although in both conversion processess solid yield decreases with the inreasing of the reaction temperature, likewise H/C and O/C ratios, carbon conversion eficiency is more pronounced in HTC [33]. Usually, in dry pyrolysis about 50% of the biomass carbon is converted to solids, while in HTC it is between 60-86% [17, 21]. By default, HC from waste feedstock has a correspondingly lower carbon content (Table 1).

Despite a significant carbon recovery during HTC, in HCs only about half of carbons are aromatic [33]. This explains relatively high O/C and H/C ratio of HCs in comparison to biochars, which is attributed to the abundance of oxygenated functional groups (OFGs) such as hydroxyl, carboxylate and carbonyl group [27, 33, 34]. Hitherto, two types of structrural models have been proposed explaining physicochemical characteristics of HCs [45]. The first model proposes a structure of HC as a polyaromatic lignin-type matrix with a shape very similar to that of a microsphere, built of a hydrophobic-core (composed of stable oxygen groups like ether, quinone, pyrone) and a hydrophilic-shell (composed of a large number of reactive oxygen functional groups like hydroxyl/ phenolic,carbonyl,or carboxylic) [33]. The second one have revealed that most of the carbon atoms in a HC samples are cross-linked directly via either sp^2 or sp^3 type carbon groups, in a similar way to that of a furan ring structure and dominated alkyl moieties [46, 47]. Such structure has been suggested to provide the increased surface reactivity, although HCs have generally lower porosity and surface area than biochars carbonized at temperatures above 400°C. These features are deemed to be benificial for sorption especially of positively charged contaminants such as heavy metals [16, 21, 23, 32-37].

3. BIOSORPTION OF HEAVY METALS

Although HCs exhibit relatively undeveloped porous structure and surface chemistry with acidic properties, high O/C ratio of HCs obtained at lower HTC temperatures indicate greater abundance of surface OFGs. Therefore, the heavy metal adsorption ability of HC has been reported to be noteworthy [36, 48].

In recent years, there is an exponential increase in the number of studies dealing with the use of different HCs as adsorbents of heavy metals. Influence of various reaction parameters on the biosorption as well as results of modeling, kinetic and thermodynamic of heavy metals adsorption using HCs obtained from various biomasses presented so far in the literature is summarized in Table 2.

Table 1 - Hydrochars properties relevant to hydrothermal conversion processes

Hydrochar feedstock	HTC temp (°C)	HTC time	Yield (%)	Elemental composition (wt, %)						VM (%)	FC (%)	Atomic ratio		HHV (MJ/kg)	pH	BET surface area, (m^2/g)
				C	H	O	N	S	Ash			O/C	H/C			
Eucaliptus sawdust [38]	250	2h	40	69.7	4.71	25	0.1	-	0.54	-	57	0.27	0.81	26.2	-	4.40
Barley straw [38]	250	2h	37	69.9	5.03	20	0.75	-	0.43	-	56	0.20	0.80	27.5	-	8.30
Corn stover [33]	250	4h	36	67.8	5.3	16.2	0.65	-	2.1	-	-	0.27	0.94	27.8	4.7	-
Coconout fiber [24]	220	30min	77	62.5	5.28	31.0	0.90	0.26	6.2	69.8	24.0	0.37	1.01	24.7	-	-
	250		66	67.1	5.20	26.4	0.98	0.29	5.0	67.9	27.1	0.30	0.93	26.7		
	300		65	73.2	5.09	20.2	1.13	0.35	4.3	53.6	42.1	0.21	0.97	29.4		
	350		56	73.4	4.52	20.6	1.17	0.35	4.9	56.6	38.5	0.21	0.74	28.7		
	375		59	78.2	4.31	15.9	1.23	0.33	8.6	42.6	48.8	0.15	0.66	30.6		
Eucaliptus leaves [24]	220		87	61.1	6.13	30.7	1.37	0.65	7.3	72.5	20.2	0.38	1.20	25.3	-	-
	250		61	62.3	5.47	30.4	1.44	0.44	6.9	70.1	23.0	0.37	1.05	25.0		
	300		61	68.9	6.00	22.8	1.62	0.72	7.1	61.2	31.7	0.25	1.05	28.7		
	350		48	70.5	5.93	20.4	1.60	1.52	9.9	56.2	33.9	0.22	1.01	29.4		
	375		43	72.2	4.81	19.8	1.64	1.51	14.2	43.2	42.6	0.21	0.80	28.7		
Grape pomace [26]	180	1h	86	56.4	6.92	32.2	2.07	0.19	3.7	67.7	25.8	0.44	1.45	24.4	-	-
	200		78	58.6	7.07	28.8	1.97	0.16	3.6	66.6	25.7	0.38	1.42	25.7		
	220		66	60.5	6.50	23.9	2.37	-	6.8	63.4	26.6	0.32	1.30	26.1		
Rice husk [40]	200	6h	58	40.8	4.31	29.9	0.44	0.04	24.5	43.1	29.4	0.05	1.27	15.7	4.2	20.7
	300		36	45.6	3.20	10.4	0.69	0.04	40.1	15.1	46.6	0.12	0.84	17.8	3.4	20.3
Corn stalk [41]	250	4h	36	71.4	5.60	16.3	2.00	0.40	4.36	-	54.2	0.17	0.94	29.2	-	-
Wood [41]	250		38	72.0	5.42	20.9	0.96	0.27	0.41	-	58.6	0.22	0.90	28.4		
Maize silage [42]	190	2h	72	59.1	6.75	30.7	-	-	11.6	-	-	0.39	1.37	25.4	-	-
	190	6h	56	61.9	6.63	28.3	-	-	8.71	-	-	0.34	.29	26.4		12.0
	190	10h	65	62.1	6.87	27.4	-	-	10.4	-	-	0.33	1.33	27.0		-
	230	2h	60	67.3	7.09	21.5	-	-	12.4	-	-	0.24	1.26	29.7		-
	230	6h	50	72.9	7.26	15.2	-	-	13.3	-	-	0.16	1.20	32.6		3.0
	230	10h	49	74.1	7.32	13.8	-	-	13.2	-	-	0.14	1.18	33.3		-
	270	2h	41	75.7	7.16	12.3	-	-	13.1	-	-	0.12	1.13	33.8		-
	270	6h	43	77.6	7.47	10.1	-	-	14.6	-	-	0.10	1.16	35.2		0.50
	270	10h	40	78.8	7.43	8.97	-	-	14.3	-	-	0.09	1.13	35.7		-
Hickory wood [43]	200	5h	44	53.5	6.13	39.8	0.25	-	-	-	-	0.74	0.11	-	6.0	2.50
Bagasse [43]			28	53.3	6.23	39.9	0.21	-	-	-	-	0.75	0.12	-	5.7	3.80
Bamboo [43]	200	20h	48	55.2	6.18	38.2	0.44	-	-	-	-	0.69	0.11	-	6.3	1.30
Sawdust [44]			55	61.5	5.83	31.6	0.08	-	1.03	-	-	0.38	1.14	-	3.4	4.41
Wheat straw [44]			47	55.3	7.19	31.5	0.27	-	5.79	-	-	0.43	1.56	-	3.9	9.14
Sewage sludge [21]	-	-	-	28.6	3.60	22.3	2.0	-	-	-	-	-	-	-	-	25.3
Anaerobically digested sludge [35]	200	24h	-	23.2	2.70	24.10	1.45	-	63.9	-	-	-	-	-	-	18.0
Pulp and paper industrial sludge [35]				34.7	3.78	15.5	1.67		47.5	-	-	-	-	-	-	9.10

VM- Volatile matter, FC-Fixed carbon, HHV-Higher heating value

Table 2 - Adsoption parameters of HTC feedstock

HTC			Adsorption parameters							
Feedstock	*Temp (°C)*	*Time*	*Metal*	*pH*	*Temp. (°C)*	*Contact time*	q_{eq} (mg/g)	*Isotherm model*	*Kinetic model*	*Thermo-dynamics*
Pinewood [16,36]	300	20 min	Pb^{2+}	5	45	5h	4.13	Langmuir	Pseudo 2nd order	Endotermic Spontaneous
			Cu^{2+}	6.2	25	5h	4.46			
Rice husk [16]	300	20 min	Pb^{2+}	5	45	5h	2.40	Langmuir	Pseudo 2nd order	Endotermic Spontaneous
Switchgrass [23, 32]	300	30 min	Cu^{2+}	5	23	24h	4.00	NM	NM	NM
			Cd^{2+}				1.50			
			U^{6+}	6.2	23	34h	2.12	Langmuir	NM	NM
Prospis Africana shell [48]	200	20 min	Pb^{2+}	6	22	30 min	45.3	Langmuir	Pseudo 2nd order	Endotermic Spontaneous
			Cd^{2+}	8			38.3			
Anaerobicaly digested sludge[35]	200	24 h	Pb^{2+}	5	NS	24h	~11	Sips	Pseudo 2nd order	NM
			Cr^{3+}	ND			ND	NM	NM	
			Cr^{6+}	3			N	NM	NM	
			As^{3+}	3			N	NM	NM	
			As^{5+}	3			N	NM	NM	
Pulp and paper industrial sludge [35]	200	24 h	Pb^{2+}	5	NS	24h	~11	Sips	Pseudo 2nd order	NM
			Cr^{3+}	ND	NS		ND	NM	NM	NM
			Cr^{6+}	3	NS		N	NM	NM	NM
			As^{3+}	3	NS		ND	NM	NM	NM
			As^{5+}	3	NS		ND	NM	NM	NM
Sewage sludge [21]	NS	NS	Cu^{2+}	5	NS	16h	15.7	Langmuir	Pseudo 2nd order	NM

ND-not detected, NM-not measured, NS-not specified, N- negligible

In two separate studies Liu et al. [36, 37] have characterized and investigated Pb^{2+} and Cu^{2+} adsorption properties of pinewood HCs. The results indicated the existence of a large amount of OFGs on the HCs surface responsible for removal capacities of 4.25 and 4.21 mg/g for Pb^{2+} and Cu^{2+}, respectively. In comparison with raw pinewood, HTC increased total OFGs for 95% in resulted solid, while pyrolized pinewood biochar exhibited significantly lower OFGs content. Same authors have used HC of rice husk prepared under similar conditions and reported adsorption of Pb^{2+} from aqueous solution of 2.40 mg/g. The adsorption data have been well described by Langmuir isotherm model and pseudo second order kinetics.

Similar conclusions have been reported by Elaigwu et al. [48] using HC prepared from microwave-assisted HTC of *Prospis afficana* shell for the removal of Pb^{2+} and Cd^{2+} from aqueous solution performed in batch experiments [48]. Maximum adsorption capacities for HC of 45.3 mg/g for Pb^{2+} and 38.3 mg/g for Cd^{2+} were higher than that of correspondent biochars. Higher adsorption of Pb^{2+} in comparison to Cd^{2+} have been attributed to better electrostatic interaction with OFGs of the chars due to smaller ionic radius of the hydrated Pb^{2+}.

Hydrochar produced from switchgrass have been used for removal of Cu^{2+} and Cd^{2+} from a single component solution system [23]. Reported adsorption capacities have been 4.0 and 1.5 mg/g for Cu^{2+} and Cd^{2+}, respectively. The importance of the presence of OFGs on the HC surface has been again confirmed, since the powdered activated carbon has exibited lower affinity for both metals (1.8 for Cu^{2+} and 1.5 mg/g for Cd^{2+}) although it has had more than twenty times greater surface area than of switchgrass HC. Kumar et al. [32] also investigated hydrothermally treated switchgrass as an adsorbent of U^{6+} (Table 2). The adsorption data have been followed Langmuir isotherm model and the sorption capacity of HC has been reported to be 2.12 mg of U per g of HC. The biosorption has been reported to be strongly pH dependent and towards neutral pH has resulted in the maximum U^{6+} adsorption of 4 mg/g.

Anaerobically digested municipal sludge (ADS) and pulp and paper industrial sludge (INS) have been investigated in study of Alatalo et al. [35] as precursors for hydrothermal production of heavy metal sorbents. The adsorption efficiencies of both HCs have been reported for Pb^{2+}, As^{3+}, As^{5+}, Cr^{3+} and Cr^{6+}(Table 2). Both materials have exhibited relatively high adsorption capacity for Pb^{2+} (around 11 mg/g) but much smaller for other investigated heavy metals (Table 2). The adsorption data have showed best fit to Sips isotherm model and pseudo second order kinetic model, and intraparticle diffusion have been partially involved in the adsorption process [35].

Application of HCs obtained from sewage sludge has also been tested as a potential sorbent of Cu^{2+} from aqueous solutions [21]. Removal of Cu^{2+} have been 15.67 mg/g at optimum experimental conditions of pH 5 and 70 mg/L metal concentration (Table 2). Pseudo second order of the kinetics and Langmuir isotherm model has showed best fit with the obtained experimantal data.

4. MECHANISMS OF METAL BINDING

All the mentioned authors, who have examined biosorption of heavy metals using different HCs, were concordant in claiming that large surface area and well developed porosity does not always indicate greater biosorption ability, and that in the adsorption, besides the structural morphology, surface functional groups perform essential role. In the main, resulting findings indicate that in the removal of heavy metals, amount of the surface OFGs are closely correlated to the adsorption capacity of HCs.

Investigating the mechanism of biochar's adsorption of Pb^{2+} from the solution, Wang et al. [49] have reported the possible coordination of metal ions due to surface complexation with carboxyl (-COOH) and/or hydroxyl (-OH) functional groups. This has been confirmed through FT-IR analysis of biochars after Pb^{2+} sorption. Furthermore, biochars pyrolized at higher temperatures (above 500°C) have not undergone changes of the characteristic –COOH and –OH bands after sorption, probably due to the lack of these functional groups [49].The coordination between OFGs and metal ions is typically followed by the release of hydrogen ions and thus the reduction of solution pH, which turned out to be characteristic in test solutions during biosorption of metals with HCs [50]. Similar mechanism for Pb^{2+} sorption with switchgrass HC has been proposed by Regmi et al. [23].

In the latter study, FT-IR spectra and NMR analysis have showed that more than 45% of the functional groups of switchgrass HCs are aromatic carbons [23]. The aromatic *π*- system behaves as an electron donor, and this feature increases with the number of associated rings [51]. Therefore, another proposed mechanism of metal binding assumes the possibility of establishing a cationic π - interaction between the metal and aromatics in chars. FT-IR analysis of biochars conducted by Wang et al. [50] have revealed changes in aromatic C=C and C=O vibrational bands before and after Pb^{2+} sorption, implying that Pb^{2+}-π interactions might be responsible for metal binding together with the coordination of the d-electron metal to the C=C (π - electron) bond of the unsaturated and aromatic systems [52].

In studies of Lima et al. [53] and Mohan et al. [54], the adsorption of heavy metals on broiler litter and alfalfa stems biochars, and pellets from fired coal fly ash was predominantly attributed to ion exchange mechanism. Similar conclusion have reported Lu et al. [55] in whose study FT-IR analysis have showed the possible presence of ion-exchange between Pb^{2+} and cations containing functional groups (R-O-M^+ or R-COO-M^+). This type of mechanism have also suggested by Regmi et al. [23] although that mechanisms of surface complexation and cationic π - interaction could not be neglected.

However, in the literature that deals with the phenomenon of heavy metal sorption on HCs, background mechanisms of metal binding are insufficiently elucidated, and therefore, further examinations regarding its relative contribution in overall adsorption process are highly needed.

5. SURFACE ACTIVATION

Recent advances in the synthesis of carbon materials using HTC have shown the possibility of tailoring HCs surface structure and chemical proprieties, thereby enhancing its efficiency as heavy metal sorbents.

The carbons derived from pine wood and rice husk HCs, after pyrolysis (800 °C) and following CO_2-activation, have exhibited significantly higher adsorption capacities for Cu^{2+} of 25.18 and 22.62 mg/g, respectively, in comparison to untreated HCs (~4 mg/g) Table 2 [36, 37].

In the work of Xue et al. [50], batch experiments have been conducted to investigate the effect of 10% H_2O_2 solution treatment on peanut hull HC to remove heavy metals. Obtained results have showed that Pb^{2+} sorption ability of modified HCs (22.82 mg/g) was twentyfold higher than that of untreated HCs (0.88 mg/g). These results have been confirmed when HCs have been used as filters in following column experiments. The activated HC except Pb^{2+} has effectively removed other heavy metals (Cu^{2+}, Ni^{2+} and Cd^{2+}) from water flow [50].

The cold alkali activation process proposed by Regmi et al. [23] using 2M KOH solution has been developed to enhance the porous structure and sorption properties of HC. As it was foreseeable, activated switchgrass HC exhibited much higher adsorption potential for Cu^{2+} and Cd^{2+} (of 31 and 34 mg/g, respectively) than untreated HC (of 4 and 1.5 mg/g, respectively, Table 2) and activated carbon (1.8 and 1.5 mg/g, respectively) [23]. Results of the same method of activation using sawdust, wheat straw and corn stalk HCs, have been reported by Sun et al. [44]. Their investigation showed that KOH treatment have increased the aromatic and OFGs in HCs, which resulted in more than a double efficient removal of Cd^{2+} from the aqueous solution (between 30.40-40.78 mg/g) in comparison with untreated HCs (between 13.92-14.52 mg/g).

More complex process of HC modification, have been presented recently by Chen et al. [56]. They have presented sorption performance of ultra-high efficient and Pb^{2+} selective amino-functionalized HC (AFHC), synthesized via HTC of watermelon extract and ammonium hydroxide. Pb^{2+} removal capacity of AFHC has been reported to be 1000 mg/g, with preserved efficiency even at lower Pb^{2+} concentrations. Reported results have indicated that excellent features of AFHC may be attributed to the formation and growth of rod-like hydroxypyromorphite crystals on AFHC surface, during which amino groups serves as bridges to interact with the crystal nucleus of Pb [56].

6. FUTURE TENDENCIES

Despite the still present knowledge gap between HC properties, specific utilization and environmental impact, there is growing number of studies that are nowadays focused on the generation of a variety of tailor-designed hydrophilic nanostructured carbon and hybrid materials using HTC. Although in the beginning, presented investigations suggested that HTC have a great potential as a method of conversion of residual lignocellulosic and unconventional biomasses, in the production of new generation of efficient low-cost heavy metal sorbents. These continuing experimental trials will very soon lead to an understanding of resolute HC traits, allowing processes to be designed to achieve the required product characteristics.

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IZVOD

HIDROČAĐI, PERSPEKTIVNI ADSORBENTI TEŠKIH METALA: - PREGLED AKTUELNIH PRAVACA U ISTRAŽIVANJIMA

Kao alternativa pirolizi, hidrotermalna karbonizacija je predložena kao perspektivan pravac konverzije širokog spektra otpadnih biomasa u biogoriva, adsorbente i specifične hemikalije. U ovom preglednom radu predstavljena su aktuelna istraživanja primene različitih otpadnih biomasa, kao prekursora za dobijanje hidročađi - efikasnih adsorbenata teških metala iz otpadnih voda postupkom hidrotermalne konverzije. Efikasnost biosorbenata je diskutovana u odnosu na strukturne karakteristike, reakcione parametre, sorpcione kapacitete i mehanizme, kao i predložene metode poboljšanja površinske reaktivnosti hidročađi. Sveukupno, biosorpcija hidročađima je identifikovana kao dobra alternativa konvencionalnim tehnologijama uklanjanja toksičnih metalnih jona iz otpadnih voda.

***Ključne reči**: hidročađi, teški metali, adsorpcija, aktivacija.*

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