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GREEN TECHNOLOGY APPROACH FOR CAPTURING POLLUTION WASHED FROM TRANSPORTATION INFRASTRUCTURES

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DISCLAIMER

1. Project Validation and Literature Review

The next few decades are predicted to be continuous challenge for the National Transportation System. Projected substantial increase of travelers and fright on the roads combined with aging infrastructures, old technologies, and reinforced environmental regulations focused on significant reduction and prevention of contamination generated by the street's runoff, are dictating intense search for new solutions. The U.S. Departments of Transportation are required to control and treat stormwater runoff from various transportation infrastructures. State departments of transportation (DOTs) are required to comply with their NPDES permits and initiate specific actions aiming reduction of stormwater pollution (http://mdot.ms.gov/portal/home.aspx).

Typical stormwater runoff from transportation infrastructures is a mixture of organic and inorganic contaminants. Heavy metals such as cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn) are one of the most common pollutants found on impervious areas, mainly released from transportation activities (Genç-Fuhrman et al., 2007; Helmreich et al., 2010; Hatt et al., 2011; Huber et al., 2016). Continuous interest in researching effective measures for their removal is due to their toxic and carcinogen nature causing serious health damages. Examination of the first flush shows that percentage in coexistence of ionic and particulate heavy metal forms (Zhao et al., 2010) depends primarily on pH of stormwater carrying pollutants. Typically, decrease in pH promotes ionic forms of different heavy metals, while increase of pH supports formation of different hydroxides and other complexes (Lima et al., 2010). Moreover, pH values in range of 5 to 7 have been reported as most effective for adsorption studies in heavy metal removal (Joseph et al., 2019). Attribution to effective adsorption media has been reported in many scientific articles and depending on the type of media, the common stormwater heavy metal pollutants (Pb, Cu, Cd, Zn, etc.) have been removed from a range of 0 to 90 % (Gill et al., 2017).

The proposed aim of this study was to investigate a carbon-based substance, namely biochar, for the *in-situ* adsorption of numerous pollutants carried by the stormwater runoff from highways. Use of biochar, if successful, it would implement green technology approach for *in situ* removal of toxic contaminants.

Biochar is well known as a common soil amendment in agricultural practices; however, only recently it has been "rediscovered" as a material with quite unique properties that make it a potential candidate for the numerous applications outside of agriculture. Biochar is formed during thermal decomposition of organic biomass under no- or limited presence of oxygen and it is defined by the International Biochar Initiative as "a solid material obtained from the carbonization of biomass" (International Biochar Initiative: http://www.biochar-international.org/). The elemental composition of biochar varies depending on the starting biomass and the setup of parameters of carbonization process (Duku, et al., 2011; Cambo, et al., 2015). Generally, biochar is produced under limited or full anaerobic conditions by slow pyrolysis at the range of temperatures (350^{o}C- 800^{o}C). From its agricultural uses, biochar is recognized as a great and very stable adsorbent. With large specific surface area, porous structure, and combination of surface's functional groups and mineral content, biochar is good candidate for adsorption of water and air pollutants, but also could serve as a catalyst to remove tar or produce biodiesel, as a soil amendment, a fuel cell, supercapacitor, and hydrogen storage. In comparison with traditional sorbents such as activated carbon or zeolites, biochar appears to be less expensive, more stable and more flexible within particular application.

The final properties of manufactured biochar heavily depend on numerous mechanisms, such as surface complexation, surface cation exchange, precipitation, etc. (Zhang et al., 2015). Formation of favorable structural properties can be altered through manipulation of pyrolytic conditions. For example, increase of temperature is affecting pore formation by removal of volatiles (Mohanty et al., 2018). On the other hand, the percentage of carbon will depend on the feedstock type and origin. Mukome et al. (2013) reported significant difference in using hard and soft-wood derived biochars, and they found greater pore formation of soft-wood derived biochar due to less density in the structure. Besides of physical properties, chemical characteristics are influenced by feedstock origin and pyrolytic conditions. Cation exchange capacity (CEC), abundance of surface functional groups and hydrophobicity represent just few of the main descriptors of how effective chosen adsorbent could be. For example, the removal of heavy metals as cations is affected by the negative surface charge of biochar (Mohanty et al., 2018) which can be approximated by the CEC, and promoted by decrease in pyrolysis' temperature (Mukherjee et al., 2011; Suliman et al., 2017).

Existence of functional groups such as hydroxyl, carboxy and phenolic would increase adsorption of heavy metals (Lu et al., 2012; Cao et al, 2009). In summary, targeted removal of a specific metal could be governed by adsorbent-adsorbate interactions through different adsorption mechanisms. Uchimiya et al., (2011a, b) reported that the governing mechanism dominating over others is a result of variating dimensions of pores, thus contributing to greater ion exchange. Lu et al, (2012) and Cao et al (2009) additionally explained that complexation and formation of heavy metal precipitates occurs in reactions with other inorganics found within material, thus promoting removal efficiency as well. Recent studies have shown similarities in adsorption capacities of heavy metals by different types of biochar. Lima et al., (2010) investigated eight types of biochar for copper, cadmium, nickel and zinc removal from polluted water resulting in different efficiency depending on the biomass used. Other studies have supported these findings. For example Wang et al. (2015a) obtained high efficiency with hickory wood biochar for Pb^{2+} and Cu^{2+} adsorption at 98.5% and 93.2%, respectively. Tong et al., (2017) obtained 98.6% for Pb^{2+} and 99.2% for Cd^{2+} adsorption efficiency by corn straw biochar.

Reddy et al., (2014) investigated biochar efficiency for adsorption in a multi-contaminant stormwater system that showed variations in adsorption efficiencies for different heavy metals (Pb, Zn, Cd, Cu, Cr and Ni). Such systems have great importance in determining the appropriate adsorption efficiency of a target heavy metal. It is not uncommon to expect decrease in adsorption efficiency when multiple ions compete for the affinity of the biochar's surface charge. For example, Han et al. (2017) showed decrease in Pb^{+2} adsorption efficiency when Cd or Al were present by 19% to 96% depending on the type of biochar.

2. Objectives of the study

The main goal of this study was to produce and extensively examine biochar as a potential material for the *in-situ* adsorption of typical pollutants carried by the stormwater runoff from the transportation infrastructures. Biochar, a product of controlled pyrolysis of carbon-rich waste material is the best known for its adsorption capacity as used for agricultural applications. The individual source of organic waste material, and parameters of pyrolysis, such as duration, temperature, limitation of oxygen, etc., would influence its final properties, which will dictate the overall efficiency of *in situ* adsorption.

The choice of waste biomass transformed into biochar is very important when final product is to be applied on commercial scale. There are several conditions that must be taken under consideration. For instance, the organic waste should be easily available for manufacturing, and be stable after pyrolysis. Mississippi is a State with heavy agriculture and farming; it is also "green" state with extensive forest and green foliage. The carbon-rich waste material used for this study represents organic waste produced by those activities: fragments of trees (bark nuggets, pine needles, and cypress mulch), waste from agriculture (corn stover) and animal waste (manure).

Long-term goal of this research was to investigate with further optimization a green technology approach for the effective, low-cost and environmentally friendly clean-up of contaminants spilled on the roads. To develop the foundation for reliable technology, the crucial parameters needed for production of biochar with designated properties had to be investigated first.

Our research was divided into several steps, as followed:

Objective 1: *Production with further optimization of biochar*. This objective was to establish the best organic waste material suitable for pyrolysis, and determine optimal conditions of pyrolysis;

Objective 2: *Characteristics of obtained biochars*. Employed techniques included FT-IR (Fourier-transform infrared spectroscopy), SEM-EDX (Scanning electron microscopy – Energy dispersive X-ray), XRD (X-ray diffraction), and elemental analysis that provided information about surface, structure, functional groups on the surface, and mineral content of final product;

Objective 3: *Test on leachability of biochar*. The aim for this part of the study was to confirm stability of biochar in retaining adsorbed pollutants;

Objective 4: *Adsorption capacity*. Biochar material was tested for removal of selected metallic contaminates under different conditions (pH of water, influence of other ions, temperature, etc.). Experiments were performed in mini columns with layer of biochar ranged 1–2 cm to investigate, what would be efficiency of adsorption in short time (30 min), when layer of biochar would be overflown with contaminated stormwater. Additional batch tests were run to establish adsorption capacities of tested biochar.

3. Methodological Approach

3.1 Materials

Five different carbon-rich waste materials were used to study the progress in transformation of organic waste into biochar. All biomass was obtained locally in Mississippi, USA. The investigated biomass included:
(a) Pine bark nuggets (PBN) and (b) Cypress mulch blend (CYMB) collected in Brookhaven, MS;
(c) Pine needles collected in Byram, MS;
(d) Cow manure from a local farm in Canton, MS., and
(e) Corn stover collected from Jackson, MS area.

As a part of preparation for pyrolysis, all biomass was cut to smaller pieces with an electric grinder and sieved to obtain designated particle size. All chemicals and standard solutions of tested metals used in adsorption experiments were analytical grade quality obtained from Fisher Scientific, USA.

3.2 Preparation of initial biomass and setup of parameters of pyrolysis

The aim of this part of the study was to test chosen biomass undergoing pyrolysis under various conditions.

Corn stover (CS), pine needles (PN), pine bark nuggets (PBN), cypress mulch blend (CYMB) and cow manure (CM) biomass were used as feedstock for biochar pyrolysis. Prior pyrolysis, the biomass material was air-dried under the fume hood for 24h, grinded to small pieces (< 2 cm) and sieved to mesh size 10-35, 35-60 and >60. Biomass was placed in stainless steel vessels with 10.2 cm x 5.4 cm x 4 cm (L x W x H) dimensions and packed until full to obtain limited oxygen conditions. Pyrolysis temperature ranged between 300 °C and 700 °C with a heating rate 26℃/min. All biochars were produced in a muffle furnace (1400 Thermolyne, Thermo Fisher Scientific, USA) with assigned temperature for 2 hours. After pyrolysis and cooling to constant temperature, biochar was stored in clean containers for further analysis.

3.3 Proximate analysis

Proximate analysis of CM, PN, CYMB and PBN biochar samples was followed adaptation of ASTM-D1762-84 method. All samples were sieved to mesh size 10-35 before analysis. Crucibles were pre-fired for 6h at 750℃ and then cooled to 105℃ to reduce any volatile residuals. For determination of moisture, biochar was heated for 18 h at 105℃, volatile matter was determined by heating biochar 10 minutes in a pre-heated furnace (950℃) and ash content was obtained by heating biochar for 6 h on 750℃. 1 g of each biochar sample was used for proximate analysis.

3.4 .Comprehensive instrumental analysis of obtained biochar

3.4.1. Determination of morphology by Scanning Electron Microscope – Energy Dispersive X-Ray (SEM – EDX)

The morphology of manufactured biochar's structures was determined by obtaining SEM images with the model FEI Quanta 200 (Thermo Fisher Scientific, Inc., MA, USA), with the acceleration voltage of SEM HV 5, 10, 15, 20 kV and magnification of 20, 50, 100 and 200 µm. EDX spectral analysis investigated all corresponding elements existed in the sample. Small specimens of biochar were mounted on an aluminum pin with carbon conductive glue, and placed for analysis.

3.4.2. Analysis of functional groups at the surface of biochar by Fourier-transform infrared spectroscopy (FT-IR)

FTIR spectroscopy was completed using Spectrum Two (PerkinElmer, Inc., MA, USA) with the LiTaO3 (lithium tantalate) MIR detector and standard optical system with a KBr window. The data collected represented results over the spectral range 400 – 4000 cm^{-1}. No special preparation of biochar was needed. Sample was directly placed on the KBr window for analysis and the readings were obtained through the Spectrum Two software.

3.4.3. Elemental analysis

Manufactured biochar samples were agitated for 24h to remove all impurities, and subjected to elemental analysis. 1 g of biochar was placed in a 50 ml test tube and mixed with 20 ml of distilled water. After 24h, the solution was vacuum-filtered through a 0.45µm glass membrane filter and stored for leachate analysis.

3.4.4. Determination of metals by inductively coupled plasma- mass spectrometry (ICP-MS)

All tested metals were analyzed with the ICPE-MS (ICPE-9000 Shimatzu) with implementation of (Quality Assurance/Quality Control) QA/QC procedures.

3.5. Adsorption and leachate testing of biochar

3.5.1. Mini column adsorption

Produced biochars were tested for their adsorption capacity. Initial experiments used mini columns, and tested contaminants were Pb^{2+} in competition with Cu^{2+}, Cd^{2+} and Zn^{2+} ions. The emphasis was given to Pb^{2+} in competition with Cu^{2+}, Cd^{2+} and Zn^{2+} ions. Stock solution of tested metals was prepared with deionized water (18 µS/cm conductivity) with following concentrations: 300 mg/l Cu^{2+}, 100 mg/l Pb^{2+}, 50 mg/l Cd^{2+} and 500 mg/l Zn^{+2}. The pH of the feed solution was adjusted to pH of 5. Column experiments were performed employing manufactured (in two different temperatures of 300°C and 600°C) biochars (PN300, PN600, CS300 and CS600) at 2 different adsorbent heights, 1 and 2 centimeters. Glass wool was placed at the bottom of the column to prevent biochar from leaking. The feed solution was pumped with a peristaltic pump with a flow of 2 ml/min in a 3cc mini column. The samples for analysis were collected after 30 minutes of adsorption and analyzed for adsorption capacity of lead in competition with copper, cadmium and zinc ions. After the adsorption was completed, samples for analysis were collected at the bottom of the column and analyzed for metals with the ICPE-MS (ICPE-9000 Shimatzu).

3.5.2. Jar tests for batch adsorption

Batch adsorption experiments were performed in jar testing apparatus to investigate the effect of pH, biochar dose and time on the adsorption efficiency of PBN700 and PBN400. Prior adsorption, 6 beakers with 150 ml of 10 mg/L Pb^{2+} solution were adjusted to different pH's ranging from 4.5 – 7.0 to investigate the influence of OH^-on formation of lead precipitates. After 15 minutes the solutions were filtered through a 0.45µm filter and analyzed for presence of free Pb^{2+} ions with the ICPE-MS (Shimadzu, Japan). During testing, solution in 6 beakers was mixed at 150 rpm. Adsorption isotherms were obtained for different doses of biochar (5-500mg), during a time of 60 min and initial pH 5.

3.5.3. Leachate tests

After adsorption was completed, biochars were investigated for their ability to retain adsorbed metals. Change of solution pH and leachate analysis was done in duplicates for each biochar. Biochar was placed in a 50 ml test tube and agitated in deionized water for 24 hours. The ratio of biochar (g) to water (ml) was 1:20. After 24h, the solution pH was measured; the leachate was filtered through a 0.45µm glass membrane filter and analyzed by the ICPE-MS for possible leakage of adsorbed metals.

4. Results and discussion

4.1. Specifics related to production of biochar in the lab

The first objective of this study was to manufacture biochar from different choices of organic waste material. The summary of typical parameters of pyrolysis is provided in Table 1. Collected biomass (5 sources) were subjected pyrolysis under the same controlled conditions, which included limited oxygen availability, time of pyrolysis, rate of temperature and initial condition of biomass used for production. The range of temperature of pyrolysis was setup either for the 300 ºC – 600ºC or 400ºC and 700ºC under limited oxygen availability. All manufactured biochars were stored for the further assessment of their properties.

Table 1 Biochar Production in temperatures 300ºC and 600ºC

Procedure	**Temperature**	**Time**	**Rate**	**Gas**	**Pre-drying**
Slow pyrolysis bathed in fire	550 - 600 ℃	Extended hours	n/a	n/a	n/a
Slow pyrolysis	300 ℃	3 h	5 ℃/min	limited N_2, 15 min	5 days air drying, 2 h at 110 ℃ before pyrolysis
Limited oxygen pyrolysis	300 ℃	2 h	n/a	limited O_2	24 h at 110 ℃
Limited oxygen pyrolysis	600 ℃	2 h	n/a	limited O_2	24 h at 110 ℃
Limited oxygen pyrolysis	300 ℃	2 h	n/a	limited O_2	24 h at 110 ℃
Limited oxygen pyrolysis	600 ℃	2 h	n/a	limited O_2	24 h at 110 ℃

An example of grinding of pine needles into mass used later for manufacturing of biochar is shown in Fig. 1. The fraction used for pyrolysis was grinded to mesh size 10 – 35 microns. This range was the optimal to obtain a uniform morphology of biochar.

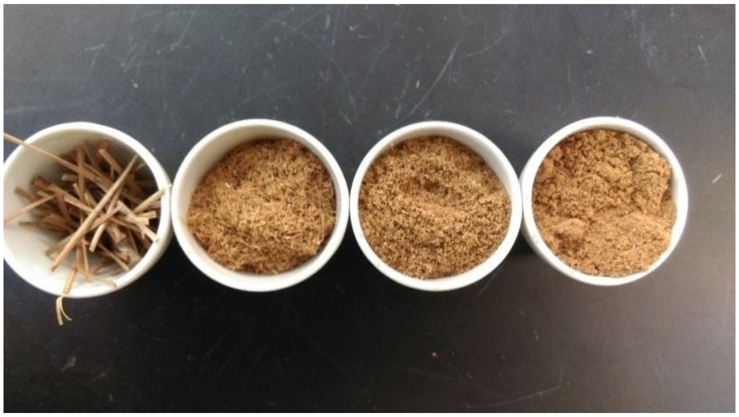


Fig. 1 Pine needles grinded to mesh size 10 – 35, 35 – 60 and > 60 microns

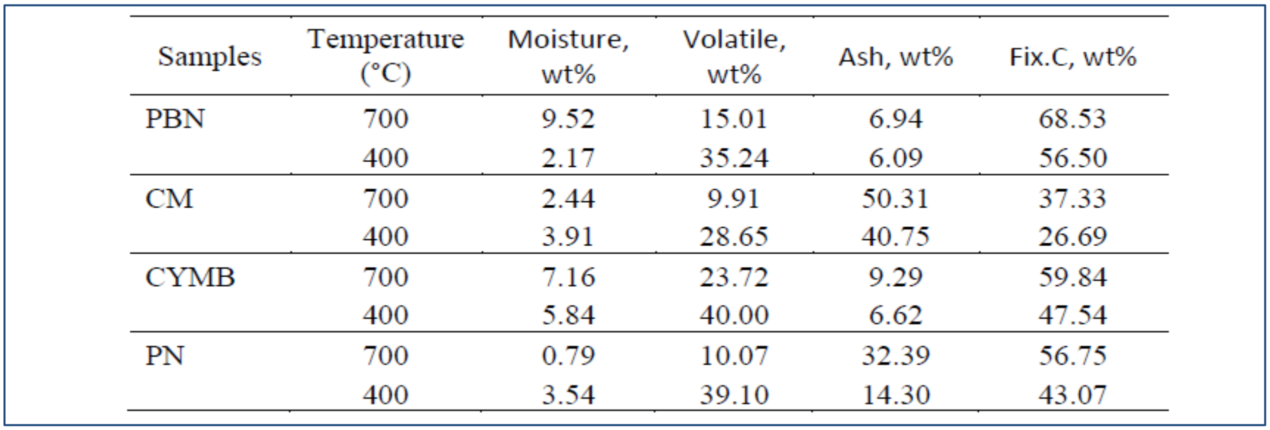
4.2. Determination of carbon, volatile and ash yield in tested biochar samples

The first step of characterization of obtained biochar was to compare carbon content, percentage of volatile products (gases) and ash yield for all manufactured samples. Carbon content was important for estimation of the percentage of final product versus initial material taken for pyrolysis. The percentage of volatile substances would be important only for production of energy gases. The content of ash indicated mineral components that may affect the overall efficiency of adsorption.

Biomass from different sources was expected to produce biochars displaying different properties. Summary of proximate analysis results is shown in Table 2. From analysis, it was obvious that high temperature pyrolysis yielded higher carbonized composition in all biochars. Volatile matter content was affected mainly by the type of biomass. Woody types of biochar (PBN and CYMB) showed greater change in volatile matter content.

It was found that higher fixed carbon content (favorable in biochar) was correlated with higher pyrolytic temperatures (700^{o}C) and more dense initial material (woody feedstock). For example, pine bark nugget (PBN) biochar contained 68.5% fixed carbon, versus only 37.3% in biochar made from cow manure (CM), when temperature of pyrolysis was 700^{o}C.

Table 2 Proximate analysis of PBN, CM, CYMB, PN biochar samples produced in adjusted temperatures of 400°C and 700°C



Samples	Temperature (°C)	Moisture, wt%	Volatile, wt%	Ash, wt%	Fix.C, wt%
PBN	700	9.52	15.01	6.94	68.53
	400	2.17	35.24	6.09	56.50
CM	700	2.44	9.91	50.31	37.33
	400	3.91	28.65	40.75	26.69
CYMB	700	7.16	23.72	9.29	59.84
	400	5.84	40.00	6.62	47.54
PN	700	0.79	10.07	32.39	56.75
	400	3.54	39.10	14.30	43.07

Figures 2, 3 and 4 provide comparison of fixed carbon, volatile portion and ash content in biochars delivered from 4 different sources of biomasses produced in two temperatures (400°C and 700°C).

Summarizing, it was found that biochar delivered from pine bark needles (PBN) contained the highest carbon content when compared to other samples. Incidentally, the cow manure (CM) has shown the lowest carbon content, and the highest ash content.

The observed trend in carbon content for the same temperature of pyrolysis could be expressed as followed (with pine bark needles as a best waste material and cow manure, as a poorest):

PBN>CYMB>PN>CM

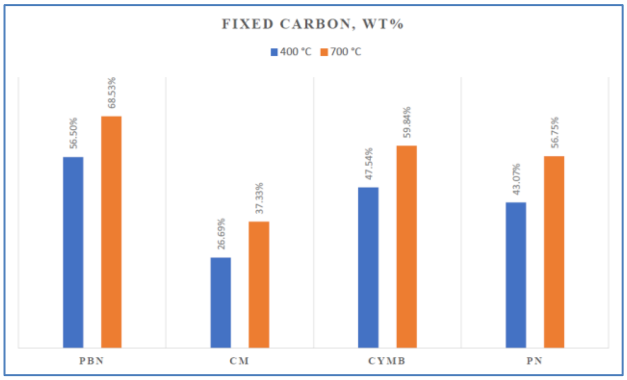


Fig. 2. Fixed carbon in different biochar samples produced at 400°C and 700°C

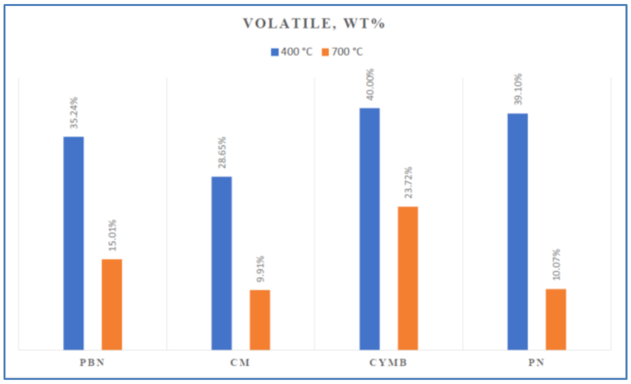


Fig. 3. Volatile content in different biochar samples produced at 400°C and 700°C

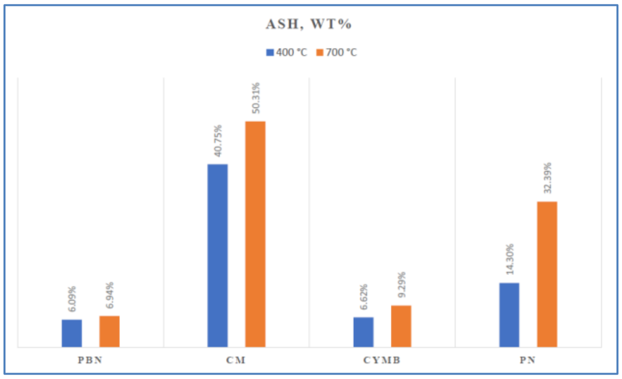


Fig. 4. Ash content in different biochar samples produced at 400°C and 700°C

4.3 Results from microstructure and elemental analyses

The next phase of the research was devoted to characterization of surface and elemental content of manufactured biochars. The surface was determined by electronic imaging, and the content – by elemental analysis. For more accurate comparison, the different pyrolysis' conditions were applied; however, the sources of initial biomass remained the same. Comparison of surfaces was done on samples prepared from two biomasses, under temperature of 300^{o}C and 600^{o}C (Table 3)

4.3.1. Investigation of morphology of tested biochars and formation of comb-like structures

The adsorption capability of any material is usually correlated with extensive surface of this material. Generally, biochar is produced in lower temperature than typical activated carbon, and does not required activation with the steam. Our testing was focused on morphology of biochar's surfaces as a function of the firing temperature (pyrolysis), type of initial biomass, limitation of oxygen during pyrolysis and time of thermal decomposition.

Scanning electron microscope imagines were obtained using the FSI Quanta 200 FSI SEM, and distribution of comb-like pores (important for efficient adsorption) with average pore diameter of 20 µm was estimated with ImageJ software.

During the first set of experiments, two types of biochar (pine wood and corn stover) were investigated. In addition, corn stover biochar was prepared under three different conditions. Summary of information about tested biochar and temperature of pyrolysis is shown in Table 3, and morphology of their surfaces is provided in the Fig 5. Tested biomass was fired with limited nitrogen gas (no oxygen) and limited oxygen gas (no nitrogen) for pine wood, and corn stover fired in two temperatures (300^{o}C and 600^{o}C).

Table 3 Samples of biochar analyzed for the surface (see Fig. 5, SEM images)

Biochar made from:	Abbreviation	Temperature of pyrolysis, ^{o}C
Pine wood	PWB	550 - 600
Corn stover (limited nitrogen gas)	CS300N2	300
Corn stover (no nitrogen gas; limited oxygen)	CS300	300
Corn stover	CS600	600

Generally, the increase in surface area and pore sizes in tested biochars could be explained by the breakage of hemicellulose, cellulose and lignin of original waste materials. Hemicellulose degradation typically occurs under 300°C and the increase of temperature above 300°C results in formation of more amorphous structures during volatilization of different compounds (Zhao S. et al, 2017). Longer exposures to higher temperatures (~ 600 °C) should promote formation of more tube-like pores in a dense structural formation as result of degradation of lignin (Zhao S. et al, 2017, Hyväluoma J. et al., 2017).

Pore formation in these four tested samples is shown in Fig.5. The formation of such structures is important for the development of large surface areas needed for adsorption. Similar morphology is typically found in activated carbon and carbon nanotubes (Zhao B. et al., 2014).

Lower pyrolysis temperatures (300°C) didn't result in any visible pore formation in CS300N2, and that could be attributed to shorter pyrolysis time when compared to PWB. As it can be seen in Fig. 5, the morphological structure of CS300N2 is continuously non-uniform; however, degradation of material was observed even for this low temperature. The overall degradation of material could be explained by the transforming existing volatile compounds into further volatile and organic molecules with smaller molecular weight (Ma X. et al., 2016). Interestingly, cellulose is seen as long fiber-alike structure with non-existence of pore formation due to insufficient cracking of molecular structure in lower temperature.

CS600 was produced from same initial biomass as CS300, but in higher temperature (600^{o}C). The increase of temperature from 300^{o}C to 600^{o}C promoted complete degradation of lignin, and formation of comb-alike pores. Longer exposure to 600°C would stimulate formation of more carbonaceous structures, and increase percentage of fixed carbon to 77.9 %.

It was concluded that higher temperature of pyrolysis, and prolonged thermal processing time was favorable toward comb-like structures needed for more efficient adsorption, and overall higher content of carbon in obtained product.

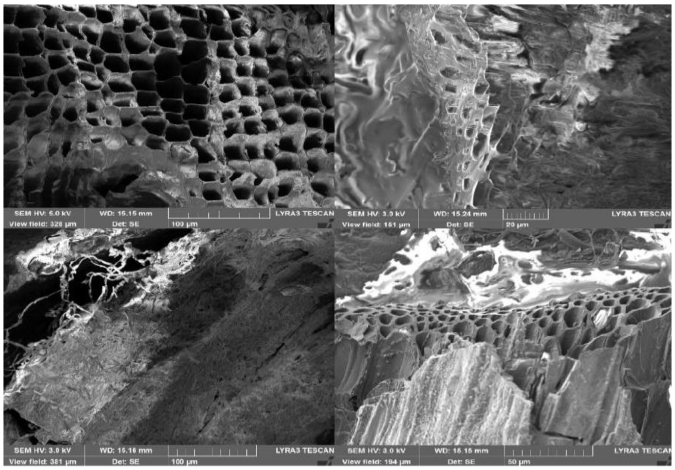


Fig. 5 Pore formation under thermal decomposition of PWB, CS300N2, CS300 and CS600

We have investigated images of other biochar samples to confirm correlation between temperature of pyrolysis, presence/absence of oxygen, and type of initial biomass.

Similar trend, as for PWB and CS biochars, was observed on SEM images of the second set of samples (CS and PN) shown in Figure 6. Increase of temperature from 300^{o}C to 600^{o}C promoted formation of more amorphous surfaces. For those conditions, elemental analysis (Table 2) showed increase in carbon content 14% (to total 72.2%) and reduction in oxygen (in oxygen bearing groups) from 46.1% to 22.7% with increased temperature of pyrolysis. Similar trend could be seen when compared SEM images of CS300 and CS600 samples. Increase of temperature stimulated raise of carbon content from 57.4% to 75.7%, and reduction in oxygen from 42.6% to 24.4%.

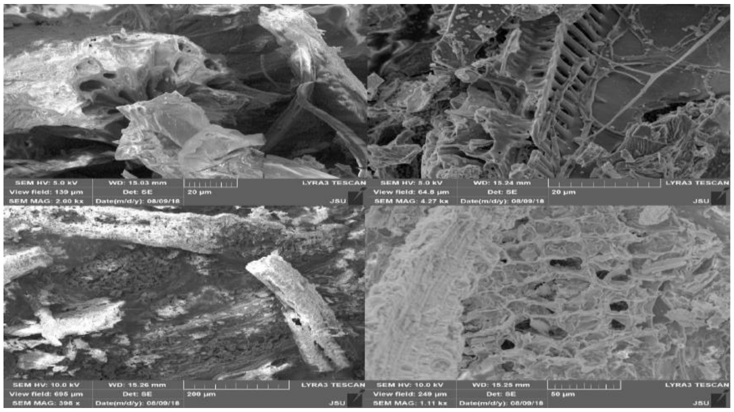
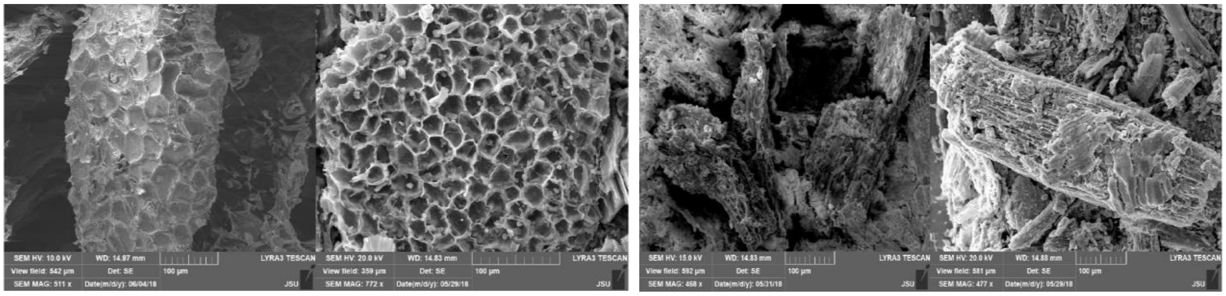


Fig. 6 SEM imaging of corn stover biochar (CS) and pine needle biochar (PN) produced at 300°C and 600°C

The same tendencies in changes in morphological structures, and in content of carbon and oxygen bearing functional groups with higher temperature of pyrolysis were seen on SEM images of biochars produced from other biomasses.

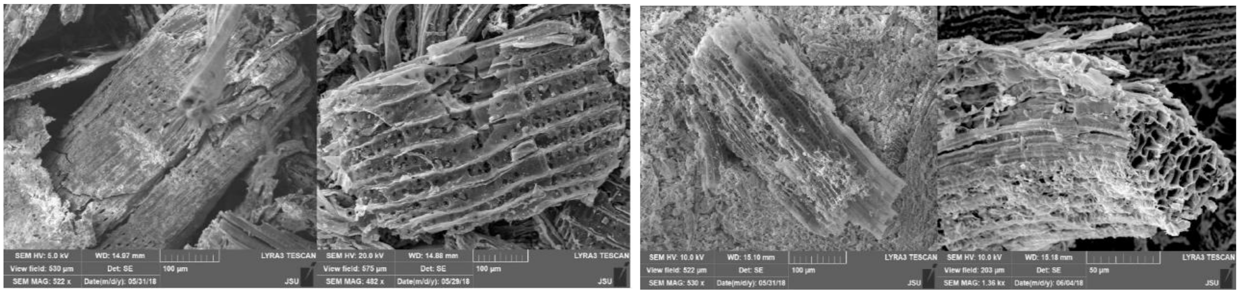
Morphological structures of PBN (Figure 7A.), CM (Figure 7B.), CYMB (Figure 8A.) and PN (Figure 8B.) determined by SEM-EDX qualitative analysis have revealed more efficient pore formation as a function of temperature as well. Only cow manure (CM) biochar (Fig. 7B) displayed low carbonization, which is attributed to the lack of volatile compounds that are responsible for the morphological structure (De Bhowmick G., et al., 2018). The enrichment of minerals (proved by ash content analysis) in CM biochar could contribute to the lower carbonization and less pore formation.

In summary, SEM-EDX analysis has confirmed that temperature, biochar feedstock, and residence time of pyrolysis has an important impact on elemental composition and structure tailoring. Incidentally, it was detected a substantial difference in morphology between biochar made from plant-based biomass and from animal waste (cow manure biochar). Lack or limited content of hemicellulose, cellulose and lignin (typical for plant-base waste) in cow manure, was affecting properties of final biochar.



A (pine bark nuggets biochar) **B (cow manure biochar)**

Fig. 7. (A) Pine bark nuggets (PBN) and (B) cow manure biochar pore-formation at 400°C and 700°C



A (cypress mulch blend biochar) **B (pine needles biochar)**

Fig. 8. (A) Cypress mulch blend (CYMB) biochar and (B) pine needles (PN) pore-formation at 400°C and 700°C

4.3.2. Manifestation of functional groups at different pyrolysis temperatures

Presence of functional groups within the structure of carbon-based sorbents (activated carbon, carbon nanotubes) is expected to increase overall efficiency of adsorption and better retention (lower leachate) of adsorbed contaminants.

In our study, the determination of functional groups was done by the FTIR analysis. Due to thermal decomposition of cellulose and lignin, functional groups such as aromatics, C-O, C-O-C were observed within the structure of biochar. Analysis was done for all studied biochars. We could observe similar pattern of changing functional groups with increase of temperature and increase density of initial biomass. The observation of aromatic groups suggested stabilization of the structure with carbon-like tubes abundantly generated within studied biochar. The example of analysis of bark nuggets biochar produced in 400°C (red) and 700°C (blue) is shown on Fig. 9.

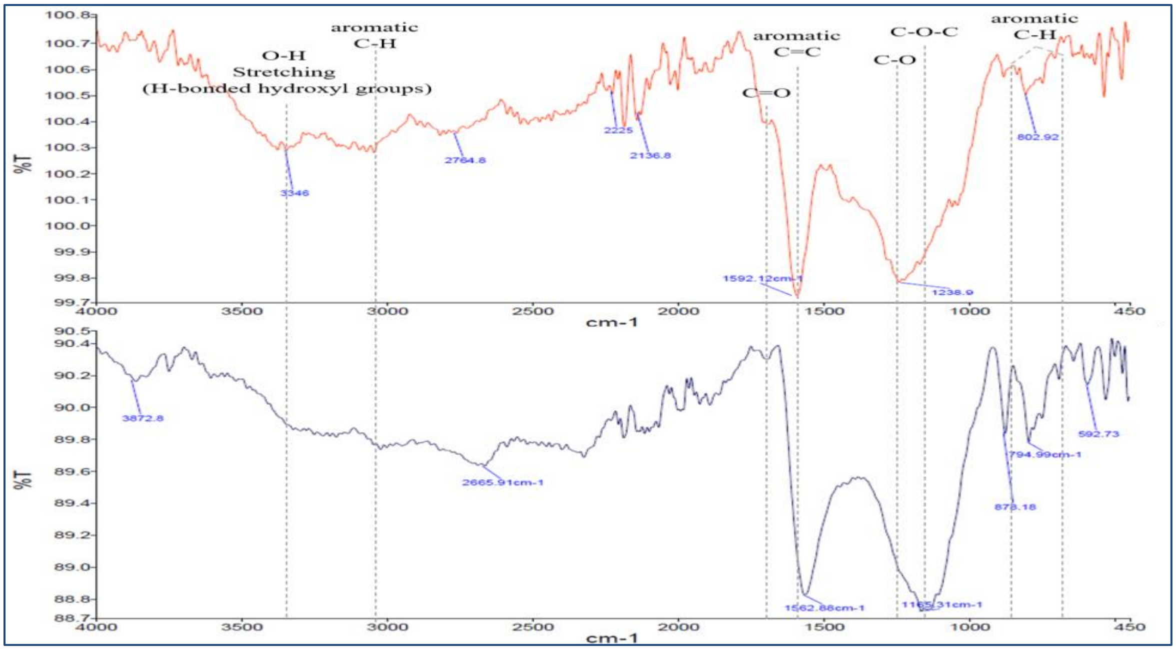
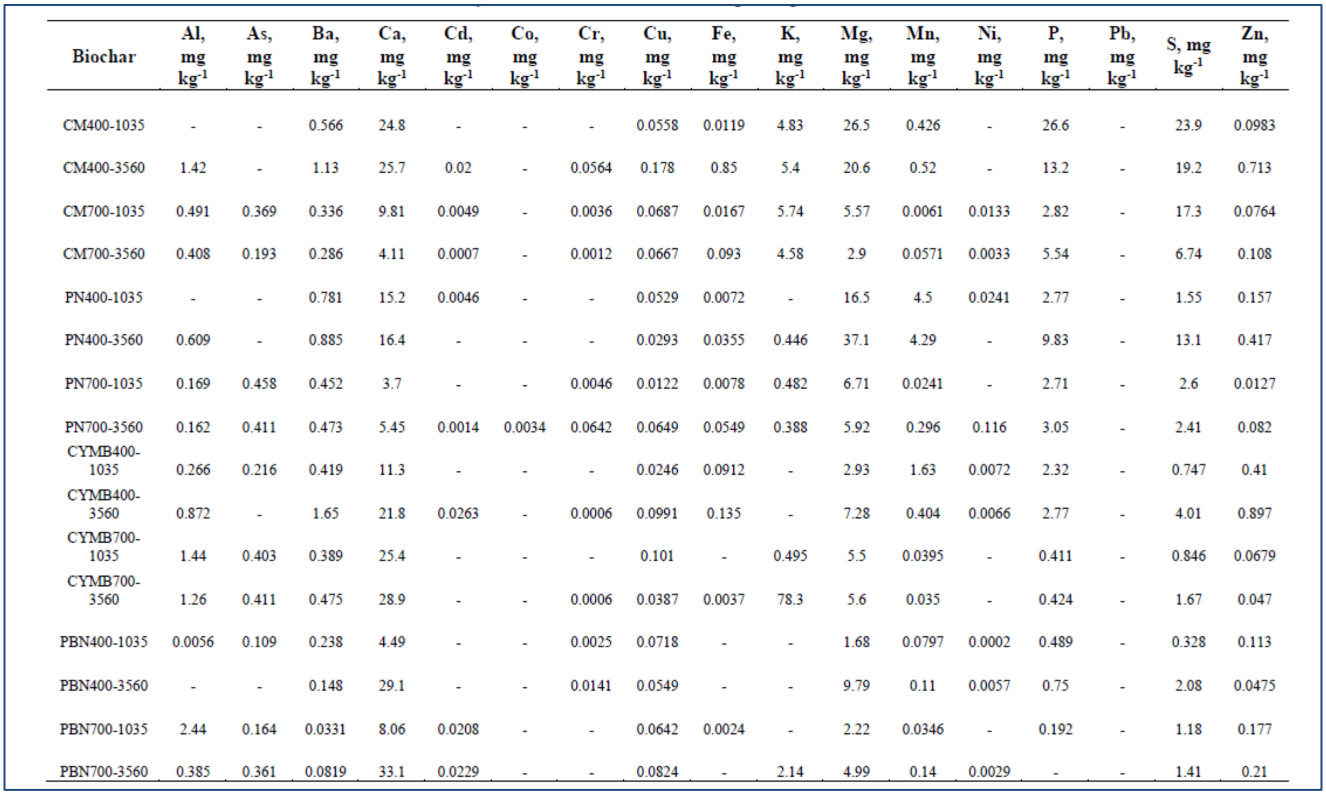


Fig. 9. FTIR spectra of pine bark nuggets biochar produced at 400°C (red) and 700°C (blue)

4.3.3 Results from elemental analysis of biochar

Biochar was manufactured from different organic waste, and depending on the initial source, the additional atoms could be identified within biochar structure. It was important to examine the differences in additional content of biochar related to the source. After agitation in 24 hours in distilled water (to wash-off possible loosely bonded contaminants), samples were subjected to elemental analysis. It was found that distribution of elements in all samples varied depending on the source of biomass and temperature of pyrolysis (Table 4). It can be noted that higher content of S and P in cow manure biochar resulted from the enrichment of nutrients in livestock food. Similar observance can be seen when study pH of same biochar samples. Cow manure (CM) biochar's pH was in alkaline range, where more woody type of biochar's pH was neutral or lightly acidic. Higher pH of cow manure biochar could be correlated with the high ash content.

Table 4. Elemental analysis of different biochar samples agitated in distilled water for 24h



Biochar	Al, mg kg^{-1}	As, mg kg^{-1}	Ba, mg kg^{-1}	Ca, mg kg^{-1}	Cd, mg kg^{-1}	Co, mg kg^{-1}	Cr, mg kg^{-1}	Cu, mg kg^{-1}	Fe, mg kg^{-1}	K, mg kg^{-1}	Mg, mg kg^{-1}	Mn, mg kg^{-1}	Ni, mg kg^{-1}	P, mg kg^{-1}	Pb, mg kg^{-1}	S, mg kg^{-1}	Zn, mg kg^{-1}
CM400-1035	-	-	0.566	24.8	-	-	-	0.0558	0.0119	4.83	26.5	0.426	-	26.6	-	23.9	0.0983
CM400-3560	1.42	-	1.13	25.7	0.02	-	0.0564	0.178	0.85	5.4	20.6	0.52	-	13.2	-	19.2	0.713
CM700-1035	0.491	0.369	0.336	9.81	0.0049	-	0.0036	0.0687	0.0167	5.74	5.57	0.0061	0.0133	2.82	-	17.3	0.0764
CM700-3560	0.408	0.193	0.286	4.11	0.0007	-	0.0012	0.0667	0.093	4.58	2.9	0.0571	0.0033	5.54	-	6.74	0.108
PN400-1035	-	-	0.781	15.2	0.0046	-	-	0.0529	0.0072	-	16.5	4.5	0.0241	2.77	-	1.55	0.157
PN400-3560	0.609	-	0.885	16.4	-	-	-	0.0293	0.0355	0.446	37.1	4.29	-	9.83	-	13.1	0.417
PN700-1035	0.169	0.458	0.452	3.7	-	-	0.0046	0.0122	0.0078	0.482	6.71	0.0241	-	2.71	-	2.6	0.0127
PN700-3560	0.162	0.411	0.473	5.45	0.0014	0.0034	0.0642	0.0649	0.0549	0.388	5.92	0.296	0.116	3.05	-	2.41	0.082
CYMB400-1035	0.266	0.216	0.419	11.3	-	-	-	0.0246	0.0912	-	2.93	1.63	0.0072	2.32	-	0.747	0.41
CYMB400-3560	0.872	-	1.65	21.8	0.0263	-	0.0006	0.0991	0.135	-	7.28	0.404	0.0066	2.77	-	4.01	0.897
CYMB700-1035	1.44	0.403	0.389	25.4	-	-	-	0.101	-	0.495	5.5	0.0395	-	0.411	-	0.846	0.0679
CYMB700-3560	1.26	0.411	0.475	28.9	-	-	0.0006	0.0387	0.0037	78.3	5.6	0.035	-	0.424	-	1.67	0.047
PBN400-1035	0.0056	0.109	0.238	4.49	-	-	0.0025	0.0718	-	-	1.68	0.0797	0.0002	0.489	-	0.328	0.113
PBN400-3560	-	-	0.148	29.1	-	-	0.0141	0.0549	-	-	9.79	0.11	0.0057	0.75	-	2.08	0.0475
PBN700-1035	2.44	0.164	0.0331	8.06	0.0208	-	-	0.0642	0.0024	-	2.22	0.0346	-	0.192	-	1.18	0.177
PBN700-3560	0.385	0.361	0.0819	33.1	0.0229	-	-	0.0824	-	2.14	4.99	0.14	0.0029	-	-	1.41	0.21

4.4. Results from leachate tests

The objective of this part of the study was to determine to what degree, biochar can be resistant to leachate of already adsorbed contaminants, when exposed to weathering conditions. We have investigated the filtrate portion of agitated for 24 hours biochar samples. The objective was two-folded: (a) determination of all washable content of biochar after manufacturing, and (b) testing if adsorbed on biochar metals could leached from the structure under standard conditions.

4.4.1 Testing occurrence of leachate when distilled water was applied.

Table 5 summarizes the results from the analysis of PBN400 and PBN700 leachate after agitation in deionized water for 24h. Release of volatile compounds in higher pyrolytic temperatures was generating an additional surface area, but also made available number of nutrients nested within original biomass. Inorganic micronutrients such as Al, Ca, Cu, K and Zn showed increase from 0.11 mg/kg, 29.10 mg/kg, 0.05 mg/kg, 0.30 mg/kg and 0.05 mg/kg for PBN400 (made in 400^{o}C) to 0.39 mg/kg, 33.10 mg/kg, 0.08 mg/kg, 2.14 mg/kg and 0.21 mg/kg for PBN700, respectively.

Overall, the heterogeneity of different types of biomass was one of the main reasons for disproportional distribution and availability of micronutrients, along with other process parameters affecting the final chemical composition.

Summarizing, the freshly-made biochar exposed to weather conditions may release nutrients from its structure. This property is valuable for agricultural conditions; however, when used as adsorber of spills and/or in situ stormwater treatment, depending on initial biomass used for production, it would be recommended to pre-wash biochar before first use, if applicable.

Table 5. Analysis of pine bark biochar leachate for nutrient availability and change of pH

Sample		**PBN400**	**PBN700**
Leachate pH		**6.45**	**6.54**
Nutrient analysis of biochar leachate	Al, mg kg^{-1}	0.11	0.39
	Ca, mg kg^{-1}	29.10	33.10
	Cu, mg kg^{-1}	0.05	0.08
	K, mg kg^{-1}	0.30	2.14
	Mg, mg kg^{-1}	9.79	4.99
	Na, mg kg^{-1}	0.14	0.06
	P, mg kg^{-1}	0.75	0.14
	S, mg kg^{-1}	2.08	1.41
	Zn, mg kg^{-1}	0.05	0.21

4.4.2. Leachability results after adsorption of metallic ions on tested biochar

When considering biochar for the application in stormwater runoff treatment, it is important to determine the stability of biochar and its capability to retain heavy metals without leaching after adsorption when exposed to weather conditions.

Figure 10 provides comparison of leachability of two biochars made from pine barks nuggets in two temperatures (PBN400 and PNB700). Tested ion was Pb^{2+} in deionized water. Investigation included determination of adsorbed lead ions on biochars, and its concentration in leachates after 2 extraction cycles with deionized water (1 cycle = 15 min, 150 rpm). The experiment confirmed that higher adsorption on PNB700 was related to the better developed comb-like structures, which allowed more efficient adsorption. Negligible concentration of lead ions in leachates after cycle 1 and 2 confirmed strong retaining capability for both biochars.

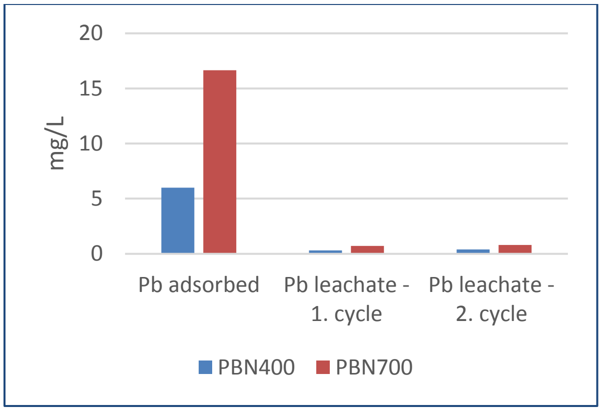


Fig. 10 Comparison of adsorbed Pb^{2+} leached from PBN400 and PNB700 after 2 extraction cycles with deionized water (1 cycle = 15 min, 150 rpm)

Experiment was repeated with the mixture of metallic ions (lead, cadmium, copper and zinc). It is known that adsorption/desorption could be affected by competition of ions toward active sites on biochar. The results show (Figure 11) that both biochars have great potential to remain stable, even after 2 extraction cycles. Interestingly, adsorption of components of mixture was different for each ion and type of biochar. Again, it was found that PBN fired in higher temperature (700^{o}C) has shown better adsorption capability, with the best results for removal of cadmium ions.

Summarizing, temperature of pyrolysis was affecting morphology of structures, and consequently, affecting adsorption/ion exchange capability of single ion and the same ion in mixture of other metals. Desorption (capability to retain adsorbed metals) was similar for both biochars made in different temperatures with exception of lead ions. It was observed that in each cycle they leached from PBN400, but not from PBN700.

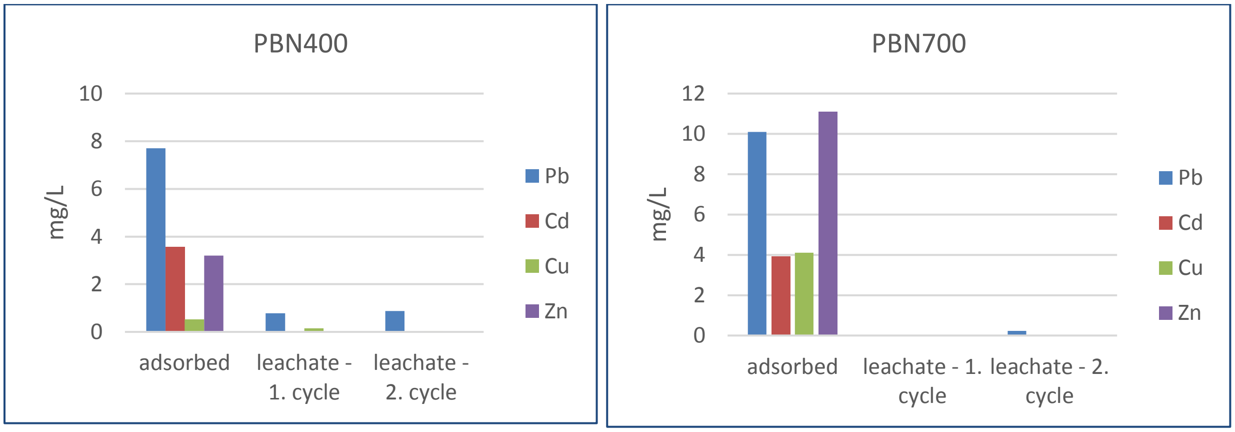


Figure 11 Leaching of mixture of adsorbed heavy metals from PBN400 and PBN700 after 2 extraction cycles with deionized water (1 cycle = 15 min, 150 rpm)

4.5 Results from adsorption experiments

The adsorption experiments were designed in two steps: (a) initial adsorption in mini-column to investigate capability of thin layer of biochar (1-2 cm) to adsorb incoming mixture of contaminants, and (b) batch test (jar test) to determine isotherms of adsorption.

4.5.*1 Results from thin-layer column adsorption experiments*

Tested mixture of metallic contamination simulated road conditions and contained Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} ions. Efficiency of adsorption was studied on the following biochar samples: PN300, PN600, CS300 and CS600. Mini column (Fig. 12) was packed with investigated sample with thickness of biochar 1 to 2 cm to imitate the single layer of biochar.

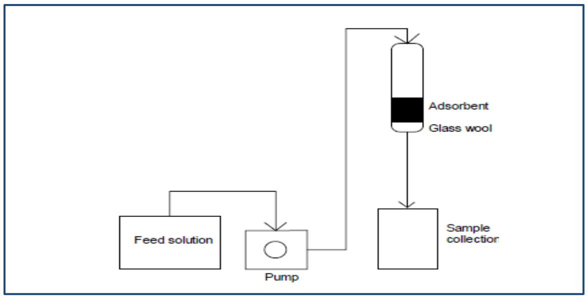


Fig. 12 Schematic representation of a mini-column adsorption set-up

Results from mini column adsorption are presented in Fig. 13. It was found that after 30 min, overall removal efficiency was 25% to 99.9% depending on the ion, ion's initial concentration and type of biochar. The best results were obtained for lead and cadmium ions (over 90% in 30 min) on all tested types of biochars. Zinc and copper adsorption was depended on type of biochar. Corn stover biochar made in 600°C performed the best, and was able to remove over 90% of all tested ions in 30 min time range.

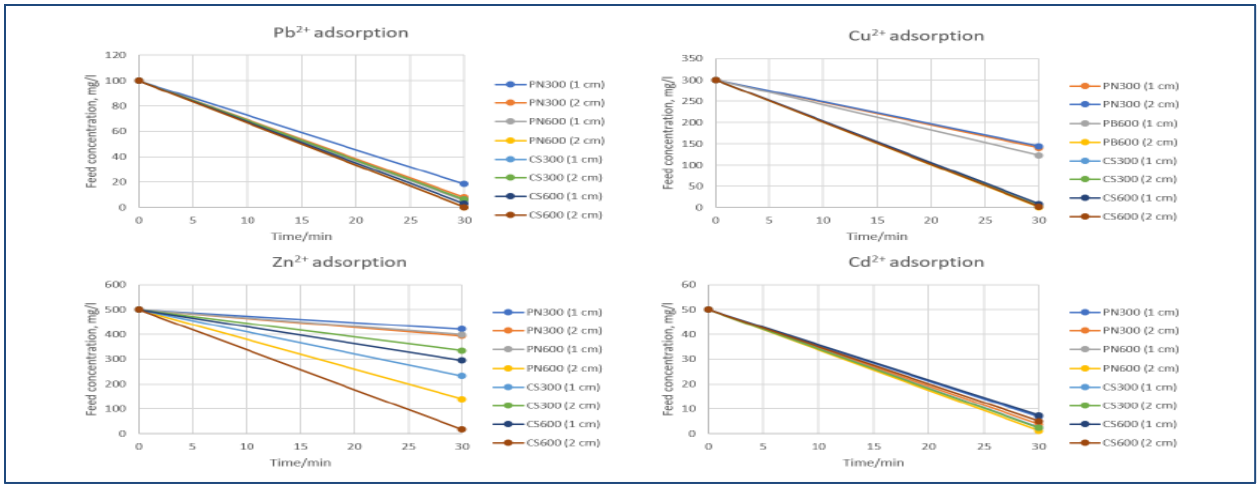


Fig. 13 Adsorption of metallic ions on various biochar

4.5.2. Results from batch adsorption experiments

The preliminary batch experiments were run as a single metal ion adsorption system to determine if firing the same biomass in different temperatures would affect overall efficiency of adsorption. Adsorption isotherms (Langmuir and Freundlich) were constructed for the pine bark nuggets biochar produced in 400°C and 700°C (PBN400 and PBN700). It was found that higher firing temperature provided a little higher adsorption capacity of biochar made from the same initial biomass. Table 6 provides comparison of parameters for Langmuir and Freundlich isotherms. Maximum adsorption capacity obtained for PBN700 was 33.9 mg/g with the removal efficiency of 97.6% for the dose of 0.5 g of biochar.

Table 6 Langmuir and Freundlich isotherm's fitted parameters of Pb^{2+} adsorption on PBN400 and PBN700 (initial concentration of Pb^{2+} = 25 mg/L)

Biochar	**Langmuir isotherm**			**Freundlich isotherm**		
	***q_m*, g/mg**	***K_L***	***R^2***	***1/n***	***K_F***	***R^2***
PBN700	33.9	0.42	0.99	2.05	9.09	0.94

Where: q_m, g/mg expresses maximum adsorption capacity,
K_L – Langmuir constant
1/n – Affinity for adsorption,
K_F – Freundlich constant
R^2 –Respective correlation coefficients

5. Impacts/Benefits of Implementation (actual, not anticipated)

The results of this study are supporting our initial hypothesis that biochar could be customized to remove various contamination from stormwater runoff from transportation infrastructures, and possibly remove various spills from the roads. Adaptation of the biochar would bring not only immediate transport-related benefits, but also would serve as an application of green approach in turning organic waste material into useful product that is easy to handle, does not required special precaution when put in use, is inexpensive to produce, and environmentally friendly.

6. Recommendations and Conclusions

This study was mainly focused on manufacturing and characterization of biochar produced under controlled conditions. When material is being developed for new application(s), it is important to understand all correlations between the production/properties/influences/stability/capacity, etc., such as:

- Properties of new material (biochar): type of surface, pores, entrapped mineral content, functional groups formed during heating process;

- <u>Controllable conditions that could influence properties of new material:</u>
    - Conditions of pyrolysis such as total time of firing, temperature, rate of rising temperature per time unit, an effect of pyrolysis under complete anaerobic conditions or under limiting oxygen presence influencing final morphology of biochar, etc.
    - Origin of starting carbon-rich waste biomass, such as plant-based, farming-based, etc.
    - Specific properties of initial waste material, such as density, other content (not organic), possible harmful by-products, etc.
- <u>Properties of new material (biochar) toward specific application:</u> capacity of sorption, leachability of already adsorbed contaminants, stability in various climatic and site conditions, etc.

This study provides results that could be used to understand and efficiently apply advantages and avoid limitations of produced biochar toward particular application.

It is recommended that long-term pilot scale testing of *in situ* adsorption to be performed to verify laboratory-scale results.

7. Addressing the MarTREC research theme "Preserving the Nation's Transportation System through Efficient, Resilient, and Sustainable Maritime and Multimodal Logistics and Infrastructure".

The rapid increase of commercial long-distance mass transportation of various chemicals, combined with sharp rise of the presence of passenger cars on the national and state roads are generating new challenges in (a) efficient control of contaminated stormwater runoff from highways, and (b) addressing hazardous spills resulted from road accidents. Prolonged clean-up after spills is usually causing the additional turbulence to already congested traffic in affected areas. Moreover, state departments of transportation (DOTs) are required to comply with their NPDES permits and initiate specific actions aiming reduction of stormwater pollution.

The aim of this research was to manufacture and investigate new materials that could serve three purposes included in MarTREC research objectives, namely: (a) control stormwater runoff, (b) in situ effectively remove pollutants from runoff, and (c) rapidly adsorb spills of various chemicals caused by road/train/water accidents.

This research has successfully generated results that are aligned with proposed objectives. New material, namely biochar, was manufactured from various waste biomasses, and investigated in correlation between sources of biomass, firing conditions, presence/absence of oxygen during production, time and temperature of pyrolysis.

The capabilities of final products were tested to identify, if they could:

(a) Serve as a fast, an efficient, and environmentally friendly adsorber/ion exchanger of pollutants carried by stormwater runoff from transportation infrastructures;
(b) Resist leaching of already absorbed pollutants while overflowing with next storm event, and
(c) Retain stability in various climatic and site conditions.

The long-term spin-offs from proposed research are aimed toward testing biochar for:

(a) Applicability as a safe to handle, and environmentally friendly material applied during emergency recovery of various spills,
(b) Improvement (through mixing) of permeability and adsorption of natural soil receiving first flush of stormwater from the roads and other transportation infrastructures;
(c) Exploring possibilities of using biochar as an addictive to pervious concrete or asphalt.

8. Glossary

FT-IR: Fourier-transform infrared spectroscopy

SEM-EDX: Scanning electron microscopy – Energy dispersive X-ray

XRD: X-ray diffraction

CS: corn stover

PN: pine needles

PBN: pine bark nuggets

PBN300: pine bark nuggets fired at 300^{o}C

PBN600: pine bark nuggets fired at 600^{o}C

CYMB: cypress mulch blend

CM: cow manure

9. References

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