

(11) Patento numeris: **6661** (51) Int. Cl. (2019.01): **B01J 8/00**

(21) Paraiškos numeris: **2018 513**

(22) Paraiškos padavimo data: **2018-03-23**

(41) Paraiškos paskelbimo data: **2019-08-26**

(45) Patento paskelbimo data: **2019-09-25**

(62) Paraiškos, iš kurios dokumentas išskirtas, numeris: —

(86) Tarptautinės paraiškos numeris: —

(86) Tarptautinės paraiškos padavimo data: —

(85) Nacionalinio PCT lygio procedūros pradžios data: —

(30) Prioritetas: —

(72) Išradėjas:

Pranas BALTRĖNAS, LT
Edita BALTRĖNAITĖ, LT
Luiza USEVIČIŪTĖ, LT

(73) Patento savininkas:

Vilniaus Gedimino technikos universitetas, Saulėtekio alėja 11, LT-10223
Vilnius, LT

(74) Patentinis patikėtinis/atstovas:

Gediminas PRANEVIČIUS, Advokatų profesinė bendrija IP FORMA, Užupio
g.30, LT-01203 Vilnius, LT

(54) Pavadinimas:

Bioanglies hidrofiliškumo didinimo įrenginys ir būdas

(57) Referatas:

Išradimas skirtas lignoceliuliozinės bioanglies vakuuminiams hidrofiliškumo didinimo įrenginiams ir būdai. Bioanglies hidrofiliškumo didinimo įrenginį sudaro ramnolipidinės medžiagos tirpalo talpa, sujungta su bioanglies vakuuminio apdorojimo talpa, kurios apatinėje dalyje, užpildytoje ramnolipidinės medžiagos tirpalu, įrengtas kaitinimo elementas, o viršutinėje dalyje, atskirtoje nuo apatinės perforuota pertvara, įrengta bioanglies vakuuminio apdorojimo ramnolipidinės medžiagos garais talpa, sujungta su vakuumine pompa ir turinti bioanglies užpildo maišytuvą. Būde bioanglies hidrofiliškumo didinimui naudojami ramnolipidinės medžiagos tirpalo garai, įkaitinti iki 100-105 °C, esant 99 990 Pa - 1333 Pa dydžio vakuumui, sukurtam vakuumine pompa bioanglies apdorojimo talpoje.

IŠRADIMO SRITIS

Išradimas skirtas lignoceliuliozinės bioanglies hidrofiliškumo didinimo įrenginiams ir būdui, konkrečiai – vakuuminiams įrenginiams, skirtiems sukurti slėgio pokyčius tarp bioanglies dalelių ir didinti skysčių infiltracijai ir eksfiltracijai iš bioanglies porų, dėl ko yra paveikiamas ne tik išorinis, bet ir vidinis bioanglies porų paviršius. Tokiu būdu didėja bioanglies geba sulaikyti vandenį bei chemines medžiagas. Tokia modifikuota bioanglis gali būti naudojama įvairiose aplinkosauginėse technologijose, pavyzdžiui, biofiltracinėse sistemose didinant drėgmės išlaikymo trukmę bioanglyje, didinant cheminių medžiagų sulaikymą bioanglyje, sumažinant vandens sunaudojimą aplinkosauginėse technologinėse sistemose, didinant organinių teršalų skaidymo efektyvumą esant mažesniai vandens sunaudojimui, gerinant mikroorganizmų gyvavimo sąlygas.

TECHNIKOS LYGIS

Bioanglies hidrofiliškumo didinimo įrenginys ir būdas gali būti taikomi iš bet kokios pradinės lignoceliuliozinės žaliavos gautos bioanglies fizikinių ir cheminių savybių, susijusių su bioanglies hidrofiliškumo didinimu, gerinimui. Vakuuminė technologija yra pranašesnė už įprastą bioanglies prisotinimą vandeniniu tirpalu, kuris paprastai paveikia tik išorinį paviršių bei mažą bioanglies vidinio paviršiaus dalį. Bioanglis gaunama biomasės pirolizės būdu. Gauta bioanglis vėliau veikiama vakuumu ir paviršiaus aktyvios medžiagos (PAM) tirpalu. Bioanglies poveikis po pirolizės reikalingas bioanglies vidiniam porų tūriui ir paviršiaus plotui padidinti. Bioanglies veikimas ramnolipidinio tirpalo garais po pirolizės tikslas – padidinti bioanglies vidinį porų tūrį ir paviršiaus plotą, pašalinti žalingus kondensuotus junginius iš bioanglies porų bei įtraukti į bioanglies struktūrą biologinės kilmės junginius, ir tai geriausiai galima pasiekti modifikuojant bioanglies chemines ir fizikines savybes, naudojantis ramnolipidinio tirpalo garais. Poveikis vakuumu paskatina tirpalo infiltraciją į ir eksfiltraciją iš bioanglies porų, dėl to yra pagreitinamas dervų kondensuotų junginių pašalinimas iš bioanglies porų. Poveikis tirpalu naudojamas dėl trijų priežasčių: 1) padidinti bioanglies poringos struktūros paviršių; 2) neutralizuoti bioanglies pH; 3) pašalinti dervų junginius iš bioanglies porų.

Šio išradimo prototipu laikytinas JAV patentas Nr. US9809502. Technologija,

aprašyta šiame išradime, apima bioanglies patalpinimą į vakuuminę talpą. Į ją įpilamas drėkinimo didinimo agentas bei sukuriamas vakuumas, naudojantis vakuumine pompa, sujungta su vakuumine žarnele, turinčia sklendę. Kuomet sklendė į talpą yra uždaryta, slėgis talpoje sumažėja nuo 99,99 kPa iki 1,33 kPa. Bioanglis gali būti laikoma vakuume nuo kelių sekundžių iki 100 minučių. Drėkimo didinimo agentas patenka į vakuuminę talpą per žarnelę, atidarius sklendę. Atidarius sklendę, poveikio tirpalas naudojamas bioanglies porų paviršiui modifikuoti. Vakuumas gali būti sukuriamas jau bioanglį paveikus tirpalu arba tuo metu, kai tirpalas patenka į talpą. Talpoje bioanglis maišoma maišykle. Po to, ramnolipidiniu tirpalu prisotinta bioanglis gali būti veikiamą oro srove pertekliniam vandeniui iš bioanglies pašalinti. Tokiu būdu modifikuota bioanglis dar gali būti impregnuojama priedais dėl papildomų porų paviršiaus savybių išvystymo.

Prototipo trūkumu galima laikyti tai, kad bioanglį siūloma modifikuoti tirpalu. Kitaip nei garai, reagento skystoji fazė paveikia tik bioanglies porų išorinį paviršiaus plotą ir tik mažą dalį vidinio paviršiaus ploto. Kitas trūkumas yra tai, kad modifikuojantį tirpalą siūloma ruošti iš cheminių paviršiaus aktyvių medžiagų, kurios yra toksiškos. Modifikacijai sunaudojamas iki 10–100 kartų didesnis cheminių medžiagų kiekis, lyginant su biologinės kilmės paviršiaus aktyviomis medžiagomis.

IŠRADIMO ESME

Šio išradimo tikslas – bioanglies hidrofiliškumo didinimas, siekiant pagerinti bioanglies drėkumą, didinant bioanglies vidinį paviršiaus plotą. Taikomas bioanglies maišymas kartu su ramnolipidinio skysčio garų prisotinimu bei slėgio pokyčių sukūrimu tarp bioanglies dalelių vakuumo sąlygomis. Tirpalas, kurio garai naudojami bioanglies hidrofiliškumui didinti, gaminamas iš dejonizuoto vandens ir ramnolipidinės paviršiaus aktyvios medžiagos dėl pastarosios didelės gebos drėkinti hidrofobinius paviršius.

Ramnolipidai yra paviršiaus aktyvūs glikolipidai, priklausantys biologinės kilmės paviršiaus aktyvioms medžiagoms ir sudaryti iš hidrofiliinės grupės, suformuotos iš vienos ar dviejų ramnozės molekulių ir iš hidrofobinės grupės, susidedančios iš vienos ar dviejų sočiųjų rūgščių grandinių. Ramnolipidinės medžiagos gaminamos iš atsinaujinančių žaliavų ir didelės įvairovės mikroorganizmų, tačiau daugiausiai – iš

Pseudomonas aeruginosa. Lyginant su jų sintetiniais analogais, ramnolipidinės medžiagos yra mažiau toksiškos, aktyvesnės drėkinimo didino gebai ir stabilesnės, esant ribinėms temperatūroms, pH, druskingumo sąlygoms. Hidrofobiškos žematemperatūrės bioanglies drėkumas gali būti padidintas, naudojantis ramnolipidinės medžiagos tirpalu, kurio koncentracija siekia 30–40 mg/l, dėl vandens įtempties paviršiaus sumažėjimo nuo 72 mN/m iki 30–35 mN/m.

Bioanglies aktyvacija garais gali padidinti bioanglies hidrofiliškumą dėl keletos priežasčių. Pirma, aktyvacija garais padidina bioanglies paviršiaus plotą, nes jos metu yra išlaisvinami kondensuoti junginiai, užkemšantys bioanglies poras. Adsorbuoto vandens kiekis ant bioanglies tiesiogiai priklauso nuo didelio bioanglies paviršiaus ploto, dėl to tokie bioanglies tipai gali adsorbuoti didelius vandens kiekius. Antra, aktyvacija garais didina mikroporingumą dėl mažų porų susijungimo bei vidinių ertmių didinimo. Trečia, aktyvacija garais oksiduoja bioanglies porų paviršių, dėl to susiformuoja paviršiaus rūgštinės deguonies turinčios funkcinės grupės (pvz.: karboksilinės, karbonilinės, eterinės ir fenolinės hidroksilinės grupės), kurios didina bioanglies hidrofiliškumą dėl vandenilinių jungčių sudarymo su vandens molekulėmis. Ketvirta, aktyvacija garais skatina kondensuotų junginių (monoaromatinių ir policiklinių aromatinių angliavandenilių, benzonitrilo, benzofuranų) pašalinimą iš bioanglies porų, kurie trukdo vandens patekimui į bioanglį. Porų užsikimšimo efektas mažina bioanglies hidrofiliškumą. Svarbu pabrėžti fizinę garų reikšmę bioanglies hidrofiliškumui didinti. Kadangi vandens garai pasižymi mažesniu tankiu ($0,59 \text{ kg/m}^3$, esant $99,63^\circ\text{C}$ virimo temperatūrai) ir klampumu ($0,000012 \text{ kg/m}\cdot\text{s}$, esant $99,63^\circ\text{C}$ virimo temperatūrai), lyginant su skystąja vandens faze (atitinkamai $997,996 \text{ kg/m}^3$ ir $0,000978 \text{ kg/m}\cdot\text{s}$, esant 21°C vandens temperatūrai), jų molekulės bioanglies aktyvacijos garais metu gali lengviau prasikverbti į poringą vidinę bioanglies struktūrą ir jos kapiliarus, dėl to pastebimas geresnis garų poveikis minėtoms bioanglies savybėms.

Bioanglies hidrofiliškumo didinimo įrenginys turi ramnolipidinės medžiagos tirpalo talpą su tirpalo padavimo anga, iš kurios ramnolipidinės medžiagos tirpalas ištekėjimo žarnele patenka į bioanglies vakuuminio apdorojimo talpos apatinę dalį. Kaitinimo elementas naudojamas ramnolipidinės medžiagos tirpalo garų, kurie naudojami bioanglies dalelių oksidacijai bei dervų išvalymui, sukūrimui. Temperatūros daviklis ir automatinis valdymo blokas naudojami ramnolipidinės medžiagos tirpalo garų temperatūros fiksavimui $100\text{--}105^\circ\text{C}$ ribose. Apatinę bioanglies vakuuminio

apdorojimo talpos dalį nuo viršutinės skiria perforuota pertvara, kuri naudojama bioanglies užpildo atskyrimui nuo ramnolipidinės medžiagos tirpalo bei modifikuotos bioanglies išėmimui, pasibaigus modifikacijos procesui. Flanšinis sujungimas su tarpine skirtas perforuotos pertvaros išėmimui, prieš pašalinant modifikuotą bioanglį. Maišyklė, susidedanti iš elektrinio variklio, veleno bei strypelių formos menčių, atlieka bioanglies užpildo maišymo funkciją ir dėl to yra skatinami tirpalo garų mainai su vidine bioanglies struktūra. Maišyklės nenutrūkstantį darbą reguliuoja automatinis valdymo blokas. Pro viršutinėje talpos dalyje esančią bioanglies padavimo angą patenka 2–4 mm frakcijos bioanglies užpildas, kuris yra veikiamas ramnolipidinės medžiagos tirpalo garais 2,5–3 val. Tirpalo garų poveikio metu slėgis talpoje sumažinamas nuo 99 900 Pa iki 1333 Pa dėl bioanglies dalelių pseudosluoksnio sukūrimo.

BRĖŽINIŲ PAVEIKSLŲ APRAŠYMAS

1 pav. pateiktas bioanglies modifikavimo ramnolipidinės medžiagos tirpalo garais ir vakuumu įrenginio schematinis vaizdas išilginiame pjūvyje.

IŠSAMUS IŠRADIMO APRAŠYMAS

Bioanglies hidrofiliškumo didinimo įrenginį sudaro ramnolipidinės medžiagos tirpalo talpa 1, užpildyta ramnolipidinės medžiagos tirpalu 2 per tirpalo užpildymo angą 3, sklendė 4, sujungianti žarnele 5 ramnolipidinės medžiagos tirpalo talpą 1 su bioanglies vakuuminio apdorojimo talpa 6, kaitinimo elementas 7, vakuuminio apdorojimo talpos 6 apatinė dalis 8, užpildyta ramnolipidinės medžiagos tirpalu 9, temperatūros daviklis 10, automatinis valdymo blokas 11, flanšinis sujungimas su tarpine 12, perforuota pertvara 13, viršutinė vakuuminio apdorojimo talpos 6 dalis 14, elektros variklis 15, velenas 16, maišymo mentės 17, bioanglies padavimo anga 18, antgalis 19, sujungiantis vakuuminio apdorojimo talpą 6 per sklendę 20 su vakuumine pompa 21, skirta sukurti vakuumą viršutinėje vakuuminio apdorojimo talpos 6 dalyje 14, užpildytoje ramnolipidinės medžiagos tirpalo 2 garais 23 ir bioanglies dalelėmis 22, ir bioanglies 22 dalelių kapiliaruose.

ĮRENGINIO VEIKIMO PRINCIPAS

Talpa 1 yra užpildyta ramnolipidinės medžiagos tirpalu 2, paduotu per angą 3. Atidarius sklendę 4, ramnolipidinės medžiagos tirpalas 2 per žarnelę 5 iš talpos 1 patenka į vakuuminio apdorojimo talpos 6 apatinę dalį 8. Kaitinimo elementu 7, įrengtu vakuuminio apdorojimo talpos 6 apatinėje dalyje 8, į ją patekęs ramnolipidinės medžiagos tirpalas 9 pakaitinamas iki virimo temperatūros tam, kad būtų gautas maksimaliai (iki 100 %) garais prisotintas oras. Pasiekus garų temperatūrą 100–105 °C, kuri yra pamatuojama temperatūros davikliu 10, sujungtu su automatinio valdymo bloku 11, kaitinimo elementas 7 automatiškai išjungiamas. Kuomet garų temperatūra krenta žemiau 100 °C, automatinis valdymo blokas 11 įjungia pakartotinį ramnolipidinės medžiagos tirpalo 9 pakaitinimą. Automatinis valdymo blokas 11 taip pat reguliuoja nenutrūkstamą maišyklės, susidedančios iš elektros variklio 15, veleno 16 ir strypelių formos menčių 17, darbą. Vykstant bioanglies 22 modifikacijos procesui, kondensuoti junginiai išlaisvinami iš vidinės ir išorinės bioanglies struktūros ir todėl skatinami ramnolipidinės medžiagos tirpalo mainai su vidine bioanglies 22 struktūra. Perforuota pertvara 13 su flanšiniu sujungimu bei tarpine 12 yra skirti tam, kad būtų galima išvengti bioanglies 22 dalelių patekimo į ramnolipidinės medžiagos tirpalą 9, o pasibaigus modifikacijos procesui, – kad būtų galima pašalinti modifikuotą bioanglį 22. Perforuota pertvara 13 taip pat prisideda prie tolygesnio garų 23 viršutinėje vakuuminio apdorojimo talpos 6 dalyje 14 pasiskirstymo bioanglyje 22. 1 kg bioanglies 22, kurios frakcija yra 2–4 mm, per angą 18 paduodama į viršutinę vakuuminio apdorojimo talpos 6 dalį 14. Bioanglis yra veikiamas ramnolipidinės medžiagos tirpalo garais 23 2,5–3 val. Yra įrodyta, kad bioanglis 22, prisotinta tirpalo garais 23, praėjus 7 dienoms praranda savo pradinį hidrofobiškumą. Tai siejama su erdvės tarp porų užpildymu ir porų paviršiaus oksidacija. Kuomet bioanglis 22 prisotinama ramnolipidinės medžiagos tirpalo garais 23, viršutinėje vakuuminio apdorojimo talpos 6 dalyje 14 sukuriamas 99 990 Pa – 1333 Pa dydžio vakuumas, naudojant vakuuminę pompą 21, kad bioanglies dalelės 22 pakibtų ramnolipidinės medžiagos tirpalo garuose 23. Tai labai pagerina kontaktą tarp bioanglies dalelių 22 ir garų 23. Kai įrenginio sklendė 20 yra atidaryta, veikiant vakuuminei pompai 21 slėgis talpoje sumažinamas nuo 99 990 Pa iki 1333 Pa. Bioanglis laikoma vakuume iki 2,5–3 val. Vakuumas pagreitina skysčių infiltraciją į ir eksfiltraciją iš bioanglies porų. Dėl bioanglies dalelių pakibimo efekto, pagerėja bioanglies kapiliarų prapūtimas ir išvalymas. Skysčio užpildymo lygis

apatinėje vakuuminio apdorojimo talpos 6 dalyje 8 siekia 20 % vakuuminio apdorojimo talpos 6 tūrio, o bioanglies lygis viršutinėje vakuuminio apdorojimo talpos 6 dalyje 14 siekia 60 % vakuuminio apdorojimo talpos 6 tūrio.

IŠRADIMO APIBRĖŽTIS

1. Įrenginys bioanglies hidrofiliškumo didinimui, turintis vakuuminę talpą, kurioje yra bioanglies maišymo velenas su elektros varikliu, bioanglies padavimo angą, tirpalo padavimo angą ir vakuuminę pompą, besiskiriantis tuo, kad turi:

- ramnolipidinės medžiagos tirpalo (2) talpą (1) su tirpalo padavimo anga (3) ir sklende (4), reguliuojančia tirpalo (2) patekimą į bioanglies vakuuminio apdorojimo talpos (6) apatinę dalį (8),

- kaitinimo elementą (7), įrengtą vakuuminio apdorojimo talpos (6) apatinėje dalyje (8), skirtą ramnolipidinės medžiagos tirpalo (9) pakaitinimui iki garų būvio,

- perforuotą pertvarą (13), atskiriančią vakuuminio apdorojimo talpos (6) viršutinę dalį (14), užpildytą bioanglimi (22), nuo vakuuminio apdorojimo talpos (6) apatinės dalies (8), užpildytos ramnolipidinės medžiagos tirpalu (9), ir skirtą ramnolipidinės medžiagos tirpalo garų (23) praleidimui į vakuuminio apdorojimo talpos 6 viršutinę dalį (14),

- vakuuminę pompą (21), sujungtą per sklendę (20) su bioanglies vakuuminio apdorojimo talpos (6) viršutine dalimi (14), skirtą vakuumo joje ir pseudosluksnio bioanglyje sukūrimui.

2. Įrenginys pagal 1 punktą, besiskiriantis tuo, kad bioanglies vakuuminio apdorojimo talpos (6) apatinė dalis (8) yra užpildyta ramnolipidinės medžiagos tirpalu (9) iki 60 % jos tūrio.

3. Įrenginys pagal 1 punktą, besiskiriantis tuo, kad bioanglies vakuuminio apdorojimo talpos (6) viršutinė dalis (14) yra užpildyta bioanglimi (22) iki 60 % jos tūrio.

4. Įrenginys pagal 3 punktą, besiskiriantis tuo, kad bioanglies (22) frakcija yra 2–4 mm.

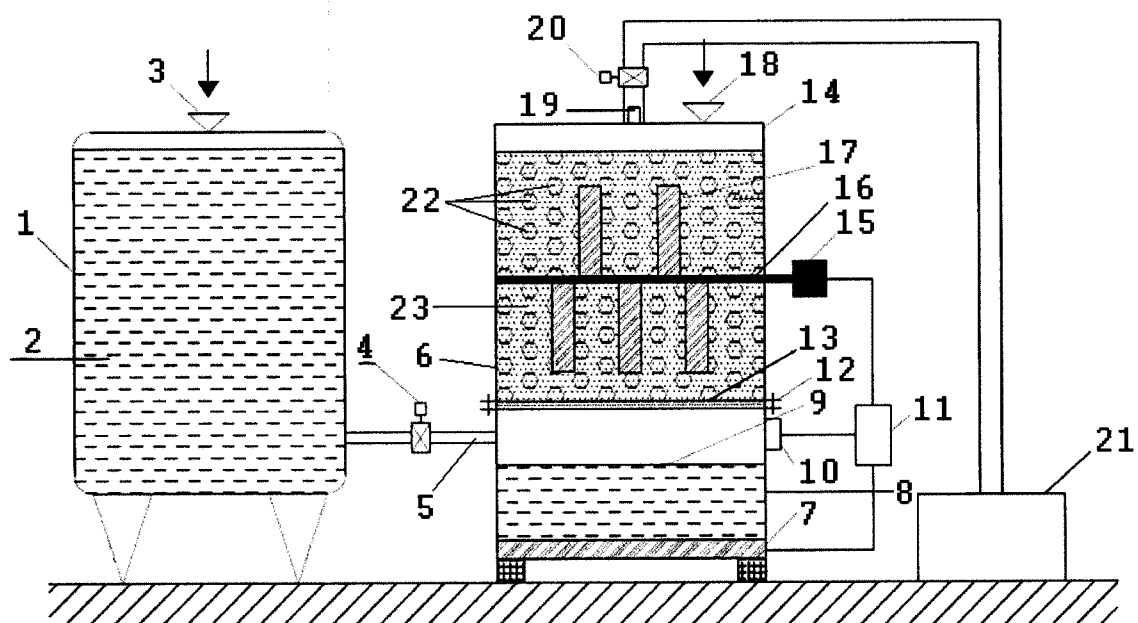
5. Bioanglies hidrofiliškumo didinimo būdas, apimantis bioanglies apdorojimą ramnolipidinės medžiagos tirpalu, maišant bioanglį vakuumo sąlygomis,

besiskiriantis tuo, kad bioanglies (22) hidrofiliškumo didinimui naudoja ramnolipidinės medžiagos tirpalo (9) garus (23), įkaitintus kaitinimo elementu (7) iki 100–105 °C, esant 99 990 Pa – 1333 Pa dydžio vakuumui, sukurtam vakuumine pompa (21) bioanglies (22) apdorojimo talpoje (14).

6. Bioanglies hidrofiliškumo didinimo būdas pagal 5 punktą, besiskiriantis tuo, kad ramnolipidinės medžiagos tirpalo koncentracija vandens tirpale yra 30–40 mg/l.

7. Bioanglies hidrofiliškumo didinimo būdas pagal 5 punktą, besiskiriantis tuo, kad maišo bioanglį (22) ramnolipidinės medžiagos tirpalo garuose (23) maišykle (16) nuo 2,5 iki 3,0 val.

8. Bioanglies hidrofiliškumo didinimo būdas pagal 5 punktą, besiskiriantis tuo, kad kaitinimo elemento (7) ir maišyklės (16) darbą reguliuoja temperatūros daviklis (10) per automatinį valdymo bloką (11).



1 pav.



Hydrophilicity enhancement of low-temperature lignocellulosic biochar modified by physical–chemical techniques

Luiza Usevičiūtė¹ · Edita Baltrėnaitė-Gedienė¹ · Pranas Baltrėnas¹

Received: 22 September 2020 / Accepted: 19 May 2021
© Springer Japan KK, part of Springer Nature 2021

Abstract

Creation of oxygen-containing functional groups on the biochar surface can highly improve its hydrophilicity and amend its behaviour in aquatic systems. Hydrogen peroxide, ozone, potassium permanganate and nitrogen acid were most usually used reagents for the surface oxidation. On the contrary, biochar activation by strong acids can be a costly process at the industrial scale and can raise environmental problems due to the disposal of activated carbon. Hence, there is a need to search for cheaper and cleaner products for the modification of biochar. For this reason, weak acids, such as solution of rhamnolipids or rainfall water solution, can be used. In this study, it was found that lower size biochar particles had higher wettability compared to larger size particles, since it was categorized as slightly hydrophobic (2.67 s). Steam of average concentration of rhamnolipid solution (20 mg/l) had the highest effect on the enhancement of biochar surface area (15.2 m²/g) and satisfactory impact on the reduction of initial hydrophobicity (4210 s). Biochar modified with increased concentration of nitric acid solution (from 65 to 20%) wettability was in accordance with the increase of surface area (from 4210 to 3907 s and from 1.27 to 4.36 m²/g).

Keywords Rhamnolipids · Low-temperature biochar · Birch bark · Steam · Rainfall water solution · Nitric acid

Introduction

Usage of oxidative agents for the modification of biochar governs creation of biochar with various functional groups containing oxygen (carboxylic, lactonic, phenolic, cetonic, quinone and ether). Many biochar adsorptive features are affected by chemically sorbed oxygen which can be found in the composition of many functional groups. When biochar is modified, its wettability changes from hydrophobic to hydrophilic [62].

Since pores are filled with tar compounds during carbonization, additional chemical and physical treatment is required to improve the properties of carbon-based material surface properties (surface area, porosity and functional

groups) for its subsequent usage in different environmental applications (e.g., for the removal of gases, metal ions). For example, Li et al. [24] used sludge biochar which was modified with nitric acid and then impregnated with iron ions to increase its adsorption capacity to phosphorus (P). The adsorption capacity for phosphorus-modified wastewater biochar reached up to 9.79 mg/g, which was 40 times higher than the original biochar. Liu et al. [28] used coconut shell activated carbon and exposed it to nitric acid due to the usage of MnO₂-based activated carbon for the removal of SO₂. Up to date, many articles have been published to address biochar modification or carbon activation techniques and widely used carbon-based adsorbent was activated carbon [8, 11, 24, 28, 39, 47, 51, 53, 54, 63]. It was showed that optimum modification/activation effect can be achieved during the management of various experimental conditions such as activation temperature, contact time, ratio of the adsorbent and the modifying agent, particular gas concentration in the mixture. However, most of these papers paid attention to carbon activation with gases (CO₂, CO₂ and N₂ mixture), salts (ZnCl₂), acids (H₃PO₄, HNO₃) and bases (KOH), when most of them can be considered as aggressive oxidizing reagents, which are not considered as environmentally friendly

✉ Luiza Usevičiūtė
luiza.useviciute@vilniustech.lt

Edita Baltrėnaitė-Gedienė
edita.baltrenaite-gediene@vilniustech.lt

Pranas Baltrėnas
pranas.baltrenas@vilniustech.lt

¹ Vilnius Gediminas Technical University, Saulėtekio Avenue 11, 10223 Vilnius, Lithuania

solution for the adsorbent's modification. Hence, biochar modification with rainwater and low concentration of rhamnolipid solution, sustainable, less-expensive and cleaner products, can be an alternative way for the improvement of its surface properties and increment of its sorption capacity to various pollutants from the liquid phase.

Modification of biochar with oxidative agents can enhance the amount of functional groups containing oxygen. Some chemical oxidative agents can be used for the modification of biochar: HNO_3 , KMnO_4 , H_2O_2 or NaOH . Weak acids (for example, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) or citric acid ($\text{C}_6\text{H}_8\text{O}_7$)) can also create carboxylic functional groups on the biochar's surface through esterification [60]. Huff and Lee [17] found that pine wood biochar modification with H_2O_2 decreased its pH from 7.16 to 5.66 and increased the amount of functional groups containing oxygen. Other study [7] found that birch wood modification with H_2O_2 can activate it through the increase of cation exchange capacity (by 6 times) and specific surface area (by 15 times). The increase of cation exchange capacity is related with carboxylic functional groups which were found and showed by the results of FTIR analysis (peaks at $1500\text{--}1750\text{ cm}^{-1}$) and pH (8.36 for the granulated biochar fraction). Li et al. [23] found that biochar modification with nitric acid (2 M) creates carboxylic, lactonic, phenolic and carbonyl groups on the surface of bamboo biochar. Steam changes biochar's properties by both removing residuals of incomplete combustion during pyrolysis and oxidation of biochar surface [1]. A surface area and functional groups can be manipulated through the modification of biochar due to its capacity to sorb-specific pollutants. Significant differences between biochar surface area and functionality can be achieved by modification of biochar with the steam of rainwater solution, steam of rhamnolipid solution and nitric acid solution.

Effect of acids creates more functional groups containing oxygen at the biochar surface and increase biochar's potential to chemically sorb pollutants through specific adsorption [48]. One of the ways to modify biochar for the enhancement of its hydrophilicity is to use rainwater solution [9]. Rainwater solution is often not characterized by high concentrations of pollutants [45]. Several studies have shown that rainwater collected from a natural area away from highways and industrial sites does not have high concentrations of air pollutants. The rainwater solution for this study was collected from an Integrated Monitoring Station (IMS) which is located in a rural area (at the site of minimum anthropogenic impact, in combination with the infrastructure of Aukštaitija National Park). Observations at this station are treated as Lithuanian background monitoring. According to pH values of rainwater found in Lithuania, most acidic rainwater was found in the Aukštaitija Integrated Monitoring Station. Annual pH value there reached 4.72 [10]. In its composition, rainwater

can also have anionic (such as compounds of methylene blue) and cationic (such as active compounds of blue disulphide) materials [40]. It was found that a mixture of active surface compounds highly improved surface activity, lower critical micelle concentration and lower surface tension of the liquid [31].

Recently it was shown that rhamnolipids have good economic potential compared to all studied biological surface active materials. This can be explained by several factors (biodegradability, low toxicity of the solution and its production from renewable sources and industrial wastes) as well as physical–chemical properties and biological origin [52]. Rhamnolipids which belong to the class of glycolipids are most widely investigated biological surface active compounds. Rhamnolipids are produced by genus *Pseudomonas aeruginosa*. Rhamnolipids are composed from a hydrophilic group which consists of one or two (l)-rhamnose units and a hydrophobic head which consists of one or two β -hydroxy-saturated acid units. The active material of the rhamnolipid surface lowers surface tension of water from 72 to 28 mN/m [25]. Rhamnolipids are weak acids due to a carboxylic acidic part which aggregates in the solution and has pKa value which is equal to approximately 5.6 [34]. The active rhamnolipid surface material has the following physical–chemical properties: boiling point is 99.0°C , it is soluble in water, steam pressure is 31 kPa, it is stable in normal conditions and in the presence of metals and metal ions, it is stable until 1 year, viscosity is 1.0 mPas, specific gravitational force is 8.51 [55].

Compared to other glycolipid bioagents, rhamnolipids have a wider application field from the remediation of the environment to its application in the industry. In the near future, rhamnolipids will be most widely used in bioremediation, biodegradability of hydrocarbons and in the removal of potentially toxic elements. Nowadays, the enhancement of biodegradation of organic compounds in the polluted areas is the most important application of rhamnolipids [58]. There is a need to conduct more research on behaviour of these compounds in the environment for the further application of rhamnolipids in bioremediation [41]. Except for biodegradability, rhamnolipids can enhance wettability of agricultural soils. Rhamnolipids can wet hydrophobic soils through the lowering of cohesion and/or adhesion surface tension, hence water can more effectively penetrate into the hydrophobic soils and distribute more evenly. The aim of the article is to analyse how wettability of hydrophobic birch bark biochar can be enhanced by different physical–chemical modification methods and how it differs in different particle sizes of the biochar. This study used birch bark for the biochar modification, because it was showed that low-cost adsorbents are usually obtained from wastes such as wood waste [6]. Successful application of wood bark for wastewater treatment has been published elsewhere [12].

Table 1 Wettability categories based on water drop penetration time test results [40]

Water drop penetration time (s)	Wettability category
≤ 1 s	Hydrophilic
1–60 s	Slightly hydrophobic
60–600 s	Strongly hydrophobic
600–3600 s	Severely hydrophobic
≥ 3600 s	Extremely hydrophobic

Materials and methods

Production of biochar and evaluation of biochar wettability

For the investigation of dependence of biochar wettability on different fractions and its modification methods, biochar was produced from birch bark in the oxygen deficiency conditions (using nitrogen gases) at temperature of 450 °C and 2 h holding time in the pipe type furnace (SNOL 0.7/1250). Then, the obtained biochar was ground and fractionated using the sieving method (Retsch sieves of 1.6 mm, 900 µm and 300 µm in size). The obtained different fractions (coarse from 900 µm to 1.6 mm, medium from 300 µm to 900 µm and fine less than 300 µm) were further investigated for the evaluation of its wettability by the water drop penetration time test [56]. In the water drop penetration time test, a drop of water was placed on the biochar's surface using a pipette and the complete drop penetration time was counted by a stopwatch. The shortest time (less than 1 s) was referred to momentum penetration. All the times exceeding 3600 s were referred to the wettability category of 3600 s. All the times and categories are shown in Table 1.

Evaluation of physical–chemical properties of the solutions

The pH of the solutions was analysed using a pH-meter Mettler MultiSeven. Electrical conductivity of the solutions was analysed using a conductometer WTW inoLab terminal 740.

Biochar modification techniques

For the enhancement of biochar's hydrophilicity, biochar was modified by physical–chemical techniques. Modification is related to the activation of the original biochar. A modifier, its concentration, modification time and temperature all together affect biochar properties [67]. Table 2 shows different techniques for modification of biochar used in this research. The coarse fraction of birch bark biochar (900 µm–1.6 mm) was chosen for modification due to its further application in the biofiltration system. After

Table 2 Physical–chemical modification techniques of biochar used in this study

Modified material	Modification technique	Reagent	Modification description	Effect of the modification
Coarse fraction (900 µm–1.6 mm) of birch bark (450 °C, 2 h) biochar	Physical	Steam of deionised water	Biochar was treated with the steam of deionised water for 1 and 3 h in biochar hydrophilicity enhancement device	Removal of tar compounds, enhancement of specific surface area, development of microporosity
		Steam of rainwater solution	Biochar was treated with the steam of rainfall water solution for 1 and 3 h in biochar hydrophilicity enhancement device	Removal of tar compounds, enhancement of specific surface area, development of microporosity
		Steam of rhamnolipid solution	Biochar was treated with the steam of rhamnolipid solution (5, 20, 40 mg/l) for 1 and 3 h in biochar hydrophilicity enhancement device	Removal of tar compounds, enhancement of specific surface area, development of microporosity
	Chemical	HNO ₃ solution	1 g of biochar was treated with 25 ml of nitric acid (20%, 40% or 65%) at 80 °C for 1 h	Development of oxygen and nitrogen containing functional groups on the biochar surface

modification, all biochar types were analysed for the wettability using the water drop penetration time test [20].

Modification of biochar with the steam of deionised water

Biochar was modified in the biochar hydrophilicity enhancement device [4] (Fig. 1). To produce steam, the solution in the lower part of the reservoir was heated by an electrical heating element. The solution was heated until it reached the water boiling temperature due to creation of maximally (100%) saturated air. The device was supported by the automatic control block which regulated the work of the automatic heating element and the electrical engine. In the middle part of the reservoir, there was a perforated plate which held biochar particles from their access to the solution. Biochar of a size of particles at 900 μm –1.6 mm was treated by the steam of deionised water for 1 and 3 h. In the upper part of the reservoir, vacuum (99.990–1.333 Pa) was created to overhang biochar particles in the steam. Modified biochar types were labelled as BC-SDW-1 h and BC-SDW-3 h, unmodified one as BC.

Modification of biochar with the steam of rainwater solution

Rainwater for the modification was collected in the Aukštaitija Integrated Monitoring Station. After collection, chemical properties, such as pH and electrical conductivity, were analysed. The pH of the rainwater was analysed using a pH-meter (Mettler MultiSeven). Electrical conductivity of the rainwater solution was analysed using a conductometer (WTW inoLab terminal 740). Properties were compared to the solutions of deionised water. Biochar was treated for 1 and 3 h. Modified biochar types were labelled as BC-SRW-1 h and BC-SRW-3 h.

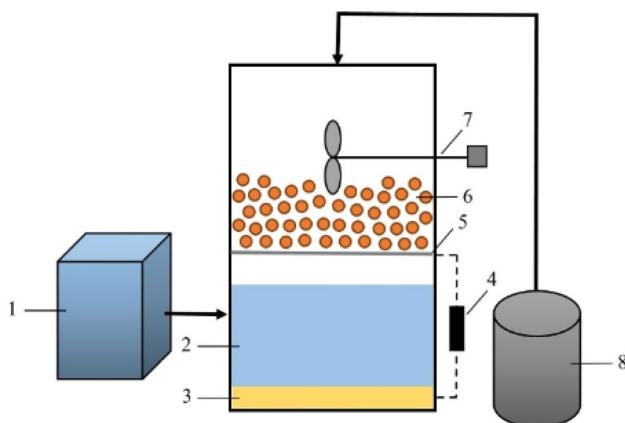


Fig. 1 Schematic picture of the biochar hydrophilicity enhancement device

Modification of biochar with the steam of rhamnolipid solution

Biochar was modified with the rhamnolipid solution using the biochar hydrophilicity enhancement device. The only difference from biochar modification with deionised water and rainwater vapour is that the lower part of the device reservoir was filled with different concentrations of rhamnolipid solution (5 mg/l, 20 mg/l and 40 mg/l) [58]. Biochar was treated for 1 and 3 h. Modified biochar types were labelled as BC-SRS5-1 h, BC-SRS5-3 h, BC-SRS20-1 h, BC-SRS20-3 h, BC-SRS40-1 h, BC-SRS40-3 h.

Modification of biochar with nitric acid

Due to the creation of groups containing oxygen and nitrogen on the biochar's surface, it was oxidised with different concentrations of HNO_3 solutions. 1.0 g of dried biochar particles were processed with 25 ml of 20%, 40% and 65% HNO_3 solution at temperature of 80 $^\circ\text{C}$ for 1 h. After the treatment, the biochar was washed with deionised water and dried at temperature of 105 $^\circ\text{C}$ [15]. Modified biochar types were labelled as BC-NA20, BC-NA40 and BC-NA65.

Statistical analysis

All experiments were performed three times. The data were processed (mean value, standard deviation) using Microsoft Excel 11 software.

Results

Chemical properties of the modified liquids

According to the results of the liquids' pH, the deionised water had the highest alkalinity (pH of 7.71) (Table 3). It was found that the acidity of the solutions increased from 6.41 to 5.83 when raising concentration of the rhamnolipid solutions (from 5 to 40 mg/l). The rainwater solution had higher acidity (pH of 4.83) compared to the highest concentration rhamnolipid solution. The rainwater solution was acidic and contained dissolved gases (dissolved in SO_3 , SO_2 , CO_2 , NO_x) that turn into acids in water and can react with biochar, thus changing its wettability. According to atmospheric precipitation studies, the rainfall solution taken from IMS in 2018 had the following chemical properties: SO_2 —0.15 $\mu\text{gS}/\text{m}^3$; NO_2 —0.52 $\mu\text{gN}/\text{m}^3$; total NO_3 —0.27 $\mu\text{gN}/\text{m}^3$; total NH_4 —0.50 $\mu\text{gN}/\text{m}^3$ [10]. Meanwhile, solutions of nitric acid, whose pH decreased from 0.53 to 0.43 when the concentration of the solution increased from 20 to 65%, had a very high level of acidity. According to the results of the electrical conductivity of the solutions,

Table 3 Chemical properties of the solutions, $n=3$, $\pm$ standard deviation

Solution	pH	Electrical conductivity, $\mu\text{S}/\text{cm}$
Deionised water	6.86 ± 0.12	15.1 ± 0.2
Rainwater	4.83 ± 0.1	38.2 ± 0.2
Rhamnolipid (5 mg/l)	6.41 ± 0.07	7.47 ± 0.25
Rhamnolipid (20 mg/l)	5.92 ± 0.05	5.07 ± 0.06
Rhamnolipid (40 mg/l)	5.83 ± 0.03	4.17 ± 0.21
HNO_3 (20%)	0.53 ± 0.01	551 ± 2.08
HNO_3 (40%)	0.47 ± 0.03	586 ± 5.57
HNO_3 (65%)	0.42 ± 0.02	634 ± 5.29

Table 4 Biochar wettability (s) dependence on different fraction, $n=3$, $\pm$ standard deviation

Fraction size	Wettability, s
$< 300 \mu\text{m}$	2.67 ± 0.58
$300 \mu\text{m} - 900 \mu\text{m}$	6120 ± 5
$900 \mu\text{m} - 1.6 \text{ mm}$	$18,541 \pm 3.21$

it decreased from $7.47 \mu\text{S}/\text{cm}$ to $4.17 \mu\text{S}/\text{cm}$ in the case of increasing concentration of the rhamnolipid solution from 5 to 40 mg/l. In the case of nitric acid solutions, the tendency was opposite, since electrical conductivity of the solutions decreased when the concentration of the solution increased from 20 to 65% (from 551 to 634 $\mu\text{S}/\text{cm}$, respectively).

Dependence of biochar wettability on different fractions

According to the results of biochar wettability dependence on different fractions, it can be seen that when the size of biochar's particles is decreasing, wettability of the material increases (Table 4). The lowest fraction ($< 300 \mu\text{m}$) of biochar had slight hydrophobicity ($\text{WDPT} > 1 \text{ s}$), since biochar samples of a medium size ($300 \mu\text{m} - 900 \mu\text{m}$) and the largest size ($900 \mu\text{m} - 1.6 \text{ mm}$) had extreme hydrophobicity (WDPT are 6120 s and 18,540 s, respectively). When biochar fractions decreased from a large size to medium, wettability of biochar altered from extreme hydrophobicity to slight hydrophobicity.

Literature sources suggest that the effect of the size of biochar particles on its wettability is not well known; however more research was done on the effect of the size of biochar particles on the soil water holding capacity. One study [26] showed that lower biochar particles had a higher water holding capacity compared to the larger biochar particles. Several mechanisms can govern this effect. Firstly, lower biochar particles can easily fill in the cavities between larger biochar particles and soil particles, and, in such a manner, mechanically fill in the pores of the soil. This increases the

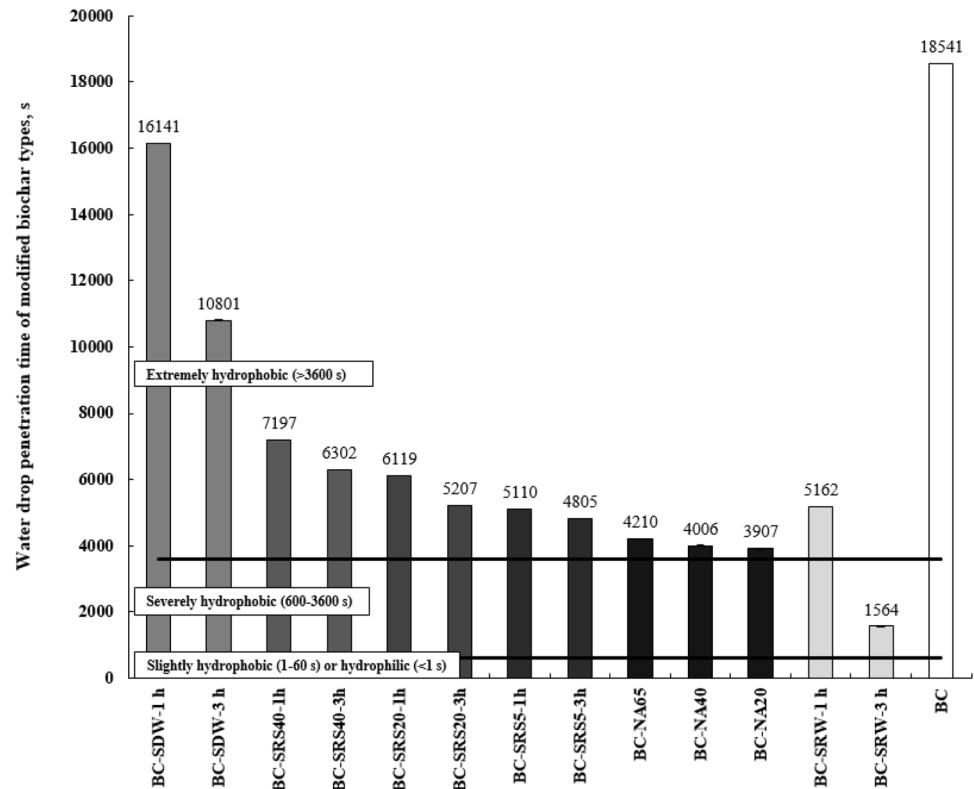
tortuosity of the water flow in the soils and lowers soil's hydraulic conductivity. Additionally, smaller biochar particles fill in the internal pores between the particles and it governs higher water retention on the biochar's surface and soil particles. Secondly, lower sizes of the biochar particles have more cracked internal macropores, which increases the amount of retained water.

Dependence of different biochar modification techniques on its wettability

According to the results of biochar wettability after its modification by applying different techniques, it can be seen that biochar modification with the steam of rhamnolipid solution had a greater effect on biochar hydrophilicity compared to the effect of the deionised water steam (Fig. 2). Steam of the deionised water had the least effect on the enhancement of biochar hydrophilicity, since biochar wettability increased only by 1.15 and 1.72 times (in the case of 1- and 3-h heating time, respectively) compared to the unmodified biochar. Meanwhile, the steam of the highest concentration rhamnolipid solution (40 mg/l) was more than two times more effective, since wettability of the biochar increased by 3.63 and 3.86 times after the modification (in the case of 1- and 3-h heating time, respectively). However, biochar modification with the nitric acid solution (20%) was more effective compared to almost all modification techniques, since biochar wettability increased by 4.75 times compared with unmodified biochar and this is 0.88 times more effective than its impact by the steam of the highest concentration rhamnolipid solution. This result obtained after modification of biochar with nitric acid solution could be explained by the potential higher amount of acidic functional groups on the biochar's surface. The steam of the rainwater (for 3 h) had the highest effect on enhancement of biochar hydrophilicity, since biochar wettability increased by 11.9 times compared to the unmodified biochar. This result could be explained by the potential anionic and cationic active surface materials which highly increase the surface activity of the solution and lower surface tension of the solution. After modification, all biochar types retained strong initial hydrophobicity (hydrophobicity differed from severely to extremely hydrophobic).

Previous studies showed how different biochar treatment techniques (activation by steam, modification with nitric acid, water) affected physical and chemical properties of biochar. Since biochar hydrophobicity mostly depends on the biochar surface area, porosity, acidic functional groups and gases which are retained in the air-filled pores, biochar activation by the steam can be a perfect technique for the enhancement of biochar hydrophilicity. Biochar activation by the steam is a common modification method which is used to increase structural porosity of biochar and remove residuals from incomplete combustion. This method

Fig. 2 Biochar wettability dependence on different modification techniques



increases biochar's surface area on which sorption occurs. Lou et al. [30] found that activation of biochar made from pine sawdust by the steam increased its surface area; however, it had little effect on its surface's functional groups. Hadjittofi et al. [16] studied cactus fibres activated by HNO_3 acid to create carboxylic functional groups on the surface. Functional groups containing oxygen were also incorporated into the structure of rice straw biochar after biochar modification with H_2SO_4 and HNO_3 and it resulted in the higher O/C ratio in the final product.

In literature, a number of studies on biochar hydrophilicity enhancement after its treatment with water can be found. Post-treatment of biochar after pyrolysis plays a significant role for the creation of the hydrophilic biochar. One study [44] showed that 350 °C temperature biochar after being quenched with water still remained hydrophobic due to absence of polar functional groups containing oxygen. When the pyrolysis temperature increased, wood biochar quenched with water decreased its hydrophobicity. According to other studies [49], biochar made from wood and bark still remains hydrophobic if it has been obtained at temperatures of 500 °C and 600 °C. In the firstly mentioned study [44], wood biochar made at temperature of 450 °C and after water quenching became hydrophilic. The conclusion was made that biochar quenching was a good method, since the effect of a hot steam can potentially crack opened pores. Biochar treatment with water after pyrolysis resulted in the

creation of pure biochar (activated char). Pure biochar's surface has many pores to absorb and retain water. In the latter study, the analysis of the FTIR and BET was used for further investigation of functional groups at biochar's surface and its structural characteristics.

Biochar surface functional groups before and after modification

Fourier-transform IR (FTIR) spectroscopy determines the type and the amount of functional groups on the biochar surface [36]. Biochar modified by the steam of various solutions and the solution of nitric acid, FTIR spectrum are shown in Figs. 3, 4 and 5. FTIR results showed that low-temperature birch bark biochar had $-\text{OH}$ functional group in its structure (peaks at 3433 cm^{-1} and 3421 cm^{-1} wavenumbers) after the effect with the steam (Figs. 3 and 4). The steam of rainwater had the highest effect on the development of biochar hydroxyl functional groups (for 1 h) due to the highest absorption intensity of the peak (Fig. 3). It shows that biochar after post-pyrolysis treatment with the steam of rainwater solution had better absorption to water compared to modification with the steam of deionised water. The highest difference between different FTIR spectrums was between different values of the absorption peaks. The higher value of light absorption is, the better adsorption and potentially higher amount of particular functional group. Higher

Fig. 3 FTIR spectra of biochar modified by the steam of deionised water and rainwater solution

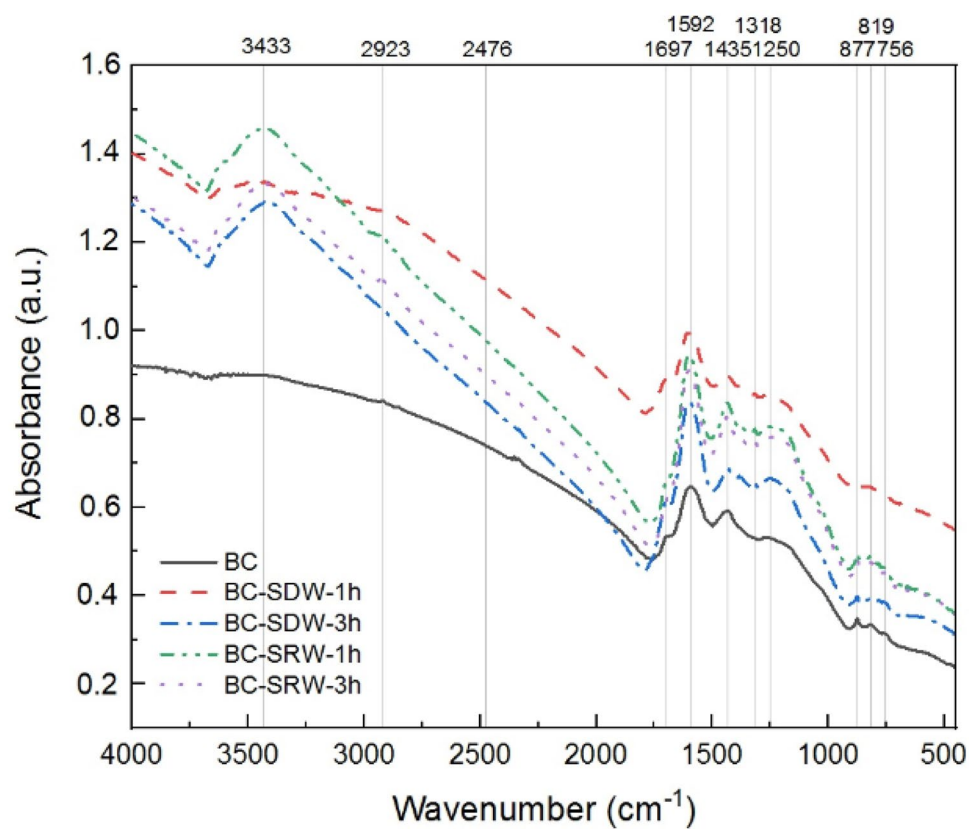


Fig. 4 FTIR spectra of biochar modified by the steam of different concentration of rhamnolipid solution

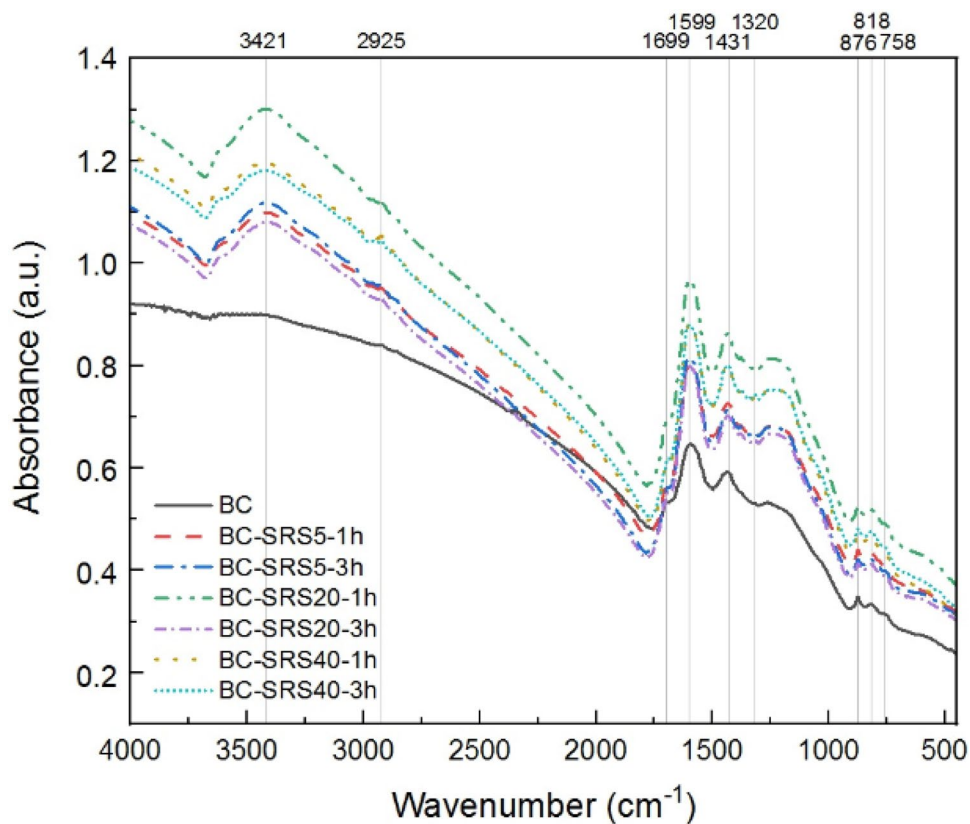
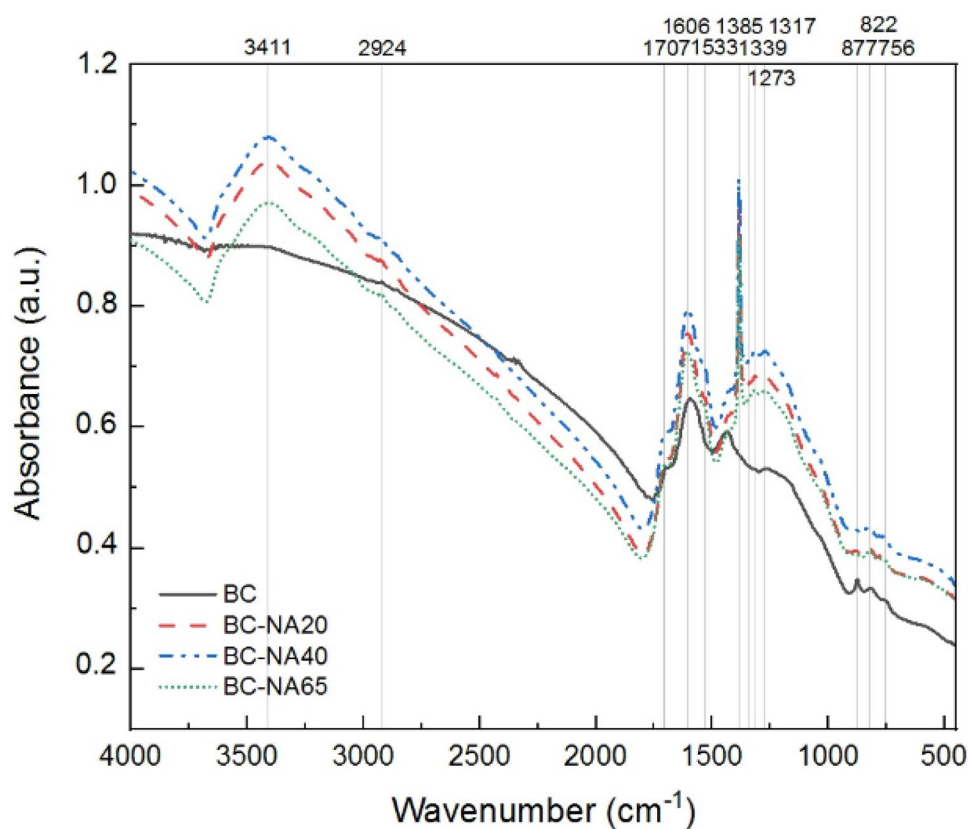


Fig. 5 FTIR spectra of biochar modified by different concentration of nitric acid solution



absorption peaks at 1697 cm^{-1} , 1592 cm^{-1} , 1435 cm^{-1} , 1250 cm^{-1} , 877 cm^{-1} , 819 cm^{-1} and 756 cm^{-1} wavenumbers showed that the amount of functional groups (C=O, C=C, C–O and C–H, respectively) was higher of biochar modified with steam compared to the unmodified one. A slight peak at 1697 cm^{-1} wavenumber shows vibration of C=O bond which corresponds to the formation of ketones, quinones, carboxylic and aromatic components [29]. Organic oxygen existing in the form of oxygen-containing functional groups enhances hydrophilicity of the biochar [65]. A weak peak at 2923 cm^{-1} wavenumber, which shows aliphatic C–H bond, did not vanish after biochar modification with steam and it shows that aliphatic structure is resistant to heat and water [29].

Comparing FTIR spectrum of unmodified and modified biochar types with the steam of various concentrations of rhamnolipid solutions (from 5 to 40 mg/l) it can be seen that absorption intensities of all functional groups were higher in the case of modified biochar, and it means that the effect of steam of rhamnolipid solution developed more oxygen-containing functional groups which are important for adsorption (Fig. 4). Higher absorption peak at 3421 cm^{-1} , 1599 cm^{-1} , 1431 cm^{-1} , 1270 cm^{-1} , 876 cm^{-1} , 818 cm^{-1} and 758 cm^{-1} wavenumbers showed that the amount of functional groups (–OH, C=O, C=C, C–O and C–H, respectively) increased after biochar modification

with the steam of rhamnolipid solution. Comparing the effect of different rhamnolipid solution concentrations and treatment times it can be stated that modification with the steam of 20 mg/l rhamnolipid solution for a shorter time (1 h) had the best effect on the development of biochar functional groups due to the highest absorption intensities.

Similarly, another study [46] showed FTIR spectrum of biochar made from *Miscanthus* and activated with steam, peaks at $3000\text{--}3700\text{ cm}^{-1}$ (which are related with hydroxyl (–OH) functional groups, including adsorbed water molecules), 1695 and 1696 cm^{-1} (which are related with C=O bond), 1605 and 1616 cm^{-1} (which are related with aromatic C=C bond) were determined. Peaks at 1384 cm^{-1} (–CH bond in alkanine and alkaline groups) and $887\text{--}823\text{ cm}^{-1}$ (aromatic –CH) were also determined in the spectrum of both biochar types. These results show that functional groups are not removed from biochar after the process of its modification with steam.

Another study [54] proposed a new procedure to convert algal waste to porous carbon. Initially, the algae were pyrolyzed at $550\text{ }^{\circ}\text{C}$, and after pyrolysis, the solid product was subjected to hydro-pyrolysis (physical steam activation) at different temperatures. The optimal temperature was determined, which resulted in a small surface area, microporosity, and mesoporosity that developed during the

activation process. Oxygen-containing functional groups with weak acidic and alkaline origin were identified.

After biochar modification with the nitric acid solution, three strongest peaks were determined: at 3411 cm^{-1} , 1606 cm^{-1} and 1385 cm^{-1} (Fig. 5). The peak at 3411 cm^{-1} wavenumber is related to hydroxyl -OH functional group [35], the peak at 1606 cm^{-1} is to C=O , C=C and C=N functional groups [42] and the peak at 1385 cm^{-1} wavenumber is with N=O vibrations. Similarly, Tan et al. [50] determined that peak at 1410 cm^{-1} which occurs due to the lactonic structure and is presented after the treatment with nitric acid. A higher amount of oxygen-containing functional groups on the biochar after its modification with nitric acid solution can explain its better adsorption to water. In this study, a better formed peak at $3450\text{--}3500\text{ cm}^{-1}$ wavenumber showed that biochar had more -OH groups due to carboxyl groups. Comparing the effect of different solution concentrations on the development of functional groups, 40% solution of nitric acid had the highest effect due to the highest absorption intensities comparing to other concentrations.

Another study [35] determined that the amount of O-H , C-H , aromatic C=C , C=O , C-O and aromatic C-H increased on the surface of biochar after its modification with nitric acid. The peak at $3200\text{--}3650\text{ cm}^{-1}$ shows -OH group which corresponds to the hydroxyl group and arises from phenols, alcohols and water. Additionally, using the Boehm titration method it was found that the amount of carboxyl, lactonic and phenolic hydroxyl groups was higher after the treatment with HNO_3 in the oxidized hydrochar. It was determined that oxygen-containing functional groups had the highest effect on the interaction of hydrochar and methylene blue. According to another study [42] when biochar was modified with the solutions of nitric and phosphorous acids it was rich in phosphates, nitrogen groups and nitrates, which were shown by FTIR analysis. Three significant signals were determined from the biochar IR spectrum: P=O vibrations at $1000\text{--}1050\text{ cm}^{-1}$, N=O vibrations at $1340\text{--}1350\text{ cm}^{-1}$, C=O , C=C and C=N vibrations at $1600\text{--}1650\text{ cm}^{-1}$. These signals are related to phosphates, nitrates, carboxylic (-COOH), carbonyl (-C=O) and imine (-C=N) bonds in the biochar structure. Since the biochar effect with HNO_3 governs nitrification of active sites, signals increased at $1340\text{--}1350\text{ cm}^{-1}$. Increase of biochar surface area and functional groups after its modification with nitric acid was determined by other studies as well [5, 27, 66]. Li et al. [22] found out that the FTIR spectrum of activated carbon modified with HNO_3 acid (AC-1) was more intensive compared to other activated carbon which was activated also with HNO_3 acid (AC-2), however, in a different way. In the case of AC-1 activated carbon, it was produced in the microwave device for 22 min in the inert nitrogen atmosphere. In the case of AC-2, activated carbon was activated in the pipe type furnace at $500\text{ }^\circ\text{C}$ for 90 min. This result was confirmed

by the Boehm titration method also. Comparing two activated carbon types modified with nitric acid, the amount of carboxyl, lactonic and phenolic hydroxyl groups was higher in AC-1 (from 0.5 to 1.52 mmol/g , from 0.05 to 0.43 mmol/g and from 0.1 to 0.51 mmol/g , respectively). A mesoporous structure has an important impact on the development of acidic functional groups after biochar treatment with HNO_3 and a higher amount of oxygen-containing functional groups explains a better absorptive capacity of HNO_3 modified biochar [50]. Jia and Thomas et al. [19] found out that after oxidation of activated carbon with HNO_3 acidic oxygen-containing functional groups developed. It was found that carboxyl acidic groups were the main incorporated surface groups during the oxidation process.

Nitric acid is the weakest of the strong acids (hydrochloric acid, sulfuric acid, bromic acid, iodic acid), which results in weak oxidation/reduction reactions at lower concentrations (e.g., up to 4%) and the acid becomes inefficient for the formation of biochar functional groups. Oxidation of one carbon atom C requires four molecules of nitric acid and, as a result, low acid concentrations are ineffective. According to literature analysis, the concentrations of nitric acid used for biochar modification ranged from 9 to 80% [13, 16, 64]. One study [64] showed that biochar (300 , 500 , and $700\text{ }^\circ\text{C}$) modified with 2 M (9%) nitric acid for 8 h at $30\text{ }^\circ\text{C}$ was characterized by lower concentrations of the main surface groups due to its effect on the dissolution of biochar ash. On the other hand, the cation exchange capacity, the number of carboxylic acids and the content of weak acid ester groups increased significantly. It was showed that oxidative functional groups of biochar can lead to its high cation exchange capacity and charge. Other study [16] used biochar made from cactus fibres ($600\text{ }^\circ\text{C}$, 1 h) for its modification with 12 M (53%) nitric acid solution. FTIR spectra results indicated that HNO_3 activation resulted basically in the formation of carboxylic moieties on the carbonized fibre surface. Absorption bands at 1588 and 1428 cm^{-1} were attributed to the asymmetric and symmetric vibrations of the carboxylic moieties and proved the formation of carboxylic acids. New peaks at 1528 cm^{-1} and 1335 cm^{-1} were attributed to asymmetric and symmetric NO_2 stretch vibrations what proves that HNO_3 oxidation promotes the addition of nitrogen containing groups on the biochar surface. Gokce and Aktas [13] used activated carbon for its modification with different concentration of nitric acid solution (from 20 to 80%). It was observed that acidic surface modification had a strong effect on the textural properties of activated carbon. The surface area decreased with increasing HNO_3 concentration. Decrease (98%) in the total pore volume was attributed to the destructed pore walls. Liu et al. [28] showed that the concentration of nitric acid did not significantly changed the structural properties of MnO_2 -based activated carbon. Oxygen-containing surface functional groups (carbonyl carbon

and transit) initially increased with increasing HNO_3 concentration and reached a maximum value when the HNO_3 concentration reached 10 mol/L (44%), which resulted in an increased SO_2 sorption capacity.

Characteristics of biochar surface structure before and after modification

Porous materials are described according to their adsorptive properties. Term adsorption originally marks condensation of gases on the material's free surface. Adsorption of gases in the porous material is qualitatively described by the adsorption isotherm, amount of the adsorbed gases in the material at fixed temperature depending on the pressure. Porous materials are most usually described according to their pore size obtained from the gas sorption data,

and the IUPAC classifies pore sizes and gas sorption isotherms reflecting the link between porosity and sorption [3].

With respect to qualitatively forecast biochar environmental benefit, it is important to characterize biochar porosity and pore size distribution. In this study, the biochar pore characteristics were determined using nitrogen adsorption. N_2 adsorption–desorption isotherms and pore size distributions of unmodified and modified biochar types are shown in Figs. 6, 7 and 8. According to the IUPAC classification, biochar modified with the steam adsorption–desorption isotherms can be classified as type I isotherms (Figs. 6a and 7a) and biochar modified with nitric acid solutions (Fig. 8a) as type II. The type I isotherm shows that biochar has microporous structure and the type II means macroporous. The rise of biochar isotherms at relative pressure (P/P_0) between 0.1

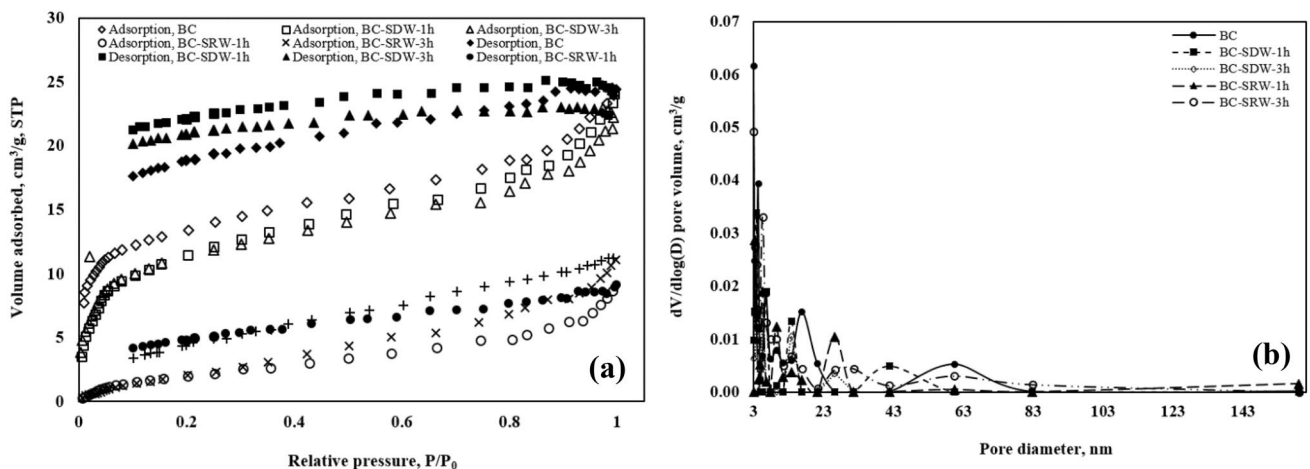


Fig. 6 Adsorption–desorption isotherms (a) and pore size distribution (b) of unmodified and modified biochar by the steam of deionised water and rainwater solution

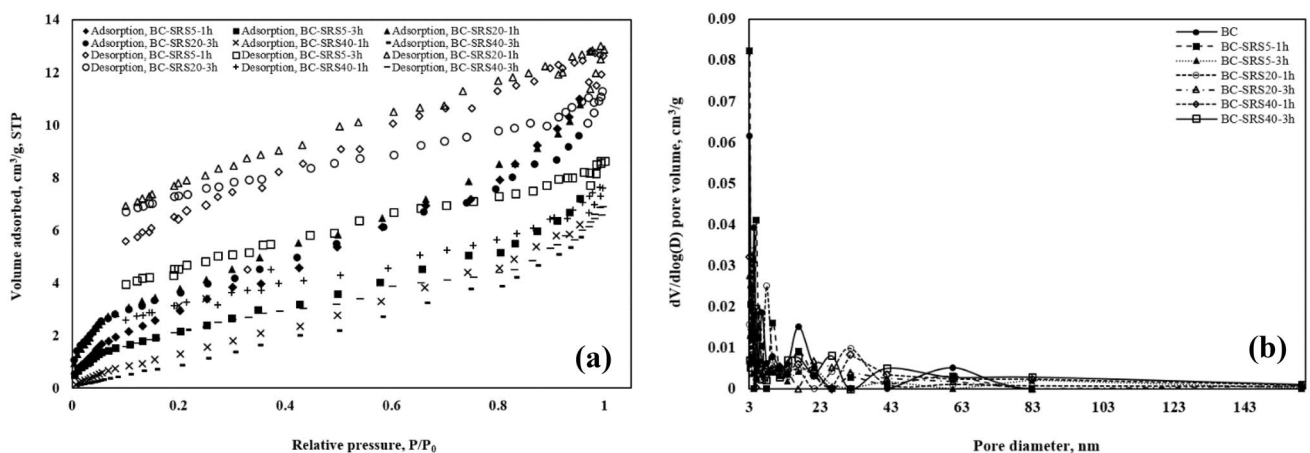


Fig. 7 Adsorption–desorption isotherms (a) and pore size distribution (b) of unmodified and modified biochar by the steam of different concentration of rhamnolipid solution

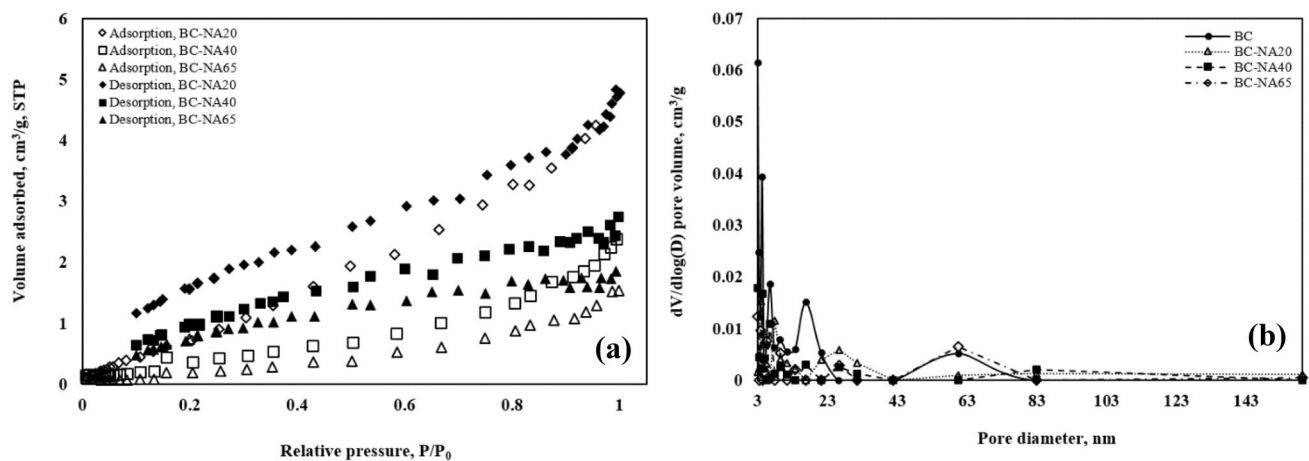


Fig. 8 Adsorption–desorption isotherms (a) and pore size distribution (b) of unmodified and modified biochar by different concentration of nitric acid solution

and 0.9 shows existence of the microporous and mesoporous structure.

The pore size was calculated according to the BJH method and it is shown in Figs. 6b, 7b and 8b. Figures 6b and 7b show modification with steam effect on the structure of the biochar samples, meanwhile Fig. 8b shows the effect of modification with nitric acid. The highest peaks of all biochar types were determined at 3.1–6.6 nm pore size, and it shows the increase of the mesopore volume. A peak at 60.5 nm pore size was observed in the case of biochar modified with 65% concentration nitric acid solution which shows macropores. In the case of unmodified biochar peaks at 4.36, 16.9, and 60.5 nm, a pore size can be observed, which shows mesoporosity and macroporosity of biochar. Wide pore size distribution across a microporous and mesoporous range and slightly heterogenous structure was determined in the case of modified biochar types. Compared to unmodified biochar, the effect with steam and nitric acid governed the development of more mesoporous structure, because of a narrow monomodal distribution which is centered in the mesoporous range (2–50 nm). It is obvious that biochar samples showed wide pore size distribution, from narrow micropores to wider mesopores and macropores. Different biochar post-pyrolysis modification techniques can significantly impact biochar pore characteristics. Using detailed characterization of the biochar pore structure, a potential impact of biochar on the amendment of soil and pollutants sorption can be effectively predicted.

Physical adsorption process is affected by the pore structure of the biochar, and the pore structure can be different according to distinct biochar types [21]. Table 5 shows the surface area, total pore volume, micropore volume and average pore size of unmodified and modified biochar types. The average pore size of biochar varied from 1.93 to 2.77 nm and it is related to the microporous and mesoporous structure.

After biochar modification with the steam of different solutions biochar surface area increased, but the total pore volume decreased, except in the case of biochar modified with the steam of deionised water. Comparing the steam of different solutions, the rhamnolipid solution (20 mg/l) had highest effect on the development of surface area (15.2 m²/g). The optimum concentration of rhamnolipid solution was 20 mg/l for the enhancement of biochar surface area, because higher rhamnolipid concentrations can bind to biochar surface radicals by clogging its pores. It was found that with increasing concentration of the modifying rhamnolipid solution from 20 mg/l to 40 mg/l, the specific surface area of biochar decreased from 15.2 to 6.15 m²/g. The decrease in the specific surface area of biochar with increasing concentration of biosurfactant may have been caused by the surfactant filling of biochar pores [33]. Biochar types according to the development of surface area can be ordered in such manner: BC-SRS20_1h (15.2 m²/g) < BC-SRW_1h (10.4 m²/g) < BC (4.42 m²/g) < BC-SDW_1h (3.95 m²/g). It can be stated that the most microporous biochar types were those which were modified with the steam of 5 mg/l (for 3 h) and 20 mg/l (for 1 h) rhamnolipid solutions, since micropore surface contained 98% and 95% of its overall surface area. It can be seen, that S_{mic}/S-BET surface area of the initial biochar (29%) has not changed considerably after the treatment with the steam of deionised water for 1 h (23%) and nitric acid solution of 65% (22%). However, the effect of strong acid on the decrease of biochar micropore surface can be explained by the destruction of pore walls during strong oxidation and the conversion of micropores and mesopores to macropores. The total pore volume varied from 0.0089 to 0.035 cm³/g in the case of steam modification and from 0.0026 to 0.0063 cm³/g in the case of nitric acid modification. It was found out that after modification with nitric acid, the BET surface area of birch bark biochar decreased from 4.36 to 1.27 m²/g when

Table 5 Characteristics of unmodified and modified birch bark biochar (450 °C) surface structure

Biochar modification technique	Treatment time, h	BET surface area (m ² /g)	Micropore surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Average pore size (nm)	S _{mic} /S _{BET} (%)	V _{mic} /V _t (%)
Unmodified	—	4.42	1.29	0.035	0.0216	1.93	29	62
Steam of deionised water	1	3.95	2.31	0.035	0.0194	1.93	58	55
Steam of deionised water	3	3.81	0.88	0.032	0.0186	1.93	23	58
Steam of rainfall solution	1	10.4	8.27	0.013	0.00368	1.93	79	28
Steam of rainfall solution	3	9.68	7.8	0.016	0.00278	2.02	81	17
Steam of rhamnolipid solution (5 mg/l)	1	12.9	11.7	0.019	0.00415	1.93	91	22
Steam of rhamnolipid solution (5 mg/l)	3	8.81	8.66	0.0313	0.012	1.93	98	38
Steam of rhamnolipid solution (20 mg/l)	1	15.2	14.4	0.018	0.0054	1.93	95	30
Steam of rhamnolipid solution (20 mg/l)	3	14.7	13.3	0.016	0.00522	1.93	90	33
Steam of rhamnolipid solution (40 mg/l)	1	6.78	5.13	0.01	0.00182	2.02	76	18
Steam of rhamnolipid solution (40 mg/l)	3	6.15	2.61	0.0089	0.000929	2.02	51	10
Nitric acid solution (20%)	1	4.36	2.31	0.0063	0.000821	2.02	53	13
Nitric acid solution (40%)	1	1.99	0.75	0.0037	0.000268	2.77	38	7
Nitric acid solution (65%)	1	1.27	0.28	0.0026	0.000101	2.77	22	4

concentration of the modifying nitric acid solution increased from 20 to 65%. The decrease of biochar total surface area in the case of HNO₃ can be explained by the decrease of the micropore volume (from 0.0008 to 0.0001 cm³/g). The micropore surface area of the same biochar modified with increasing concentration of nitric acid solution decreased from 2.31 to 0.28 m²/g. In the case of HNO₃ modification, the pore diameter of biochar increased from 2.02 to 2.77 nm.

Another study [66] similarly found that after modification with nitric acid surface area of rice straw biochar decreased from 76.2 to 68.8 m²/g. The micropore surface area decreased in the case of the nitric acid modification (from 52.8 to 33.2 m²/g) due to the part of oxygen-containing functional groups which prevent the entrance of nitrogen molecules into the pores. A significant increase of pore diameter was observed in the case of HNO₃ modification and it increased from 1.6 to 2.4 nm. It shows that unmodified biochar treatment with acids governs collapse of micropores which form mesopores and increase pore diameter. Additionally, a percentage equivalent of micropores decreased after modification with HNO₃ (from 53 to 28%), since an equivalent of mesopores increased (from 47 to 72%). The decrease of the biochar total surface area in the case of HNO₃ was explained by the decrease of micropore volume. The biochar effect with acid governed the widening of the pores when pore walls and pore structure were destructed, which decreases the biochar surface area. Similarly, to this study,

Guzel et al. [15] found that surface area, total pore volume and pore diameter of weed biochar (500 °C) decreased when modifying HNO₃ concentration increased from 20 to 65% (from 25.6 to 5.14 m²/g, from 0.019 to 0.006 cm³/g and from 3.74 to 3.57 nm, respectively). This decrease can be explained by the narrowness of pore openings, formation of oxygen groups near pore openings and walls, by the destruction of pore walls, micropores and mesopores conversion to macropores due to strong oxidative conditions.

Discussion and future research

In order for biochar to be actively used in industry, researchers need to ensure its specific physical and chemical properties. Therefore, current research focused on the modification and characterization of low temperature birch bark biochar. The objectives of this study were to evaluate the effect of biochar modified with high acidity traditional chemical solutions (HNO₃) and the steam of lower acidity solutions (rain, rhamnolipid) on its physicochemical properties.

Physical and chemical properties of biochar which is produced using different thermochemical conversion techniques can differ and mostly affected by the process conditions (holding time and temperature), initial feedstock and modification technique [18]. Typically, biochar types made by low temperature thermochemical conversion technique have less polar oxidative surface groups such as C–O, C=O and OH

and have limited porosity and surface area (typically $< 150 \text{ m}^2/\text{g}$). Even though low-temperature biochar types have porous structure, they can be less accessible for water due to lesser pores, lesser pore interconnectivity and components of residual tars which block the pores. The biochar aliphatic functional groups also determine hydrophobicity of the biochar because they vapour only at high pyrolysis temperatures [14]. These drawbacks limit wide applicability of biochar as beneficial functional material. For example, abundant surface functional groups are important for the creation of biochar as catalyst or adsorbent [65]. Biochar porosity and high surface area are favourable properties which are important for its application as a hydrophilic material in biofiltration for removal of volatile pollutants or enhancement of water holding capacity in dry sandy soils.

Biochar modification is an important area for the possibility to use tailored material for the removal of specific pollutants from a liquid phase [37]. Biochar properties including surface acidic functional groups or microporosity and high surface area which are important for biochar wettability can be further improved using different modification techniques [2]. Due to modification or incorporation of modified materials, biochar types have improved properties (pore volume, specific surface area, pore size distribution, active surface sites) which affect the adsorption of water, so the removal of the pollutants [61].

Physical activation which is called gaseous activation uses various gases, for example: steam and carbon dioxide. Physical activation can improve physical–chemical properties of new biochar types by removing secondary products of incomplete combustion, oxidizing carbon surface and further enhancing biochar surface area. Physical activation methods are often simple, more economically available and effective for enhancing more carbon surface area than chemical modification techniques. Li et al. [23] determined that the surface area of a new biochar type activated by heating increased by 11.5 times compared to the initial biochar. In the case of biochar activated by chemical modification technique, the surface area was only 0.009–0.63 times lower than that of the initial biochar [68]. Another study [48] showed that higher vapouring speeds and longer activation time increased sorption of Cd, Cu and Zn on the surface of biochar. Though activation by steam increased biochar surface area and porosity, Shim et al. [46] determined that the sorption capacity of Cu^{2+} insignificantly changed on the elephant grass biochar made by slow pyrolysis under 500°C temperature and its activation by steam under 800°C temperature. They found that, despite the fact that biochar activation by steam increased its surface area, the amount of biochar functional groups was reduced. Similarly, Lou et al. [30] showed that biochar made from pine sawdust activation by steam increased its surface area; however, it had a low effect on functional groups on its surface. The effect of steam did

not have impact on the sorptive capacity of phosphate due to electrostatic repulsion which is formed by the negative charge of the biochar. In the context of sorption of inorganic pollutants, the activation by steam is more effective, which is used before the second activation/modification step [48]. Physical modification increases the adsorptive capacity of modified biochar for the potentially toxic elements, nutrients and organic pollutants due to the increase of a specific surface area and development of micropores and mesopores on the biochar [59].

Although chemical activation has got some disadvantages, such as corrosion of used devices and high price, its activation effect in creation of additional and abundant functional groups on the biochar surface is better compared to physical activation. Chemical oxidation using mixtures of HNO_3 , KMnO_4 or $\text{HNO}_3/\text{H}_2\text{SO}_4$ can create acidic functional groups on the biochar surface, such as carboxylic, phenolic and hydroxyl [68]. Biochar modification by acids and bases can change the surface area and the amount and types of functional groups on the biochar surface. In one study [66], biochar originated from rice straw was produced at different temperatures (550 , 650 , 750°C); then it was modified using different oxidizing agents, including KOH , HNO_3 , H_2SO_4 , H_2O_2 and KMnO_4 . The effect of carbonization temperature and oxidizing agent on chemical properties of the biochar surface was investigated. Ketone, carbonyl, quinone, carboxyl-carbonate and alcoholic groups were found in many oxygenated samples. Modified biochar types had a low pH values compared to the initial biochar. This can be explained by many effects which increase the amount of acidic functional groups on the surface of the biochar. Modified biochar types had higher capacity for the adsorption of different molecular size organic pollutants, e.g., for iodine, phenol and methylene blue from solutions. This shows that alkalinity/acidity and hydrophilicity are main biochar surface properties which affect their adsorption from solutions. It is known that low-temperature biochar chemical oxidation using KMnO_4 , H_3PO_4 , HNO_3 and H_2O_2 mixtures can create acidic adsorptive sites, such as phenolic, carbonyl, carboxylic and lactonic on the biochar surface [57]. Besides O containing functional groups, the development of N containing functional groups (such as imide and amide) also accomplishes an important role in the environmental remediation due to their high complexation capacity with various potentially toxic elements (Cd, Zn and Cu). Unpaired oxygen electrons (such as carbonyls) and nitrogen enhance adsorption of polar and polarized compounds through the Lewis acids-bases interaction [43].

Changes in the chemical composition of biochar are minimal after exposure to water vapor because the water is inert and does not have high reactivity. Major modifications by vapor are based on the increment of biochar porosity, and there are no significant changes for

functional radicals. For example, Lou et al. [30] found that biochar made from sawdust and activated with steam increased its surface area, but had negligible effect on its surface functional groups. Meanwhile, chemical modifications occur by oxidation/reduction of biochar, which creates new functional groups.

In summary, the modification of biochar by exposing the surface to acidic solutions forms carboxylic groups on its surface and develops micropores that lead to an increase in the surface area [48]. Nitric acid causes fixation of functional groups through nitrification and oxidation, which inserts nitrogen moieties on the surface of biochar through electrophilic substitution [38]. However, activation of biochar with strong acids can be expensive in large scale and present environmental issues during the disposal of activation media, hence activation with rainwater and low concentration rhamnolipid solution, less-expensive and cleaner products, can be an alternative for biochar modification and increment of sorption capacity. Surfactant modification can provide positive and negative charges to the modified surface. One study [32] showed that surfactant can be adsorbed onto rice husk biochar through Van der Waals force. Surfactant binding also affects biochar surface properties. It was showed that surfactant-modified biochar had decreased specific surface area and total pore volume. It can be expected that biosurfactant (such as rhamnolipids) may have similar effect on the biochar surface properties.

In the future it is important to perform studies on various biochar modification techniques and different pollutant adsorption and desorption mechanisms [37]. There is a need to use cheap methods for the development of innovative and sustainable environmental technologies for the production of biochar which has multifunctionality. Clean biochar can be transformed to functional groups containing biochar after its modification, and this is the reason why functional groups in biochar matrix can enhance the amount of surface reactive groups, specific surface area and surface exchange sites. For example, waste water from agriculture treated by biochar can be held as a renewable source used for the irrigation or in agriculture. However, in the future there is a need to search for the environmentally friendly materials which could improve functionality of the biochar [61]. Another reason of this is a huge gap between demand and supply of activated carbon which is an economically expensive material (e.g., 246 \$/t of inactivated carbon compared to 1500 \$/t of activated carbon) [18]. This is the reason why it is important to search for novel sources for the production of carbonaceous material with desirable physical–chemical properties (e.g., high specific surface area, micro and mesoporosity, surface functionality, thermal stability, purity of the carbon, adsorptive capacity and chemical composition).

Conclusions

1. Decrease of biochar fraction increases its wettability. In this study, fine fraction of low-temperature birch bark biochar ($< 300\ \mu\text{m}$) had slight hydrophobicity (water drop penetration time was 3 s), since medium ($300\ \mu\text{m}$ – $900\ \mu\text{m}$) and coarse ($900\ \mu\text{m}$ – $1.6\ \text{mm}$) fractions were extremely hydrophobic (water drop penetration times of 6120 s and 18,541 s, respectively).
2. Steam of rainwater solution had the highest effect on the alteration of low-temperature birch bark biochar wettability. After modification, its wettability increased when water drop penetration time decreased from 18,541 s to 1564 s, although it still remained severely hydrophobic. It can be explained by the creation of hydroxyl, carboxyl and carbonyl functional groups, which showed higher peaks at $3433\ \text{cm}^{-1}$, $1697\ \text{cm}^{-1}$ and $1592\ \text{cm}^{-1}$ wavenumbers compared to the unmodified biochar.
3. Biochar modification with steam of 20 mg/l rhamnolipid solution had the highest effect on the enhancement of BET surface area, which was $15.2\ \text{m}^2/\text{g}$. This biochar type was highly microporous because its micropore surface area contained 98% of its total surface area. The rate of the micropore surface area to the total surface area showed that biochar modified with the steam of rhamnolipid solution had a higher proportion of their total surface area as micropores. It can be attributed to the fact that the modifying agent benefitted in removing tarry compounds that block the pores.
4. Comparing the effect of different nitric acid solution concentrations on the biochar wettability, 20% nitric acid solution concentration affected biochar wettability better, since its wettability was higher (3907 s) compared to biochar types modified with 40% and 65% nitric acid solution concentrations (4006 s and 4210 s, respectively). This can be explained by the modified biochar with the lowest solution concentration higher BET surface area ($4.36\ \text{m}^2/\text{g}$), higher micropore volume ($0.0008\ \text{cm}^3/\text{g}$) and development of oxygen–nitrogen containing functional groups, which were observed by the absorbance peaks at $3411\ \text{cm}^{-1}$, $1606\ \text{cm}^{-1}$ and $1385\ \text{cm}^{-1}$ wavenumbers. O and N containing functional groups have an important role in environmental protection technologies due to their high complexation capacity with various polar and polarized compounds through the Lewis acids–bases interaction.
5. Adsorption–desorption isotherms and pore size distribution showed that biochar modified with steam had more microporous and mesoporous structure compared to unmodified biochar and biochar modified with nitric acid solutions. In the case of biochar modified with the steam, pore volumes were higher at 3.1 to 16.9 nm pore

size range, which shows mesoporosity. In the case of unmodified biochar and biochar modified with the highest concentration nitric acid solution (65%), an additional peak at 60.5 nm pore size can be observed, which shows macroporosity.

References

- Ahmed MB, Zhou JL, Ngo HH, Guo W, Chen M (2016) Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresour Technol* 214:836–851. <https://doi.org/10.1016/j.biortech.2016.05.057>
- Ahmed MB, Zhou JL, Ngo HH, Guo W, Johir MAH, Sornalingam K, Rahman MS (2017) Chloramphenicol interaction with functionalized biochar in water: sorptive mechanism, molecular imprinting effect and repeatable application. *Sci Total Environ* 609:885–895. <https://doi.org/10.1016/j.scitotenv.2017.07.239>
- Alothman ZA (2012) A review: fundamental aspects of silicate mesoporous materials. *Mater* 5(12):2874–2902. <https://doi.org/10.3390/ma5122874>
- Baltrėnas P, Baltrėnaitė E, Usevičiūtė L (2019) Bioanglies hidrofiliškumo didinimo įrenginys ir būdas (LT patent No. LT 6661 B). Lithuanian Patent Office
- Bhatnagar A, Hoagland W, Marques M, Sillanpaa M (2013) An overview of the modification methods of activated carbon for its water treatment applications. *Chem Eng J* 219:499–511. <https://doi.org/10.1016/j.cej.2012.12.038>
- Chan WH, Mazlee MN, Ahmad ZA, Ishak MAM, Shamsul JB (2017) The development of low cost adsorbents from clay and waste materials: a review. *J Mater Cycles Waste Manag* 19:1–14
- Chemerys V, Baltrėnaitė-Gedienė E, Baltrėnas P, Dobelev G (2020) Influence of H₂O₂ modification on the adsorptive properties of birch-derived biochar. *Pol J Environl Stud* 29(1):579–588. <https://doi.org/10.15244/pjoes/105241>
- Chen W, Zhang S, He F, Lu W, Xu H (2019) Porosity and surface chemistry development and thermal degradation of textile waste jute during recycling as activated carbon. *J Mater Cycles Waste Manag* 21:315–325
- Das O, Sarmah AK (2015) The love-hate relationship of pyrolysis biochar and water: a perspective. *Sci Total Environ* 512–513:682–685. <https://doi.org/10.1016/j.scitotenv.2015.01.061>
- Fizinių ir technologijos mokslų centras (2019) Tolimųjų oro teršalų pernašų iš kitų valstybių poveikio bendram Lietuvos oro baseino užterštumo lygiui Lietuvoje įvertinimas—2016. Ataskaita [Report]
- Gao X, Wu L, Li Z, Xu Q, Tian W, Wang R (2018) Preparation and characterization of high surface area activated carbon from pine wood sawdust by fast activation with H₃PO₄ in a spouted bed. *J Mater Cycles Waste Manag* 20:925–936
- Godwin PM, Pan Y, Xiao H, Afzal MT (2019) Progress in preparation and application of modified biochar for improving heavy metal ion removal from wastewater. *J Mater Cycles Waste Manag* 4(1):31–42
- Gokce Y, Aktas Z (2014) Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol. *Appl Surf Sci* 313:352–359
- Gray M, Johnson MG, Dragila MI, Kleber M (2014) Water uptake in biochars: the roles of porosity and hydrophobicity. *Biomass Bioenerg* 61:196–205. <https://doi.org/10.1016/j.biombioe.2013.12.010>
- Guzel F, Saygili H, Saygili GA, Koyuncu F, Yilmaz C (2017) Optimal oxidation with nitric acid of biochar derived from pyrolysis of weeds and its application in removal of hazardous dye methylene blue from aqueous solution. *J Clean Prod* 144:260–265. <https://doi.org/10.1016/j.jclepro.2017.01.029>
- Hadjittofi L, Prodromou M, Pashalidis I (2014) Activated biochar derived from cactus fibre—preparation, characterization and application on Cu(II) removal from aqueous solutions. *Bioresour Technol* 159:460–464
- Huff MD, Lee JW (2016) Biochar-surface oxygenation with hydrogen peroxide. *J Environ Manage* 165:17–21. <https://doi.org/10.1016/j.envman.2015.08.046>
- Inyang M, Dickenson E (2015) The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: a review. *Chemosphere* 134:232–240. <https://doi.org/10.1016/j.chemosphere.2015.03.072>
- Jia YF, Thomas KM (2000) Adsorption of cadmium ions on oxygen surface sites in activated carbon. *Langmuir* 16(3):1114–1122. <https://doi.org/10.1021/la990436w>
- Kinney TJ, Masiello CA, Dugan B, Hockaday WC, Dean MR, Zygourakis K, Barnes RT (2012) Hydrologic properties of biochars produced at different temperatures. *Biomass Bioenerg* 41:34–43. <https://doi.org/10.1016/j.biombioe.2012.01.033>
- Li B, Yang L, Wang CQ, Zhang QP, Liu QC, Li YD, Xiao R (2017) Adsorption of Cd(II) from aqueous solutions by rape straw biochar derived from different modification processes. *Chemosphere* 175:332–340. <https://doi.org/10.1016/j.chemosphere.2017.02.061>
- Li K, Jiang Y, Wang X, Bai D, Li H, Zheng Z (2016) Effect of nitric acid modification on the lead(II) adsorption of mesoporous biochars with different mesopore size distributions. *Clean Technol Environ Policy* 18:797–805. <https://doi.org/10.1007/s10098-015-1056-0>
- Li Y, Shao J, Wang X, Deng Y, Yang H, Chen H (2014) Characterization of modified biochars derived from bamboo pyrolysis and their utilization for target component (furfural) adsorption. *Energy Fuels* 28(8):5119–5127. <https://doi.org/10.1021/ef500725c>
- Li Z, Liu X, Wang Y (2019) Modification of sludge-based biochar and its application to phosphorus adsorption from aqueous solution. *J Mater Cycles Waste Manag* 22:123–132
- Li Z, Zhang Y, Lin J, Wang W, Li S (2019) High-yield di-rhamnolipid production by *Pseudomonas aeruginosa* YM4 and its potential application in MEOR. *Molecules* 24(7):1433. <https://doi.org/10.3390/molecules24071433>
- Liao W, Thomas SC (2019) Biochar particle size and post-pyrolysis mechanical processing affect soil pH, water retention capacity, and plant performance. *Soil Syst* 3(1):14. <https://doi.org/10.3390/soilsystems3010014>
- Liu P, Liu WJ, Jiang H, Chen JJ, Li WW, Yu HQ (2012) Modification of biochar derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution. *Bioresour Technol* 121:235–240. <https://doi.org/10.1016/j.biortech.2012.06.085>
- Liu X, Liu L, Osaka Y, Huang H, He Z, Bai Y, Li S, Li J, Li H (2018) Study on desulfurization performance of MnO₂-based activated carbon from waste coconut shell for diesel emissions control. *J Mater Cycles Waste Manag* 20:1499–1506
- Liu Z, Niu W, Chu H, Zhou T, Niu Z (2018) Effect of the carbonization temperature on the properties of biochar produced from the pyrolysis of crop residues. *Biores* 13(2):3429–3446. <https://doi.org/10.15376/biores.13.2.3429-3446>
- Lou K, Rajapaksha AU, Ok YS, Chang SX (2016) Pyrolysis temperature and steam activation effects on sorption of phosphate on pine sawdust biochars in aqueous solutions. *Chem Spec bioavailab* 28(1–4):42–50. <https://doi.org/10.1080/09542299.2016.1165080>

31. Maneedaeng A, Flood AE (2016) Synergisms in binary mixtures of anionic and pH-insensitive zwitterionic surfactants and their precipitation behavior with calcium ions. *J Surfactants Deterg* 20:263–275. <https://doi.org/10.1007/s11743-016-1902-z>
32. Mathurasa L, Damrongsiri S (2017) Possibility of using surfactants to increase nitrogen adsorption on rice husk. *Appl Environ Res* 31:11–22
33. Mathurasa L, Damrongsiri S (2018) Low cost and easy rice husk modification to efficiently enhance ammonium and nitrate adsorption. *Int J Recycl Org Waste Agric* 7:143–151
34. Mendes AN, Filgueiras LA, Pinto CP, Nele M (2015) Physicochemical properties of Rhamnolipid biosurfactant from *Pseudomonas aeruginosa* PA1 to applications in microemulsions. *J Biomater Nanobiotechnol* 06(01):64–79. <https://doi.org/10.4236/jbnb.2015.61007>
35. Nguyen DH, Tran HN, Chao HP, Lin CC (2019) Effect of nitric acid oxidation of hydrochars to sorb methylene blue: an adsorption mechanism comparison. *Adsorpt Sci Technol* 37(7–8):607–622. <https://doi.org/10.1177/0263617419867519>
36. O'Reilly JM, Mosher RA (1983) Functional groups in carbon black by FTIR spectroscopy. *Carbon* 21(1):47–51. [https://doi.org/10.1016/0008-6223\(83\)90155-0](https://doi.org/10.1016/0008-6223(83)90155-0)
37. Oliveira FR, Patel AK, Jaisi DP, Adhikari S, Lu H, Khanal SK (2017) Environmental application of biochar: current status and perspectives. *Bioresour Technol* 246:110–122. <https://doi.org/10.1016/j.biortech.2017.08.122>
38. Peiris C, Nayanathara O, Navarathna CM, Jayawardhana Y, Nawalage S, Burk G, Karunanayake AG, Madduri SB, Vithanage M, Kaumal MN, Mlsna TE, Hassan EB, Abeysundara S, Perez F, Gunatilake SR (2019) The influence of three acid modifications on the physicochemical characteristics of tea-waste biochar pyrolyzed at different temperatures: a comparative study. *RSC Adv* 9:17612–17622
39. Qian Q, Machida M, Aikawa M, Tatsumoto H (2008) Effect of ZnCl₂ impregnation ratio on pore structure of activated carbons prepared from cattle manure compost: application of N₂ adsorption-desorption isotherms. *J Mater Cycles Waste Manag* 10:53–61
40. Razak IS, Latif MT, Jaafar SA, Khan MF, Mushrifah I (2015) Surfactants in atmospheric aerosols and rainwater around lake ecosystem. *Environ Sci Pollut Res Int* 22(8):6024–6033. <https://doi.org/10.1007/s11356-014-3781-z>
41. Rikalović MG, Vrvíč M, Karadžić IM (2015) Rhamnolipid biosurfactant from *Pseudomonas aeruginosa*—from discovery to application in contemporary technology. *J Serb Chem Soc* 80(3):279–304. <https://doi.org/10.2298/JSC140627096R>
42. Sahin O, Taskin MB, Kaya EC, Atakol O, Emir E, Inal A, Gunes A (2017) Effect of acid modification of biochar on nutrient availability and maize growth in a calcareous soil. *Soil Use Manag* 33:447–456. <https://doi.org/10.1111/sum.12360>
43. Sajjadi B, Chen WY, Egiebor NO (2018) A comprehensive review on physical activation of biochar for energy and environmental applications. *Rev Chem Eng*. <https://doi.org/10.1515/revce-2017-0113>
44. Setiawati E, Prijono S, Mardiana D, Prayogo C, Soemarno W (2019) Impact of pyrolysis temperature and water quenching on hydrophilicity of biochar derived from durian wood waste. *Biosci Res* 16(2):2047–2062
45. Shaheed R, Wan Mohtar WM, Ahmed ES (2017) Ensuring water security by utilizing roof-harvested rainwater and lake water treated with a low-cost integrated adsorption-filtration system. *Water Sci Eng* 10(2):115–124
46. Shim T, Yoo J, Ryu C, Park YK, Jung J (2015) Effect of steam activation of biochar produced from a giant Miscanthus on copper sorption and toxicity. *Bioresour Technol* 197:85–90. <https://doi.org/10.1016/j.biortech.2015.08.055>
47. Shimada M, Iida T, Kawarada K, Chiba Y, Momoto T, Pkayama T (2000) Porous structure of activated carbon prepared from waste newspaper. *J Mater Cycles Waste Manag* 2:100–108
48. Sizmur T, Fresno T, Akgul G, Frost H, Moreno-Jimenez E (2017) Biochar modification to enhance sorption of inorganics from water. *Bioresour Technol* 246:34–47. <https://doi.org/10.1016/j.biortech.2017.07.082>
49. Smetanova A, Dotterweich D, Ulrich U, Fohrer N (2013) Influence of biochar and terra preta substrates on wettability and erodibility of soil. *Z Geomorphol* 57:111–134. <https://doi.org/10.1127/0372-8854/2012/S-00117>
50. Tan IAW, Abdullah MO, Lim LLP, Yeo THC (2017) Surface modification and characterization of coconut shell-based activated carbon subjected to acidic and alkaline treatments. *J Appl Sci Eng* 4(2):186–194. <https://doi.org/10.33736/jaspe.435.2017>
51. Tasca AL, Puccini M, Stefanelli E, Gori R (2020) Investigating the activation of hydrochar from sewage sludge for the removal of terbuthylazine from aqueous solutions. *J Mater Cycles Waste Manag* 22(5):1539–1551
52. Tiso T, Zauter R, Tulke H, Lauchtle B, Li WJ, Behrens B, Wittgens A, Rosenau F, Hayen H, Blank LM (2017) Designer rhamnolipids by reduction of congener diversity: production and characterization. *Microb Cell Fact* 16:225. <https://doi.org/10.1186/s12934-017-0838-y>
53. Tsai WT, Jiang TJ, Lin YQ (2018) Conversion of de-ashed cocoa pod husk into high-surface-area microporous carbon materials by CO₂ physical activation. *J Mater Cycles Waste Manag* 21(2):308–314
54. Tsyntarski B, Toteva VB, Nickolov RN, Banchev I, Stoycheva I, Gonsalvesh L, Petrova B, Georgiev G, Vasileva M, Budinova T, Petrov N (2020) Conversion of waste algae from biodiesel production to valuable gas, liquid and solid products. *J Mater Cycles Waste Manag* 22:1176–1183
55. US Environmental Protection Agency (2004) Biopesticides registration action document, rhamnolipid biosurfactant (PC Code 110029)
56. Usevičiūtė L, Baltrėnaitė E (2020) Methods for determining lignocellulosic biochar wettability. *Waste Biomass Valori* 11:4457–4468. <https://doi.org/10.1007/s12649-019-00713-x>
57. Vijayaraghavan, (2019) Recent advancements in biochar preparation, feedstocks, modification, characterization and future applications. *Environ Technol Rev* 8(1):47–64
58. Vu KA, Tawiq K, Chen G (2015) Rhamnolipid transport in biochar-amended agricultural soil. *Water Air Soil Pollut* 226:256. <https://doi.org/10.1007/s11270-015-2497-0>
59. Wang B, Gao B, Fang J (2017) Recent advances in engineered biochar productions and applications. *Crit Rev Environ Sci Technol* 47(22):2158–2207
60. Wang J, Wang S (2019) Preparation, modification and environmental application of biochar: a review. *J Clean Prod* 227(1):1002–1022
61. Wei D, Li B, Huang H, Luo L, Zhang J, Yang Y, Guo J, Tang L, Zeng G, Zhou Y (2018) Biochar-based functional materials in the purification of agricultural wastewater: fabrication, application and future research needs. *Chemosphere* 197:165–180
62. Wolak E, Vogt E, Szczurowski J (2017) Chemical and hydrophobic modification of activated WD-axtra carbon. *Energ Fuel* 14:1–8
63. Wu L, Shang Z, Wang H, Wan W, Gao X, Li Z, Kobayashi N (2018) Production of activated carbon from walnut shell by CO₂ activation in a fluidized bed reactor and its adsorption performance of copper ion. *J Mater Cycles Waste Manag* 20:1676–1688
64. Wu W, Li J, Niazi NK, Muller K, Chu Y, Zhang L, Yuan G, Lu K, Song Z, Wang H (2016) Influence of pyrolysis temperature on lead immobilization by chemically modified coconut fiber-derived biochars in aqueous environments. *Environ Sci Pollut Res* 23(22):22890–22896

65. Xu C, Zhou G, Qiu H (2017) Analysis of the microscopic mechanism of coal wettability evolution in different metamorphic states based on NMR and XPS experiments. *RSC Adv* 7(76):47954–47965. <https://doi.org/10.1039/C7RA07905B>
66. Yakout SM, Daifullah AEHM, El-Reefy SA (2015) Pore structure characterization of chemically modified biochar derived from rice straw. *Environ Eng Manag J* 14(2):473–480
67. Yang X, Zhang S, Ju M, Liu L (2019) Preparation and modification of biochar materials and their application in soil remediation. *Appl Sci* 9(7):1365
68. Zakaria ZA (2018) Sustainable technologies for the management of agricultural wastes. Springer, Singapore

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Application of pyrogenic carbonaceous product for immobilisation of potentially toxic elements in railway sleepers and polluted soil

L. Usevičiūtė¹ · E. Baltrėnaite¹

Received: 28 May 2017 / Revised: 18 September 2017 / Accepted: 3 January 2018 / Published online: 17 July 2018
© Islamic Azad University (IAU) 2018

Abstract

In the last decades, there is a growing concern about soils polluted with potentially toxic elements (PTE) and their negative impact on the ecosystems. In the recent year, biochar is intensively investigated not only for carbon sequestration or soil productivity enhancement but also like a new sorbent for polluted soils' remediation. The aim of this work is: (1) to assess the effect of two pine wood biochar types (produced at 450 and 700 °C temperatures) on the PTE mobility in the solution of the former sewage sludge soil; (2) to make risk assessment of pyrogenic carbonaceous product made from railway sleepers and (3) to assess pine wood biochar (700 °C) impact on the PTE uptake to oat (*Avena sativa* L.). Three different experiments were done: (1) incubation; (2) leaching and (3) bioaccumulation. Incubation experiment showed that both pine wood biochar types showed good immobilisation efficiency in the case of Cd (> 85%), but lower temperature biochar (450 °C) had higher efficiency used in the immobilisation of Zn (78%) and Cu (76%) in multi-polluted soil. Leaching experiment showed that both biochar types well retained Pb (> 99%), but lower temperature biochar had greater retention efficiency in the case of Cu (93%).

Keywords Pyrogenic carbonaceous product · Leaching test · Pine wood · Potentially toxic elements · Pyrolysis · Soil pollution · Immobilisation of elements

Introduction

Soil pollution with potentially toxic elements poses a global challenges in mining sites and industrially urban soils which represent a wide range of total organic carbon (TOC) (Uchimiya et al. 2011). PTEs are released into the environment by both natural and anthropogenic sources. Some soils have higher levels of PTE due to volcanic activity or erosion of natural rocks. Anthropogenic activities such as smelting, mining, use of pesticides, fertilisation, amending of sludge are also responsible for PTEs accumulation in soils (Gul et al. 2014). Soil contamination with PTEs is a very serious problem, especially in the agricultural lands (Khan et al. 2015). The most important contaminants are cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni) and zinc (Zn). Because these metallic PTEs from

polluted soils can become bioavailable and/or phytoavailable they may accumulate into the environment and enter the food chains. This contamination threatens soil quality, plant survival and human health. Excessive PTEs concentrations may cause hazards both for humans and ecosystems through direct consumption or contact with the contaminated soil, food chains and drinking of polluted groundwater (Yathavakulasingam et al. 2016).

PTEs in the soil can be divided into these two fractions: (1) inert fraction, assumed as the nontoxic fraction; (2) the labile fraction, assumed to be potentially toxic. To assess the bioavailability of PTEs, only the soil labile fraction is taken into account because this fraction is often called the bioavailable fraction. The availability of PTEs for plants and microorganisms in the soil depends on different constituents of soil, such as carbonates, metal hydroxides, organic matter and silica (Yobouet et al. 2010). PTEs bioavailability is one of the most serious problems in agricultural and environmental investigations (Gul et al. 2014). The mobility and bioavailability of PTEs are controlled by complex redox and acid–base chemistry and the availability of sorption sites, such as the iron and aluminium (hydr)oxides, clay and natural organic matter (Uchimiya et al. 2011). Carboxyl,

Editorial responsibility: M. Abbaspour

✉ L. Usevičiūtė
luiza.useviciute@vgtu.lt

¹ Department of Environmental Protection, Vilnius Gediminas Technical University, Saulėtekio Av. 11, Vilnius, Lithuania



phenolic hydroxyl and other oxygen-containing surface functional groups of these soil components play central roles in binding metal ions (Sposito 1989).

A variety of methods have been developed for remediation of contaminated soils and groundwater. Conventional soil remediation techniques (soil washing by acids, soil digging *ex situ*) contribute to environmental degradation and are not economically feasible on a large scale (Houben et al. 2013a, b), especially in developing countries (Rajakaruna et al. 2006). Due to this, recent research has focused on the sustainable remediation techniques (Al-Wabel et al. 2015). Remediation of PTEs-contaminated soil with various organic (compost, fertilisers, agricultural residues) and inorganic amendments (biochar, red mud, limestone) has attracted attention due its low cost and environmental benefits. The use of organic and inorganic by-products as soil amendments exemplifies a strategy for converting wastes into resources. Inorganic amendments are effective in reducing metal bioavailability due to the introduction of additional binding sites for PTEs and due to the pH effects (Gul et al. 2014). Many of these amendments are by-products of industrial activities and, therefore, cheaper and available in large quantities. Different kinds of inorganic materials have been used to decrease soil pollution with PTEs.

Biochar is a pyrolysed carbon rich by-product of plant and animal origin, organic substances produced by heating (at $> 250\text{ }^{\circ}\text{C}$ temperature) under low oxygen conditions (Antal and Gronli 2003). In the recent years, biochar is gaining attention by scientists due to its impending role in carbon sequestration, reducing greenhouse gas emissions, nutrient leaching and use for irrigation and fertilisers (Nguyen et al. 2009). Biochar physical–chemical properties can differ among different feedstock and pyrolysis conditions (Meyer et al. 2011). It is proved that biochar has magnificent potential in stabilising many organic (aromatic hydrocarbons) and inorganic pollutants which are present in soil and groundwater (Barrow 2012). Biochar application can also significantly reduce the availability of trace elements to plants. It can significantly immobilise Cd, Zn and Pb in soil (Beesley et al. 2010; Cao et al. 2011; Uchimiya et al. 2012), complex metal ions on its surface and, therefore, reduce their bioavailability (Beesley et al. 2011).

In recent years, studies have highlighted biochar as an effective soil amendment to immobilise PTEs in soils (Ahmad et al. 2014; Rajapaksha et al. 2012). Herath et al. (2017) documented that the addition of biochar to serpentine soil immobilises Cr, Ni and Mn by reducing metal toxicity in tomato plant. Wagner and Kaupenjohann (2014) compared biochar (corn, $750\text{ }^{\circ}\text{C}$) and hydrochar (poplar, $200\text{ }^{\circ}\text{C}$) regarding their possibility in immobilisation of PTEs in former sewage sludge fields. Hydrochar had no effect on metals mobility despite the fact that yields of grains were reduced (because of reduced N availability). Biochar

reduced bioavailable metal forms in plants, especially for Zn and Cd. Otherwise, biochar increased concentrations of metals in filtrates, especially for Pb and Cu. Wagner and Kaupenjohann (2014) concluded this could happened because of the complexation of organic substances or development of mobile colloids. Rees et al. (2014) investigated biochar (mixed wood, $450\text{ }^{\circ}\text{C}$) effect on the Cu, Cd and Ni mobility and sorption of metals in polluted soils (Cambisols) in northern France. They found effective metals immobilisation in soils amended with biochar when particles size distribution of biochar and increase of soil pH controlled short-time sorption of these metals. Understanding the behaviour to avoid ecotoxicological impacts, the effects of biochar on nutrient and PTEs behaviour as well as transport are some of the areas that require more attention.

The aim of this research was to assess the biochar effect on PTE (Pb, Cr, Cd, Zn, Cu and Ni) bioavailability in soil and uptake by oat (*Avena sativa* L.), PTE immobilisation in polluted soil depending on time and PTE leaching from polluted soil amended with biochar and two pyrogenic carbonaceous products made from railway sleepers. For this reason, there were made 28 days long incubation experiment with soil from former sewage sludge fields amended with two biochar types (PB450—pine wood biochar produced at $450\text{ }^{\circ}\text{C}$ temperature and PB700—pine wood biochar produced at $700\text{ }^{\circ}\text{C}$ temperature) mixed at different ratios (1/5, 1/10 and 1/20), 35 days long plant experiment with oat and leaching experiment when waste (polluted soil amended with two pine wood biochar types and two railway sleepers pyrogenic products) were percolated by one-way stream with deionised water.

Materials and methods

PTE-polluted soil

PTE-polluted soil was collected from the former sewage sludge amended fields from Molainiai (district of Panevėžys, Lithuania; E 519428; N 6176087). In 1961–1963, the fields were operated for the industrial waste. The exploitation ended in 1978. Former sewage filtration fields were amended with sludge. That sludge was severely polluted with PTE. The most common pollutant was Cd, which exceeded limit values more than 160 times (Ataskaita...2010). The territory was also polluted with Cu, which exceeded limited values by 16.5 times. In the sewage sludge, there were higher concentrations of Ni, Cr and Zn. The overall area of polluted soil formed about 27.13 ha in the former filtration fields. For the sake of experiments, there were collected about 20 kg of the top soil (15 cm depth). There were taken 20 samples which later were homogenised. Samples were taken by the method of digging by the hand with a stainless shovel (ISO 10381-2:2002). Then, soil was dried at $105\text{ }^{\circ}\text{C}$ temperature



for 2 days, crushed and sieved with < 4 mm size sieve. The prepared samples were subjected for the following parameters: pH, humidity, density, total carbon, organic matter and PTEs concentration.

Production of pyrogenic carbonaceous product (PCP)

Potentially clean pine wood biomass (pine (*Pinus sylvestris* L.) for PCP production was collected from a potentially clean territory in Vilnius city which is located in the south-east region of Lithuania (54°43'37"25°20'12") (Komkiene and Baltreinaite 2016). Samples were carved to blocks of 15 mm³ volume. There were used 4.5 kg of clean pine wood for the production of PCP. Contaminated woody biomass (pine wood railway sleepers) was collected from the railway station which was located in Vilnius city. Pine wood pyrolysis was performed in the muffle furnace (E5CK-T) at 450 and 700 °C temperature for 2 h. There were produced four different types of PCP: pine wood PCP made at 450 °C temperature (PB450), pine wood PCP made at 700 °C temperature (PB700), pine wood railway sleepers PCP made at 450 °C temperature (PSB450) and pine wood railway sleepers PCP made at 700 °C temperature (PSB700). The following properties for PCP were investigated: yield, ash content, density, pH, total carbon, PTE concentration and cation exchange capacity (Šilinskaitė 2014).

Incubation experiment

The 0.01 M CaCl₂ extraction provides information about the soil solution and exchangeable metal pools and can be regarded as an indicator of metal solubility, bioavailability and mobility in soils (Lambrechts et al. 2011). This procedure has also been used to study the influence of ageing and bioavailability of metals in soils (Schreck et al. 2011). The effect of biochar on PTEs immobilisation can be assessed by monitoring CaCl₂-extractable metal concentrations released by soil and soil-biochar mixtures during the incubation experiment (Houben et al. 2013a, b). Plastic plant pots (400 cm³) were filled with 400 g of soil and biochar mixture. Incubation lasted for 28 days at 20 ± 1 °C temperature. Throughout the experiment, the moisture content of each mixture was kept at 75% water holding capacity by adding water and weighing the pots on a weekly basis. After 1 h, 7, 14, 21 and 28 days, 10 g of each soil was sampled and subjected to a CaCl₂ (0.01 M) extraction. Samples were prepared from 100 ml of 0.01 M CaCl₂ solution and shaken at 20 °C temperature for 2 h. After shaking, the pH was measured and the extract was separated from the solid residue by filtration. PTEs concentration in the extract was determined by flame atomic spectrophotometer (FAAS).

PTE leaching from polluted soil and pine biochar mixture/sleepers pyrogenic product experiment

Analysis of PTEs mobility in PTEs polluted soil mixed with two pine wood biochar types (PB450 and PB700) and two pyrogenic product types from sleepers were investigated using up-flow percolation test (CEN/TS 14405). Leaching tests are designed with specific objectives, such as to determine the effectiveness of a waste treatment process, to estimate a source term or end point for risk assessment purposes (An assessment... 2003).

The up-flow percolation test was carried out using columns of 5 cm diameter and 30 cm height (Pečkaitė and Baltrėnaitė 2015). Leaching equipment was made from water container, four columns, inlet and outlet hoses and eluate collection bottles. Samples were prepared of polluted soil from former sewage sludge fields mixed with two pine biochar types at three different ratios (1/5, 1/10 and 1/20) and from two PCP types (PSB450 and PSB700) made from railway sleepers. Equipment (columns, filters, hoses, bottles) was rinsed with distilled water. The empty column was filled with well-crushed material and weighed to an accuracy of 1 g. The bottom section was equipped with a filter plate and a pre-filter to the column. When columns were filled in wastes (soil amended with PB450 and PB700; PSB450 and PSB700), the column was saturated with deionised water. The saturation was stopped when a column with a sample was fully saturated. In order to balance a process, a column with soil/carbonaceous product was left for at least 2 days. The flow rate was set 15 ± 2 cm through the empty column. To control leaching process, the first eluate was collected. Solubility of inorganic constituents is strongly influenced by pH and redox potential. Then, pH in eluate was measured. The outlet hose was connected to an eluate collection bottle. The hydrostatic pressure and eluate samples collection then started. The first eluate was taken when volume of eluate reached $(0.1 \pm 0.002) \times$ the mass of the test portion (m_o). The second and following eluates were collected into the bottle. According to different fraction volumes, all seven eluates were collected and pH was measured in each.

Time, volume, pH and L/S ratio were noted just after collection. PTEs (Cd, Pb, Cr, Ni, Zn and Cu) concentrations were measured in the eluates using a flame atomic spectrophotometer (FAAS).

Experiment of PTE bioavailability and uptake by oat (*Avena sativa* L.)

An experiment with plants was performed to assess the effect of pine biochar (PB700) on the PTE bioavailability in oat grown in polluted soil from former sewage sludge fields amended with biochar at three different ratios (1/5; 1/10; 1/20). Plastic pots (400 cm³) were filled in



with 200 g of soil and biochar mixture. Plants from soil amended with biochar were compared to plants from unamended soil (control). All treatments were carried out in three replicates. Each pot was visually checked for sufficient water content which was necessary for optimal plant growth conditions. Pots were kept in a room temperature. In the beginning of the experiment, there were 10 seeds of oat planted in every pot. After 10 days, the plants were thinned to three plants per pot.

The shoots were harvested after 35 days and fresh weight was determined immediately. The plants were washed with deionised water and dried at 60 °C temperature for 24 h before dry mass was determined (Wagner 2014). Then, PTEs concentration in plants was determined using a flame atomic spectrophotometer (Buck Scientific—210VGP). Total PTE concentration was measured after the acid digestion process. The acid digestion process consisted of every sample (50 mg) mixed with 3 ml HNO₃ (65%) and 9 ml (HCl). After that, the samples were placed in special vessels and then into Ethos 900 Milestone Microwave apparatus and heated for 43 min. Then, solutions were poured into bottles of 50 ml volume which then were supplemented with deionised water till the limit of 50 ml (Butkus and Baltrėnaitė 2007).

Statistical analysis

Statistical analysis to compare the average results of the different treatments was performed using one-way analysis of variance (ANOVA) (Houben et al. 2013a, b). Homogeneity of variances was tested using Levene's test. Paired comparisons between the treated and the control soils were carried out using Student's *t* test.

Results and discussion

Physical–chemical properties of pyrogenic carbonaceous products and soil

In this work, yield of pine wood biochar and pine sleepers pyrogenic products decreased from 27.34–15 to

21.64–11.81%, when pyrolysis temperature increased from 450 to 700 °C (Table 1).

A similar biochar productivity tendency with rising pyrolysis temperature was determined by Gai et al. (2014), when productivity of wheat, corn straw and peanut shell biochar decreased from 36.8–32.4 to 25.8–22.8%, when pyrolysis temperature increased from 400 to 700 °C. One explanation could be that there is higher loss of volatile compounds in higher pyrolysis temperatures (Novak et al. 2009). It could be concluded that in lower pyrolysis temperatures, there is a higher biochar yield and it has richer composition of volatile compounds compared to high pyrolysis temperatures (Jindo et al. 2014). A high amount of lignin in biomass material determines higher biochar yield (Amonette and Joseph 2009).

Ash content differed from 23.25 to 23.97% in the case of pine wood biochar types and from 26.95 to 30.91% in the case of pine sleepers pyrogenic product types and it increased with the increase of temperature. A similar tendency occurred in Mukherjee et al. (2011), when biomass of oak wood (*Quercus lobata*), pine wood (*Pinus taeda*) and grass (*Tripsacum floridanum*) was pyrolysed at 400 and 650 °C temperatures. Biochar ash content increased in higher pyrolysis temperatures mainly due to rising content of minerals (Cao et al. 2009). Tendency of increasing biochar ash content with increasing pyrolysis temperature was similar in different biochar types produced both from pine wood and both from animals' manures (Chen et al. 2008).

pH of pine wood biochar types increased from 7.3 to 8.36 and in the case of sleepers pyrogenic product types—from 6.63 to 7.87 when pyrolysis temperature increased. The biochar pH value rose in a higher pyrolysis temperature probably due to concentrations of unpyrolysed inorganic elements which have already been in the original material (Novak et al. 2009). Normally, biochar types with higher ash content have higher pH values compared to those with low ash content (Lehmann et al. 2011). Biochar pH can change with time and it can both decrease and increase depending on the feedstock.

Content of total carbon rose with increasing pyrolysis temperature from 450 to 700 °C in all PCP types. Amount of total carbon in the case of pine biochar increased from 86.48 to 93.01% and in the case of pine sleepers from 80.92 to 89.91%.

Table 1 Physical–chemical properties of polluted soil and carbonaceous products

Pyrogenic carbonaceous product type	Pyrolysis temperature (°C)	Yield (%)	Ash content (%)	Density (g/cm ³)	pH	Total organic carbon C (%)	Cation exchange capacity (cmol _c /kg)
Clean pine wood	450	27.34 ± 0.13	26.95 ± 1.70	0.22 ± 0.01	7.3 ± 0.11	86.48 ± 0.54	0.48 ± 0.12
	700	15 ± 2.46	30.91 ± 2.02	0.27 ± 0.01	8.36 ± 0.02	93.01 ± 0.99	2.07 ± 1.26
Railway sleepers (pine wood)	450	21.64 ± 1.12	23.84 ± 1.09	0.19 ± 0.004	6.63 ± 0.99	80.92 ± 0.93	0.77 ± 0.3
	700	11.81 ± 1.94	23.97 ± 2.04	0.15 ± 0.003	7.87 ± 0.13	89.91 ± 0.86	0.11 ± 0.09



All pyrolysis product types corresponded to standards of the European Biochar Certificate for total carbon content and exceeded 50% C_{tot} value. All pyrogenic product types corresponded to the parameter that organic carbon content in pyrolysed char differed from 5 to 95% depending on used temperature and temperature of the process. Pyrolysed organic matter which has < 50% of carbon content is classified as pyrogenic carbonaceous matter (EBC 2016).

Cation exchange capacity (CEC) is the ability of matter to retain positive charged cations and in this work CEC of biochar types significantly differed among different feedstock types and pyrolysis temperature. In the case of clean pine wood, when pyrolysis temperature rose from 450 to 700 °C CEC also increased (from 0.48 to 2.07 cmol_c/kg). A similar tendency was obtained in other works (Nelissen et al. 2014; Gaskin et al. 2008) when CEC of pine wood biochar rose (from 38.6 to 68.8 cmol_c/kg) when pyrolysis temperature increased from 450 to 650 °C (Nelissen et al. 2014). An opposite tendency occurred in the case of sleepers pyrogenic product types. This work showed that when pyrolysis temperature (450–700 °C) rises CEC of sleepers pyrogenic product types decreases (0.77–0.11 cmol_c/kg). These results are similar to Gai et al. (2014) and Crombie et al. (2014) results, when all biochar types (from wheat, corn straw, peanut shell) had higher CEC at 400 and 500 °C pyrolysis temperatures compared to those which were produced at 600 and 700 °C temperatures.

Soil pH is one of the most important indicators of chemical properties of soil (Sujetovienė 2011). Soil acidity directly impact availability of nutrients in plants, their development, productivity, composition of soil microorganisms, decomposition of organic matter, carbon and nitrogen immobilisation in soil, leaching of the elements and their emissions to the atmosphere (Mažvila et al. 2011). In this research, soil pH value reached 7.55 (Table 2); therefore, this soil from Molainiai was classified as average alkaline (pH from 7.5 to 8.5).

Soil density is an essential and widely used soil indicator. It describes soil's aeration and penetrability (Sujetovienė 2011). It was determined that the analysed soil density was 0.95 g/cm³. This density is similar to other work where fine sand particles dominated in sludge granular composition and density of the natural sludge varied from 0.926 to 2.138 g/cm³ (DGE Baltic... 2010). According to the density (0.8–1.2 g/cm³), investigated soil is optimal for growing plants.

Soil water content is an important parameter for all types of soil analysis: measuring water holding capacity, available moisture content to plants, infiltration, pores' size distribution and soil penetrability (Sujetovienė 2011). In this work, soil moisture reached 22.43%. According to moisture values,

investigated soil is near to optimal conditions for growing plants, when pores are filled with air and water up to 25%.

Organic matter and especially humus content is one of the indicators of soil quality showing soil's resistance to physical degradation (Liaudanskienė et al. 2008). Most usually soil consists of 80–90% of the mineral part and less than 10% of the organic part. Soil's organic part is made of organic residues and humus (Jackson 1993). In this research, organic matter in soil reached 8.77%. According to dry organic matter mass (%) this soil is classified as having average organic matter (from 6 to 20%) (EN ISO 14688-2 2004).

Carbon (C) is the main soil's organic matter component. Soil's organic carbon forms a huge part of the global carbon cycle; its content depends on photosynthesis input in soil and respiration, erosion and leaching loss (Liaudanskienė et al. 2008). The amount of total carbon in soil reached 9.64% in this study.

According to the European Biochar Certificate, certain thresholds for PTE must be kept. The following maximum values for PTE, for the basic quality grade (Pb < 150 mg/kg DM; Cd < 1.5 mg/kg DM; Cu < 100 mg/kg DM; Ni < 50 mg/kg DM; Zn < 400 mg/kg DM; Cr < 90 mg/kg DM), correspond to the German Federal Soil Protection Act (Bundes-Bodenschutzverordnung) and for the premium quality grade (Pb < 120 mg/kg DM; Cd < 1 mg/kg DM; Cu < 100 mg/kg DM; Ni < 30 mg/kg DM; Zn < 400 mg/kg DM; Cr < 80 mg/kg DM), correspond to the Swiss Chemical Risk Reduction Act. These thresholds which relate to the total dry biochar mass are shown in Table 3.

According to the PTE concentrations (mg/kg DW) in four pyrogenic product types, all types corresponded to premium biochar quality except for Ni in PSB700 type which corresponded to the values of the biochar of the basic quality grade.

The highest PTE concentrations in the contaminated soil which exceeded thresholds (HN 60:2015) were in the case of Cu (276.47 mg/kg), Ni (100.74 mg/kg) and Cd (9.56 mg/kg) (Table 3). Cd concentration in the soil for approx. 637% exceeded the threshold for Cd (1.5 mg/kg), Cu for 3.69 times and Ni for 134%. Cd concentrations in soil were similar to the research conducted in 2013, when in the top layer of the soil the thresholds were exceeded more than one hundred times and in deeper layers—1.5 to 2 times (Geotestus 2013). Pb concentration in soil reached 15.44 mg/kg and did not exceed the threshold for Pb in soil (80.00 mg/kg). In the research carried out in 2013, Pb concentrations did not exceed the thresholds and were close to natural background values (Geotestus 2013).

Table 2 Physical–chemical properties of different pyrogenic carbonaceous product types (mean value ± SD, $n = 4$)

Soil	pH	Moisture (%)	Density (g/cm ³)	Total carbon (%)	Organic matter (%)
From Molainiai	7.55 ± 0.08	22.43 ± 10.28	0.95 ± 0.02	9.64 ± 0.09	8.77 ± 2.57



Table 3 PTEs concentrations (mg/kg DW) in polluted soil and carbonaceous products (average $\pm$ SD, $n = 9$)

PTE	Polluted soil	Pine wood biochar, 450 °C temperature (PB450)	Pine wood biochar, 700 °C temperature (PB700)	Pine sleepers carbonaceous product, 450 °C temperature (PSB450)	Pine sleepers carbonaceous product, 700 °C temperature (PSB700)	Threshold for premium biochar quality grade (according to EBC)	Maximum PTE concentration in soil (HN 60:2015)
Cd	9.56 $\pm$ 1.75	0.27 $\pm$ 0.04	0.9 $\pm$ 0.59	0.9 $\pm$ 0.05	0.18 $\pm$ 0.15	1	1.5
Pb	15.44 $\pm$ 2.09	6.22 $\pm$ 1.62	13.44 $\pm$ 13.97	8.07 $\pm$ 3.09	9.03 $\pm$ 3.49	120	80
Zn	228.68 $\pm$ 29.09	330.37 $\pm$ 150.85	82.44 $\pm$ 19.98	118.3 $\pm$ 8.74	140.71 $\pm$ 9.3	400	300
Cu	276.47 $\pm$ 18.45	16.87 $\pm$ 4.05	25.99 $\pm$ 20.93	22.41 $\pm$ 22.17	32.74 $\pm$ 6.26	100	75
Ni	100.74 $\pm$ 6.89	17.76 $\pm$ 4.93	10.75 $\pm$ 6.04	17.92 $\pm$ 3.83	32.74 $\pm$ 5.36	30	75
Cr	98.53 $\pm$ 7.92	25.75 $\pm$ 4.9	7.47 $\pm$ 3.96	19.72 $\pm$ 3.14	35.4 $\pm$ 9.64	80	80

Soil pH

Figure 1 shows that soil pH from the incubation experiment reached maximum value ($= 7.2$) after 336 h ($= 14$ days) in the case of both biochar types, and later, it gradually decreased in the case of PB700 and increased in the case of PB450. In the leaching experiment, eluates' pH decreased with time in the case of both biochar types (Fig. 2). In the case of both biochar types, maximum pH (> 8) values reached after the first minute and later gradually decreased. According to Wong and Swift (2003), insignificant pH increase in the beginning of the experiment could be explained by decarboxylation of organic anions and ammonification and gradual pH decrease could be explained by nitrification.

Comparing two biochar types, PB450 increased soil pH after biochar addition ($p = 0.22$ insignificant; Fig. 1a), and in the case of PB700 soil, pH insignificantly decreased with time ($p = 0.66$; Fig. 2b). This growth of pH is constant when biochar has alkaline origin. Basic cations (Ca, Mg, K, Na) which are in the biomass are transferred into oxides, hydroxides and carbonates during pyrolysis process (Yuan et al. 2011). Due to these alkaline compounds solubility, many

biochar types serve the alkaline function in the soil (Hass et al. 2012).

Immobilisation of PTE in polluted soil using the incubation experiment

In the beginning of the experiment, after 1 h, better element's immobilisation effect between two pine carbonaceous product types was determined in the case of PB700 type (Fig. 3). Comparing all PTEs Cu concentration decreased the most in the extracts of PB700 and soil mixtures: 79.2, 75.27 and 76.28% at the ratios of 1/5, 1/10 or 1/20. Ni immobilisation by this biochar reached 12.32, 27.4 and 23.28% at the ratios of 1/5, 1/10 or 1/20. Biochar, respectively, produced at lower temperature (450 °C) in the beginning of the experiment retained Cu (76.76%, 76.21% or 73.39% at the ratios of 1/5, 1/10 and 1/20, respectively).

At the end of the experiment (after 672 h/28 days), PB450 immobilised four elements out of six ($\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb}$) (Fig. 4). However, this biochar type had no effect on the immobilisation of Cd and Ni. The most immobilised element was Cd (57.89 and 86.01% at the ratios of 1/10 and 1/20), Zn (63.26, 78.1 and 77.62% at the ratios of 1/5, 1/10

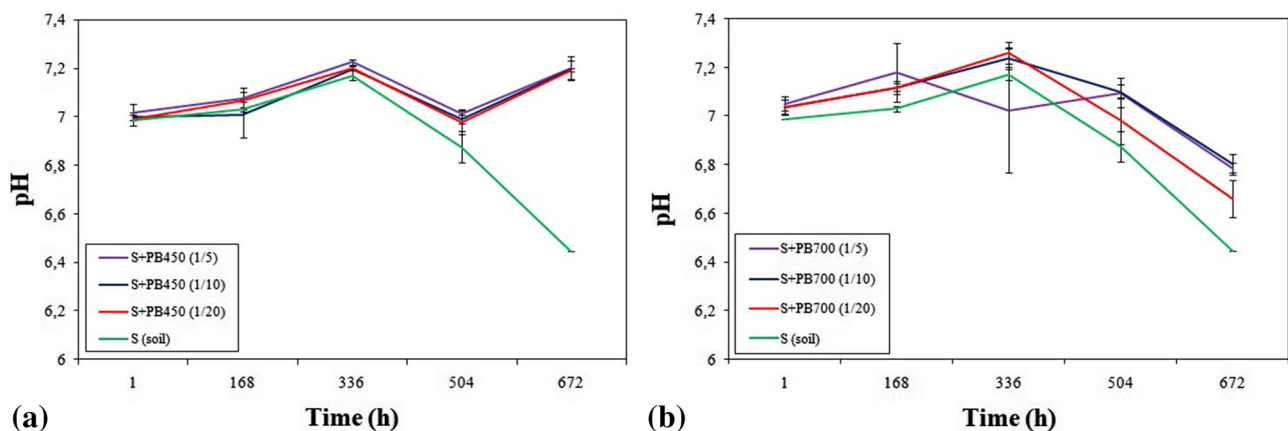


Fig. 1 pH differences in the CaCl_2 extracts depending on time (h), **a** PB450 and **b** PB700 biochar (S—polluted soil; average $\pm$ SD (0–0.009))



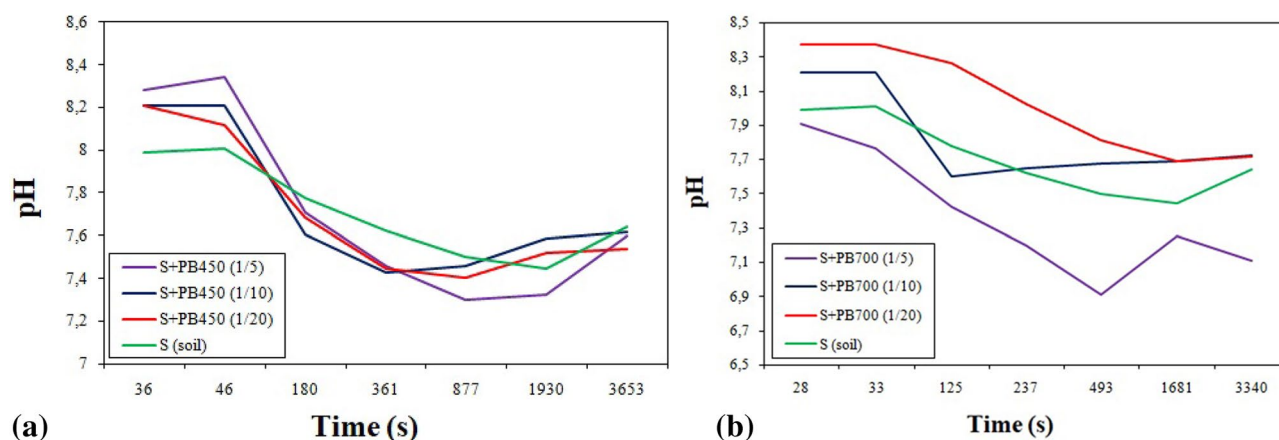


Fig. 2 pH differences in the eluates depending on time (s), **a** PB450 and **b** PB700 biochar types (S—polluted soil)

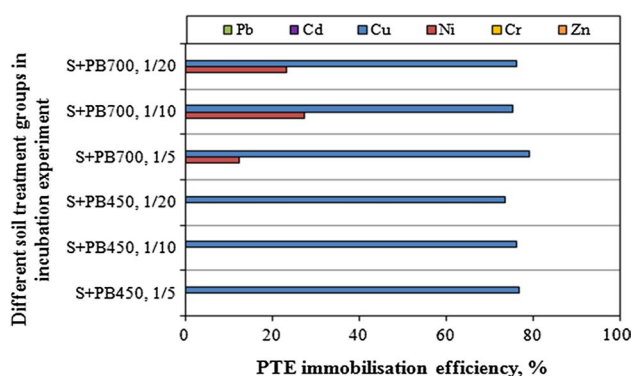


Fig. 3 PTE immobilisation efficiency in the soil amended with PB450 and PB700 biochar types in the beginning of the incubation experiment (after 1 h)

and 1/20, respectively), Cu (69.01, 70.29 and 76.03% at the ratios of 1/5, 1/10 and 1/20, respectively) and Pb (46% at the ratio of 1/5). Biochar produced at higher temperature also immobilised four elements out of six (Cd > Cu > Pb > Cr). Like biochar made at lower temperature, this biochar type immobilised Cd the most (88.32% at the ratio of 1/5).

Immobilisation of other three elements was below than average: Cu: 44.33, 45.21% at the ratios of 1/10 and 1/20; Pb: 22% at the ratio of 1/10; Cr: 20.66, 9.92 and 14.05% at the ratios of 1/5, 1/10 and 1/20, respectively). In conclusion, these two carbonaceous product types immobilised the Cd and Cu most at the end of the experiment (after 28 days). Two biochar types showed similar high retention effectivity of Cd (> 85%), but in the case of Zn retention this element was better retained (78%) by the biochar made at lower temperature (450 °C) which also effectively immobilised Cu (> 76%). Similar results were obtained by other investigation when canal bank soil severely polluted with Cd and Zn was amended with wood biochar.

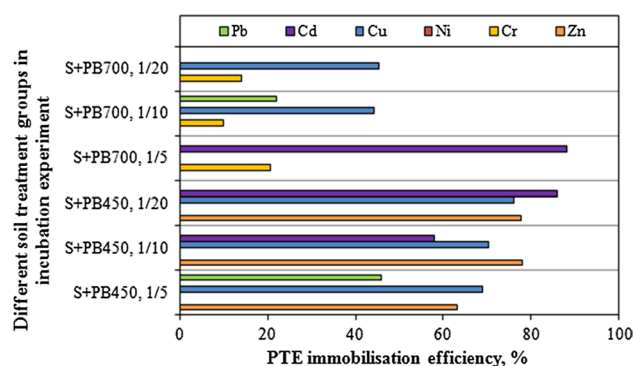


Fig. 4 PTE immobilisation efficiency in the soil amended with PB450 and PB700 biochar types at the end of the incubation experiment (after 672 h/28 days)

It showed a significant decrease of Cd concentrations in pore water after 60 days field experiment (Beesley et al. 2010). In the column analysis with the same soil, biochar similarly decreased Cd and Zn concentrations in the filtrates, which shows sorption of Cd and Zn on the biochar surface (Beesley and Marmiroli 2011) using Scanning Electron Microscopy (SEM). Zheng et al. (2015) showed that biochar both from bean stems and rice stems effectively immobilised Cd, Zn and Pb in historically polluted soil from rice fields (Zheng et al. 2015). Biochar had most significant effect on the availability of Cd and its gradual phytoaccumulation. When soil was amended with biochar, Cd concentrations in the plants decreased by 71%.

When soil is highly contaminated with Cd, both biochar types could be used for this element retention, but if soil is multi-polluted (Cd, Zn, Cu), biochar made at lower temperature (450 °C) could be a better product for immobilisation of the elements because effectiveness of immobilisation of these elements was better comparing it with biochar made at higher temperature (700 °C).



Figures 5 and 6 show that in the beginning of the incubation experiment (after 1 h) in the soil amended with two carbonaceous product types, the highest PTE bioavailable part (%) (by 2.5%) (Fig. 5) was that for Ni and at the end of the experiment bioavailable part of this element decreased by 1.9% (Fig. 6). Results showed that the PTE bioavailable part (%) was growing most significantly in the case of Zn (in soil amended with PB700 (1/10)—4.64 times and in unamended soil—6.04 times) and Cd (in soil amended with PB450 (1/5)—79.66 times and unamended soil—6.81 times) (Fig. 6).

This decrease of PTE mobility could be explained by ageing, which relates with processes affecting elements mobility and bioavailability decrease with time (Ma et al. 2006). Usually with time sorption of elements increases and this mechanism is determined by low rate of reactions, organic and inorganic pollutants diffusion into micropores and nuclear-precipitation on the surface (Ma et al. 2006). Mechanisms of elements sorption and sorbtive capacity significantly vary between source material and elements. Biochar properties highly differ due to feedstock and pyrolysis temperature, when in higher temperature biochar has major surface area, pH value and mineral content though less functional groups content. Most importantly because of a favourable structure of pores and various functional groups (carboxyl, hydroxyl and phenolic) biochar highly attracts PTEs (Park et al. 2011).

PTE immobilisation in polluted soil using the leaching experiment

In this research we investigated six PTEs (Cu, Cr, Zn, Ni, Cd and Pb) leaching from polluted soil amended with two pine wood biochar types (PB450 and PB700) made in two different temperatures, 450 and 700 °C and mixed at three different ratios (1/5, 1/10, 1/20) and from two sleepers pyrogenic carbonaceous product types (PSB450 and PSB700).

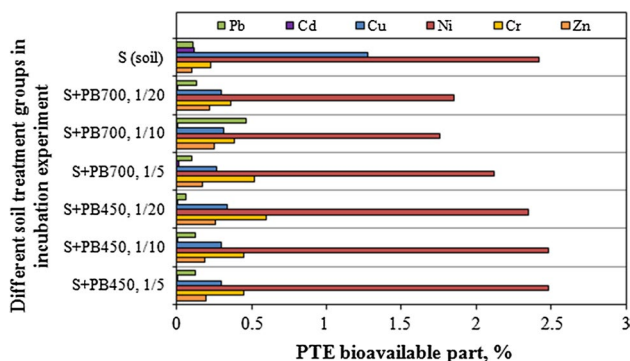


Fig. 5 PTE bioavailable part (%) compared to initial elements amount in the soil amended with two carbonaceous product types in the beginning of the incubation experiment (after 1 h)

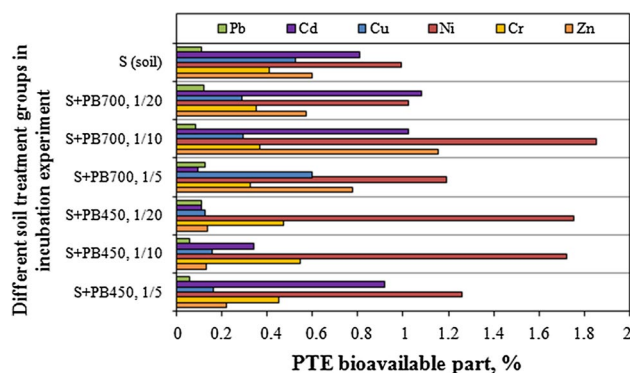


Fig. 6 PTE bioavailable part (%) compared to initial elements amount in the soil amended with two carbonaceous product types in the end of the incubation experiment (after 672 h/28 days)

Figures 7 and 8 show that from unamended soil, Pb (19.59%) and Cu (5.21%) were the highest leached PTEs part (%) comparing with initial elements concentration in the soil and Cr (0.18%) and Cd (0.02%) were the lowest. When soil was amended with two different pine wood PCPs, there was different PTE retention efficiency for different elements and mixing ratios (Figs. 9, 10). In the case of biochar produced at 450 °C temperature, the best retention efficiency was for Pb and Cu (Fig. 9). Pb retention efficiency by this biochar reached more than 99% (99.57, 99.48, and 99.45% at the ratios of 1/5, 1/10 and 1/20, respectively). In other study (Mohan et al. 2007), oak bark biochar (400–450 °C) was more effective in Pb retention compared to other types and removed similar Pb content like activated char (about 100% of Pb). The authors made a conclusion that metal adsorption by biochar was explained by the mechanisms of ion exchange. Karami et al. (2011) concluded that P could affect Pb retention by hard wood biochar in severely polluted mining soil. In the same work, biochar influenced the reduction of Pb concentrations in pore water from 80 mg/l

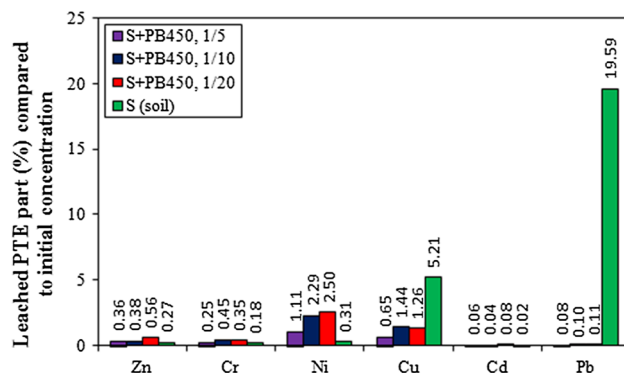


Fig. 7 Leached PTEs part (%) from soil amended with carbonaceous product (PB450) compared to initial concentration



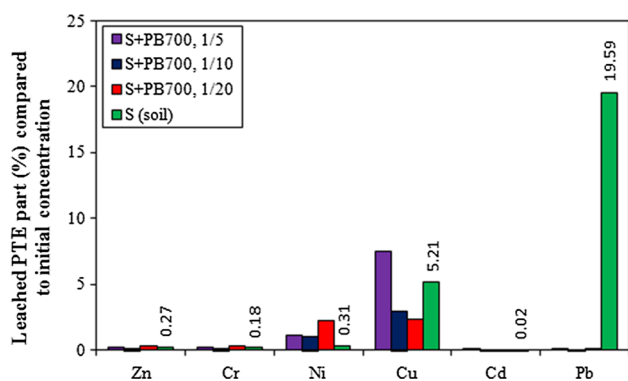


Fig. 8 Leached PTEs part (%) from soil amended with carbonaceous product (PB700) compared to initial concentration

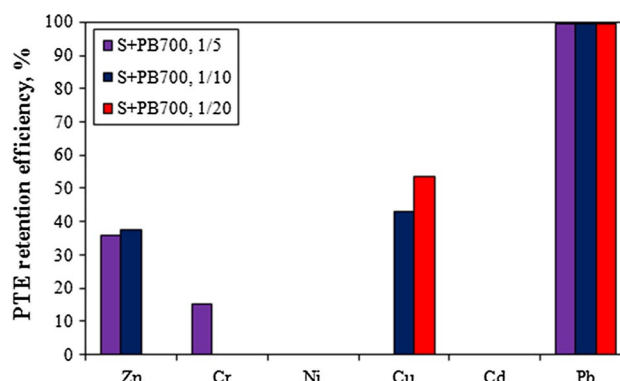


Fig. 10 PTE retention efficiency (%) in polluted soil amended with biochar (PB700)

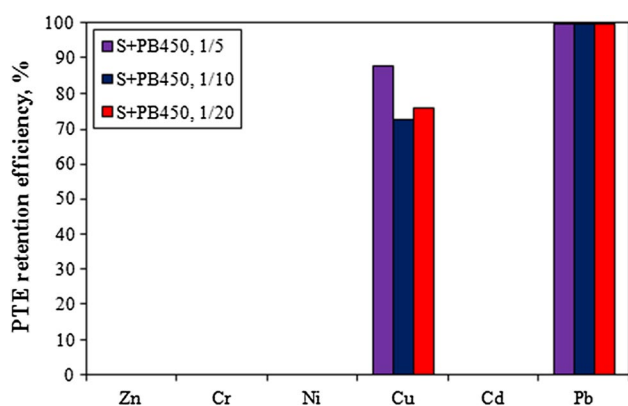


Fig. 9 PTE retention efficiency (%) in polluted soil amended with biochar (PB450)

to a half of this value. Otherwise, when biochar was mixed with compost of green wastes, Pb concentrations in soil's pore water decreased even more; therefore, there is a suggestion to combine the effects and to experiment not only with physical retention of the pollutants but also with chemical and biological drivers. Cu retention efficiency reached 93, 82.16 and 73.17% at the ratios of 1/5, 1/10 and 1/20, respectively, when soil was amended with PB450 biochar type. Jones et al. (2016) made an experiment with plants and estimated combined biochar and compost effect on the growing of plants and Cu immobilisation in polluted soil. Cu mobility in amended soils was evaluated using leaching tests before and after incubation and growing of plants. All amended soils significantly reduced leached Cu contents compared to the unamended soil. However, biochar made at 700 °C temperature retained more PTEs (Zn, Cr, Cu and Pb) compared with biochar made at lower temperature (Fig. 10). The highest retention efficiency by this biochar was for Pb, and it reached 99.63, 99.52 and 99.52% at the ratios of 1/5, 1/10 and 1/20, respectively. Cu was retained averagely (43.23 and 53.78% at the ratios of 1/10 or 1/20). Similarly to Jones et al.

(2016) study, the highest decrease in the Cu content was at the highest biochar and soil mixing ratio. Zn retention efficiency by this biochar was below average (35.72 and 37.56% at the ratios of 1/5 and 1/10, respectively) and Cr was retained at the lowest level (15.15% at the ratio of 1/5). Higher pyrolysis temperature determines higher Zn^{2+} sorption capacity and higher Zn precipitates/minerals fraction in the biochar (Wagner et al. 2015). Wagner et al. (2015) found that when biochar was used for Zn immobilisation in the sewage sludge soil, hopeite ($Zn_3(PO_4)_2 \cdot 2H_2O$) and similar Zn–P phase started to form.

In conclusion, pine wood biochar produced at 450 °C temperature in soil polluted with PTEs retained Pb (retention efficiency reached 99.57%, 1/5) and Cu (retention efficiency reached 93%, 1/5) the most. This biochar highly retained Pb when its concentration in soil was not very high, 1.75 mg/kg (by 46 times lower than limited value), but Cu was 1.4 times higher than a limited value (Fig. 11), according to Lithuanian hygienic standard HN 60:2015. This biochar had no positive effect on other soil elements (Zn, Cr, Cd and Ni). In the case of pine wood biochar made at 700 °C temperature,

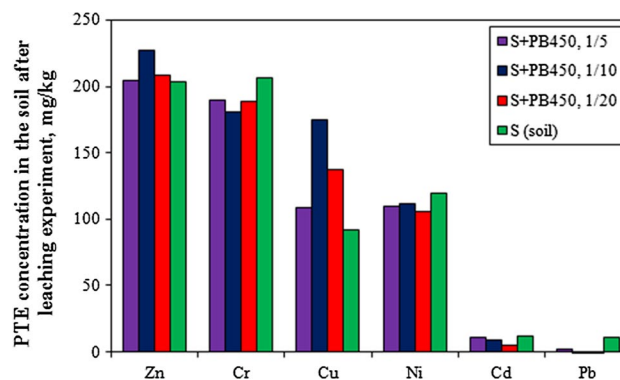


Fig. 11 PTE concentration (mg/kg DW) in soil amended with biochar (PB450) after the leaching experiment



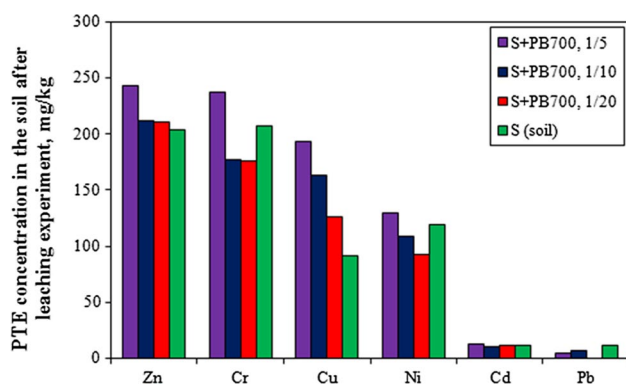


Fig. 12 PTE concentration (mg/kg DW) in soil amended with biochar (PB700) after the leaching experiment

PTEs retention efficiency decreased in the following order: Pb > Cu > Zn > Cr. This biochar effectively retained Pb (99.63%), Cu (49.34%), Zn (37.56%) and not significantly Cr (15.15%). Like biochar produced at a lower temperature, this PCP retained the highest amount of Pb when its concentration in soil was sufficiently low (7.33 mg/kg), retained Cu more when its concentration in soil was sufficiently high (126.83 mg/kg), Zn was lower (211.83 mg/kg) than the limited value (300 mg/kg) and Cr was three times higher than the limited value (237.37 mg/kg) (Fig. 12).

The most negative effect on the PTE leaching from two PCP types was for Ni (7 times higher leaching compared to control soil). When soil is highly polluted with Pb and Cu, biochar made at 450 °C temperature is a more suitable carbonaceous product because of more effective retention of these elements, but when soil is overpolluted with multi-elements (Pb, Cu, Zn and Cr) biochar made at 700 °C temperature could be more suitable carbonaceous product type for these elements retention because four elements out of six were retained.

Evaluating PTEs leaching from two sleepers pyrogenic carbonaceous product types (PSB450 and PSB700), all six PTEs (Zn, Cr, Ni, Cu, Cd and Pb) leached amounts were not significant (Table 4). Their leaching compared to the initial PTE concentrations in the pyrogenic products types varied from 0.07% for Cu and to 11.29% for Ni. It could be stated

that pyrogenic products made from railway sleepers do not make hazards to environmental quality according to soil protection acts.

Comparing two different PCP types, PSB700 type affects the environment in a lesser extent in the case of Ni, Zn and Pb because leached amounts of these elements were by 40.4% (for Ni) lower compared to PSB450 type. In the case of Cr, Cu and Cd, PSB450 type affects the environment in a lesser extent because leached amounts of these elements were by 18.12% (for Cu) lower compared to PSB700 type. According to the leaching (mg/kg DW) from PSB450 type, PTEs range in this order: Ni(2.02) > Zn(0.51) > Cr(0.35) > Cu(0.0196) > Pb(0.01) > Cd(0.00097). According to the leaching (mg/kg DW) from PSB700 type, PTEs range in this order: Ni(0.84) > Cr(0.41) > Zn(0.34) > Cu(0.0239) > Pb(0.01) > Cd(0.001). Ni was the most leached element (0.84–2.02 mg/kg) but Cd was the lowest (0.0009–0.0011 mg/kg). Slightly higher leached amount of PTEs were from PSB450. It could be explained by the fact that at 400–500 °C temperature PTEs retain in the state of mobile ions, but at 600 °C temperature elements form stable oxides (Volungevičienė et al. 2014).

PTE bioavailability in soil and bioaccumulation in oat (*Avena sativa* L.)

Carbonaceous product made from pine wood (*Pinus sylvestris*) and pyrolysed at 700 °C temperature, insignificantly affected fresh ($p = 0.595$) and dry ($p = 0.871$) mass of oat to 33.76 and to 12.07% (Figs. 13, 14) compared to the control. On the other hand, compared to other study (Wagner 2014), biochar made from corns (*Zea mays* L.) and pyrolysed at 750 °C temperature (heating time 2 h) increased oat's (which was grown in the soil from the former sewage sludge filtration fields) fresh and dry mass by 60% compared to the control. This increase was highly significant for the fresh ($p = 0.006$) and almost significant for the dry ($p = 0.05$) mass.

Specific phytotoxicity of plants and its response to volatile and leached compounds from fresh biochar could explain zero and negative response of growing plants to biochar as soil additive in this research. Several works showed phytotoxic effect of plants to fresh biochar; however, there is less information

Table 4 (a) Leached PTEs part (%) from two sleepers pyrogenic carbonaceous product types compared to initial concentration; (b) initial PTEs concentration (mg/kg DW) in two PCP types from sleepers

Pyrogenic product type	Zn	Cr	Ni	Cu	Cd	Pb
(a)						
PSB450	0.43	1.78	11.29	0.009	0.11	0.18
PSB700	0.24	1.15	2.57	0.07	0.59	0.15
(b)						
PSB450	118.3	19.72	17.92	22.41	0.9	8.07
PSB700	140.71	35.4	32.74	32.74	0.18	9.03



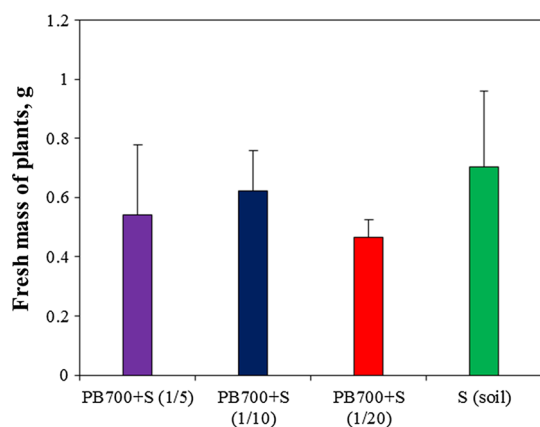


Fig. 13 Oat fresh mass after experiment with plants (after 35 days) (in abscissa axis are different treatment groups)

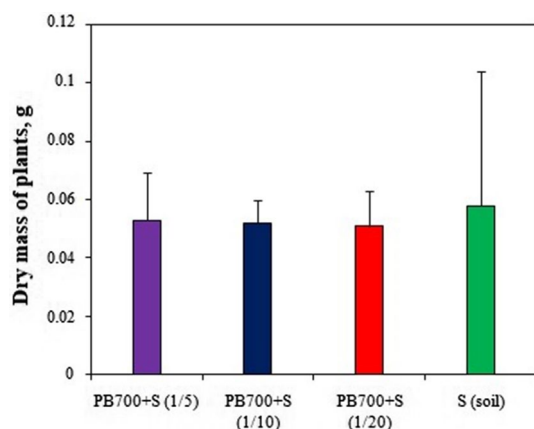


Fig. 14 Oat dry mass after plants experiment with plants (after 35 days) (in abscissa axis are different treatment groups)

about toxin sources and their chemistry (Buss and Masek 2014; Koltowski and Oleszczuk 2015). Low and average temperatures of wood material pyrolysis produce high concentrations of initial decomposition of low molecular weight compounds due to high concentrations of cellulose and lignin. For this reason, it is very important to properly choose material for biochar production and when it is used in environmental remediation and has good sorptive properties and low potential phytotoxicity.

There are two main biochar pollution reasons caused by these mobile compounds: first, biochar production time can be too short for proper transformation and diffusion of pollutants in the pyrolysis system and due to this these can be sorbed by the biochar surface or retained in the porous structure. It can usually occur in the case of fast pyrolysis, though slow pyrolysis time (from 0.5 to 2 h or less) can be too short as well (Novak et al. 2014). Second, the reason of biochar pollution can be attributed to secondary volatile compounds condensation in pyrolysis and due to isolation, blockade or biochar cooling (Buss and Masek 2014). It is thought that

one or more of these reasons can be responsible for leached and volatile compounds which occur in many biochar types (Spokas et al. 2011) and that is why there is determined zero or neutral plants response for the use of biochar (Spokas et al. 2012). It is thought that chars mineralisation under natural conditions eliminates the phytotoxic effect from volatile and leached compounds. It is possible that longer biochar heating and leaching before and after it used as a soil amendment could determine plant's positive response to biochar addition.

Table 5 show that PB700 biochar addition to soil changed PTE distribution in plants, and there is a tendency that Pb accumulates in oat in higher amounts (Antonićević and Maric 2008). Pb accumulation in oat could be explained by amended soil acidification from 6.79 (in the beginning) to 6.44 (at the end) which was reflected in the 35 days long incubation experiment. Soil acidification occurred due to oxidation of sulphide minerals, and this determines continuous increase in Pb^{2+} ions in the soil solution (Antonićević and Maric 2008).

Many investigations showed that increase in metal concentrations in various cultural plants was related to metal concentrations in the sewage sludge and with soil properties, such as, pH and which significantly affected availability of the elements to the plants (Chaney and Giordano 1977; Sommers 1980). Oat is a plant species which has low capacity for Cd and Pb accumulation compared to other plants which are known as hyperaccumulators or PTE accumulators. For example, in other studies, there were found 0.21 mg/kg concentration of Cd and 2.28 mg/kg concentration of Pb in oat's grain and 6 mg/kg in leaves (Fergusson 1990). Pb concentrations are similar the findings of this study, when Pb concentration in plants reached 1.73 mg/kg DW and Cd concentration reached 0.79 mg/kg DW. The most significant decrease in PTE concentrations in the plants from amended soils was in the case of Cr (91.7%) and Zn (66.69%). Average PTEs concentrations decrease in amended soil ranges in this order: Cr(71.28%) > Zn(53.45%) > Cd(45.36%) > Cu(11.39%) > Ni(5.09%). Mean distribution of PTEs in the oat from amended soil followed in this order: Cu(38.28 mg/kg) > Zn(25.9 mg/kg) > Ni(16.13 mg/kg) > Cr(11.42 mg/kg) > Pb(1.65 mg/kg) > Cd(0.43 mg/kg). The mean distribution of PTEs in oat from unamended soil decreased in the following order: Zn(55.69 mg/kg) > Cu(43.2 mg/kg) > Cr(39.77 mg/kg) > Ni(17 mg/kg) > Cd(0.79 mg/kg) > Cd(0.79 mg/kg).

Table 5 demonstrates that insoluble PTEs (Zn, Cr, Ni, Cu, Cd and Pb) concentrations in amended soil decreased if compared to those from unamended soil after the experiment with plants. The most significant PB700 and oat effect on the soil PTEs is for Pb (97.78% (1/5) decrease compared to unamended soil), Cr (37.03% (1/5)) and Zn (to 20.83% (1/5)). In all amended soil mixtures, four elements (Zn, Cr, Cd and Pb) decreased if compared to unamended soil.



Table 5 Concentration (mg/kg DW) of PTE in plants and soil after the experiment with plants (average $\pm$ SD, $n = 3$)

PTE	In plants, PB700 + S, 1/5	In plants, PB700 + S, 1/10	In plants, PB700 + S, 1/20	In plants, S (soil)	In soil after plants growing, PB700 + S, 1/5	In soil after plants growing, PB700 + S, 1/10	In soil after plants growing, PB700 + S, 1/20	In soil after plants growing, S (soil)
Cd	0.46 $\pm$ 0.04	0.42 $\pm$ 0.02	0.41 $\pm$ 0.004	0.79 $\pm$ 0.49	12.07 $\pm$ 0.16	6.27 $\pm$ 4.65	12.69 $\pm$ 0.01	14.45 $\pm$ 2.28
Pb	1.61 $\pm$ 1.43	1.61 $\pm$ 1.34	1.73 $\pm$ 1.48	0.32 $\pm$ 0.16	0.2 $\pm$ 0.02	1.36 $\pm$ 1.16	3.26 $\pm$ 3.11	9.14 $\pm$ 0.87
Zn	37.67 $\pm$ 3.35	18.53 $\pm$ 4.45	21.5 $\pm$ 1.97	55.63 $\pm$ 4.28	245.83 $\pm$ 5.51	266.17 $\pm$ 5.11	289.17 $\pm$ 10.69	310.5 $\pm$ 5.41
Cu	33.6 $\pm$ 15.91	41.23 $\pm$ 24.39	40 $\pm$ 13.09	43.2 $\pm$ 9.57	155.42 $\pm$ 9.81	174.25 $\pm$ 95.62	146.75 $\pm$ 10.15	151.67 $\pm$ 12.37
Ni	16.57 $\pm$ 1.4	15.73 $\pm$ 0.38	16.1 $\pm$ 0.79	17 $\pm$ 1.73	119.23 $\pm$ 4.19	104.97 $\pm$ 1.99	126.73 $\pm$ 11.72	119.23 $\pm$ 3.09
Cr	15.43 $\pm$ 0.38	15.53 $\pm$ 0.31	3.3 $\pm$ 0.17	39.77 $\pm$ 5.52	157.27 $\pm$ 120.28	231.27 $\pm$ 2.04	239.37 $\pm$ 5.95	249.73 $\pm$ 13.45

Conclusion

1. Assessing physical and chemical properties of pine wood and sleepers carbonaceous product according to pyrolysis temperature, it was shown that increase in pyrolysis temperature (from 450 to 700 °C) resulted in decreasing yield, increased ash content, pH and total carbon content, while density, cation exchange capacity and amount of potential toxic elements differed depending on the type of the feed-stock and pyrolysis temperature. Higher cation exchange capacity which is important for biochar adsorptive properties, had pine wood biochar made at 700 °C temperature (2.07 cmol_c/kg). According to PTE concentrations, all carbonaceous product types were of premium quality, except for sleepers carbonaceous product type (PSB700) in the case of Ni. According to moisture content and density, this soil is optimal for growth of plants; it has average organic matter content and is average alkaline.
2. Evaluating results of incubation experiment, similarly high retention effectivity of Cd (> 85%) had both biochar types, however, evaluating Zn retention, higher retention effectivity (78%, 1/10) of this element had biochar made at lower temperature (450 °C) which also efficiently well-immobilised Cu (76%, 1/20). When soil is highly polluted with Cd, this element could be retained by both biochar types but if soil is highly polluted with many elements (Cd, Zn, Cu, Pb), PB450 type could be a more suitable sorbative product in the long time perspective.
3. Assessing the results of leaching experiment, pine wood biochar (PB450) most effectively retained Pb (retention efficiency reached 99.57%, 1/5) and Cu (retention effectivity reached 93%, 1/5). It had not any positive retention effect on other elements (Zn, Cr, Cd and Ni). In the case of other biochar type (PB700), PTEs retention effectivity decreased in the following order: Pb > Cu > Zn > Cr. This biochar retained the most of Pb (99.63%), Cu (49.34%), Zn (37.56%) and slightly Cr (15.15%). When soil is overpolluted with Pb and Cu, PB450 type could be a better sorbative product; however, when soil is overpolluted with many elements (Pb, Cu, Zn and Cr), PB700 type could be a better biochar type for elements immobilisation in soil in the short time perspective. Assessing PTEs leaching from two pyrogenic carbonaceous product types from sleepers (PSB450 and PSB700), all leached PTEs (Zn, Cr, Ni, Cu, Cd and Pb) amounts were not significant concerning both types. Their leaching compared to initial concentration of elements in pyrogenic product types reached from 0.07% in the case of Cu and to 11.29% in the case of Ni. It could be stated that in the case of PTE in the pyrogenic product made from wooden slippers, it does not cause risk to the environment according to soil protection acts.
4. According to the incubation experiment results, pine carbonaceous product produced at lower temperature (450 °C) should be added at highest amount (1/20) to the soil polluted with Cd and the lowest amount (1/5) to the soil polluted with Cd, Zn and Cu. In the case of pine carbonaceous product produced at higher temperature (700 °C), it should be added at highest amount (1/20) to the soil polluted with Cu, at average amount (1/10) to the soil polluted with Pb and at the lowest amount (1/5) to the soil polluted with Cd and Cr. According to the results of the leaching experiment, pine carbonaceous product produced at lower temperature (450 °C) should be added at average amount (1/10) into the soil polluted with Pb and at lowest amount (1/5) to the soil polluted with Cu. In the case of carbonaceous product produced at higher temperature (700 °C), there is an opposite tendency concerning Cu: it should be added at the highest amount (1/20) to the soil polluted with Cu, at average amount (1/10) to the soil polluted with Zn and at lowest amount (1/5) to the soil polluted with Cr and Pb.
5. Pine carbonaceous product produced at 700 °C temperature had negative or zero effect on the fresh and dry oat mass. It decreased by 33.76% in the case of fresh and by 12.07% in the case of dry mass compared to the control group. Specific phytotoxicity of plants and its response to volatile and leached compounds from the fresh biochar could explain zero or negative response of growing plants to biochar addition to the soil in this research.



Pine biochar addition to the soil changed PTEs distribution in plants. PTEs (Zn, Cr, Ni, Cu, Cd) concentrations in plants grown on the amended soil decreased comparing to plants from unamended soil, except for the case of Pb: its concentration in plants increased. It is possible that Pb accumulates in oat at high amounts due to soil acidification which determines continuous increase of concentration of Pb^{2+} ions in the soil solution.

Acknowledgements The authors wish to thank all who assisted in conducting this work.

References

- Ahmad M, Lee SS, Lim JE, Lee SE, Cho JS, Moon DH, Hashimoto Y, Ok YS (2014) Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. *Chemosphere* 95:433–441
- Al-Wabel MI, Usman AR, El-Naggar AH, Aly AA, Ibrahim HM, Elmaghraby S, Al-Omran A (2015) Conocarpus biochar as a soil amendment for reducing heavy metal availability and uptake by maize plants. *Saudi J Biol Sci* 22:503–511
- Amonette J, Joseph S (2009) Characteristics of biochar: micro chemical properties. In: Lehmann J, Joseph S (eds) *Biochar for environmental management: science and technology*. Earthscan, London, pp 33–52
- An assessment of laboratory leaching tests for predicting the impacts of fill material on ground water and surface water quality 2003. A report for the legislature. Publication No. 03–09107
- Antal MJ, Gronli M (2003) The art, science and technology of charcoal production. *Ind Eng Chem Res* 42(8):1619–1640
- Antonićević MM, Maric M (2008) Determination of the content of heavy metals in pyrite contaminated soil and plants. *Sensors* 8(9):5857–5865
- Barrow CJ (2012) Biochar: potential for countering land degradation and for improving agriculture. *Appl Geogr* 34:21–28
- Beesley L, Marmiroli M (2011) The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environ Pollut* 159(2):474–480
- Beesley L, Moreno-Jiménez E, Gomex-Eyles JL (2010) Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environ Pollut* 158(6):2282–2287
- Beesley L, Moreno-Jiménez E, Gomex-Eyles JL, Harris E, Robinson B, Sizmur T (2011) A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soil. *Environ Pollut* 159:3269–3282
- Buss W, Masek O (2014) Mobile organic compounds in biochar—a potential source of contamination—phytotoxic effects on cress seed (*Lepidium sativum*) germination. *J Environ Manag* 137:111–119
- Butkus D, Baltrėnaitė E (2007) Accumulation of heavy metals in tree seedlings from soil amended with sewage sludge. *Ekologija* 53(4):68–76
- Cao XD, Ma LN, Gao B, Harris W (2009) Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environ Sci Technol* 43:3285–3291
- Cao XD, Ma L, Liang Y, Gao B, Harris W (2011) Simultaneous immobilization of lead and Atrazine in contaminated soils using dairy-manure biochar. *Environ Sci Technol* 45:4884–4889
- Chaney RL, Giordano PM (1977) Microelements as related to plant deficiencies and toxicities. In: Elliott LF, Stevenson FJ (eds) *Soils for management of organic wastes and waste waters*. American Society of Agronomy, Madison, pp 233–280
- Chen B, Zhou D, Zhu L (2008) Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environ Sci Technol* 42:5137–5143
- Crombie K, Mašek O, Cross A, Sohi S (2014) Biochar-synergies and trade-offs between soil enhancing properties and C sequestration potential. *Edinburgh Research Explorer*, Edinburgh
- DGE Baltic Soil and Environment (2010) Panevėžio miesto savivaldybės Molainių buvusių nuotekų filtracijos laukų detalieji ekogeologiniai tyrimai, Vilnius
- European Biochar Foundation (2016) European biochar certificate—guidelines for a sustainable production of biochar. <http://www.european-biochar.org/en>. Accessed 4 Feb 2016
- Fergusson JE (1990) *The heavy elements: chemistry, environmental impact, and health effects*. Pergamon Press, Oxford
- Gai X, Wang H, Liu J, Zhai L, Liu S, Ren T, Liu H (2014) Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. *PLoS ONE* 9:12
- Gaskin JW, Steiner C, Harris K, Das KC, Bibens B (2008) Effect of low temperature pyrolysis conditions on biochar for agricultural use. *Trans ASABE* 51(6):2061–2069
- Geotestus (2013) Buvusių nuotekų filtracijos laukų užterštos teritorijos kontrolinis ekogeologinis tyrimas Panevėžio apskr., Panevėžio m. sav., Molainių g. Vilnius
- Gul S, Naz A, Fareed I, Irshad M (2014) Reducing heavy metals extraction from contaminated soils using organic and inorganic amendments—review. *Polish J Environ Stud* 24(3):1423–1426
- Hass A, Gonzalez JM, Lima IM, Godwin HW, Halvorson JJ, Boyer DG (2012) Chicken manure biochar as liming and nutrient source for acid Appalachian soil. *J Environ Qual* 41:1096–1106
- Herath I, Iqbal MCM, Al-Wabel MI, Abduljabbar A, Ahmad M, Usman ARA, Ok YS, Vithanage M (2017) Bioenergy-derived waste biochar for reducing mobility, bioavailability, and phytotoxicity of chromium in anthropized tannery soil. *J Soils Sediments* 17:731–740
- Houben D, Evrard L, Sonnet P (2013a) Beneficial effects of biochar application to contaminated soils on the bioavailability of Cd, Pb and Zn and the biomass production of rapeseed (*Brassica napus* L.). *Biomass Bioenergy* 57:196–204
- Houben D, Evrard L, Sonnet P (2013b) Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. *Chemosphere* 92:1450–1457
- ISO 10381-2:2002. Ėminių ėmimas. 2 dalis. Ėmimo būdų vadovas, p 10
- ISO 14688-2:2004. Geotechniniai tyrinėjimai ir bandymai. Gruntų atpažintis ir klasifikavimas. 2 dalis. Klasifikavimo principai
- Jackson TJ (1993) Measuring surface soil moisture using passive microwave remote sensing. *Hydr Proc* 7:139–152
- Jindo K, Mizumoto H, Sawada Y, Sanchez-Monedero MA, Sonoki T (2014) Physical and chemical characterization of biochars derived from different agricultural residues. *Biogeosciences* 11:6613–6621
- Jones S, Bardos RP, Kidd PS, Mench M, de Leij F, Hutchings T, Cundy A, Joyce C, Soja G, Friesl-Hanl W, Herzig R, Menger P (2016) Biochar and compost amendments enhance copper immobilisation and support plant growth in contaminated soils. *J Environ Manag* 171:101–112
- Karami N, Clemente R, Moreno-Jimenez E, Lepp N, Beesley L (2011) Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass (*Lolium perenne*). *J Hazard Mater* 191:41–48



- Khan KT, Chowdhury MTA, Imamul Huq SM (2015) Effects of biochar on the fate of heavy metals Cd, Cu, Pb and Zn in soil. *Bangladesh J Sci Res* 28:17–26
- Koltowski M, Oleszczuk P (2015) Toxicity of biochars after polycyclic aromatic hydrocarbons removal by thermal treatment. *Ecol Eng* 75:79–85
- Komkiene J, Baltreinaite E (2016) Biochar as adsorbent for removal of heavy metal ions [Cadmium(II), Copper(II), Lead(II), Zinc(II)] from aqueous phase. *Int J Environ Sci Technol* 13:471–482
- Lambrechts T, Couder E, Bernal MP, Faz A, Iserentant A, Lutts S (2011) An assessment of heavy metals bioavailability in contaminated soils from a former mining area (La Union, Spain) using a rhizospheric test. *Water Air Soil Pollut* 217:333–346
- Lehmann J, Rillig MC, Thies J, Masiello CA, Hockaday WC, Crowley D (2011) Biochar effects on soil biota—a review. *Soil Biol Biochem* 43:1812–1836
- Liaudanskienė I, Šlepetienė A, Velykis A (2008) Žemės dirbimo ir sąjomainos įtaka dirvožemio anglies pokyčiams ekstrakciuose frakcijose. *Žemdirbystė* 95:19–28
- LST CEN/TS 14405. Documentation. Bibliographical references. Content, form and structure [Dokumentai. Bibliografinės nuorodos. Turinys. Forma ir sandara], p 26
- Ma Y, Lombi E, Oliver IW, Nolan AL, McLaughlin MJ (2006) Long-term aging of copper added to soils. *Environ Sci Technol* 40:6310–6317
- Mažvila J, Vaišvila Z, Staugaitis G (2011) Dirvožemio agrocheminių savybių įtaka žemės ūkio augalų derlingumui. *Lietuvos žemės našumas*, pp 124–128
- Meyer S, Glaser B, Quicker P (2011) Technical, economical and climate related aspects of biochar production technologies: a literature review. *Environ Sci Technol* 45:9473–9483
- Mohan D, Pittman CU, Bricka M, Smith F, Yancey B, Mohammad J, Steele PH, Alexandre-Franco MF, Gomez-Serrano V, Gong H (2007) Sorption of arsenic, cadmium and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J Colloid Interface Sci* 310:57
- Mukherjee A, Zimmerman AR, Harris W (2011) Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma* 163:247–255
- Nelissen V, Ruyschaert G, Müller-Stöver D, Bodé S, Cook J, Ronsse F, Shackley S, Boeckx P, Hauggaard-Nielsen H (2014) Short-term effect of feedstock and pyrolysis temperature on biochar characteristics, soil and crop response in temperate soils. *Agronomy* 4:52–73
- Nguyen B, Lehmann J, Kinvangi J, Smernik R, Riha S, Engelhard M (2009) Long-term black carbon dynamics in cultivated soil. *Biogeochemistry* 89:163–176
- Novak JM, Lima I, Xing B, Gaskin JW, Steiner C, Das KC, Ahmedna M, Rehrich D, Watts DW, Busscher WJ, Harry S (2009) Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Ann Environ Sci* 3:195–206
- Novak JM, Cantrell KB, Watts DW, Busscher WJ, Johnson MG (2014) Designing relevant biochars as soil amendments using lignocellulosic-based and manure-based feedstocks. *J Soils Sediments* 14(2):330–334
- Park J, Choppala G, Bolan N, Chung J, Chuasavathi T (2011) Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant Soil* 348:439–451
- Pečkaitė J, Baltreinaite E (2015) Assessment of heavy metals leaching from (bio)char obtained from industrial sewage sludge. *Moksl Liet Ateitis* 7(4):399–406
- Rajakaruna N, Tompkins KM, Pavicevic PG (2006) Phytoremediation: an affordable green technology for the clean-up of metal-contaminated sites in Sri Lanka. *Ceylon J Sci* 35:25–39
- Rajapaksha AU, Vithanage M, Oze C, Bandara WMAT, Weerasooriya R (2012) Nickel and manganese release in serpentine soil from the Ussangoda Ultramafic Complex, Sri Lanka. *Geoderma* 189(190):1–9
- Rees F, Simonnot MO, Morel JL (2014) Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase. *Eur J Soil Sci* 65(1):149–161
- Schreck E, Foucault Y, Geret F, Pradere P, Dumat C (2011) Influence of soil ageing on bioavailability and ecotoxicity of lead carried by process waste metallic ultrafine particles. *Chemosphere* 85:1555–1562
- Šilinskaitė J (2014) Research and evaluation of biochar adsorption capacity from heavy metal ions from aqueous phase. Master thesis, Vilnius Gediminas Technical University, Vilnius, p 45
- Sommers LE (1980) Toxic metals in agricultural crops. In: Bitton G, Damron BL, Edds GT, Davidson JM (eds) *Sludge health risks of land application*. Ann Arbor Science Publishers, Ann Arbor, pp 105–140
- Spokas KA, Novak JM, Stewart CE, Cantrell KB, Uchimiya M, DuSaire MG, Ro KS (2011) Qualitative analysis of volatile organic compounds on biochar. *Chemosphere* 85(5):869–882
- Spokas KA, Cantrell KB, Novak JM, Archer DW, Ippolito JA, Collins HP, Boateng AA, Lima IM, Lamb MC, McAloon AJ, Lentz RD, Nichols KA (2012) Biochar: a synthesis of its agronomic impact beyond carbon sequestration. *J Environ Qual* 41(4):973–989
- Sposito G (1989) *The chemistry of soils*. Oxford University Press, New York
- Sujetovienė G (2011) *Dirvožemio ekologija*. Naujo studijų dalyko programos parengimas, Kaunas
- Uchimiya M, Chang S, Klasson T (2011) Screening biochars for heavy metal retention in soil: role of oxygen functional groups. *J Hazard Mater* 190(2011):432–441
- Uchimiya M, Cantrell KB, Hunt PG, Novak JM, Chang S (2012) Retention of heavy metals in a Typic Kandudult amended with different manure-based biochars. *J Environ Qual* 41:1138–1149
- Volungevičienė R, Bolutienė V, Buinevičius K (2014) Elektronikos plokščių pelenų tyrimai ir jų pavojingumo vertinimas. *Moksl Liet Ateitis* 6(4):400–406
- Wagner A (2014) Biochar as soil amendment for the immobilization of copper, zinc, cadmium and lead on former sewage fields. Doctoral dissertation, pp 14–32
- Wagner A, Kaupenjohann M (2014) Suitability of biochars (pyro- and hydrochars) for metal immobilization on former sewage-field soils. *Eur J Soil Sci* 65(1):139–148
- Wagner A, Kaupenjohann M, Hu Y, Kruse J, Leinweber P (2015) Biochar-induced formation of Zn-P-phases in former sewage field soils studied by PK-edge XANES spectroscopy. *J Plant Nutr Soil Sci* 178:582–585
- Wong M, Swift RS (2003) Role of organic matter in alleviating soil acidity. In: Rengel Z (ed) *Handbook of soil acidity*. Marcel Dekker, New York, pp 337–358
- Yathavakulasingam T, Mikunthan T, Vithanage M (2016) Biochar produced at different temperatures as bioamendment to reduce bioavailability of heavy metals. *Am Eurasian J Agric Environ Sci* 16(3):512–517
- Yobouet YA, Adouby K, Trokourey A, Yao B (2010) Cadmium, copper, lead and zinc speciation in contaminated soils. *Int J Eng Sci* 2(5):802
- Yuan JH, Xu RK, Zhang H (2011) The forms of alkalis in the biochar produced from crop residues at different temperatures. *Biores Technol* 102:3488–3497
- Zheng R, Chen Z, Cai C, Tie B, Liu X, Reid BJ, Huang Q, Lei M, Sun G, Baltreinaite E (2015) Mitigating heavy metal accumulation into rice (*Oryza sativa* L.) using biochar amendment—a field experiment in Hunan, China. *Environ Sci Pollut Res* 22(14):11097–11108





Methods for Determining Lignocellulosic Biochar Wettability

Luiza Usevičiūtė¹ · Edita Baltrėnaitė¹

Received: 1 November 2018 / Accepted: 28 May 2019 / Published online: 4 June 2019
© Springer Nature B.V. 2019

Abstract

It was shown that many various biochar types are hydrophobic in low temperature (< 500 °C), but high temperature biochar (> 500 °C) has a tendency of increasing hydrophilicity. Hydrophobicity of low temperature biochar is the most often referred to the effect of pores clogging with tars, since aliphatic compounds vapour only at high temperatures. This research used various methods for the evaluation of biochar wettability, such as the water drop penetration time (WDPT) test, the molarity of an ethanol droplet (MED) test and optical determination of a contact angle (CA). Selection of the best method is difficult because of the fact that many studies used different methods, they have been compared with each other, they refer to different theoretical assumptions and they differ technically. The aim of this article is to compare the three methods used for the evaluation of biochar wettability. The chosen techniques include WDPT, MED and CA measurement. Two different temperatures (450 °C and 700 °C) and two different holding times (1 h and 2 h) were used for the production of different wettability biochar types from five different lignocellulosic feedstocks (pine bark, birch bark, pine wood, birch wood and hems). Results of wettability and all used techniques overlapped; and this means that it had the same tendency in characterising biochar wettability. Mechanical and practical arguments have been made for the selection of the most suitable method for determination of biochar wettability.

Keywords Wettability · Biochar · Lignocellulose · Molarity of ethanol droplet test · Water drop penetration time test · Contact angle

Statement of Novelty

Originality of this work is that water drop penetration time (WDPT) test showed the highest variability of wettability degree (from hydrophilic to very strongly hydrophobic) in the case of lignocellulosic biochar, made at different pyrolysis temperatures (450 °C and 700 °C) and holding times (1 h and 2 h). As it is known from literature, that low temperature (< 500 °C) biochar is hydrophobic and high temperature (> 500 °C) biochar is hydrophilic, this test reflected it the best compared to molarity of an ethanol droplet (MED) test and analysis of contact angle.

Introduction

Biochar wettability has effect on many processes which are related to the interaction between biochar and water. Some researchers suggest using biochar for the sorption of pollutants from aqueous environment, such as for the removal of organic and inorganic compounds [1]. Biochar has a capacity to remove various pollutants (including synthetic, natural organic compounds and inorganic compounds) from aqueous solution and this makes biochar a good adsorbent which is used for the treatment of water [2]. Biochar can be applied in many industrial processes, such as treatment of sewage water from town and village, treatment of filtrates from dumps and effluents from industries [3]. Biochar capacity to remove many pollutants from aqueous solution governs the decrease of pollutants' availability and toxicity to living organisms [4]. Hydrophilic biochar is more suitable for the removal of organic pollutants in filtration. However, addition of hydrophobic biochar to soil can enhance soil's hydrophobicity, reduce adsorptive capacity of water, inhibit microbiological activity and change soil's filtration and transformative

✉ Luiza Usevičiūtė
luiza.useviciute@vgtu.lt
Edita Baltrėnaitė
edita.baltrenaite@vgtu.lt

¹ Vilnius Gediminas Technical University, Saulėtekio Avenue 11, 10223 Vilnius, Lithuania

functions [5]. Since different biochar wettability can influence its role in various environmental systems, it is very important to assess it precisely.

Biochar has its wide applicability in environment because of its different features, such as high adsorptive capacity, high surface area, microporosity and ions exchange capacity. Various properties of biochar are linked with the primary feedstock and the pyrolysis conditions. These two factors have a high impact on biochar physical and chemical properties, such as surface area, polarity, wettability, atomic ratio, elemental composition and surface functional groups. Functional groups affect biochar's wettability [6]. Biochar's surface and production temperature govern adsorptive and hydrophobic functional groups. The initial group consists of carboxylic, hydroxylic and methoxy- and the later groups composed of aliphatic and aromatic non-polar groups [7]. Polar functional groups of biochar's surface increase water uptake due to electrostatic interactions and hydrogen bonds. Reduction of them can govern biochar's higher hydrophobicity. Variety of biochar's characteristics has a high impact on its suitability and effectivity for the removal of some pollutants [8]. For example, biochar functional groups containing oxygen can inhibit adsorption of hydrophobic organic pollutants, since the groups containing oxygen are hydrophilic and can form strong hydrogen bonds with water molecules [9]. Hagemann et al. [10] show that biochar interaction with water can be enhanced due to higher biochar's mesoporosity, reductive active sites and biochar's surface hydrophilicity. A better role of biochar in the retention of water is caused by a complex effect of different properties (such as porosity, acidic functional groups) and it cannot be related only with biochar's one property [11].

Many techniques, such as WDPT test [12, 13, 14], MED test [13, 15, 16], determination of CA [6, 17], capillary absorption [6] and nuclear magnetic relaxometry (NMR) [5, 10] were used for the assessment of biochar wettability. The WDPT and MED tests were the two most widely used techniques for the determination of biochar wettability. Since the WDPT test has no physical meaning and the obtainment of the physical meaning from the MED test requires deeper knowledge, the contact angle measurement using the capillary rise method can be regarded as having the highest physical meaning [18], since the contact angle measurement can provide more meaningful information, such as energy value of a solid surface. Surface free energy of solids can be used for the wettability determination of the material instead of the contact angle [19]. Results of the MED test can be used for the counting of approximate tension of solid/air surface [20]. Practically, some research works demonstrate that the MED test is more suitable than the WDPT test in the case of hydrophobic biochar due to a long WDPT [13]. If all previously mentioned tests give information about biochar wettability at

a macroscopic level, NMR provides a possibility to gain much information at a microscopic level. NMR provides information about mechanisms of water molecular dynamics at a microscopic level and this ensures an opportunity to understand the biochar's role in increasing the quality of soil [5].

The WDPT test and the MED test are the frequently used techniques for the determination of biochar wettability. The WDPT test is easy to conduct and useful for the rapid determination of biochar wettability, especially when there is a need to assess many samples. Its drawback is that for the penetration of a water drop into hydrophobic biochar takes a long time, has no physical meaning and a water drop can be affected by some factors, such as roughness of surface and geometry of the pores. Additionally, WDPT values cannot be easily repeated and they give only qualitative information about hydrophobicity stability; however, they do not provide quantitative information about the contact angle [21]. The WDPT test consists of pulling down of a water drop on the surface of biochar and fixation of time for the complete infiltration. If biochar is hydrophobic, a water drop will not penetrate into the surface of biochar, will form a spherical form and retain on the biochar's surface for some time instead. This period of time which is needed for the water drop to retain on the biochar's surface is called the WDPT test and depends on a degree of biochar hydrophobicity. If a water drop retains on the biochar's surface for a longer time, biochar has a higher degree of hydrophobicity [22].

The MED test, which is also known as the "percentage of an ethanol" or "critical surface tension" test, is a modified form of the WDPT test and uses different concentrations of ethanol for the alteration of liquid's surface tension. The MED test quantitatively determines biochar wettability, like the lowest ethanol concentration which allows for the drop to penetrate during first 3 or 5 s. It effectively determines how strongly a water drop is repelled and this property is best related to the degree of hydrophobicity [22]. Since these methods are simpler and easier to conduct, they have less scientific background. This shows a need for more accurate and quantitative methods which could determine biochar wettability. For example, some quantitative methods were used for the evaluation of biochar's physical processes (such as the sessile drop method). In the case of the sessile drop method, a contact angle of a water drop on the smooth biochar's surface is assessed [21].

The aim of this article is to compare wettability of biochar types made of different lignocellulosic biomass using three different methods: WDPT test, molarity of ethanol drop test and measurement of contact angle. Since wettability of biochar assessed by different methods statistically correlates, practical and mechanistical arguments have been made, which shows that the WDPT test is the most suitable in the case of biochar.

Materials and Methods

Samples

Biochar was made from five varieties of lignocellulosic feedstock (pine bark, birch bark, pine wood, birch wood and hems) at two different pyrolysis temperatures (450 °C and 700 °C) and two different holding times (1 and 2 h) for the determination of its wettability. Pine and birch are the most widely distributed coniferous and deciduous tree species in Lithuania. Pyrolysis was performed in a muffle furnace (SNOL). The muffle furnace is designed in such way that it does not allow inflow of air/oxygen. The pyrolyzer was sealed (to prevent oxygen flow) and heated to 450 °C and 700 °C at a rate of 10 °C/min. Before pyrolysis, the samples were rolled in aluminium foil for the creation of oxygen deficiency conditions [23]. 20 different biochar types were produced: four pine bark biochar types made at 450 °C and 700 °C temperatures and for 1 and 2 h holding times (respectively PB450_1, PB450_2, PB700_1, PB700_2), four birch bark biochar types (BB450_1, BB450_2, BB700_1, BB700_2), four pine wood biochar types (PW450_1, PW450_2, PW700_1, PW700_2), four birch wood biochar types (BW450_1, BW450_2, BW700_1, BW700_2) and four hems biochar types (H450_1, H450_2, H700_1, H700_2). The desired temperature was held for 1 and 2 h (slow pyrolysis), after which the pyrolyzed materials were left to slowly cool down to room temperature. During the pyrolysis process, the non-condensable gases exited through the fumehood. The entire unit was placed in a fumehood, so that the produced smoke could be adequately ventilated. Once the experiment reached terminal temperature, it was maintained for 1/2 h until no further significant release of gas was observed. The weights of the biomass and of the final biochar were recorded to determine the biochar yield. The experiments were performed three times for each pyrolysis temperature and holding time. All biochar samples were milled and homogenised to obtain continuous mass before determining the wettability by applying different methods (WDPT, MED, CA).

Water Drop Penetration Time Test

The procedure to determine biochar wettability by the WDPT test consists of a water drop pulled down on the surface of the analysed material and assessment of the time for a complete drop penetration. 5 g of homogenised biochar samples were placed in 12 ml volume bottles. Then, using a pipette, three drops of water were placed on the biochar's surface from a modest distance (< 10 mm

height) for the creation of a permanent volume of a drop and, using a stop-watch, the WDPT was assessed [13]. The shortest time (≤ 1 s) corresponds to instant penetration of a drop. Such material is regarded as hydrophilic. If a water drop cannot spontaneously penetrate, the material is referred to as hydrophobic [24]. All analyses were finished after 3600 s. Table 1 presents categories of hydrophobicity with corresponding WDPTs.

The WDPT test is regarded as an indicator which shows the consequences of material's hydrophobicity. WDPT directly refers to soil erosion, since the surface flow is impacted by time which is needed for the penetration of rainfall water [19].

Molarity of the Ethanol Droplet Test

MED tests used mixtures of ethanol and deionised water which were used for the assessment of their sorption in 3 s on the biochar's surface. Seven mixtures of different concentrations (0, 3, 5, 11, 13, 18, 24 and 36%) were used to test. Droplets (0.05 ml) of prepared solutions were pulled down on the plane surface of biochar from a short distance (< 5 mm) with a pipette. A droplet of the solution was pulled down from a short distance for the reason to avoid excess of kinetic energy, which can demolish biochar's surface [25]. The test was started with deionised water. If the solution penetrated into the surface of biochar within 3 s, that material got a corresponding index. The material got a number of the hydrophobicity index which corresponded to the concentration near it. The indices of hydrophobicity and corresponding concentrations of ethanol solutions are shown in Table 2.

MED values were categorised from 1 (very hydrophilic) to 7 (extremely hydrophobic), when 0% concentration of an ethanol solution corresponded to a very hydrophilic and 36% concentration of an ethanol solution corresponded to an extremely hydrophobic material. A higher value of the MED index is related with a higher degree of hydrophobicity. The surface tension of an ethanol solution is decreasing with the increasing concentration of an ethanol solution; therefore, a droplet with a lower surface tension (respectively, a higher concentration of an ethanol solution) will infiltrate into the porous solid material faster than solution with a high surface

Table 1 Categories of hydrophobicity with corresponding WDPTs

WDPT (s)	Category of hydrophobicity
≤ 1	Hydrophilic
1–60	Slightly hydrophobic
60–600	Strongly hydrophobic
600–3600	Very strongly hydrophobic
≥ 3600	Extremely hydrophobic

Table 2 Indices of hydrophobicity and corresponding concentrations of ethanol solutions [44]

Ethanol (%)	Index of hydrophobicity
0	0 veryhydrophilic
3	1 hydrophilic
5	2 slightly hydrophilic
11	3 slightly hydrophobic
13	4 moderate hydrophobic
18	5 strongly hydrophobic
24	6 very strongly hydrophobic
36	7 extremely hydrophobic

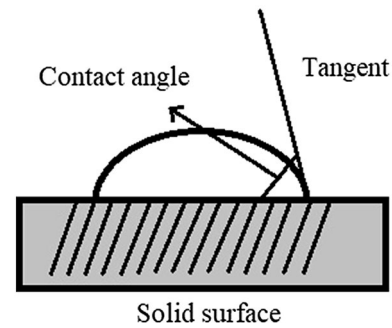
tension (respectively, a lower concentration of an ethanol solution) [20].

In the beginning of the research the material under analysis was placed in a suitable opened container. Before that the material was being dried at 110 °C temperature for 8 h and then cooled down in the ambient conditions. The analysis was started with deionised water without ethanol. Then more droplets were placed on the surface of the substrate. If droplets could penetrate it in <3 s, the tested substrate obtained the value of “0”. If a tested droplet needed more time than 3 s to penetrate, the first tested ethanol solution was used. Then, using the tested solution’s number 1, many droplets were pulled down on the surface from a short distance. If droplets could penetrate faster than within 3 s, the material got the index “1”. The previously mentioned process was repeated progressively using a higher number of MED solutions until the solution which penetrated into the material within 3 s or less period of time was found. The material obtained a number of the hydrophobicity index which corresponded to the concentration of the solution near it.

Determination of the Contact Angle

Wettability of different biochar types was assessed employing the sessile drop method which was used to determine the contact angle between water drop and biochar surface. The contact angle can be defined as the angle between the tangent to the periphery of the point of the fluid contact with the biochar’s surface and the surface of the biochar in the direction where the droplet exists (Fig. 1) [26]. A modified preparation method of the sample proposed by Shang et al. [27] was used. Biochar was sieved through 600 µm sieve for the purpose to remove big particles and get a planar surface. Biochar dried in the air was placed on the microscopic slide and smoothed using another slide on it which then was removed. All slides were cleaned with acetone and washed with deionized water before the analysis.

For the determination of the contact angle, a 0.5 ml droplet of deionised water was pulled down with a pipette for 5 s

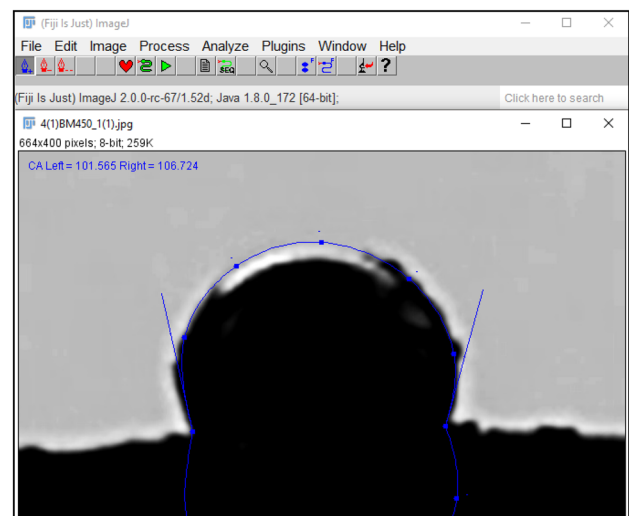
**Fig. 1** Schematic view of the contact angle. (Color figure online)

at approx. 1 cm height above the biochar’s surface. Then profile photo of a water drop was made using *Alcatel Idol-4* camera from the 10 cm distance to the sample. Photos were converted into the grey scale colour using *PhotoScape* and trimmed. Photos (Fig. 2) were analysed employing *ImageJ* software with the *DropSnake* plugin [17].

Five different photos were analysed for every biochar type. The contact angle for the determination of wettability was counted as an average value of the left and right contact angles. The contact angle less than 90° shows hydrophilic biochar and the angle larger than 90° shows hydrophobic biochar.

Statistical Analysis

In this research, statistical parameters, such as average values, standard deviations and Pearson’s correlation coefficients, were calculated and compared with different wettability data assessed by different methods using *Statistica10*.

**Fig. 2** *DropSnake* plugin in *ImageJ* software

Results and Discussion

Biochar Yield

Increasing of the pyrolysis temperature led to reduction in the yield of different biochar types, which decreased from 22 to 20% of total pine bark biomass, from 25 to 17% of birch bark biomass, from 24 to 16% of pine wood biomass, from 21 to 13% of birch wood biomass and from 28 to 15% of hems biomass respectively at 450 °C and 700 °C temperatures in the case of 2 h holding time (Table 3).

Comparing low temperature (450 °C) biochar yields made for different holding times, 1 h pyrolysis produced higher yields of various biochar types except in the case of hems. Additionally, comparing high temperature (700 °C) biochar yields, 1 h pyrolysis produced higher biochar yields in the case of birch bark, pine wood and hems. In general, biochar yields decreases as the holding time increases. The highest value of biochar yield was obtained in the case of low temperature (450 °C) and shorter holding time (1 h) pine bark biochar (37%) and the smallest value of biochar yield was obtained in the case of high temperature (700 °C) birch wood biochar (13%, 1 and 2 h holding times). It was observed that different type of feedstock led different percentage of biochar yield. This is influenced by the variation of lignocellulosic component and ash content in the

feedstock. Higher lignin composition in the feedstock will result in higher biochar yield [28]. Coniferous lignin is found to be more stable than deciduous lignin and former produces larger biochar yields [29].

Results of the Contact Angle Analysis

According to the results of the contact angle between biochar solid material and water drop, almost in all cases of all biochar types (except hems) wettability is increasing (respectively, the contact angles are decreasing) when the pyrolysis temperature (from 450 to 700 °C) and holding times (from 1 to 2 h) increase (Fig. 3). A grey dotted line in Fig. 1 marks 90° boundary which separates hydrophilic (< 90°) and hydrophobic (> 90°) biochar. The highest degree of hydrophobicity was obtained by birch bark biochar (BB450_1) and the highest hydrophilicity was demonstrated by hems biochar (H450_2) in all biochar types. Different biochar types made from hems wetting behaviour could be explained by its higher polarity, hydrophilicity and microporosity what is necessary for physical water attraction. According to determined contact angles, all biochar types of pine wood and hems can be referred to as hydrophilic (< 90°). Low temperature biochar types of pine bark (PB450_1 and PB450_2), birch bark (BB450_1) and birch wood (BW450_1) are hydrophobic according to the contact angles (respectively, 101.19°, 98.69°, 107.14° and 101.84°).

The contact angle results (86.99°) in pine wood biochar (PW450_1) are similar to those obtained by another researcher [6], when wood biochar had a contact angle close to 90°, except for the PW600_40 type, but biochar from corn digestate had slightly lower contact angles. Biochar type PW600_40 corresponds to pine wood biochar type made at 600 °C temperature and 40 min holding time. Even though, theoretically, the material can be named hydrophobic when the contact angle is larger than 90°, but when the values are close to 90° they show high potential hydrophobicity.

Table 3 Quantity of pyrolyzed biomass and solid yield of biochar

Biochar type	Quantity of biomass (g)	Biomass yield (%)
Pine bark, 450 °C, 2 h	222.57	22.42
Birch bark, 450 °C, 2 h	570.91	24.65
Pine wood, 450 °C, 2 h	1168.76	24.19
Birch wood, 450 °C, 2 h	1757.83	20.65
Hemps, 450 °C, 2 h	207.14	28.09
Pine bark, 450 °C, 1 h	38.1	37.17
Birch bark, 450 °C, 1 h	204.11	29.22
Pine wood, 450 °C, 1 h	314.23	27.42
Birch wood, 450 °C, 1 h	481.2	25.14
Hemps, 450 °C, 1 h	225.85	26.59
Pine bark, 700 °C, 2 h	1225.63	19.88
Birch bark, 700 °C, 2 h	554.02	16.73
Pine wood, 700 °C, 2 h	782.89	16.07
Birch wood, 700 °C, 2 h	1313.16	13.35
Hemps, 700 °C, 2 h	226	15.25
Pine bark, 700 °C, 1 h	349.42	14.18
Birch bark, 700 °C, 1 h	284.26	18.59
Pine wood, 700 °C, 1 h	541.42	33.17
Birch wood, 700 °C, 1 h	800.36	13.15
Hemps, 700 °C, 1 h	238.05	16.34

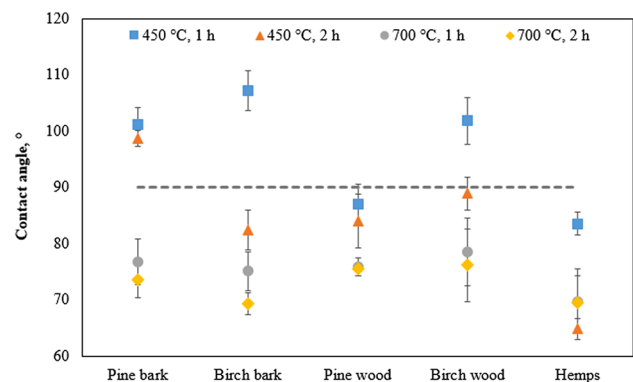


Fig. 3 Contact angles between biochar surfaces of different types and a water droplet (n = 5)

This study shows a tendency of a decreasing contact angle with an increasing pyrolysis temperature in the case of all analysed biochar types (pine bark, birch bark, pine wood, birch wood and hemsps) and it is similar to the results of other scientific studies [17]. One study on contact angles demonstrates that low temperature (400 °C) biochar from herbaceous biomass CA reached 118° and in the case of high temperature (600 °C) biochar it reached 101°. Since CA was larger than 90°, they both were referred to as hydrophobic. Low temperature (400 °C) biochar was more hydrophobic compared to high temperature biochar. It is supplemented by the fact that in the case of low temperature biochar WDPT was higher (> 1 min) compared to high temperature biochar WDPT (< 10 s).

Another study [30] on the contact angles makes a presumption that wettability of biochar is not stable with time. Ojeda et al. [30] showed that the contact angle of biochar decreased by 69.5% after 1 year of amendment of soil, and this meant that hydrophobicity of biochar disappeared after 1 year. This decrease of hydrophobicity can improve soil's water holding capacity. Hydrophobicity, which is referred to a higher biochar contact angle than 90°, can inhibit water infiltration to its internal pores and this weakens soil's capacity to hold water [31].

Analysis of photos of water droplets on the surface of different biochar shows that their shapes vary from elliptical (e.g. in the case of birch wood (BW700_1)) to spherical (e.g. in the case of pine bark biochar (PB450_1)) (Fig. 4). Contact angles of biochar from pine bark vary from 73.62° (PB700_2) to 101.19° (PB450_1), from birch bark from 69.36° (BB700_2) to 107.14° (BB450_1), from pine wood from 75.43° (PB700_2) to 86.99° (PB450_1), from birch wood from 76.15° (BW700_2) to 101.84° (BW450_1) and from hemsps from 64.83° (H450_2) to 83.52° (H450_1).

Results of Water Drop Penetration Time Test

According to the WDPT test, in the cases of all biochar types, made at low temperature (450 °C) and holding times of 1 and 2 h (except of one pine wood biochar type (PW450_2) and biochar types from birch wood and hemsps), they had high hydrophobicity (600–3600 s, the substrate is hydrophobic). According to the WDPT, biochar from birch bark (BB450_1) had the highest hydrophobicity, since its WDPT reached 1904s. All remaining low temperature biochar types had slight hydrophobicity (WDPT from 1 to 60 s). Three high temperature (700 °C) biochar types were hydrophilic: from birch bark BB700_1, WDPT = 1.33 s), from pine wood (PW700_1, WDPT = 1 s) and from hemsps (H700_1, H700_2, WDPT = 1 s). All remaining high temperature biochar types had slight hydrophobicity (WDPT from 1 to 4 s) (Figs. 5, 6). The results of WDPT test confirm

the idea that when pyrolysis temperature is increasing, hydrophobicity of biochar decreases [12].

The WDPT test shows the same tendency that biochar wettability is increasing with the rise of the pyrolysis temperature as it was proved by the CA results. This tendency was reflected especially in the case of biochar types from pine and birch barks with 1 and 2 h holding times. In the case of pine bark biochar with 1 h holding time, biochar wettability varied from very strongly hydrophobic (PB450_1, WDPT = 1333 s) to slightly hydrophobic (PB700_1, WDPT = 2.33 s). The same tendency is reflected in the case of pine bark biochar with 2 h holding time (PB450_2, WDPT = 1465 s; PB700_1, WDPT = 4 s). In the case of birch biochar, wettability varied similarly to pine bark biochar according to the rising temperature and holding time, since wettability differed from very strongly hydrophobic to slightly hydrophobic (BB450_1, WDPT = 1904 s and BB700_1, WDPT = 1.33 s; BB450_2, WDPT = 1351 s and BB700_2, WDPT = 4 s). These results resemble the results of another study [12] when biochar made from pig manures, cotton residues and municipal solid waste obtained at 300 °C were classified as very strongly hydrophobic (> 3600 s). At 400 °C and holding times of 1 and 2 h, they were strongly hydrophobic with the categories of 901 s and > 3600 s. Hydrophobicity of all samples completely disappeared over 500 °C temperature. Hydrophobicity of low temperature biochar was explained by aliphatic functional groups determined by the FTIR technique. Das and Sarmah [32] also showed that low temperature biochar had lower availability to water due to its lower surface area, lower porosity and aliphatic functional groups which govern hydrophobicity.

Another study [33] assessed biochar types made from corn stover, soy beans, switch-grass and hardwood (500–600 °C) wettability employing the WDPT test. In this research, biochar types which had WDPT from 0 to 5 s were referred to as hydrophilic, from 5 to 60 s as slightly hydrophobic, from 60 to 600 s as strongly hydrophobic, from 600 to 3600 s as highly hydrophobic and over 3600 s as extremely hydrophobic. The main classification difference of this study is that the category of hydrophilicity is prolonged up to 5 s. The results show that all fresh biochar types were more hydrophobic when compared with the aged ones. Age of biochar types was related with additional wetting–drying periods of biochar. It was shown, that after additional wetting/drying treatment biochar became less hydrophobic and therefore aged biochars were more hydrophilic than fresh biochars. Wettability of biochar types was investigated after different treatments: after drying (referred as time 1) and after second wetting–drying period (time 2). Fresh biochar was referred to sieved (< 1 mm) and dried biochar, meanwhile aged biochar was related to biochar incubated in special conditions (with dissolved organic carbon) for 2 months. Most hydrophobic biochar types were made from soy beans

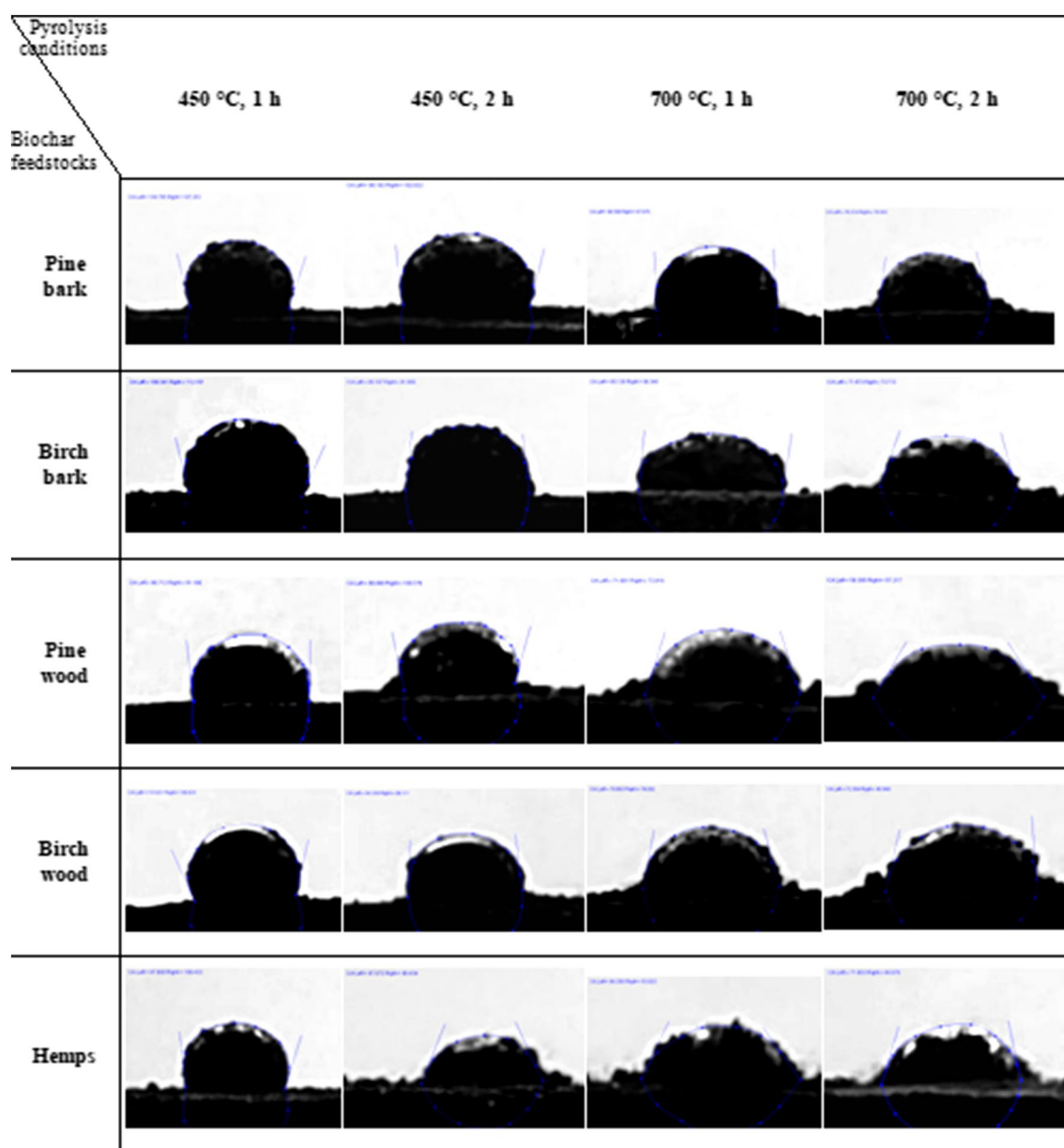


Fig. 4 Water droplets on the surfaces of different biochar types

and hardwood by flash pyrolysis and from hardwood by slow pyrolysis, since WDPT reached more than 3600 s and were referred to as extremely hydrophobic. In the case of this research, most hydrophobic biochar types were less hydrophobic compared to the previously mentioned study, since they were referred to as highly hydrophobic. The WDPT test showed that aged biochar types were more hydrophilic compared to fresh ones and the biochar types after the additional effect of wetting/drying were less hydrophobic. In the case of some fresh extremely hydrophobic biochar types (made from soy beans and hardwood by flash pyrolysis and hardwood by slow pyrolysis) with WDPT more than

3600 s, hydrophobicity decreased after 2 weeks and obtained the categories of slightly hydrophobic (< 60 s) and strongly hydrophobic (750 s). Another study [14] also shows that freshly made biochar from yellow pine (*Pinus ponderosa*) has hydrophobic characteristic, since WDPT reached more than 2 h.

The classification provided in one study [12] differs from this research by the highest degree of hydrophobicity (> 3600 s) which was identified as strongly hydrophobic. However, in the cases of this and another [11] studies, the highest degree of hydrophobicity was identified as extremely hydrophobic (> 3600 s).

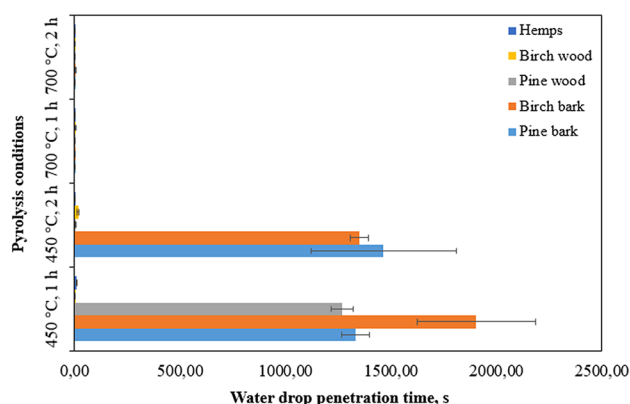


Fig. 5 WDPT of different biochar types (n = 3)

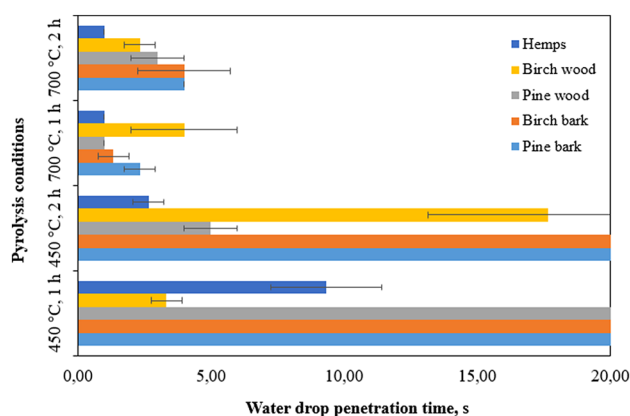


Fig. 6 Zoomed view of WDPT of different biochar types (n = 3)

Results of Molarity of the Ethanol Droplet Test

According to the results of the ethanol droplet test, all biochar types made from different types of feedstock and under pyrolysis conditions were hydrophilic (MED index varied from 0 to 2). Biochar types made from pine and birch barks at 450 °C temperature and with holding times of 1 and 2 h were slightly hydrophilic (MED = 2), since biochar types made from pine wood (PW450_1 and PW450_2), birch wood (BW450_1 and BW450_2) and

hemp (H450_1) were hydrophilic (MED = 1). All biochar types made at 700 °C temperature and holding times of 1 and 2 h were highly hydrophilic (MED = 0) (Table 4).

One study [13] analysed wettability of biochar produced from pine wood, pine bark and hybrid poplar wood employing the WDPT and MED tests. The MED test showed that hydrophobicity of biochar decreased when pyrolysis temperature increased; however, the WDPT test did not show any similar tendency. Wettability of biochar varied from extremely hydrophobic (MED = 30 in the case of pine bark biochar, 350 °C) to hydrophilic (MED = 0.1 in the case of pine wood biochar, 600 °C). Across all feedstock types, pine bark (350 °C) and hybrid poplar wood (350 °C) biochar types were extremely hydrophobic compared to pine wood biochar (350 °C), and this shows differences related to chemical and physical properties of the feedstock. Compared to the results of the MED test, a tendency that low temperature (450 °C) pine bark biochar is less wettable compared to pine wood biochar produced in the same temperature (respectively MED indices were equal to 2 and 1) was shown too.

Another study [15] showed that wettability values of biochar made from pine wood relating to pyrolysis temperature were different from those of the present study. Hale et al. [15] analysed surface wettability of biochar made from palm leaves, pine wood, coconut husks, pistachio husks and fruit stones at 300 °C (holding time of 2–2.5 h) and 600 °C (holding time of 1–1.5 h), which was assessed using dried and fresh biochar samples sieved through 0.5 mm screen applying MED test. MED values of 1 to 2 showed that samples were hydrophilic, those of 3 to 4 that slightly and moderately hydrophobic and values 5–7 showed extremely high hydrophobicity of the materials.

Assessing the time period which was used for the complete penetration of an ethanol solution to the surface of carbon, it varied in the wide time interval (3–10 s). For example, one study [16] suggested using 10 s, which was applied for the complete infiltration of an ethanol solution (with concentrations of 0 to 6 M). Meanwhile, this study applied the time interval of 3 s for the MED test. These methodological differences can govern significant distinctions between biochar types from the same feedstock.

Table 4 Hydrophobicity of biochar types determined by molarity of the ethanol droplet test (n = 3)

Pyrolysis conditions	Biochar feedstock types				
	Pine bark	Birch bark	Pine wood	Birch wood	Hemps
450 °C, 1 h	2	2	1	1	1
450 °C, 2 h	2	2	1	1	0
700 °C, 1 h	0	0	0	0	0
700 °C, 2 h	0	0	0	0	0

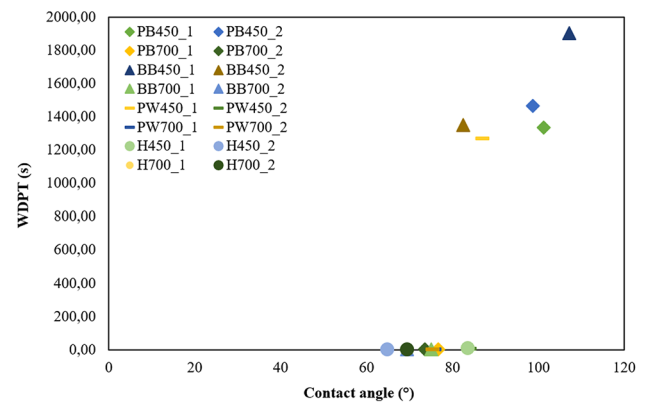
Table 5 Pearson correlation coefficients (r) for wettability parameters of different biochar types determined by different methods ($n = 12$)

Correlated parameters	Biochar type				
	Pine bark	Birch bark	Pine wood	Birch wood	Hemps
WDPT	0.985	0.971	0.518	0.555	0.949
MED					
WDPT	0.969	0.84	0.645	0.085	0.732
CA					
MED	0.987	0.718	0.935	0.809	0.869
CA					

Correlation of Biochar Wettability Results While Using Different Methods

Pearson correlation (Table 5) was carried out to determine a potential link for biochar wettability which was determined by different methods (WDPT test, molarity of the ethanol droplet test and contact angle method). The black colour marks a very strong positive or negative relation between two independent variables ($r \geq 0.7$ or $r \leq -0.7$). A dark grey colour marks strong relation between two independent variables ($0.4 \leq r \leq 0.69$ or $-0.4 \leq r \leq -0.69$). A light grey colour marks no relation among the variables (zero correlation, $r = 0$). Pearson correlation for biochar wettability determined by different methods show a very strong positive or strong positive linear correlation between results of the WDPT (s) and MED index as well as between MED index and a contact angle ($^\circ$) for all biochar types. Pearson correlation between WDPT and contact angle was very strongly and strongly positive for almost all biochar types (except for the case of birch wood biochar, $r = 0.085$). The results of correlation coefficients show that all three methods for the determination wettability are suitable for the determination of biochar wettability.

Response of the WDPT to the changes of the contact angle in the interval 64.83 – 101.84° was insignificant in the case of biochar types made from hemps and birch wood, and almost in all cases of pine wood biochar (except PW450_1) (Fig. 7). Hydrophilicity ($\text{WDPT} \leq 1$ s) of high temperature biochar from hemps and pine wood (respectively H700_1, H700_2, PW700_1) is related with a lower contact angle (in the case of PW700_1, $\text{CA} = 75.78^\circ$); however, very strong hydrophobicity ($600 \text{ s} < \text{WDPT} < 3600 \text{ s}$) is related to higher contact angles (in the case of BB450_2, $\text{CA} = 82.46^\circ$; in the case of BB450_1, $\text{CA} = 107.14^\circ$). In the interval of 64.83 – 101.84° , all types of biochar from birch wood and some other biochar types (except PB450_1, PB450_2, BB450_1, BB450_2, PW450_1, PW700_1, H700_1, H700_2) show slight hydrophobicity ($1 \text{ s} < \text{WDPT} < 60 \text{ s}$). In the case of biochar from pine bark, WDPT was the most susceptible in the CA interval of 77 – 99° , biochar from birch bark was 75 – 82° , biochar from

**Fig. 7** Relation between contact angles of different biochar types and WDPT, $n = 3$

pine wood was 83 – 86° , since slight increase of the contact angle changed the WDPT category from hydrophilic to hydrophobic. The correlation between contact angle and WDPT is useful in extending knowledge about hydrophobic biochar, whereas the WDPT could help to understand contact angles of particular biochar.

Practically, though the highest variation of wettability showed molarity of the ethanol droplet test which can provide eight different categories according to the degree of wettability (three categories are referred to hydrophilicity, two to slight and moderate hydrophobicity and other three to very strong and extreme hydrophobicity), this study did not show wide variation of wettability for the biochar types from five different feedstock types, since all types got hydrophilicity categories. The contact angle can provide two categories depending on whether the contact angle between biochar's surface and water drop can exceed 90° or not. Therefore, all biochar types received two categories of wettability—either hydrophilic or hydrophobic. Assessing the results of the WDPT, all biochar types had the highest variety of wettability: they were categorised as hydrophilic and very strongly hydrophobic. For this reason, the WDPT test can be considered as the most suitable test for the biochar. Besides, it is simple and does not require special equipment. The only drawback of this test is that it takes a long time and does not have physical meaning in the theory of wettability compared to assessment of the contact angle which can be used for the determination of the energetic value of the solid material. If only wettability values are required, the WDPT test is suitable in the case of biochar.

Discussion

For understanding wettability of biochar made from different lignocellulosic materials, it is important to know its chemical composition, as wettability is a function of material's

surface chemistry. Wood is chemically composed of macromolecular compounds (holocellulose (cellulose, hemicellulose) and lignin) and components with low molecular weight (extractives) [34]. Macromolecular compounds are located in the cell walls and known as the structural components, and nonstructural components have low molecular weight (extractives). Extraneous materials, mostly in the form of organic extractives and inorganic minerals (ash), present in wood in minor amounts (usually 4–10%) [35]. In general, wood species contain about 40–50% cellulose, 20–30% hemicellulose, 20–35% lignin and up to 10% extractives. Softwoods normally contain more cellulose and lignin than hardwoods [36]. Comparing morphological components of trees, Scots pine stem wood consists of 27.0% of lignin and its bark consists less more than two times of the same component (13.1%). In the case of silver birch, its stem wood contains 20.2% of lignin and its bark has about 5% lesser lignin compared to the wood (14.7%) [34]. Meanwhile, lignocellulosic crop-residues like hemp straw has less lignin compared to softwood, but a slightly more than hardwood (21.65% compared to 27.0% and 20.2%, respectively). This trend could explain in this study slightly higher hydrophobicity of low-temperature (450 °C, 1 h) hemp biochar compared to low-temperature birch wood biochar, since lignin is related with higher hydrophobicity compared to holocellulose.

Since higher lignin content is related with the higher biochar yield, it can be predicted, that lignin content in the softwood biochar (pine wood) in this study is higher compared to the hardwood (birch wood) and the difference of the biochar yield in this study is clearly seen in the case of low temperature (450 °C, 2 h) biochar (24.24% biochar yield compared to 20.71%, respectively). Since pine wood contains more lignin (27.2%) than other wood species (19.4–23.9%), it could contribute to the lower wettability of pine wood surfaces [37]. Similarly, this study showed that low-temperature pine wood biochar (450 °C, 1 h) was severely hydrophobic (1269.5 s of WDPT) compared to birch wood biochar made at the same conditions (3.3 s of WDPT), which was only slightly hydrophobic. Since lignin generally pyrolyzes at a slower rate than cellulose and holocellulose (Wood and wood-based... 1989), this could explain why biochar made at lower temperature was more hydrophobic compared to higher temperature in this study. According to literature, lignin is more hydrophobic material compared to cellulose considering analyzed contact angles (55–77° and 20–30°, respectively) [36]. As it is known, lesser contact angles of specific material are linked with higher hydrophilicity. Cellulose, hemicellulose are more or less hydrophilic in their nature. Lignin, however, is considered as less hydrophilic compared to the cellulose and hemicelluloses [38]. Earlier it was found [39] that natural lignin of the vessel walls in the xylem of plants was unwettable. Microscopical

investigations of wood samples of several species of trees showed apparently well-planned pattern of distribution of lignin over the water-contacted surface of the vessel wall. Strongly lignified unwettable domains were surrounded by very wettable cellulose.

The presence of extractives at the wood surface can also influence the wettability depending upon wood species. The extractives play a significant role affecting the water wettability of wood by two effects. One is direct on the wettability of the true surface and the other effect is the blockage by extractives of the openings between cells, thus preventing penetration of a droplet below the surface of the wood. It was found that specific wettability of wood (four species) in water was inversely correlated with the percentage of extractives within the wood species [40]. Wood extractives can be classified as lipophilic (e.g. terpenes, waxes, triglycerides (fats), steryl esters and sterols) and hydrophilic (carbohydrates and phenolic compounds). Lipophilic extractives (i.e. wood resin) are the main source of the wood surface inactivation, since they can migrate to the surface and make it more hydrophobic [36]. Most extractives are hydrophobic. Higher pine wood hydrophobicity (contact angle of 54.19°) compared to birch venner samples (contact angle of 45.34°) could be also related with higher amount of extractives (4.4–5.6%) in comparison to the other investigated wood species (0.8–3.8%) [37]. Extractives of pine include most of the wood resins, including nonpolar terpenes, since hardwoods have extractives, which are more polar.

High wettability difference between biochar made from different tree species stem wood and bark in this study could be also linked to the high content of certain soluble constituents, e.g. extractives and mineral content. Comparing low-temperature (450 °C, 2 h) pine wood biochar wettability with its bark it can be seen, that biochar from bark was severely hydrophobic (1464.5 s of WDPT) compared to biochar from wood (5 s of WDPT), which was only slightly hydrophobic. The same tendency was observed in the case of biochar made from birch wood and bark (1350.5 s of WDPT compared to 17.7 s of WDPT). One of the governing factor of such wettability differences could be lipophilic extractives, which are found in the bark. The total content of both lipophilic and hydrophilic extractives usually corresponds to 20–40% of the dry weight of bark. The lipophilic fraction consists mainly of fats, waxes, terpenoids and higher aliphatic alcohols [41]. Non-polymeric lipids, the „waxes“, are deposited in suberized and cutinized cells, sometimes in very significant amounts, and probably have a major role in the hydrophobicity and low permeability of these cell walls [42]. Similarly, since hemp fiber has lesser amount of fat and wax (0.7–1.3) compared to woody material [43], it could also explain why low temperature hemp biochar was more hydrophilic compared to biochar from woody biomass in this study. Another factor, affecting wettability of

biochar made from different morphological tree elements and crop-residues, could be the percentage amount of cellulose, which is more hydrophilic in nature compared to the lignin. For example, stem wood of pine has 43.9% of cellulose, since pine bark has only 10.7% (A sustainable... 2017). Hemp fiber tends to have higher amount cellulose (55–72%) compared to woody biomass [43]. This could explain high difference of wettability of low-temperature (450 °C, 2 h) biochar types, made from different bark of pine and birch compared to hemp (1464.5 s, 1350.5 s and 2.7 s of WDPT, respectively).

Conclusions

1. Assessment of wettability of biochar types made from five feedstock types by different methods demonstrates that the WDPT test is the most suitable for biochar, since it shows the highest variation of wettability compared to molarity of the ethanol droplet test and analysis of the contact angle. Wettability of all biochar types varies from hydrophilic to very strongly hydrophobic.
2. Results of the WDPT test can predict wettability of a specific biochar type. Hydrophilicity is connected with lower contact angles (75.78°, PW700_1) and hydrophobicity with higher ones (107.14°, BB450_1).
3. Analysis of correlation concludes that all three methods used to determine wettability are suitable for assessment of biochar wettability, since almost all types of biochar exhibit strong or very strong correlation between wettability values. Correlation of wettability determined by different methods in the case of biochar from pine and birch barks and hems show a very strong positive correlation. It means that all three methods are suitable for the prediction of similar tendency of biochar wettability.
4. Practically, the WDPT can last long on the hydrophobic biochar surface (> 3600 s); therefore, some research studies prove that this test is not suitable for the fresh biochar. Indeed, a water drop can be impacted by several factors, such as surface roughness and geometry of the pores. Biochar wettability values determined by this test are not easily repeated and it supports only qualitative information about the stability of wettability. Analysis of contact angles cannot be suitable in the case of powder biochar with very small sizes of particles because of very rapid penetration and significantly more difficult determination compared to a flat surface of the biochar. Therefore, for the assessment of wettability of powdery porous materials, it is often suggested to use the capillary rise method instead of the analysis of contact angles. Many additional factors can affect inaccurate determination of a contact angle, such as intensiveness of lightning, focusing, quality of the solid material's sur-

face (heterogeneity, roughness), purity of the tested liquid, skills of a researcher, methodology and performance of the procedure (such as compression of the material). Besides, this analysis can provide only two values of contact angles for the droplet. Therefore, the gained data can characterise only two points of the surface. However, the surface of all solid materials has some degree of heterogeneity. To estimate surfaces adequately, it is necessary to analyse several droplets. This makes the analysis of contact angles time consuming. The main disadvantage of molarity of the ethanol droplet test is that it cannot precisely assess wettability of biochar in the wide range of interval from hydrophobic to hydrophilic according to this study.

5. Even though the WDPT test and molarity of the ethanol droplet test are simpler and easier to perform, they have little scientific meaning. Due to the investigation of physical processes of biochar and water droplet, such as critical surface tension of the solid, it is reasonable to conduct the analysis of the contact angle.

References

1. Werner, S., Katzi, K., Wichern, M., Buekert, A., Steiner, C., Marschner, B.: Agronomic benefits of biochar as a soil amendment after its use as waste water filtration medium. *Environ. Pollut.* **233**, 561–568 (2018)
2. Gwenzi, W., Chaukura, N., Noubactep, C., Mukome, F.N.D.: Biochar-based water treatment systems as a potential low-cost and sustainable technology for clean water provision. *J. Environ. Manag.* **197**, 732–749 (2017)
3. Duwiejua, A.B., Cobbina, S.J., Bakobie, N.: Review of eco-friendly biochar used in the removal of trace metals on aqueous phases. *Int. J. Environ. Bioremediat. Biodegrad.* **5**(2), 27–40 (2017)
4. Rao, M.A., Simeone, G.D.S., Scelza, R., Conte, P.: Biochar based remediation of water and soil contaminated by phenanthrene and pentachlorophenol. *Chemosphere* **186**, 193–201 (2017)
5. Bubici, S., Korb, J.-P., Kučerik, J., Conte, P.: Evaluation of the surface affinity of water in three biochars using fast field cycling NMR relaxometry. *Magn. Reson. Chem.* **54**, 365–370 (2016)
6. Dieguez-Alonso, A., Funke, A., Anca-Couce, A., Rombola, A.G., Ojeda, G., Bachmann, J., Behrendt, F.: Towards biochar and hydrochar engineering—influence of process conditions on surface physical and chemical properties, thermal stability, nutrient availability, toxicity and wettability. *Energies* **11**(3), 496 (2018)
7. Abel, S., Peters, A., Trinks, S., Schonsky, H., Facklam, M., Wesolek, G.: Impact of biochar and hydrochar addition on water retention and water repellency of sandy soil. *Geoderma* **202–203**, 183–191 (2013)
8. Oliveira, F.R., Patel, A.K., Jaisi, D.P., Adhikari, S., Lu, H., Khalal, S.K.: Environmental application of biochar: current status and perspectives. *Bioresour. Technol.* **246**, 110–122 (2017)
9. Yang, K., Jiang, Y., Yang, J., Lin, D.: Correlations and adsorption mechanisms of aromatic compounds on biochars produced from various biomass at 700 °C. *Environ. Pollut.* **233**, 64–70 (2018)
10. Hagemann, N., Joseph, S., Schmidt, H.P., Kammann, C.I., Harter, J., Borch, T., Young, R.B., Varga, K., Taherymoosavi, S., Elliott,

- K.W.: Organic coating on biochar explains its nutrient retention and stimulation of soil fertility. *Nat. Commun.* **8**, 1089 (2017)
11. Suliman, W., Harsh, J.B., Abu-Lail, N.I., Fortuna, A.-M., Dallmeyer, I., Garcia-Perez, M.: The role of biochar porosity and surface functionality in augmenting hydrologic properties of a sandy soil. *Sci. Total Environ.* **574**, 139–147 (2017)
 12. Zornoza, R., Moreno-Barriga, F., Acosta, J.A., Munoz, M.A., Faz, A.: Stability, nutrient availability and hydrophobicity of biochars derived from manure, crop residues, and municipal solid waste for their use as soil amendments. *Chemosphere* **144**, 122–130 (2016)
 13. Kinney, T.J., Masiello, C.A., Dugan, B., Hockaday, W.C., Dean, M.R., Zygourakis, K., Barnes, R.T.: Hydrologic properties of biochars produced at different temperatures. *Biomass Bioenergy* **41**, 34–43 (2012)
 14. Briggs, C., Breiner, J.M., Graham, R.C.: Physical and chemical properties of *Pinus Ponderosa* charcoal: implications for soil modification. *Soil Sci.* **177**(4), 263–268 (2012)
 15. Hale, L., Luth, M., Crowley, D.: Biochar characteristics relate to its utility as an alternative soil inoculum carrier to peat and vermiculite. *Soil Biol. Chem.* **81**, 228–235 (2015)
 16. Amonette, J.E.: Letter Report for Characterization of Biochar. Pacific Northwest National Laboratory, Washington (2013)
 17. Jeffery, S., Meinders, M.B.J., Stoof, C.R., Bezemer, T.M., van de Voorde, T.F.J., Mommer, L., van Groenigen, J.W.: Biochar application does not improve the soil hydrological function of a sandy soil. *Geoderma* **251–252**, 47–54 (2015)
 18. Hallet, P. D. (2007): An introduction to soil water repellency, *Proceedings of the 8th International Symposium on Adjuvants for Agrochemicals*, 6–9 August, Columbus, Ohio, USA
 19. Leelamanie, D.A.L., Karube, J., Yoshida, A.: Characterizing water repellency indices: contact angle and water drop penetration time of hydrophobized sand. *Soil Sci. Plant Nutr.* **54**, 179–187 (2008)
 20. Korenkova, L., Šimkovic, I., Dlapa, P., Jurani, B., Matuš, P.: Identifying the origin of soil water repellency at regional level using multiple soil characteristics: the White Carpathians and Myjavská Pahorkatina Upland case study. *Soil Water Resour.* **10**(2), 78–89 (2015)
 21. Lourenco, S.D.N., Saulick, Y., Zheng, S., Kang, H., Liu, D., Lin, H., Yao, T.: Soil wettability in ground engineering: fundamentals, methods, and applications. *Acta peotechnica* **13**(1), 1–14 (2018)
 22. Olorunfemi, I.E., Ogunrinde, T.A., Fasinmirin, J.T.: Soil hydrophobicity: an overview. *J. Sci. Res. Rep.* **3**(8), 1003–1037 (2014)
 23. Baltrėnaitė, E., Baltrėnas, P., Bhatnagar, A., Vilppu, T., Selenius, M., Koistinen, A., Dahl, M., Penttinen, O.-P.: A multicomponent approach to using waste-derived biochar in biofiltration: A case study based on dissimilar types of waste. *Int. Biodeter. Biodegr.* **119**, 565–576 (2017)
 24. Stevenson, W.: Evaluating Soaking Times on the Hydrophobicity of Biochar Using the Water Droplet Penetration Time Method. University of Amsterdam, The soil fertility project (2016)
 25. Page-Dumroese, D.S., Robichaud, P.R., Brown, R.E., Tirocke, J.M.: Water repellency of two forest soils after biochar addition. *Am. Soc. Agric. Biol. Eng.* **58**(2), 335–342 (2015)
 26. Biria, D., Maghsoudi, E., Roostaazad, R.: Application of biosurfactants to wettability alteration and IFT reduction in enhanced oil recovery from oil-wet carbonates. *Pet. Sci. Technol.* **32**(12), 1259–1267 (2013)
 27. Shang, J., Flury, M., Harsh, J.B., Zollars, R.L.: Comparison of different methods to measure contact angles of soil colloids. *J. Colloid Interface Sci.* **328**(2), 299–307 (2008)
 28. Shariff, A., Aziz, N.S.M., Saleh, N.M., Ruzali, N.S.I.: The effect of feedstock type and slow pyrolysis temperature on biochar yield from coconut wastes. *Int. J. Chem. Mol. Eng.* **10**(12), 1410–1414 (2016)
 29. Tripathi, M., Sahu, J.N., Ganesan, P.: Effect of process parameters on production of biochar from biomass waste through pyrolysis: a review. *Renew. Sustain. Energy Rev.* **55**, 467–481 (2016)
 30. Ojeda, G., Mattana, S., Avila, A., Alcaniz, J.M., Volkmann, M., Bachmann, J.: Are soil-water functions affected by biochar application? *Geoderma* **49**, 1–11 (2015)
 31. Liu, Z., Dugan, B., Masiello, C.A., Gonnermann, H.M.: Biochar particle size, shape, and porosity act together to influence soil water properties. *PLoS ONE* **12**(6), e0179079 (2017)
 32. Das, O., Sarmah, A.K.: The love-hate relationship of pyrolysis biochar and water: a perspective. *Sci. Total Environ.* **512–513**, 682–685 (2015)
 33. Aller, D., Rathke, S., Laird, D., Cruse, R., Hatfield, J.: Impacts of fresh and aged biochars on plant available water use efficiency. *Geoderma* **307**, 114–121 (2017)
 34. Raisanen, T., Anthanassiadis, D.: Basic chemical composition of the biomass components of pine, spruce and birch. *For. Refin.* **31**, 4 (2013)
 35. Pettersen, R.C.: The chemical composition of wood. *Chem. Solid Wood* **207**(2), 57–126 (1984)
 36. Moghaddam, M. S.: Wettability of modified wood, doctoral thesis, KTH Royal Institute of Technology, Stockholm (2015)
 37. Bekhta, P., Krystofiak, T.: The influence of short-term thermomechanical densification on the surface wettability of wood veneers. *Maderas Cienc Technol.* **18**(1), 79–90 (2016)
 38. Bryne, L. E.: Aspects on wettability and surface composition of modified wood. Licentiate Thesis, KTH-Stockholm, Sweden (2008)
 39. Laschimke, R.: Investigation of the wetting behaviour of natural lignin—a contribution to the cohesion theory of water transport in plant. *Thermochim. Acta* **151**, 35–56 (1989)
 40. Mantanis, G.I., Young, R.A.: Wetting of wood. *Wood Sci. Technol.* **31**, 339–353 (1997)
 41. Yang, G., Jaakkola, P.: Wood Chemistry and Isolation of Extractives from Wood. Saimaa university of applied sciences, Literature study for BIOTULI project (2011)
 42. Graca, J.: Suberin: the biopolyester at the frontier of plants. *Front. Chem.* **3**, 62 (2015)
 43. Thomsen, A.B., Rasmussen, S., Bohn, V., Nielsen, K.V., Thygesen, A.: Hemp Raw Materials: The Effect of Cultivar, Growth Conditions and Pretreatment on the Chemical Composition of the Fibres. Risø National Laboratory, Roskilde (2005)
 44. Bontchev, R.; Kim, H. S.; Wilson, R. W.; Belcher, R. W.; Cheyney, C.; Manzer, L. E.; Jarand, M. L.; Wan, H.; Malyala, R.: 2016 12 22. Enhanced biochar. US patent No. 62/162, 219

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Dependence of pyrolysis temperature and lignocellulosic physical-chemical properties of biochar on its wettability

Luiza Usevičiūtė¹ · Edita Baltrėnaitė-Gedienė¹

Received: 22 November 2019 / Revised: 20 March 2020 / Accepted: 31 March 2020
© Springer-Verlag GmbH Germany, part of Springer Nature 2020

Abstract

Nowadays, high attention is paid to the knowledge on wettability of biochar, which is still very complicated, since it is acknowledged that it can depend either on primary feedstock, pyrolysis conditions or on environmental factors. Until now, it is known that the main factor responsible for the production of hydrophobic biochar is aliphatic functional groups forming tar compounds which vapour only at a high temperature. High-temperature ($> 500\text{ }^{\circ}\text{C}$) biochar types are considered as hydrophilic due to the effect of the release of pores from the tars. However, it is still not known what the relation between wettability of biochar and other physical-chemical properties of it is and, if it is possible, is there a need to predict wettability of biochar based on other available properties. The article focuses main attention on the determination of physical-chemical properties of biochar made of five different lignocellulosic feedstocks depending on the pyrolysis temperature ($300\text{--}700\text{ }^{\circ}\text{C}$) and their relation with the water holding capacity and wettability of biochar using the multiple regression analysis. The results showed that 54% of variation of biochar wettability could be predicted by its average pore size and 77% of variation of biochar water holding capacity could be predicted according to its ash content. Relation of wettability of biochar with its average pore size can be explained by the physical capacity of biochar to adsorb water on its surface and internal pores as well as retention of water among its particles due to capillary forces.

Keywords Wettability · Water holding capacity · Biochar · Physical-chemical properties · Multiple regression analysis · Lignocellulose

1 Introduction

Biochar is a renewable material which can be produced by pyrolysing organic biomass (from forestry, agricultural wastes, poultry and cattle manures, etc.) under the oxygen deficiency conditions [15]. Biochar has wide application in the environment because of its different properties such as high adsorptive capacity, high surface area, microporosity and ion exchange capacity [43]. For the optimisation of specific application of biochar, it is necessary to carefully choose the biomass feedstock and pyrolysis conditions for the

production of biochar having different characteristics. Many studies were conducted to relate conditions for production of biochar, its characteristics and final application of biochar [19].

Physical and chemical properties of biochar can differ and are mostly affected by the conditions of the pyrolysis process (holding time, temperature) and primary feedstock [26]. Unexploitative sources, such as sewage sludge, poultry manure and kitchen wastes, usually are not used for the production of biochar due to the risk of potential pollution and its effects. Meanwhile, biochar made from cheap and available forestry and agricultural wastes does not create hazards to water bodies, solid environmental components, human health and atmosphere due to reduced emissions of greenhouse gases [72]. Application of cheap and locally available biomass for the biochar production gains more and more attention from scientific communities [65]. Moreover, such biomass is uniformly distributed in the whole world similarly to the coal or petroleum. This makes lignocellulosic material, which is renewable natural source, a good choice for the production of

✉ Luiza Usevičiūtė
luiza.useviciute@vgtu.lt

Edita Baltrėnaitė-Gedienė
edita.baltrenaite-gediene@vgtu.lt

¹ Vilnius Gediminas Technical University, Saulėtekio Avenue 11,
LT-10223 Vilnius, Lithuania

biochar materials compared to fossil fuels [66]. Especially green wastes, including leaves, tree branches, timber and bushes, can be effectively converted into biochar [63].

Though biochar was widely studied, its interaction with water is still not well understood yet since contrasting results of dependence of wettability of biochar on pyrolysis temperature can be found in literature [9]. Some studies showed that low-temperature (< 500 °C) biochar was often hydrophobic, since in low temperature, it retains many organic functional groups from the primary feedstock [25]. Similarly, Kinney et al. [32] showed that biochar types, made from different feedstocks, had a similar tendency: pyrolysis at 300 °C produced very hydrophobic biochar; however, hydrophobicity was reduced when temperature increased and biochar types produced at 500 °C were highly wettable. One more study showed that at low-temperature (300 °C) biochar types made from crop wastes and pig manure had high hydrophobicity which was lost at temperature higher than 500 °C [81]. These findings contradict results of earlier studies where the idea is proposed that biochar types made at higher temperatures have higher hydrophobicity. Chun et al. [12] and Pimchuai et al. [45] showed that higher temperature influenced less water adsorption on the char's internal surface and it substantiated the idea that char's hydrophobicity is increasing with the rise of pyrolysis temperature until 700 °C [67]. It is thought that further increase of pyrolysis temperature determines hydrophobicity of biochar due to higher loss of polar surface functional groups and increase of biochar's aromaticity which is reflected through the reduction of O/C ratio. Hydrophobic surface of biochar can inhibit entrance of water into the porous structure of carbon.

Wettability of most natural materials, including soil and biochar, is a very complex phenomenon which is still not well understood [49]. Wettability is considered as a quantitative indicator of water-biochar relations. When these liquid-solid interactions are stronger, the material is more wettable. However, when mentioned interactions are weaker, wettability of the material is lower. Typically, hydrophobicity of biochar is explained by the presence of aliphatic functional groups. Other research [14] also claimed that biochar types made at lower pyrolysis temperatures (< 500 °C) had lower attraction to water due to low surface area, low porosity and presence of aliphatic functional groups which enhance hydrophobicity of the material. In conclusion, wettability is one of the most important parameters, which estimates the role of biochar in many environmental technologies [9]. Hydrophobicity of biochar can be an important factor affecting changes in fertility of plants, cycle of nutrients and production of greenhouse gasses in soils amended by biochar through the partitioning of water and flow alterations [7]. Meanwhile, hydrophilicity of biochar can be an important feature of biochar for its application in the removal of volatile organic compounds from the air stream or for the

enhancement of the water holding capacity in sandy soils. Such features of biochar like surface acidic functional groups, microporosity and high surface area are important properties of biochar for enhancement of its wettability [1].

The aim of the article is to determine how different primary lignocellulosic feedstocks and pyrolysis temperature influence physical-chemical properties of biochar and, using multiple regression analysis, to find particular properties which are the most suitable for the prediction of wettability of biochar. Physical-chemical properties of biochar, such as wettability, pH, electrical conductivity, ash content, water holding capacity, elemental (C, H, N, O) composition, surface functional groups, specific surface area, pore volume and pore size according to various pyrolysis temperatures (300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C) were analysed. Two equations were obtained using multiple regression analysis, and it was estimated which biochar properties were best suited for the prediction of its water holding capacity and wettability.

2 Materials and methods

2.1 Collection of the feedstocks and biochar production

Biochar types were made from five different types of lignocellulosic materials: pine (*Pinus sylvestris*) wood, pine bark, birch (*Betula pendula*) wood, birch bark and hemp (*Cannabis*). Pine and birch wood was collected from Dūkštai-Šilėnai forest which can be found on the territory outside Vilnius, 14 km north-west of Vilnius. Pine and birch bark was collected from Gaidės forest which can be found in the north-east part of Lithuania, 2 km outside Visaginas town. Pine forests are the main forests in Lithuania (35.8%). Fir forests (21.4%) and birch forests (21.1%) are the second and third largest forests in the country. Hemp was collected from Panevėžys district, Lithuania, Hemp strain—Futura 75, which is high-quality French industrial hemp strain that is grown in Europe.

Feedstocks were pyrolysed at various pyrolysis temperatures (300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C) lasting for 2 h holding time and approximately at 10 °C/min heating rate in the muffle furnace (SNOL). Temperature was controlled in the furnace by thermocouple inside the bed. Sample weights were of 200 g, which were later rolled in the aluminium foil for the creation of oxygen deficiency conditions [5]. After pyrolysis, the biochar yield was determined. All biochar samples were milled and homogenised to obtain particle size lower than 2 mm, which was used for the further analysis.

2.2 Methodology of the determination of physical-chemical properties of biochar

Biochar yield was expressed in the percentages according to the dry weight of the sample [40]:

$$Y_{\text{biochar}}(\%) = \frac{\text{biochar weight}}{\text{Feedstock weight}} \times 100 \quad (1)$$

where Y_{biochar} (%) is the yield of the dried biochar in the ambient atmosphere. Ash content, electrical conductivity and water holding capacity of biochar were determined according to the requirements of the European Biochar Certificate [20]. Samples were heated in the furnace at 550 °C for 1 h. A crucible was used for the determination of the content of biochar ash. The crucible containing the sample was weighed and placed in the furnace. After the heating, residual mass was expressed as an ashy mass [39, 62]. According to the results of ash weights, the ash content was calculated according to the equation [4]:

$$\text{Ash content} = \frac{W_2 - W_c}{W_1 - W_c} \times 100, \% \quad (2)$$

where W_c is the mass of an empty crucible, g; W_1 is the mass of the crucible containing the sample mass before the heating, g; W_2 is the mass of the crucible containing the ashes after the heating, g. Minimum amount of 5 ml of air dried sample was placed in a glass bottle. Five times more (25 ml) of 0.01 M CaCl₂ solution was poured into the same bottle. The suspension was shaken for 1 h. pH was analysed directly from the suspension using the pH-meter Mettler Toledo Seven Multi [20]. Ten grams of the sample was placed in 100 ml desalinated water and shaken for 1 h. Then, solution was filtered through the filter paper (VWR 413, particles retention 5/13 µm). Electrical conductivity was determined in the filtration water using InoLab WTW serial 740 electrical conductivity meter. The elemental composition of biochar (C, H, N, O) was analysed using the EuroEA3000-Single analyser. A total of 1.5–3 mg of air dried sample was weighed directly in the tiny capsule. After that, the capsule was closed and placed in the EuroEA3000-Single analyser for the determination of elemental composition [20]. EA3000 analyzers refer to a very well-established principle of dynamic flash combustion after which chromatographic separation of gasses (N₂, CO₂, H₂O, SO₂) and then detection of TCD proceed. Using the Callidus software package, accurate analytical results can be obtained. Wettability of biochar was determined using the water drop penetration time test. Using a pipette, a drop of water was placed on the biochar's surface and, using a stopwatch, the time was counted for the complete penetration of the drop of water [32]. The shortest time was 0.2 s and it shows complete penetration of the drop of water. Evaluations were completed after 3600 s. All times exceeding

3600 s was attributed to the category of 3600 s. All categories are shown in Table 1.

The water holding capacity was analysed saturating biochar for 24 h, and after that, biochar was placed into the filter for 2 h to remove excessive water [76]. Then, the saturated material was weighed and dried in the furnace at 40 °C temperature [20]. The dried material was weighed again for the determination of the water holding capacity. The water holding capacity was calculated according to the Eq. 3:

$$\text{WHC} = \frac{M_2 - M_3}{M_3 - M_1} \times 100 \quad (3)$$

where M_2 is biochar mass after saturation for 24 h period of time, g; M_3 is biochar mass after the removal of excessive water content, g; M_1 is dried biochar mass, g.

The Fourier transformation infrared spectroscopy (FTIR) analysis was performed using Spectrum One spectrometer (Perkin Elmer, UK) in the range of 450–4000 cm⁻¹ wavenumbers to characterize the surface functional groups for different biochar types. Special sample preparation method including usage of potassium bromide (KBr) was used to prepare pressed pellets. FTIR is frequently used to identify and qualitatively track changes in functional groups in biochar samples [8]. Chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule. The correlation of the band wavenumber position with the chemical structure is used to identify a functional group in a sample. The presence of specific functional groups can be monitored by these types of infrared bands, which are called group wavenumbers. For the determination of biochar physical properties (specific surface area (SSA), pores volume and average pore size) NOVA 4200 analyser (Quantachrome Instruments, United States of America) was used. For N₂ isotherms, the BET SSA was determined using BET equation [53]. Both (FTIR and BET) analyses were conducted at the laboratory of the Latvian State Institute of Wood Chemistry.

2.3 Statistical analysis

Descriptive analysis (average value, standard deviation, minimum and maximum values) was conducted using Microsoft

Table 1 Categories of wettability of biochar referring to water drop penetration times (WDPT)

WDPT (s)	Category of wettability
≤ 1 s	Hydrophilic
1–60 s	Slightly hydrophobic
60–600 s	Highly hydrophobic
600–3600 s	Severely hydrophobic
≥ 3600 s	Extremely hydrophobic

Excel 2016 software. For the determination of the relation of water holding capacity and wettability of biochar with other physical-chemical properties of it, the multiple regression analysis was carried out using the Statistical Package for the Social Sciences (SPSS) software (International Business Machines Corporation (IBM), USA). The step-wise regression analysis was used to select significant variables, by either accepting or eliminating the respective predictor variables, based on the probability level (P value). A predictor variable associated with a P value less than predetermined significance level was added; otherwise, the variable was dropped [52]. Two regression analyses were performed: (1) for the prediction of biochar water holding capacity (biochar water holding capacity was the dependent variable and other biochar physical-chemical properties (C, H, O concentrations, pH, electrical conductivity, ash content, total volume of pores, volume of micropores, average size of pores) were independent variables; (2) for the prediction of biochar wettability (biochar wettability was the dependent variable and C, H, O concentrations, pH, electrical conductivity, ash content, total volume of pores, volume of micropores, average size of pores, intensities of hydroxyl functional group ($-OH$) and phenolic functional group ($C-O$) were independent variables). The root mean square deviation (RMSE) was counted according to the equation no. 4 [44]:

$$RMSE = \sqrt{\frac{\sum (f(x_i) - y_i)^2}{n}} \quad (4)$$

The mean absolute percentage error (MAPE) was calculated using Eq. 5 [27, 39]:

$$MAPE = \frac{1}{n} \sum \frac{|y_i - x_i|}{x_i} \times 100 \quad (5)$$

The mean squared error (MSE) was calculated according to the Eq. 6:

$$MSE = \frac{1}{n} \sum (x_i - y_i)^2 \quad (6)$$

The median absolute deviation (MAD) can be calculated according to the Eq. 7:

$$MAD = \frac{1}{n} \sum |x_i - y_i| \quad (7)$$

3 Results and discussion

3.1 Biochar yield

Biochar yield made from different lignocellulosic materials is shown in Fig. 1. The yield decreased when the temperature

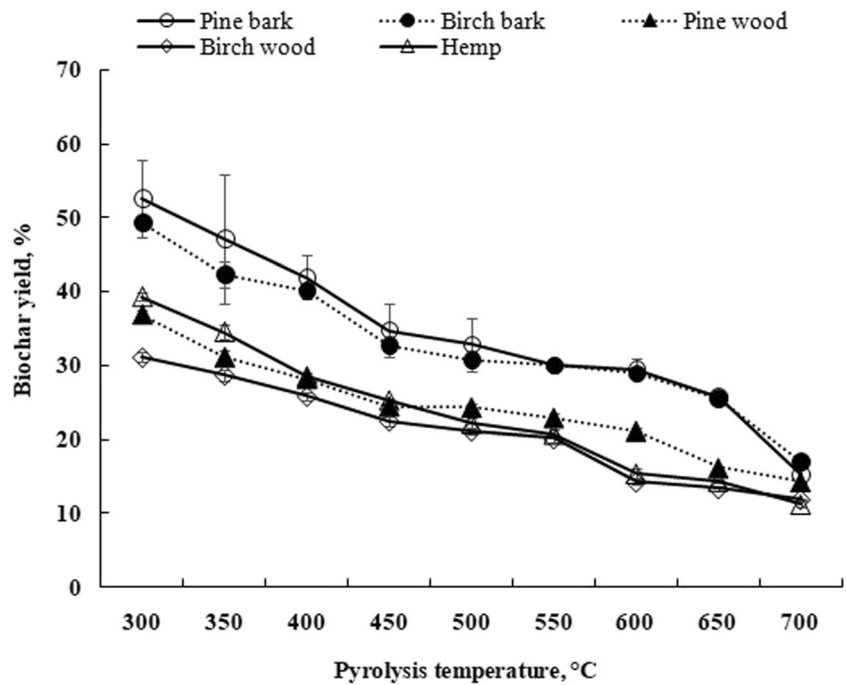
increased in the case of all feedstocks. Biochar made from pine bark, birch bark, pine wood, birch wood and hemp yield decreased respectively from 55 to 15.09%, 49.22 to 16.85%, 36.84 to 14.19%, 31.05 to 11.76% and 93.26 to 11.18%. It can be explained by the higher loss of volatile compounds at higher pyrolysis temperatures [23]. Highest yield of all feedstocks was obtained at the lowest temperature (300 °C) and pine bark biochar had the highest yield (52.55%) compared to other feedstocks. Meanwhile, the lowest yield of all biochar types was obtained at the highest temperature (700 °C) and hemp had the lowest yield (11.18%) compared to other biochar types. The decrease of biochar yield is related with primary thermal biomass degradation [48]. When pyrolysis temperatures increase, pyrolytic volatile compounds are further decomposed into the low-molecular-weight organic compounds and gasses. Similarly, other study [31] showed that biochar made from sewage sludge yield significantly decreased with increasing pyrolysis temperature from 72.5% at 300 °C to 52.9% at 700 °C.

Figure 1 demonstrates that biochar yield differs not only in respect to different temperatures but also between different feedstocks (wooden biomass and non-wooden biomass) and even between different components of the same tree species (wood and bark). There are only a few studies which analysed the effect of temperature on the biochar yield, elemental composition, ash content, pH and electrical conductivity. Quantitative knowledge on parameters of biochar is important for the evaluation of quality and commercial value of biochar and its potential suitability, stability and performance in the environmental systems. Mathematical relation between process conditions (such as pyrolysis temperature) and physical-chemical properties of biochar allows choosing suitable process conditions for the production of biochar containing its desirable properties [48].

3.2 Ash content in biochar

According to the results of ash content in all biochar types, it can be concluded that it increased with the rise of the pyrolysis temperature from 300 to 700 °C. The ash content in pine bark, birch bark, pine wood, birch wood and hemp differs according to the increase of the temperature, respectively from 3.22 to 5.57%, 2.16 to 6.89%, 0.58 to 3.99%, 0.82 to 2.77% and 2.95 to 32.1%. From all biochar types, the highest ash content was in the high temperature (700 °C) hemp biochar (32.1%). To sum up, the ash content in all biochar types rose when pyrolysis temperature increased due to higher concentrations of minerals from organic wastes [23]. The progressive increase of the ash content is related to the increase of inorganic compounds in biochar [80]. Biochar made from hemp showed high ash content near all temperatures and it was partly governed by the changes in biomass composition, which occur due to possible links between organic and inorganic

Fig. 1 Yields of different biochar types (%), $n = 2$

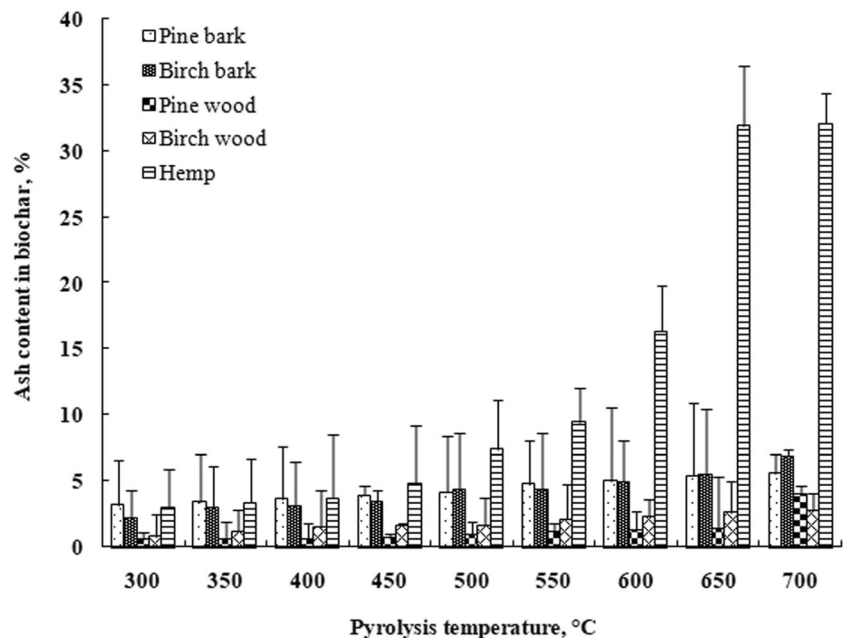


compounds in the feedstock during pyrolysis when biochar has ash content higher than 20% [28]. This tendency was similar to other studies which used different lignocellulosic wastes for the biochar production, such as pine needles or animal manure [23].

Similarly, one study showed that the ash content in pine wood biochar increased from 2.5 to 4.7% when pyrolysis temperature rose from 300 to 700 °C [73]. Biochar types having low amount of ashes (<2.5%) do not provide sufficient amount of nutrients into the soil compared

to biochar types having high amount of ashes (made from manure or bones) [17]. One study [3] showed that ash content of the rapeseed (made at 400 °C, 450 °C, 500 °C, 550 °C and 700 °C) biochars was quite high and increased with the increasing temperature from 19.3 at 400 °C to 26.1% at 700 °C. The ash content is a measure of the non-volatile matter and non-combustible component of the biochar. The ash content of biochars increased due to reduction of other elements like carbon, nitrogen, hydrogen and oxygen.

Fig. 2 Ash content in different biochar types (%), $n = 3$

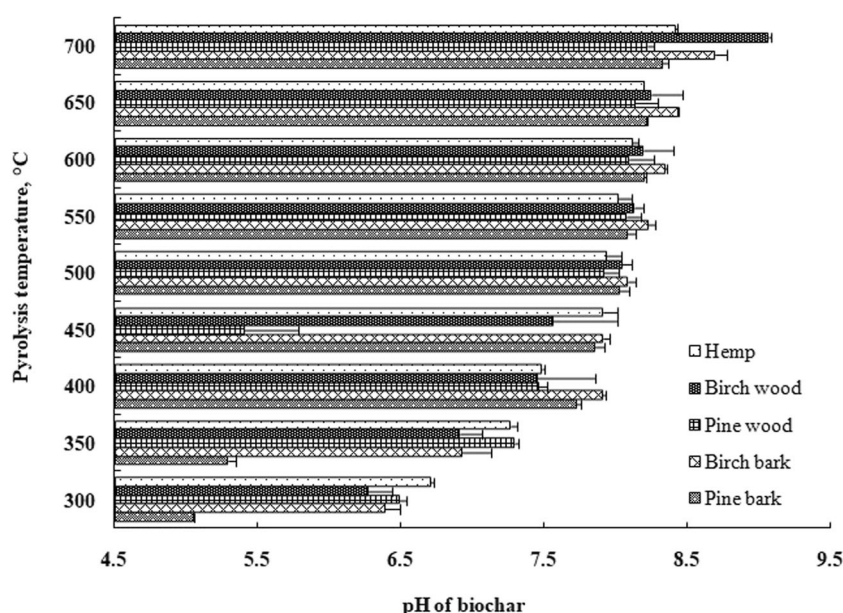


3.3 pH of biochar

According to pH values of different biochar types, it is shown (Fig. 3) that pH of biochar increases when pyrolysis temperature rises in the case of all feedstocks. pH of pine bark biochar increases from 5.05 to 8.32; in the case of birch bark biochar, it rises from 6.39 to 8.69; pine wood biochar goes up from 6.48 to 8.22; birch wood biochar increases from 6.27 to 9.06 and hemp biochar is from 6.7 to 8.41. The pH increase with the rising temperature can be related with the higher ash content in high temperature biochar types due to hydrolysis of Ca, K and Mg salts [42]. The pH increase is governed by higher concentration of unpyrolysed inorganic elements which are found in original feedstock [28].

The increase of biochar pH according to the rising pyrolysis temperature was found in the case of biochar made from corn cob straw, sewage sludge, pine wood, poultry manure and sugarcane straw. When pyrolysis temperature rises, ashes are enriched with the main cations which relate to alkaline compounds, such as carbonates, oxides and hydroxides. Previously, it was found that carbonates were the main alkaline components of biochar. Biochar's alkaline value is principally regulated by the amount of ashes in biochar and chemical composition (main cations) and by the lower extent by pH of biochar [18]. Biochar typically becomes alkaline in the case of high pyrolytic temperatures, since heating increases the ash content and the loss of acidic functional groups [51]. Type of the feedstock (crop wastes, wood biomass) is a strong indicator of the pH. Functional groups ($-OH$, $-COOH$) mainly evaluate the reactivity of biochar decompose at high pyrolytic temperatures ($> 500\text{ }^{\circ}\text{C}$) [58]. One study [31] showed that biochar pH significantly increased with increasing pyrolysis temperature from 7.8 at $300\text{ }^{\circ}\text{C}$ to 9.0 at $500\text{ }^{\circ}\text{C}$.

Fig. 3 pH of different biochar types, $n = 3$



3.4 Electrical conductivity of biochar

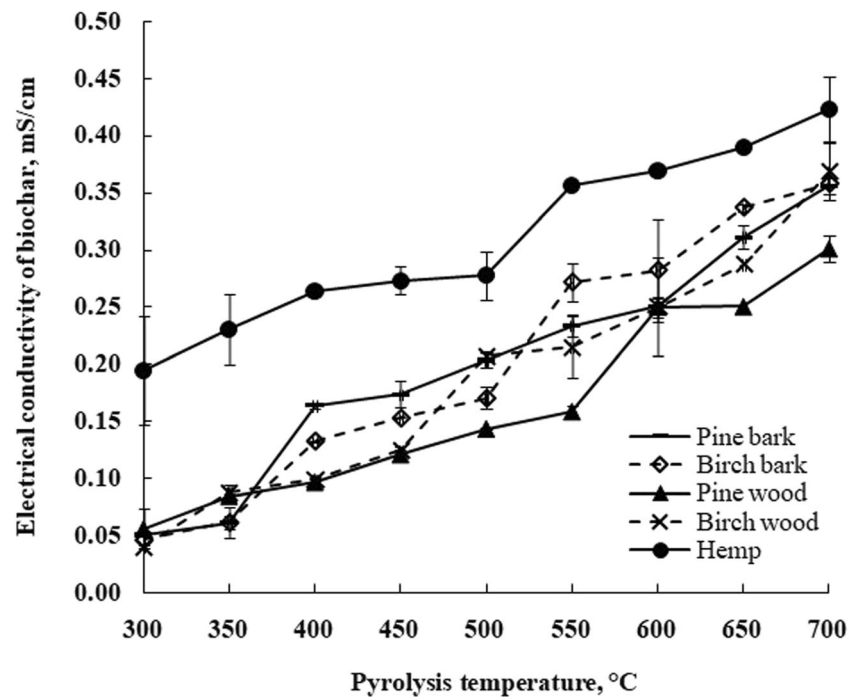
According to the results of the biochar electrical conductivity, it increased when pyrolysis temperature rose from 300 to $700\text{ }^{\circ}\text{C}$ in the case of all feedstocks: from 0.05 to 0.36 mS/cm (in the case of pine bark biochar), from 0.05 to 0.36 mS/cm (in the case of birch bark biochar), from 0.06 to 0.3 mS/cm (in the case of pine wood biochar), from 0.04 to 0.37 mS/cm (in the case of birch wood biochar) and from 0.19 to 0.42 mS/cm (in the case of hemp biochar) (Fig. 4).

Electrical conductivity shows a common amount of dissolved salts or common amount of dissolved ions in the sample. Electrical conductivity of the biochar increases when temperature rises due to the loss of volatile compounds, and it is governed by the higher concentration of salts in the ash fraction [42]. Some researchers [31] showed that electrical conductivity of sewage sludge biochar increased with temperature and biochar made at the lowest temperature ($300\text{ }^{\circ}\text{C}$) had the lowest electrical conductivity.

3.5 Water holding capacity of biochar

The water holding capacity of all biochar types increased when pyrolysis temperature rose from 1.09 to 3.09 times in the case of pine bark, birch bark from 0.9 to 2.13 times, pine wood from 1.47 to 3.97 times, birch wood from 1.33 to 2.16 times and hemp from 1.99 to 9.12 times (Fig. 5). The water holding capacity or material's capacity to retain water depends on porosity and interconnectivity of pores in the material. This explains why high-temperature biochar types can retain more water in its porous structure. Since low-temperature biochar types have porous structure as well, they can be lesser available for water due to lower pores, lower interconnectivity of

Fig. 4 Electrical conductivity of different biochar types, $n = 3$



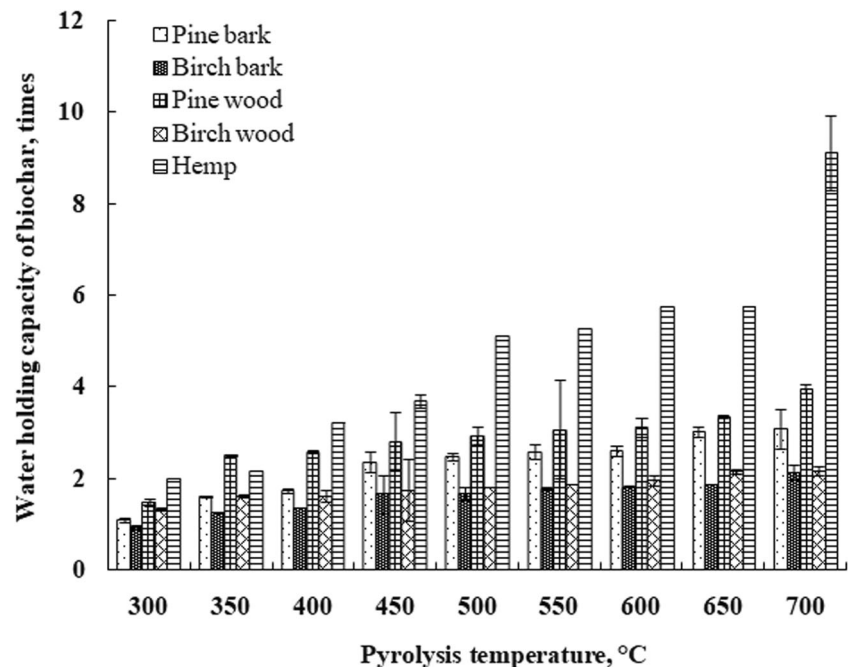
pores and residual tar components which block biochar pores [67].

Similarly, one study showed that biochar made from switchgrass had the water holding capacity of 448.69% compared to its primary mass, and biochar made from hemlock had the water holding capacity of 268.34% [75]. It was concluded that switchgrass biochar can be more favourable for enhancing the water holding capacity of the sandy soils. Meanwhile, pine wood biochar could retain 274% of water

and it was similar to hemlock's capacity. The water holding capacity is an important property when biochar is used in sandy soils which quickly dry. It could reduce the amount of water used for irrigation of land.

The water holding capacity of biochar can impact the water holding capacity of soil depending on biochar wettability and environmental conditions. Jeffery et al. [27] showed that biochar made from grass did not improve the water holding capacity of soil. It is explained by hydrophobicity of biochar

Fig. 5 Water holding capacity of different biochar types (times), $n = 3$



(average contact angle of 118°), since grass biochar has lower hydrophobicity compared to biochar made from leaves or wood. Hydrophobicity of biochar varies according to the production temperature and the feedstock; however, it is usually removed after the effect of the environment. Mollinedo et al. [38] found that Maddock and Langhei soils amendment with corn stover (*Z. mays* L.) and switchgrass (*P. virgatum* L.) biochar resulted in the increase of water holding capacity by 25% compared to the soil with no biochar amendment. Biochar incorporation into the soils increased water amount and improved plant available water holding capacity. The study was conducted using single application rate of 104 Mg/ha biochar.

In conclusion, effectivity of the water holding capacity of soil will be reduced if hydrophobic biochar is incorporated; however, hydrophobicity of biochar can be impacted by additional treatment. Hydrophobic biochar has positive pressure for the entrance of water, and it means that additional force is needed for the availability of water to the internal biochar pores. Effect of external forces will impede availability of water into the pores, and it will limit internal pore saturation with water and potential benefit of the water holding capacity of biochar. An additional effect upon biochar with water saturation or composting can significantly reduce problems related with hydrophobicity of biochar [34].

3.6 Wettability of biochar

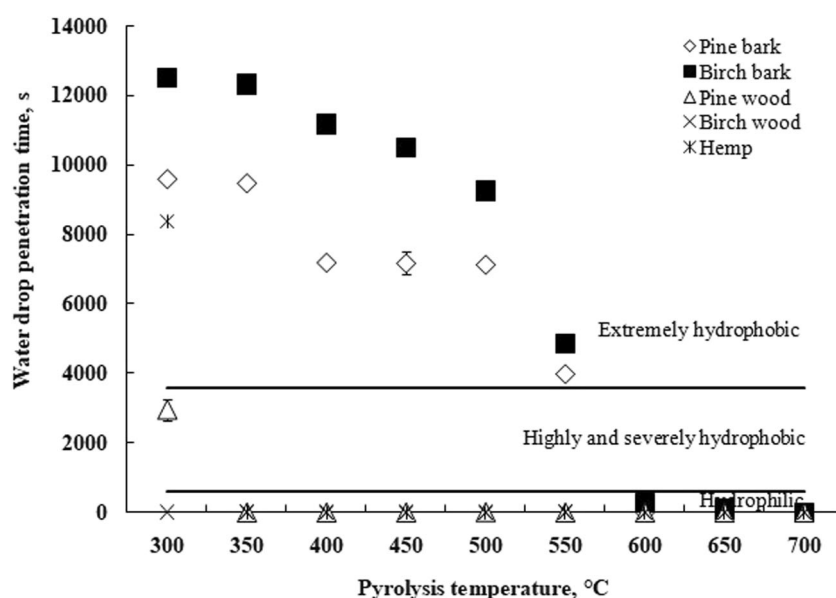
Comparing wettability of biochar according to pyrolysis temperature, a tendency of the increase in wettability of biochar can be observed (Fig. 6). Comparing different feedstock types, birch and pine bark biochar types were the most hydrophobic at all temperatures. These biochar types were extremely hydrophobic even until 550°C . When temperature further

increased until 700°C , their hydrophobicity completely vanished. It can be explained by the blockage of low temperature biochar pores with the tars, since aliphatic compounds which form tars vapour only at high temperatures. Birch wood biochar at all temperatures retained high hydrophilicity (WDPT from 2.33 to 2.47). Similarly, biochar types made from hemp and pine wood which lost their hydrophobicity at 350°C temperature (respectively from 8340 s to 14.13 s and from 2945.33 s to 3.53 s) were highly wettable.

Comparing these results with other studies, a similar tendency of different biochar types was found. One study [74] showed how pyrolysis temperature impacted wettability of poultry manure biochar. Using the analysis of a contact angle, it was shown that wettability of biochar increased from 300 to 600°C (respectively contact angle decrease from 101.1° to 20.6°). The highest difference of wettabilities occurred between temperatures 350 and 450°C . Biochar pyrolysed at 450°C and higher temperatures were only slightly hydrophobic compared to pure quartz sand. These findings support the hypothesis that hydrophobicity is affected by the vapouring of condensed organic compounds [56]. When pyrolysis is finished and samples are cooled down, amount of the concentrated organic compounds on the pyrolysed upper zone is lower at higher temperatures and it governs lower mass of condensates on the surface of biochar as well as lower hydrophobicity and contact angles.

Other research [32] showed that different biochar types made from corncob, magnolia leaves and apple tree wood were hydrophobic when they were pyrolysed at temperature from 300 to 400°C ; however, they became hydrophilic when they were made at temperatures 500°C and 600°C . Intervals of pyrolysis temperatures at which biochar changes from hydrophobic to hydrophilic are not universal, since one study [54] showed that wood and bark biochar made from 500 to

Fig. 6 Water drop penetration times of different biochar types (s), $n = 3$



600 °C retained their hydrophobicity. Similarly, this study showed that pine and bark biochar lost its hydrophobicity at the temperature of 600 °C.

In conclusion, hydrophobicity of biochar decreases when pyrolysis temperature increases and it can be explained by the aliphatic functional groups which vapour and are lost at higher pyrolysis temperatures [24]. Aliphatic functional group loss at higher pyrolysis temperatures governs that surface of biochar becomes less hydrophobic and even has hydrophilic tendency and then capillary forces enhance water availability into the biochar pores.

When biochar is saturated with water, two different mechanisms occur depending on the wettability of biochar surface: (1) in the case of hydrophilic biochar adhesive forces dominate, which causes formation of water H-links and lets water to wet higher surface of biochar; (2) in the case of hydrophobic biochar water clusters retain the same amount of H-links like in the bulk material (when there is no surface) and material-surface interactions occur mainly because of Van der Waals forces [9].

3.7 Elemental composition and atomic ratios of biochar

All elemental (C, H, N, O) composition and atomic ratios of different biochar types are shown in Table 2. In the case of all feedstocks when pyrolysis temperature increased from 300 to 700 °C, the amount of C also increased, but the amount of H, O and N decreased. Amount of C in the case of all feedstocks varied in the wide range, and in the case of pine bark, it was the highest (47.47–85.72%). Similarly, Conz et al. [13] showed that in the case of wood biochar (made from sawdust), amount of C varied in the highest range, and it differed from 51 to 77%. Similar results were obtained in another study [59] when amount of C in the case of pine bark biochar differed from 66.1 to 85.72% (when temperature increased from 350 to 600 °C). The highest amount of C was evaluated in birch bark biochar which reached 92.3% at 700 °C temperature in this study. High increase of C content from 300 to 350 °C could be governed by devolatilisation of pine bark. Similarly, another study [50] showed a high jump of C content from 270 to 400 °C temperature in the case of wood biochar. When pyrolysis temperature increased, the amount of C also rose in the case of all feedstocks, and the highest increase of C was obtained in the case of pine bark biochar (by 37.75%). Meanwhile, elemental concentrations of O, H and N decreased when temperature increased in the case of all feedstocks. The highest decrease of O content (by 75.03%) was in pine wood biochar. Some biochar types (birch bark and pine wood) had 100% decrease of H content when temperature increased from 300 to 700 °C. Other biochar types (made from pine bark, birch wood and hemp) also showed decrease of H content (respectively by 89.82%, 73.8% and 90.52%).

Increase of pyrolysis temperature caused complete loss (100%) of N in the case of all feedstocks. Similarly, other studies showed that increase of pyrolysis temperature governed higher feedstock carbonisation and it destined higher amount of C and lower amounts of H and O [51]. This can be explained by natural feedstock response to the pyrolysis process, since feedstocks lose surface –OH groups due to dehydration as well as H and O atoms connected with C due to structural degradation [47].

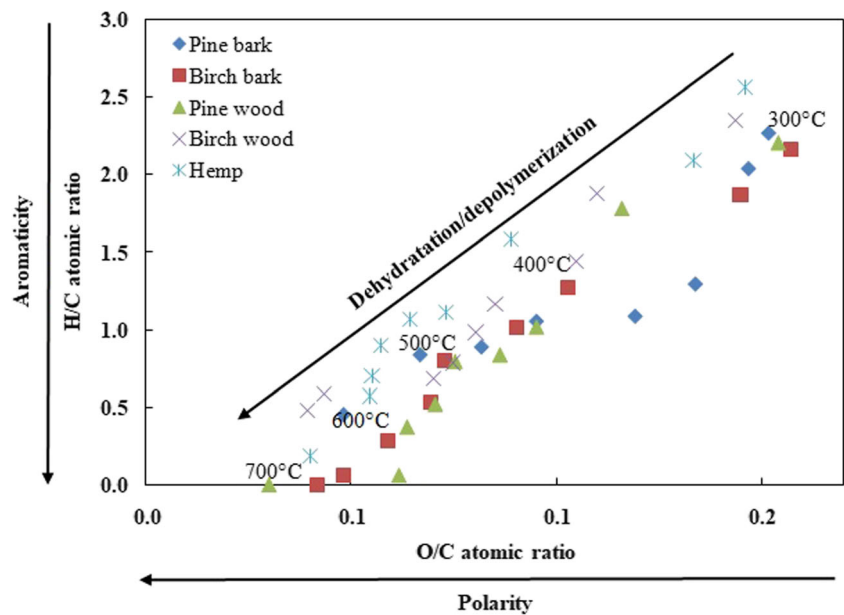
O/C and H/C ratios of different feedstocks are shown in Van Krevelen's diagram (Fig. 7) which shows clear differences between distinct degrees of pyrolytic temperatures for biochar carbonisation. When O/C and H/C ratios are lower, then there is a higher loss of oxygen and hydrogen during the thermal treatment. All biochar feedstocks had high percentage decrease of O/C and H/C ratios when carbonisation temperatures increased from 300 to 700 °C. O/C percentage ratios decreased in such order: pine bark (84.87%) > pine wood (80.48%) > birch bark (73.4%) > hemp (73.33%) > birch wood (71.43%). Meanwhile, H/C ratios decreased in such order: birch bark (100%) > pine wood (100%) > pine bark (94.36%) > hemp (92.72%) > birch wood (79.36%). Loss of CH₃ (demethylation) is evaluated by the H/C ratio, and loss of CO₂ (decarboxylation) governs lower O/C ratios and final carbonisation products enriched with C [68]. Polar functional groups which exist in the feedstock and low-temperature biochar are presented by higher O/C ratios. In other words, a high O/C ratio shows a low carbonisation degree and more likely lower stability of biochar for degradation in the soil, but it shows higher reactivity [68]. According to EBC recommendations, H/C ratio should be less than 0.6 and O/C ratio should be less than 0.4 in the case of biochar material. In this study, all biochar types had lower O/C ratio than 0.4 and high-temperature (550–700 °C) biochar types had lower H/C ratio than 0.6. It was shown that high-temperature biochar types had high aromaticity and low polarity. Similarly, one study [79] showed that biochar made from pine needles had lower H/C and O/C ratios when temperature increased, and it was related with higher aromaticity and lower polarity. Higher O/C ratio of low temperature biochar types shows that these biochar types have more hydroxyl, carboxyl and carbonyl functional groups which govern higher cation exchange capacity of biochar.

One study [29] showed that H/C and O/C atomic ratios of both biochar types (from grass and wood) followed the trajectory associated with dehydration reactions. The greatest loss of H and O appeared between 300 and 500 °C temperature. At 300 °C, biochar is affected to initial dehydration and depolymerization reactions, which produce small, volatile dissociation products. At 400 and 500 °C, “amorphous” biochar phase is composed from volatile, low-molecular-weight aliphatic and aromatic compounds, which arise from thermal transformation of lignin and cellulose.

Table 2 Elemental composition and atomic ratios of different biochar types, $n = 3$

Feedstock type	Temperature, °C	Elemental composition, %				Atomic ratios	
		C	H	N	O	O/C	H/C
Pine bark	300	47.47	32.23	0.20	20.10	7.20	0.28
	350	71.06	13.52	0.20	14.38	2.27	0.15
	400	72.30	12.37	0.19	14.15	2.04	0.15
	450	77.54	8.43	0.19	13.84	1.27	0.13
	500	79.85	7.29	0.15	12.69	1.09	0.12
	550	81.77	7.24	0.14	10.37	1.06	0.10
	600	83.41	6.23	0.04	9.08	0.89	0.08
	650	84.96	5.98	—	7.56	0.84	0.07
	700	85.72	3.28	—	5.49	0.46	0.05
Birch bark	300	71.28	12.96	0.84	14.92	1.94	0.14
	350	73.78	11.62	0.36	14.24	1.72	0.13
	400	80.16	8.57	0.29	10.98	1.23	0.10
	450	82.71	7.05	0.27	9.97	1.01	0.09
	500	85.71	5.79	0.18	8.32	0.80	0.07
	550	87.83	3.96	0.09	8.12	0.53	0.07
	600	90.69	2.19	—	7.12	0.29	0.06
	650	91.76	0.48	—	5.89	0.06	0.05
	700	92.32	0.00	—	5.14	0.00	0.04
Pine wood	300	71.7	13.29	0.29	14.72	0.14	2.07
	350	76.47	11.44	0.27	11.82	0.11	1.69
	400	82.3	7.04	0.22	10.44	0.09	1.02
	450	84.34	5.93	0.03	9.70	0.09	0.84
	500	84.78	5.67	0.02	8.52	0.08	0.80
	550	85.82	3.75	—	8.07	0.07	0.52
	600	89.59	2.81	—	7.60	0.06	0.37
	650	90.39	0.46	—	7.43	0.06	0.06
	700	91.74	0.00	—	3.68	0.03	0.00
Birch wood	300	71.93	14.19	0.13	13.75	0.13	2.14
	350	76.61	12.11	0.08	11.20	0.11	1.82
	400	79.28	9.59	0.07	11.06	0.10	1.41
	450	82.53	8.09	0.03	9.35	0.08	1.16
	500	83.73	6.92	0.01	8.96	0.08	0.99
	550	85.77	5.70	—	8.53	0.07	0.79
	600	86.26	5.00	—	8.04	0.07	0.69
	650	90.34	4.46	—	5.20	0.04	0.58
	700	91.34	3.72	—	4.79	0.04	0.49
Hemp	300	70.55	15.20	0.52	13.73	0.14	2.40
	350	73.71	12.97	0.21	13.11	0.12	1.96
	400	79.72	10.60	0.21	9.47	0.09	1.53
	450	82.93	7.77	0.19	8.09	0.07	1.12
	500	84.92	7.61	0.18	7.29	0.06	1.05
	550	86.69	6.55	0.12	6.64	0.06	0.89
	600	88.29	5.20	—	6.50	0.06	0.70
	650	89.22	4.29	—	6.49	0.05	0.57
	700	91.91	1.44	—	4.93	0.04	0.19

Fig. 7 Van Krevelen diagram of the obtained biochar types, $n = 3$



3.8 Specific surface area, volume and size of pores in biochar

The surface area, volume of pores (total and micropores) and pore size of pores in biochar were analysed using N_2 absorption; the results are shown in Table 3. The relation between feedstock surface area and temperature was positive, and similar results were obtained by other authors [46]. In the case of all feedstocks, from 500 °C temperature, the surface area sharply increased which was 191 times (in the case of pine bark biochar), 38 times (pine wood biochar), 14 times (birch wood biochar) and 134 times (hemp biochar) more than compared to 400 °C temperature. Almost in the case of all feedstocks (except for birch wood), the highest surface area was obtained at 700 °C temperature. The highest surface area was obtained in the case of high-temperature pine bark biochar (421 m^2/g).

The total volume of pores increased almost in the case of all feedstocks (except for birch bark) until 600 °C temperature. Sharp increase of the total volume of pores by 19 and 2 times when temperature increased from 500 to 600 °C was obtained in the case of pine and birch bark biochar types. However, other biochar types (made from pine wood, birch wood and hemp) showed the total volume of pores increase at a lower temperature range (from 400 to 500 °C). Another study [46] also showed that volumes of pores counted from N_2 isotherms also increased in the case of all feedstocks when pyrolysis temperatures increased. The effect of temperature on the volume of pores was clear from 450 to 550 °C temperature in the case of biochar made from fermentation wastes and vineyard wastes when volumes increased respectively by 4 and 9 times.

The increase of the surface area and volume of pores respectively with the temperature was governed by

progressive degradation of organic materials (hemicellulose, cellulose and lignin) and formation of fibre and channel structures during the pyrolysis process. Hemicellulose has high reactivity during thermal treatment at low (generally lower than 300 °C) temperature. One study [80] showed that porosity of biochar made from apple tree wood increased at 500 °C temperature due to degradation of lignin and quick release of H_2 and CH_4 . It was governed by the sharp increase of the surface area and volume of pores. Further increase of temperature until 600 °C caused dramatic increase of BET surface area and total volume of pores (respectively from 37.24 to 108.59 m^2/g and from 12.41 to 58.54 cm^3/g). Angin and Senzor [3] showed that BET surface areas were generally low for rapeseed biochars produced at all pyrolysis temperatures but did slightly increase while increasing the temperature up to 550 °C (25.4 m^2/g) and decreased thereafter (to 22.9 m^2/g at 700 °C). Similarly, micropore surface area and volume reached its maximum values at 500 °C (18.3 m^2/g and 0.039 cm^3/g , respectively). Due to high temperature, the porous structure cracked and the pores might be partially blocked as a result of the softening and melting of the rapeseed constituents, which could be responsible for a low surface area. In another study [21], the surface area and pore volume of lignocellulosic wastes biochar produced at 700 °C was found to be 249.1 m^2/g and 0.03 cm^3/g , respectively. On the other hand, biochar made at 300 °C exhibited surface area of 2 m^2/g and pore volume of 0.006 cm^3/g .

Biochar particle size affects water and nutrient retention potential. Smaller size biochar particles have greater surface area that can increase retention of nutrients and water holding

Table 3 Surface area, pore volume and pore size of different biochar types, $n = 3$

Feedstock type	Pyrolysis temperature, °C	BET surface area, m ² /g	Total volume, cm ³ /g	Micropores volume, cm ³ /g	Average pore size, nm
Pine bark	300	No data	No data	No data	No data
	400	1.67	0.0098	0.0012	2.42
	500	319	0.1837	0.1831	1.23
	600	383	0.216	0.19	1.23
	700	421	0.254	0.209	1.23
Birch bark	300	0.47	0.0032	$2.55 \cdot 10^{-8}$	3.17
	400	No data	No data	No data	No data
	500	111	0.0887	0.0584	1.93
	600	329	0.186	0.177	1.18
	700	381	0.224	0.198	1.18
Pine wood	300	4.81	0.0034	$4.03 \cdot 10^{-11}$	6.23
	400	8.93	0.01	0.004	1.93
	500	337	0.1913	0.2073	1.29
	600	360	0.202	0.179	1.18
	700	380.36	0.189	0.079	No data
Birch wood	300	2.43	0.0033	$4.03 \cdot 10^{-12}$	3.32
	400	21.88	0.024	0.012	1.85
	500	304	0.175	0.192	1.41
	600	345	0.189	0.175	1.18
	700	291	0.155	0.119	No data
Hemp	300	6.99	0.007	$2.22 \cdot 10^{-12}$	4.54
	400	2.15	0.0258	$6.07 \cdot 10^{-8}$	1.85
	500	334	0.196	0.181	1.23
	600	391	0.262	0.186	1.29
	700	392	0.239	0.191	1.13

capacity. Biochar also has great porosity and therefore can increase water holding capacity in soils [38].

3.9 Surface functional groups of biochar

Oxygen-containing functional groups (OCFGs) can be divided into two subgroups: (1) acidic (including carboxyl, anhydride, lactone, lactol and phenol and (2) neutral/weakly basic (including carbonyl, quinone, ether and pyrone) [33]. The concentration and distribution of these different groups have a major impact on the adsorptive performance of biochar. Surface acidic functional groups are by far most important surface functional groups that not only influence the surface characteristics (polarity, acidity and wettability) but also physicochemical properties (catalytic, electrical and chemical reactivity) of the biochar [61]. Increasing acidic functional groups could increase the hydrophilicity of biochar [10]. One study [60] showed that oxidized biochar types possessed better wettability compared to unoxidized. The hydrophilic groups on the biochar surface play a critical role in water adsorption, because water molecules can bind with these groups through H-bonding [35]. Hydrophobic and hydrophilic regions of the

biochar surface can serve as adsorbents for non-polar and polar organic molecules in the environment, respectively [8]. One study [70] proposed that introduction of carboxyl group on the biochar can enhance adsorption of ionizable compounds by providing strong charge-induced hydrogen bonding sites. Carboxyl group on the surface of biochar is essential for improving the biochar nutrient holding capacity, as well as polarizing the surface which may also increase water retention of the biochar [22].

There are several techniques that have been used for characterizing OCFGs. One of these techniques includes Fourier-transform infrared spectrometry (FTIR). This method can qualitatively characterize OCFGs of biochar with acceptable accuracy. The observed characteristic peaks (strength of the absorption band) by FTIR analysis indicate the functional groups on the biochar surface which may differ from the original wavenumber due to different pyrolysis conditions or initial feedstocks, of which heat treatment is mostly responsible for eliminating or rearranging functional groups on biochar surface [2].

According to Fig. 8, groups N–H ($1550\text{--}1640\text{ cm}^{-1}$) decreased when pyrolysis temperature increased in the case of

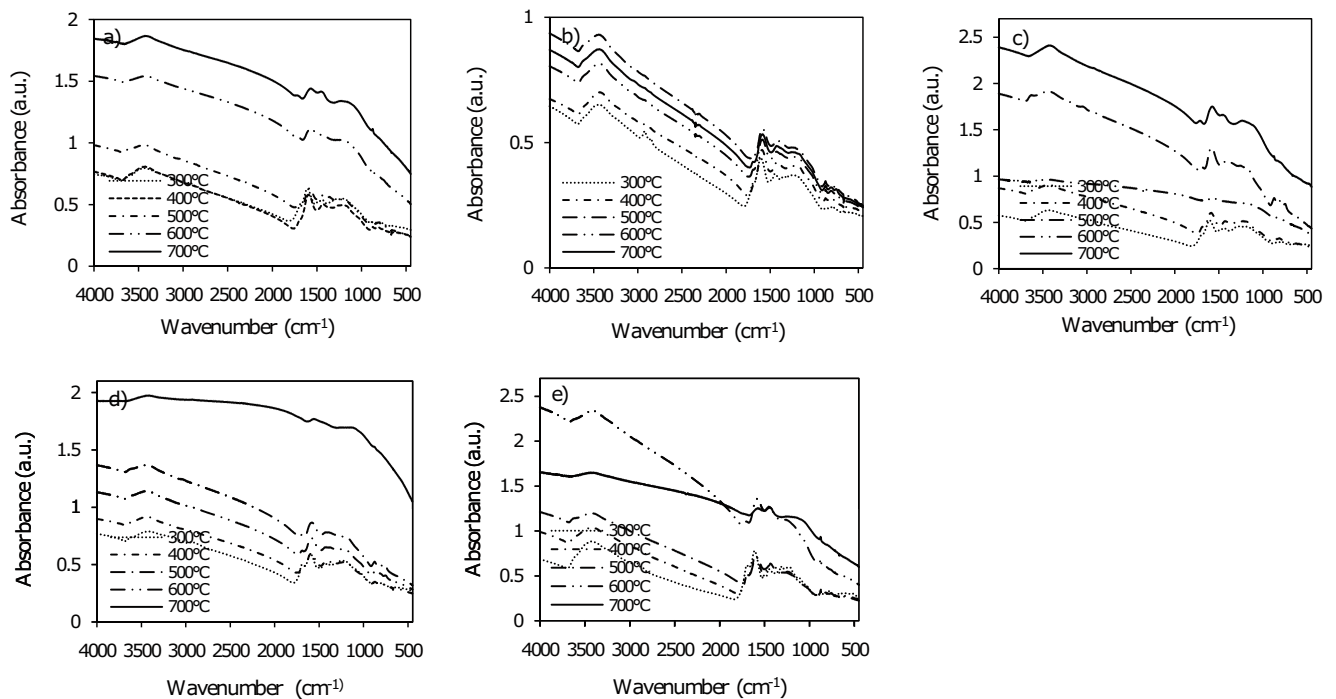


Fig. 8 FTIR analysis results of different biochar types made from distinct temperatures and feedstocks. **a** Pine bark. **b** Birch bark. **c** Pine wood. **d** Birch wood. **e** Hemp, $n = 2$

pine bark biochar due to visible decrease of peaks (Fig. 8a), and groups C–H ($2850\text{--}3000\text{ cm}^{-1}$) decreased in the case of birch bark, pine wood and hemp (respectively Fig. 8 b, c and e). All analysed groups decreased in the case of birch wood biochar (Fig. 8d). Peaks between 2850 and 2970 cm^{-1} are related with aliphatic functional groups (bonds C–H) [57], which were best expressed in the case of low temperature ($300\text{ }^{\circ}\text{C}$) for birch bark biochar. In this study, it was shown that aromatic C=C functional groups dominated in all ligno-cellulosic biochar types and had the sharpest peaks compared to other peaks. It can be concluded that the aromatic group was a dominating characteristic of these materials. Similarly, a similar tendency was shown in another study [29] when vibrations of 1600 cm^{-1} of analysed wood and grass biochar were obtained.

Using FTIR analysis results, Yuan et al. [77] showed that absorbance peak of aliphatic C–H stretching (at 2985 cm^{-1}) decreased slightly when temperature increased, but it did not disappear, which shows that aliphatic compounds were heat resistant. Another study [80] showed that when pyrolysis temperature increased, the FTIR spectrum of biochar showed narrowness of peaks O–H ($3200\text{--}3500\text{ cm}^{-1}$) and C–H (2935 cm^{-1}), and it was related with the increase of dehydration reactions in the biomass and this shows the decrease of polar functional groups during increase of pyrolysis temperature. Biochar increased expansion of aromatic bond C=C and plane deformation of aromatic group C–H (885 cm^{-1}), since a

symmetric bond C–O ($1030\text{--}1110\text{ cm}^{-1}$) started to vanish when pyrolysis temperature increased. Meanwhile, the bond O–H (1325 cm^{-1}) and aromatic bonds C=C, C=O which present conjugated ketones and quinones decreased during the increase of the temperature and it showed the degradation of lignin phenol and carboxyl compounds. Pyridine was detected (781 cm^{-1}) as well, which is one of heterocyclic nitrogen compounds. In conclusion, maximum loss was obtained in the case of functional groups –OH, $-\text{CH}_2$ and C–O according to the increase of temperature and it can be clearly seen from elemental analysis [80].

Wood cellulose is a polymer which is enriched with hydroxide groups, and even after pyrolysis, some hydroxides and water retain in the sample, since peak of 3640 cm^{-1} is related with the bond OH; however, the bond of Si–OH can be expected. An aliphatic bond C–H of 2920 cm^{-1} shows that cellulose is not completely carbonised during pyrolysis. The aromatic bond C–H of 3050 cm^{-1} shows the value which arises from aromatic residual compounds of lignin. A wide asymmetric peak of 1744 cm^{-1} shows the bond C=O. This peak consists of various functional groups C=O including ketones, carboxyl acidic esters and anhydrides. The peak of 1605 cm^{-1} is related with the bond C=C which arises from aromatic rings of lignin as well as from newly aromated and carbonised material due to dehydration of hydrocarbon rings and cyclic pyrolysis [11].

In the case of low temperature (350 °C) for sugarcane biochar, there was a high absorption from 1700 cm⁻¹ to 1740 cm⁻¹ and it corresponded to carboxyl groups (C=O) and aromatic compounds bond (1600 cm⁻¹ until 1475 cm⁻¹) which was created at a higher temperature (500 °C). At 500 °C temperature, molecular vibrations C=O were observed, which indicates the ketones group (2300 cm⁻¹). Other vibrations of the sample from 1300 to 1000 cm⁻¹ are related with bonds C–O and C–H which show formation of alcoholic and ester groups as well as typical aromatic groups.

In another study [37], pea shell biochar showed 5 strong peaks: peak near 3408 cm⁻¹ was related with carboxyl group O–H; peak near 1600 cm⁻¹ showed conjugated phenyl rings C=C [30]; peak near 1417 cm⁻¹ was related with the bond C–H; peak near 1060 cm⁻¹ was related with the secondary alcohol bond C–O; peak near 600 cm⁻¹ showed aliphatic compounds of bromine (C–Br). Biochar made from cauliflower showed 6 peaks near 3400–600 cm⁻¹ region. A wide absorption peak near 3397 cm⁻¹ was related with carboxyl acids O–H; peak near 1582 cm⁻¹ showed weak bond of rings (C=C); peak near 1437 cm⁻¹ showed various groups of alkenes C–H; peak near 1093 cm⁻¹ showed the secondary alcohol bond C–O and peak near 875–602 cm⁻¹ showed strong C–H bond of phenyl rings. Most chemical reactions between biochar and environment are directly related with chemical properties of its surface. Existence of such functional groups, such as carboxyl and hydroxyl, shows that all these biochar types have a possibility to be used as soil amendments for the enhancement of cation exchange capacity and be used as potential adsorbent.

In conclusion, existence of organic components with particular chemical responses and different structure govern reactivity of different biochar types. In one study [16], the FTIR analysis showed that biochar types made from sugarcane wastes and sewage sludge were composed from carboxylic acids, ketones, alcohol and ester functional groups and, additionally, sugarcane biochar had ether and phenolic groups. Eucalyptus biochar had only a group of ketones and aromatic compounds were identified in all biochar types. Functional groups, particularly carboxyl and phenols, can ionise and have impact on the formation of the charge of soil. Long-term retention of carbon in the environment is related with its polycyclic aromatic structure. When biochar is incorporated into the soil, its stability and resistance can contribute to the retention of water and ions in the soil.

3.10 Dependence of physical-chemical properties of biochar on its water holding capacity and wettability

Soil and water are two main resources in agriculture [75]. Potential benefits of biochar in soil refer to its capacity to retain water and nutrients. Biochar's wettability is one of the

most important features which evaluates biochar's role in soils [9]. Unsuitable biochar types and amount of the amendment can affect soil's hydrophobicity influencing soil's capacity to sorb water, inhibiting microbiological activity and weakening soil's filtration and retention functions. Designed biochar can be produced selecting particular feedstock and pyrolysis conditions for the improvement of soil's physical and chemical properties [41]. Two regression models were developed for the prediction of biochar's hydrophysical (wettability and water holding capacity) properties which save expenses and time for experiments.

Determination of a quantitative link between biochar's hydrophysical (wettability, water holding capacity) and its other physical-chemical properties was not evaluated before. For the revealing of a clear link between these properties, two equations were obtained using the step-wise multiple linear regression analysis. For the determination of a possible link between water holding capacity (dependent variable) of biochar with its other physical-chemical properties (independent variables: C, H, O concentrations, pH, electrical conductivity, ash content, total volume of pores, volume of micropores, average size of pores), the first equation was obtained using the multiple regression analysis. Meanwhile, for the determination of a possible link between wettability (dependent variable) of biochar with its other physical-chemical properties (independent variables: C, H, O concentrations, pH, electrical conductivity, ash content, total volume of pores, volume of micropores, average size of pores, intensities of hydroxyl functional group (–OH) and phenolic functional group (C–O)), the second equation was obtained. Variables which were included in the second regression analysis were transformed to logarithmic due to the simplification of the model. Equations were derived for the prediction of biochar water holding capacity (8) and wettability (9):

$$Y = 1.508 + (0.27 \cdot AX) \quad (8)$$

$$\text{Log}(Y) = 0.796 - (2.13 \cdot \text{Log}(APS)) \quad (9)$$

where AC was the ash content of the biochar, %.

APS was the average pore size of the biochar, nm.

Regression coefficients and statistical analysis of each forecasting model is shown in Table 4. It can be stated that the water holding capacity of biochar can be predicted by the ash content (%), since modelled results of the water holding capacity (expressed in WHC, times) were similar to the experimental values in the case of 14 different biochar types (made from pine wood, birch wood, pine bark, birch bark and hemp). Using Eq. (8), the water holding capacity of hemp biochar (600 °C) was predicted most precisely when the difference between real and calculated values reached 0.18 times. A high coefficient of

Table 4 Results of two multiple regression analysis ($n = 14$)

Dependent variable	Independent variable	Regression equation	R^2	F	p
Water holding capacity	Ash content	$Y = 1.508 + (0.27 * P)$	0.77	22.9	0.001
Wettability	Average pore size	$\text{Log}(Y) = 0.796 - (2.13 * \text{Log}(APS))$	0.54	8.16	0.024

determination $R^2 (=0.77)$ shows that the model is good, since it explains 77% of scattering of dependant variable around its mean value. Since p value of the first model was lower than 0.05 (0.001), the obtained regression model was significantly favourable for the prediction of the biochar water holding capacity (Fig. 9).

It can be stated that wettability of biochar can be predicted by the average pore size (nm), since modelled results of wettability (expressed in WDPT, s) were similar to the experimental values in the case of 14 different biochar types (made from pine wood, birch wood, pine bark, birch bark and hemp). Using Eq. (9), wettability of pine bark biochar (500 °C) was predicted most precisely when the difference between real and calculated values reached 0.01 s. An average coefficient of determination $R^2 (=0.54)$ shows that the model is good, since it explains 54% of scattering of dependant variable around its mean value. Since p value of the first model was lower than 0.05 (0.024), the obtained regression model was significantly favourable for the prediction of biochar wettability (Fig. 10).

However, the question remains why the average pore size is the dominant factor for the prediction of biochar's wettability and the factor of ash content is relevant for the prediction of the water holding capacity. The first case could be explained by the reduction of pore sizes of the biochar governing physical water adsorption, when

the pyrolysis temperature is increasing. Biochar can physically adsorb water on its external surface and retain water between particles due to capillary action [71]. In the second case, the relation between biochar's water holding capacity and ash content can be explained by the fact that biochar produced from the feedstocks containing a higher amount of ashes (in this case, bark) typically has a lower surface area compared to the feedstocks containing a lower amount of ashes (in this case, wood), since ashes block the pore spaces, despite wood biochar has a higher water holding capacity. Previous studies show that biochar's water holding capacity is related to zeta potential and amount of carbon and ions. The principal component analysis showed that variation of vineyard biochar's water retention was highly associated with the zeta potential and the amount of carbon and ions, and it shows that surface charge and hydrophobicity were the main properties which governed the capacity of water retention [36]. Another study [6] showed that porosity was the primary factor affecting biochar's water holding capacity, and the cation exchange capacity and zeta potential were the secondary factor. It is thought that the linkage between water and biochar's aromatic rings is highly affected by the presence of cations. Polar components also contribute to water holding

Fig. 9 Relation between evaluated and predicted water holding capacity of biochar, $n = 14$

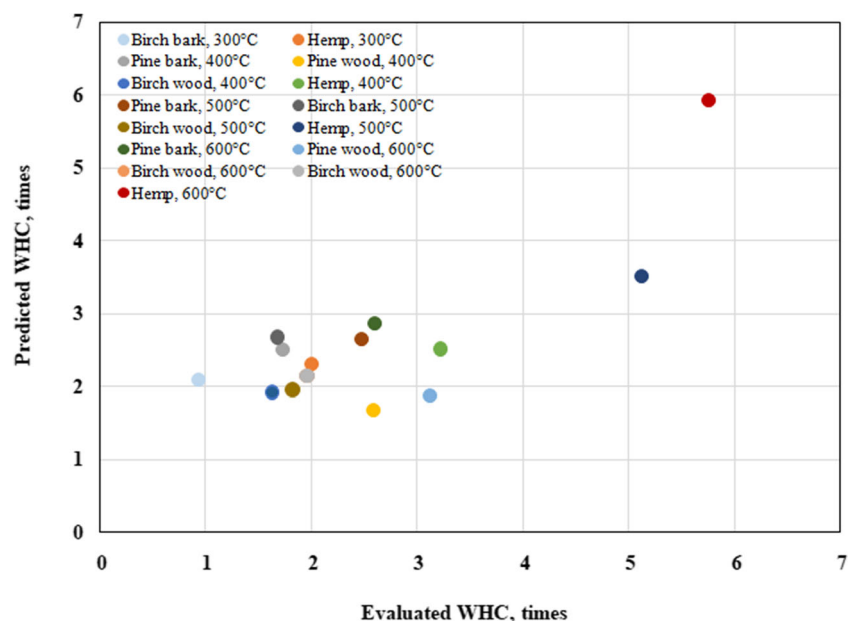
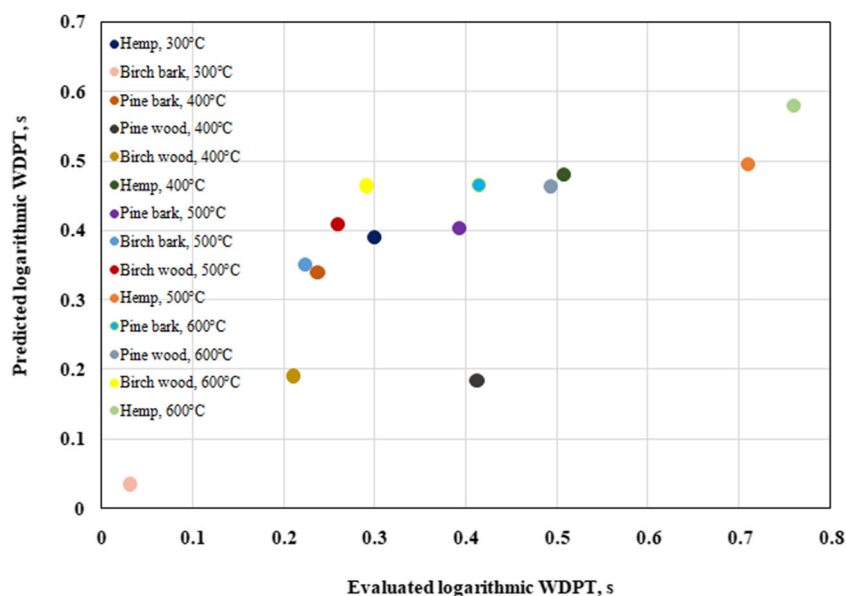


Fig. 10 Relation between logarithmic evaluated and predicted wettability of biochar, $n = 14$



capacity, since biochar types having a higher amount of polar components showed higher water retention effectiveness [6]. One more study [78] showed that biochar's rate of water adsorption was affected by the total pore volume and average pore size. Major pores not only can retain more water, but also can perform the function of transportation of water to the lower pores. Surface roughness, which well correlates with BET surface area, can impact surface wettability [64]. Biochar's mineral and chemical surface analysis showed that fine biochar particles and salts can be removed after its impact with water which opens new pores and alters biochar's roughness and wettability [55]

The results of the biochar water holding capacity and wettability were statistically validated. The experimentally obtained water holding capacities of biochar types were compared to the predicted values in terms of several parameters. In the case of the water holding capacity, R^2 (0.77) shows strong correlation which is supported by some other tests: RMSE = 0.79, MAPE = 30.6%, MSE = 0.63 and MAD = 0.64. In the case of wettability, R^2 (0.54) shows a significantly average correlation which is supported by some other parameters: RMSE = 0.13, MAPE = 28.4%, MSE = 0.02 and MAD = 0.1. The types of obtained models can be successfully used to predict the biochar water holding capacity and

wettability. Lower values of all parameters typically show better data equivalency to the model. According to the MAPE parameter, both models can be held as acceptable, since this value is between 20 and 50. Meanwhile, when the RMSE value is lower, then there is a better forecasting capacity of the model and a better simulative performance [69]. According to the RMSE criterion, the wettability model is slightly better than the hydrophilic biochar model (Table 5).

The article deals with the evaluation of the water holding capacity and wettability for five different feedstocks and nine pyrolysis temperatures. Two regression models were obtained according to the analytically evaluated biochar properties. Two equations were validated by the obtained results and forecasted values of biochar hydrophysical properties which were similar with the experimental data. It shows the universality of the models for the prediction of the biochar water holding capacity and wettability.

4 Conclusions

1. All physical-chemical properties of all biochar types differed according to the pyrolysis temperature. When the temperature increased from 300 to 700 °C, pH, electrical conductivity, ash content, water holding capacity, amount

Table 5 Statistical parameters which were used for the comparison of experimentally evaluated and predicted water holding capacities and wettabilities of different biochar types, $n = 14$

Statistical parameter	Biochar water holding capacity	Biochar wettability
Median absolute deviation (MAD)	0.64	0.1
Mean squared error (MSE)	0.63	0.02
Root mean square deviation (RMSE)	0.79	0.13
Mean absolute percentage error (MAPE), %	30.6	28.4

of C, specific surface area, total and micropore volume and wettability increased, too. Meanwhile, biochar yield, amounts of O, H and N, average size of pores and organic functional groups tendentially decreased when the pyrolysis temperature increased.

2. Hydrophobicity of biochar was lost in various temperature intervals and it differed according to distinct feedstocks. Hydrophobicity of bark biochar is most resistant to the effect of temperature, which was lost only at 600 °C temperature. In the case of birch wood and hemp, their hydrophobicity vanished at near comparatively low temperature (350 °C). Birch wood biochar types can be considered the most hydrophilic materials in the wide range of temperature (300–700 °C), and all biochar types made from this feedstock were considered slightly hydrophobic or hydrophilic.
3. According to wettability results, hydrophilicity increased in the case of all feedstocks when pyrolysis temperature increased from 300 to 700 °C. This can be explained by hydrophobic aliphatic functional groups which vapour at higher temperatures. This was confirmed by the FTIR results when obtained peaks at 2850 cm⁻¹ wavelength were sharpest in the case of low-temperature (300 °C) biochar types and completely flattened when temperature rose (until 700 °C). Low-temperature (300 °C) pine and birch bark biochar types were extremely hydrophobic (respectively 12,480 and 9600 s). Extremely high hydrophobicity of bark biochar types can be related with lipophilic compounds which are found in the feedstocks which account 20% of dry bark weight.
4. According to the results of the multiple regression analysis, the variation of the water holding capacity for 77% of biochar can be predicted using values of its ash content. Meanwhile, the wettability variation of 54% can be predicted using values of the average pore size. The differences between real and predicted values were only 0.18 times and 0.01 s, respectively. Usage of the already known values of hydrophysical properties of biochar can save expenses and time for experiments.

References

1. Ahmed MB, Zhou JL, Ngo HH, Guo W, Johir MAH, Sornalingam K, Rahman MS (2017) Chloramphenicol interaction with functionalized biochar in water: sorptive mechanism, molecular imprinting effect and repeatable application. *Sci Total Environ* 609:885–895
2. Ahmed MB, Zhou JL, Ngo HH, Guo W, Chen M (2016) Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresour Technol* 214:836–851
3. Angin D, Senzor S (2014) Effect of pyrolysis temperature on chemical and surface properties of biochar of rapeseed (*Brassica napus* L.). *Int J Phytoremediation* 16(7–8):684–693
4. ASTM (2005) D2216–98. Standard test method for laboratory determination of water content of soil and rock by mass. ASTM, West Conshohocken
5. Baltrėnaitė E, Baltrėnas P, Bhatnagar A, Vilppu T, Selenius M, Koistinen A, Dahl M, Penttinen O-P (2017) A multicomponent approach to using waste-derived biochar in biofiltration: a case study based on dissimilar types of waste. *Int Biodeterior Biodegrad* 119:565–576
6. Batista EMCC, Shultz J, Matos TTS, Fornari MR, Ferreira TM, Szpoganicz B, de Freitas RA, Mangrich AS (2018) Effect of surface and porosity of biochar on water holding capacity aiming indirectly at preservation of the Amazon biome. *Sci Rep* 8(1):10677
7. Bauters TWJ, Steenhuis TSS, DiCarlo DA, Nieber JL, Dekker LW, Ritsema CJ, Parlange J-Y, Haverkamp R (2000) Physics of water repellent soils. *J Hydrol* 231–232:233–243
8. Brewer CE (2012) Biochar characterization and engineering. In: Doctoral dissertation. Iowa State University, pp 55–57
9. Bubici S, Korb J-P, Kucirik J, Conte P (2016) Evaluation of the surface affinity of water in three biochars using fast field cycling NMR relaxometry. *Magn Reson Chem* 54:365–370
10. Cheng C-H, Lehmann J, Thies JE, Burton SD, Engelhard MH (2006) Oxidation of the black carbon by biotic and abiotic processes. *Org Geochem* 37(11):1477–1488
11. Chia CH, Gong B, Joseph SD, Marjo C, Munroe P, Rich AM (2012) Imaging of mineral-enriched biochar by FTIR, Raman and SEM-EDX. *Vib Spectrosc* 62:248–257
12. Chun Y, Sheng G, Chiou T, Xing B (2004) Compositions and sorptive properties of crop residue-derived chars. *Environ Sci Technol* 38:4649–4655
13. Conz RF, Abbruzzini TF, de Andrade CA, Milori DMBP, Cerri CEP (2017) Effect of pyrolysis temperature and feedstock type on agricultural properties and stability of biochars. *Agric Sci* 8:914–933
14. Das O, Sarmah AK (2015) The love-hate relationship of pyrolysis biochar and water: a perspective. *Sci Total Environ* 512–513:682–685
15. Das O, Hedenqvist M (2018) Wettability properties of biochar added wood / polypropylene composites. *Acad J Polym Sci* 1(4). <https://doi.org/10.19080/AJOP.2018.01.555570>
16. de Figueredo NA, de Costa LM, Melo LCA, Siebeneichler EA, Tronto J (2017) Characterization of biochars from different sources and evaluation of release of nutrients and contaminants. *Rev Ciênc Agron* 48(3):395–403
17. Denyes MJ, Parisien MA, Rutter A, Zeeb BA (2014) Physical, chemical and biological characterization of six biochars produced for the remediation of contaminated sites. *J Vis Exp* 93:52183
18. Domingues RR, Trugilho PF, Silva CA, de Melo ICNA, Melo LCA, Magriotis ZM, Sanchez-Monedero (2017) Properties of biochar derived from wood and high-nutrient biomasses with the aim of agronomic and environmental benefits. *PLoS One* 12(5): e0176884. <https://doi.org/10.1371/journal.pone.0176884>
19. Duwiejua AB, Cobbina SJ, Bakobie N (2017) Review of eco-friendly biochar used in the removal of trace metals on aqueous phases. *Int J Environ Bioremed Biodegr* 5(2):27–40
20. EBC, 2012. European biochar certificate – guidelines for a sustainable production of biochar. European Biochar Foundation (EBC), Arbaz, Switzerland. <http://http://www.european-biochar.org/en>. Version 6.3E of 14th August 2017: <http://www.european-biochar.org/en/download%20the%20certificate>
21. Elnour AY, Alghyamah AA, Shaikh HM, Poulouse AM, Al-Zahrani SM, Anis A, Al-Wabel MI (2019) Effect of pyrolysis temperature on biochar microstructural evolution, physicochemical characteristics, and its influence on biochar/polypropylene composites. *Appl Sci* 9(6):1149

22. Fuschs M, Garcia-Perez M, Sjoding D (2012) Biochar: background and early steps to market development. Washington State Department of Ecology, Olympia, p 9
23. Gai X, Wang H, Liu J, Zhai L, Liu S, Ren T, Liu H (2014) Effects of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. *PLoS One* 9(12):e113888. <https://doi.org/10.1371/journal.pone.0113888>
24. Gray M, Johnson MG, Dragila MI, Kleber M (2014) Water uptake in biochars: the roles of porosity and hydrophobicity. *Biomass Bioenergy* 61:196–205
25. Hallin IL, Douglas P, Doerr SH, Bryant R (2015) The effect of addition of a wettable biochar on soil water repellency. *Eur J Soil Sci* 66:1063–1073
26. Inyang M, Dickenson E (2015) The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: a review. *Chemosphere* 134:232–240
27. Jeffery S, Meinders MJB, Stoof CR, Bezemer TM, van de Voorde TFJ, Mommer L, van Groenigen JW (2015) Biochar application does not improve the soil hydrological function of a sandy soil. *Geoderma* 251–252:47–54
28. Jindo K, Mizumoto H, Sawada Y, Sanchez-Monedero MA, Sonoki T (2014) Physical and chemical characterization of biochars derived from different agricultural residues. *Biogeosciences* 11: 6613–6621
29. Keiluweit M, Kleber M, Sparrow MA, Simoneit BRT, Prah FG (2012) Solvent-extractable polycyclic aromatic hydrocarbons in biochar: influence of pyrolysis temperature and feedstock. *Environ Sci Technol* 46(17):9333–9341
30. Keiluweit M, Nico PS, Johnson MG, Kleber M (2010) Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ Sci Technol* 44:1247–1253
31. Khanmohammadi Z, Afyuni M, Mosaddeghi MR (2015) Effect of pyrolysis temperature on chemical and physical properties of sewage sludge biochar. *Waste Manag Res* 33(3):275–83
32. Kinney TJ, Masiello CA, Dugan B, Hockaday WC, Dean MR, Zygourakis K, Barnes RT (2012) Hydrologic properties of biochars produced at different temperatures. *Biomass Bioenergy* 41:34–43
33. Li N, Ma X, Zha Q, Kim K, Chen Y (2011) Maximizing the number of oxygen-containing functional groups on activated carbon by using ammonium persulfate and improving the temperature-programmed desorption characterization of carbon surface chemistry. *Carbon* 49(15):5002–5013
34. Liu Z, Dugan B, Masiello CA, Gonneermann HM (2017) Biochar particle size, shape, and porosity act together to influence soil water properties. *PLoS One* 12(6):e0179079. <https://doi.org/10.1371/journal.pone.0179079>
35. Ma W, Li H, Yao X, Li L, Shih K (2015) Preparation of hydrophilic activated carbon through alkaline hydrolysis of ester for effective water-vapor adsorption. *Sep Sci Technol* 51(2):193–201
36. Marshall J, Muhlack R, Morton BJ, Dunnigan L, Chittleborough D, Kwong CW (2019) Pyrolysis temperature effects on biochar-water interactions and application for improved water holding capacity in vineyard soils. *Soil Systems* 3(27). <https://doi.org/10.3390/soilsystems30220027>
37. Mary GS, Sugumaran P, Niveditha S, Ramalakshmi B, Ravichandran P, Seshadri S (2016) Production, characterization and evaluation of biochar from pod (*Pisum sativum*), leaf (*Brassica oleracea*) and peel (*Citrus sinensis*) wastes. *Int J Recycl Org Waste* 5:43–53
38. Mollinedo J, Schumacher TE, Chintala R (2015) Influence of feedstocks and pyrolysis on biochar's capacity to modify soil water retention characteristics. *J Anal Appl Pyrolysis* 114:100–108
39. Moreno JJM, Pol AP, Abad AS, Blasco BC (2013) Using the R-MAPE index as a resistant measure of forecast accuracy. *Psicothema* 25(4):500–506
40. Naeem MA, Khalid M, Arshad M, Ahmad R (2014) Yield and nutrient composition of biochar produced from different feedstocks at varying pyrolytic temperatures. *Pak J Agric Sci* 51(1):75–82
41. Narzari R, Bordoloi N, Sarma B (2017) Fabrication of biochars obtained from valorization of biowaste and evaluation of its physicochemical properties. *Bioresour Technol* 242:324–328
42. Nwajiaku IM, Olanrewaju JS, Sato K, Tokunari T, Kitano S, Masunaga T (2018) Change in nutrient composition of biochar from rice husk and sugarcane bagasse at varying pyrolytic temperatures. *Int J Recycl Org Waste Agric* 7(4):269–276
43. Oliveira FR, Patel AK, Jaisi DP, Adhikari S, Lu H, Khanal SK (2017) Environmental application of biochar: current status and perspectives. *Bioresour Technol* 246:110–122
44. Patle GT, Sikar TT, Rawat KS, Singh SK (2017) Estimation of infiltration rate from soil properties using regression model for cultivated land. *Geol Ecol Landscapes* 3(1):1–13
45. Pimchua A, Dutta A, Basu P (2010) Torrefaction of agriculture residue to enhance combustible properties. *Energy Fuels* 24: 4638–4645
46. Pituello C, Francioso O, Simonetti G, Pisi A (2014) Characterization of chemical-physical, structural and morphological properties of biochars from biowastes produced at different temperatures. *J Soils Sediments* 15(4):792–804
47. Pituya P, Sriburi T, Wijitkosum S Properties of biochar prepared from Acacia wood and coconut shell for soil amendment. *Environ Energy Nat Resour* 21(3). <https://doi.org/10.4186/ej.2017.21.3.63>
48. Rafiq MK, Bachmann RT, Rafiq MT, Shang Z, Joseph S, Long R (2016) Influence of pyrolysis temperature on physico-chemical properties of corn stover (*Zea mays* L.) biochar and feasibility for carbon capture and energy balance. *Plos One* 11(6):e0156894. <https://doi.org/10.1371/journal.pone.0156894>
49. Rasa K, Heikkinen J, Hannula M, Arstila K, Kulju S, Hyvaluoma J (2018) How and why does willow biochar increase a clay soil water retention capacity? *Biomass Bioenergy* 119:346–353
50. Ronewicz K, Kluskas J, Heda L, Kardas D (2016) Chemical and physical properties of pine wood during pyrolysis. *Drv Ind* 68(1): 29–36
51. Saletnik B, Zagula G, Bajcar M, Tarapatsky M, Bobula G, Puchalski C (2019) Biochar as multifunctional component of the environment – a review. *Appl Sci* 9:1139. <https://doi.org/10.3390/app9061139>
52. Shelukindo HB, Semu E, Msanya BM, Singh BR, Munishi PKT (2014) Predictor variables for soil organic carbon contents in the Miombo woodlands ecosystem of Kitonga forest reserve, Tanzania. *Int J Agric Sci* 4(7):222–231
53. Sigmund G, Huffer T, Hofmann T, Kah M (2017) Biochar total surface area and total pore volume determined by N₂ and CO₂ physisorption are strongly influenced by degassing temperature. *Sci Total Environ* 580:770–775
54. Smetanova A, Dotterweich D, Ulrich U, Fohrer N (2013) Influence of biochar and terra preta substrates on wettability and erodibility of soil. *Z Geomorphologie* 57:111–134
55. Spokas KA, Novak JM, Masiello CA, Johnson MG, Colosky EC, Ippolito JA, Trigo C (2014) Physical disintegration of biochar: an overlooked process. *Environ Sci Technol Lett* 1(8):326–332
56. Spokas KA, Novak JM, Stewart CE, Cantrell KB, Uchimiya M, DuSaire MG, Ro KS (2011) Qualitative analysis of volatile organic compounds on biochar. *Chemosphere* 85(5):869–882
57. Suarez-Hernandez L, Ardila- A, Alba N, Barrera R (2017) Morphological and physicochemical characterization of biochar produced by gasification of selected forestry species. *Rev Fac Ingenieria* 26(46):123–130
58. Subedi R, Bertora C, Zavattaro L, Grignani C (2017) Crop response to soils amended with biochar: expected benefits and unintended risks. *Ital J Agron* 12:794

59. Suliman WSO (2015) Toward an understanding of the role of biochar as an agro-environmental tool: potential for control water release, bacterial retention, and greenhouse gas emissions, dissertation of philosophy. Washington State university, pp 49–53
60. Suliman W, Harsh JB, Abu-Lail NI, Fortuna A-M, Dallmeyer I, Garcia-Perez M (2017) The role of biochar porosity and surface functionality in augmenting hydrologic properties of a sandy soil. *Sci Total Environ* 574:139–147
61. Suliman W, Harsh JB, Abu-Lail NI, Fortuna A-M, Dallmeyer I, Garcia-Perez M (2016) Modification of biochar surface by air oxidation: role of pyrolysis temperature. *Biomass Bioenergy* 85:1–11
62. Sun X, Shan R, Li X, Pan J, Liu X, Deng R, Song J (2017) Characterization of 60 types of Chinese biomass waste and resultant biochars in terms of their candidacy for soil application. *GCB Bioenergy* 9:1423–1435
63. Usman ARA, Ahmad M, El-Mahrouky M, Al-Omran A, Sik Ok Y, Sallam AS, El-Naggar AH, Al-Wabel M (2015) Chemically modified biochar produced from conocarpus waste increases NO₃ removal from aqueous solutions. *Environ Geochem Health* 38(2): 511–521
64. Valipour NM, Birjandi FC, Sargolzaei J (2014) Super-non-wettable surfaces: a review. *Colloids Surf A Physicochem Eng Asp* 448:93–106
65. Vikrant K, Kim K-H, Ok YS, Tsang DCW, Tsang YF, Giri BS, Singh RS (2018) Engineered/designer biochar for the removal of phosphate in water and wastewater. *Sci Total Environ* 616–617: 1242–1260
66. Viswanathan B, Neel IN, Varadarajan TK (2009) Methods of activation and specific applications of carbon materials, p 160
67. Weber K, Quicker P (2018) Properties of biochar. *Fuel* 217:240–261
68. Wiedner K, Rumpel C, Steiner C, Pozzi A, Maas R, Glaser B (2013) Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale. *Biomass Bioenergy* 59:264–278
69. Woschnagg E, Cipan J (2004) Evaluating forecast accuracy, 406347 *Okonometrische Prognose*. University of Vienna, Austria, Department of Economics, pp 13–14
70. Xiao F, Pignatello JJ (2016) Effects of post-pyrolysis air oxidation of biomass chars on adsorption of neutral and ionizable compounds. *Environ Sci Technol* 50(12):6276–6283
71. Xiao Q, Zhu L-X, Shen Y-F, Li S-Q (2016) Sensitivity of soil water retention and availability to biochar addition in rainfed semi-arid farmland during a three-year field experiment. *Field Crop Res* 196: 284–293
72. Yakout SM (2015) Monitoring the changes of chemical properties of rice straw-derived biochars modified by different oxidizing agents and their adsorptive performance for organics. *Bioremed J* 19(2):171–182
73. Yang H, Sheng K (2012) Characterization of biochar properties affected by different pyrolysis temperature using visible-near-infrared spectroscopy. *Int Scholar Res Network Spectrosc* 2012:7
74. Yi, S. C. 2018. The impact of biochar surface properties on sand and on sandy loam regarding water repellency, water retention, and gas transmissivity, dissertation of philosophy in civil engineering
75. Yu O-Y, Harper M, Hoepfl M, Domermuth D (2017) Characterization of biochar and its effects on the water holding capacity of loamy sand soil: comparison of hemlock biochar and switchblade grass biochar characteristics. *Environ Prog Sustain Energy* 36(5). <https://doi.org/10.1002/ep.12592>
76. Yu O-Y, Raichle B, Sink S (2013) Impact of biochar on the water holding capacity of loamy sand soil. *Int J Energy Environ Eng* 4:44
77. Yuan JH, Xu RK, Zhang H (2011) The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour Technol* 102(3):3488–3497
78. Zhang J, You C (2013) Water holding capacity and absorption properties of wood shars. *Energy Fuel* 27(5):2643–2648
79. Zhang Z, Zhu Z, Shen B, Liu L (2019) Insights into biochar and hydrochar production and applications: a review. *Energy* 171:581–598
80. Zhao S-X, Ta N, Wang X-D (2017) Effect of temperature on the structural and physicochemical properties of biochar with apple tree branches as feedstock material. *Energies* 10(9):1293
81. Zornoza R, Moreno-Barriga JA, Acosta MA, Munoz AF (2016) Stability, nutrient availability and hydrophobicity of biochars derived from manure, crop residues, and municipal solid waste for their use as soil amendments. *Chemosphere* 144:122–130

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Modelling of a Capillary Rise Height of Biochar by Modified Lucas–Washburn Equation

Luiza Usevičiūtė¹ · Edita Baltrėnaitė-Gedienė¹

Received: 1 June 2020 / Accepted: 16 June 2021

© The Author(s), under exclusive licence to Springer Nature Switzerland AG 2021

Abstract

Lucas–Washburn equation is a fundamental expression which is used to describe capillary rise in porous materials according to average pore radius, liquid viscosity, surface tension, contact angle and time. However, a traditional equation is overestimating a real capillary rise height of liquid in the material, since it models pores as straight and circular capillaries, though in reality porous materials, such as biochar, have tortuous capillaries with different aperture forms. It is also known that cellulosic materials are characterised by their swelling capacity, which also can affect the process of capillary rise. Therefore, a modified model including a parameter describing the pores' form and swelling parameters (volumetric swelling, energy loss coefficient and radius of swelled capillary) was developed. Experiments of water capillary rise in the biofilter tubes were conducted: the biochar made from different primary feedstocks, size of particles and modifications with steam of the biomedica. It was shown that the model is suitable for the prediction of short time (until 5 h) water capillary rise process in biochar due to low relative maximum error. Both experimental and modelling results showed that higher biochar porosity, average capillary radius, volumetric swelling and wettability govern higher velocity of capillary rise. Meanwhile, liquids with higher surface tension and dynamic viscosity lower the capillary rise speed in the biochar.

Keywords Modified Lucas–Washburn equation · Height of capillary rise · Biochar · Volatile organic and inorganic compounds · Biofilter

1 Introduction

Capillary rise is a function of material's microporous and macroporous structure, characteristic of liquid and a function of time [1]. The main link between capillary rise velocity and liquids' characteristics is well defined in traditional capillary rise models. Two main theories which are used to describe velocity of capillary rise in porous materials are as follows: based on Washburn equation (also known as Lucas–Washburn equation) and another is based on the Darcy's law. Evaluation of the link between velocity of capillary rise and material's structure raises main difficulties, since the structure of the porous material has many variations. Natural porous media usually have extremely complex pore structure with pore sizes extended over several orders of magnitude [2].

The history of studying phenomena of capillary rise goes back to the pioneering work of Washburn [3], where he concluded that the volume of the liquid which penetrates into the porous material in a time is proportional to time square root. For a long time of using this equation, many modifications have been applied, since previous models had poor agreement with the natural porous media. Authors including Cai et al. [4, 5] contributed to this area for further understanding of the capillary rise phenomena via different mathematical models. Mathematical model is an important tool which is used when experimentation is expensive. All these attempts well described the mechanism of capillary rise into rigid porous material. However, in many industrial as well as biological processes, the porous material is not rigid anymore, as they deform when liquid passes through them. These materials exist in biomechanics, soil science, infiltration and textile engineering [6].

Wicking plays an important role in many phenomena observed in science, industry, and nature. Spontaneous imbibition is a ubiquitous natural phenomenon in many fields such as groundwater engineering, engineering

✉ Luiza Usevičiūtė
luiza.useviciute@vilniustech.lt

¹ Vilnius Gediminas Technical University, Saulėtekio avenue 11, 10223 Vilnius, Lithuania

geology, soil physics and civil engineering [2]. Wicking or spontaneous liquid absorption into dry porous media is an industrial problem, and it finds application on a range of fields from textile processing to food processing to the processing of composite materials [7]. Wicking also takes place in nature: in green plants, both capillary and osmotic pressures are responsible for carrying water and minerals from the roots up to leaves [7].

The phenomenon of capillarity is important not only in nature, but also in the processes which occur in irrigated biofilter media. The biofiltration system with capillary wetting of the media is a comparatively new method of pollution control. However, the problem is that biofilter media can serve for 5–7 years and for the permanent maintenance of moisture increased the demand for energy. It utilises many environmental resources. The wetting system by capillary action reduces exploitation costs of the device, since it no longer needs artificial wetting system. Due to capillary wetting, media is preserved from overwetting, and anaerobic zones do not form inside the biofilter which can increase the aerodynamic resistance. Additionally, biofilter media must be wetted due to effective removal of the pollutants [8]. Moisture is important for microorganisms which perform decomposition, and it is crucial for their growth and survival. The recommended moisture content in the biofilter should be 40–80% according to the dry mass. According to this, biochar and commercial activated carbon have the highest water holding capacity and due to this can be used for the water retention in poorly wetted biofilters [9].

The swelling of the fibres is an important phenomenon which affects a capillary rise height in biofibres and plant origin materials [10]. Since swelling affects material's structure and molecular arrangement, it affects both wettability of porous material and capillary absorption. Biochar is a complex material which has thermoplastic properties, such as swelling, fluidity and viscosity [11]. Biochar swelling is related with its physical and morphological changes, which occur when biochar is immersed into the solution [12]. Volumetric swelling differs both in raw and processed biochar types. In raw biochar types, it is not significant; however, variation exists in different fraction sizes. At present, there is no clear understanding of biochar swelling during capillary rise when biochar interacts with the liquid.

The aim of the study is to evaluate biochar media which is used in a tube type biofilter with capillary wetting system, volatile organic and inorganic compounds physical properties and their impact on the capillary rise height when different biochar types were used: made from different feedstocks (pine wood, pine bark and hemp), different particle sizes (fine, medium and coarse), modified by the steam of different solutions (rainfall water and rhamnolipid solution).

1.1 Basic Theories and Models for the Evaluation of Capillary Rise in Swelling Porous Materials

One of the first models developed for the evaluation of a capillary rise height in porous materials was formulated by Lucas [13] and Washburn [3]. The liquid capillary rise height, h , can be calculated according to the well-known Lucas–Washburn (L-W) equation:

$$h^2 = \frac{r\sigma\cos\theta}{2\mu}t, \quad (1)$$

where h is the capillary rise height (m), r is the radius of capillary (m), σ is the liquid surface tension (mJ/m²), θ is the contact angle between material and liquid (°), μ is the liquid dynamic viscosity (mN·s/m²) and t is the time (s). Previous studies determined that h - t link which is evaluated by L-W equation is not suitable for the prediction of real, experimental data. Methods which improve L-W equation include alterations of contact angle, pore radius unevenness, tortuosity of the pores, uncircular cross section of the pores and effect of inertia, especially in the early stages of the capillary rise [14].

In the later models of capillary rise, it was analysed how swelling affected capillary process in various materials (pharmaceuticals, fibrous filter, wood, cellulose sponges, food biopolymers (e.g. alginates)). Shi and Gardner [15] analysed the effect of swelling for the liquid capillary rise height in three materials: polyethylene, wood and nylon. A new model which describes velocity of capillary rise according to swelled capillary radius (r_s), volumetric swelling (δ_v) and energy loss coefficient (C) was developed:

$$h^2 \frac{r_s^2 \sigma \cos\theta}{2\mu r} t - \frac{C\delta_v}{4\mu\pi} \left(\frac{r_s}{r}\right)^2 t, \quad (2)$$

where h is the capillary rise height (m), r is the capillary radius (m), r_s is the swelled capillary radius (m), σ is the liquid surface tension (mJ/m²), θ is the contact angle between material and liquid (°), μ is the liquid dynamic viscosity (mN·s/m²), C is the energy loss coefficient (J/m), δ_v is the volumetric swelling (%) and t is the time (s). Equation 2 is based on a force balance condition, since in the derivation of Washburn's equation, the total effective driving force (effective driving pressure) of the capillary rise is only the capillary pressure neglecting the hydrostatic pressure. Because the capillaries are very small, hydrostatic pressure can be neglected compared to the capillary pressure. The Washburn equation was derived assuming that the capillary force was the only effective driving force occurring during the capillary rise process. The modified Washburn equation, including the effect of particle swelling, was developed considering Poiseuille's viscous flow. According to the mentioned Poiseuille's law, liquid movement in each capillary was

regarded as viscous flow. The r value in Poiseuille's law was substituted to capillary radius after swelling (r_s).

Markl et al. [16] developed a new model which describes liquid capillary rise in pharmaceutical tablets. When tablets swell, capillary rise height is increasing and swelled capillary radius (r_s) is decreasing (Fig. 1). Liquid capillary rise in porous media is calculated by the equation:

$$h^2 = \frac{2P_c}{\varepsilon_0 \mu} \int_0^t K(t') dt', \quad (3)$$

where h is the capillary rise height (m), P_c is the capillary pressure, ε_0 is the initial porosity of the material (%), μ is the liquid dynamic viscosity (mN·s/m²), K is the permeability of the material and t is the time (s). In this model, intrinsic permeability varies with time. Permeability is considered globally for the whole wet area. Thus, it is a function of time only [1]. If global values are considered for permeability throughout the wetted porous medium, then local effects are neglected and permeability can then be just a function of time. Neglecting the local spatial dependence in this parameter simplifies the governing equation (Eq. 3) from a nonlinear partial differential equation to an ordinary differential equation that can be solved analytically.

Cellulosic porous materials, when they come into contact with water or dyes, absorb liquid and, at the same time, swell. Cellulose is a polymer whose chains are connected with hydrogen bonds and water molecules, and it participates in adsorptive sites, which causes increase of the polymer volume. Such physical–chemical interaction of water and porous structure is called hygroscopic expansion. In one

study [17], capillary rise of liquid in cellulosic porous material in later stages is described by Darcy's law:

$$u \approx \frac{\sigma^3}{\mu(\rho g)^2 r h^3}, \quad (4)$$

where u is the volumetric average Darcy's law velocity (m/s), σ is the liquid surface tension (mJ/m²), μ is the liquid dynamic viscosity (mN·s/m²), ρ is the liquid density (g/cm³), g is the free fall acceleration (m/s²), r is the capillary radius (m) and h is the height (m). This theory is based on a primary presumption that pores' pressure increases according to water content, which promotes swelling of the pores.

1.2 Development of Modified Lucas–Washburn Model

In this study, the main equation for the evaluation of a capillary rise height (h) dependency on time (t) was taken from another study [5]. The model of Cai et al. [5] evaluates saturated mass dependence on time during the capillary rise process. This model differs from other previously mentioned models for it includes a composite parameter (ξ), liquid density (ρ_s), initial (S_{wi}) and final (S_{wf}) liquid saturation states:

$$m^2 = \xi \frac{\rho_s^2 A^2 \phi^2 (S_{wf} - S_{wi})^2 r \sigma \cos \theta}{2\mu} t, \quad (5)$$

where m is the mass of the material during capillary rise (g), ρ_s is the liquid density (g/cm³), A is the material's cross-sectional area (cm²), ϕ is the porosity of the material (%), S_{wf} is the final saturation state of the material, S_{wi} is the initial saturation state of the material, r is the capillary radius (m), σ is the liquid surface tension (mJ/m²), θ is the contact angle between material and liquid (°), μ is the liquid dynamic viscosity (mN·s/m²) and t is the time (s).

Instead of a dry capillary radius r , the new model includes effective capillary radius r_e which is equal to the swelled capillary radius square (r_s^2) and dry capillary radius (r) quotient ($r_e = \frac{r_s^2}{r}$). Therefore, the capillary effective radius (r_e) and similarly to another study [15], volumetric swelling of the material (δ_v) and energy loss coefficient (C) are included into the final form of the new model. The new model obtains the final form:

$$m^2 = \xi \frac{\rho_s^2 A^2 \phi^2 (S_{wf} - S_{wi})^2 r_e \sigma \cos \theta}{2\mu} t - \frac{C \delta_v}{4\mu\pi} \left(\frac{r_s}{r} \right)^2 t, \quad (6)$$

where ξ is the composite parameter, m is the accumulated imbibition weight (g), ρ is the liquid density (g/cm³), A is the material's cross-sectional area (cm²), ϕ is the porosity of the material (%), S_{wf} is the final saturation state of the material, S_{wi} is the initial saturation state of the material, r_e is the effective capillary radius (m), σ is the liquid surface

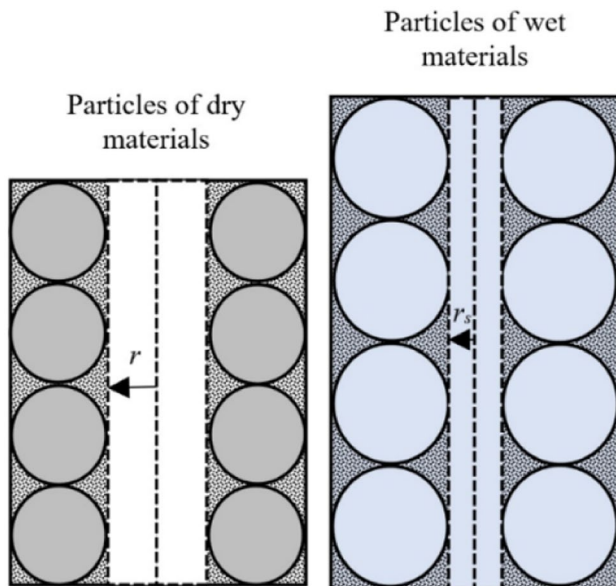


Fig. 1 Scheme of particles swelling (particle radius directly impact capillary radius (r and r_s))

tension (mJ/m²), θ is the contact angle between material and liquid (°), μ is the liquid dynamic density (mN·s/m²), t is the time (s), r is the average capillary radius (m), r_s is the average capillary radius after swelling (m), C is the energy loss coefficient (J/m) and δ_v is the volumetric swelling of particles (%). According to Eq. 6, saturated mass of the material (g) was recalculated to the height (cm) in every analysed moment of time. Therefore, final graphs of modelling results were presented as a function of capillary rise height (cm) and time (s). The results of saturated material mass due to the wicking were recalculated knowing the volume equation, which is equal to the mass divided by the density ($V=m/\rho$) and equation of filled column volume with the saturated material after the capillary rise ($V=\pi r^2 \cdot h$). Equation 6 is based on a force balance condition, since when a tortuous capillary tube is brought into the contact with liquid, the liquid will impregnate capillary tube due to balance among the atmospheric pressure, the hydrostatic pressure and the capillary pressure. However, Eq. 6 is only valid for early imbibition times. Therefore, analytical model including gravity should be used for long-term imbibition process, since the effect of gravity increases with the uptake height/time.

Similarly, to another study [16], instead of the swelled capillary radius, hydraulic capillary radius is included and effective capillary radius of the material is calculated according to the equation: $r_e = \frac{r^2}{r_s}$. Since hydraulic radius (r_h) is more common term for pharmaceutical tablets [16] and fibres, swelled radius (r_s) was chosen because this term is more common for materials which have more complex structures for their pore spaces (such as wood particles, polyethylene, etc.). In this model, radius of swelled capillary is calculated according to the equation [15]:

$$r_s = \sqrt{\frac{\pi R^2 \rho_m - (1 + \delta_v) G_m}{\pi \rho_m R^2 - G_m}} \cdot r, \quad (7)$$

where R is the radius of the column (m), ρ_m is the material's density (g/cm³), δ_v is the volumetric swelling of the material (%), G_m is the mass of the column (g) and r is the capillary radius (m).

The number of capillaries in the column can be calculated using the equation [15]:

$$N = \left(\frac{R}{r}\right)^2 - \frac{G_m}{\pi R^2 \rho_m}, \quad (8)$$

where N is the number of capillaries in the column, R is the inner radius of the column (m), G_m is the unit column mass (g/m), r is the average capillary radius (m) and ρ_m is the material density (g/cm³). After polymer swelling, the number of capillaries in the column (N) should remain the same. If expansion due to swelling is neglected, the following equation also holds:

$$N \cdot \pi r_s^2 h + (1 + \delta_v) \frac{M_m}{\rho_m} = \pi R^2 h, \quad (9)$$

where r_s is the swelled average capillary radius (m), δ_v is the volumetric swelling of the particles (%), M_m is the mass of swelling material in the column (g) and h is the height of the capillary rise (m). Combining Eqs. 8 and 9, the relationship between r_s and r can be established as it has been shown in Eq. 7.

2 Materials and Methods

2.1 Production of Biochar

For the capillary rise experiment in the biofilter, seven biochar types were used: coarse fraction (900 µm–1.6 mm), medium fraction (300–900 µm) and fine fraction (<300 µm) of pine wood biochar (PW_CF, PW_MF and PW_FF, respectively), coarse fraction of pine bark and hemp biochar (PB_CF and H_CF, respectively) and pine wood biochar types modified with steam of rhamnolipid solution (40 mg/l, 3 h) and rainfall water (3 h) (PW_CF_SRW and PW_CF_SRS, respectively). All biochar types were produced in low pyrolysis temperature (450 °C) and 2-h holding time at 10 °C/min heating rate. Biochar was produced in muffle furnace (E5CK-T) and, to create oxygen deficiency conditions, feedstocks were rolled in the aluminium foil [18].

2.2 Evaluation of Biochar and Liquids' Properties

At the beginning of the study, before the capillary rise experiment, biochar's physical properties were analysed: porosity (ϕ), contact angle (θ), average capillary radius (r) (Table 3). Additionally, liquid properties were analysed: density (ρ_s), dynamic viscosity (μ) and surface tension (σ) (Tables 1 and 2). According to Eq. 7, radius of swelled capillaries (r_s) was calculated, and according to Eq. 2, the energy loss coefficient (C) was calculated in the case of hexane. It is accepted that the cross-sectional area (A) in the case of biochar is 10.2 cm², and it is equal to the radius of the filled column. Values of the composite parameter (ζ) were taken from the literature [5]. For the modelling of liquid capillary height dependence on time, four volatile organic compounds (acetone, toluene, xylene and hexane) and one volatile inorganic compound (ammonium) were chosen (Table 1). Volatile organic compounds were chosen according to their different hydrophilicity/hydrophobicity with reference to Henry's law constant (K_H). Henry's law constant (also called gases-water distribution coefficient) is a ratio between gases partial pressure in the air and its concentration in water at a particular temperature [19].

Table 1 Surface tension (σ), dynamic viscosity (μ), density (ρ_s), Henry's law constant (K_H) of different liquids and contact angles (θ) between liquid and coarse pine wood biochar at ambient temperature (25 °C)

Solution	Surface tension	Dynamic viscosity	Density	Contact angle	Henry's law constants	
	σ (mJ/m ²)	μ (mN·s/m ²)	ρ_s (g/cm ³)	θ (°)	K_H (dimensionless)	Reference
Water	72.8	1	0.99	84	-	-
Acetone	22.8	0.32	0.78	26	0.00159	Peng and Wan [20]
Toluene	28.4	0.55	0.87	33	0.235	
Xylene	28.9	0.78	0.86	33	0.3	
Hexane	18.4	0.14	0.66	21	1.802	
Ammonium	75	0.13	0.61	87	-	-

For the modelling of a capillary rise height according to different concentration of the solution, acetone whose concentration ranged from 0.15 to 1 mol/l was chosen (Table 2). It can be seen that when molar concentration of acetone increased, its dynamic viscosity and surface tension decreased.

Porosity of the biochar was determined using the method of mercury porosimeter [21]. A mercury intrusion porosimeter Quantachrome PoreMaster PM-33-12 was used for the analysis. Before the analysis, the material was dried until constant mass at 105 °C temperature (Table 3).

A contact angle is defined as an angle whose liquid surface centres on material's surface [22]. The modified method proposed by Shang et al. [23] was used. Biochar was sieved through a 600 μ m sieve for the removal of coarse particles and obtainment of flattened surface. Biochar was dried in the air and was placed on the microscope slide and flattened using the other slide. For the evaluation of contact angle, 0.5 ml of deionised water droplet was placed on the biochar surface using a pipette for 5 s from 1 cm height. Then, pictures of droplet profiles were taken using a camera of *Alcatel Idol-4*, photographing at a distance of 10 cm from the sample. Then, the pictures were converted into the grey scale using *PhotoScape*. The pictures were analysed using *ImageJ* software with *DropSnake* plugin [24].

The pore radius of biochar was evaluated using SEM macrostructure pictures. Morphological biochar analysis

was conducted using a scanning electron microscope [25]. Then, the obtained pictures were converted to the black/white colour scale using *ImageJ* software due to evaluation of average capillary diameter (μ m). In each picture, diameters of 30 capillaries were analysed.

Biochar volumetric swelling was analysed in the column, 24 h after the capillary rise experiment. Biochar volumetric swelling is expressed by the swelling ratio [26]:

$$S = \frac{V_s - V_d}{V_d} \times 100\%, \quad (10)$$

where S is the increase of the material volume (%), V_s is the volume of the swelled material and V_d is the volume of the dry material.

Liquid absolute (dynamic) viscosity was evaluated using Ostwald's viscometer [27]. The bigger sphere of the viscometer was filled with a particular amount of liquid and was pulled off until the smaller sphere filled. The viscometer was vertically placed into the bath at a particular temperature. Water freely flew into a capillary tube and, when the liquid reached the mark, the stop-watch was stopped. The experiment was repeated with all liquids of unknown viscosity. For the calculation of liquid dynamic viscosity, Eq. 11 was used [28]:

$$\frac{\eta_1}{\eta_2} = \frac{t_1 d_1}{t_2 d_2}, \quad (11)$$

where η_1 is the viscosity of the first liquid, poise; η_2 is the viscosity of water, which is equal to 0.891, poise; t_1 is the velocity of first liquid, cm/s; t_1 and t_2 is the time, s; d_1 is the density of first liquid, g/cm³; d_2 is the density of water which is equal to 0.997 g/cm³. The surface tension of liquids was evaluated according to the liquid height and density in the narrow tube. The surface tension of liquid was calculated according to the equation:

$$\sigma = \frac{\rho_s h g a}{2}, \quad (12)$$

Table 2 Characteristics of acetone solutions according to different molar concentrations at ambient temperature

Concentration of acetone (mol/l)	Surface tension σ (mJ/m ²)	Dynamic viscosity μ (mN·s/m ²)	Density ρ_s (g/cm ³)	Contact angle θ (°)
1	23	0.32	0.78	26
0.6	30	0.5	0.8	35
0.3	39	1.1	0.82	45
0.15	50	1.2	0.85	58

Table 3 Characteristics of porous material (biochar) used in the model

Type of the biochar	Parameter of the composite	Cross-sectional area of the material	Porosity	Capillary radius	Swelled capillary radius	Contact angle	Energy loss coefficient	Volumetric swelling
	ξ	A (cm ²)	ϕ (a part per hundred)	r (m)	r_s (m)	θ (°)	C (J/m)	δ (a part per hundred)
PW_CF	0.51	10.2	0.77	$1.22 \cdot 10^{-5}$	$1.17 \cdot 10^{-5}$	84 ± 4.71	0.123	0.025
PW_MD	0.51	10.2	0.8	$1.38 \cdot 10^{-5}$	$1.32 \cdot 10^{-5}$	82	0.123	0.029
PW_FF	1	10.2	0.82	$6.66 \cdot 10^{-6}$	$6.38 \cdot 10^{-6}$	79	0.059	0.053
PB_CF	0.51	10.2	0.65	$1.25 \cdot 10^{-5}$	$1.25 \cdot 10^{-5}$	89	0.099	0.005
H_CF	0.51	10.2	0.86	$1.48 \cdot 10^{-5}$	$1.42 \cdot 10^{-5}$	65 ± 1.83	0.094	0.03
PW_CF_SRW	0.51	10.2	0.78	$1.21 \cdot 10^{-5}$	$1.16 \cdot 10^{-5}$	66	0.102	0.03
PW_CF_SRS	0.51	10.2	0.79	$1.1 \cdot 10^{-5}$	$1.05 \cdot 10^{-5}$	54	0.08	0.04

where σ is the liquid surface tension, N/m; ρ_s is the liquid density, kg/m³; g is the free fall acceleration which is equal to 9.8 m/s²; α is the tube radius, m. For the evaluation of liquid density, a bath was filled with the liquid until 2.54 cm height. A transparent and narrow tube was placed into the bath, in which the capillary rise height (m) of the liquid was measured. The diameter of the tube was measured using a ruler. Density of the liquid was calculated according to the equation [29]:

$$\rho_s = \frac{m_s}{V_s}, \quad (13)$$

where ρ_s is the liquid density, kg/m³; m_s is the liquid mass of a particular volume (50 ml), kg; V_s is the volume of the liquid (50 ml).

2.3 Evaluation of the Swelling Phenomenon: Temperature Rise

For the determination of temperature rise in biochar during capillary rise, a J-type thermopore was placed in the tube's hole which was dug at the beginning of the column (at height of 2 cm from the tubes' holder). Loss of energy (J/m) in the tube during capillary rise occurs due to the liquid penetration into material's micropores, and it governs formation of swelling heat (adsorption heat) which is expelled from the capillary system [15]. The temperature rise phenomenon shows that during capillary rise particles swell in the system of material and liquid. When temperature stops rising after some time, it can be stated that the swelling does not occur anymore.

2.4 Experiment of Capillary Rise

For the determination of capillary rise velocity, a tube type biofilter with capillary wetting was used (Fig. 2). For the

analysis of biomedica capillarity, the biofilter's lower part was filled with water in which seven of 30-cm length and 1.8-cm internal diameter perforated organic glass tubes filled with biochar were immersed until 7.5-cm depth. Bottoms of the tubes were supported with fine steel screens which prevent water from contamination with solid particles [30].

A graduated metallic ruler was attached to the side of one tube. Zones of wetted and dry material visually differed and heights of wetted material were fixed according to time [14]. The duration of the experiment was 24 h. Capillary rise heights were fixated for nine time intervals (after 1, 2, 3, 4, 5, 6, 7, 8 and 24 h), and at the same time, variation of temperature in the wetted biochar was analysed with the thermopore [15]. The scheme of the biofilter for the evaluation of capillary

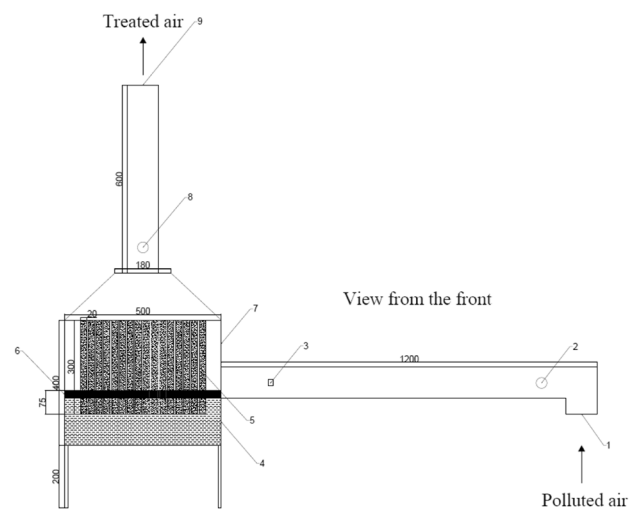


Fig. 2 Biofilter: 1, opening hole of volatile compounds; 2, closing valve of the opening; 3, temperature regulator; 4, reservoir of solution (water with biogenic elements); 5, tube filled with biochar; 6, tubes holder; 7, reservoir filled with steam of volatile compounds; 8, measuring hole of concentration of volatile compounds; 9, exhaustion hole of volatile compounds

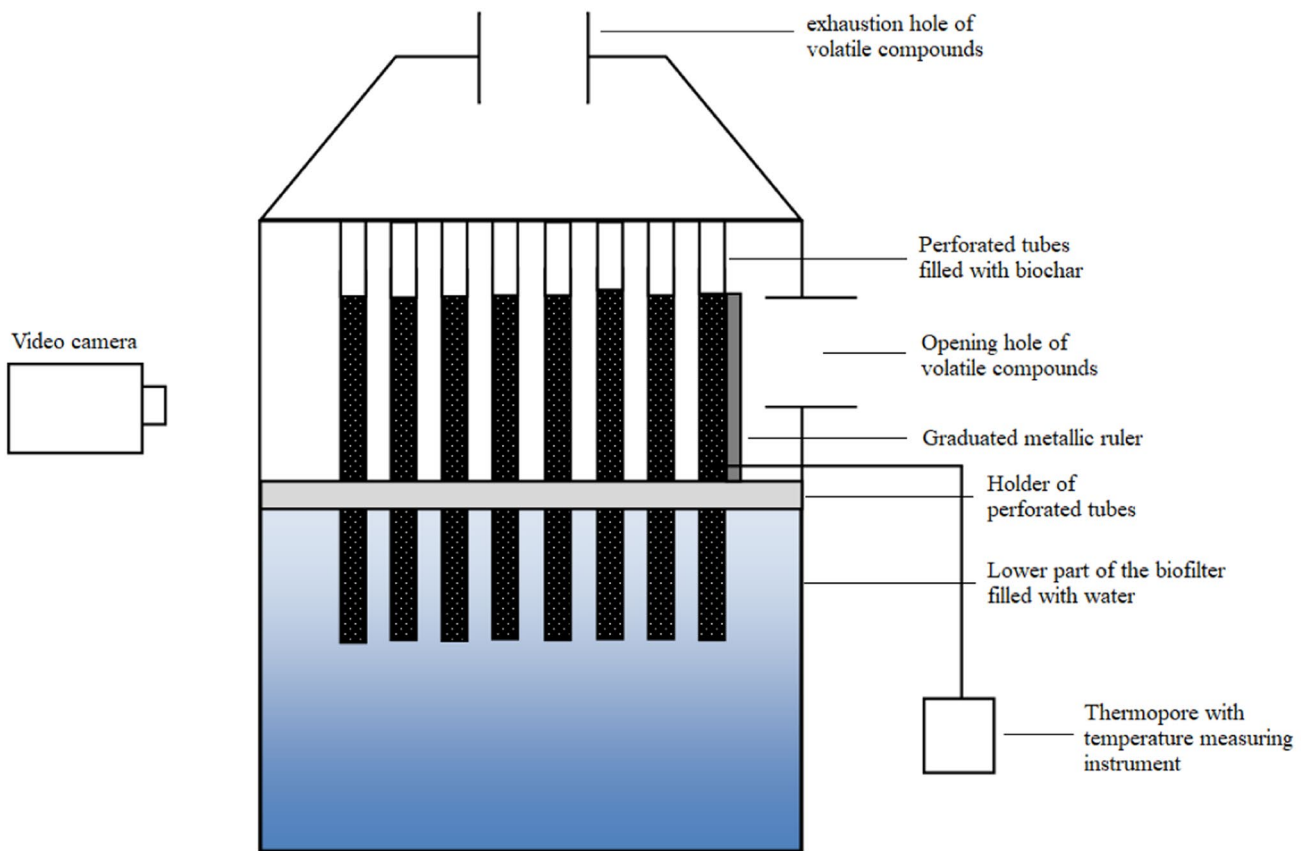


Fig. 3 Scheme for the evaluation of capillary height in biochar, placed in biofilter tubes

height is shown in Fig. 3. Until the end of the experiment, a continuous filling of tubes until 7.5-cm depth was ensured at the bottom part of the biofilter's reservoir [31].

2.5 Statistical Analysis

Calculations of capillary rise height (cm) as a function of time (s) were performed using *Microsoft Excel 2016*. All capillary rise experiments were done in triplicate. Average values and standard deviations of capillary rise height (cm) and average pore diameter (μm) were calculated and showed in the graphs.

3 Results

3.1 Dependence of Biochar Morphological Characterisation on initial Feedstock, Particle Size and Modification

Morphology of biochar types was characterised according to SEM pictures (Fig. 4a–g). An average pore diameter of the pine wood biochar pores decreased after crushing, and,

in the case of fine fraction ($< 300 \mu\text{m}$) average macropore, diameter decreased by 13% and 37% compared to the coarse and medium fractions, respectively. The pores' diameter of medium size in biochar particles was similar to the coarse biochar (28 and $20 \mu\text{m}$, respectively). Comparing three feedstocks (pine wood, pine bark and hemp), hemp biochar had the averagely highest size of macropores ($30 \mu\text{m}$), which was by 16% and 32% higher than pine bark and pine wood biochar types (Fig. 4h). Comparing modification techniques (with steam of rainfall water and rhamnolipid solution), biochar modified by the steam of rainfall water had by 17% and biochar modified by the steam of rhamnolipid solution had by 8% higher average macropore diameter compared to the unmodified biochar.

Biochar has a porous structure, a complex pore network and various cracks which form during the process of biomass pyrolysis due to fast rate of external and internal decomposition of biomass. This structure can be decomposed when it is affected by additional mechanical stress and then it can form colloids [32]. Physical crushing of biochar is the most common technique used to decrease the size of particles. Meanwhile, biochar modification by steam facilitates merging of fine pores and enlarges internal cavities that increase microporosity of the material [33].

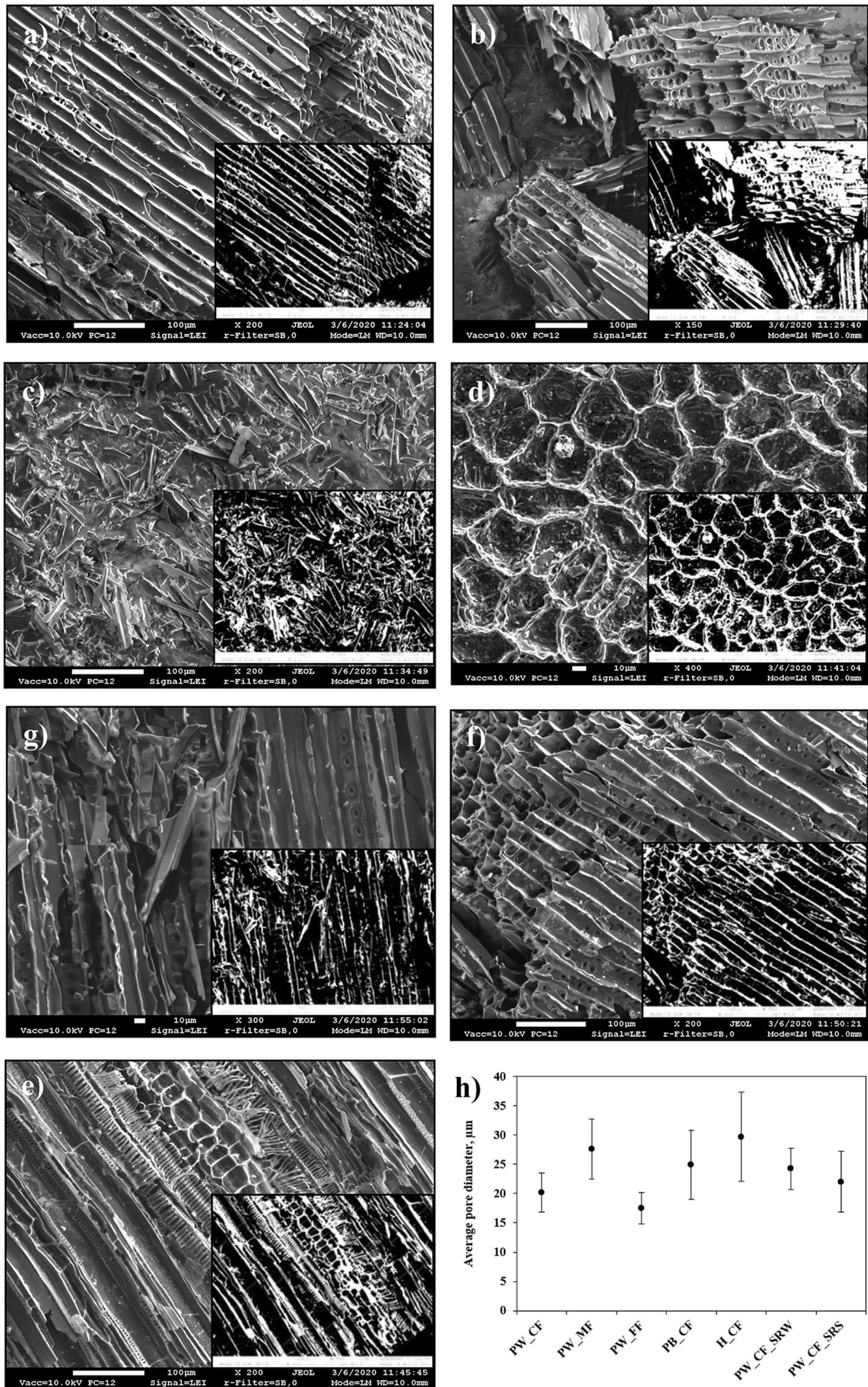


Fig. 4 SEM pictures of biochar types: **a** coarse fraction (900 μm –1.6 mm) pine wood biochar; **b** medium fraction (300–900 μm) pine wood biochar; **c** fine fraction (<300 μm) pine wood biochar; **d** coarse fraction pine bark biochar; **e** coarse fraction hemp biochar; **f** coarse fraction pine wood biochar modified by the steam of rainfall water; **g** coarse fraction pine wood biochar modified by the steam of rhamnolipid solution; **h** average diameter of the macropores (μm) according to SEM pictures, $n=30$

3.2 Evaluation of the Swelling Effect on Water Capillary Rise in Biochar

Heat of adsorption is a typical phenomenon which occurs during swelling of the materials [15]. When liquid penetrates and is adsorbed on the surface of internal micropores, energy of the material and liquid typically decreases. Part of the system energy excludes in the form of heat, which is called the heat of swelling or adsorption. Figure 5 shows evaluation of temperature change during water capillary rise in pine wood biochar, which was determined with the thermopore. The results showed that the highest jump of temperature occurred after 4 h when temperature changed from 24.2 to 27.5 $^{\circ}\text{C}$. At the same time, the capillary rise height increased from 2.6 to 6.6 cm. This temperature rise phenomenon shows that the swelling occurred at the beginning of the capillary rise experiment (until 6 h) and, later on, the heat did not exclude and started decreasing in the case of long-term capillary rise (from 6 to 24 h).

Decrease of temperature during capillary rise is related to (1) liquid in the tube which absorbs the heat of the adsorption, (2) release of the adsorption heat into the environment. Biochar swelling during capillary rise process shows that calculated swelled capillary radius was smaller than compared to the dry capillaries which were analysed by the SEM pictures.

3.3 Fitting of Composite Parameter to Experimental Data

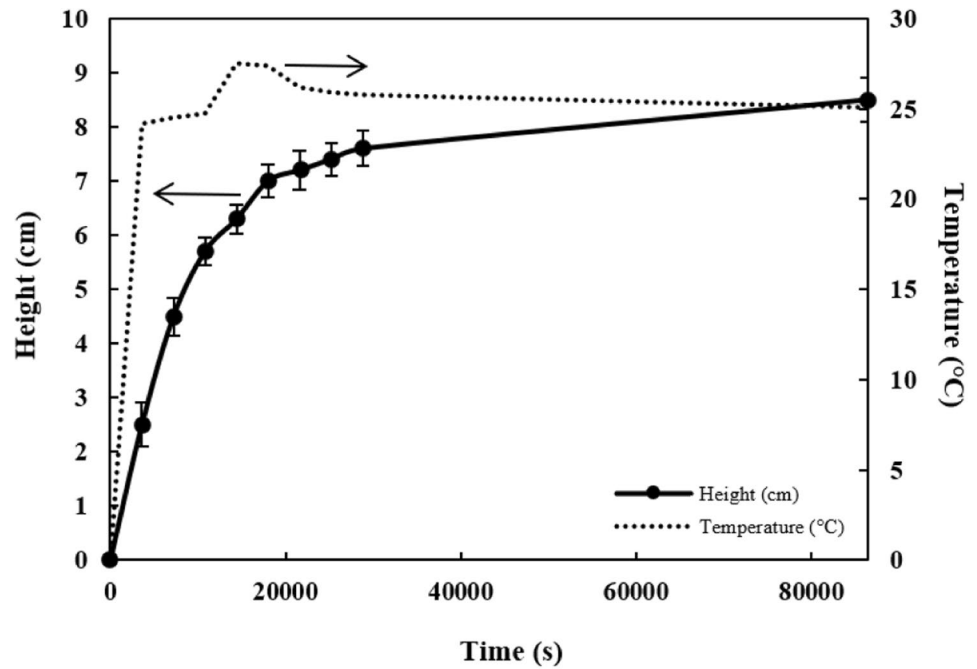
The value of the composite parameter was obtained when modelling results were fitted to experimental (Fig. 6a, b). Figure 6a shows that, in the case of coarse pine wood biochar type, the modelling results better fitted experimental data when the value of the composite parameter reached 0.513. For almost all biochar types, except fine fraction of pine wood biochar, best modelling results were obtained when the value of this parameter was 0.513. In the case of fine fraction pine wood biochar, this value was 1 (Fig. 6b). Compared to other studies, this value can reach from 0.463 (in the case of greywacke) to 1.032 (in the case of natural rock, Berea) [34]. Almost for all biochar types the value of the composite was equal to the value of silica glass (0.513) [35]. The composite parameter includes the form of the pores and tortuosity of capillary stream.

An accumulated capillary rise height increases with time until the constant time is reached, after which the experiment becomes stable. In the case of coarse pine wood biochar, this constant reached 7 cm in the case of the accumulated water capillary rise height. It can be seen that the modelled accumulated capillary rise height well fits experimental results at the beginning of the experiment (until 8 h). Meanwhile, in the long-term case (> 8 h), it is possible that the gravitational force starts acting and the modified Lucas–Washburn model is not suitable for the prediction of capillary rise height. For the long-term capillary rise including gravitational force, Darcy’s law or Lambert function can be used. Models based on Darcy’s law have some advantages against the methods based on Washburn equation, since the latter can be developed into two-dimensional or three-dimensional capillary rise situations. Washburn models are limited with one-dimensional streams [1]. Pezron et al. [36] noticed a steep increase of the mass of saturated materials in the early capillary rise stages and it was related with the force of wetting liquid, which affects the lower part of the tube when it starts to contact with the liquid. Lucas–Washburn equation is preferable due to its simplicity; however, it is not valid for increasing time. It raises the question to which time it may be used and for later times extended solution including gravity should be considered. One study [37] showed that, in the beginning, the Lucas–Washburn solution fitted well to the extended solution; however, it tended to deviate to higher values for longer times due to the neglect of gravity. Fried and Dryer [37] used Lambert W function for mathematical Washburn solution rearrangement, and the final solution including gravity (hydrostatic pressure) was proposed for the calculation of liquid rise behaviour for longer times. Another study [2] showed that liquid maximum relative error for long imbibition time (until 20,000 s) in porous media was less than 0.1%. Validity of the Lambert W function introduced there was verified. Barry et al. [38] mentioned that Lambert W function can be used to calculate infiltration as well as capillary rise of moisture in soils.

3.4 Dependence of Capillary Rise Velocity on Initial Feedstock

Results of the capillary rise experiment in the case of biochar types made from different initial feedstocks are shown in Fig. 7 which shows the height (cm) of water rise according to temperature due to capillary force. Hemp biochar had the highest capillary rise height (9 cm) at the beginning of the experiment (until 8 h) compared to other biochar types. The modelling results also showed that hemp biochar had the highest capillary rise height (10 cm). The modelling showed that hemp biochar had by 28% and 19% higher capillary rise height compared to pine bark and pine wood biochar types, respectively. Such results can be explained by higher hemp biochar

Fig. 5 Alteration of temperature (dotted line) in pine wood biochar during capillary rise experiment, $n=3$



porosity (86%), wettability (65°) and swelling (3%). According to the modelling results, biochar types made from different initial feedstocks can be ordered in such a way: hemp > pine wood > pine bark. The order of the feedstocks partly can be explained by the porosity of the biochar types: hemp (86%) > pine wood (77%) > pine bark (65%). Biochar porosity can vary from 55 to 86%, and it mainly depends on initial feedstock (wood < grass) [42]. Differences between experimental and modelling results of heights were by 3.89%, 10.2% and 13.8% in the case of pine wood, pine bark and hemp biochar types after 8 h, respectively.

These results confirm the idea that higher porosity materials govern higher capillary rise velocity [5]. Additionally, a diameter of the pores was an important factor for the capillary rise height, which was higher in the case of hemp biochar ($29.7\ \mu\text{m}$) compared to pine wood or pine bark biochar types (20.2 and $24.7\ \mu\text{m}$, respectively). Similarly, another study [14] showed that the modelled capillary rise height in the case of coarse soil pores was higher compared to fine pores. The latter study showed that soil with higher average capillary radius ($10\ \mu\text{m}$) was characterised by a higher modelled capillary rise height ($12.5\ \text{cm} > 2.5\ \text{cm}$) compared to fine capillary radius of pores ($0.35\ \mu\text{m}$) after 10 min.

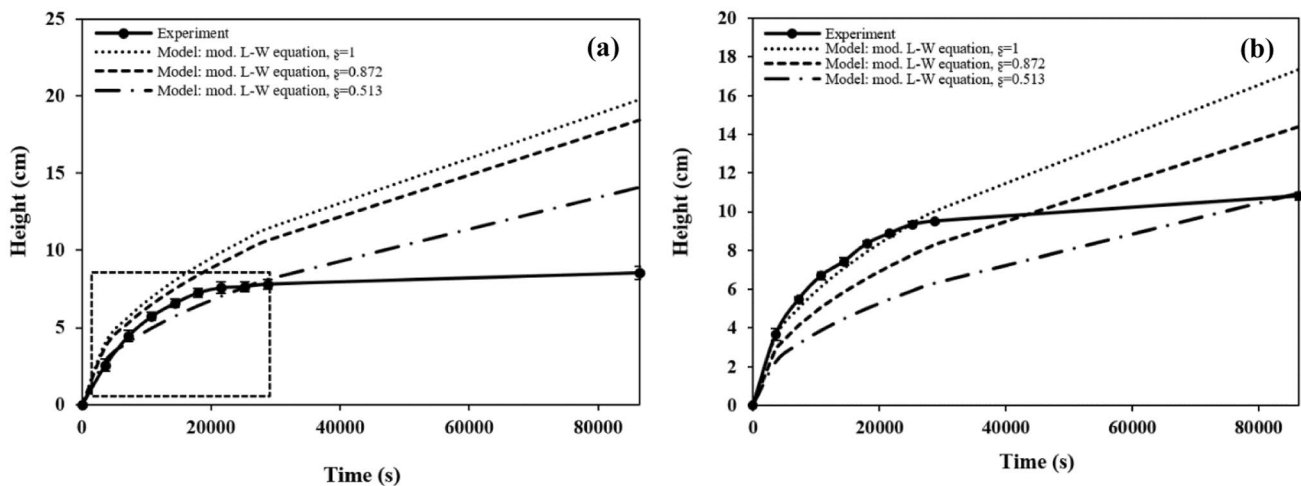


Fig. 6 Experimental (solid line) and modelling (dash line) results of capillary rise height (cm) in the case of coarse biochar (a) and fine biochar (b) according to different value of composite parameter, $n=3$

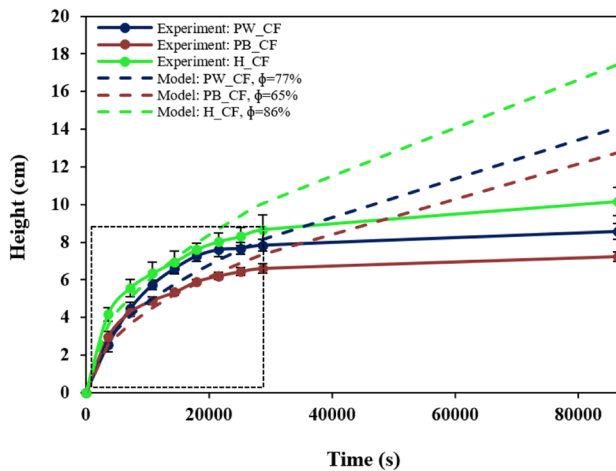


Fig. 7 Experimental (solid line) and modelling (dash line) results of capillary rise height (cm) according to different biochar initial feedstock, $n=3$

In this study, capillary rise curves can be divided into two zones: fast capillary rise zone until 8 h and stable zone after this time. This property confirms the theoretical analysis that the gravitational force can be neglected during the capillary rise process in the early stages which are predicted by Washburn equation [39]. In the early stages, the capillary rise height is proportional to the square root of time ($h(t) \approx t^{1/2}$); however, the gravitational force gains a more significant meaning when the liquid raises further and kinetics of capillary rise decreases from $h(t) \approx t^{1/2}$ to $h(t) \approx t^{1/3}$.

3.5 Dependence of Capillary Rise Velocity on the Particle Size of Biochar

During the capillary rise experiment, the experimental capillary rise height of the finest particle size was the highest compared to the coarse and medium particle sizes (Fig. 8). A similar tendency was obtained comparing the modelling results, when water capillary rise heights in the finest particle size were by 15% and 25% higher compared to medium and coarse size of biochar, respectively. It was experimentally shown that the water capillary rise height was by 17% and 34% higher compared to medium and coarse biochar after 8 h, respectively. When biochar particles are smaller, the capillary rise height is higher. Differences between the experimental and the modelling results of heights were by 11.7%, 7.63% and 5.09% in the case of coarse, medium and fine particle size of pine wood biochar after 8 h, respectively. Similarly, to the experiment of capillary rise height, dependence on the initial feedstock, curves of capillary rise can be divided into two zones: zone of fast capillary rise height until 8 h and stable zone after that time.

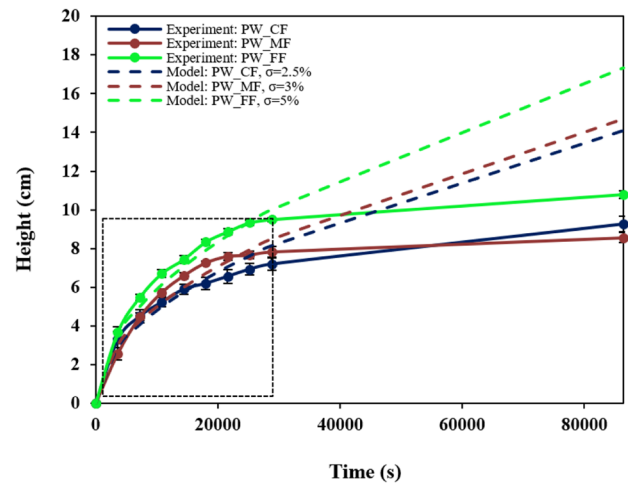


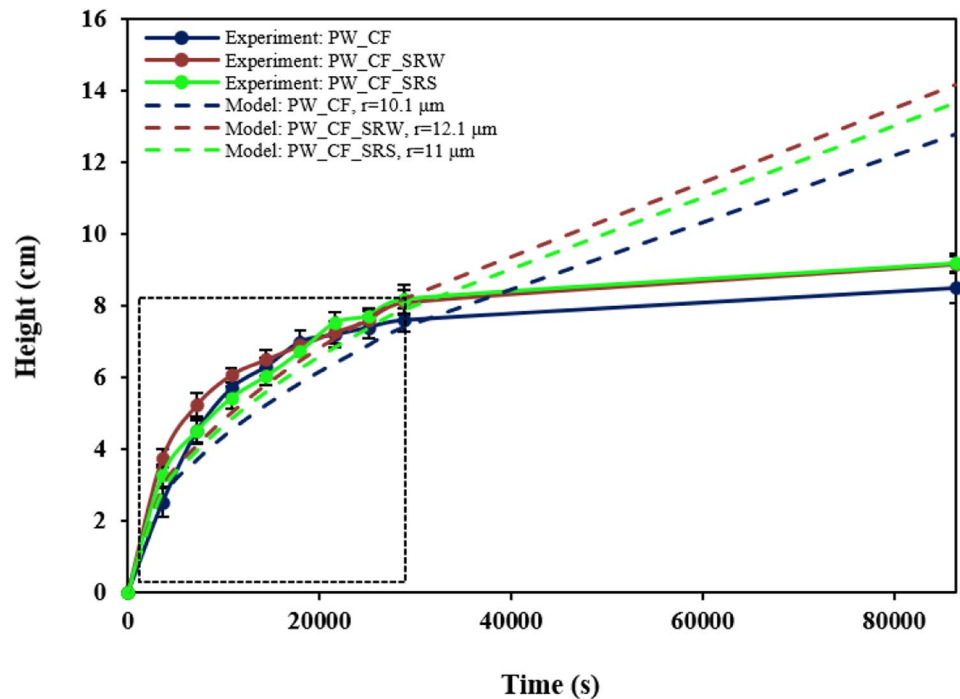
Fig. 8 Experimental (solid line) and modelling (dash line) results of capillary rise height (cm) according to different particle size of pine wood biochar, $n=3$

Comparing how biochar volumetric swelling varies among different biochar fractions, finest pine wood biochar had the higher swelling (5.3%) and the coarsest biochar had smaller (2.5%). Similarly, the finest biochar had higher porosity (82%) than coarse biochar (77%). Despite similar chemical composition of the materials, a higher porosity material (with higher specific surface area) has a higher ability to swell compared to a lower porosity material [26]. A small difference exists between swelling of coarse and fine particles.

3.6 Dependence of Capillary Rise Velocity on a Different Technique of Modification by Steam

From both the experimental and the modelling results, it can be seen that the water capillary rise height in the case of biochar modified by the steam of rhamnolipid solution and steam of rainfall water had slightly higher capillary heights compared to unmodified biochar (Fig. 9). Comparing the modelling results, after 8 h from the beginning of the experiment, biochar modified by the steam of rainfall water had a capillary rise height by 11% and biochar modified by the rhamnolipid solution had by 7% higher compared to the unmodified one. Analysing the experimental results, the difference between biochar types can be more clearly seen after 24 h, when the height of modified biochar was by 8% higher compared to the unmodified biochar. Differences between the experimental and the modelling results of heights were by 3.89%, 0.98% and 4.06% in the case of the unmodified pine wood biochar, biochar modified by the steam of rainfall water and biochar modified by the steam of rhamnolipid solution after 8 h, respectively.

Fig. 9 Experimental (solid line) and modelling (dash line) results of capillary rise height (cm) according to different biochar modifications with steam, $n=3$



It is important to notice that, in this modelling (describing the modification effect on the capillarity of biochar), the used capillary radius can be ordered in such a manner: unmodified biochar ($1.01 \cdot 10^{-5}$ m) < biochar modified by the steam of rhamnolipid solution ($1.01 \cdot 10^{-5}$ m) < biochar modified by the steam of rainfall water ($1.21 \cdot 10^{-5}$ m). Therefore, when the diameter of biochar pores (capillaries) is higher, the capillary rise height is also better. Biochar modification by the steam facilitates the blending of small pores and increases internal cavities [33]. Similar to another study [40], it was found that the maximum capillary rise height of the soil was mainly determined by the distribution of large size pore, and meanwhile, the effect of small pore size was quite insignificant.

3.7 Dependence of Capillary Rise Velocity on the Properties of the Liquid

Analysing a theoretical capillary rise height of volatile organic compounds (acetone, toluene, xylene and hexane) and inorganic (ammonium) in the coarse pine wood biochar, it can be seen that hexane had the highest capillary rise which reached 26 cm after 8 h from the beginning of the experiment (Fig. 10). Such result can be explained by the lowest surface tension of this compound (18.4 mJ/m²) and comparable low dynamic viscosity (0.14 mN·s/m²). Meanwhile, the lowest capillary rise height had water and ammonium (9.87 and 11.8 cm after 8 h, respectively). It can be explained by a similar surface tension

of these liquids, which were 72.8 and 75 mJ/m² in the cases of water and ammonium, respectively. Water also had the highest dynamic viscosity (1 mN·s/m²) and density (0.995 g/cm³). The theoretical maximum capillary height of analysed liquids can be ordered in such a way: water (17.1 cm) < ammonium (21.7 cm) < xylene (30.3 cm) < toluene (36.8 cm) < acetone (39.5 cm) < hexane (45.9 cm). Similarly, however, in an opposite manner, liquids can be ordered in such a way according to surface tensions: ammonium (75 mJ/m²) < water (72.8 mJ/m²) < xylene (28.9 mJ/m²) < toluene (28.4 mJ/m²) < acetone (22.8 mJ/m²) < hexane (18.4 mJ/m²).

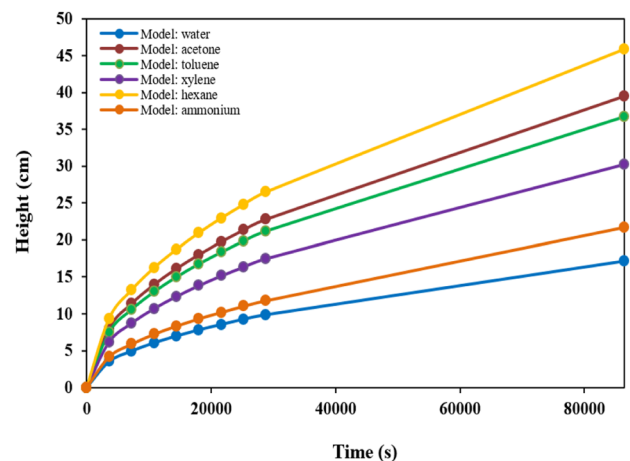


Fig. 10 Modelling results of capillary height (cm) dependence on different solutions of volatile organic compounds (1 mol/l)

Comparing capillary rise heights of volatile organic compounds according to their Henry's law constant, it can be seen that when this constant is lower, the capillary rise height is higher. Heights of capillary rise depending on different volatile organic compounds and their Henry's constants can be ordered in such a way: acetone ($h(8) = 22.8$ cm, $K_H = 0.00159$) > toluene ($h(8) = 21.2$ cm, $K_H = 0.235$) > xylene ($h(8) = 17.49$ cm, $K_H = 0.3$).

4 Dependence of Capillary Rise Velocity on the Acetone Concentration in the Liquid

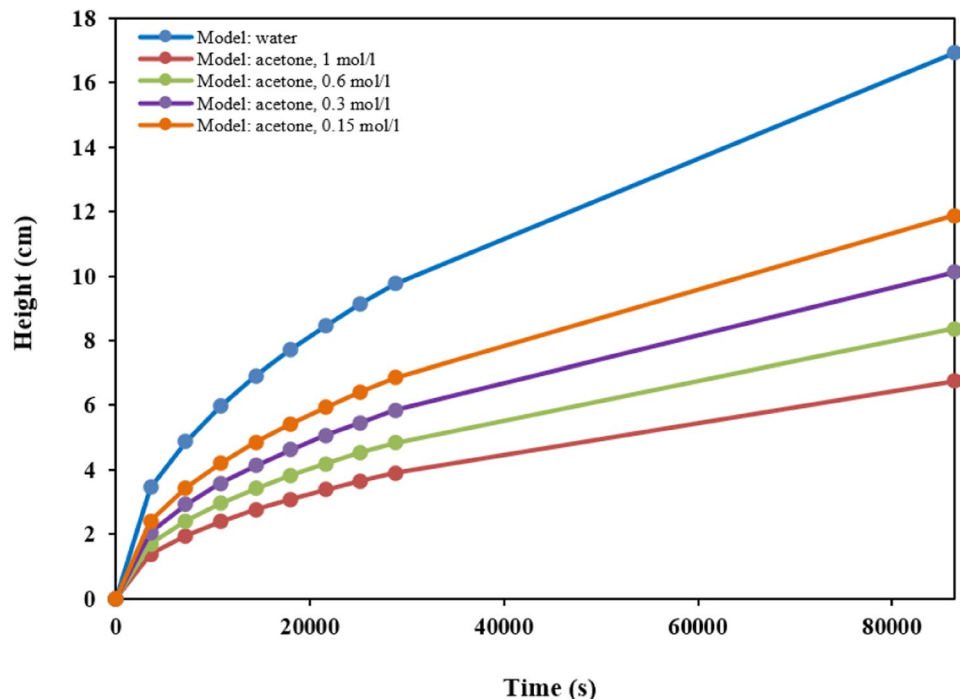
Figure 11 shows theoretical acetone capillary rise heights in the coarse pine wood biochar according to different concentration of acetone in the liquid. It can be seen that when the acetone concentration increased from 0.15 to 1 mol/l, the capillary rise height also increased from 14.4 to 22.8 cm after 8 h from the beginning of the experiment. When the acetone concentration increased by 7 times (from 0.15 to 1 mol/l), the maximum capillary rise height increased by 1.6 times (from 24.9 to 39.5 cm). It can be stated that surface tension and dynamic viscosity are the parameters which mostly affected the capillary rise height, since the best capillary rise velocity had acetone solutions with an increased concentration and decreased

surface tension and dynamic viscosity. Acetone solutions of different concentration (mol/l) according to the surface tension can be ordered in such a manner: 0.15 mol/l (50 mN/m) > 0.3 mol/l (39 mN/m) > 0.6 mol/l (30 mN/m) > 1 mol/l (23 mN/m). Similarly, when the concentration increases, dynamic viscosity decreases: 0.15 mol/l (1.2 mN·s/m²) > 0.3 mol/l (1.1 mN·s/m²) > 0.6 mol/l (0.5 mN·s/m²) > 1 mol/l (0.32 mN·s/m²). It is worth mentioning that the concentrated solution of acetone (1 mol/l) has lower density than water (0.784 and 0.995 g/cm³, respectively).

According to the literature, the surface tension (mJ/m²) of acetone has a linear decrease compared to its concentration (mol/l) [10]. The dynamic viscosity of acetone varies depending on the molar fraction of acetone (in the interval of 0.3–1.4 mN·s/m²) and can reach a maximum value in the case of 0.15 molar fraction in the solution. It is important to mention that viscosity of the solution does not have linear variation depending on the concentration of the solution.

Washburn method can possess a number of limitations. Regardless of many difficulties the technique remains valuable tool for investigating wetting properties of solids [41]. This study hence describes a novel application of the Washburn technique. This technique is experimentally simple and highly versatile, allowing users to screen a wide range of solvents for their ability to wet and penetrate into biochar in a short period of time.

Fig. 11 Modelling results of capillary height (cm) dependence on different molar concentration of acetone solution



5 Conclusions

The modified Lucas–Washburn equation was proposed to model the capillary rise height of liquid in a porous material such as biochar which absorbs liquid and swells. The presented model considered almost all the properties of porous media and the wetting liquid, which control the process of spontaneous imbibition; this model considered not only the mass of the liquid imbibed between the pores by capillary wicking but also the effect of volumetric particle swelling what has not been addressed in the literature about capillary wicking in swelling biochar. The change of effective capillary radius during swelling, the swelled capillary radius and the volumetric swelling can be taken into account by modelling the liquid capillary rise rate. As it can be seen from the obtained SEM pictures, biochar has non-uniform distribution of pores' diameter. Hence, mathematical model including composite parameter relating to flow tortuosity and the pore shape of the porous media was adopted to represent different pores' aperture forms in lignocellulosic biochar. The experimental results showed distinguished features between biochar's initial feedstocks (pine wood, hems, birch bark) and its fractions (fine, medium and coarse). It was shown that higher volumetric swelling (5%), porosity (86%), wettability (contact angle of 65°) and average pore radius ($1.48 \cdot 10^{-5}$ m) of biochar is more favourable for the higher capillary rise height at the fixed time. As the radius of the pores available for capillary rise increased, the rate of capillary rise increased too. Comparing different fractions, fine fraction ($< 300 \mu\text{m}$) of pine wood biochar showed the highest capillary rise rate compared to medium and coarse fractions. The proposed model was validated for the short-term (8 h) behaviour of capillary rise of liquid. However, the model was not suitable for the long-term (24 h) behaviour. Comparing results obtained by fitting experimental data showed that generalized expression can be used not only for water but also for many other liquids in natural and artificial porous material.

This preliminary study aimed at representing study in environmental engineering to study the interactions between biochar and water. These interactions are important not only in soil but also in environmental technologies (e.g. biofilters). Modified model can save not only the cost of expensive experimentation but also time and effort. The proposed model may be further developed by including gravity (hydrostatic pressure) for the modelling of liquid rise in swelling material for longer times. More capillary rise tests on different types of biochar would be very beneficial. Some other factors affecting capillary rise height such as temperature need further investigations.

Author Contribution Both authors have contributed equally to the work.

Availability of Data and Material Due to the nature of this research, participants of this study did not agree for their data to be shared publicly, so supporting data is not available.

Declarations

Conflict of Interest The authors declare no competing interests.

References

- Masoodi, R., & Pillai, K. M. (2010). Darcy's law-based model for wicking in paper-like swelling porous media. *AICHE Journal*, 56(9), 2257–2267. <https://doi.org/10.1002/aic.12163>
- Cai, J., Hu, X., Standnes, D. C., & You, L. (2012). An analytical model for spontaneous imbibition in fractal porous media including gravity. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 414, 228–233.
- Washburn, E. W. (1921). The dynamics of capillary flow. *Physics Review*, 17(3), 273–283.
- Cai, J., Yu, B., Zou, M., & Luo, L. (2010). Fractal characterization of spontaneous co-current imbibition in porous media. *Energy & Fuels*, 24, 1860–1867.
- Cai, J., Perfect, E., Cheng, C. -L., & Hu, X. (2014). Generalized modeling of spontaneous imbibition based on Hagen-Poiseuille flow in tortuous capillaries with variably shaped apertures. *Langmuir*, 30(18), 5142–5151.
- Siddique, J. I., & Kara, A. (2016). Capillary rise of magnetohydrodynamics liquid into deformable porous material. *Journal of Applied Fluid Mechanics*, 9(6), 2837–2843.
- Masoodi, R., & Pillai, K. M. (2013). *Wicking in porous materials* (p. 2). Traditional and modern modeling approaches: CRC Press.
- Ima, C. S., & Mann, D. D. (2011). Hygroscopic expansion of biofilter media consisting of woodchips. *Australian Journal of Agricultural Engineering*, 2(1), 5–7.
- Dorado, A. D., Lafuente, F. J., Gabriel, D., & Gamisans, X. (2010). A comparative study based on physical characteristics of suitable packing materials in biofiltration. *Environmental Technology*, 31(2), 193–204.
- Mochado, D. R., Hasson, D., & Semiat, R. (1999). Effect of solvent properties on permeate flow through nanofiltration membranes. Part I: Investigation of parameters affecting solvent flux. *Journal of Membrane Science*, 163, 93–102.
- Fu, Z., Guo, Z., Yuan, Z., & Wang, Z. (2007). Swelling and shrinkage behavior of raw and processed coals during pyrolysis. *Fuel*, 86, 418–425.
- Xie, K. C. (2015). Coal swelling. In: *Structure and Reactivity of Coal: A Survey of Selected Chinese Coals*, 305–335.
- Lucas, R. (1918). Ueber das Zeitgesetz des Kapillaren Aufstiegs von Flüssigkeiten. *Kolloid-Z*, 23, 15–22.
- Tsunawaza, Y., Yokoyama, T., & Nishiyama, N. (2016). An experimental study on the rate and mechanism of capillary rise in sandstone. *Progress in Earth and Planetary Science*, 3(8), 1–10.
- Shi, S., & Gardner, D. J. (2000). A new model to determine contact angles on swelling polymer particles by the column wicking method. *Journal of Adhesion Science and Technology*, 14(2), 301–314.
- Markl, D., Yassin, S., Wilson, D. I., Goodwin, D. J., Anderson, A., & Zeitler, J. A. (2017). Mathematical modelling of liquid transport in swelling pharmaceutical immediate release tablets. *International Journal of Pharmaceutics*, 526, 1–10.
- Ha, J., Kim, J., Jung, Y., Yun, G., Kim, D. -N., Kim, H. -Y. (2018). Poro-elasto-capillary wicking of cellulose sponges. *Science Advances*, 4(3). <https://doi.org/10.1016/B978-012369522-2/50012-9>

18. Komkiene, J., & Baltreinaite, E. (2015). Biochar as adsorbent for removal of heavy metal ions [Cadmium(II), Copper(II), Lead(II), Zinc(II)] from aqueous phase. *International Journal of Environmental Science and Technology*, 13, 471–482. <https://doi.org/10.1007/s13762-015-0873-3>
19. Katyal, A., & Morisson, R. D. (2007). Forensic applications of contaminant transport models in the subsurface. In: *Introduction to Environmental Forensics*, Second Edition 513–575.
20. Peng, J., & Wan, A. (1998). Effect of ionic strength on Henry's constants of volatile organic compound. *Chemosphere*, 36(13), 2731–2741.
21. Baltrėnas, P., Baltrėnaitė, E., & Spudulis, E. (2015). Biochar from pine and birch morphology and pore structure change by treatment in biofilter. *Water, Air and Soil Pollution*, 226(3), 1–14.
22. Liu, Q., Yasufuku, N., Miao, J., & Ren, J. (2014). An approach for quick estimation of maximum height of capillary rise. *Soils and Foundations*, 54(6), 1241–1245.
23. Shang, J., Flury, M., Harsh, J. B., & Zollars, R. L. (2008). Comparison of different methods to measure contact angles of soil colloids. *Journal of Colloid and Interface Science*, 328(2), 299–307.
24. Jeffery, S., Meinders, M. B. J., Stoof, C. R., Bezemer, T. M., van de Voorde, T. F. J., Mommer, L., & van Groenigen, J. W. (2015). Biochar application does not improve the soil hydrological function of a sandy soil. *Geoderma*, 251–252, 47–54.
25. Giffin, S., Littke, R., Klaver, J., & Urai, J. L. (2013). Application of BIB-SEM technology to characterize macropore morphology in coal. *International Journal of Coal Geology*, 114, 85–95.
26. Sienkiewicz, A., Krasucka, P., Charnas, B., Stefaniak, W., & Goworek, J. (2017). Swelling effects in cross-linked polymers by thermogravimetry. *Journal of Thermal Analysis and Calorimetry*, 130, 85–93.
27. Okechukwu, I. K. (2019). Determination of contact angle measurement of sub-bituminous and bituminous coal particles through capillary rise method using washburn equation for surface free energy and interfacial energy. *International Journal of Advances Engineering and Technology*, 3(2), 58–62.
28. Vinš, V., Hruby, J., Hykl, J., Blaha, J., & Šmid, B. (2013). Design of an experimental apparatus for measurement of the surface tension of metastable fluids. *EPJ Web of Conferences*, 45, 5.
29. A & D 2005. GX-13 Instruction Manual. Retrieved from https://www.aandd.jp/products/manual/manual_balances.html
30. Wangler, J., & Kohlus, R. (2017). Dynamics of capillary wetting of biopolymer powders. *Chemical Engineering Technology*, 40(9), 1552–1560.
31. Nagy, E., & Deak, A. J. (2013). Investigation of water capillary rise in soil columns made from clay mineral mixtures pretreated with cationic surfactants. *Communications in Soil Science and Plant Analysis*, 44(1–4), 749–757.
32. Yang, W., Shang, J., Baoguo, L., & Flury, M. (2019). Surface and colloid properties of biochar and implications for transport in porous media. *Critical Reviews in Environmental Science and Technology*, 50(23), 2484–2522. <https://doi.org/10.1080/10643389.2019.1699381>
33. Lou, K., Rajapaksha, A. U., Ok, Y. S., & Chang, S. X. (2016). Pyrolysis temperature and steam activation effects on sorption of phosphate on pine sawdust biochars in aqueous solutions. *Chemical Speciation and Bioavailability*, 28(1–4), 42–50. <https://doi.org/10.1080/09542299.2016.1165080>
34. Li, K. W., & Horne, R. N. (2004). An analytical scaling method for spontaneous imbibition in gas-water-rock systems. *SPE Journal*, 9, 322–329.
35. Huber, P., Gruner, S., Schafer, C., Knorr, K., & Kityk, A. V. (2007). Rheology of liquids in nanopores: A study on the capillary rise of water, n-Hexadecane and n-Tetracosane in mesoporous silica. *The European Physical Journal Special Topics*, 141, 101–105.
36. Pezron, I., Bourgain, G., & Quere, D. (1995). Imbibition of a fabric. *Journal of Colloid and Interface Science*, 173, 319–327.
37. Fries, N., & Dreyer, M. (2008). An analytical solution of capillary rise restrained by gravity. *Colloid and Interface Science*, 320, 259–263.
38. Barry, D. A., Parlange, J. Y., Sander, M., & Sivaplan, M. (1993). A class of exact-solutions for Richards equation. *Journal of Hydrology*, 142, 29–46.
39. Zeng, J., Lin, L., Tang, Y., Sun, Y., & Yuan, W. (2017). Fabrication and capillary characterization of micro-grooved wicks with reentrant cavity array. *International Journal of Heat and Mass Transfer*, 104, 918–929.
40. Li, Y., Zhang, C., Chen, C., Chen, H. (2018). Calculation of capillary rise of soils by SWCC model. *Advances in Civil Engineering*, 10. <https://doi.org/10.1155/2018/5190354>
41. Jaine, J. E., & Mucalo, M. R. (2015). Measurements of the wettability of catalyst support materials using the Washburn capillary rise technique. *Powder Technology*, 276, 123–128.
42. Brewer, C. E., Chuang, V. J., Masiello, C. A., Gonnermann, H., Gao, X., Dugan, B., Driver, L. E., Panzacchi, P., Zygourakis, K., & Davies, C. A. (2014). New approaches to measuring biochar density and porosity. *Biomass and Bioenergy*, 66, 176–185.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.