A Review on Biochar as Catalyst/Catalyst Support for

Oxidation/Reduction/Redox Reactions

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Abstract. Biochar is a low-cost carbon material derived from the thermal or chemical treatment of biomass. Due to its chemical structure, biochar has a high surface area and functional groups can be attached to its surface using some activation methods. This property makes it versatile to use as catalyst /catalyst support for various chemical reactions. The carbonaceous material derived from biomass is environment friendly and cost-effective as compared to existing heterogeneous catalyst. The hydrophobicity, tunable surface properties, thermal stability, and chemically inert nature make

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biochar suitable for catalyst support at extreme operating conditions.This paper focuses on the different methods for the preparation of biochar for heterogeneous chemical reactions. In this paper, the production of pyrochar and hydrochar is discussed, and its activation and/or functionalization methods are also included. Subsequently, the application of biochar-based catalysts in the various heterogeneous catalytic reaction are discussed.

Keywords: Biochar, Catalyst support, Pyrolysis, Hydrochar, Pyrochar.

1. Introduction

Biochar is the carbon-rich material derived from biomass such as wood, manure, and other carbon-rich solid materials by the thermal decomposition under a limited supply of oxygen and at relatively low temperature (< 700°C)[1]. At present, biochar is utilized as process fuel, material for soil amendment, and carbon sequestration [2-4]. The surface properties of biochar can be modified by using thermal/chemical treatment. Therefore, biochar can be utilized for the development of a variety of catalysts and catalyst supports. To disperse the active components uniformly without sintering, a well-developed pore structure and high surface area are necessary. The original biochar has a low density of pores, an activation process is needed before using as catalyst support[5]. After activating or functionalizing, the biochar shows properties, such as large surface area, multi-scale porous structure, and abundant surface functional groups.

Because of the high potential of catalytic biomass upgrading,this review is completely devoted to discussing the various applications of biochar as catalysts for biomass upgrading, including biocharbased solid acids for biomass hydrolysis and dehydration,biochar-based catalysts for biodiesel production, and biocharsas catalyst support for biomass pyrolysis, gasification, and bio-oil upgrading. Considering the fact that the formation, activation, andfunctionalization of biochar have been widely reviewedbymany researchers, these research topics are brieflydiscussed here.
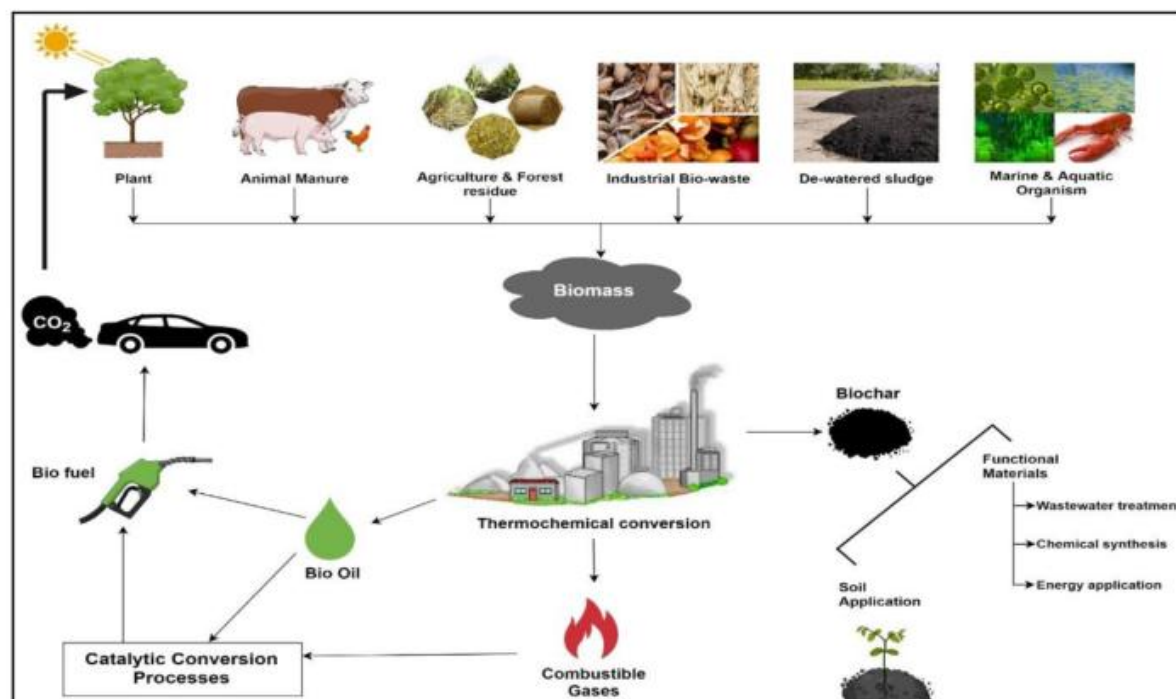
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Fig 1. Production and application of biochar (Ref:Chemical Engineering Journal 394 (2020) 124856)

2. Catalyst support preparation

Biochar can be produced using different carbonization processes, such as pyrolysis, gasification, hydrothermal carbonization, and torrefaction. Lignocellulosic composition of biomass includes cellulose (38–50%), hemicelluloses (23–32%), lignin (15–25%), and small amounts of extractives[6]. The structural differences of cellulose, hemicelluloses, and lignin, changes the biochar yield, degradation rate, degradation mechanism. This section focuses on explaining the degradation of biomassin the pyrolysis and hydrothermal carbonization processes, and further discussing the formation pathways of pyrochar and hydrochar.

The pathways for the formation of biochars (pyrochar and hydrochar) vary significantly according to the reaction medium[7]. Numerous reactions will be taking place during biomass pyrolysis, in which the free radical reaction is one of the most important ones [8,9]. These radicals, being very active, further react with other compounds or radicals through free-radical substitution, free-radical addition, carbon-carbon coupling, etc., and thus result in the formation of syngas, bio-

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oils, and biochars. Some important intermediates and/or product, such as retroaldol products (hydroxyacetaldehyde, pyruvaldehyde, etc.), dehydrated species (furfural, 5-hydroxymethyl furfural, etc.), anhydromonosaccharides (levoglucosan, levoglucosenone, etc.), and phenolic compounds (4-vinylguaiacol, eugenol, etc.) have alsobeen found among the volatile products of biomass pyrolysis. This indicates that the reactions, like retroaldol condensation,dehydration, isomerization, etc., also occur during the pyrolysisprocess[10-14].Thus,the product mixture observed is very complex in nature[11,8,13,15].However, the morphology and the microstructure of the biomass are not changed over the pyrolysis[16].Figure 2 shows the possible formation pathway of biochar. During the pyrolysis process, the volatile products are released from the biomass leaves carbonaceous pyrochar material.

Comparing with pyrolysis, ionic reactions are conducted in anaqueous medium. The depolymerization of cellulose,hemicelluloses, and lignin occurs at relatively low temperaturesunder hydrothermal conditions [7,17,18]. Unlike pyrochar, thehydrochar obtained through a different pathway resulting in the formation of abundant functional groups, such as hydroxyl and carboxylgroups. The formation pathway of hydrochar is illustratedin Fig. 3.During the hydrothermal carbonization process, celluloseand hemicelluloses are initially hydrolyzed into oligosaccharides and monosaccharides through the breakage of theirglycosidic bonds in hot compressed water. These water-solubleoligo and monosaccharides are further degradedinto small molecule compounds, such as 5-hydroxymethylfurfural (HMF), furfural (FF), acetic acid, etc., at relatively mildconditions or decomposed into syngas at more severe conditions. Meanwhile, the ether linkages of lignin (mainly b-O-4 anda-O-4 linkages) are also unstable under hydrothermal conditions, and a large amount of lignin is converted into variouswater-soluble phenolic compounds when the lignocellulosicmaterial is hydrothermally treated at 240^0C [19]. However, mostcarbon-carbon bonds in lignin (mainly b-b, b-5, b-1, and 5-5linkages) are more stable than oligo and monosaccharides, and they are leftas "aggregated hydrochars"[20].The furan compounds(FF and HMF), derived from hemicelluloses and

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cellulose, then react with the soluble phenolic compounds derived from lignin, forming "dispersed hydrochars" through polymerization[21].The "dispersed hydrochar" surface which contains reactive oxygen-containing groups further reacts with the"aggregated hydrochars" and covers the surface of the "aggregated hydrochars", resulting in a hydrochar with lowspecific surface area and poor porosity[21,22].
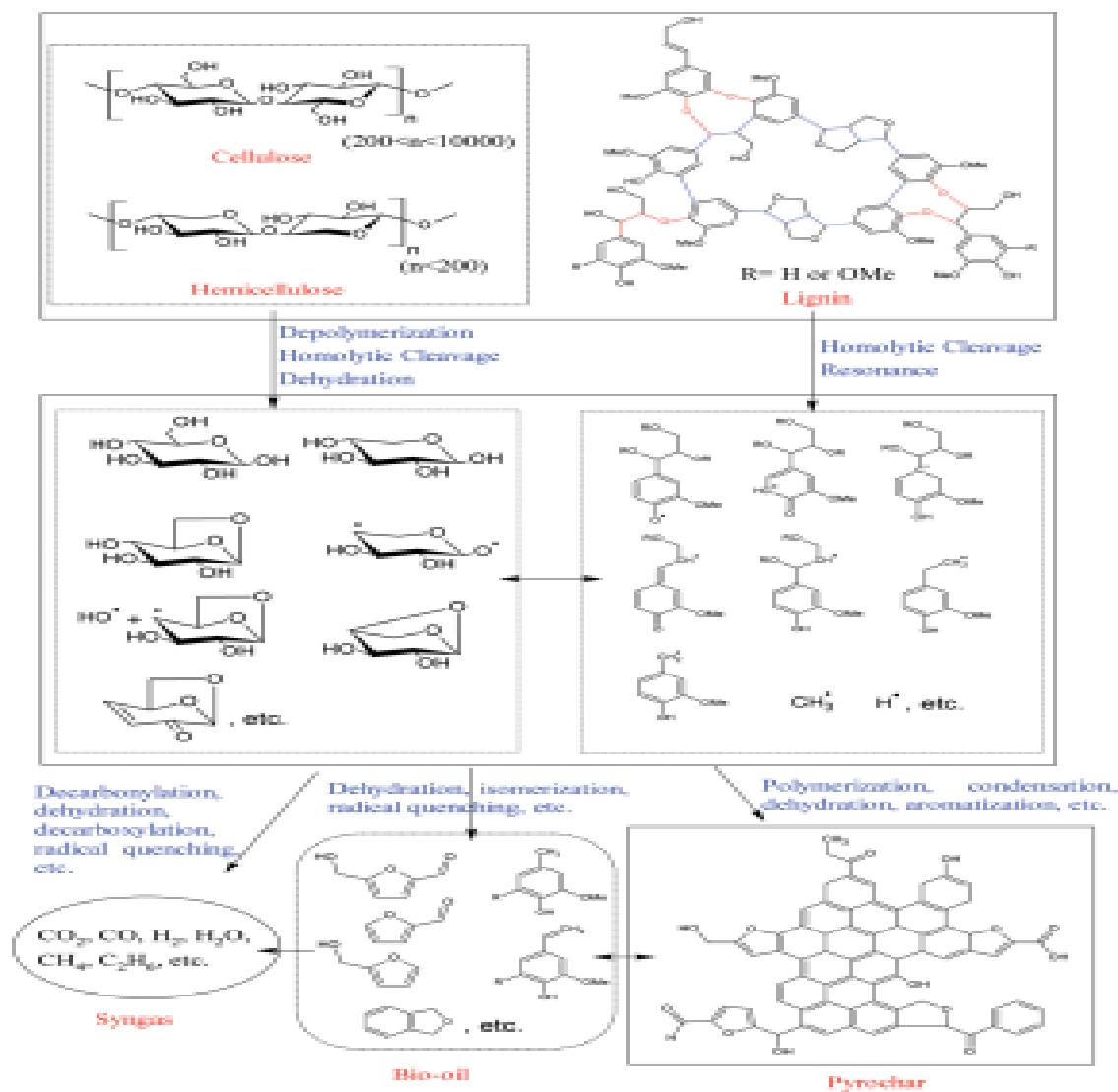

Fig 2. Formation pathway of pyrochar (Ref. RSC Adv., 2017, 7, 48793–48805)

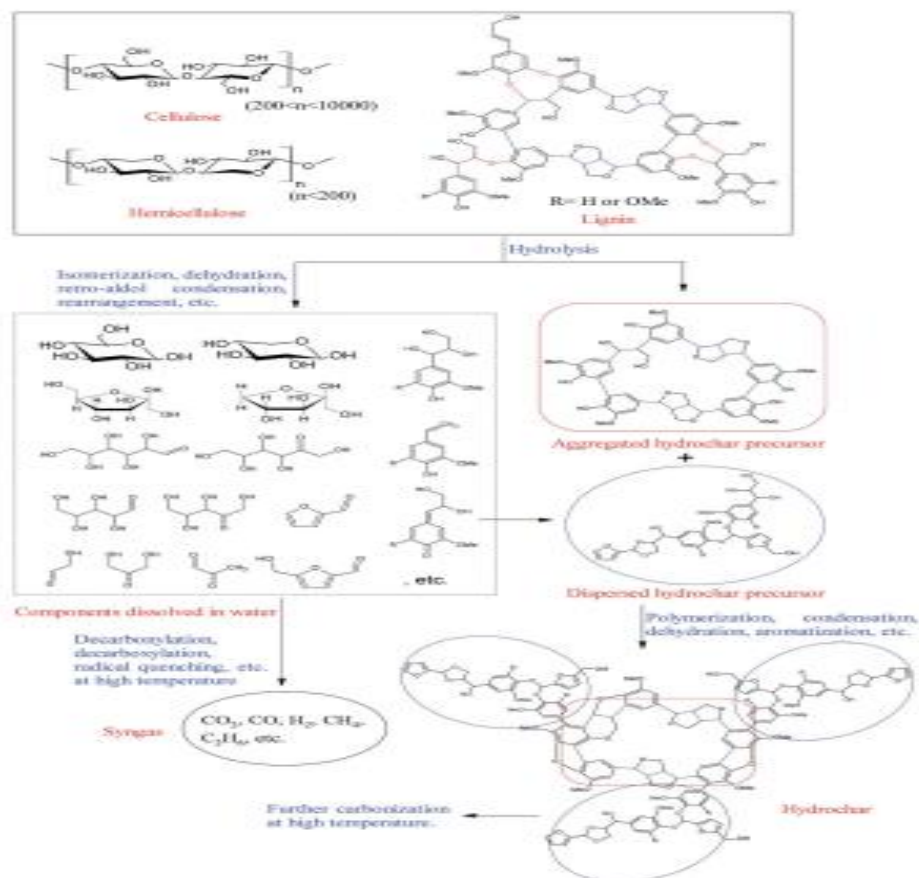*Eur. Chem. Bull. 2023,12(4), 3255-3279*

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Fig 3. Formation pathway of hydrochar (Ref. RSC Adv., 2017, 7, 48793–48805)

Various approaches have been developed for biochar production from different feedstocks. Among these, torrefaction, pyrolysis, gasification, hydrothermal carbonization (HTC), and flash carbonization are thermochemical conversion technologies discussed here.

2.1 Torrefaction

Torrefaction is a mild preheat treatment before pyrolysis or gasification. The treatment temperature varies from 200–300 °C with a slow heating rate and short retention time.[119]. The solid product obtained from torrefaction will be carbon enriched, porous, high energy density, low dense, low O/C ratio, more easily grindable, low moisture content, easily stored and transported[22,23]. The variables that are affecting the yield of carbon content include temperature, retention time, raw material, and furnace types[23]. For example, at 200 °C beechlignin initiated a transformation, while

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the majority of biomass started their transformationfrom 230 °C while cellulose only degraded above 270 °C [22]. Solid yields of more than 77 wt% were found for hardwood and switchgrass pellets[24]. Torrefaction of oil palm fiber pellets at a temperature range from 275–350 °C in inert and oxidative atmospheres produced 43 and 65% biochar respectively[25].

2.2 Pyrolysis

Pyrolysis is the decomposition of biomass at 300–1200 °C in the absence (or limited) of oxygen produces pyrochar. Biochar production can be favored at temperatures between 300–700 °C. The pyrolysis can be divided into slow, fast, intermediate, flash, and vacuum pyrolysis [26-29].

2.2.1 Slow pyrolysis

*S*low pyrolysis employs low operating temperatures(400-650°C), slow heating rate(~5-10 °C min-1), high vapor residence time (5-60 min), and long holding times(hours to days) [30-34]. The yield from the pyrolysis setup ranges from 20 to 40% and decreases with increasing pyrolysis temperature and heating rate [30-36]. The properties of biochar can also depend upon the properties of feedstock.Biochars produced frombagasse and wood stem showed various pore size and large Surface area as compared to the biochar produced from cocopeat, paddy straw, and palm kernel shell. The SBETand pore structures of biochar are found to be sufficiently developed at around 500 °C[37] with high thermal stability and a wide range of mineral composition [38].

2.2.2. Fast pyrolysis

Fast pyrolysis employs rapid, high-temperature treatment of biomass in the absence of oxygen [39]. In order to increase heat transfer and conversion, the biomass drying and grinding is necessary[27,40]. Fast pyrolysis gives high yield of bio-oil instead of biochar(15-25wt%)[27,30]. The fast pyrolysis of biochar produced from wheat straw contains an un-pyrolyzed carbohydrate fraction (8.8%) but completely carbonized in the slow pyrolysis process[40]. The two pyrolysis

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methods resulted in different characteristics of biochar including pH, particle size, and surface area, by the formation of highly ordered aromatics at 400 °C and increased surface area at 500 °C (175.4 m^2 g-1) compared to 300 °C (2.9 m^2 g-1) and 400 °C (4.8 m^2 g-1)[41,42].

2.2.3. Intermediate pyrolysis

Intermediate pyrolysis operates at the condition between slow and fast pyrolysis. Operating temperature up to 500 °C, residence times of 0.5-25 min vapor residence times of 2–4 s, yields 15–35 wt% of dry and brittle biochar[43-46]. Biochar produced from a pilot plant that uses wood and barley straw pellets yielded 30 wt% char containing 75 wt% carbon [47].Organic fractions of municipal solid waste under intermediate pyrolysis yielded 51.7 wt% char because of the presence of inert fractions in the biomass[48].

2.2.4 Other methods

Other methods of pyrolysis include flash and vacuum pyrolysis. During the flash pyrolysis, the temperature is raised to 1000 °C at a heating rate of 1000 °C s-1 for less than 1s, gives high bio-oil yield, and low char production [28, 49-50]. Vacuum pyrolysis is conducted at a process condition the same as that of slow pyrolysis except the pressure is reduced to 10-100kPa. The bio-oil yield is more for vacuum pyrolysis as compared to flash pyrolysis[51]. On vacuum pyrolysis of South African sugarcane bagasse, yielded only 18.1wt% char which was found to be a good adsorbent with surface area (418 m^2g-1) and ion exchange capacity (122 $cmol_c$ kg-1)[51-52].

2.2.5 Gasification

Gasification converts carbonaceous materials into syngas, tars, and char at around a temperature of 800°C in the presence of active gaseous like oxygen, nitrogen, air, CO_2, steam, or other gas mixture medium (e.g. oxygen, nitrogen, air, carbon dioxide, steam or gas mixture) [28]. Gasification involves drying, pyrolysis, partial oxidation, and reduction. The yield of char is only 5–10 wt% of the

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feedstock

mass[53,54]. The process can be scaled up to large capacity, thus producing several tons of biochar per day as a co-product[55]. In comparison with the biochar produced by pyrolysis, gasification char usually has small particle size[54], low surface area, and pore volumes[56]. Char from gasification is low in carbon content (20–60 wt%), but because of the condensation of aromatic rings enables strong resistance to chemical oxidation and microbial mineralization though it has limited surface chemistry[53-57]. A two-stage process combining both pyrolysis and gasification of straw and wood in separate reactors at around 730 °C produces chars of high porosity and Surface area, can be used as an additive for soil remediation[57].

2.2.6 Hydrothermal carbonization

Hydrothermal carbonization (HTC) is another approach toprocess biomass to yield biochar. The feedstock is heated at 200–300 °C in a closed vessel, under the pressure of 2–10 MPa with the presence of liquid water, yields hydrochar [58,59]. At a temperature of 300 °C, it is possible to produce the hydrochar with better thermal stability. Hydrothermal carbonisation is also termed as wet torrefaction[60] or wet pyrolysis [61], which produces the biochar with smaller pore volume and low ash and carbon content[62].

2.2.7 Flash carbonization

The Flash carbonization process produces biocarbon (i.e. charcoal) via an ignition and controlled flash fire at the high temperature inside a packed bed at a pressure of 1MPa frombiomass quickly and efficiently [63-65]. The combustion flame moves in opposite to that of the airflow, transforming the biomass into gas and charcoal in less than30 min. Typically, the charcoal yield was found to be around 40 wt%.
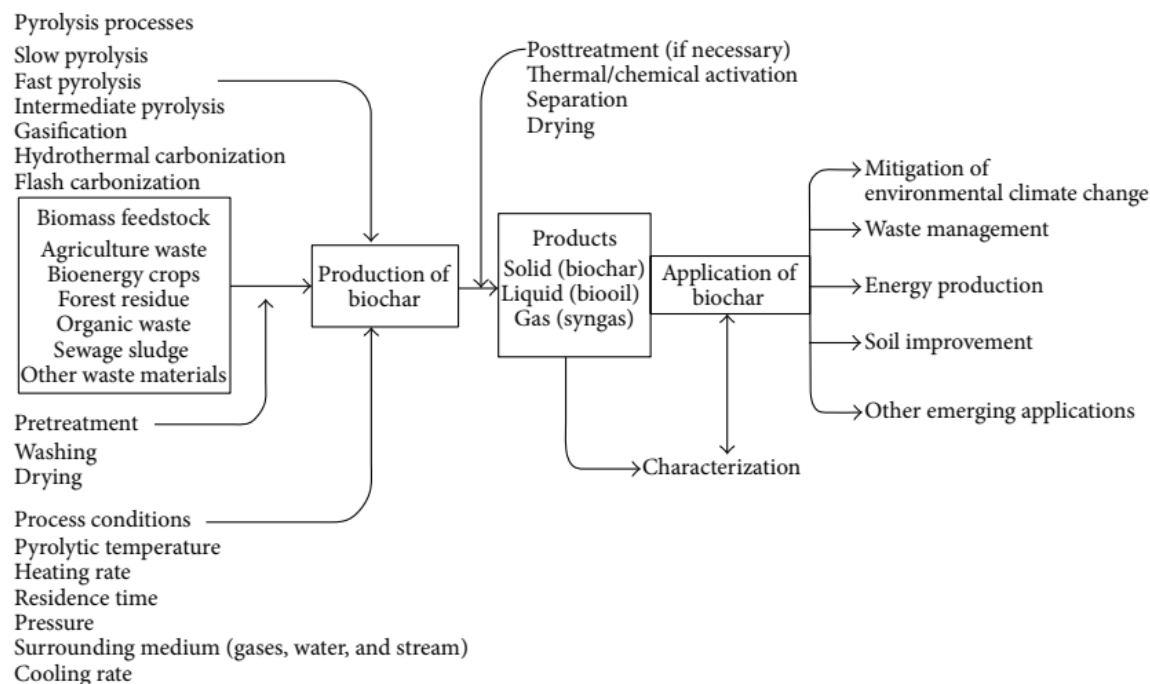
Fig3.Production and application of biochar (Advances in Materials Science and Engineering

Volume 2014)

3. Activation and functionalization of supported catalysts

Activation of biochar is done to increase the specific surface area and porosity prior to use as catalyst support. The improvement in specific surface area and porosity is due to the development and opening of internal porous structure[7,66]. Thus, activated biochar can be used in soil amendments, environmental adsorbents, carbon sequestration, and support for various catalytic reactions. Activated biochar provides more active sites, high active loading surface, high mass transfer capacities for catalytic reactions[12,67]. The activation methods can be broadly classified into three categories: impregnation methods to incorporate active components, physical activation, and chemical activation[68].

3.1 Physical activation

Physical activation is a process, where the prepared biochar is further exposed to a controlled flow of steam/CO_2 / mixture of steam and CO_2 at high temperatures (above 700 °C). At high temperatures, carbon atoms of the biochar are partially eroded via C–H_2O and/or C–CO_2 gasification reactions[26]. Most of the reactive carbon present in the carbonized material can be selectively removed and can open the enclosed pores during the physical activation[12]. Thus, it is possible to get improved specific surface area and well-developed pore structure(micropores with a low contribution of mesopores) as a result of physical activation[12,69,70]. The choice of feedstock, activating gas, and reaction conditions have a significant effect on porosity, pore size distribution, and specific surface area of the activated biochar[26]. Adsorptive properties of the steam activated biochars produced from fast pyrolysis of several substrates for metal ion uptake are studied [71].The surface area and micropore volume of biochars improved from 4m2/g to 136-793m2/g, when on activation at 800°C for 45 min. Thus the metal ion adsorption was also improved as a result of improved surface area and porosity[71]. Activation of biochars produced from the slow pyrolysis of willow using steam and carbon dioxide significantly improved the surface area and porosity of the biochar [72]. It was found that the surface area of steam activated carbon(840.6 m^2 g-1) is greater than that of CO_2-activated biochar (512 m^2 g-1) [72]. In contrast, the biochars activated using CO_2 of coffee endocarp showed the higher surface area and pore volumes than the corresponding steam activated biochars. The conclusion was made that the contradiction is because of the change in microstructures of the feed stock[73].

3.2 Chemical activation

The prepared biochar is first impregnated in a solution containing activation agents like KOH, $ZnCl_2$, K_2CO_3, H_2SO_4, H_3PO_4, etc followed by heating at elevated temperatures under an inert gas flow [26,36,74,12,75,76]. These chemicals remove the partial carbon atoms and volatile matter from the biochar, suppress the tar formation, and thus develop the pores of the biochar matrix [12,77].

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The activation efficiency of chemical activation is always higher than physical activation which produces high porosity and surface area at low operating temperatures [60]. It is necessary to wash the biochar after chemical activation to remove the impregnating agents and its salts[78,79]. Since the chemical activation also aggravates equipment corrosion and creates secondary pollution, affects the application of chemical activation[60]. The activation temperature, activating agent, type of feed also affect the porosity, pore size, and specific surface area of the activated char[26,80]. It was found that short activation time and low activation temperature increases chemical activation. But, high usage of chemicals, equipment corrosion, and risk in wastewater treatment limit the application of chemical activation.

3.3 Impregnation

The impregnation method was used to incorporate the active metallic component to the biochar matrix by mixing the feedstocks with the metal precursors. This produces active interfaces and binding sites[81-87]. Iron incorporated biochar produced from ligninmagnetite pellet at 900°C is used for the adsorption and degradation of trichloroethylene [81].A rice straw-derived biochar-Co_3O_4 composite has been prepared by impregnating the biochar with $Co(NO_3)_2$, followed by hydrothermal treatment and calcinations[83]. The composite showed higher surface area (62.7 m^2 g-1) and total pore volume (0.207 cm^3 g-1) than those of pristine biochar (43.0 m^2 g-1, 0.081 cm^3 g-1) and Co_3O_4 (37.0 m^2 g-1, 0.184 cm^3 g-1). The adhesion of the metallic species was highly influenced by the nature of the biomass used.

4. Biochar based catalytic reactions-Oxidation/Reduction/Redox reactions

The high surface area and pore volume make the biochar suitable for catalyst support and even as a catalyst for many chemical reactions. Oxidation/reduction reactions are the major reactions at which the catalyst supports (metal oxide supports) are being replaced by the carbonaceous material derived

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from biomass. Also in the removal of heavy metals from the wastewater/drinking water, the biochar found to be very useful as it has a high surface area and pore volume. The following paragraph deals with some oxidation/reduction reaction at which biochar is used in place of metal oxide catalysts and for the abatement of environmental pollutants from the water resources.

For oxidation/reduction/redox reactions, several methods have been developed to activate the carbon lattice and improve their oxidation resistance. The addition of some compounds can be used to tune the catalytic activity and recoverability. Metal species wrapped in heteroatom-doped graphitic carbon layers were used to boost the reactivity, at temperatures $\geq$ 700 °C. This entangles the meaningful comparison of biochar reactivity and the modes of interaction in redox conversions over highly graphitic pyrogenic carbons [88,89]. By modifying the textural, chemical, and electronic states enables it a more resilient photo, electro, and chemocatalyst and can be used as metal-free carbocatalysis [90].Biochar derived from poultry litter and wastewater biosolids reduced the hydrophobic dinitro herbicides (pendimethalin and trifluralin) and explosives (2,4/dinitrotoluene and hexahydro/1,3,5/trinitro/1,3,5/triazine) completely. Because of low surface area, the biochar quickly adsorbed 28% of pendimethalin while up to 95% of the herbicide was reduced after 2 h and 62% of Trifluralin. The redox of explosive substances significantly improved in the presence of biochars bearing graphene-like structures. The biochar produced through very ill-defined carbonization made it thermallyunstable and vulnerable to harsh oxidative environments. Highly graphitised biochar is more electrochemically positive and thus greater redox reactivity than nongraphitised biochar[91].Incorporating different components, biochar exhibits mixed behaviors. The derived biochars from Polyacrylamide and polyferricsulfate-flocculated sludge with iron-heteroatom-carbon interfaces highly active for tetracycline degradation[92]. Oak wood-derived char has been found to be the main facilitator in the dechlorination of 1,1-trichloro-2,2-di(4-chlorophenyl)ethane and its various metabolites[93].

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The behavior of two types of modified biochar (functional and iron composite biochars) as a catalyst derived from pyrolysis of Cladophora glomerata (C. glomerata) macroalgae. Two catalytic pyrolysis experiments were conducted in a 25 mL slow pyrolysis reactor in the presence of biochar-based catalysts at the temperature of 500 ◦C. For activated functional biochar, no clear effect on biogas production was observed, whereas iron composite biochar increased the hydrogen content by 7.99 mml/g algae. Iron composite biochar showed remarkable catalytic behaviors (especially toward hydrogen production) due to its wonderful surface area, high dispersion of iron particles and particular structures and compositions. Thus this process provided a promising path for the low-cost, efficient, renewable and environmental friendly catalysts[94].

Biochar (BC), produced by fast pyrolysis of rice husk, was activatedby chemical and physical processes. The activated biochar (ABC) showed graphite-like morphology and had a large number of pores with a high surfacearea of 1058 m^2/g. The biochar produced through fast pyrolysis is used as catalyst support for Ru metal for syngas methanation. Thecatalytic performance of the Ru/ABC catalyst in methanation was superior orcomparable to the conventional activated carbon (AC) supported Ru catalyst. High CH_4 selectivity of 98% and a CO conversion of 100% were obtained underthe proper reaction conditions over the Ru/ABC catalyst[95].

Carbon nanoparticles have provided new solutions for the removal of various environmental contaminants. In this paper,two carbon nanomaterial–biochar nanocomposites (SG–PySA–CNT and SG–PySA–GO) were derived from sweetgum biomass pretreated with carbon nanotubes (CNTs) and graphene oxide (GO) through slow pyrolysis at 600 ◦C. Both SG–PySA–CNT and SG–PySA–GO had higher surface area but much lower pore volume than the pristine biochar (SG). Batch sorption experimental results showed that SG– PySA–CNT and SG–PySA–GO had greater sorption ability to Pb(II) and Cd(II) from an aqueous solution than SG. SG–PySA–GO was the best sorbent with maximum sorption capacities higher than 40 and 10 mg g1 for Pb(II) and Cd(II), respectively. The enhanced metal sorption by the biochar nanocomposites is because of theexcellent sorptive

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properties of the carbon nanoparticles distributed and stabilized on the biochar surfaces within the matrix.Because of its facile synthesis and good sorptive properties, biocharsupported CNT and GO nanocomposites have great potential to beused in various environmental applications for the removal of metaland metalloid contaminants[96].

5. Conclusion

Different methods for the preparation of biomass derived carbon catalyst supports and catalysis applications have been reviewed in this article. Direct hydrothermal carbonization (HTC) of biomass-derived precursors can result in porous structured carbons with different oxygen functionalities that facilitate the anchoring of active catalysts on their surface. The structure-directing the role of templates in making porous carbons with high surface area and tunable porosity is discussed with suitable examples. Active metal catalysts supported on porous carbon performed several organic reactions including hydrogenation, oxidation, methanation, etc. Carbon-based catalysts for environmental applications have become a research hot-spot in recent years, owing to their low cost, simple synthesis method, and environmentally safe nature. Considering that biomass is a renewable, highly abundant, and low-cost precursor, the direct preparation of carbonaceous materials from biomass would have a potential advantage. Under a controlled pyrolysis process, the inbuilt ordered porous structure of natural raw biomass can retain their textural properties in the final carbon materials which are highly demanding in various potential technological applications. Some of these functionalized carbonaceous materials have been already demonstrated in a wide range of advanced catalytic applications. Apart from the proper selection of biomass precursors, the preparation method is also an important factor to achieve carbon materials with excellent physicochemical properties. Consequently, more efforts have to be given on the development of greener synthetic protocols to design biomass-derived carbon materials with required features for their catalysis-related applications of future relevance. These will include biomass conversion,

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photochemical processes, advanced electrocatalysis, aqueous chemistries (i.e. in organic synthesis and in biomass/waste valorization) as well as continuous flow processes. Various examples of catalytic applications of carbonaceous materials illustrate the potential of designer nanomaterials and (nano)composites for a wide range of applications in catalysis, which will serve the future of a more sustainable and benign-by-design preparation of nanocatalysts as a potential replacement of currentindustrial catalytic systems.

Conflicts of Interest

No conflicts of interest.

References

[1]   S.J.Lehmann, Biochar for Environmental Management , Earthscan, Oxford,UK,2009

[2]   Abdullah, H., K. A. Mediaswanti, and H. Wu. 2010. Biochar as a fuel: 2. Significant differences in fuel quality and ash properties of biochars from various biomass components of Mallee trees. Energy Fuels 24:1972–1979.

[3]   Kim, Y., and W. Parker. 2008. A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil. Bioresour. Technol. 99:1409–1416.

[4]   Bird, C. M., C. M. Wurster, P. H. Paula Silva, A. M. Bass, and de Nys R. 2011. Algal biochar – production and properties. Bioresour. Technol. 102: 1886–1891.

[5]   Azargohar, R. and A. K. Dalai 2006. Biochar as a precursor of activated carbon. Appl. Biochem. Biotechnol.131:762–773.

[6]   S. Du, J. A. Valla and G. M. Bollas, Green Chem., 2013, 15,3214–3229

[7]   H. S. Kambo and A. Dutta, Renewable Sustainable Energy Rev., 2015, 45, 359–378

[8]   A. Demirbas ¸, Energy Convers. Manage., 2000, 41, 633–646.

[9]   M. L. Poutsma, J. Anal. Appl. Pyrolysis, 2000, 54, 5–35.

[10] F. X. Collard and J. Blin, Renewable Sustainable Energy Rev., 2014, 38, 594–608

[11] P. R. Patwardhan, R. C. Brown and B. H. Shanks, Chemsuschem, 2011, 4, 636–643.

[12] W. J. Liu, H. Jiang and H. Q. Yu, Chem. Rev., 2015, 115,12251–12285.

[13] Y. C. Lin, J. Cho, G. A. Tompsett, P. R. Westmoreland and G. W. Huber, J. Phys. Chem. C, 2009, 113, 20097–20107.

[14]   D. K. Shen, S. Gu and A. V. Bridgwater, J. Anal. Appl.Pyrolysis, 2010, 87, 199–206

[15] Q. Liu, S. Wang, Y. Zheng, Z. Luo and K. Cen, J. Anal. Appl. Pyrolysis, 2008, 82, 170–177.

[16] Y. Zhang, S. Liu, X. Zheng, X. Wang, Y. Xu, H. Tang, F. Kang, Q.-H. Yang and J. Luo, Adv. Funct. Mater., 2017, 27, 1604687.

[17] D. Kim, K. Lee and K. Y. Park, J. Ind. Eng. Chem., 2016, 42, 95–100.

[18]   H. P. Yang, R. Yan, H. P. Chen, D. H. Lee and C. G. Zheng, Fuel, 2007, 86, 1781–1788.

[19] X. F. Cao, X. W. Peng, S. N. Sun, L. X. Zhong and R. C. Sun, J. Agric. Food Chem., 2014, 62, 12360–12365.

[20] S. Kang, X. Li, J. Fan and J. Chang, Ind. Eng. Chem. Res., 2012, 51, 9023–9031.

[21] J. Ryu, Y. W. Suh, D. J. Suh and D. J. Ahn, Carbon, 2010, 48, 1990–1998.

[22] T. Melkior, S. Jacob, G. Gerbaud, S. Hediger, L. Le Pape, L. Bonnefois, M. Bardet, NMR analysis of the transformation of wood constituents by torrefaction, Fuel 92 (2012) 271–280, https://doi.org/10.1016/J.FUEL.2011.06.042.

[23] W.-H. Chen, H.-C. Hsu, K.-M. Lu, W.-J. Lee, T.-C. Lin, Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass, Energy. 36 (2011) 3012–3021, https://doi.org/10.1016/J.ENERGY. 2011.02.045.

[24] A.A. Boateng, C.A. Mullen, Fast pyrolysis of biomass thermally pretreated by torrefaction, J. Anal. Appl. Pyrolysis. 100 (2013) 95–102, https://doi.org/10. 1016/J.JAAP.2012.12.002.

[25] W.-H. Chen, Y.-Q. Zhuang, S.-H. Liu, T.-T. Juang, C.-M. Tsai, Product characteristics from the torrefaction of oil palm fiber pellets in inert and oxidative atmospheres, Bioresour. Technol. 199

(2016) 367–374, https://doi.org/10.1016/J. BIORTECH.2015.08.066.

[26] J.S. Cha, S.H. Park, S.-C.C. Jung, C. Ryu, J.-K.K. Jeon, M.-C.C. Shin, Y.-K.K. Park, Production and utilization of biochar: a review, J. Ind. Eng. Chem. 40 (2016) 1–15, https://doi.org/10.1016/j.jiec.2016.06.002.

[27] A.V. Bridgwater, The production of biofuels and renewable chemicals by fast pyrolysis of biomass, Int. J. Glob. Energy Issues. 27 (2007) 160–203.

[28] M. Tripathi, J.N. Sahu, P. Ganesan, Effect of process parameters on production of biochar from biomass waste through pyrolysis: a review, Renew. Sustain. Energy Rev. 55 (2016) 467–481, https://doi.org/10.1016/J.RSER.2015.10.122.

[29] D. Angın, Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake, Bioresour. Technol. 128 (2013) 593–597, https://doi.org/10.1016/J.BIORTECH.2012.10.150.

[30] Y. Lee, P.-R.-B. Eum, C. Ryu, Y.-K. Park, J.-H. Jung, S. Hyun, Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1, Bioresour. Technol. 130 (2013) 345–350, https://doi.org/10.1016/J.BIORTECH.2012.12.012.

[31] D. Mohan, C.U. Pittman, P.H. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review, Energy Fuels 20 (2006) 848–889, https://doi.org/10.1021/ ef0502397.

[32] S. Chellappan, V. Nair, S. V, A. K, Experimental validation of biochar based green Bronsted acid catalysts for simultaneous esterification and transesterification in biodiesel production, Bioresour. Technol. Reports. 2 (2018) 38–44. doi:10.1016/j. biteb.2018.04.002.

[33] X. Xiong, I.K.M. Yu, S.S. Chen, D.C.W. Tsang, L. Cao, H. Song, E.E. Kwon, Y.S. Ok, S. Zhang, C.S. Poon, Sulfonated biochar as acid catalyst for sugar hydrolysis and dehydration, Catal. Today. 314 (2018) 52–61, https://doi.org/10.1016/j.cattod. 2018.02.034.

[34] S. Meyer, B. Glaser, P. Quicker, Technical, economical, and climate-related aspects of biochar production technologies: a literature review, Environ. Sci. Technol. 45(2011) 9473–9483,

Eur. Chem. Bull. 2023,12(4), 3255-3279

3272

https://doi.org/10.1021/es201792c.

[35] M.I. Al-Wabel, A. Al-Omran, A.H. El-Naggar, M. Nadeem, A.R.A. Usman, Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes, Bioresour. Technol. 131 (2013) 374–379, https://doi.org/10.1016/J.BIORTECH.2012.12.165

[36] D. Angın, Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake, Bioresour. Technol. 128 (2013) 593–597, https://doi.org/10.1016/J.BIORTECH.2012.10.150

[37] Y. Lee, J. Park, C. Ryu, K.S. Gang, W. Yang, Y.-K. Park, J. Jung, S. Hyun, Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 °C, Bioresour. Technol. 148 (2013) 196–201, https://doi.org/10.1016/J.BIORTECH.2013.08.135

[38] M. Waqas, A.S. Aburiazaiza, R. Miandad, M. Rehan, M.A. Barakat, A.S. Nizami, Development of biochar as fuel and catalyst in energy recovery technologies, J. Clean. Prod. 188 (2018) 477–488, https://doi.org/10.1016/j.jclepro.2018.04.017

[39] D. Mohan, C.U. Pittman, P.H. Steele, Pyrolysis of wood/biomass for bio-oil: ancritical review, Energy Fuels 20 (2006) 848–889, https://doi.org/10.1021/ ef0502397.

[40] E.W. Bruun, P. Ambus, H. Egsgaard, H. Hauggaard-Nielsen, Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics, Soil Biol. Biochem. 46 (2012) 73–79, https://doi.org/10.1016/J.SOILBIO.2011.11.019.

[41] E.W. Bruun, H. Hauggaard-Nielsen, N. Ibrahim, H. Egsgaard, P. Ambus P.A. Jensen, K. Dam-Johansen, Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil, Biomass Bioenergy 35 (2011) 1182–1189, https://doi.org/10.1016/J.BIOMBIOE.2010.12.008.

[42] K.H. Kim, J.-Y. Kim, T.-S. Cho, J.W. Choi, Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida),

Bioresour. Technol. 118 (2012) 158–162, https://doi.org/10.1016/J.BIORTECH.2012.04.094.

[43] M. Uchimiya, S. Hiradate, M.J. Antal, Dissolved phosphorus speciation of flash carbonization, slow pyrolysis, and fast pyrolysis biochars, ACS Sustain. Chem. Eng. 3 (2015) 1642–1649, https://doi.org/10.1021/acssuschemeng.5b00336 .

[44]   M. Uchimiya, S. Hiradate, M.J. Antal, Influence of carbonization methods on then aromaticity of pyrogenic dissolved organic carbon, Energy Fuels 29 (2015) 2503–2513, https://doi.org/10.1021/acs.energyfuels.5b00146.

[45] J.-H. Park, J.J. Wang, N. Tafti, R.D. Delaune, Removal of Eriochrome Black T by sulfate radical generated from Fe-impregnated biochar/persulfate in Fenton-like reaction, J. Ind. Eng. Chem. 71 (2019) 201–209, https://doi.org/10.1016/J.JIEC. 2018.11.026.

[46] S. Zhu, X. Huang, F. Ma, L. Wang, X. Duan, S. Wang, Catalytic removal of aqueous contaminants on N-doped graphitic biochars: inherent roles of adsorption and nonradical mechanisms, Environ. Sci. Technol. (2018), https://doi.org/10.1021/acs.est.8b01817.

[47] Y. Yang, J.G. Brammer, A.S.N. Mahmood, A. Hornung, Intermediate pyrolysis of biomass energy pellets for producing sustainable liquid, gaseous and solid fuels, Bioresour. Technol. 169 (2014) 794–799, https://doi.org/10.1016/J.BIORTECH. 2014.07.044.

[48] Y. Yang, Y. Zhang, E. Omairey, J. Cai, F. Gu, A.V. Bridgwater, Intermediate pyrolysis of organic fraction of municipal solid waste and rheological study of the pyrolysis oil for potential use as bio-bitumen, J. Clean. Prod. 187 (2018) 390–399, https://doi.org/10.1016/J.JCLEPRO.2018.03.205

[49] A.W. Palumbo, C.J. Bartel, J.C. Sorli, A.W. Weimer, Characterization of products derived from the high temperature flash pyrolysis of microalgae and rice hulls, Chem. Eng. Sci. 196 (2019) 527–537, https://doi.org/10.1016/J.CES.2018.11.029.

[50]   I. Aarum, H. Devle, D. Ekeberg, S.J. Horn, Y. Stenstrøm, The effect of flash pyrolysis temperature on compositional variability of pyrolyzates from birch lignin, J. Anal. Appl. Pyrolysis.

127 (2017) 211–222, https://doi.org/10.1016/J.JAAP.2017.08.003

[51] M. Carrier, T. Hugo, J. Gorgens, H. Knoetze, Comparison of slow and vacuum pyrolysis of sugar cane bagasse, J. Anal. Appl. Pyrolysis. 90 (2011) 18–26, https://doi.org/10.1016/J.JAAP.2010.10.001

[52] M. Carrier, A.G. Hardie, Ü. Uras, J. Görgens, J. (Hansie) Knoetze, Production of char from vacuum pyrolysis of South-African sugar cane bagasse and its characterization as activated carbon and biochar, J. Anal. Appl. Pyrolysis. 96 (2012) 24–32. doi:10.1016/J.JAAP.2012.02.016.

[53] S. You, Y.S. Ok, S.S. Chen, D.C.W. Tsang, E.E. Kwon, J. Lee, C. Wang, A critical review on sustainable biochar system through gasification: Energy and environmental applications, Bioresour. Technol. 246 (2017) 242–253, https://doi.org/10.1016/j.biortech.2017.06.177.

[54] C.E. Brewer, K. Schmidt-Rohr, J.A. Satrio, R.C. Brown, Characterization of biochar from fast pyrolysis and gasification systems, Environ. Prog. Sustain. Energy. 28 (2009) 386–396, https://doi.org/10.1002/ep.10378.

[55] C. Deal, C.E. Brewer, R.C. Brown, M.A.E. Okure, A. Amoding, Comparison of kilnderived and gasifier-derived biochars as soil amendments in the humid tropics, Biomass Bioenergy 37 (2012) 161–168, https://doi.org/10.1016/J.BIOMBIOE.2011.12.017.

[56] S.C. Peterson, M.A. Jackson, Simplifying pyrolysis: using gasification to produce corn stover and wheat straw biochar for sorptive and horticultural media, Ind. Crops Prod. 53 (2014) 228–235, https://doi.org/10.1016/J.INDCROP.2013.12.028.

[57] V. Hansen, D. Müller-Stöver, J. Ahrenfeldt, J.K. Holm, U.B. Henriksen, H. Hauggaard-Nielsen, Gasification biochar as a valuable by-product for carbon sequestration and soil amendment, Biomass Bioenergy 72 (2015) 300–308, https://doi.org/10.1016/J.BIOMBIOE.2014.10.013.

[58] J. Fang, L. Zhan, Y.S. Ok, B. Gao, Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass, J. Ind. Eng. Chem. 57 (2018) 15–21, https://doi.org/10.1016/J.JIEC.2017.08.026.

[59]   J. Mumme, L. Eckervogt, J. Pielert, M. Diakité, F. Rupp, J. Kern, Hydrothermal carbonization of anaerobically digested maize silage, Bioresour. Technol. 102 (2011) 9255–9260, https://doi.org/10.1016/j.biortech.2011.06.099.

[60]   H.S. Kambo, A. Dutta, A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications, Renew. Sustain. Energy Rev. 45 (2015) 359–378, https://doi.org/10.1016/J.RSER.2015.01.050.

[61]   J.A.J.A. Libra, K.S.K.S. Ro, C. Kammann, A. Funke, N.D.N.D. Berge, Y. Neubauer M.-M.M.-M. Titirici, F. C., O. Bens, J. Kern, K.-H.K.-H. Emmerich, C. Fühner, O. Bens, J. Kern, K.-H.K.-H. Emmerich, Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis, Biofuels. 2 (2011) 71–106. doi:10.4155/bfs.10.81.

[62]   Y. Sun, B. Gao, Y. Yao, J. Fang, M. Zhang, Y. Zhou, H. Chen, L. Yang, Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties, Chem. Eng. J. 240 (2014) 574–578. doi:10.1016/J.CEJ.2013.10.081.

[63]   T. Yoshida, M.J. Antal, Sewage sludge carbonization for terra preta applications, Energy Fuels 23 (2009) 5454–5459, https://doi.org/10.1021/ef900610k.

[64]   M. Uchimiya, S. Hiradate, M.J. Antal, Dissolved phosphorus speciation of flash carbonization, slow pyrolysis, and fast pyrolysis biochars, ACS Sustain. Chem. Eng. 3 (2015) 1642–1649, https://doi.org/10.1021/acssuschemeng.5b00336.

[65]   M. Uchimiya, S. Hiradate, M.J. Antal, Influence of carbonization methods on the aromaticity of pyrogenic dissolved organic carbon, Energy Fuels 29 (2015) 2503–2513, https://doi.org/10.1021/acs.energyfuels.5b00146

[66]   J. Li, H. Zhang, X. Tang and H. Lu, RSC Adv., 2016, 6, 100352–100360.

[67]   J. Lee, K. H. Kim and E. E. Kwon, Renewable Sustainable Energy Rev., 2017, 77, 70–79.

[68]   M. B. Ahmed, J. L. Zhou, H. H. Ngo, W. Guo and M. Chen, Bioresour. Technol., 2016, 214,

836–851

[69]   T. Shim, J. Yoo, C. Ryu, Y. K. Park and J. Jung, Bioresour.Technol., 2015, 197, 85–90.

[70]   D. Jimenez-Cordero, F. Heras, N. Alonso-Morales, M. A. Gilarranz and J. J. Rodriguez, Fuel Process. Technol., 2015, 139, 42–48.

[71]   I. M. Lima, A. A. Boateng and K. T. Klasson, J. Chem. Technol. Biotechnol., 2010, 85, 1515–1521.

[72]   M. Koltowski, B. Charmas, J. Skubiszewska-Zieba and P. Oleszczuk, Ecotoxicol. Environ. Saf., 2017, 136, 119–125.

[73]   J. M. V. Nabais, P. Nunes, P. J. M. Carrott, M. M. L. RibeiroCarrott, A. M. Garc´ıa and M. A. D´ıaz-D´ıez, Fuel Process.Technol., 2008, 89, 262–268.

[74]   S. Yorgun, N. Vural and H. Demiral, Microporous Mesoporous Mater., 2009, 122, 189–194.

[75]   H. Jin, S. Capareda, Z. Chang, J. Gao, Y. Xu and J. Zhang, Bioresour. Technol., 2014, 169, 622–629

[76]   A. M. Dehkhoda, N. Ellis and E. Gyenge, J. Appl.Electrochem., 2014, 44, 141–157.

[77]   R. Azargohar and A. K. Dalai, Microporous Mesoporous Mater., 2008, 110, 413–421

[78]   S. Prapagdee, S. Piyatiratitivorakul and A. Petsom, Asian J. Water, Environ. Pollut., 2016, 13, 27–34

[79]   D. Angin, E. Altintig and T. E. Kose, Bioresour. Technol., 2013, 148, 542–549.

[80]   Y. Ding, Y. Liu, S. Liu, Z. Li, X. Tan, X. Huang, G. Zeng, L. Zhou and B. Zheng, Agron. Sustainable Dev., 2016, 36, 1–18

[81]   M. Lawrinenko, Z. Wang, R. Horton, D. Mendivelso-Perez, E.A. Smith, T.E. Webster, D.A. Laird, J.H. Van Leeuwen, Macroporous carbon supported zerovalent iron for remediation of trichloroethylene,   ACS   Sustain.   Chem.   Eng.   5   (2017)   1586–1593, https://doi.org/10.1021/acssuschemeng.6b02375.

[82]   M.L. Nieva Lobos, J.M. Sieben, V. Comignani, M. Duarte, M.A. Volpe, E.L. Moyano,

Biochar from pyrolysis of cellulose: a alternative catalyst support for the electrooxidation of methanol, Int. J. Hydrogen Energy. 41 (2016) 10695–10706, https://doi.org/10.1016/J.IJHYDENE.2016.04.041

[83] L. Chen, S. Yang, X. Zuo, Y. Huang, T. Cai, D. Ding, Biochar modification significantly promotes the activity of Co3O4 towards heterogeneous activation of peroxymonosulfate, Chem. Eng. J. 354 (2018) 856–865, https://doi.org/10.1016/ J.CEJ.2018.08.098.

[84] P. Lisowski, J.C. Colmenares, O. Mašek, W. Lisowski, D. Lisovytskiy, A. Kamińska D. Łomot, Dual functionality of TiO2/biochar hybrid materials: photocatalytic phenol degradation in the liquid phase and selective oxidation of methanol in the gas phase, ACS Sustain. Chem. Eng. 5 (2017) 6274–6287, https://doi.org/10.1021/acssuschemeng.7b01251

[85] M.B. Ahmed, J.L. Zhou, H.H. Ngo, W. Guo, M. Chen, Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater, Bioresour. Technol. 214 (2016) 836–851, https://doi.org/10.1016/J.BIORTECH.2016.05.057.

[86] D.-W. Cho, G. Kwon, Y.S. Ok, E.E. Kwon, H. Song, Reduction of bromate by cobaltimpregnated biochar fabricated via pyrolysis of lignin using CO2 as a reaction medium, ACS Appl. Mater. Interfaces. 9 (2017) 13142–13150, https://doi.org/10.1021/acsami.7b00619.

[87] J.-H. Park, J.J. Wang, R. Xiao, N. Tafti, R.D. DeLaune, D.-C. Seo, Degradation of Orange G by Fenton-like reaction with Fe-impregnated biochar catalyst, Bioresour.Technol. 249 (2018) 368–376, https://doi.org/10.1016/J.BIORTECH.2017.10.030

[88] M. Lawrinenko, D.A. Laird, J.H. Van Leeuwen, Sustainable pyrolytic production of zerovalent iron, ACS Sustain. Chem. Eng. 5 (2017) 767–773, https://doi.org/10.1021/acssuschemeng.6b02105.

[89] S.-H. Ho, Y. Chen, R. Li, C. Zhang, Y. Ge, G. Cao, M. Ma, X. Duan, S. Wang, N. Ren,N-doped graphitic biochars from C-phycocyanin extracted Spirulina residue forcatalytic persulfate activation toward nonradical disinfection and organic oxidation, Water Res. 159 (2019) 77–86,https://doi.org/10.1016/j.watres.2019.05.008

[90] M. Antonietti, N. Lopez-Salas, A. Primo, Adjusting the structure and electronicproperties of carbons for metal-free carbocatalysis of organic transformations,Adv. Mater. (2018) 1–15, https://doi.org/10.1002/adma.201805719.

[91] S.Y. Oh, J.G. Son, P.C. Chiu, Biochar-mediated reductive transformation of nitroherbicides and explosives, Environ. Toxicol. Chem. (2013), https://doi.org/10.1002/etc.2087.

[92] J. Yu, L. Tang, Y. Pang, G. Zeng, J. Wang, Y. Deng, Y. Liu, H. Feng, S. Chen, X. Ren, Magnetic nitrogen-doped sludge-derived biochar catalysts for persulfate activation: Internal electron transfer mechanism, Elsevier B.V. (2019), https://doi.org/ 10.1016/j.cej.2019.01.163.

[93] K. Ding, W. Xu, Black carbon facilitated dechlorination of DDT and its metabolites by sulfide, Environ. Sci. Technol. 50 (2016) 12976–12983, https://doi.org/10.1021/acs.est.6b03154.

[94] Omid Norouzi and Francesco Di Maria, Catalytic Effect of Functional and Fe Composite Biochars on Biofuel and Biochemical Derived from the Pyrolysis of Green Marine Biomass, Fermentation 2018, 4, 96; doi:10.3390/fermentation4040096.

[95] Lingjun Zhu, Shi Yin, Qianqian Yin, Haixia Wang &Shurong Wang, Biochar: a new promising catalyst support using methanation as a probe reaction, Energy Science and Engineering 2015; 3(2): 126–134 doi: 10.1002/ese3.58

[96] TaozeLiu,ab Bin Gao,*b June Fang,b Bing Wanga and Xinde Cao, Biochar-supported carbon nanotube and grapheme oxide nanocomposites for Pb(II) and Cd(II) removal, RSC Adv., 2016, 6, 24314, DOI: 10.1039/c6ra01895e