

**Production and use of biochar from lignin and lignin-rich residues (such as digestate
and olive stones) for wastewater treatment**

Eid Gul^a, Khalideh Al Bkoor Alrawashdeh^b, Ondrej Masek^c, Øyvind Skreiberg^d, Andrea Corona^e,
Mauro Zampilli^e, Liang Wang^c, Petros Samaras^f, Qing Yang^g, Hewen Zhou^g, Pietro Bartocci^e,
Francesco Fantozzi^e

^aBiomass Research Centre, University of Perugia, Via G. Duranti - Strada S. Lucia Canetola s.n.c,
Perugia, Italy

^bMechanical Engineering Department, Al-Huson University College, Al- Balqa' Applied University,
Al-Huson- Irbid, P. O. Box 50, 21510, Jordan

^cUK Biochar Research Centre, School of GeoSciences, University of Edinburgh, Edinburgh, EH9
3FF, United Kingdom

^dSINTEF Energy Research, Postboks 4761 Torgarden, Trondheim, Norway

^eDepartment of Engineering, University of Perugia, Via G. Duranti 67, Perugia, 06125, Italy

^fLaboratory of Technologies of Environmental Protection and Utilization of Food By-Products,
Department of Food Science and Technology, International Hellenic University, Thessaloniki, GR-
57400, Greece

^gState Key Laboratory of Coal Combustion, Huazhong University of Science and Technology,
Wuhan 430074, PR China

^hChina-EU Institute for Clean and Renewable Energy, Huazhong University of Science and
Technology, Wuhan 430074, PR China

ⁱDepartment of New Energy Science and Technology, School of Energy and Power Engineering,

^jHuazhong University of Science and Technology, Wuhan 430074, PR China

John A. Paulson School of Engineering and Applied Sciences, Harvard University,
Cambridge, MA 02138, USA

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Abstract: Clean water is an essential source of life, and its demand is continuously increasing with the rapid growth in population, while the freshwater reserves are also depleting. A large amount of wastewater is released by different industries, which is affecting the environment as well as polluting the freshwater reserves. Recycling and treatment of wastewater are highly essential to meet the demand for clean water and to protect the environment. Activated carbon can be used in primary, secondary and tertiary wastewater treatment steps. It can be used to capture pollutants which stop microbial activity or to produce clean water with high purity. About 3 million tons of activated carbon are produced per year and it is mainly used for fluid purification. The objective of this review is to investigate the preparation and production of biochar from lignin which is an important resource available in great quantities (about 100 Million tons per year) and the practical application of it for wastewater treatment. Biochar can be produced through pyrolysis (at temperatures of 600-700°C) and Hydrothermal carbonization (at temperature between 180-300°C). Subsequent activation can be performed in two ways (physical and chemical) usually at temperatures between 600-800°C. The quality of biochar and activated carbon produced from lignin-rich residue can be very high, even though the costs also are higher respect to other fossil derived materials (carbon black, lignite and pet coke).

Keywords, Biochar technologies; Wastewater treatment, Heavy metals; Dyes; Pyrolysis; HTC

1. INTRODUCTION

1.1 Lignin as a subproduct

Lignin is becoming a more and more abundant resource, as this is a subproduct of many important industrial sectors. It can for example be produced from the paper industry, by recovering it from the black liquor fraction. The total lignin amount produced by the pulping industry is estimated to be around 40 million tons per year [1]. This lignin accounts for about 55% of the total lignin production [2]. The remaining production is represented mainly by lignosulfonate lignin (a byproduct from the production of wood pulp), while a small part is represented by organosolv lignin (mainly coming from 2nd

generation bioethanol production). The total lignin production in 2015 was estimated to be about 100 tons per year, and it is forecasted to increase of about 20% in 2025 [2]. Lignin is the second most abundant compound after cellulose in the plant world.

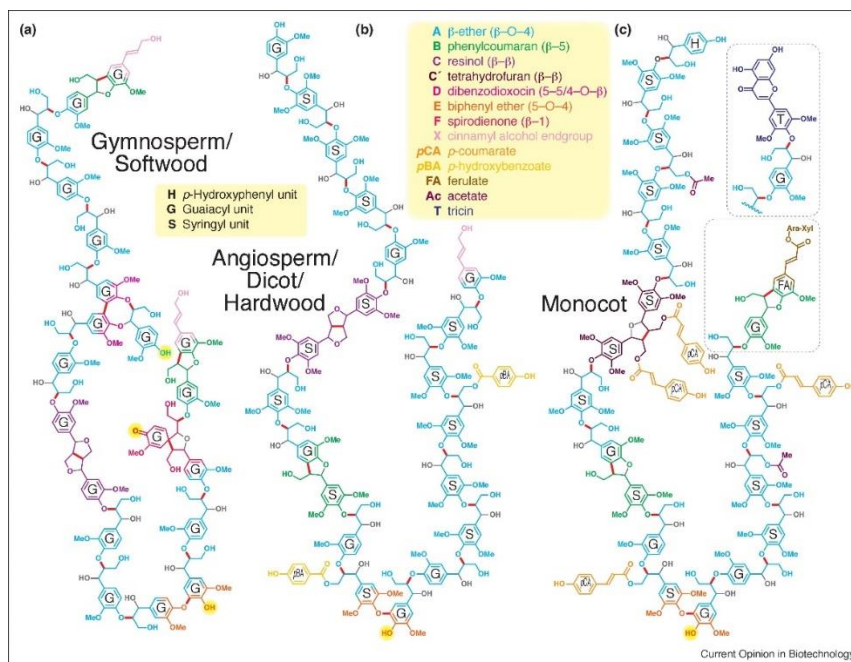


Figure 1. Lignin model structures. Model lignin oligomers are shown for: (a) A gymnosperm/softwood, (b) An angiosperm/dicot/hardwood, and (c) A (commelinid) monocot [3].

Lignin is a branched polymer, where the different units can be classified in H, G and S monolignols [3]. The composition of lignin varies between different vegetal phyla. The detailed biological synthesis of the monolignols is shown in [4].

Lignin can be used to produce many chemicals and materials, among which: adhesives, carbon fibers, thermoplastics, emulsifiers, concrete mixtures etc. These routes are under analysis in many projects at European level and especially under the LIGNOCOST action, which is chaired by Wageningen University (Netherland) and co-chaired by VTT (Finland), see: <https://lignocost.eu/>.

Together with lignin also lignin rich residues have to be considered, such as digestate (at least the solid separated part) and olive pits. If we assume that for an average biogas plant of the power capacity of 500 kWe ,about 10,000 t of digestate are produced [5], given a total installed capacity of 12,000 MWe in the EU [6] we can assume a production of digestate of about 240 Mt, which is relevant.

1 Assuming that the digestate has a remaining solid content of 10% (which can be also much higher), we
2 have a production of solid digestate of about 24 Mt per year. If we consider olive stones, we have to
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4 take into account that the average global production of olives is about 3 Mt per year, they contain about
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6 18 wt% [7] of stones and so about 0.54 Mt of olive stones are produced per year.
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10 **1.2 Charcoal and activated charcoal production**

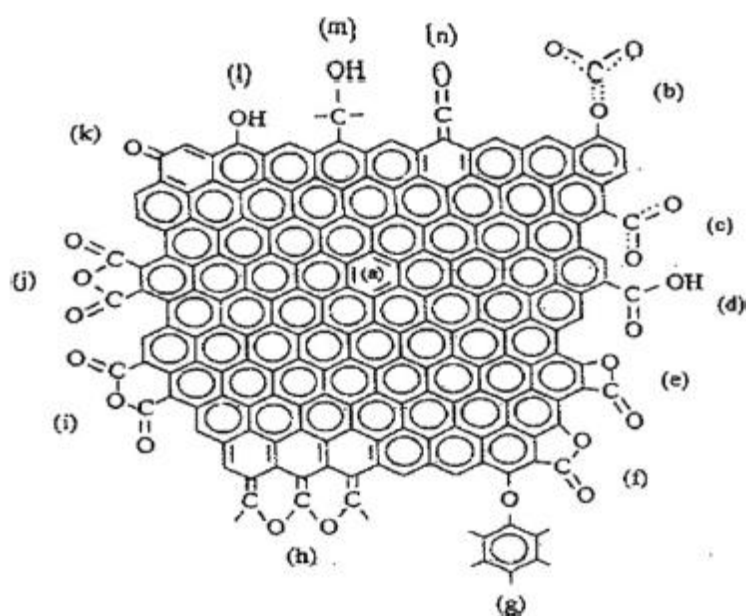
13 All these lignin rich bio-based compounds can be used to produce activated charcoal, see for
14 example [8]. In this contribution we see that agricultural residues, which are rich in lignin are e.g.
15 coconut shell and palm shell. So, what is activated charcoal and how can we produce it? Activated
16 charcoal can be considered as a highly porous material, which can be produced from organic substrates
17 and it is used for many applications, among them for the sorption of contaminants from fluids [9]. The
18 production of activated carbon is usually more complex than that of biochar. Assuming that activated
19 carbon is produced from biomass, biochar can be a precursor in its supply chain. So, if biochar can be
20 produced through pyrolysis and hydrothermal carbonization (HTC), as a second step activation is then
21 required to produce the final activated carbon from it. We don't consider gasification as a thermal
22 treatment to produce biochar because in the case of activated carbons the biochar obtained from
23 gasification would have a high ash content and this can limit the activation phase and the formation of
24 a high porosity material.
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40 As we will see in this review, activation can be performed by using chemical and physical methods,
41 the final aim of this step is to increase the porosity of the biochar, which can be measured with the
42 Brunauer–Emmett–Teller (BET) analysis. Dealing with pyrolysis, this is a thermal treatment, which
43 happens in the absence of oxygen and produces three phases: a liquid (pyrolysis oil) a solid (char) and
44 a gas (pyrogas). The process begins at temperature around 300°C and can continue till very high
45 temperatures are reached (usually not more than 900°C) [10]. Like the pyrolysis process, also
46 hydrothermal carbonization is a biochar production process, which happens at temperatures of about
47 180-300°C in a suspension containing biomass and water, with a pressure high enough to prevent water
48 evaporation, for several hours [11]. Main reaction mechanisms happening in the HTC process are
49 hydrolysis, dehydration, decarboxylation, aromatization, and condensation polymerization.
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1 Physical activation can be performed using gaseous reagents (air or CO₂), steam, or both [12]. The
2 temperature usually is about 700°C [13]. In chemical activation the temperature is lower, compared to
3 the physical one (about 500°C). In both types of activation, the chemical reactions happening are mainly
4 based on oxidation. In the first case oxidation is performed by gases or steam (in a similar way in which
5 the gasification process is performed) and in the second case oxidation is performed by chemical agents
6 which are adsorbed on the charcoal powder to be activated. Chemical agents can be ZnCl₂ and H₃PO₄
7 [14-16]; H₂SO₄, K₂S and KCNS [17]; HNO₃, H₂O₂, KMnO₄ and (NH₄)₂S₂O₈ [13]; NaOH and KOH
8 [18]; K₂CO₃ [19, 20]. The surface area yields are a key aspect for both chemical and physical activation.
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10 The versatile characteristics of charcoal and its capacity to adsorb many pollutants are due to two
11 mechanisms: chemisorption and physisorption. The chemisorption mechanism is due to the presence of
12 functional groups in the porous internal surface of the activated charcoal [21].
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14 Those functional groups derive from the elements which are present in the activated charcoal
15 composition, some of those can be: O, S, H, N, Cl, K, Na, Mg, Ca [22-24]. Oxygen for example can
16 form many functional groups, such as carboxyl, carbonyl, phenols, lactone and others [25-27]. The
17 groups which are available on the surface can be classified as protonated (C-OH₂⁺), neutral (COH) or
18 ionized (CO⁻). The groups are shown in Figure 2, as measured with IR.
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Figure 2. IR-active functional groups on carbon surface: (a) aromatic C¹/C stretching; (b) and (c) carboxyl-carbonates; (d) carboxylic acid; (e) lactone(4-memberedring); (f) lactone(5-memberedring); (g) ether bridge; (h) cyclic ether; (i) cyclican hydride (5-membered ring); (j) cyclican hydride (6-membered-ring); (k) quinine; (l) phenol; (m) alcohol; and (n) ketene [8]

1.3 Wastewater treatment

The physisorption and chemisorption mechanisms can be used for water purification, which is the subject of this work. Clean water is the most essential source for all living species and the clean water reserves are now decreasing [28]. If we consider the UN SDG 6 (sustainable management of water and sanitation for all), this is linked with many other SDGs (particularly SDG 1 (No poverty), 2 (Zero hunger), 3 (Good health and well-being), 14 (Life below water) and 15 (Life on land)) [29]. This importance is highly felt in African territories. Another way to consider the importance of water is the so-called Food-Energy-Water NEXUS which has already been shown to involve a great part of the 17 UN SDGs [30]. The use of charcoal in water treatment is done with the aim of reducing three types of contaminants [31]:

- Natural organic matter (NOM, mainly consisting of residues of the metabolism of living things);
- Synthetic organic matter (e.g. oil, benzene and toluene, phenols and chlorophenols, trichloromethane and carbon tetrachloride, detergents, pesticides, dyes, surfactants etc.);
- by-products of chemical water treatment (for example the byproducts of the drinking water disinfection step, which is usually done with chlorine compounds and it is followed by the treatment with activated charcoal to adsorb the formed trihalomethanes).

Dealing with the AC market in the US, 50% of it is used in drinking water sanitation, 40% is used in wastewater treatment and the remaining is used in ground water treatment [31]. The total market of activated charcoal was about 2.7 Mt in 2015 and it is projected to reach about 5.4 Mt in 2021 for a total market value of 8.1 billion dollars with a unit price of 1.5 €/kg [32]. Higher values are reported by [33], so this can be evaluated as a very interesting market and as mentioned before, the

1 total production of lignin worldwide can easily cover the current demand of activated charcoal, with
2 interesting economic benefits.

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4 Wastewater treatment can be divided into the following phases:

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7 1. the first (or pre-treatment) stage happens when the effluent contains toxic substances, which
8 can influence the activity of the biological treatment. In this phase we can apply redox reactions,
9 followed by precipitation to separate metals; ozonation followed by filters based on granular
10 AC, to eliminate big organic molecules; air stripping to eliminate light organics and ammonia;
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15 2. secondary treatment is based on the use of lime and other chemicals, followed by nitrification and
16 neutralization using acids or bases; this will remove suspended solids, oils and floating
17 materials; then follows the removal of proteins, starches and sugars and phenols by biological
18 treatment in aerobic conditions;
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24 3. the tertiary phase consists of the removal of inorganic and organic compounds by adsorption,
25 obtaining an extremely pure effluent with 99% BOD reduction.
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29 The use of activated charcoal in the above-mentioned cleaning processes can be done in many ways:
30 it can be inserted as an adsorbent after the primary and after the secondary biological processes directly
31 in the reactors; or it can be used in a separate reactor (especially during the tertiary treatment). An
32 example of 20 m³ reactor used with powdered activated carbon (PAC) is shown in Figure 3.
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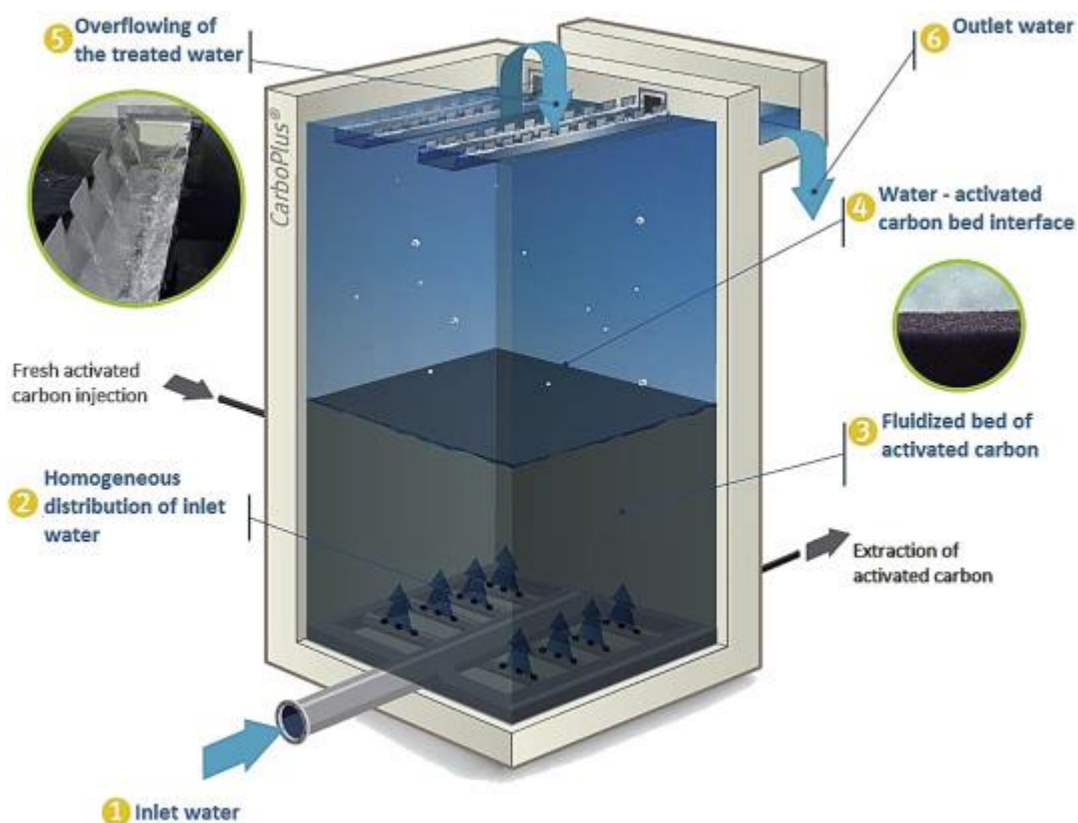


Figure 3: Layout of the 20 m³ (5 m × 4 m²) CarboPlus® pilot (SAUR source), adapted from [34]

2. AIM OF THE WORK AND METHODS

Few reviews are available on the topic of activated charcoal production from lignin (or lignin rich residues) and its use in wastewater treatment. One is that presented by [35], but in that work it is missing a detailed part on adsorption performance, which is only treated shortly. Besides this, economic considerations on the feasibility of the whole supply chain are missing and also the comparison with other possible uses of lignin. The works [36-39] take into consideration the production and the use of biochar in wastewater treatment, but the quality and properties of biochar are much different from those of activated charcoal. According to [40], if digestate sludge has a porosity of 1.92 m²/g, the porosity of biochar is about 20.86 m²/g. This is very low, if we consider that the porosity of activated charcoal can reach more than 2000 m²/g [35]. Other works [41, 42] take into consideration the modification of biochar through the use of chemicals, oxidation, carboxylation and amination, treatment with organic

solvents and use of Fe to produce magnetic biochar, and the use of biochar in the adsorption of heavy metals is also considered. Still modified biochar is different from activated charcoal.

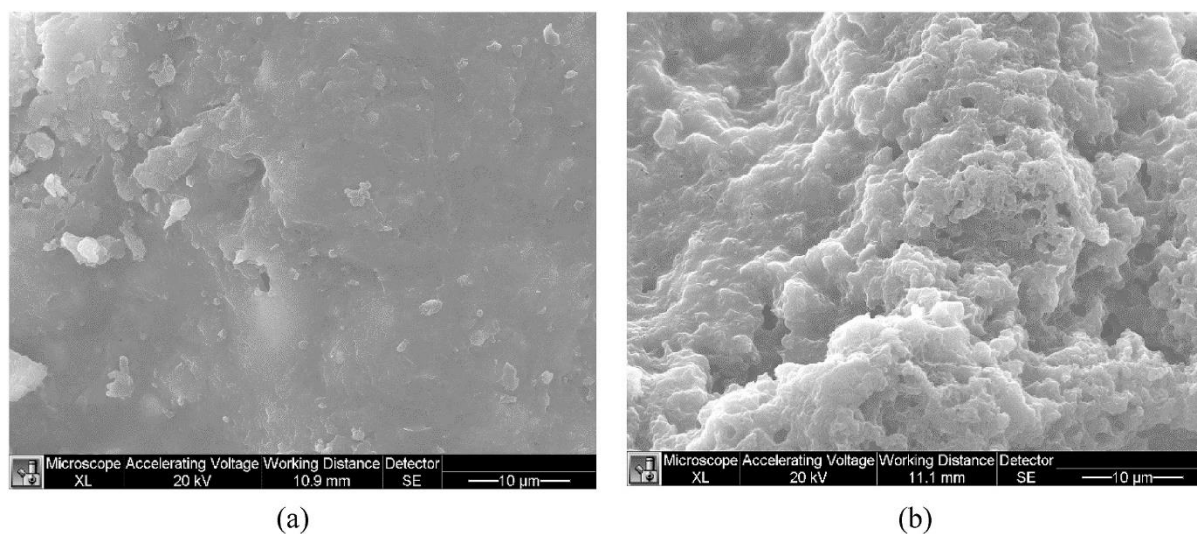


Figure 4: SEM image of (a) digested sludge and (b) biochar sample BC450 [40].

Dealing with the use of activated carbon and more broadly with the application of adsorption in WWTP, some relevant books have been written, such as: [43-46]. To these important publications it has to be added also the book of Harry Marsh on activated carbon production [31]. We also have to remember the review of lignin materials adsorption capacities [47], this is an important work showing all the sorbents which can be derived from lignin and their sorption capacity, nevertheless the work is not sufficiently focused on activated carbons. The work [48] is focused on lignin activated carbon production and modeling of the adsorption process, but little information is available on the actual adsorption capacity. Also the work [49] is very general, adsorption application are not dealt with in detail and lignin-rich residues are not taken into account.

So, none of the above-mentioned works gets a sufficiently detailed insight on lignin activated charcoal production and use in wastewater treatment and to the best of the authors' knowledge, there is no work considering the economic aspects of activated carbon production from lignin and comparing the economic performance with other possible uses.

For these reasons this work aims at:

- describing biochar production technologies from lignin and examine lignin pyrolysis and HTC, focusing on yields, solid products characterization (through BET, ashes, total porous volume analysis etc.) and chemical and kinetic aspects;
- describing the activation step, taking into consideration the chemical activation process and also the physical activation process;
- describing the pollutants adsorption process, focusing on process parameters, efficiency adsorption capacity, activated charcoal dose, process kinetics;
- describing the pollutants adsorption performance of activated charcoal derived from lignin compared to other activated charcoals;
- compare the economic feasibility of producing activated charcoal from lignin with other possible uses.

To do this, detailed searches have been performed in google scholar using the keywords shown in table S1 of the supplementary material. About 348 papers in the literature have been consulted. Their distribution among the main topics of research is shown in Figure 5.

As it can be seen from Figure 5, about 8 hot topics have been identified for the production of activated charcoal from lignin: pyrolysis; hydrothermal carbonization (HTC); physical activation; chemical activation; modification; adsorption process modelling (Ad modelling); wastewater treatment and technical economic performance. This last aspect is considered only for lignin, while for digestate and olive stone it is neglected. This is due to the wider market which is now growing for lignin valorization, as also demonstrated by the EU cost action LIGNOCOST (<https://lignocost.eu/>). It can be easily understood that in the case of lignin it is very important to discern the most economically attractive uses. Dealing with the pyrolysis conversion technology, which can be both conventional pyrolysis or microwave pyrolysis, much research has been done with digestate, while with olive stone more research is needed. For this last residue of the olive production the most interesting technologies are based on activation. Chemical and physical activation are performed for both olive stones and lignin; while for digestate no activation is performed.

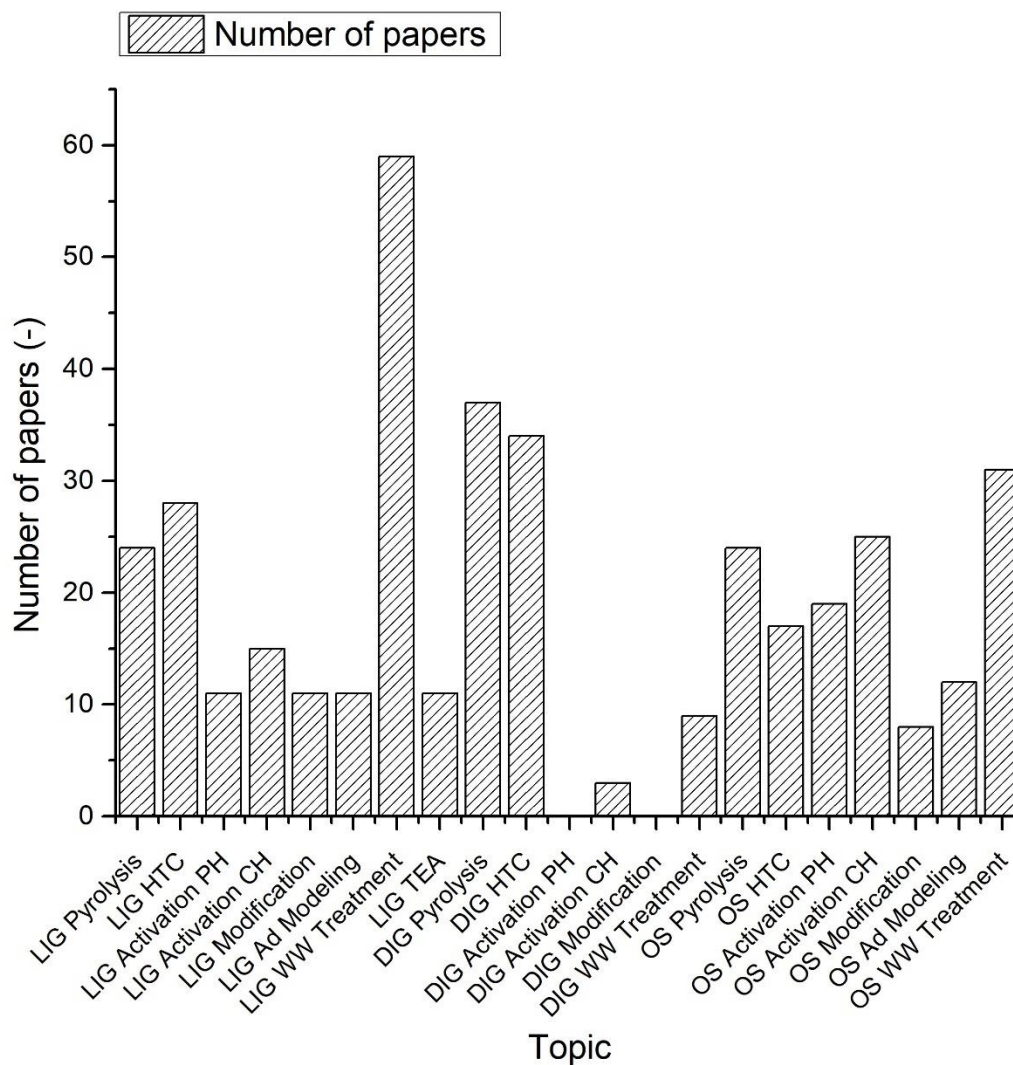


Figure 5: Literature review, LIG = lignin; HTC = Hydrothermal Carbonization; PH = Physical; CH = chemical; Ad = Adsorption; WW = Wastewater; TEA = Technoeconomic analysis; DIG = digestate; OS = Olive Stones

We will deal in the following sections with: lignin, digestate and olive stones characterization and thermal treatment, charcoal modification and activation, wastewaters treatment and technical economic feasibility of producing activated carbons from lignin.

3. LIGNIN, DIGESTATE AND OLIVE STONES CHARACTERIZATION

3.1 Lignin characterization

The most important lignin characteristics are clearly presented in [50], these are reported also in Table

1. Different lignins are taken into consideration: organosolv eucalyptus lignin, kraft eucalyptus lignin, organosolv spruce lignin, kraft spruce lignin.

Table 1: Lignin characterization [50]

Parameter	Organosolv eucalyptus lignin	Kraft eucalyptus lignin	Organosolv spruce lignin	Kraft spruce lignin
Klason lignin (%)	83.7	58.6	94.3	88.5
Acid soluble lignin (%)	1.6	6.3	3.1	2.3
Ash (%)	3.6	22.4	3.2	2.5
Total sugars (%)	2.9	2.2	0.5	1.0
C (%)	61.4	49.8	68.8	63.7
H (%)	6.0	5.0	6.3	6.1
N (%)	0.13	0.11	0.08	0.10
S (%)	0.06	0.78	0.20	1.45
Number-average molecular weight	1567	1059	1065	1540
Molecular Weight	5079	2653	3081	7195
PDI	3.24	2.51	2.89	4.67
Ash (%)	3.6 ± 1.9	22.4 ± 0.3	3.2 ± 0.3	2.5 ± 0.0
Volatiles (%)	63.4 ± 1.7	49.1 ± 0.0	55.0 ± 0.2	63.9 ± 2.0
Fixed carbon (%)	32.9 ± 0.0	27.2 ± 0.0	41.7 ± 0.0	33.5 ± 2.5
Organic matter (%)	96.3 ± 1.9	76.3 ± 0.1	96.7 ± 0.3	97.4 ± 0.0
HHV (MJ/kg) [51]	22.7	18.3	24.0	23.0
HHV (MJ/kg) [52]	22.5	18.0	24.2	22.8

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It can be seen from Table 1 that kraft lignins have usually higher content of nitrogen and sulfur compared to organosolv lignins. The presence of sulfur can be explained with the fact that some acids used for lignin isolation can remain in the compound when analyzed. Organosolv lignin has a high carbon content so it is the more suitable for active carbon production. Organosolv lignin is also purer than kraft lignin, having higher Klason lignin concentration. Lignin molecular weight average (Mw) can be different depending on the feedstock and the extraction process [53]. For this reason, the samples shown in Table 1 have values that differ in an important way and this is due probably to the fact that they have been extracted in two different ways. The polydispersivity (PDI) values are generally high for all the samples considered, which is confirmed also by [54]. From the proximate analysis we can see that the moisture content is very low, so lignin can be transformed easily with thermochemical processes. Also the ash content is quite limited (with the exception of eucalyptus kraft lignin), while fixed carbon content is important and this means that we expect interesting yields of charcoal after the thermal treatment. Lignins have also an interesting heating value.

3.2 Digestate characterization

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In Table 2 we find the characterization analysis of a digestate obtained from a biogas plant realized in a farm in the Umbria region (Italy), which is mainly fed with energy crops (maize and sorghum silage). Compared with other digestates, which are obtained when the anaerobic digestion plant is fed with animal wastes, the ones obtained using energy crops have surely a higher content of lignin. In this case the lignin content is about 41 wt%. The high content of lignin implies also an interesting heating value of the residue. Ash concentration is also important, if compared for example with that of pure lignin. The heating value is slightly lower than that of lignin, the same is also for the fixed carbon content. This means that pure lignin is potentially a better substrate for activated carbon production. Digestate produced from energy crops seems to have better characteristics, if compared with olive stones, for example.

Table 2: Digestate characterization [55, 56]

Parameter	Value	Unit of measure
Ash	12.38	wt% d.b.
Volatile matter	67.07	wt% d.b.
Fixed carbon	20.55	wt% d.b.
VM/FC	3.29	wt% d.b.
C	42.52	wt% d.b.
H	5.94	wt% d.b.
N	1.79	wt% d.b.
O	49.75	wt% d.b.
Cellulose	21.64	wt% d.b.
Hemicellulose	15.08	wt% d.b.
Lignin	40.88	wt% d.b.
Extractives	10.02	wt% d.b.
Higher Heating Value	19.74	MJ/kg d.b.

3.3 Olive stones characterization

If we consider olive stones, they have a lignin content of about 26.5 ± 0.42 wt%, according to [57]. Other components are cellulose (31.9 ± 0.34 wt%) and hemicellulose (21.9 ± 1.62 wt%) [57]. Lignin content is lower than that of the digestate reported in Table 2; this explains also the reason why the fixed carbon content is lower than that of digestate. It seems that olive stones can give less yield of charcoal compared to the other two considered raw materials (lignin and digestate). The advantage for the olive stones is that they have a lower moisture content, compared to olive pomace and so they can be easily be converted through thermochemical processes. Cellulose and hemicellulose will produce some charcoal also even though with less efficiency, compared to lignin.

Table 3: Olive stones and olive pomace characterization [58]

Parameter	Olive Stone	Wet Pomace
Moisture (wt% d.b.)	4.53	49.02
Ash (wt% d.b.)	0.49	0.84
Volatiles (wt% d.b.)	87.06	42.35
Fixed carbon (wt% d.b.)	12.45	7.79
C	50.00	55.54
H	6.17	7.98
N	0.42	1.98
O	43.41	34.5
HHV (wt% w.b.)	19.21	5.7

4. BIOCHAR PRODUCTION FROM LIGNIN RICH SUBSTRATES

4.1 Biochar production technologies from lignin-rich substrates

Biochar production technologies are basically thermochemical processes. They can be pyrolysis, gasification and hydrothermal carbonization. Gasification is not considered in this work because it produces a charcoal which has a high concentration of ashes. This can generally limit the porosity of the charcoal and so limit its adsorption efficiency. Another important aspect to take into consideration is that if we want to obtain activated carbon as a final product, we have to consider that two ways are possible: direct activation (physical or chemical) or thermal treatment (pyrolysis or HTC), followed by activation. In this sense biochar can be an intermediate product for activated charcoal production [35].

4.2 Lignin and lignin-rich residues pyrolysis

From a chemical point of view, during pyrolysis lignin decomposition starts with the breaking of the bonds which are weaker (e.g. hydrogen bonds and C-OH bonds), and with the increase of temperature stronger bonds are broken, such as the β -O-4 linkages. In the first low-temperature phase of the pyrolysis process aldehydes, toluols, styrenes, and guaiacyl hydroxyls are formed. In the second step of the pyrolysis, which happens at higher temperatures, p-hydroxy-phenols, catechols, and cresols are produced. When the β -O-4 linkages are broken, free radicals are liberated and they start the depolymerization reaction of lignin [59-61]. The radicals can form compounds like vanillin and 2-methoxy-4-methylphenol. The formation of important quantities of radicals starts the chain propagation reaction. At temperatures higher than 350°C through the random repolymerization of radicals, biochar is formed [59].

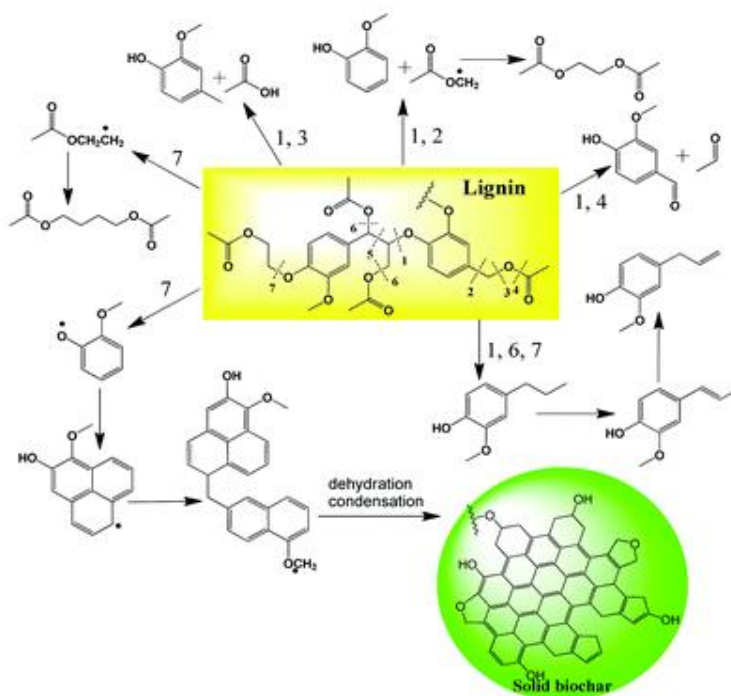
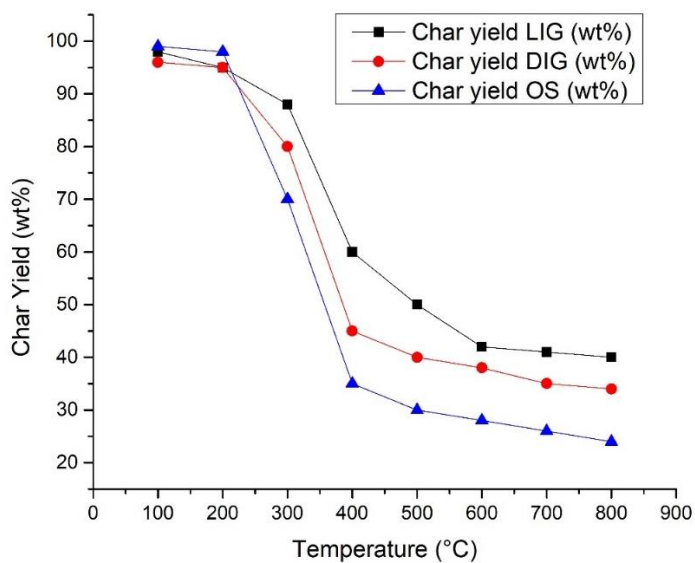


Figure 6: Pyrolysis of lignin, depolymerization mechanism [61]

A key parameter to take into consideration when performing lignin pyrolysis is the effect of temperature on biochar yield. This is reported for example in [62], but it can also be derived from TG diagrams, given that the residue that it is weighted by the thermal balance is the charcoal itself. So, if we consider

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2 the values presented in the TG diagram shown in [50] we can derive the values reported in Figure 7 on
3 char yields obtained during lignin pyrolysis.



26 Figure 7: Comparison of TG curves between: lignin [50], digestate [55] and olive stones [63, 64]

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33 Another important aspect is the effect of temperature on the porosity of the final material, as reported
34 in [65].

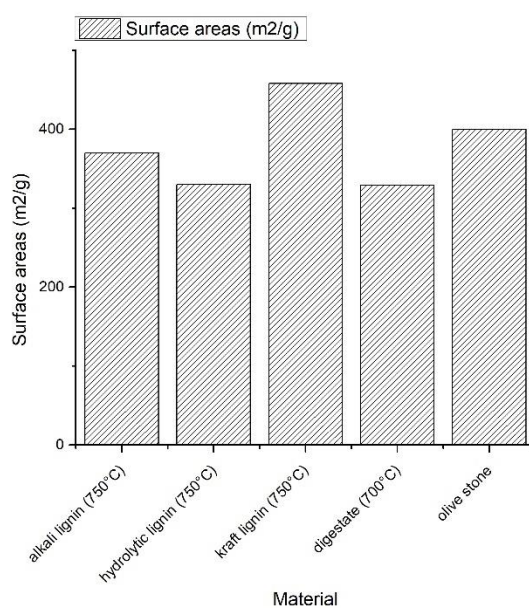


Figure 8: Surfaces areas of charcoals produced from different lignins and lignin-rich residues [65-67]

As it can be seen from Figure 8, different types of lignin and also the lignin-rich residues seem to have a similar surface area. It is important so, to understanding the role played by hemicellulose, cellulose and lignin on porosity development and main characteristics [68]. To consider the effect of the three components of biomass the TG and DTG diagrams shown in Figure 9 can be useful.

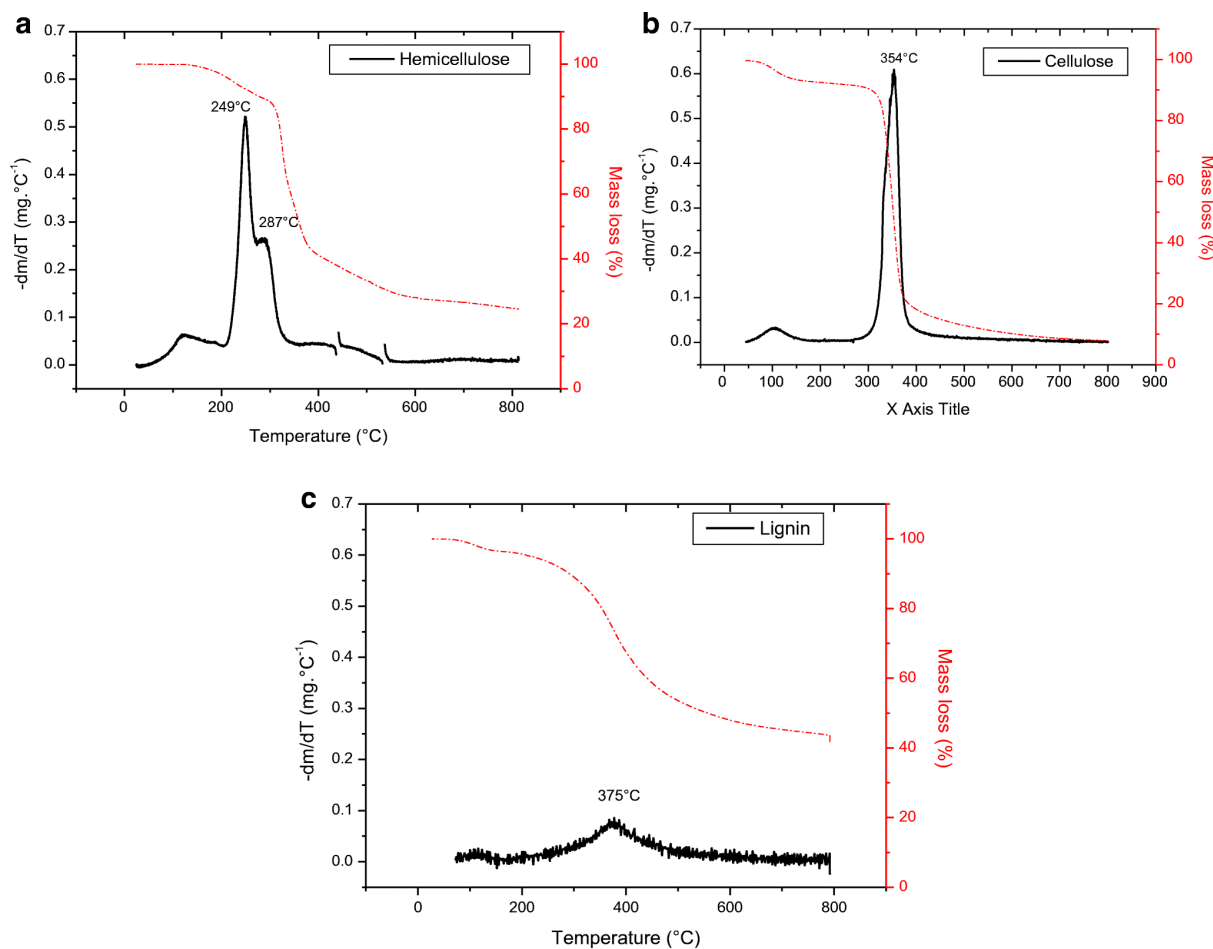


Figure 9: Thermal behavior of lignin, cellulose and hemicellulose [68]

It can be seen from Figure 9 that the total mass losses (in %) for hemicellulose, cellulose and lignin are 76.5 %, 80.9 % and 55.1%. So, the final charcoal yields at 800°C are 23.5% (for hemicellulose), 19.1% (for cellulose) and 45.9% (for lignin). From this data it seems that lignin is the major contributor to charcoal formation, but it is not so simple as it seems. In the study of Boundzanga et al. [68], in fact, an

1 interesting method to calculate the contribution of hemicellulose, cellulose and lignin to the final mass
2 of the formed charcoal is proposed. The contribution is estimated using a predictive method based on
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4 Cagnon equations [69], such as:
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$$7 \quad Y = 100 - ((1-x) \cdot 100) \quad (1)$$

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10 with:

$$11 \quad x = H \cdot y_{c,H} + C \cdot y_{c,C} + L \cdot y_{c,L} \quad (2)$$

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14 being Y the charcoal yield expressed in percentage. H, C and L are respectively the percentage of
15 hemicellulose, cellulose and lignin in the precursor (in %) and $y_{c,i}$ are the heat treatment yields of each
16 individual component (in %).
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25 Considering the initial mass of the raw material, the contribution of each component can be calculated
26 based on the following equation, which takes into consideration, as an example, lignin:
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$$34 \quad L_c = (1-(x-(L \cdot y_{c,L}))/x) \cdot 100 \quad (3)$$

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40 Where L_c is the production of charcoal from the lignin in the sample after pyrolysis (expressed in wt%),
41 x is the calculated char mass after heat treatment, $y_{c,L}$ is the yield of charcoal from the pyrolysis of pure
42 lignin (expressed in %). If we consider the values of the contributions of cellulose, hemicellulose and
43 lignin to char formation, from olive pomace, reported in [68], these are the following: 36.9 wt%
44 (hemicellulose), 18.5 wt% (cellulose) and 44.6 wt% (lignin). Based on these data lignin cannot be
45 considered as the major component of charcoal, also cellulose and hemicellulose are playing an
46 important role.
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4.3 Lignin and lignin-rich residues HTC

Hydrothermal carbonization of biomass is a thermal treatment which happens in the liquid phase at moderate temperature and high pressure (above the saturation pressure of water) [70]. The most common reactions in hydrothermal treatment of biomass are: the cleavage of C-O-C and C-C bonds; de-methoxylation; alkylation, and condensation. The cleavage of the β -O-4 linkages and $^{\alpha}$ C- β C linkages happens first, while aromatic bonds are not broken during HTC. The changes in structure of char during HTC of lignin are presented in [1]. Usually, lignin decomposition increases with the increase of temperature. With higher temperature HTC char tends to have a more crystalline structure; besides above 350°C many functional groups tend to disappear and only OH groups are left.

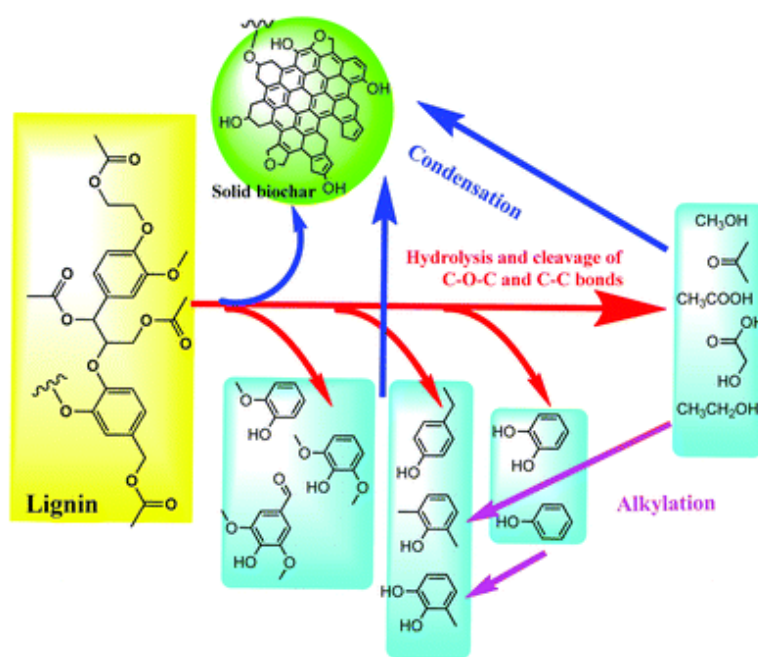


Figure 10: Mechanism of lignin HTC [61]

If compared with lignin pyrolysis, lignin HTC generally yields more charcoal, but this is a less stable product, so when activation is performed the final yield of activated product is in many cases less for HTC than for pyrolysis [71].

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Dealing with the porosity of the obtained hydrochars, few data are available. This is mainly because a simple HTC treatment does not produce a sufficiently porous carbon and the hydrochar has to be activated in a second step, to have a final product to be used as an adsorbent. The porosity of lignin hydrochar, obtained with a thermal treatment lasting 4 hours at a temperature equal to 360°C, is about 12.5 m²/g [72]. This value is much lower than that of pyrochar.

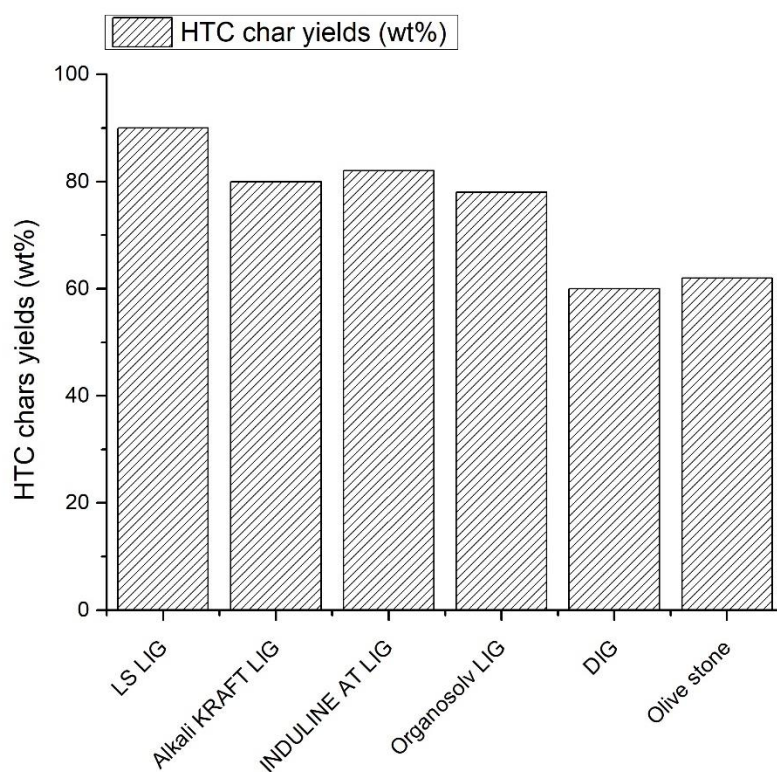


Figure 11: Hydrochar yields obtained at a temperature of 220°C [71, 73, 74], where LS = Low sulfonate; LIG = Lignin; DIG = digestate.

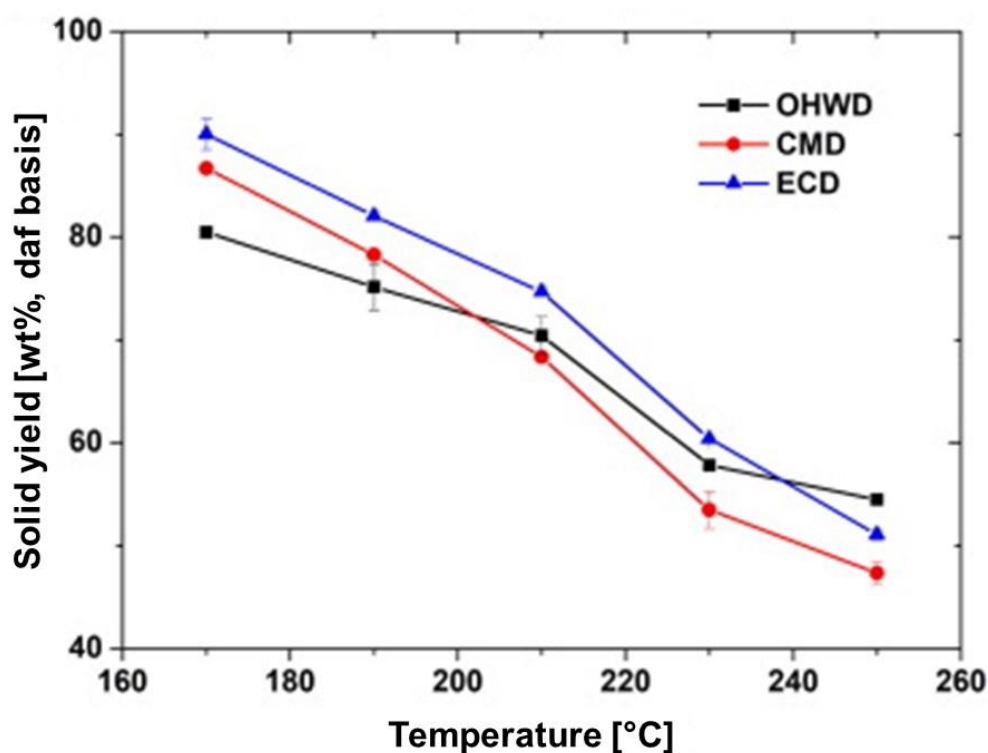
Where Indulin AT is a type of lignin derived from a purified form of kraft pine lignin. It has to be considered that the yields of hydrochar obtained with digestate and olive stones at the same temperature of 220°C (typical of wet torrefaction) are much lower than those obtained from lignin. This can be explained with the following facts:

1 -first the yields reported in Figure 11 with regard to lignins are maybe too high if we consider that [75]
2 reports a yield of hydrochar at 225°C equal to 60%;

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5 - general hydrochar yields obtained with lignin are higher than those obtained with cellulose and
6 hemicellulose;

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11 - this is due to the fact that the phenolic structure of lignin is more thermally stable.

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14 It has also to be considered that HTC temperature has an important effect on lignin hydrochar yields,
15 as it is reported in [74] and this is shown in Figure 12.



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55 Figure 12: Effect of temperature on hydrochar yields [74], where OHWD = organic household waste
56 digestate; CMD = Cow Manure Digestate; ECD = energy crops digestate.

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3 From Figure 12 it can be seen that compared to biochar obtained from pyrolysis the yields of hydrochar
4 are generally higher, this is due to the lower process temperature which makes hydrochar in general
5 more reactive than pyrolysis biochar.
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10 11 12 13 14 15 16 **4.4 Biochar modification processes**

17 18 19 20 **4.4.1 Influence of process parameters on final porosity and activated carbon yields**

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23 Given that lignin has a good sorption capacity, even without being modified, and also a high carbon
24 content, it is an ideal raw material for the production of activated carbons [35, 76-78]. As reported by
25 Mackay and Roberts [79, 80] the final porosity and textural characteristics of activated carbons strongly
26 depend on both raw materials properties and the process parameters. Dealing with raw materials
27 properties, the influence of their carbon content, lignin content and fixed carbon content have been
28 clearly explained in the previous paragraphs. We have also to take into consideration that the contents
29 of cellulose, hemicellulose and lignin have important effects on the final porosity of the material. In
30 fact, in cellulose charcoal the volume occupied by mesopores is 82% of the total porosity volume; in
31 the hemicellulose charcoal the volume occupied by the mesopores is about 45% of the total, while the
32 micropores occupy about 54% of the total; in the lignin the volume occupied by the micropores is about
33 63% of the total [68]. Depending on the final application the average diameter of the obtained pores can
34 be changed by changing the raw material. The important parameters that have to be taken into account
35 when dealing with activation are shown in Table 4.
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56 Table 4: Key Parameters during chemical and physical activation of lignin [35]
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58 59 60 61 62 63 64 65	ACTIVATION OF LIGNIN
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Source	Precursor	Activation	Temperature	Time	Surface area (m ² /g)	Micropore volume (cm ³ /g)
[81]	Indulin C ^a	(Ph) Carbonization with N ₂	300°C	1 h	<10	<0.01
[82]	Kraft Lignin	(Ph) Carbonization with N ₂ Activation with CO ₂	350°C	2h	1613	0.47
			800°C	40 h		
		(Ph) Carbonization with N ₂ Activation with CO ₂	350°C	2h	1853	0.57
			850°C	20 h		
[83]	Lignin ^b	(Ph) Carbonization with N ₂	500-900°C	-	10-50	-
[84]	Hydrolytic lignin	(Ph) Carbonization with Ar Activation with steam	600°C	2 h	865	0.365
			800°C	-		
[85]	Hydrolytic lignin	(Ph) carbonization with Ar Activation with steam	700°C	-	769	-
			780°C	-		
[86]	Hydrolytic lignin	(Ph) Activation with steam	700°C	2h	-	0.33
[81]	Indulin C ^a	(Ch) carbonization and Activation with KOH (Lignin:KOH = 4:1)	700°C	1	514	0.214
[83]	Lignin ^b	(Ch) ZnCl ₂ , H ₂ PO ₄ , K ₂ CO ₃ , Na ₂ CO ₃ , KOH, NaOH. Impregnation ratio (1)	-	-	800-2000	-
[87]	Kraft Lignin	(Ch): ZnCl ₂ , Lignin:1:2.3	500°C	1h	1800	1.039
[88]	Kraft Lignin	(Ch): H ₃ PO ₄ , Lignin:H ₃ PO ₄ :1:2	427°C	2h	1459	0.82
[89]	Hydrolysis lignin	(Ch): Carbonization and Activation with KOH. Lignin:KOH: 1:4	850°C	15	2753	1.37
[90]	Kraft Lignin	(Ch) H ₃ PO ₄ . Lignin:H ₃ PO ₄ : 1:1.4	600°C	1 h	1370	0.78
^a From black liquors of kraft pulping						
^b From strong black liquor of kraft pulping, acidulated with CO ₂ to obtain the lignin.						

As it can be seen from table 4 that an important parameter is the process temperature, this has influence on both yields and porosity. A clear view of the effects on porosity is shown in Figure 13 where SEM images of activated carbon produced from lignin at different temperatures are shown.

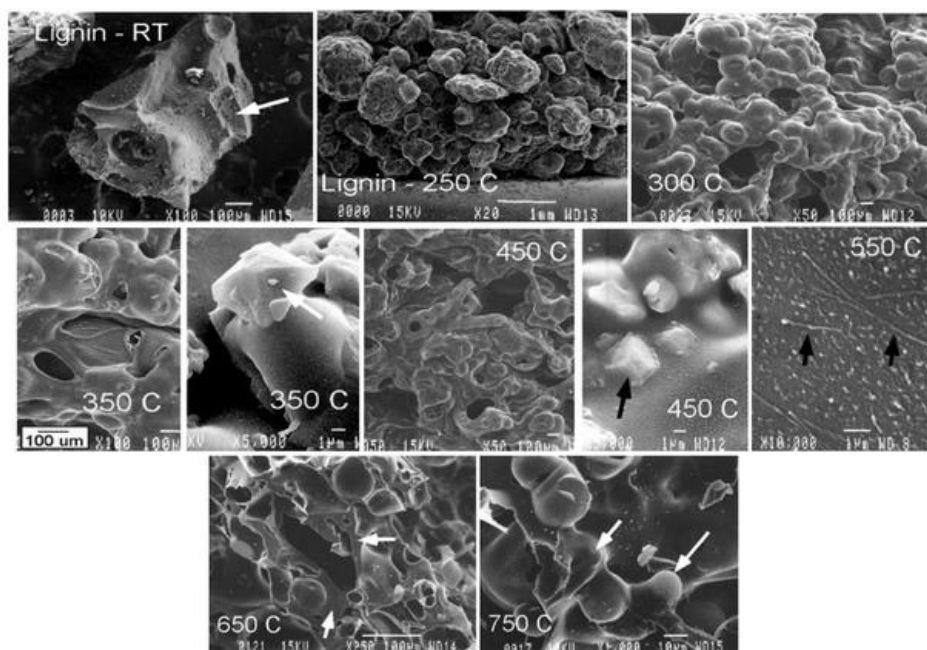


Figure 13: SEM images of lignin and lignin charcoals produced at different temperatures [61]

Table 5: Key Parameters during chemical and physical activation of digestate

ACTIVATION OF DIGESTATE						
Source	Precursor	Activation	Temperature	Time	Surface area (m ² /g)	Micropore volume (cm ³ /g)
[91]	Digestate	HTC and (Ch) KOH:Char: 4:1	190 °C	3 h	854	0.324
			600°C	2h		
[91]	Digestate	HTC and (Ch) KOH:Char: 4:1	220 °C	3 h	1178	0.440
			600°C	2h		
[91]	Digestate	HTC and (Ch) KOH:Char: 4:1	250°C	3 h	1609	0.596
			600°C	2h		
[91]	Leached Digestate	HTC and (Ch) KOH:Char: 4:1	190 °C	3 h	1180	0.502
			600°C	2h		
[91]	Leached Digestate	HTC and (Ch) KOH:Char: 4:1	220 °C	3 h	1317	0.563
			600°C	2h		
[91]	Leached Digestate	HTC and (Ch) KOH:Char: 4:1	250°C	3 h	1762	0.665
			600°C	2 h		
[92]	Digestate	HTC and (Ch) KOH:Char: 3:1	250°C	1 h	1106	0.54
			600°C	2 h		

[92]	Digestate	HTC with H ₂ SO ₄ and (Ch) KOH:Char: 3:1	250°C 600°C	1 h 2 h	503	0.30
[93]	Digestate	Carbonization and (Ch) KOH:char:	400°C 850°C 850°C	+ 1 h + 3.5 h 1 h	1754	-

Table 6: Key Parameters during chemical and physical activation of olive stone; Ch = Chemical activation; Ph= physical activation; BO=Burn-off

ACTIVATION OF OLIVE STONE						
Source	Precursor	Activation	Temperature	Time	Surface area (m ² /g)	Micropore volume (cm ³ /g)
[94]	Olive stone	(Ch) Impregnation with H ₃ PO ₄ (60 wt%) and carbonization	500°C	2 h	257	0.123
[94]	Olive stone	(Ch) Impregnation with H ₃ PO ₄ (70 wt%) and carbonization	500°C	2 h	779	0.35
[94]	Olive Stone	(Ch) Impregnation with H ₃ PO ₄ (80 wt%) and carbonization	500°C	2 h	1218	0.6
[95]	Olive Stone	Carbonization and (Ch) KOH (50wt%):Char:1:1	600°C 900°C	1 h 3 h	-	-
[95]	Olive Stone	Carbonization and (Ch) KOH (75wt%):Char:1:1	600°C 900°C	1 h 3 h	-	-
[96, 97]	Olive stone	(Ch) Impregnation with ZnCl ₂ (20wt%)	650°C	2 h	790.25	-
[98]	Olive stone	Carbonization and (Ch) KOH:char: 0.5:1	350°C 800°C	1 h 2 h	1500	0.31
[98]	Olive stone	Carbonization and (Ch) KOH:char: 1:1	350°C 800°C	1 h 2 h	1635	0.52
[98]	Olive stone	Carbonization and (Ch) KOH:char: 2:1	350°C 800°C	1 h 2 h	1768	0.80
[98]	Olive stones	Carbonization and (Ch) H ₃ PO ₄ (75wt%):char: 2.4:1; steam	350°C 500°C	1 h 1 h	393	0.12
[98]	Olive stones	Carbonization and (Ph) CO ₂	350°C 840°C	1 h 11% BO	584	0.11
[98]	Olive stones	Carbonization and (Ph) CO ₂	350°C 840°C	1 h 27% BO	793	0.14
[98]	Olive stones		350°C	1 h	1038	0.17

		Carbonization and (Ph) CO ₂	840°C	57%BO		
[99]	Olive stone	(Ch) Impregnation with H ₃ PO ₄ (50wt%):char = 10ml/g	400°C	2 h	1740	0.89

Those shown in Table 6 are only some examples on the production of activated carbons from olive stones, they are interesting because they show the influence of different activating agents. It is shown in the literature also that chemical activation is more effective than physical activation in many cases [98]. Chemical activation is generally preferred for olive stones (and also other precursors). More activation examples performed with olive stones are presented in the review [100]. From this review we can see that about 25 chemical activation tests have been performed in the literature, while the performed physical activation tests are only 2. Generally chemical activation produces activated carbons with higher porosity, compared to physical activation.

Dealing with the final yields of activated carbons, some values are presented in Figure 14. These values are taken from [71] and we see that the yields of activated carbons from lignin in most of the cases range from 20 wt% to 30 wt%, referring to the initial total mass of lignin used. The most important aspect to take into consideration in the activation (especially if it is chemical) is the reactant and the ratio between it and the precursor). In [91] KOH is used as an activating agent.

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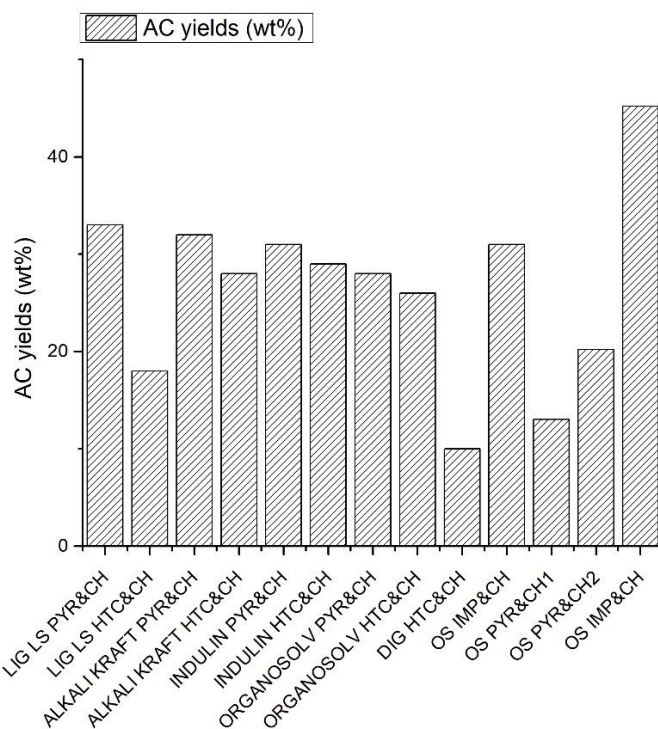


Figure 14: Activated carbon yields obtained with different activation methods and different lignins and lignin-rich substrates [71, 91, 94-96]

KOH at first during activation reacts with the carbon of the hydrochar and forms K_2CO_3 and metallic K and releases H_2 . The unstable organic compounds of the hydrochar when heated gasify also and release from these reactions CO_2 , which is responsible of the increase in porosity. The metallic K which has been formed by the previous reactions finally reacts again with C and promotes further gasification. It is possible that the high ratio between KOH and hydrochar (equal to 4:1) is the reason why the activated carbon yield obtained with the digestate is quite low, if compared to that obtained with lignin. On the other hand the activated carbon from lignin, which is shown in Figure 14, has been obtained through KOH activation at similar conditions, as it is reported in [71]; so in general it can be inferred that activated carbon yields from digestate are usually lower than those obtained with lignin. This can be explained with the fact that the carbon contained in lignin is more thermally stable. When we consider the case of olive stone, this is quite similar to that of digestate. The only cases in which higher yields are obtained are those in which activation is not performed with a two-step process, so we don't have two thermal treatments: carbonization and activation; but we have only impregnation, followed

1 by activation. In this case the final yields of activated carbons can reach easily about 40 wt%. The main
2 differences between the yields of activated carbon obtained with lignin and those obtained with lignin-
3 rich residues are due to the behavior of cellulose, hemicellulose and lignin during carbonization. As it
4 has been previously reported, the concentration of lignin is high in pure lignin (obviously), then it
5 decreases in digestate (also depending on the feedstock used in the anaerobic digestion process) and it
6 decreases again in the olive stone.
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13 Regarding the contribution of hemicellulose, cellulose and lignin to final activated carbon mass we can
14 take into consideration the data reported in [68]. The contribution of lignin is estimated to be about 44.6
15 wt%, the contribution of cellulose is estimated at about 18.5 wt%; the contribution of hemicellulose is
16 estimated at about 36.9 wt%.
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33 **4.4.2 Further insights on the influence of process parameters on final porosity and activated** 34 **carbon yields** 35

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38 As it can be seen from Table 6 an important parameter in the activation process is the burn-off, which
39 can be calculated with the following simple equation [101]:
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$$45 \text{BO} = (m_i - m_f) / m_f \quad (4)$$

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48 Where m_i is the initial mass (d.a.f.b.) and m_f is the final mass (d.a.f.b.) after activation. An interesting
49 analysis on the effect of burn-off on the final properties of the activated carbon is reported in [102]. As
50 we know the burn-off is dependent on both process variables: temperature and time of activation. It was
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observed that the BO has the most important influence on the development of the porosity, this is clearly shown in Figure 15.

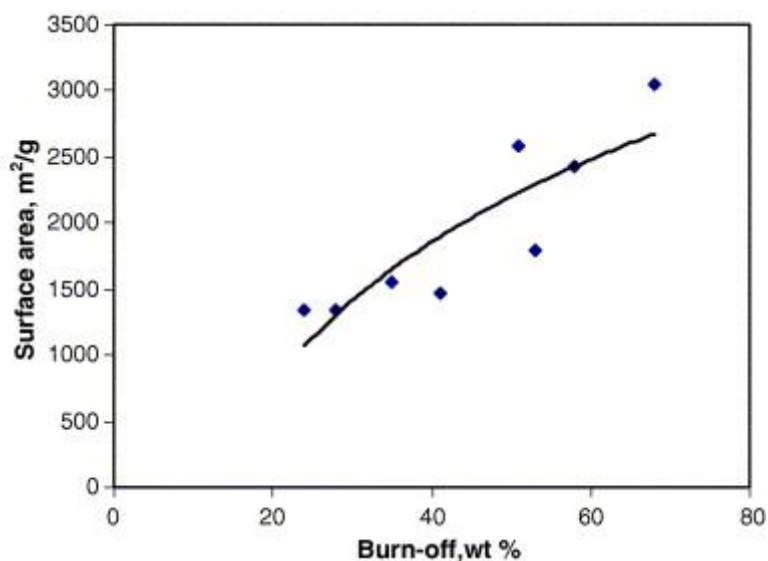


Figure 15: Influence of the burn-off on the development of the surface area in olive stone activated carbon [102]

In the experiments of Zabanotou et al. [102] it is also shown that the methylene blue adsorption is proportional to the surface area of the charcoal, these experiments so confirm that BET analysis is important to understand what will be the adsorption capacity of the produced carbon.

4.4.3 Lignin and lignin-rich substrates modification processes

The most interesting way to modify the charcoal is to functionalize its surface as it is explained in [61]. In fact, the charcoal produced through pyrolysis and hydrothermal carbonization has generally a low number of functional groups, such as: C-O-C, C=O and OH. It has also a limited surface area and porosity. Surface modification of the charcoal can be performed through the following processes:

- oxidation
- amination

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- sulfonation

The first modification can be performed using the following agents: H₂O₂, O₃, KMnO₄ and HNO₃ [103-106]. These reagents are useful if we want to introduce into the char functional groups such as carboxyl, phenolic hydroxyl, lactones and peroxides. Sulfonation is usually performed using H₂SO₄ and its derivatives (e.g. fuming H₂SO₄ and ClSO₃H). Sulfonation is performed to introduce SO₃H groups in the charcoal [107-111]. Amination is usually performed through NH₃ treatment at high temperatures [112-114]. Other possible modifications include the use of amino-containing compounds, such as: 3-chloropropylamine, tris(2-aminoethyl)amine, and polyethylenimine. These treatments are more environmentally friendly than the treatment with NH₃ because the production of NH₃ is highly energy intensive and also polluting. Amino loaded charcoal has the important advantage of being able to chemically retain acidic pollutants.

4.4.4 Modification of lignin through the production of magnetic charcoal

Another way to modify lignin is to produce from it magnetic charcoal. The process flow is shown in figure 16, as it is reported in [115].

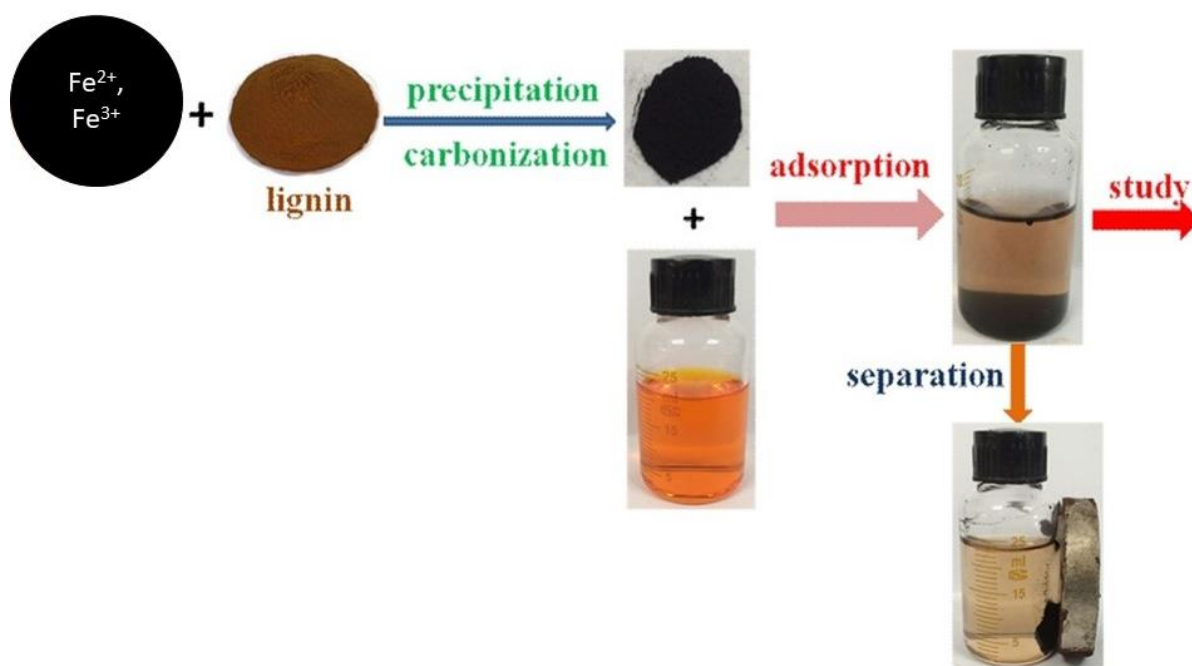


Figure 16: Magnetic lignin-based carbon nanoparticles production process, as reported in [115]

In the particular case 5.4 g of ferric chloride hexahydrate are mixed together with 3.5g of ferrous sulfate heptahydrate in 100 mL deionized water. Also 30 mL of 10 wt% ammonia are added to the solution and the temperature is increased to 90°C. 3g of Lignin were added to the solution, using again ammonia to regulate the pH and incubating the solution at 90°C for 2 h. the detailed procedure is found in [115].

Once the reaction is completed the magnetic particles (made of lignin coated with iron oxide) were separated from the solution using a permanent magnet, they were then washed with ethanol and dried.

Then the particles were carbonized in nitrogen atmosphere at 500°C for 3 hours. The adsorption capacity was tested using wastewaters polluted with methylene orange and the performance was interesting: 113 mg/g of adsorption capacity was reached, which proved to be quite high respect to the literature. This sorbent in fact has two big advantages:

- on one hand the nanoparticles and dissolve in the solution very efficiently and adsorb the polluting substances;

1 - on the other hand being magnetic, the sorbent can also be easily separated from the wastewater and
2 recycled.

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5 Similar other experiments have been put in place by [116], using lignin and dopamine they reached an
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7 adsorption capacity on Cr(III) equal to 44.56 mg/g which has proven to be quite higher respect to other
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9 sorbents developed in the literature. Even more interesting is the final price of the sorbent, which is
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11 equal to about 500 \$/t so more than half the price of conventional activated charcoal.

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14 Other researchers [117] have produced composite magnetic lignin with good adsorption performances
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16 on Congo Red (198.24 mg/g) and Titan Yellow (192.51 mg/g).

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19 Also red mud and lignin wastes can be used as raw materials to produce metal biochar composites [118],
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21 If the production of magnetic carbon and aerogels from lignin is quite common [119-123], the
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23 production of magnetic carbon from digestate and olive stone is more rare.
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30 **5. The adsorption process theory**

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33 Adsorption can be defined in [45] as the enrichment of a compound from a fluid phase on the surface
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35 of a solid (which in this case is the activated charcoal). Generally, the adsorption efficiency is
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37 proportional to the surface area of the sorbent (at least this is valid if we are talking about physisorption).
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39 If we consider the adsorption process from a thermodynamic point of view, we have to take into
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41 consideration that in the adsorption process the Gibbs free energy is not only a function of the system
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43 temperature, pressure and composition (expressed in number of moles), but also is a function of the
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45 surface (indicated with the letter A). So, the change in the Gibbs free energy equation is given by:
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$$49 \quad dG = -SdT + Vdp + \sum_i \mu_i dn_i + \sigma dA \quad (5)$$

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52 where S is the Entropy, V is the volume, μ is the chemical potential and σ is the surface free energy,
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54 which can be indicated also as the surface tension. When adsorption happens, the surface free energy
55
56 decreases from a value of σ_{ws} (surface tension at the interface between the water and the activated
57
58 carbon) to the value of σ_{as} (surface tension between adsorbate and solid). The difference between the
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1 two surface tensions is proportional to the amount of compound which is adsorbed and it is indicated
2 as the spreading pressure, π .

$$3 \quad 4 \quad 5 \quad \sigma_{ws} - \sigma_{as} = \pi > 0 \quad (6)$$

6
7
8 The variation of enthalpy and the variation of entropy can be used to define the variation of the free
9 energy during adsorption, assuming adsorption is a spontaneous process:

$$10 \quad 11 \quad 12 \quad \Delta G_{ads} = \Delta H_{ads} - T\Delta s_{ads} < 0 \quad (7)$$

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16 The reaction is negative because the adsorption process is considered to be spontaneous. Given that the
17 adsorption process generally produces a decrease in the disorder of the system, the change of entropy
18 is usually negative. If the change in entropy is negative, equation 7 implies that the change of enthalpy
19 should be negative also, and so the reaction is exothermic (it releases heat in the environment). The
20 adsorption enthalpy is an interesting parameter, which allows us also to evaluate the difference between
21 different adsorption processes (e.g. chemisorption and physisorption). Physical adsorption is usually
22 due to van der Waals forces (such as: dipole-dipole interactions, dispersion forces, induction forces).
23 These interactions are relatively weak (the enthalpy in this case can be evaluated to be lower than 50
24 kJ/mol). On the other hand, chemical sorption is based on chemical reactions which retain the adsorbate
25 on the surface of the activated carbon (in this case the enthalpy is higher than 50 kJ/mol).

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29 The adsorption process efficiency can be defined by the adsorption capacity, expressed in
30 mg_adsorbate/g_adsorbent. This parameter can be referred to also as adsorbent loading. The loading or
31 the adsorption capacity depends not only on the parameters of the adsorbent (such as its surface area
32 and its functional groups) but also on the adsorption parameters (such as pH, temperature, pressure etc.).

33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 **6. Wastewaters treatment**

53 54 55 **6.1 Adsorption performance of activated carbon from lignin**

56
57 While some important reviews have been already published on the sorption capacity of activated
58 charcoals produced from olive stones (as it will be shown in paragraph 6.2), no literature review is

available on the adsorption of pollutant on activated charcoal produced from lignin. Some reviews are available on the adsorption which happens directly on the charcoal produced from lignin, without activation [124, 125].

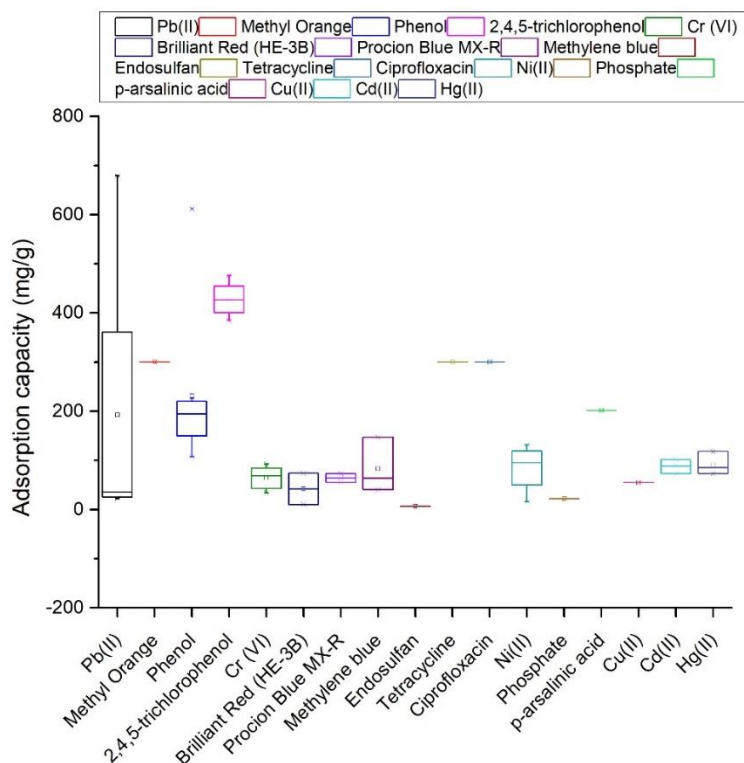


Figure 17: Adsorption capacity of activated carbon produced from lignin

From Figure 17 we see that the adsorption is very variable, depending on the characteristics of the activated carbons and on the process parameters. Generally, higher adsorption is measured for activated carbons with higher surface areas. Activated carbons produced from lignin have also important variations in the adsorption capacities of phenol, reaching very high values for 2,4,5-trichlorophenol.

6.2 Adsorption performance activated carbons from digestate and olive stone

As far as olive stone are concerned in the review presented in [100] it can be seen that the activated carbons produced from olive stones have very good adsorption performance, if compared with commercial activated carbons.

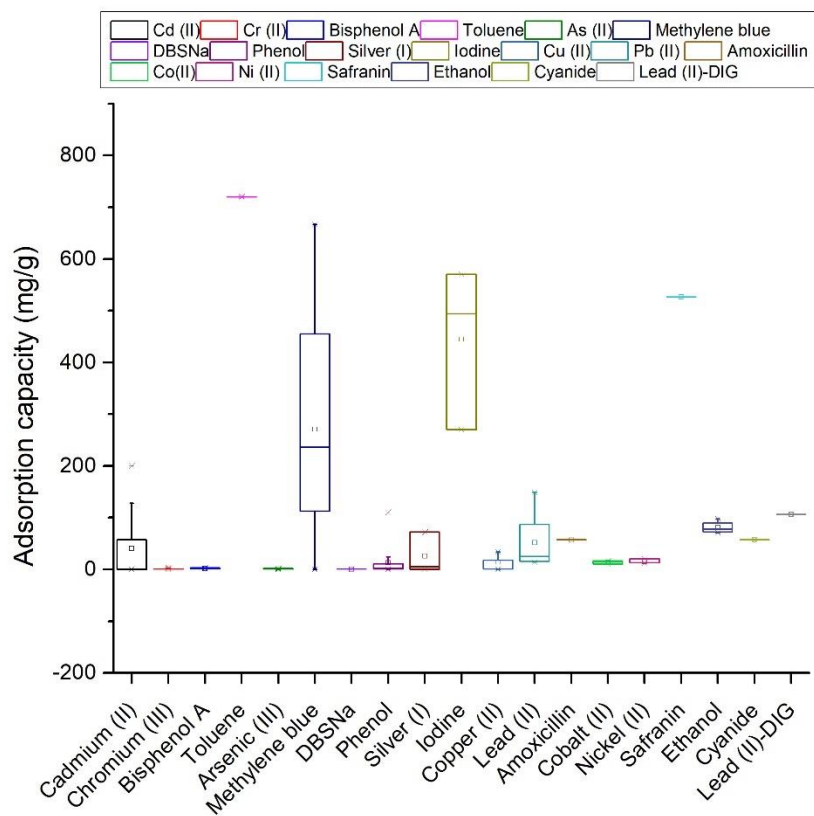


Figure 18: Adsorption capacity of activated carbons produced from olive stones and digestate [100]

The detailed adsorption capacities proposed in Figure 18 are taken from [100], which is a complete review on the performance of sorbents produced from olive stones. According to what is reported in [100], olive stone is a very competitive raw material for the production of activated carbon and can have interesting performances. Particularly interesting is the adsorption of phenolic compounds with activated carbons. This is the topic of the SURFOLY project recently founded under the PRIMA EU funds and managed by the University of Perugia.

7. Technical and Economic analysis on the production of activated charcoal from lignin rich biomass

7.1 Background

In the work of [126] it is proposed a detailed analysis on the production of alternatives to petroleum-based polymers through technical lignins; where with the term “technical” the following types are indicated:

- lignosulfonates, which are obtained as byproducts of sulphite pulping;
- Kraft Lignin, which is produced from wood kraft pulping process;
- soda lignin, which is generated in the soda pulping process;
- hydrolysis lignin, obtained as a subproducts of second-generation ethanol production;
- organosolv lignin, which is produced from pulping processes that employ organic solvents to separate cellulose from lignin.

Dealing with the identification of best commercial products to be produced using lignin, a screening study [127] has selected the following promising products: phenol produced from Kraft lignin to be used in the synthesis of phenol-formaldehyde (PF) resins; polyols produced from lignosulfonate to be used in the synthesis of polyurethane (PU) foam; carbon fiber produced from organosolv lignin. In [127] it is presented also an interesting figure in which it is clearly identified the market price and the market size of different added value products which can be produced from lignin. The diameter of the bubbles in the graph is given by the product of the market value and the market price of the added value product. The percentage associated to each bubble represents the market share of the product respect to the total sum of the market shares of all the products. Three categories of final uses can be identified:

- high volume and low value (eg. bioenergy);
- low volume and high value (eg. carbon fibers);
- medium volume and medium value (eg. phenol).

The dotted square in figure 19 represents the most interesting productions which can give the highest return. BTX, bitumen and phenols represent the markets with the highest volumes. Lignosulfonates can be successfully transformed in vanillin, additives and dispersants.

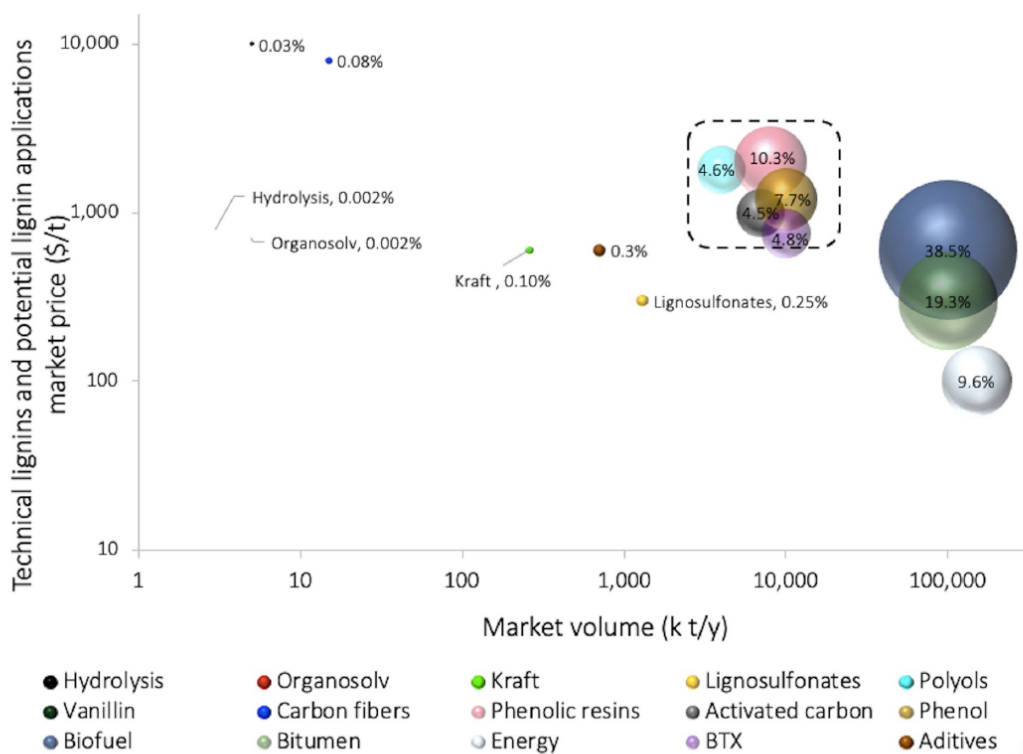


Figure 19: Potential market of added value products produced from lignin [127]

Other useful added value products are thermoplastics. The entire annual production of lignin could cover about 2% of the global consumption of plastics in the world [128]. The market of thermoplastics in fact is characterized by an annual demand of 280 Mt/y [129].

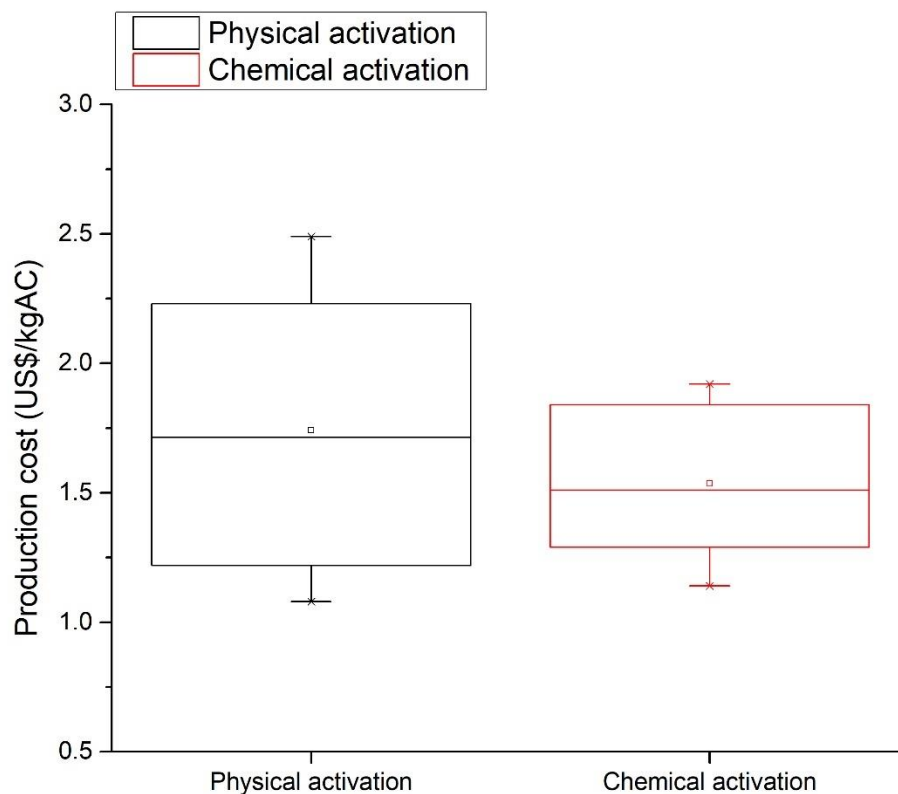
7.2 Activated charcoal production costs

An important work on the estimation of the production costs of activated carbons is reported in [33]. The analysis starts with the identification of potential yields and also of product quality (based on surface area), see table 7.

Table 7: Activated carbon yields and surface areas

Raw material	Type of activation	Activated carbon yield (wt%)			Surface Area (m ² /g)
		Pyrolysis yield	Activation yield	Total carbon yield	
Wood	Activation with steam	25	50	12.5	800
Used tires	Activation with steam	30	50	15	500
Pet coke	Activation with steam	90	70	63	1000
Carbon Black	Activation with steam	95	50	47.5	500
Charcoal	Activation with steam	90	50	45	900
Lignite	Activation with steam	52	30	15.6	800
Wood	Activation with KOH	N/A	N/A	22	800
Used tires	Activation with KOH	N/A	N/A	20	700
Pet coke	Activation with KOH	N/A	N/A	45	3000
Carbon black	Activation with KOH	N/A	N/A	60	500
Charcoal	Activation with KOH	N/A	N/A	44	2000
Lignite	Activation with KOH	N/A	N/A	25	2200

The final costs of the produced activated carbon for a plant with production capacity of 4.5 t/day are reported in figure 20. The two alternatives are compared (with the assumption that the raw material has zero cost of supply): chemical activation (with KOH) and physical activation (with steam). We can see from figure 20 that in general chemical activation has better performance than physical activation, this is due to the higher yields. The payback period of the plants range from 3 to 12 years, depending on the feedstock. The best performances in physical activation are achieved by pet coke: 3.12 years. The best performance for chemical activation are achieved by carbon black: 3.94 years.



8. Conclusions

Lignin used as a precursor for the preparation of magnetic activated charcoal has been investigated and reviewed based on relevant articles published. Magnetic activated charcoal adsorbents are highly efficient for the removal of pollutants such as heavy metal ions, dyes, and organic and inorganic compounds. In past years a lot of low-cost biomass-based adsorbents has been synthesized and characterized, such as commercially activated carbon, but for large scale application they showed many complications, such as the separation process of activated carbon. On the other hand, magnetic activated materials showed great scope and application for wastewater treatment because of their physicochemical properties, large surface area and volume, great affinity toward pollutants and easy separation process. Based on detailed reviewed research articles it is concluded that the lignin based magnetic activated materials such as carbon nanotubes, nanoporous materials, are highly efficient for the wastewater treatment from small scale to large scale.

Acknowledgement

This work is supported by the e-COST European Cooperation in Science and Technology, UK Biochar research center at Edinburgh University UK, the BioCarbUp project at SINTEF Energy Research and Biomass research center at Perugia University Italy.

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