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A Review: Coffee and Tea Potential Materials for Carboneous Material Synthesis

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Abstract

Coffee and tea are classified as the biomass due to their characteristic lignocellulosic main content, including lignin, cellulose, and hemicellulose. However, their each most content is cellulose and lignin, respectively. Both coffee and tea have been used for preparation of biochar, activated carbon, and CNM/CNS. Biochar and activated carbon (AC) have different chemically structure, especially related to oxy groups and hydrocarbon aliphatic chain. CNM can has same or different crystal structure with activated carbon depend on the preparation way. As the adsorbent, activated carbon had higher average specific surface area (11x) and higher average pore volume (6X) than biochar. In other side, it had higher average specific surface area (4X) but same average pore volume compared to CNT. Using 3 different activators (H_3PO_4, KOH, CO_2), hydrothermal pyrolysis produced the activated carbon which had 86X higher specific surface than without activator. In other side, it gave 6X higher specific surface area than slow pyrolysis method with those 3 activators. For the same metal cation adsorbate (Cu^{2+}), each maximum adsorption ratio of AC to biochar, AC to CNT, and NaOCl-modified CNT to AC was about 2.4. For 4 different metal cations (Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}), the average maximum adsorption ratio of the functionalized CNT to AC was about 3.2.

Key words: Biochar; activated carbon; carbon nanomaterial; carbon nanostructure; coffee; tea.

1. Introduction

Coffee and tea are 2 drink types which are popular in Indonesia due to their characteristic tastes and colors. Even tea is one of the most drinks in the world, with a consumption in 2020 about 6.3 billion kilograms and estimated about 7.4 billion kilograms at 2025 [1]. Both materials have been used to prepare biochar [2-5], activated carbon [6-9], and CNM/CNS [10-13]. The chemical reasons why coffee and tea can be used as the carbon precursors are discussed in this paper.

Biochar, activated carbon, and CNM are the porous materials which have different porosity and surface functional groups as consequence of the different synthesis methods. Comparison of application for the three materials are given to understand how effect of their properties toward their different performances. The different synthesis methods are also described to give the real examples.

2. Tea and coffee as biomass sources of carbon precursor

Biomass is an organic complexe or organic solid product of organism and provided in the nature. Various waste such as manure, pulp waste, lumpur, various industry waste can be categorized as biomass because they can be processed to be energy. Generally, biomass is derived from product fraction which is biodegradable, agriculture waste, animal, fishery, and aquaculture [14]. Biomass or called bioresource is all organic substances derived from green plants which their molecules are destroyed after processes of digestion, burning, or decomposition [15]. Biomass is an organic material obtained from the photosynthesis process, either in the form of products or waste [16]. Tea is one of biomass sourcess, including tea leaves [17-20], stem, branches, and roots [21]. Coffee is also the biomass source, including spent coffee grounds [7,22], coffee dreg [16], coffee residue [23], coffee husk, mucilage, parchment, and silverskin [24].

The main contents of biomassa is cellulose, hemicellulose, and lignin, i.e. 40-60%, 10-30%, 20-30%, respectively [14]. Coffee dregs (Coffea arabica L.) contains hemicellulose which is composed of mannose (21.2%), galactose (13.8%), and arabinose (1.7%), also cellulose which consists of glucose (8.6% b/b). Coffee dregs also contain proteins (glutamic acid, leucine, glycine, valine, phenylalanine, alanine) and ash minerals, such as potassium, phosphorus, magnesium, and calcium [16]. As general biomass, coffee waste contain lignocellulosic substances with the highest cellulose amount of cellulose [24]. Tea leaves are composed of cellulose, hemicellulose, lignin, polyphenols, and proteins [4]. Among all those chemical contents, the lignocellulosic substances (lignin, hemicellulose, and cellulose) which are important for carbon preparations. Even each lignin [25-29], cellulose [30-33], and hemicellulose [34] have been used individually as carbon precursors for synthesis of carboneous materials. The lignocellulosic contents in various coffee and tea biomass are listed in Table 1 and Table 2, respectively. Based on both table the most average content in coffee and tea are cellulose and lignin, respectively. Lignin, cellulose, and hemicellulose have different range temperatures of thermal reactions in pyrolysis process, including dehydration, degradation and decarbonization reactions [35]. These different thermal characteristics make them create different characteristics of the

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carbon products. For example, individually lignin produced the biochar which had more C=O and C-O functional groups and much more percentage yield at the same pyrolysis temperature range of 500 – 800ºC than cellulose [36].

Table 1: Lignocellulosic contents in coffee biomass

No.	Coffee biomass	% Cellulose	% Lignin	% Hemicellulose	References
1.	Pure SCG	49.8	31.9	15.4	[46]
2.	Blended SCG	48.9	36.7	10.5	[46]
3.	Spent coffee ground	47.3	29.3	19.0	[46]
4.	Spent coffee ground	47.3	24.6	19	[47]
5.	Cofee husk	43.0	9.0	7.0	[46, 48]
6.	Coffee cherry	27.6	13.7	12.5	[24]
7.	Coffee husk	43	9	7	[24]
8.	Spent coffee ground	23.6	17.8	12.1	[24]

Table 2: Lignocellulosic contents in tea biomass

No.	Tea biomass	% Cellulose	% Lignin	% Hemicellulose	References
1.	SGT	21.5	32.7	34.0	[46]
2.	Tea waste	25.4	25.7	31.1	[46]
3.	Green tea	14.26	52.44	33.33	[49]
5.	Black tea	28.13	61.34	10.53	[49]

3. Definition

Biochar is a solid which is rich of carbon atoms and produced by pyrolysis or carbonization of biomass without or limited oxygen gas. The activated biochar is the biochar which is prepared by involving activation process [14]. Biochar is a carbon-rich solid material produced by thermal decomposition of diverse waste biomass species under oxygen limited conditions [37]. Biochar is a porous carbonaceous solid material with a high aromatization degree, high decomposition resistance, formed by thermal breakdown of plant or animal biomass in thermal decomposition without oxygen [38]. Biochar is a carbonaceous material obtained by pyrolysis biomasses such as wood waste, sewage sludge, plant leaves, and crop residues, using an inert atmosphere or oxygen-free [39].

Biochar is obtained by biomass pyrolysis, whereas activated carbon is produced by chemical or physical activation of the biochar [40]. Activated biochar is biochar which is prepared by involving activation process [14]. Therefore, activated biochar and activated carbon is same material. Carbon nanomaterial (CNM) or carbon nanostructure (CNS) is a carbon material which has particle size of 1–100 nm [41,42].

4. Characteristics

There are differences of biochar, activated carbon, and CNM properties. First, based on material solid particle size, the biochar and activated carbon are not nanomaterials, whereas CNM is the nanomaterial. Nanomaterial can be verified by several methods, including dispersion test : the nanomaterial will be dispersed [11]. However, the activated carbon can be changed to CNM by grinding, blending, mixing, stirring or sonicating. Formation as colloid is needed for application of the CNM/CNS as the additive in fertilizer solution to make easy to spread it on the farm land [10-12,43]. The other methods are XRD by calculating the crystallite size based on FWHM, SEM and TEM through particle size on their images [41].

The second difference is about the crystal structure. Both biochar and activated carbon are mixture of amorph and graphite structure. Graphite is a carbon structure which is constructed by layers of graphene with space between layer is 3.35 Angstrom. In other side, the amorphous carbon has space between layer of 3.44 Angstrom [44]. Those spaces can be detected from d-spacing of the main peak of the activated carbon diffractograms [41]. Imagination about graphite and amorphous carbon are presented in Figure 2 based on HRTEM images in Figure 3. CNM has various crystal structures such as graphene, CNT, CNF, CND, CNH, fullerene, etc. The CNM structures are presented in Figure 4.

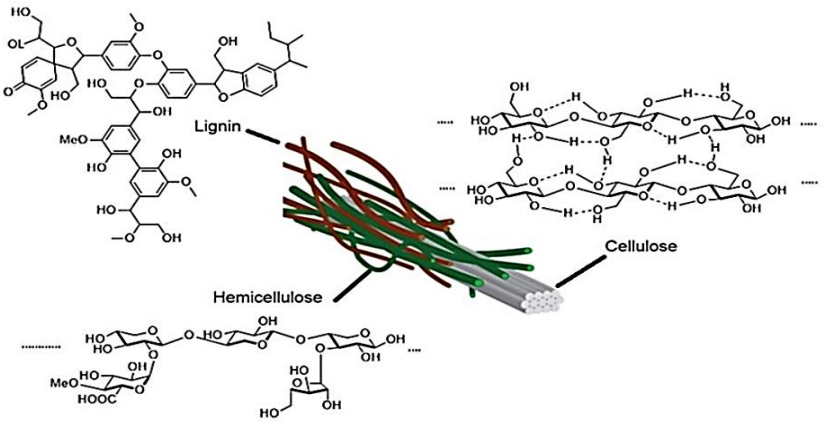

Fig. 1. Lignosecclulosic substances in biomass [45].

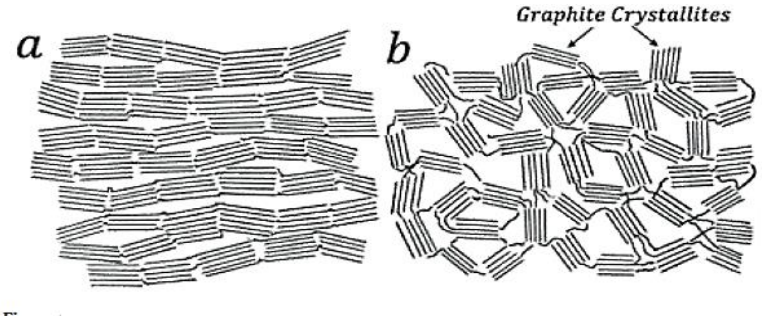

Fig.2. Structure of graphite and non graphite [50].

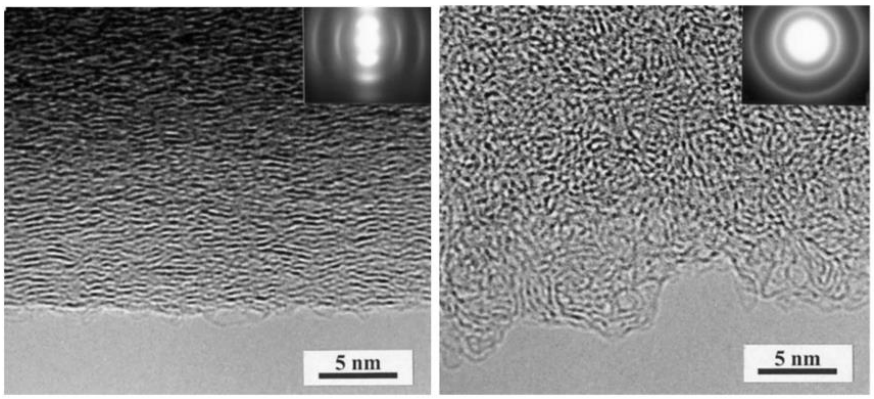

Fig. 3. HRTEM images of antrachen based graphite and sucrose based non graphite [51]

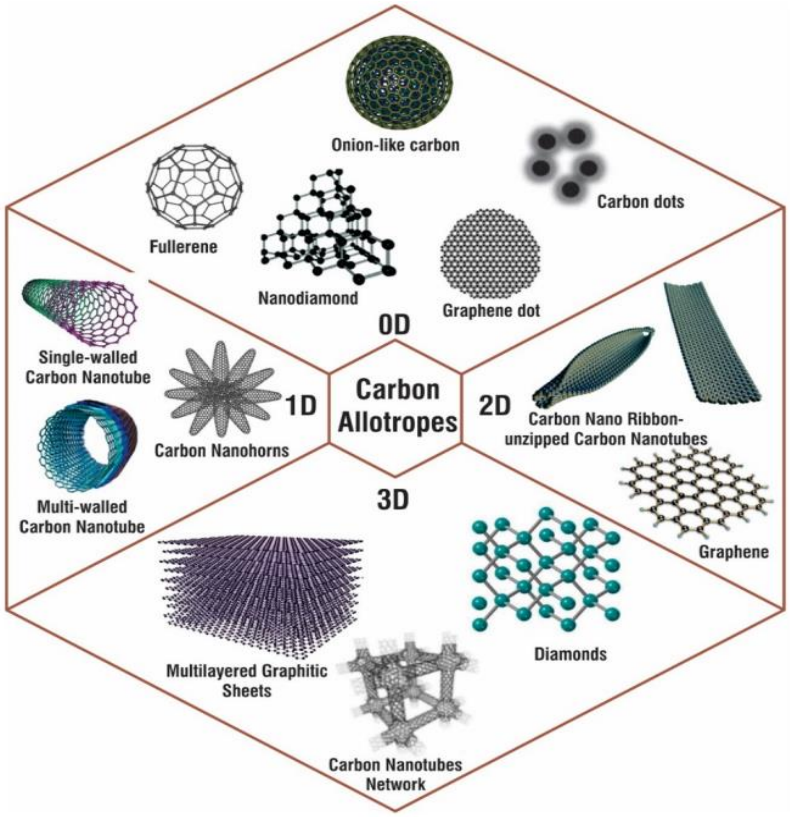

Fig. 4. CNM atom models in various dimension [52].

Based on surface area, AC is a carbonaceous material with better pore structure, larger specific surface area than biochar as the consequence of activation treatments, including physical activations and chemical activations [53]. Among all chemical activators, potassium hydroxide (KOH) is one of the most effective for obtaining large surface area of carbons. For example the activated carbon from birch wood by KOH activation using tube furnace under nitrogen gas stream had S_{BET} of 3160 m^2/g [54]. The activated carbons from spruce cone, silver spruce cone and full spruce cone with KOH activator, same tube furnace under argon stream have large specific surface area (SSA) of 3565, 3497, and 3067 m^2/g, respectively [55]. However, the opinion about KOH is right for slow pyrolysis, but not for hydrothermal pyrolysis [53] as listed in Table 3.

Table 3: Effect of activator toward porosity of the activated carbon

Pyrolysis type	Activator	S_{BET} (m^2/g)	V_p (cm^3/g)	References
Hydrothermal	No activator	23.1	0.1175	[53]
	H_3PO_4	2595	1.625	[53]
	KOH	857	0.3435	[53]
	CO_2	2475	0.1445	[53]
Slow pyrolysis	No activator	13.7	0.006	[53]
	H_3PO_4	357	0.1565	[53]
	KOH	1325	0.483	[53]
	CO_2	343	0.142	[53]

Lower surface area obtained by usage of KOH as the chemical activator in hydrothermal method is probably related to presence of water solvent which dissolve the KOH and lower temperature of hydrothermal method which is impossible to make dry condition in the autoclave. Both makes KOH can not worked as well as in the dry pyrolysis as the template of pore. In other side, phosphoric acid and CO_2 worked better in presence of water solvent in chemical activation reaction than worked as the pore template.

Comparison of specific surface area and pore volume for the 3 different carbons can be seen in Table 4. Table 4 shows that CNM (CNT type) has larger specific surface area than biochar. It is probably caused by smaller size of solid particle. However, compared to activated carbon CNT have much lower specific surface area than activated carbon. It is possibly also caused the much smaller solid particle size which unfortunately reduces pore numbers due to destructed pores by reducing of solid particle.

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Table 4: Specific surface area and pore volume of CNT, biochar and activated carbon

No.	Carbon type	SSA (m^2/g)	V_p (cm^3/g)	References
1.	MWCNT	175	0.664	[56]
2.	SWCNT	557	1.043	[56]
3.	Biochar (1)	85	0.057	[56]
4.	Biochar (2)	142	0.185	[56]
5.	Powder Activated Carbon	1255	0.757	[56]
6.	Granule Activated Carbon	1354	0.778	[56]

Chemically, biochar has both lower oxygenated functional group density and higher content of aliphatic hydrocarbon probably due to incomplete cellulose and lignin combustion. Activation makes formation of more aromatic structure and oxygenated functional groups on activated carbon, as shown in Figure 5 and 6.

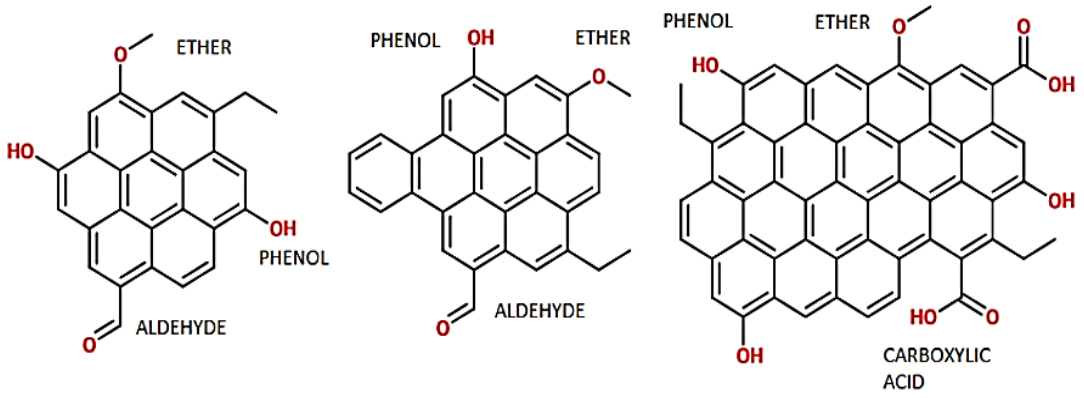

Fig. 5. Structure of biochar based on different temperature and pyrolysis type , from left to right: fast pyrolysis 500ºC, slow pyrolysis 500ºC, gasification 760ºC [57].

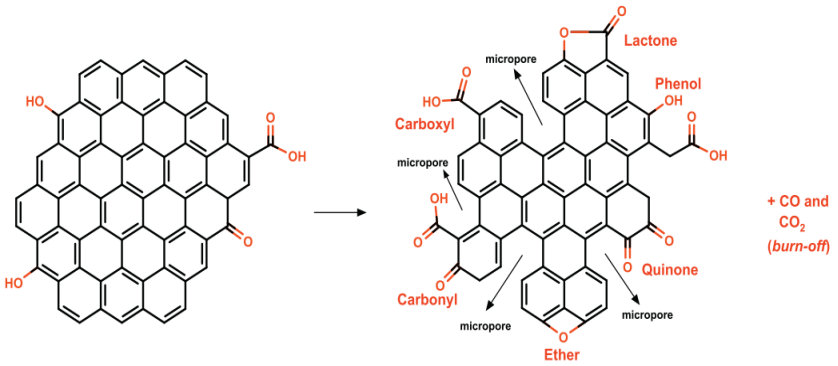

Fig. 6. Improvement of functional group before and after thermal air oxidation [58].

Number of aromatic structure in biochar also is affected by production route. Thermal pyrolysis route gives higher density of aromatic structure than hydrothermal pyrolysis, such as shown by Figure 7 and 8. Dry pyrolysis tends to work better in formation of the aromatic structure network than hydrothermal. Principally, presence of H_2O in the hydrothermal pyrolysis can make the activator enter into all part of the precursor. However higher temperature in the dry pyrolysis makes the thermal reactions and the pore templating in dry pyrolysis process more effective than in the hydrothermal one.

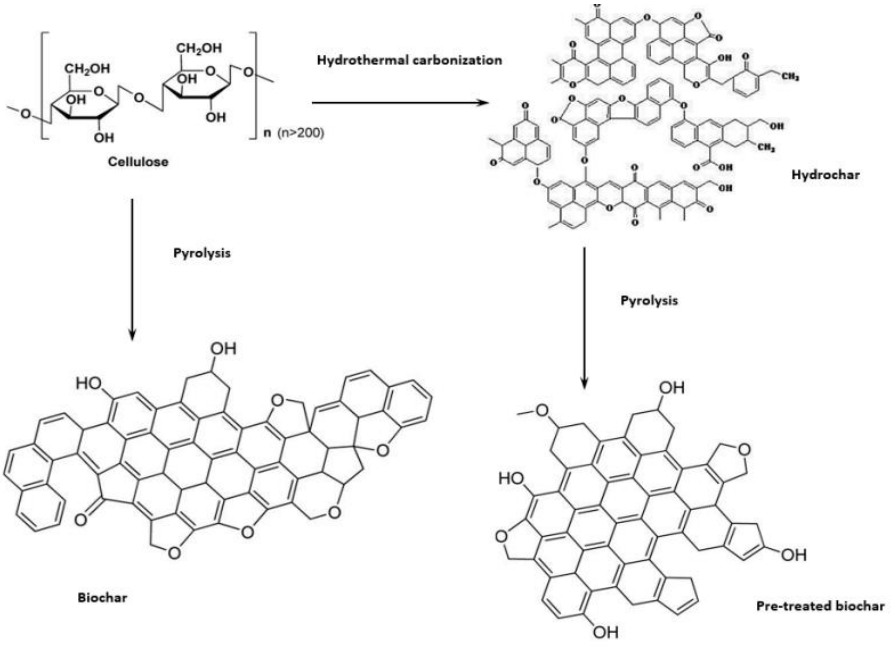

Fig. 7. Structure of biochar based on different method : thermal pyrolysis VS hydrothermal pyrolysis followed thermal pyrolysis [59].

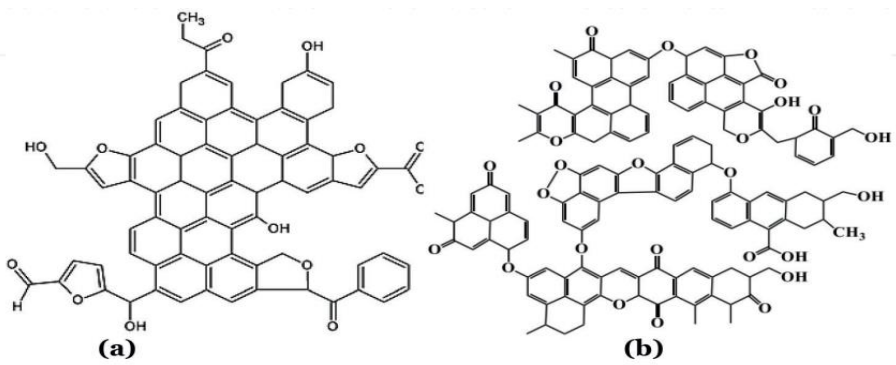

Fig. 8. Chemical structure : a) pyrochar and b) hydrochar [60].

The surface area of biochar are also affected by the pyrolysis temperature. The formation of microstructure and surface area of biochar increase by increasing pyrolysis temperature. The opened internal structure of biochar was observed for pyrolysis temperature ≥ 450 ◦C [61]. For example, by using miscanthatus as the feedstock, the surface area of the biochar increased from 2.41 to 382 m^2/g by increasing of temperature from 400 to 600°C [62]. With same tendency but higher value is about activated carbon, using blue coke powder precursor, the surface area improved from 75.50 to 636.91 m^2/g and total pore volume of 0.059 to 0.363 cm^3/g for increasing of temperature from 500 to 1000°C [63]. Fig 9 describe that temperature affected the pore and oxy functional group formation. For range temperature more than 450°C, the higher temperature the larger numbers of the pore and oxy groups the less remain unpyrolyzed organic substances.

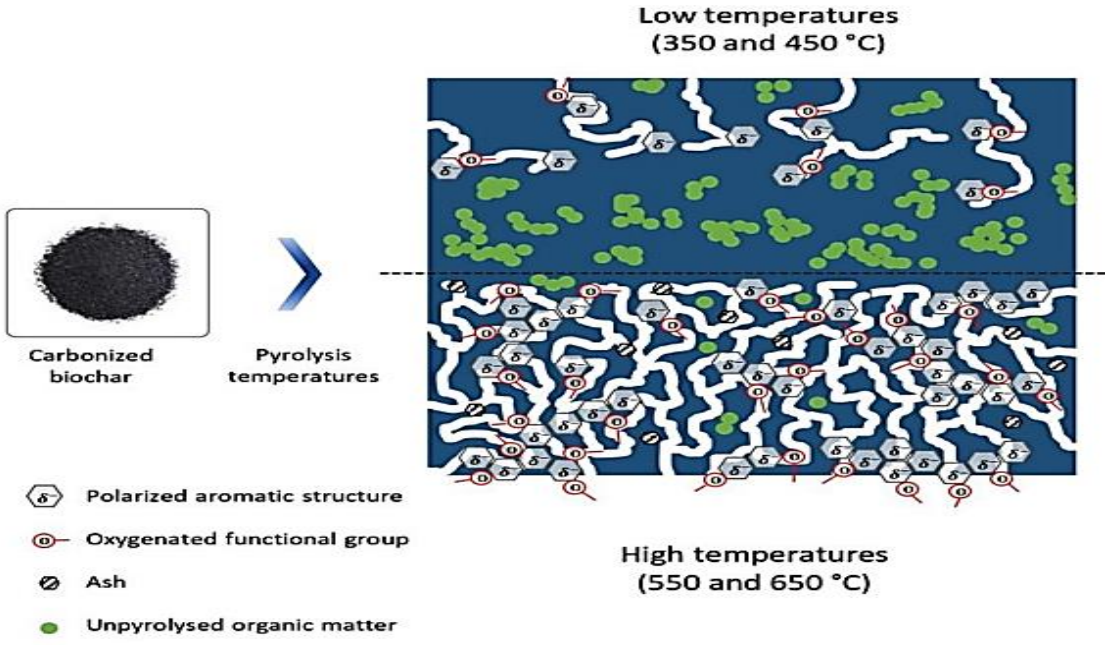

Fig. 9. Effect of temperature on porosity, surface oxy functional groups and unpyrolized organic mater of the biochar [61].

4. Applications

This session presents applications of biochar, activated carbon, and CNM as individual and in comparisons. For the comparison study, their different performances are discussed based on chemical and physical characteristics provided in the same references or predicted based on data of characteristics in session 4 as long as possible. Biochar can be applied as catalyst, energy storage such as electrode, soil amandement to increase soil fertility and quality, adsorbent of organic and inorganic contaminant in the soil and aquatic environment, and composting to enhance microbial population and minerals [38]. Biochar in compost with sewage sludge decreased the abundance of Escherichia coli and Salmonella ssp [64]. The biochars made from woody or leafy material have high porosity and improve water content in the soils [65]. Biochar reduce greenhouse gas emissions from the soil and remove pollutans of heavy metals, pigments, pharmaceuticals, aromatic and polyaromatic hydrocarbons, also pathogenic organism from aqueous solutions [39].

Activated carbon widely is used as adsorbent, catalyst and catalyst supports. The matchness of adsorbent pore size and adsorbate size determines effectivity of adsorption [23]. Carboxyl, carbonyl, lactone, phenol and quinone are the main functional groups of the activated carbon which are responsible to adsorb pollutants [66]. Activated carbons (ACs) are widely also applied in medical, electronic and environment products [6].

CNS have developed tremendous interest in the world because of their remarkable structural, electrical, optical, thermal, mechanical and chemical properties. By designing novel arrangements such as ribbon, hybrid, polymer, dopping, and hetero-structures, the carbon nanomaterials were moved by researches of various disciplines [67].

CNS such as CNT and graphene were used as Pt and platinum oxide nanoparticles matrix to control their size, distribution and amount of the deposited particles. As matrix, CNT provides additional advantages, such as a conductive characteristics, large surface area, fast response time, high electron transfer rate, easy immobilization [68]. CNTs have attractive electronic and optical properties, small size, good biocompatibility, good surface function, and high reactivity. Therefore, CNTs can be widely used in the fields of energy, biomedicine, electronics, photoelectricity, analysis, and catalysis [69].

Compared to activated carbon, biochar makes the anaerobic metabolism of the biofilm higher and has a longer lifetime than GACs in bioelectrochemical systems. Therefore, the wood-derived biochar has been studied to replace GACs in contaminant removal applications [37]. Increasing applications of biochar are determined by its characteristics such as surface

area, pore volume, pore size, pH, cation exchange capacity (CEC), electrical conductivity (EC) and surface functional groups, as well as its sustainable, easy and low cost production process [39].

Comparison of the three materials in their applications as adsorbents have been conducted by some research. For example, removal of Pb(II) cations by CNT, AC (activator of H_3PO_4) and AC (activator of KOH). After adsorption process in various times (1, 24, and 72 h), the adsorption effectivity showed in sequence of AC (KOH) > AC (H_3PO_4) > CNT. Physically, data of specific surface area (S_{BET}) and pore volume characterizations shows in the same sequences. XPS characterization reported that chemically AC (H_3PO_4) and CNT had surface functional groups of C-O and O-C=O in similar intensities [70]. The Pb(II) cation is Lewis acid and those oxygenated functional groups are the Lewis base which attracted the Pb(II) cations in the adsorption process. Therefore, the adsorption difference is probably more affected by difference of the physical properties.

The other comparison is about adsorption of ^{14}C-catechol by various carbons (biochar, AC, SWCNT, and MWCNT) and soil. The sequence of the adsorbed cathecol as follows: SWCNT > MWCNT > AC > biochar > soil. The other experiment, the extracted microbe from the fresh soil by addition of various carbons (0,2 mg/Kg) after incubation at 25°C in the dark for 61 days were in sequence: control = biochar > MWCNT > SWCNT > AC. It means that growth of the microbe in the soil is not affected by biochar but reduced by the other carbons' adsorptions. No characterizations of functional groups, surface area, and pore volume were reported to discuss [71]. However, based on characteristics of AC and CNT in Table 4 it can be predicted that physical properties including specific surface area and pore volume may determine the sequence.

Comparison among the activated carbons with different pyrolysis methods and different activators affect the adsorption capacity of dyes and metal cation, as listed in Table 5. The pyrolysis methods include hydrothermal (HTC) and slow pyrolysis (SP). The used activators are H_3PO_4, CO_2, and KOH. Table 5 confirms that the highest adsorption capacity of the both dyes was achieved by AC (HTC H_3PO_4) due to the lowest AC pH (most acid). Oppositely, the largest one of Zn^{2+} was obtained by AC (SP CO_2) due to the highest AC pH (most base). It means that dyes and Zn^{2+} prefer the AC surfaces with the most acid groups and the least acid groups, respectively. The kind of the oxy groups role in the adsorption capacity can be determined by Pierson correlation coefficient as presented in Table 6. Based on Table 6 the phenolic groups have the most role for adsorption of dyes, whereas the lactonic has the most role for Zn^{2+} adsorption. The imagination of interaction is given in Figure 10.

Table 5: Adsorption capacity of dyes and metal cation by AC with different pyrolysis method and activator (%)

AC	Methylen blue	Acid orange II	Zn^{2+}	AC pH	References
HTC H_3PO_4	92	95	7	3.9	[53]
HTC CO_2	55	47	13	5.4	[53]
HTC KOH	80	50	61	6.2	[53]
SP H_3PO_4	62	52	5	4.2	[53]
SP CO_2	54	52	98	9.5	[53]
SP KOH	91	67	88	7.2	[53]

Table 6: Pierson correlation coefficient of acidic surface groups and adsorption capacity

Oxy groups	Methylene blue	Acid orange II	Zn^{2+}	References
Carboxyl	0.57	0.47	-0.48	[53]
Lactone	0.63	0.11	0.36*	[53]
Phenol	0.8*	0.7*	-0.56	[53]
Total acidity	0.8	0.48	-0.15	[53]

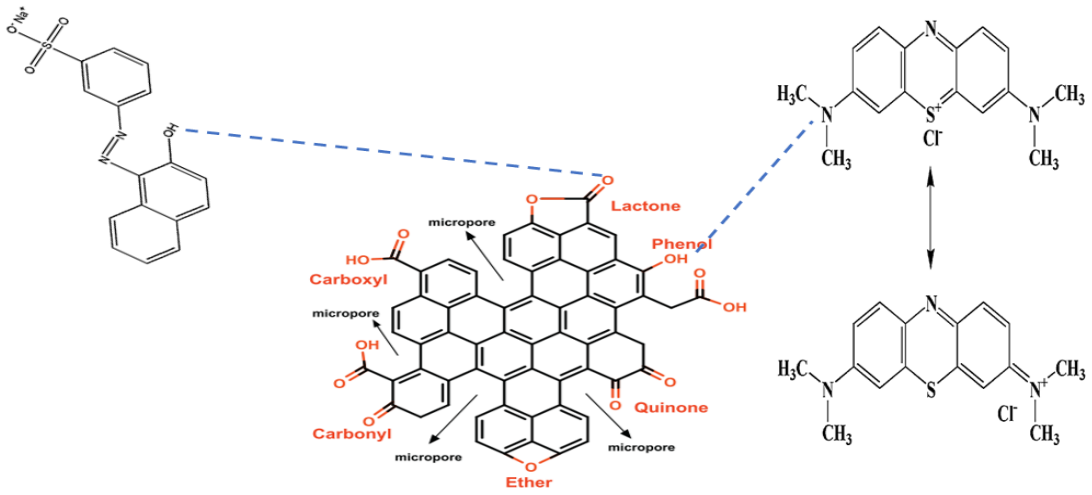

Fig. 10. Chemical interactions of methylene blue – phenolic group(AC) and acid orange II – lactonic group (AC) [58, 72,73]

Adsorptions of multi component solutions by different adsorbents such as biochar and activated magnetic biochar are presented in Figure 11. The multi components include Cu(II)-sulfamethoxazole and Cu(II)-17β-estradiol for adsorption of rice straw biochar and of rice straw activated magnetic biochar, respectively. Figure 11 confirms that the activated magnetic biochar has higher maximum adsorption than the biochar.

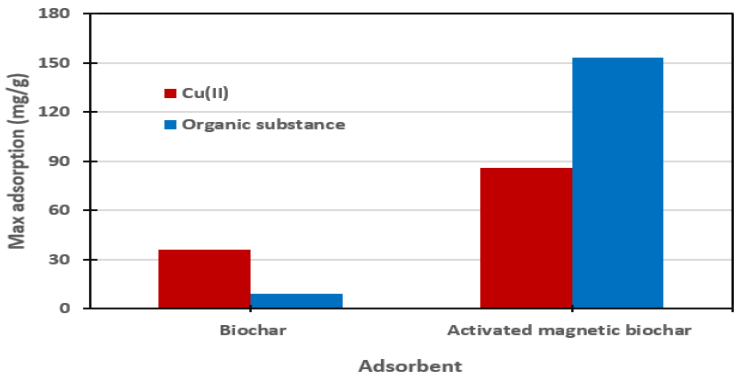

Fig. 11. Maximum adsorption of Cu(II) cations and organic substances by different rice straw adsorbents [40]

Possible adsorption mechanisms of inorganic ions and organic compounds by both adsorbents were designed in Figure 12 to explain the difference of adsorption. The possibilities of mechanisms include adsorption of organic molecules then followed by adsorption of metal cations, adsorption of the metal cations then followed by the organic molecules, and adsorption of the cation – organic molecules as the complexe molecules [40]. The formation of the complexe compound before adsorption or sequent adsorption of metal cations and organic molecules are supported by attraction force of Cu(II) as Lewis acid and the organic molecules as Lewis bases. Based on general comparison properties of the biochar to of the activated carbon, higher adsorption of both Cu(II) cation and the organic molecules by the activated carbon than the biochar might be caused by its higher surface area and pore volume and richer oxygenated functional groups due to activation treatment.

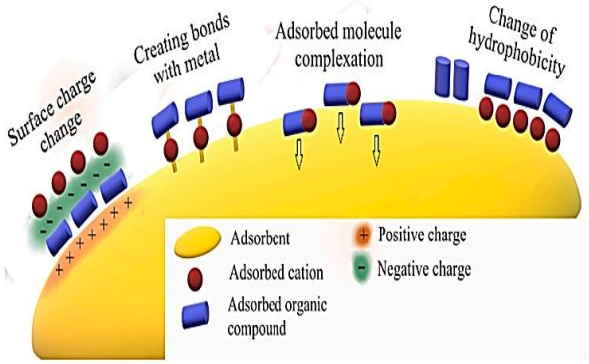

Fig. 12. Possible mechanism of metal cation and organic substance adsorption on activated carbon and biochar surfaces [40]

Comparison of Pb(II) adsorption by biochar VS biochar-CNT composite was reported in Table 7. The Langmuir isotherm model in Table 7 suggests that the interactions between Pb(II) and the sorbents might be mainly the mono-layer adsorption. The maximum adsorption amount of Pb(II) on CS-CNT was significantly higher than that on CS, indicating that CNT can enhance the Pb(II) sorption ability of biochar due to the improved surface area and pore volume. The characterization by FTIR spectrometry confirm similar functional groups of the adsorbent's surfaces including types and intensities. The functional groups which may have the role in interaction with Pb(II) Lewis acid are C=O, -OH, COO-, and C-O Lewis bases can be designed as adsorption mechanism in Figure 13.

Table 7: Adsorption of Pb(II) cations by biochar and biochar-CNT composite

Sample	SSA	Pore volume	Langmuir model		References
	(m^2/g)	(cm^3/g)	q_m(308°C)	R^2	
Pristine biochar	193.52	0.077	1294.44	0.998	[74]
Biochar-CNT	231.6	0.09	1334.65	0.999	[74]

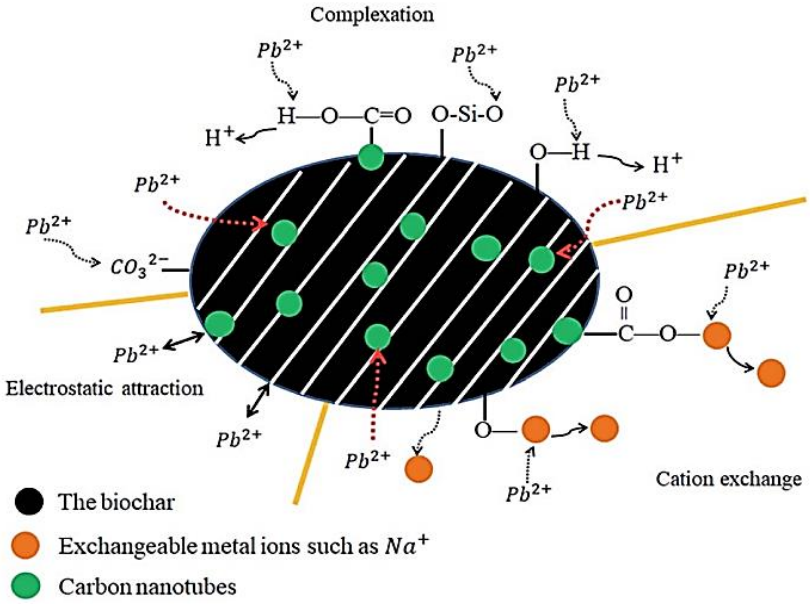

Fig. 13. Proposed adsorption mechanism of Pb(II) on biochar-CNT [74]

Comparison of SDS adsorption by activated carbon and biochar is listed in Table 8. The Langmuir model in Table 8 reported higher maximum adsorption of SDS by activated carbon than biochar. Physically, it can be related to much higher surface area of the activated carbon than of the biochar. The chemical interactions of the SDS and the adsorbents were explained based on the functional groups which were identified from their FTIR spectra. Prior to SDS adsorption, the adsorbents exhibited oxygen-containing functional groups, including hydroxyl (–O-H) and carbonyl (C=O) stretching of carboxylic, ester, ketone and aldehyde groups. After SDS adsorption, the FTIR spectra absorption intensity difference were observed. Therefore, chemically the adsorption may be controlled by interaction between negative charges of the deprotoned hydroxyl of the adsorbents and the positive charges of SDS heads. The additional weak chemical interaction may be between hydrophobic aliphatic hydrocarbon of the adsorbent and hydrophobic chains of the SDS surfactant. Those chemical interactions are designed in Figure 14.

Table 8: Sodium dodecyl sulphate (SDS) adsorption by activated carbon and biochar

Sample	SSA (m^2/g)	Langmuir model		References
		q_{max} (mg/g)	R^2	
Activated carbon	1500–3000	80.65	0.963	[75]
Biochar	300	45.87	0.955	[75]

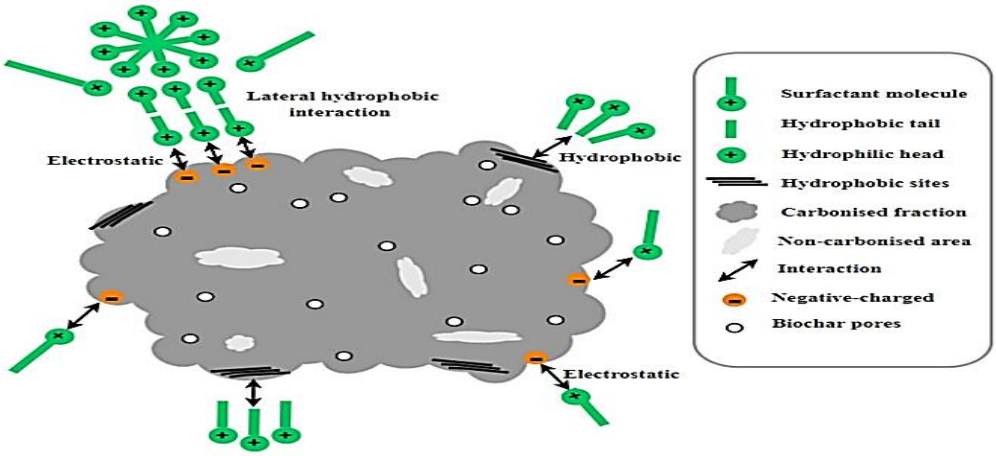

Fig. 14. Surfactant adsorption mechanism [75].

Adsorptions of different metal cations by 4 different adsorbents are presented in Table 9. Generally, adsorption data in Table 9 shows that adsorption of metal cations by activated carbon is higher than CNT, but less than both oxidized CNT and NaOCl-modified CNT. No data of surface area and functional groups type of the carbon based on characterization, but based on oxidation and NaOCl modification treatments, the main mechanism is probably due to the chemical interactions of the metal ions and surface functional groups of CNTs, including surface anion OCl- from modification and oxy functional groups which were ctreated by oxidation reaction.

Table 9: Metal cation adsorptions by activated carbon, CNT, oxidized CNT and modified CNT

Adsorbates	Adsorbents	Q (mg/g)	Adsorption condition	References
Cu^{2+}	As-produced CNTs	8.25	pH 6, 300K	[67]
	NaOCl-modified CNTs	47.4	pH 6, 300K	[67]
	Activated carbon	19.5	pH 6, 300K	[67]
Ni^{2+}	NaOCl-modified MWCNTs	38.5	pH 5, 298K	[67]
	Granule activated carbon	2.88	pH 5, 298K	[67]
Pb^{2+}	Oxidized MWCNTs	97.1	pH 5, 298K	[67]
	AC/ F-400	30.1	pH 5, 298K	[67]
Cd^{2+}	Oxidized MWCNTs	10.9	pH 5, 298K	[67]
	AC/ F-400	8	pH 5, 298K	[67]

5. Synthesis methods

Combustion and pyrolysis are same termochemical conversion techniques which employ heat to break down the organic material bonds with different concepts. Chemically, combustion is the thermal oxidation reaction in oxygen presence to produce CO_2 and H_2O (hot flue gas) with ash as the side product. Pyrolysis products are solid (char), liquid (tar, water) and non-condensable gases (H_2, CO, CO_2 and CH_4) [76].

Synthesis method of biochar

The biochar fraction is determined by pyrolysis types, including slow pyrolysis, intermediate pyrolysis, fast pyrolysis gives biochar product of 35%, 25%, and 12 %, respectively. Those pyrolysis methods can have same temperature range (450 – 500°C) but exactly different residence time, including hours to days, 10-20 s, and < 2 s, respectively. The slow pyrolysis by torrefaction, hydrothermal, and microwave assistance tehniques achieve the biochar product of 75%, 35%, and about 30% respectively.

In pyrolysis process, the lignocellulosic substances of biomass (hemicellulose, cellulose, and lignin) experience the decomposition reactions in the different temperatures, such as 200-300°C, 400°C and 500°C, respectively [38].

For example, dried spent coffee grounds (SCG) was used to produce biochar by slow pyrolysis at three different temperatures: 300, 450, and 600 °C. A heating rate of 5 °C.min^{-1} was applied with a residence time at the set temperature of 30 min. No explanation about nitrogen gas stream. There was decreasing of yield, bulk density, O/C ratio of biochar, but increasing of electric conductivity, pH, oil holding capacity, and metal content (K, Fe, Cu, Mn) by increasing temperature. [2].

Coffee-ground biochar (CGB) was synthesized from spent coffee grounds (SCG) through slow pyrolysis experiments to 500 °C for 1 h under nitrogen gas streaming. The CGB was modified with TiO_2 using a sol–gel method and labelled as CGBT. The CGBT has lower crystal size, larger S_{BET} and pore volume and smaller pore size, aand smaller band gap than TiO_2. Photocatalytic degradation of pentachlorophenol (PCP) by CGBT has higher k (11.4 X), higher % degradation (3,7 X), dectruction rate (14 X) than by CGB [3].

Tea waste was torrefied in a Thermogravimetric analyzer LECO TGA 701 at a rate of 10 ◦C. min^{-1} at 250, 300, 350, 450, 550°C. Analysis of element with the Elemental analyzer shows that there are increasing of carbon and ash but decreasing of hidrogen and oxygen by increasing of temperature. The phytotoxicity test show that untorrified tea and torrefied at 250 ◦C are toxic and unsuitable for soil application. Heat treatment at higher temperatures decomposes substances that have a negative effect on germination. The sample treated at 350 ◦C showed the highest germination index for all grinding fraction sizes. [4].

The waste tea was pyrolysed at 500 °C for 2 h in tube furnace under a N_2 atmosphere, then calcined by an activation gas of steam and nitrogen flow at 700°C for 45 min. The activated biochar (HC) was modified by NH_4Cl solution by magnetic stirring and then ultrasonic. The modified biochar has higher both S_{BET} and V_p (141.53 m^2/g ; 0,084 cm^3/g) than activated biochar (122.53 m^2/g; 0.055 cm^3/g). It has Hg removal capacity of 1079 µg/g [5].

Synthesis method of activated carbon

Activated carbon are produced in 2 steps including carbonization and activation [6,23]. Carbonization is pyrolysis reaction of the raw materials [23]. Carbonization converses biomass to carbonaceous structure and activation forms the carbon pores physically or chemically. Both processes increase the oxygenated functional group and porosity structure on carbon surface and consequently improve water adsorption [6]. Activation can also enlarge fine pores besides create new pores after carbonization. Activation is performed physically using steam (H_2O) or CO_2 gas at high temperatures (800 – 1300 °C). The chemical activation uses acidic agents (HCl, H_3PO_4, H_2SO_4, $ZnCl_2$) or basic reagents (KOH, NaOH, etc). However carbonization and activation processes can be carried out simultaneously by thermal decomposition of the chemical activator impregnated precursors [23].

AC and biochar are samely produced from pyrolysis of biomass under oxygen devoid conditions. The major difference of biochar and AC is other production process condition. AC, is produced at higher temperatures than biochar. Biochar is produced at around 400°C or less, while AC is produced at about 700 to 900°C. Activation step is compulsory either before or after carbonization for AC, but not compulsory for biochar. In both carbon materials, the thermal treatment stabilizes the biomass core-structure by improving the physicochemical properties of the materials [77].

Dried fresh coffee grounds and dried fresh tea leaves were carbonized at 560 °C for 4h and then was activated with nitric acid (HNO_3) and then by 1 molar of potassium hydroxide (KOH). Washing with DI water and drying at 100 °C was conducted every after activation process. The ACs based on the coffee grounds and tea leaves have the codes of CA and TA, respectively. There is similarity of FTIR spectra patterns, including kind of peaks at ~3420 cm^{-1} (OH), at ~1583 cm^{-1} (C=C) and at ~1384 cm^{-1} (C-O) except CA has sharper peak than TA. Adsorption capacity of iron (II) by TA was higher than CA. The Fe(II) cation concentration in the filtrate after filtration by TA and CA is 0.13 and 0.2 mg/L, compared to unfiltered water (0.3 mg/L) [6].

Potassium hydroxide (KOH) and dried spent coffee grounds (SCG) were mixed in mass ratios of 1:1 and 2:1 (KOH: SCG), weighed in crucibles and placed in the tubular furnace with nitrogen gas flow and the temperature was set to 400 or 600◦C for 1 or 2 h, then washed with distilled water until a neutral pH to remove the KOH residual, then dried at 105 ◦C for ~12 h [7].

The dried waste tea (WT) was pyrolized using KOH (KWT) and NaOH (NWT) activators at impregnation ratio of activating agent: biomass 1:1 and the activation temperature of 600 ◦C. Small quantities of SiO_2 nanoparticles (2.5, 5, and 7.5%) were physically added to AC by hand dry-mixing method and designated as K.WT.Sx (x is the weight percentage of silica). There was increasing of S_{BET}(59.15 to 453.18 m^2/g) and V_{BJH} (0.03 to 0.307 cm^3/g) for sequence of WT < NWT < KWT < KWTS2.5. The decreasing is available for more silica addition treatment. The FTIR spectra showed weaker bands at 3391-3404, 1557-1647, 997-1052 cm^{-1} related to the -OH, aromatic C=C, and C-O functional groups respectively for sequence of WT > KWT > NWT. There was increasing of carbon dioxide capture capacity by same sequence of specific surface area and pore volume [8].

Waste tea were carbonized at room temperature by addition of piranha solution (75 mL H_2SO_4 98 %-25 mL H_2O_2 30 %) at ratio of 2:5. The fast (10-15 min) and exothermic reactions complete carbonization of the waste tea by formation of CO_2 gas and hot steam vapor (H_2O). The XRD pattern shows a very broad (002) reflection with d_{002} = 4.5 Å, larger than crystalline graphite with d_{002} = 3.4 Å indicating amorph, highly disordered carbon. Raman spectroscopy shows intensity ratio ID/IG = 0.49, indicative of amorphous carbon. XPS spectra shows ratio of sp^2/sp^3 carbons (58.7 %), the functional groups contents of C-O (23.5 %), C=O (9.5 %) and O-C=O (6.8 %). SEM and TEM confirms the presence of large nanosheets. AFM confirms that the nanosheets consist of both thin sheets with thickness 1-2.5 nm and thick sheets with thickness 2.5-35 nm. The waste tea-derived carbon reacts hypergolically with fuming nitric acid (HNO_3) at ambient conditions probably due to large space between graphene layers [9].

Synthesis method of CNM or CNS

Carbon nanomaterial can be produced from AC in 2 ways, including by physical and chemical treatments. For the physical way, the AC particle size is directly reduced to achieve 1-100 nm, including mixing by mixer, blending by blender, sonication by sonicator, and stirring by stirrer. Among those all mixer is the best technique. By these technique, the structure of CNM will be same (turbostratics) with the AC [10,41]. The CNM synthesis route is described in Figure 15. For the chemical way, the AC was pyrolyzed again using other organic precursor and chemical activator. For example, CNT was prepared by dry pyrolysis of activated carbon, melamine, and iron (III) oxalate mixture at 600 and 900ºC sequently. The structure of CNT was proved virtually by SEM and TEM [78]. CNM was also prepared from biochar by ball milling of the biochar. The product was called as nano-biochar [79].

CNM can be also prepared directly from biomass with activator such as preparation of AC but involving mechanical treatment such as ball milling of precursor before pyrolysis. For example, waste coffee ground was grinded by ball milling at 1000 rpm then carbonized together with a chemical activator of KOH at 700ºC under nitrogen flow. The product was named nano porous carbon (NPC). The product was mixed with CNT and grinded by ball milling again at 1000 rpm. The scheme of preparation is given in Figure 16. The NPC has S(BET) of 706.5 m^2/g and V_p 0.23 cm^3/g. The mixture of NPC and CNT (3%) increase both specific surface area and pore volume to 1158 m^2/g and 0.34 cm^3/g [13]. The other example, carbon nanoflake was prepared by pyrolysis of ferrocene ($Fe(C_5H_5)_2$) and tea waste mixture in tubular furnace at 900ºC for 1 h under argon streaming. No additional treatment to conditionize the solid particle size. FE-SEM confirmed the width range of these nanoflakes from 15- 55 nm and few of 65-75 nm. Raman spectra of carbon nanoflakes show ratio of relative intensity (D/G = 1.24), suggesting the low disorder. The oxy functional group of the surface is C-O and S=O [1].

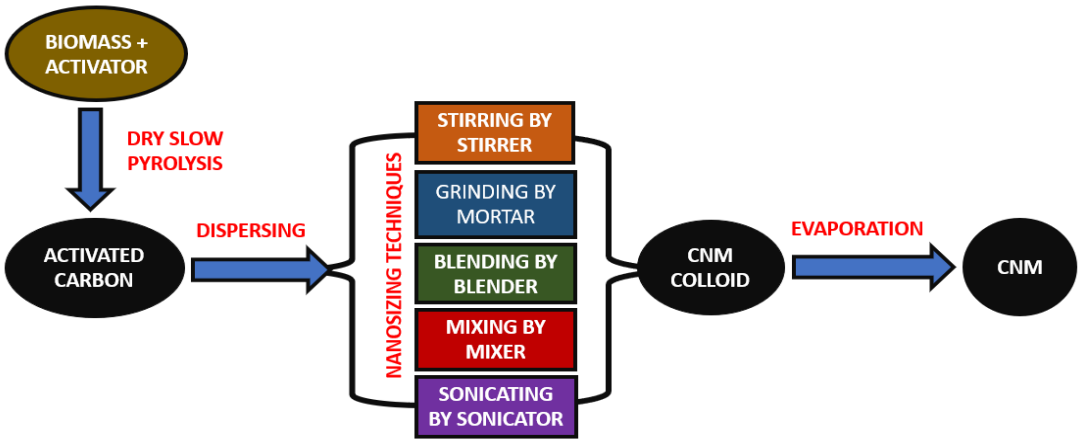

Fig. 15. Scheme of CNM synthesis route using various nanosizing techniques [10-12,43]

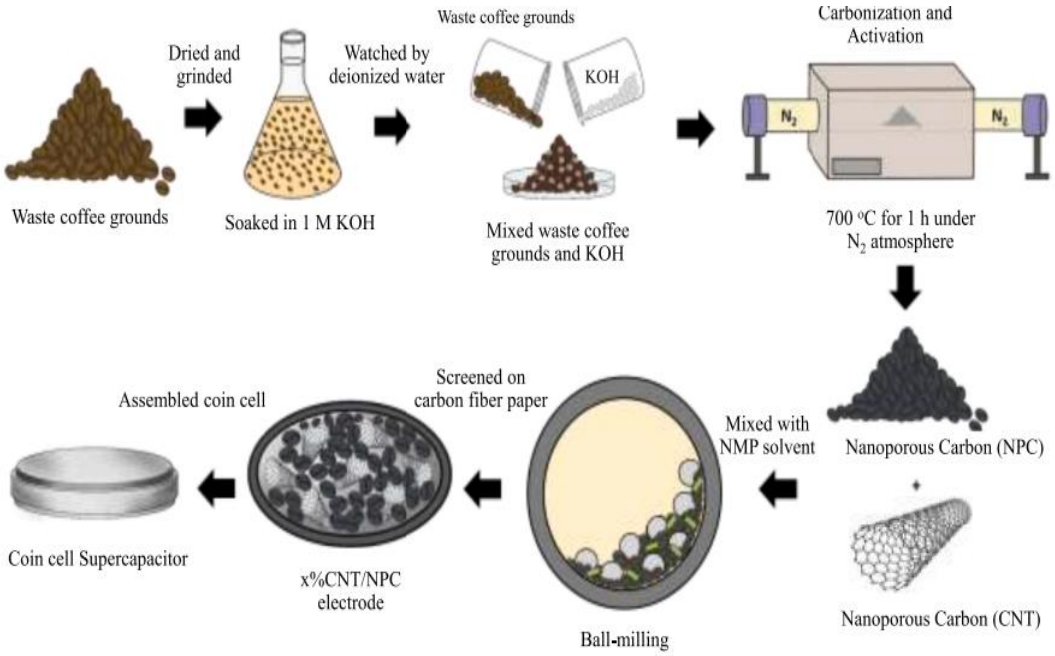

Fig. 16. Scheme of NPC preparation from waste coffee ground [13]

6. Conclusions

Biochar, activated carbon, and CNM are 3 physically and chemically different materials but have same carbon atoms as the main content. Physically, they have different surface area and pore volume. Chemically, they have different chemical structures due to their different preparation methods. Those materials can be prepared from coffee and tea due to their lignocellulosic substances, including cellulose, lignin, and hemicellulose.

7. Conflicts of interest

"There are no conflicts to declare".

8. References

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