PREPARATION AND CHARACTERIZATION OF NANO-ACTIVATED CARBON FROM AGRICULTURAL WASTE FOR WASTEWATER TREATMENT: A REVIEW

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ABSTRACT

Activated carbon generated from cellulosic material such as agriculture wastes received great attention. The synthesis of activated carbon from biomass by physical and chemical activation methods and its classification were reviewed. The effect of carbonization parameters (chemicals activation reagent, temperature) on surface area and pore volume of activated carbon was discussed. Nano-carbon forms and applications are considered. Also the effect of milling on carbon structures was discussed.

Keywords: *Activated carbon, Agriculture waste, Chemical activation, Application of Nano-carbon.*

1. INTRODUCTION

Many types of toxic substances are present in wastewater from different industries such as fabric, paper, construction materials, leather, plastic, cosmetic and printing industries [1]. The rapid pace of industrialization and urbanization activities has become an important environmental concern because of the disposal of wastes generated to the ecosystem. Heavy elements have specific gravity greater than 4 [2]. The effects of these pollutants on the environment and humans are dangerous. Searching for efficient methods to remove these pollutants is necessary for both human's health and aquatic organisms [3]. Many types of adsorbents such as carbon filters, silt materials, biomaterials, nanoparticles, fly ash and leaves have been widely used to remove harmful pollutant

from aqueous stream [4, 5–6]. Oxidation using safe oxidizing agents such as ozone and adsorption to activated carbon (AC) are the most used treatment to remove contaminants [7]. One future aspect of nanotechnology depends on the ability to produce new nanomaterial that has structural and functional features that are effective for this purpose [8]. The unique magnetic, surface chemistry, optical characteristics and the properties of corresponding bulk materials of nanomaterials make them desirable for different applications including adsorption, electronic sensing, medical applications, and drug delivery [9]. Mesoporous carbon has been major research topic because of its distinctive competent properties such as low density, high surface area, large pore size, electrophoresis, thermal conductivity, good

mechanical and chemical stability [10]. Improved AC properties such as increased surface area, pore size distribution and functional surface groups can be obtained from various precursors with high carbon content such as agriculture wastes [11]. In general, the characteristics of the final AC product depend primarily on the nature of the raw materials containing the carbon and also, the mechanical and thermal processing for carbon production [12]. One of the main interests that has recently emerged is the production of carbon using biological waste materials that not only reduces the impact of the environment, but can also be more effective than available polychlorinated naphthalene [13]. The advantage of vital clean materials such as rice husk, wheat straw, seaweed, wood pulp, tea waste, maize cob, sugar cane, sawdust, wool, olive shells, almond shells, cactus leaves, banana and orange peel, cellulose, lignin and hemicellulose compared with fossil fuels. On the other hand, biomass wastes have harmful effect on the ecosystem [14-16]. The use of rice husk not only has benefits of valuable carbon production but also reduces the problems of wastes and pollution [17]. Many investigations show that pure amorphous carbon can be prepared from cheap rice wastes [18, 19]. In addition, the presence of surface functional groups on carbon materials has a significant role in improving adsorption performance and also in the preparation of highly stable AC [20]. Because of their chemically inert nature, most carbon materials usually do not have the desired functional groups on their surfaces. So additional surface modifications are made; for example oxidation treatment is applied to provide functional oxygen groups [21, 22]. Powder AC is often seen as an alternative to the current advanced

wastewater treatment. The nature of AC surfaces, particularly active carbon nanotubes, has made the absorption of heavy metals from industrial wastewater applicable. Activated Carbon Fiber (ACF) is an amorphous carbon fiber with high surface area and functional groups used in the industrial processes [23, 24]. Activated carbon fiber has structure with many small porous opening and large surface area; which makes it denser, faster and more efficient than powder AC [25]. Several reports have emerged on the development of low-cost AC from easily available agricultural residues [26- 28]. Furthermore, the mechanical and thermal treatment of these waste materials is carried out through the process of carbonization and grinding, in order to achieve AC in nano-scale structure and to have aloft adsorption properties. The pore size of the AC has been classified into three types, According to International Union of Pure and Applied Chemistry (IUPAC) [29].

1. Micropore (pore size < 2nm) - (8–100 Å) [30, 31] which may be divided into ultra micropore (< 0.5 nm) and super micropore (1-2nm) [32]. The micropore size distribution determined by nonlocal density functional theory (NLDFT), N₂ adsorption isotherms, t-plot method, Dubinin–Raduskevich (DR) method, the alpha method or immersion micro calorimeter of liquids.
2. Mesopore (2 nm < pore size < 50 nm) - (100–500 Å) [30, 31]. The mesopore volume (V_{me}) is calculated as the difference between total pore volume (V_T) and micropore volume (V_{mi}).
3. Macropore (pore size > 50 nm) - (500–20,000 Å) [30, 31].

Incorporation of macropores in mesoporous materials combines benefits from both of them.

The pore size distribution of activated carbon and pore structure depends originally on the nature of the starting material [33, 34]. The distribution of pore size of AC depends mainly on the degree of thermal treatment and the catalyst used. Shapes and sizes depend on the type of activation [34]. The resulting porosity is due to increase the burning of the carbon [35]. Raw materials and the state of carbonization and activation are the most important factors affecting on porosity types and their distribution of activated carbon prepared [36, 37].

2. AGRICULTURAL WASTE MATERIAL AS AC PRECURSORS

Activated carbon can be generated naturally from carbonaceous wastes [38]. Characteristics of starting material, its property and the used activation process also may influence the properties and structure of the final AC product [39-40] and qualities, as well as the activation procedures [41]. Abandoned agricultural wastes are of the best potential sources used as alternatives to high-cost capacitors for the removal of wastewater pollutants [42]. Wastes such as agriculture wastes are the main sources of biomass; which is chemically composed of carbon, hydrogen, oxygen, nitrogen and traces of chlorine and sulfur in different functional groups forms [43]. Various biomass materials have been developed from agricultural wastes such as wheat straw, rice husk, seaweed, wood bark, tea waste, corn flour, cane cub, sawdust, wool, sugarcane bagasse, olive cake, pine needles, almond shells, cactus leaves, bananas, orange peel, etc. [44, 45]. All materials have their own advantages and limitations, so there is still a

need to improve the properties of resulted adsorbents. The conversion of solid wastes such as biomass to activated carbon to treat polluted water will add economic value by providing an alternative to activated carbon with low cost and better characteristics [17, 46]. Any cheap wastes with low inorganic content and high carbon content can be used for producing the AC.

3. PREPARATION OF ACTIVATED CARBON

The preparation of AC commonly consists of carbonization and activation that can be done either merged in a single stage process or separately in two-stage process. The carbonization of the precursors takes place at high temperature in the absence of oxygen. Thermal decomposition can convert materials containing carbon into activated carbon [43]. Highly porous AC can be produced using three processes: chemical, physical and physico-chemical activation [46].

3.1 PHYSICAL ACTIVATION

The physical activation consists of carbonaceous material carbonization followed by activation of the resulting char at high temperature in the presence of oxidizing gases such as carbon dioxide, steam, air or their mixtures. Higher temperatures improve the diameter of the pores, where as the pore volume increases substantially [47]. Physical activation using steam as oxidizing gas is the best potential for producing ACs with good pore ratio and high surface area [48]. The carbonization occurs as pyrolysis of the precursors at an appropriate temperature (500-1000°C) in an inert atmosphere gas in order to eliminate hydrogen and oxygen [49]. Temperatures (400:600°C) are required before partial gasification to develop the porosity at higher

temperature [23]. The thermal activation occurs at a temperature higher than the temperature of the pyrolysis or at the same temperature of pyrolysis in the presence of oxidant gas [50]. The produced activated carbon is affected by the activation agent, the activation method, and other factors parameters such as pressure, flow rate of oxidizing gas and heating rate, etc. [51]. Long pyrolysis period, high temperature, and loss of volatile components increase the ash content [52].

3.2 CHEMICAL ACTIVATION

The chemical activation has more advantages than physical activation, including higher yield, shorter time, lower temperature, larger surface area [53] and greater micro-pore structure [54]. Chemical

activation is carried out in a single step, combining activation and carbonization [55]. The chemical activation involves impregnation the carbonaceous material with a chemical oxidizing agent such as H_2SO_4 [47], $ZnCl_2$ [56, 57], KOH [58], H_3PO_4 [59, 60], K_2CO_3 [61]. The porosity of ACs is formed by dehydration reactions of activating reagent [23]. This activation requires a relatively low temperature of range from 300 to 800 °C [29] which is lower than physical activation temperature [62]. Activated carbons characteristics produced from various agricultural precursors by physical and chemical activation are present in Tables 1 and 2, respectively.

TABLE 1: CHARACTERISTICS OF ACS FROM VARIOUS AGRICULTURAL MATERIALS USING PHYSICAL ACTIVATION

Precursor	Activation Agent	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{mi} (cm^3/g)	V_{mc} (cm^3/g)	Ref.
Corn shell	CO_2 & H_2O	1779	0.927	-	-	[47]
Olive-tree wood	Air	481	-	0.226	0.046	[48]
Sawdust	N_2 flow	515.4	0.208	0.195	0.013	[51]
Sawdust	Under CO_2 flow	1003	0.538	0.462	0.076	[51]
Corrugated cardboard	Stream of argon	268	0.18	0.12	-	[52]
Waste tea	H_3PO_4	1327	1.142	0.2778	0.8651	[54]
	K_2CO_3	1125	0.592	0.5420	0.050	
Bamboo waste	Steam flush	363	0.15	0.13	-	[63]
Bagasse	CO_2	1433	0.91	-	-	[64]
	Steam	1579	1.1	-	-	[65]
Date stones	CO_2	604	0.34	0.29	-	[66]
Palm shell	CO_2	984	0.76		-	[67]
Coconut shell	Steam	1054	0.517	0.092	-	[68]
Peach and apricot stone	Steam	1150	0.44	-	-	[69]
Moso bamboo	Steam	1135	0.718	0.521	-	[70]

TABLE 2: CHARACTERISTICS OF ACS FROM VARIOUS AGRICULTURAL MATERIALS USING CHEMICAL ACTIVATION

Precursor	Activation Agent	$S_{BET} (m^2/g)$	$V_t (cm^3/g)$	$V_{mi} (cm^3/g)$	$V_{me} (cm^3/g)$	Ref.
Silkworm cocoon waste	$(NH_4)_2HPO_4/KOH$	2797.30	1.735	1.409	-	[23]
Crab shell	KOH	2197	1.192	0.832	-	[53]
	NaOH	2126	1.321	0.655	-	
	H_3PO_4	300	0.208	0.118		
	$H_4P_2O_7$	309	0.268	0.080		
Pomegranate seeds	$ZnCl_2$	978.8	0.563	0.283	0.280	[56]
Cassava peel	KOH	1378	0.520			[58]
Moso bamboo	KOH	2527	1.52	0.962		[70]
Potato residue	$ZnCl_2$ solutions (50 wt.%)	1357	1.065	0.083	0.982	[71]
Grape waste	$ZnCl_2$	1455	2.318		-	[72]
Tomato solid waste	$ZnCl_2$	1093	1.569	0.129	1.440	[73]
Rubber tires	NaOH	369.27	0.69	-	-	[74]
	HNO_3	473.35	0.70	-	-	
Wood	H_3PO_4	1708		-	-	[75]
Rice husk	KOH	3263	1.772	1.132	0.640	[76]
Chinese sargassum	H_3PO_4	1337.0	0.8	-	-	[77]
Plum stones	KOH	3228	1.61	1.57	-	[78]
Grape seeds	$ZnCl_2$	497	0.12	-	-	[79]
Almond shells	$ZnCl_2$	998	0.40	-	-	[79]
Apricot stones	$ZnCl_2$	1190	0.50	-	-	[79]
Papaya peel	Phosphoric acid	15.26		-	-	[80]
Cocoa pod husk	KOH	490	0.24	-	-	[81]
Sugarcane bagasse	$ZnCl_2$	1788	1.74	0.19	1.55	[82]
Coconut shells	$ZnCl_2$	2114	1.307	1.142	-	[83]
Camellia oleifera argan	$ZnCl_2$	2080	1.18	0.12	1.06	[84]
Sunflower seed shell waste	KOH	1235	0.67	0.59	0.08	[85]

4. EFFECT OF OPERATIONAL PARAMETERS ON THE RESULTED AC

Characterization of activated carbon is done by various instruments such as scanning electron microscope (SEM), x-ray diffraction (XRD), N_2 adsorption/desorption and Fourier transform infrared spectroscopy (FTIR). These techniques are used to determine surface area, pore size distribution, pore volume and function groups structure which helps choose the best conditions for producing AC at its best properties.

4.1 EFFECT OF CARBONIZATION TEMPERATURE (CT) ON SURFACE AREA AND PORE VOLUME

One of the most important synthesis factors affecting the textural properties of the AC is carbonization temperature (CT). The S_{BET} , V_T , $V_{mes}(\%)$ and $D_p(nm)$ values are increased as CT increased, due to the creation of new pores [72]. When the raw materials were activated at low CT, predominantly micro porous was observed, while meso porous were formed gradually with CT increasing [63]. Zhang et al. [86] studied the effects of

the CT on the physical properties of the AC generated from waste potato. It was observed that S_{BET} and V_T increased as CT increased from 400 to 600 °C and then gradually decreased when CT increased from 600 to 800 °C. The surface area and pore volume decreased because of heat shrinkage [87]. Also, carbonization temperature plays an important role in the AC production. At CT range of 450 to 550 °C, the loss of weight is primarily high because the amount of volatiles released as well as the loss of moisture. The yield of the AC at temperatures more than 650 °C is less than fixed carbon in initial precursor. However, increasing the CT from 450 to 750 °C results in creation of new pores, due to increasing the evolution of volatile matters [58]. The effect of the carbonization temperature on the specific capacitance of RH carbon was investigated as shown in Figure 1. The temperature was increased from 500 to 900 °C, keeping the activation time and KOH-to-RHC ratio constant at 1 h and 3:1. The highest specific surface area and specific capacitance 2,367 m² g⁻¹ and 288 F g⁻¹, respectively were achieved at CT 700 °C. It was found that as CT was increased, the activation reaction increased and caused the formation of much more pores and specific surface area. When CT surpassed 700 °C, the activation reaction became so fast, resulting in over-etching and lower specific surface area was obtained. When the CT reached 900 °C, the specific surface area decreased to 2,031 m²g⁻¹ [76]. The pore volumes of the AC generated from lignin by chemical activation using ZnCl₂ and H₃PO₄ as oxidizing agent were studied. The activation increased with increase in temperature over the range 500 to 600 °C, and decreased with increase temperature over the range of 600 to 900 °C.

When the temperatures were higher than 600 °C, the surface areas of AC decreased and the carbon structure shrunk. The pore volumes of the AC produced using alkali metals compound generally increase with CT up to about 800 °C. This referred to the pores enlarge up to this temperature. When the temperature is higher than 800 °C, the excess enlargement induces combination of pores, resulting in a decrease of surface area and micropore volume and an increase in mesopores, [87].

Fig.1. Effect of CT on the specific capacitances and specific surface area of rice husk-AC [76].

4.2 EFFECT OF CHEMICAL ACTIVATION REAGENTS ON SURFACE AREA AND PORE VOLUME

Cross-linking structures in the form of phosphate ester can be developed by activation with H₃PO₄ which is directly related to porosity improvement. These cross links reach a limit of thermal stability when the temperature maintained at 450-500 °C. The higher temperatures cause a reduction of cross-links and minimize the development of porosity [29]. AC was produced from pomegranate seeds using ZnCl₂ at 600 and 800 °C as shown in Figure 2. The recovery was found to be from 74.43 to 81.24 wt.%. The final yield of AC was affected by the concentration of zinc chloride. The benefit of ZnCl₂ was inhibition of tar formation and dehydration that influenced pyrolysis decomposition [56]. Although, AC was prepared from grape industry waste without any activating agent,

Fig.2. SEM images of AC produced from pomegranate by ZnCl_2 activation at 600 and 800 °C [56].

the produced AC had very low S_{BET} , V_{T} , V_{mic} , V_{mes} and $D_{\text{p}}(\text{nm})$. In case of activation using ZnCl_2 , the resulted AC had high porosity and surface area due to increase of the raw material degradation. ZnCl_2 causes dehydration of the raw material, burning of the carbon skeleton and creates new porous structure during the carbonization [72]. However, the impregnation of the precursors with alkaline hydroxides agent such as (NaOH and KOH) generated AC with higher specific surface area [59]. Waste tire also have been used for AC preparation using acid and base activation at different temperatures. Saleh et al. observed that AC treated with acids had better properties than that treated with bases. The pore volumes and surface area of AC activated with HNO_3 at 90°C were 0.70 cm^3/g and 473.35 m^2/g , respectively, which were higher than that activated with NaOH at 60 °C (V_{p} , 0.69 cm^3/g , S_{BET} , 369 m^2/g) [74]. Activation for long time may have a negative effect on the AC generated from silkworm cocoons by KOH activation. It was observed that S_{BET} decreased from 2797 to 1163 m^2/g and pore volume decreased

from 82.34 to 75.18% when increasing activation time from 1 to 4 h. This may be attributed to the reduction of KOH to metallic potassium, as KOH may be associated with the gasification reaction. In addition, pretreatment with $(\text{NH}_4)_2\text{HPO}_4$ increases the carbon yield [23]. Gergova et al. [50] prepared AC with high porosity from date stones by pyrolysis using (H_2O) as oxidant gas. This high porosity was due to the production of new pores in the carbon structure resulted from the elimination of volatile matters and recycling of the carbon atoms in the glycoside rings. Activated carbon of high surface area was produced from crab shell using KOH and NaOH activation. The produced AC was effective for removal of contaminants and pollutants from wastewater stream [53].

4.3. EFFECT OF MILLING ON NAC STRUCTURES

Applying of ball milling is common to materials which need to be transformed to nano-size. Ball milling used for the production of single-wall CNTs to produce highly curved nanostructures. Morphology of cup-stacked CNTs affected by ball

milling. High energy milling also used to reduce the length of the single-walled CNTs, to form nanobarrels and to shorten the nanotubes, and to increase the number of consenting active sites and the anisotropic characteristic at both ends [88, 89]. High-energy ball milling decreases their particle sizes and increases the amount of amorphous carbon. Increasing the grinding time shortens the multi-wall CNTs entangling each other. Some multi-wall nanotubes are broken and subsequently their closed ends become opened during the milling. There are compatible conditions for modification the opened structure of multi-wall nanotubes. Ball milling is able to affect the morphology of particles and also introduces crystal defects and refines the microstructure. Ball milling is performed in atmosphere to produce samples reinforced with a presumably higher amount of in-situ reinforcement. Ball milling is also expected to destroy the outer surface of the ceramic shells and to disperse the oxide fragments in the metal matrix leading to dispersion hardening (in-situ reinforcement) the morphology of the as received powders is made up of quasi-spherical particles with diameter lower than 45 μm [90].

5. PREPARATION OF DIFFERENT TYPES OF NANO-CARBON

Nano-AC appears after preparation in different forms such as carbon nano-spheres, carbon nano-tube and carbon nano-fiber depending on type of preparation method.

5.1. CARBON NANO-SPHERES (CNS)

Nano-size spherical particles of AC are produced from raw Magahara coal by thermal and chemical activation process using KOH followed by carbonization at 600 °C for 90 min. The nano-size spherical particles of pronounced porosity and series

of irregular cavities distributed over the surface of the AC can be observed [86]. Carbon nano-spheres can be obtained by the pairing of pentagonal and heptagonal carbon rings, used in some specific applications. Bio-waste materials as a source of carbon containing materials have been used for preparation of CNS. The results showed wonderful particle size along with high zeta potential values. Quality and crystallographic properties were determined by TEM and XRD analyses. It was an easily CNS synthesis method using convenient and safety catalyst-free pyrolysis technique [91]. Shuo et al. [92] prepared CNS from potato starch with perfectly retaining of the original morphology. A destruction of the regular super molecular structure in the potato starch has been done during stabilization and carbonization. As stabilization was carried out intensively, the inter molecular cross-linking and rearrangement of porosity were the dominating parameters on the structural change. Meso-phase pitches were converted to carbon nanoparticle using hot injection method using oleic acid solution, H_2SO_4 as activation agent at 180 °C. They are important synthesis conditions to produce carbon nano-structures with various morphologies [93]. It was more efficiently to produce uniform CNS when sucrose molten with KOH was used as precursor without any catalysts using hydrothermal route. A mono-disperse between 100–150 nm CNS was obtained [94]. Another agriculture waste, namely oil palm leaves has been used as a source of carbon to produce carbon nanoparticles. Ali et al. [13] generated porous carbon structure in Nano-scale in one step by pyrolysis in inert atmosphere (N_2). Firstly oil palm leaves were separated from a local oil palm and dried at 60 °C for

48 h to remove all the water content. Then, the dry oil palm leaves were crushed, grinded and sieved. Finally, the powder underwent pyrolysis in a furnace tube at 500 and 600°C for 2 h and cooled down to room temperature in N₂ atmosphere to get the porous carbon nanoparticles. Irregular porous CNS has resulted, when adding of Na₂SnO₃ on corn porous starch as a precursor [95]. Carbon nano spheres also have been produced from saturated hydrocarbons. A liquid hydrocarbon was introduced carefully into double furnace apparatus for the pyrolysis with the desired feed rate controlled by a pump at 250 °C, resulting in 99% carbon as CNS (1-5 nm) [96].

5.2. CARBON NANO-TUBE (CNTs)

Preparing CNTs has quickly improved every year, to synthesis large amount of size-controlled CNTs for commercial applications. CNTs are classified into two types: (1) multi-walled CNTs (MWCNTs) and (2) single-walled CNTs (SWCNTs) [97, 98]. Many methods were tried to get short and open ended CNTs. Examples of these methods are acid etching, scanning tunnelling microscope (STM) voltage, radiation treatment, ultrasonic treatment and ball milling. Among them, ball milling appears to be the easier process for cutting CNTs. ball milling is a reasonable method to crack and to open the closed ends of CNTs [99]. More recently, SWCNTs have been prepared based on the pyrolysis of hydrocarbon by catalytic chemical vapor deposition at relatively low temperatures [100]. Zhu et al. [101] prepared Multi-walled carbon nano tubes CNTs from bamboo plants using tube furnace. The bamboo plants were placed on an alumina substrate and then inserted into tube furnace to obtain bamboo charcoals, heated at

temperatures between 1200 and 1500 °C and then passing through a bath of ethanol under flowing of Ar. Multi-walled CNTs have been synthesized from graphite by ball milling and annealing. Mechanical milling produces a disordered and nano-porous structure, which provides nanotube nucleation sites [102]. Immobilizing CNTs onto a carbon support was done to shuffle the unparalleled properties of CNTs with those of conventional AC, and to maintain the chemical compatibility between these two phases of different dimensionality. A hierarchically carbon structure, consisting of CNFs supported on AC, was successfully produced by CVD of C₂H₄ on an AC-supported iron catalyst. Agriculture-derived AC contains iron was directly used for synthesis CNF as a catalyst. The process involved preparation of Fe particles on the AC was circumvented and the overall process was simplified. Differing from other natural materials for CNT synthesis, AC may suffer gasification during CVD treatment at high temperatures in the presence of oxygen. The generation of CNFs on the AC was organized to be non-proportional to the amount of iron in the starting AC. The diameters of the CNFs were less than of 300 nm, with a small number having diameters as large as 500 nm [103]. Natural resources such as stone garnet sand as a catalyst and support, and city gas based natural gas as the carbon source are efficient method and environmentally friendly for growing multi walled carbon nanotubes (MWCNTs). Garnet powder consists of Fe₂O₃, FeO, Al₂O₃, and SiO₂, among other things. The air oxidation of the garnet sand (~ 200 µm) at 1000°C for 6 h is a decisive step to enhance the production and growth rate of CNTs before introducing garnet powder into the

reaction chamber. Gas for urban consumption was used as the carbon source. It contains propane, ethane, methane, dimethyl sulfide, n-butane, and isobutene as an additive so that the gas can be detected by smell [104]. Acetylene gas as a carbon source is used for producing MWCNTs by catalytic CVD method at 600–900 °C for 20 min. Two different morphologies of MWCNTs synthesized well-aligned bundles and entangled aggregates [99]. Pierard et al. [88] synthesized SWNTs from methane by catalytic decomposition using Co supported on MgO as catalyst. Also decomposition of Acetylene for creating nano carbon structure using Kaolin supported Co catalyst has been investigated. CNTs grown over the catalyst have diameter of 30–40 nm, 20µm in length. A mixture of carbon nanotubes and carbon spheres were obtained using ceramic plate as substrate [105]. Using acid-attapulgit as template and furfuryl alcohol as carbon source were investigated for synthesis the carbon nanotubes through a vapor deposition polymerization (VDP) method. Carbonized furfuryl alcohol-attapulgit in furnace under N₂ atmosphere was tested [106]. Chen and Wang prepared MWCNTs using acetylene in hydrogen flow at 760 °C by chemical vapor deposition (CVD) and Ni-Fe nanoparticles as catalysts. N₂-BET method showed the specific surface area of MWCNTs to be 197 m²g⁻¹ [107].

5.3. CARBON NANO-FIBER (CNFs)

Fibrous carbon nano-materials, such as carbon Nano fibers (CNFs), have attracted a lot of attention because of their unique crystalline structure as well as excellent physical and chemical characteristics. Because of these characteristics, a variety of potential applications have been reported [108]. The major processing route towards the CNFs has been the catalytic

decomposition of molecules containing the carbon atoms such as hydrocarbons. Jia and Zhang [109] synthesized CNFs by CVD using acetylene (C₂H₂) gas as the carbon precursor and the water-soluble salt from KI as the catalyst. Chemical vapor deposition can be applied without the need for an iron incorporation step, Carbon Nano fibers on activated carbons produced from agricultural waste, since the biomass already contains iron. This iron, present in the ash content of the ACs, acts as a “natural catalyst” and can catalyze the formation of CNFs from ethylene on biomass derived ACs [110]. Also platelet CNF was synthesized from carbon monoxide over an iron catalyst [111, 112]. Romero et al. [113] prepared carbon nanofibers by the decomposition of C₂H₄ using different metal phase over Y zeolite. It was found that the metal phase had very plentiful effects on CNFs growth, including the extinction rate and the CNF production. Poly ethylene glycol can be used as the carbon source and NiCl₂ as the catalytic for synthesis of carbon nano fibers by thermal decomposition from polymer and a catalyst. Heated this mixture at 400 °C and then increasing the temperature to 600–850 °C for the produce of carbon Nano fiber [114]. CNFs were synthesized by CVD method using ultra-fine Fe₃O₄ as the catalyst and CO as the carbon source [115]. Oil palm shell powdered activated carbon (PAC) was used as carbon resource for production. Carbon Nano fibers have been prepared from C₂H₂ by impregnation with nickel and using CVD in the presence of hydrogen gas. CNFs were synthesised directly on the surface of the impregnated oil palm shell [116]. High quality carbon Nano fibers were synthesized by CVD method using acetylene as carbon source and γ-alumina-supported iron as catalyst in a tubular quartz reactor

[117]. Preparation of porous carbon that exhibits nano structure with high surface area and large-level nitrogen has been also investigated by doping polypyrrole (PPy). Nanofiber webs with a high N content (~ 16 wt%) were selected as precursor, and KOH served as an activation reagent to form porous structure. Benefiting from the unique porous nano structure and high-level N doping, the CNF exhibit excellent rate capability [118]. Carbon nanotube and carbon nanofiber can be generated by an alumina template membrane with Ni catalyst using CVD method. Using ethylene used as carbon source, the carbon tubes can be converted into carbon nano fibers with increasing the deposition time [119].

6. ACTIVATED CARBON APPLICATIONS

Activated carbon is the most widely used adsorbent for removal of heavy metals, dyes, organic compounds, other pollutants in waste water treatment [120], petroleum industries [121], purification and separation of gaseous and liquid phase mixtures [108, 109], catalysis [122, 123], super capacitors [43], energy storage [124], fuel cells batteries [125], nuclear power stations [126], electric double layer capacitors [127], pharmaceutical industries [128], and hydrometallurgy [129, 130]. Gold can be separated from liquors by activated carbon as sorbent [131]. Activated carbon is used in purposes of deodorization and decolourization in food industries [132]. Abrasion resistance and hardness properties are very important factor for the AC. If an application needs to frequent back-washing such as air conditioning, AC will be a good choice for this purpose, due to ability to air filtration [133].

6.1. CAPACITY OF AC FOR REMOVING POLLUTANT

Properties of AC are determined by its pore volume, surface area and presence of different functional groups such as aldehydes, ketones, phenols, lactones, anhydrides, quinones, hydroquinone and carboxyl [134]. However, removal of pollutant by adsorption from liquid needs large surface area [39].

7. APPLICATION OF NANO-CARBON

Presence of heavy metals like Cd, Pb, Ni, Hg and Cause major pollution problems in water stream. Carbon nano-tubes (CNTs) can be used as adsorbent of heavy metals contaminated from waste steam. Elimination of Nickel by adsorption method can be performed using multiwall carbon nanotubes (MWCNTs). Among the different parameters that may affect on adsorption process, Ni (II) adsorption onto MWCNTs was found to depend on pH and oxidized MWCNT concentration [107]. The sorption capacities of metal ions by oxidized CNTs are better than raw CNTs due to oxidation process upgrade. Their dispersivity and increases amount of oxygen-containing functional groups like $-\text{COOH}$, $-\text{OH}$, or $-\text{CO}$ on the surface site of CNTs are important properties [135-137]. The carbon nano tube sheets were then oxidized with concentrated acid for elimination of some heavy metal ions from pollutant water. The demonstrated adsorption capacity of the CNT sheets increases significantly after oxidation process. Also, the adsorption capacity of the CNT increasing with increases the initial salts concentration [138]. The functional groups present on AC surface cause a rise in negative charge on carbon surface and the oxygen atoms in functional groups donate single pair of electrons to metal ions, so increasing their

cation exchange capacity. MWCNTs have good adsorption capacity for chromium ions. The adsorption capability is increased by increasing the sediment speed and it is pH dependent. Our results demonstrate that the MWCNTs/Nano-iron oxide magnetic composites, whose surface area is large, are very promising materials as adsorbent for pollutant in water with good performances [139]. The properties of CNTs such as purity, structure and nature of the surface could be highly improved by acid treatment which made CNTs become more hydrophilic and convenient for adsorption of low molecular weight and relatively polar tri halo methane (THM). Molecules such as CHCl_3 , CHBr_3 , CHBrCl_2 , CHBr_2Cl , and CHCl_3 , are the most suitable adsorbed onto CNTs [140]. Multi-walled carbon nanotubes (CNTs) were thermally treated used as adsorbents to remove some natural organic matter from aqueous solutions. The amount of adsorbed natural organic matter onto CNTs increased with increasing an initial concentration of contaminants, but decreased with a rise in solution pH [141]. Multi-walled carbon nanotubes (MWNT) and single-walled carbon nanotubes (SWNT) are efficient adsorbents for removal of tetracycline from contaminated aqueous solutions. The results of the present work tick that the adsorption selectivity and efficiency has evolved through specific molecular-level interactions between organic contaminants and carbon nanotubes [142]. Liao and Gao used multi-walled carbon nanotubes as efficient adsorbents for adsorbed resorcinol and other phenolic derivatives from water. They showed that multi-walled carbon nanotubes have ideal performance for adsorption of phenolic derivatives, which can be utilize not only in the environmental protection but also in

many scientific fields such as catalyst support and chemical sensors. The potential of adsorption process depended on contact time, pH range, Acid-treated MWCNTs, hydroxyl and its location in meta-position on aromatic ring [143].

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تحضير وتوصيف جزيئات الكربون المنشط النانومترية من المخلفات الزراعية لمعالجة مياه الصرف

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الملخص:

يعد الصرف الصناعي أحد أخطر الملوثات التي تهدد البيئة لما يحتويه من عناصر سامة تؤثر علي الحياة المائية، ويعد البحث عن طرق لازالة هذه الملوثات ضروري للمحافظة علي صحة الانسان والموارد المائية، وقد استخدم الكربون المنشط على نطاق واسع كمادة مازة للتخلص من هذه الملوثات وذلك لخصائصه الفريدة، وفي المقام الاول تعتمد خصائص الكربون الناتج على المادة الخام المستخدمة، ولقد لقيت أبحاث تحضير وتوصيف الكربون المنشط من المواد الغنية بالكربون مثل المخلفات الزراعيه اهتماما كبيرا من الباحثين، وفي هذا العرض تم مناقشة تحضير جزيئات الكربون المنشط النانومترية بالطرق الفيزيائية والكيميائية بالإضافة الى توصيفها، كما تم مناقشه العوامل المؤثرة على عملية التنشيط والتفحم مثل (المواد الكيميائيه المستخدمه في التنشيط – درجة الحرارة) وتأثيرها على مساحة السطح وحجم المسام. أشكال الكربون الناتجة وتطبيقاتها تم عرضها ايضا. كما تم عرض تأثير عملية الطحن علي اشكال الكربون الناتجة.