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Preparation and characterization of activated carbons derived from bio-solid: a review

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ABSTRACT

Preparation of activated carbons from bio-solid is a promising way to dispose bio-solid as well as to produce a low-cost adsorbent for pollutant removal. Various physical and chemical processes are in use for the activation of the activated carbon derived from bio-solid (ACBS). Both physical and chemical characterizations provide fundamental knowledge for its potential application for pollutants removal. The literature illustrates that KOH, the chemical activation procedure is found to be the most effective technique for producing high BET surface area ACBS, with areas in excess of 1,882 m^2/g being reported. In this review, the results reveal that the ACBS is comparable with commercially activated carbons.

Keywords: Bio-solid; Activated carbon; Production; Characterization; Application

1. Introduction

Sewage sludge is generated in gigantic amounts due to rapid urbanization. Increasing urbanization and industrialization have led to a dramatic increase in the intensity of wastewater produced around the world [1]. Without proper treatment and disposal, it will cause a secondary pollution problem for the environment. Landfill, application to farmland and forestry, and incineration are the conventional disposal options. Protein, carbohydrates, fats, and oils are the main entities of the organic solids in the sludge [2]. These varied from each other in origin, system, and efficiency of the wastewater treatment each other [3].

Sewage treatment effluent is the largest contributor of organic pollution in Malaysia, to water resources and environment. Its contribution is top listed (64.4%), followed by animal husbandry wastes (32.2%), agro-based (1.7%) and industrial effluent (1.3%) measured in terms of BOD load [4]. In Malaysia, Indah Water Konsortium produces approximately 3.8 million m^3 of sewage treatment plant sludge. This sludge volume is expected to rise up to 7 million m^3 by the year 2020. The management of the ever increasing organic wastes is one of the important issues in Malaysia for a clean environmental. It requires a pragmatic economical approach and research to utilize this bio-solid in friendly environmental way [5]. Landfill has long been a major option in disposal of bio-solid. But it will not be sustainable owing to increasing competition for landfill space, higher costs, and more stringent environmental standards applied. Incineration is playing an important role in recent years. However, its rising energy cost, ash disposal, and gaseous emissions are the significant constraints for its more widespread use

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[6]. Eventually, a cost-effective and innovative solution to the problem caused by the sludge disposal is desirable. The thermal application such as pyrolysis is the promising way for bio-solid disposal [7]. Bio-solid is carbonaceous in nature and rich in organic materials. Hence, it has the potential to be converted into activated carbon, if it is pyrolyzed under controlled conditions or by some other chemical treatment [8]. Many researchers recognize bio-solid as a resource more potential for beneficial reuse than direct disposal [9–12].

Activated carbons preparation from bio-solid can be considered as one of the attractive method in reducing sludge volume. Moreover, it produces reusable by-products. Activated carbon demonstrated significant adsorption in gas and liquid phases due to its high micropore volume, large specific surface area, favorable pore size distribution, thermal stability, and capability for rapid adsorption [13]. Adsorption onto activated carbon has been found to be superior compared to other physical and chemical techniques because it has simplicity of design, easy of operation, and high quality of effluent achieved. Activated carbons can be used to adsorb organic and inorganic species [14]. The chemical structure on the carbon surface will influence the interaction between polar and non-polar adsorbates. Activated carbon adsorption process is recognized as the most promising treatment technology. It is a surface phenomenon by which a multi-components fluid mixture is attracted to the surface of solid adsorbent and forms attachments via physical or chemical bonds [15]. The application of bio-solid-based materials has been successfully reported for the uptake of metal ions [16], dyes [17], phenolic compounds [18,19], and gas purification, such as NO treatment and H_2S removal [20,21].

The objective of this study is to present a detailed review on preparation of activated carbons derived from bio-solid. Various methods for preparation of activated carbon derived from bio-solid (ACBS) are reviewed. The effect of several process parameters of the generated ACBS, such as BET surface area, surface morphology, and surface chemistry, were discussed and the obtained results from the literature were reported. Ultimately, it describes and discusses the reported ACBS uptakes and potential techniques for improving their performance.

2. Sewage sludge

Wastewater is a combination of the liquids or water-carried wastes removed from residential, institutional, commercial, and industrial establishments, together with ground water, surface water, and storm water. Wastewater treatment plants (WWTP) generate two output streams: sewage sludge and treated effluent. Sewage sludge is generated through the removal of suspended solids and sludge from the influent wastewater, and treated effluent is discharged to watercourses. In primary treatment, all wastes that either float or sink are removed by screening. This primarily removes debris from the raw sewage, but most of the organic waste stays in the suspension or solution. After the initial screening, most of the organic waste is removed from the sewage through settling in tanks. From there, the organic waste is subsequently removed into separate sludge treatment [22]. Most wastewater treatment processes produce primary sludge in the primary sedimentation stage of treatment and a secondary, biological, sludge in final sedimentation after the biological process (Fig. 1). Approximately 70% of the main raw sewage is composed of proteins, urea (nitrogenous compounds), sugars, cellulose, starches (carbon hydrates), cooking oil, greases, and soaps (fats) [23], whereas, 30% of the solids consist of inorganic components such as metallic salts, road grit, and chloride mix up with sewerage and storm water [24]. Chemical sludge is another common form of sludge. It is produced from the sludge dewatering facilities of water treatment works and it constitutes sludge that is dewatered by the aid of polymer chemicals. Typically, the chemicals are used either to facilitate the precipitation of hard-to-remove substances, or to improve suspended solid removal [25]. The characteristics of the activated sludge sample are shown in Table 1. It was obtained from Bayan Baru sewage treatment plant located in Penang, Malaysia [26].

3. The composition of raw sewage sludge

Proximate analysis provides information on the content of moisture, volatile matter, fixed carbon, and the ash of a material. Table 2 listed some of the previous studies carried out on proximate analysis and ultimate analysis for raw sewage sludge. From proximate analysis (Thermogravimetric Analysis), the raw sludge was found plenteous in volatile matters. The fixed carbon contents are considered satisfactorily high. These depict the raw sludge as suitable material which can be converted into activated carbon. The fixed carbon content increases steadily while volatile declines over temperatures. At higher temperature, organic substances remain unstable. Heat provides energy to the molecules to break the bonding and linking. Once it is broken, the substances will be discharged both as gas and liquid products. After the carbonization process, the volatile matter content of the sludge decreases

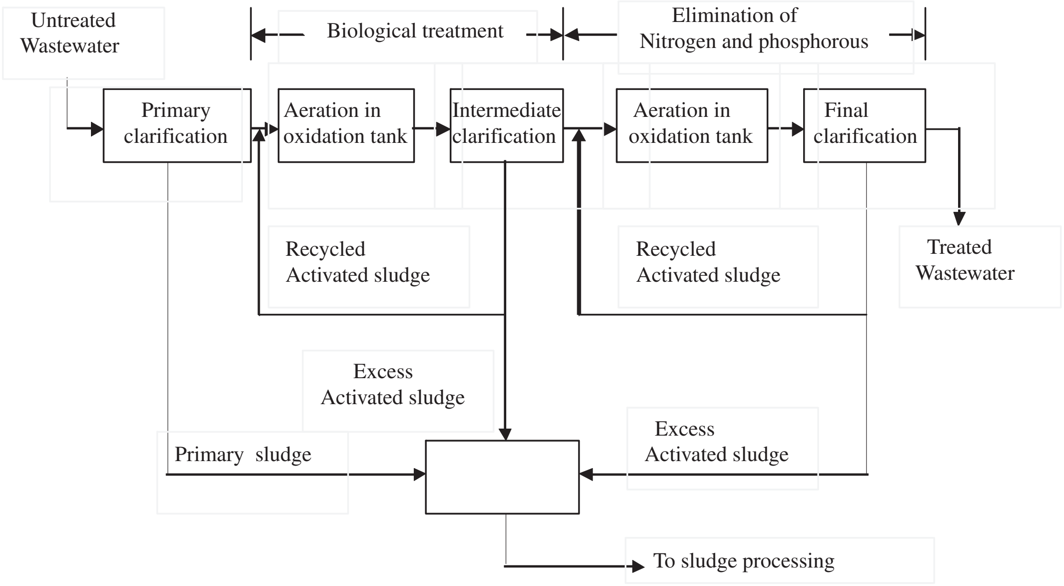

Fig. 1. Scheme of an activated sludge wastewater treatment plant [24].

Table 1
Characteristics of activated sludge sample [26]

Parameter	Average value
Temperature (°C)	26.95
Total solids (mg/L)	11,540
Suspended solids (mg/L)	9,893
MLVSS/MLSS	0.84
Electrical conductivity (ms/cm)	2.02
Total dissolved salts (%)	1.31
Salinity (g/L)	1.03
ORP (mV)	−139.6
NH_3–N (mg/L)	143
COD (mg/L)	4,055
pH	6.75

significantly, whereas the fixed carbon content increases in the activated carbon. It is observed that sewage sludge contains large amount of ash. The ash consists of minerals such as silica, aluminum, iron, magnesium and calcium. Ash in activated carbon is undesirable. It is regarded as impurity. Usually, materials with the lowest ash content produce the most active products [27]. Sewage sludge is rich in Fe species. Its content in sludge-based activated carbon has the concentration higher than 72,000 μg/g [28]. Other elements (N, H, S, and O content) varied in concentration. These might result in different chemical characteristics of the activated carbon by forming various functional groups [29]. Malaysian sewage sludge contains moisture content of about 80 wt% of the total weight of the sludge. The high moisture content and the heavy amount of water must be dried off from the sample before the start of pyrolysis. The ash content of the sludge sample is 30.83 wt%. It shows the amount of inorganic matter present in the sewage sludge (Table 2).

4. Preparation of ACBS

Carbonization is the process to remove the volatile matters from the carbonaceous material by thermal decomposition under the inert atmosphere, usually nitrogen atmosphere to eliminate the bulk of the volatile matter [39]. Pyrolytic temperature, heating rate, nitrogen flow rate, and time of pyrolysis are the main operation parameters involved in carbonization process. Pyrolytic conversion of bio-solid generates three phases of char, oils (tar), and gases. Carbonization also serves to stabilize and indeed consolidate the fixed carbon: the energy provided during this process enables it to assume a more stable structure [40]. The purpose of carbonization is to produce the carbon structure and to create an initial porosity in the char [41]. A schematic diagram of the process of producing activated carbons from bio-solid generally adopted by the researchers is shown in Fig. 2.

4.1. Effect of temperature

The application of heat accelerates the thermal degradation and the carbonization process. This leads to the development of pores, increase of surface area,

Table 2
Some of the previous works carried out on physicochemical characteristics of sewage sludge

Property	[30]	[31]	[32]	[33]	[34]	[35]	[36]	[37]	[38]
Proximate analysis (wt%)									
Moisture	–	–	–	80.4	–	–	5.74	5.2 ± 1.1	32.6
Volatile matter	49.4	–	–	54.7	–	45.97	42.6 ± 4.9	54.7	49.4
Fixed carbon	30.7	–	–	14.5	–	6.88	4.6 ± 1.1	6.2	30.7
Ash	22.0	–	22.0	30.8	31.2	22.0	47.15	52.8 ± 5.7	39.1
BET surface area									
BET (m^2/g)	2.9	–	2.9	–	<5	–	–	–	–
Ultimate analysis (wt%)									
Carbon content	39.4	27.2	39.4	33.8	31.4	57.7	29.84	21.1 ± 3.2	32.51
Hydrogen content	5.6	3.60	5.6	5.4	4.8	8.5	4.08	3.4 ± 0.4	5.08
Nitrogen content	6.4	1.34	6.4	5.7	4.4	9.3	3.76	3.2 ± 0.6	19.81
Sulfur content	0.9	1.11	0.9	0.9	1.0	0.5	0.94	1.1 ± 0.3	2.05

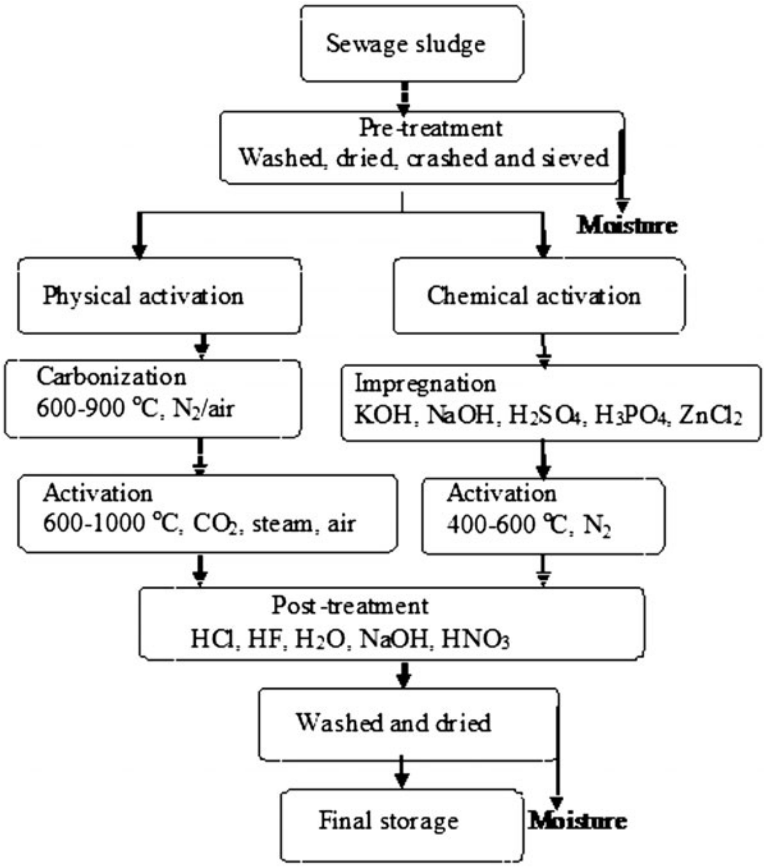

Fig. 2. Principle scheme of the activated carbons preparation from bio-solid.

and the subsequent mass loss. The activation temperature is selected by several factors, which include the type of precursor and the chemical agent used. Most literatures report that the temperature has the greatest effect on activated carbons preparation. The activation temperature is a very influential parameter on the pore structure of activated carbon, which determines the adsorption capacity. The pyrolysis of sewage sludge is usually performed under inert atmosphere at 400–1,000˚C to release volatile matters and produce chars with rudimentary pore structures [42]. Pyrolysis of activated carbon from paper mill bio-solid is carried out in an inert environment (70 mL/min flow of nitrogen) at 800˚C for 2 h. The BET surface areas, total pore volumes, and average diameter of the carbons produced are 1,249 m^2/g, 0.411 cm^3/g, and 29.62 A°, respectively [43].

4.2. Effect of duration

The activation duration has a significant effect on the development of the carbons' porous networks [44]. Proper time is required to eliminate all the moisture and most of the volatile components in the precursor so that the pores develop. The activation should be limited to the end of the volatile evolution that marks the formation of the basic pore structure. Longer activation durations cause enlargement of pores at the expense of the surface area. The controlled activation duration is economical. The shorter time period is generally desired. It reduces the energy consumption. Yield also depends on the activation duration as it drops when an optimum point is reached. Low activation time causes an incomplete burn-off. Ultimately, the result is a higher carbon yield.

4.3. Impregnation ratio

In a chemical activation process, the impregnation ratio, the ratio of the weights of the chemical agent and the dry precursor are the variables which have major effect on the characteristics of the final carbons produced. The chemical agents in the process are dehydrating agents that penetrate deep into the structure of the carbon pores to develop [44]. Ahmad and Do [45] reported that the most important variable to porosity of activated carbon development is the ratio of the chemical agent to the precursor. All precursors generally believe that as the concentration increases, the surface area also increases. An optimum concentration is evident in most cases. Larger pores, which correspond to smaller surface area, develop as more acids as are used. The strong sorbed KOH resists washing with distilled water. It still remains, causing partial blockage of the existing pores. Therefore, activation with KOH may need subsequent gasification with CO_2 or steam as combined activation procedure to affect pore opening and lead to well-developed pore structure [46]. KOH activation alone can only produce microporous activated carbon. The process of KOH plus CO_2 gasification can produce activated carbon of higher ratio mesopores. The combination improves mass transfer within the activated carbon pores [47]. KOH is found as the most effective technique for producing high BET surface area ACBS, with areas in excess of 1,882 m^2/g being reported, as shown in Table 4.

4.4. Other parameters

Parameters such as particle size and method of mixing are also affecting the pore evolution of carbon samples during the chemical or physical activation [45]. Particle size is a known parameter which has a direct effect on the physical properties of the resulting carbon during the carbonization stage. The samples with small particle size are superior in terms of their surface area and micropore volume. The reason is the higher surface of the small particles compared with that of the larger particles [45]. The impregnation method has advantages over the physical mixing method on account of better distribution of chemical agents into the carbonaceous particle mass.

Washing stage is the final stage in the preparation of activated carbons. The products of carbonization are washed with acid and water. During the final stage, the different metallic salts, acid, basic and water-soluble components are removed from the carbon structure. It is observes that the removal process of chemicals will yield porosity in the carbon structure. The distribution of these chemicals in the precursor prior to carbonization governs the pore size distribution in the final products [48]. Ros et al. [34] calculated that the BET surface area of the carbonaceous fraction alone of the HCl washed carbon was 897 m^2/g, while it was 7 m^2/g without the HCl washing step. Thus, further improvements are evidently attainable by improving the washing procedure's efficiency at removing the inorganic fraction.

5. Activation of ACBS

The activation process is needed to enhance the porosity and clean out the pores. During carbonization, the pores structure is filled with tar products. When it is decomposed, it blocks the pores [49].

Commonly, there are two methods to activate the carbon; physical and chemical methods as it is shown in Fig. 2. Physical activation is a two-step process. It involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air, or their mixtures [50,51]. Chemical activation is performed by chemical treatment of the starting material with a dehydrating agent such as KOH, NaOH, K2CO$_3$, ZnCl$_2$, H_2SO_4, H_3PO_4, and HNO_3 followed by heat treatment of the impregnated material in an inert atmosphere [52–54]. Chemical activation is carried out in a single step at lower temperatures between 400 and 700°C (fewer energy costs) and higher carbon yields [55]. Besides, part of the added chemicals, such as zinc salts and phosphoric acid, can be easily recovered.

5.1. Physical activation

Physical activation is a process in which the precursor is developed into activated carbons. Gases are used in this process. When volatile matter is eliminated during carbonization, the porous structure creates [56]. The main function of gasification is to widen the pores and create large mesoporosity. Carbon dioxide is the most commonly used activating gas in this process. It is clean and easy to handle, and has slow reaction rate. It facilitates and controls the activation process due to the slow reaction rate at temperatures around 800°C [57]. In process of carbonization, a carbon skeleton with a rudimentary porous structure is formed, which is known as char. The pores of the produced char can be blocked by the tar formed in thermal process and result in a low adsorption capacity. Therefore, thermal activation after the carbonization process is required to remove the blockage caused by tar. This activation process develops the porosity of the char and makes it suitable for adsorption purposes [58]. The reactions that may occur under such condition to extract carbon atoms from the char structure are summarized as under [59]:

$$C + H_2O \rightarrow CO + H_2, \qquad \Delta H = +117\ \text{kJ/mol}$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2, \qquad \Delta H = +75\ \text{kJ/mol}$$

$$C + CO_2 \rightarrow 2CO, \qquad \Delta H = +159\ \text{kJ/mol}$$

All of these reactions are endothermic; therefore external energy is required to supply the high activation temperature, which is almost above 800°C [60]. The H_2O molecule is smaller than the CO_2 molecule and diffuses faster into the pores of the carbon. Consequently, reaction with steam is faster than that with CO_2. Activation with CO_2 promotes external oxidation and development of larger pores as compared to activation with steam. For activated carbon, time and temperature are found to increase the carbon CO_2 reaction resulting in the enhancement of pores and formation of new pores. However, the prolonged time or too high temperature would cause the widening of pores and the collapse of some pore walls [57]. This process is referred as burn-off [61]. It is generally recognized that carbon dioxide develops mainly microporosity, and that steam produces a wider pore size distribution with larger development of wide micropores and mesopores [62]. Table 3 shows that the activated carbons obtained from bio-solid exhibit low specific surface areas when physical activation is applied due to its high ash content [8]. Therefore, the inorganic content of bio-solid, which is essentially nonporous, is high. Table 3 shows the highest BET surface area of activated carbon-derived bio-solid achieved by physical activation is between 155 and 265 m^2/g.

5.2. Chemical activation

The chemical activation is carried out simultaneously in two steps (carbonization and activation). It involves impregnation of the carbonaceous precursor with chemical activating as dehydrating agents' oxidants. Chemical activation offers several advantagessince it is carried out in a single step, combining carbonization and activation, performed at lower temperatures. Therefore, it affects the development of a better porous structure. The inorganic chemicals degrade and dehydrate the lignocellulosic materials and simultaneously to prevent the shrinkage during carbonization, whereby reducing the amount of volatile matters released and so increasing the carbon yield [69]. This is the main concept of the higher carbon yield achieved in chemical activation than the physical activation process [58]. Activation agent plays a decisive role in affecting the carbon yield and adsorption performance of the carbon adsorbents. The potassium compound which is formed during the activation step can diffuse into the internal structure of char matrix, widen the existing pores, and create new porosities, in accordance with the reactions [70,71].

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3$$

Lillo-Rodenas et al. [72] studied the gasification of graphite by alkali metal. He found that K_2CO_3 was reduced in inert atmosphere by carbon as follows:

Table 3
Some of the previous works carried out on physical activation condition of bio-solid

Sludge type	Carbonization conditions	Activation conditions	BET (m^2/g)	Ref.
Aerobic sewage sludge from WWTP	450°C/1 h	O_2:N_2 (1:29 by vol), 275°C/4 h	102	[1]
Municipal wastewater treatment plant	N_2, 750–850°C/30–90 min	–	226–217	[30]
Paper-mill sewage treatment plant	Steam, 300°C/60 min	Steam, 850°CFor 40 min	130–140	[31]
Wastewater treatment plant	N_2, 700°C/10–20 min, 100 mL/min, 5°C/ min	CO_2, 670–800°C/2–4 h, 100 mL/min	62	[34]
Municipal waste water treatment plants	Not carbonized	Steam, 550°C/60 min	97	[38]
Municipal wastewater treatment plant	N_2, 850°C/1 h	CO_2, 550°C,/0.5 h Air, 335°C, 3 h	88	[63]
	Not carbonized		80	
Municipal WWTP	N_2, 350–750°C/30 min 20°C/min	CO_2, 350–550°C	34.3–60.7	[64]
Municipal sludge	700°C/1 h	Steam, 800°C	123	[65]
Secondary biological from wastewater treatment Plant	Not carbonized	Air, 700°C/3 h	18	[66]
Anaerobically digested from municipal sewage sludge	Steam, 838°C/73 min, 10 °C/min,	Steam, 838°C/73 min,	107.7	[67]
Municipal wastewater treatment plants sludge	N_2, 250–1,000°C/5 or 10°C/min	CO_2, 838°C/80 and 73 min	155–265	[68]

$$K_2CO_3 + 2C \rightarrow 2K + 3CO$$

$$K_2CO_3 \rightarrow K_2O + CO_2$$

$$K_2O + 2C \rightarrow 2K + CO$$

The pores development in the char during pyrolysis was also important as this would enhance the surface area and pore volume of the activated carbon by promoting the diffusion of KOH and CO_2 molecules into the pores and thereby increasing the KOH-carbon and CO_2 carbon reactions. It would then create more pores in the activated carbon [73]. It can also be deduced because the pore enlargement related to NaOH activation is associated to the redox reduction and oxidative modification responsible for the development of micro- and mesoporosity according to the reaction [74]:

$$6NaOH + C \rightarrow 2Na + 3H_2 + 2Na_2CO_3$$

$$Na_2CO_3 + C \rightarrow NaO + 2CO_2$$

$$2Na + CO_2 \rightarrow Na_2O + 2CO$$

Therefore, by increasing the ratio of NaOH to char, the activation process is accelerated and correspondingly, the adsorption uptake is further enhanced [74]. As shown in Table 4, NaOH is the second most-effective reagent for generating high BET surface areas, yielding, at best, a surface area of 1,224 m^2/g. The activation of sulfuric acid into the interior char matrix may retard the formation of tar and promote the introduction of oxygen functionalities according to the reaction [75]:

$$2H_2SO_4 + C \rightarrow 2SO_2 + CO_2 + 2H_2O$$

Furthermore, H_2SO_4 activation may induce the formation of stable C–O complexes, which accounts for the internal porosities. Similarly, phosphoric acid (H_3PO_4) activation improved the adsorptive property of the carbonized char. It can be deduced. The phosphoric acid may act as an acid catalyst to promote bond cleavage, hydrolysis, dehydration, and condensation accompanied by cross-linking reactions which serve to improve the interior structure of the char matrix [76]. Additionally, H_3PO_4 molecules can be converted into phosphorus-containing constituents such as polyphosphoric acid ($H_{n+2}P_nO_{3n+1}$) and H_2O.

Table 4
Some of the previous works carried out on chemical activation condition of bio-solid

Sludge type	Chemical treatment	Activation conditions	BET (m^2/g)	Ref.
Municipal wastewater treatment plant	H_2SO_4	N_2, 600–800℃/60–180 min, 20℃/min	353–352	[32]
Wastewater treatment plant	NaOH	N_2 and CO_2, 700℃/15 min, 15℃/min	1,224	[34]
Secondary sludge from the urban wastewater treatment plant	H_2SO_4	N2, 700 ℃/30 min, 15℃/min	253	[35]
Anaerobically digested sewage sludge	$ZnCl_2$	N_2, 500℃/2 h, 400 cm^3/min, 15℃/min	647.4	[79]
WWTP	KOH	700℃/60 min	1882	[80]
Alum coagulation sludge	K_2S	700℃/60 min	1,160	[81]
Paper mill wastewater treatment	$ZnCl_2$	N_2, 800℃/2 h, 70 mL/min	1,249	[82]
Anaerobically digested sludge from an urban wastewater treatment plant	$ZnCl_2$	650℃/5 h	472	[83]
Municipal sewage sludge	H_3PO_4	650℃/60 min	289	[84]
Paper-mill wastewater treatment	KOH	700℃/90 min	900	[85]
Municipal sewage treatment plants	H_2SO_4, $ZnCl_2$	N_2, 450℃/30 min, 200 mL/min, 125℃/min	210.2	[86]
WWTP	$ZnCl_2$	N_2, 500℃/2 h, 10–20℃/min	394.1	[87]

These accelerate the carbonization of volatile components, resulting in increased porosity [77]. The mechanism for the formation of pores in activated carbon by H_3PO_4 is as follows [78]:

$$nH_3PO_4 \rightarrow H_{n+2}P_nO_{3n+1} + (n-1)H_2O$$

$$2H_3PO_4 \rightarrow P_2O_5 + 3H_2O$$

$$2P_2O_5 + 5C \rightarrow P_4 + 5CO_2$$

As shown in Table 4, the greatest BET surface area activated with H_2SO_4 ranges from 353 to 352 m^2/g. H_3PO_4 is a widely used activation reagent because it is easily used for the post-activation extraction process and has relatively low activation temperature. It is not an effective reagent for activating bio-solid, with the highest BET surface area attained being only 289 m^2/g. Chemical activation using alkali metal hydroxide reagents is found to be the most effective technique for producing high BET surface area and shows improved pore development in the carbons structure.

6. Characteristics of ACBS

6.1. BET surface area and pore size

Brunaeur, Emmett, and Teller suggested a method (BET method) to determine the surface area and pore characteristics of activated carbons [88]. BET method is based on adsorption of gas, such as nitrogen at low temperatures and conditions, which allows adsorption through purely physical forces and the amount of gas required to form a monolayer is obtained from the slope and intercept of the adsorption isotherm. The development of surface area is shown to have a linear relationship with the degree of burn-off, which is a function of different factors such as the activation temperature, gas pressure, and holding time [89]. Generally, increasing temperatures and holding time would result in a rise of burn-off due to the burn-out of micropore walls. Both the size and distribution of micropores, mesopores, and macropores determine the adsorptive properties of the activated carbons. For instance, small pore size will not trap large adsorbate molecules and large pores may not be able to retain small adsorbates, whether they are charged, polar molecules or uncharged, non-polar compounds [90]. The presence of micro- and mesopores in activated carbons enhance the adsorption of large adsorbates such as dye molecules [91]. Activated carbon includes a wide range of pores that can be classified according to the International Union of Pure and Applied Chemistry (IUPAC) definition; pores can be distinguished in three groups with respect to their dimensions (IUPAC) [92].

1. Micropores type (pore size <2 nm).
2. Mesopores type (pore size 2–50 nm).
3. Macropores type (pore size > 50 nm).

Jindarom et al. [64] reported that the BET surface areas and micropore surface areas of bio-solid-derived char as shown in Fig. 3. The BET surface areas of the as-received sludge are considerably low, 3.4 m^2/g. Under either N_2 or CO_2 atmosphere, the porosity of the materials was found to increase when volatile matter removes during pyrolysis [93]. Under the N_2 atmosphere, the BET surface area of char slightly increases when the pyrolysis temperature increases from 14.0 m^2/g at 350°C to 15.3 m^2/g at 650°C. At 750°C, the BET surface areas of char increase substantially, up to 34.3 m^2/g. As CO_2 is introduced, the BET surface areas of the char prepared at medium temperatures (350–550°C) are quite similar to those of the char derived under nitrogen atmosphere. However, above 550°C, the surface area improves dramatically from 20.0 m^2/g (550°C) to 60.7 m^2/g (750°C) owing to the CO_2 gasification effect. It is reported that the gasification removes carbon atoms from the interior of the particle. Eventually, the opened micropores and the closed micropores open [94]. The presence of CO_2 is found to enhance the formation of micropore of bio-solid char. The micropore is found at lower temperature, 650°C, in case of the char prepared by CO_2 pyrolysis, while the micropore in the char prepared by N_2 pyrolysis is found at 750°C. Pore widening occurs as a result of wall burning between micropores. This leads to an increase in internal porosity and decrease in micropores associated with high surface area. The high BET surface area and total pore volume of the activated carbon are appeared by the activation process. The process involves chemical agents, physical activating, and CO_2. Pore development during carbonization is important. It enhances the BET surface area and pore volume of the activated carbon by promoting the diffusion of chemical agent and CO_2 molecules into the pores to create more pores in the activated carbon [95]. An increase is observed in specific surface area of ACBS after carbonization and activation. Tables 3 and 4 illustrate the BET and some previous works carried out on physical and chemical activation conditions of bio-solid.

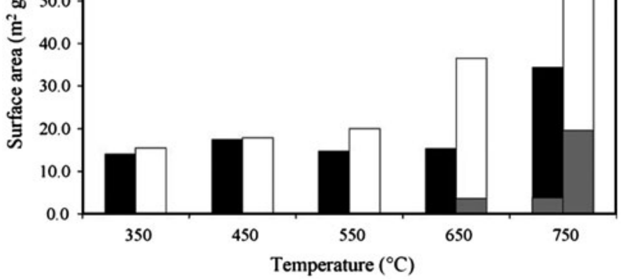

Fig. 3. BET surface area of the N_2-char and CO_2-char as a function of temperature [64].

6.2. Surface morphology

Surface morphology is considered as an important parameter when it is produced or selected an adsorbent. Scanning electron microscopy (SEM) is widely used to study the surface morphology, including the pore structure, surface structure, and pore arrangement of the material. In activated carbon production, the SEM analysis can be used to verify the presence of porosity and pore development during pyrolysis and activation processes. Fig. 4 shows the SEM images of the raw bio-solid precursor, carbonization, and the derived activated carbon, respectively. The structure of raw sludge is dense and there are almost no pores in it (Fig. 4(a)). After the carbonization and activation process, the structure appears in a different way. The surface of carbonized product is loose. Pores of different sizes and shapes appear as these are shown in Fig. 4(b) due to the decomposition of organic matters during carbonization process. Meanwhile, the pores on the surface of ACBS (Fig. 4(c)) are different from that of carbonized product, contributing to the drilling and expansion of steam to pores during activation process. These results support the increase in the BET surface area as a function of temperature. When the pyrolysis temperature increases, an increase in the solid porosity can be found. Chen et al. [79] reported that after N_2 activation of the ACBS, a clear and well-developed pore structure was obtained on the bio-solid-based activated carbon by 5M$ZnCl_2$ activation. The SEM photographs of the activated carbon show the pores of different size and shapes. The merit mentions that there is a noticeable scattering of salt particles, probably attributed to the remaining of the metal compounds on the activated carbon. Some particles are even trapped into the pores and can possibly block the entry of pores to some extent. Therefore, it seems that the adsorptive capacity of the products can further increase if the washing procedure is improved to develop the pores of activated carbon.

6.3. Surface chemistry

The surface chemistry of carbon materials is basically determined by the acidity and basicity of their surface. The existence of functional groups, such as carboxyls, phenols, lactones, aldehydes, ketones, quinones, hydroquinones, and anhydrides on activated carbon surfaces is postulated. These functional groups

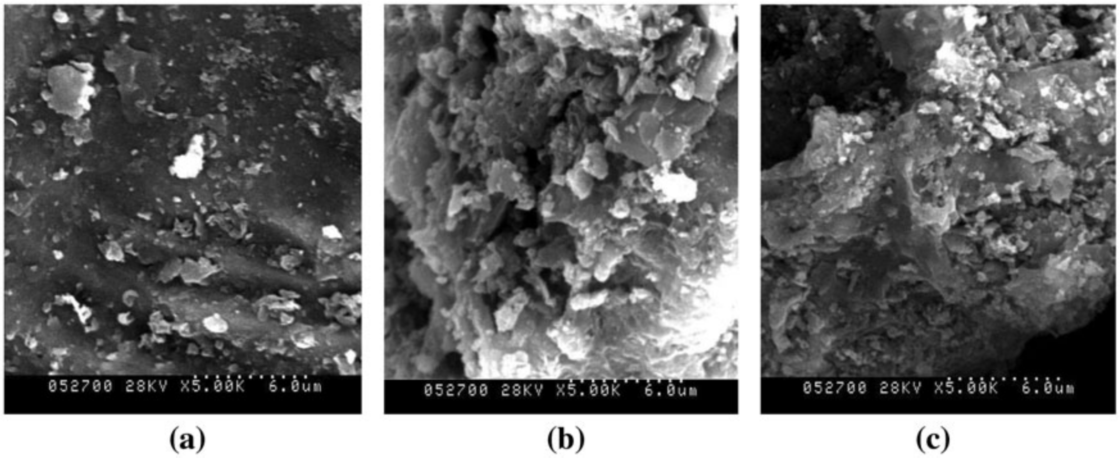

Fig. 4. SEM images of (a) bio-solid, (b) bio-char and (c) ACBS [31].

determine the acid–base character of carbon materials. The acidic and basic properties are caused by the oxygen-containing groups [96].

Cao et al. [97] used the DRIFTS technique with high sensitivity to determine the organic functional groups in bio-solid (Fig. 5). The spectrum exhibits intense characteristic absorptions of the amide groups at 3,275 cm^{-1} (O–H and N–H stretching). The strong absorbance between 2,800 and 3,000 cm^{-1} and an additional band around 1,455 cm^{-1} are assigned to aliphatic C–H stretching and bending, respectively. It shows a high degree of aliphaticity of bio-solid. The shoulder at 1,730 cm^{-1} is assigned to C=O stretching of ester carbonyl groups [98]. These aliphatic and carbonyl structures reflect the occurrence of lipids in bio-solid [99]. Furthermore, the weak band around 1,230 cm^{-1} is attributed to C–O stretch vibrations of carboxylic acids or C–N stretch vibrations, and the weak and broad band at around 2,120 cm^{-1} can be assigned to nitrile (–C≡N) and isonitrile (–N=C) stretching. The broad and strong band in the 940–1,190 cm^{-1} region, which was reported to be a typical absorbance of wastes, including bio-solid, is assigned to be C–O stretching of polysaccharide and Si–O of silicate [100]. Amira et al. [101] studded the structure of humic acids during composting of activated sludge-green waste. The main absorbance bands in FTIR spectra of the humic acids on composting bio-solid and their assignments are listed in Table 5.

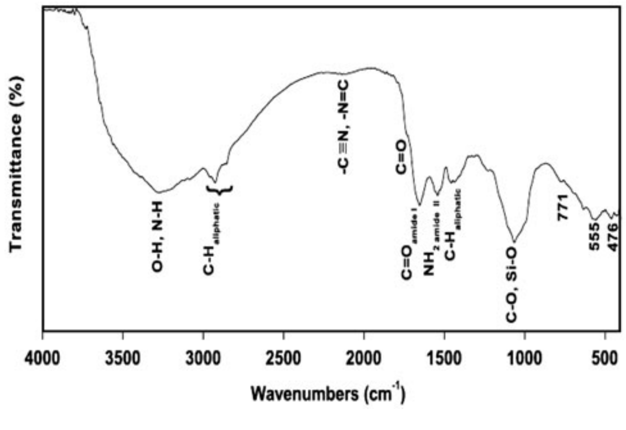

Fig. 5. DRIFTS spectrum of bio-solid [102].

Jindarom et al. [64] analyzed the functional groups on the surface of the char obtained from pyrolysis/gasification of bio-solid. The results show that the –OH and –NH of either alcohols or phenols, and nitrogen-containing surface group; and the C=O of carbonyl groups, indicated by the peaks at the bands

Table 5
The main absorbance bands in FT-IR spectra of the humic acids on composting bio-solid and their assignments

Bands and peaks (cm^{-1})	Assignments
3,300–3,400 cm^{-1}	H-bonded OH groups of alcohols, phenols, and organic acids, as well as H-bonded N–H groups
2,920–2,930 cm^{-1}	C–H stretching of alkyl structures
1,660–1,600 cm^{-1}	Aromatic and olefinic C=C, C=O in carboxyl; amide I, ketone and quinone groups
1,550 cm^{-1}	Amides II, aromatic C=C
1,450 and 1,380 cm^{-1}	OH of phenols, COO−, –CH3, amide II
1,260–1,200 cm^{-1}	Amide III or aromatic ethers C–O–C
1,070–1,030 cm^{-1}	–C–O–C of carbohydrates, aromatic ethers, Si–O–C groupments

The interpretations are based on data of numerous studies [102].

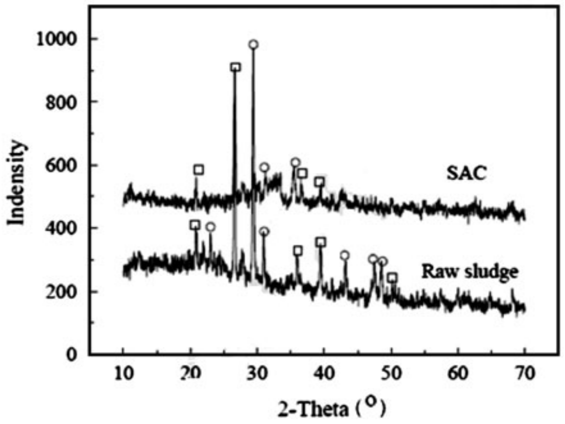

Fig. 6. XRD patterns of bio-solid and ACBS (□, quartz; ○, calcite) [31].

of 3,650–3,200 and 1,760–1,650 cm^{-1}, respectively. These oxygenated functional groups are normally related to the acidity of the carbon. The evidence of the C=C bond of aromatic rings is polarized by oxygen atoms bound near one of the carbon atoms is observed at the band of 1,450–1,428 cm^{-1}, suggesting the presence of basic oxygen-containing functionalities such as chromene structures, diketones or quinone groups, and pyrone-like groups [103]. The major absorption band of the char is 1,040 cm^{-1} assigned to either Si–O–Si or Si–O–C structures, which is associated with the silicon content in bio-solid and char [104]. The results also indicates a slight decrease in the –OH, –NH, and C=O functionalities with increasing pyrolysis temperature, resulting in a decreasing in the char acidity of char. Wen et al. [29] reported that the FT-IR spectrum of the ACBS presented with the similar shape but different strength. This indicates that the activated carbon has almost the same species but different content of functional groups on their surface. The main functional groups of the ACBS are deduced as follows: 3,450 cm^{-1}, –OH and $–NH_2$; 1,650 cm^{-1}, C=O; 1,560 cm^{-1}, $–NO_2$; and 1,385 cm^{-1}, –CH. In conclusion, there are mainly hydrophilic groups such as –OH, $–NH_2$, $–NO_2$, and C=O on the surface of the activated carbon and the major hydrophobic group is –CH.

6.4. X-ray diffraction

ACBS using $ZnCl_2$ activation can be crystallographically characterized by means of X-ray diffraction. XRD patterns of bio-solid and ACBS (Fig. 6) reveal the presence of important amounts of quartz and calcite. After activation, the amount of calcite is significantly lowered due to the decomposition of some calcite at 850°C. Then, the produced CaO could

Table 6
Previous researches in the utilization of ACBS as adsorbent for different applications

Sludge type	Adsorbate	Activation method	Adsorption capacity (mg/g)	Ref.
Sewage sludge—wastewater treatment processes	Phenol	Steam activation	36–48	[30]
	Acid red 18 dye		48–57	
	Basic violet 4 dye		69–81	
	COV		15–33	
Sewage treatment plant	Methylene blue dye	Chemical activation	139.4	[36]
	Iodine		1358.5	
Anaerobically digested sewage sludge	Phenol	Physical activation	46.95	[79]
	CCl_4		7.73	
Anaerobically sludge urban wastewater treatment plant	Methylene blue dye	Chemical activation	194.3	[83]
	Saphranine dye		250.2	
Municipal wastewater treatment plant	Methylene blue dye	Chemical activation	260	[106]
Industrial−Municipal sludge	Basic fuchsin dye	Physical activation	73	[107]
	Acid red 1 dye		127	
Municipal sewage sludge-second wastewater treatment plant	Cd^{2+}	Chemical activation	16	[108]
	Ni^{2+}		9	
Sewage sludge-urban wastewater treatment plant	Hg(II)	Chemical activation	175.4	[109]
	Pb(II)		64.1	
	Cu(II)		30.7	
	Cr(III)		15.4	

react with water and OH would be introduced, which may be the cause of negative zeta potential for ABSS in deionized water [31]. For this activated carbon, the occurrence of broad peaks at these 2θ indicates an increase of crystal structure resulting in better layer alignment [105]. Lillo-Rodenas et al. [80] observed a decrease of the main diffraction peaks of the starting inorganic compounds, indicating that the activating agent is acting as a reactive (alkaline fusion starting between 135 and 365℃). From the results discussed, the alkaline fusion should be responsible of the porosity development in the inorganic matter as well as ion recombination leading to and improving the solubilisation of most inorganic species.

7. Application of ACBS

Table 6 lists previous researches in the utilization of ACBS as adsorbents for different applications. The adsorption capacities of ACBS depend on the different sources of raw materials, the history of its preparation, and experimental condition such as pyrolysis temperature, activation time, and chemical activation agents. Many other factors can also affect the adsorption capacity in the same adsorption conditions such as surface chemistry (heteroatom content), surface charge, surface area, and pore structure. There is a significant need for more extensive applications testing of ACBS for a wider range of industrial pollutants in wastewaters and also for gas-phase applications. Wang et al. [110] used sludge-based activated carbon for its adsorption efficiency for color and TOC in the dye solutions. About 100.0% color and 99.9% TOC were removed from solution at an initial concentration of 50 mg/L, while 98.0% color and 97.9% TOC were removed at 500 mg/L. Twenty grams per liter of carbon dosage was sufficient for the removal of the dye in the solution with an initial concentration of 300 mg/L. Over the range of initial concentration investigated, the dye removal efficiency remained above 97%, indicating that the produced carbon had large adsorption capacity. Ultimately, it is clear from the present literature survey that ACBS has the potential as readily available, inexpensive, and effective adsorbents.

8. Conclusion

This review shows that thermal processing of bio-solid, especially pyrolysis, plays an important role for bio-solid disposal method. Preparation of activated carbon from bio-solid is suitable to produce a useful adsorbent for pollutants removal. The influences of activating conditions, physical and chemical, and nature of activation chemicals were discussed. The characterization of the ACBS provides a basic understanding of its structure. Most applications of ACBS concern the removal of pollutants from gas and wastewater via adsorption process. The literature review mentions that pyrolysis of bio-solid can be a proof of an interesting alternative route for the economical and environmentally acceptable synthesis of carbon-based adsorbents.

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