

Development of carbon dioxide adsorbents from renewable and non-renewable sources: A review

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Abstract

High concentration of carbon dioxide in the atmosphere which consistently and gradually increased every year imposed a serious impact especially to the environment such as climate change and global warming. Several methods have been established to mitigate this issue such as through absorption and adsorption technique. Carbon dioxide absorption using amine-based absorbent have been commonly used due to its rapid reaction. However, it has several major drawbacks such as its production of harmful by-product and high-energy demand. Contrary to absorption method, adsorption of carbon dioxide via adsorbents is simpler, environmentally friendly and high-energy efficiency. Availability of several type of adsorbents provides researchers and industries with a broad choice of selection, for example carbon-based adsorbents. In this review, development process of carbon-based adsorbents from renewable and non-renewable sources such as biomass, polysaccharides, microorganisms, coal, petroleum, and synthetic polymers are summarized. Other than that, the physical and chemical properties of the prepared adsorbents which influenced the adsorption of carbon dioxide are also reviewed. This review is expected to stimulate sustainable development of carbon dioxide adsorbent which benefits both environment and industry.

Keywords: carbon precursor, renewable sources, non-renewable sources, adsorption

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INTRODUCTION

Air pollution is a condition where harmful or excessive quantities of substances such as gases, particles, and biological molecules are introduced into the atmosphere. Air pollution can be grouped into several groups such as; indoor or outdoor and naturally occurred or anthropogenic-introduced. Often the danger of air pollution is neglected because it is too small to be seen with naked eyes and the effects usually developed gradually rather than instantly. The adverse effects cause by air pollution are manifest in health problems and environmental degradation. Particulate matter (PM) such as PM_{2.5} has been reported to cause health problems as it can travel through and deposited in the respiratory system (Okuda et al., 2015; Surib et al., 2019). Climate change and global warming that can be felt around the world are commonly associate to greenhouse gases emission such as methane, ozone, and carbon dioxide. Among different types of greenhouse gases, carbon dioxide is the main culprit to the emission (Firouzi, Sobri, Yasin, & Ahmadun, 2011; Solomon, Plattner, Knutti, & Friedlingstein, 2009).

Carbon dioxide is a natural gas which is colourless, odourless, and slightly acidic. This gas is essential for plant growth, chemical uses, as refrigerant, in production of alcoholic and fizzy drinks, and other uses (Padalkar & Kadam, 2010). However, this natural gas has been identified as one type of air pollution due to its high concentration in the atmosphere. Moreover, its concentration is predicted to gradually increase in the future and surely will impose a greater impact.

Therefore, a solution known as carbon capture, utilisation, and storage (CCUS) is established.

Carbon dioxide capture methods, as illustrated in Fig. 1, can be done either in pre-combustion, post-combustion, and oxyfuels combustion and there are several methods available (D'Alessandro, Smit, & Long, 2010). Each method has its advantages and disadvantages. Among all of these methods that are available, carbon dioxide capture through adsorption has grabbed the interest of researchers and industries as it is easy to operate, environmentally friendly, and high energy efficiency (Younas, Sohail, Leong, Bashir, & Sumathi, 2016). Adsorption is a process where gas molecules known as adsorbate are trapped inside the pores of the solid adsorbents (Saha & Kienbaum, 2019). Commercially, there are numerous types of adsorbents for carbon dioxide such as silica-based, zeolite-based, and carbon-based adsorbent. Interestingly about carbon-based adsorbent is it can be developed from renewable and non-renewable sources.

Carbonaceous materials with unique properties have been widely used in several applications such as in battery system and others (Faizal, Khairunnisa, Yokote, & Lenggoro, 2018). In this review, carbon-based adsorbents from renewable and non-renewable sources are reviewed and the preparation process of the adsorbents from different sources are further discussed in details. Other than that, the characteristics and adsorption mechanisms of the synthesised adsorbents are also explained and compared.

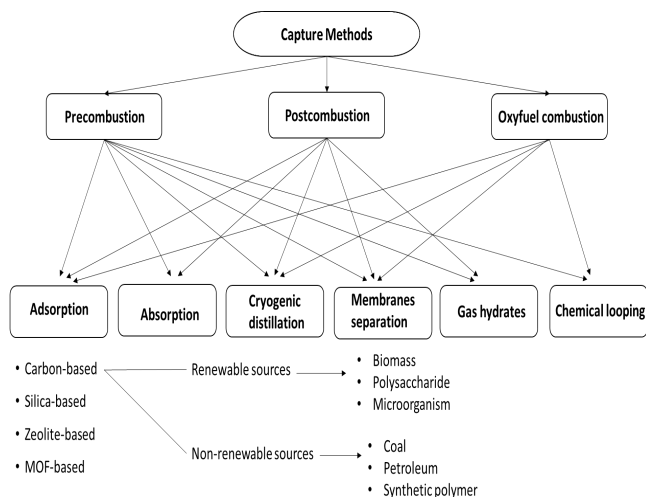


Fig. 1 Carbon dioxide capture method.

RENEWABLE SOURCES

Biomass

Biomass is any material produced by the growth of microorganisms, plants, and animals. The materials have been used in various fields such as in energy production, manufacturing industry, and many more (Heinimö & Junginger, 2009; Saygin, Gielen, Draeck, Worrell, & Patel, 2014). Recently, biomass also has been widely used in the production of adsorbents to adsorb carbon dioxide and other type of gases and also used in wastewater treatment. In general, biomass is available in the form of raw material and waste material which benefitted the economy and environment. As shown in Fig. 2, several studies have been carried out to adsorb carbon dioxide by using various materials such as sugarcane bagasse, coconut shell, peanut shell, almond shells, sunflower seed, rice husk, and many more. These materials were used by the researchers as carbon precursors and further developed it into adsorbents through several process such as char production and activation.

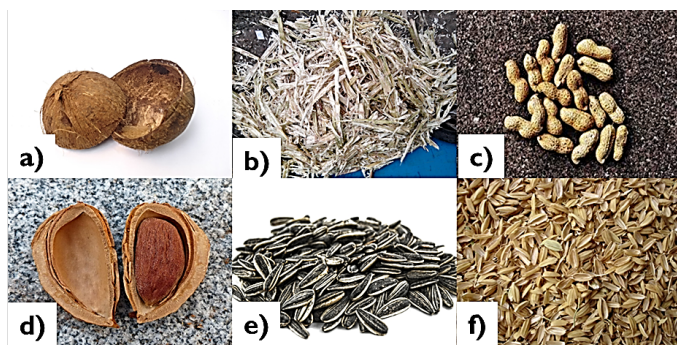


Fig. 2 Some biomass used as carbon precursor. a) coconut shell; b) sugarcane bagasse; c) peanut shell; d) almond shell; e) sunflower seed; f) rice husk.

Preparation process of biomass-based adsorbents

Production of char is common in production of non-activated and activated carbon dioxide adsorbent. The first route involves production of biochar when biomass undergo slow pyrolysis. Slow pyrolysis is the slow heating of organic material in oxygen-limited environment or also known as carbonisation. There are 4 categories of pyrolysis; slow, fast, flash, and intermediate pyrolysis. Biochar production usually conducted in temperature range between 300-650 °C and residence time of few minutes to couple of hours (Kambo & Dutta, 2015). Additionally, this carbonisation process can be conducted under nitrogen flow (Alabadi, Razzaque, Yang, Chen, & Tan, 2015; Deng et al., 2015; A. Kumar & Jena, 2016). Meanwhile, the second route in char production is a process known as hydrothermal carbonisation (HTC) where the biomass is heated in the presence of water and heated in a

confined system producing a solid by-product called hydrochar. In hydrochar production, the raw material will be mixed with distilled water to obtain an intermediate product known as aqueous dispersion which will be autoclaved at temperatures ranging from 150 °C to 350 °C for at least 20 minutes up to 24 hours. Jujun grass, camellia japonica, starch, and cellulose were among biomass used to synthesis carbon dioxide adsorbents in several studies (Bhatta et al., 2015; Coromina, Walsh, & Mokaya, 2015; Sevilla & Fuertes, 2011). An advantage to be noted in hydrochar production is it does not require pre-drying process of wet biomass with moisture content (>30%). However, it has a more complex after process where several treatments such as mechanical dewatering, filtering, solar/thermal drying, and pulverisation are required which makes the process costlier. Usually, the product of biochar and hydrochar are further chemically activated by several activating agents to produce activated carbons as illustrated in Fig. 3.

The most widely used method for the past few years in preparation of carbon dioxide adsorbent is through activation process, either by chemical activation or physical activation. In chemical activation, activating agents which belong to different categories such as acids, bases, and salts were normally used for activation of biomass materials. One-step activation process is a process where the raw precursor is impregnated with chemical agents prior the heat treatment which enable to shorten the preparation time. Meanwhile in two-step process activation, the carbon precursor is carbonised to obtain bio-solid and impregnation with chemical agent were carried out followed by second heat treatment (Ukanwa, Patchigolla, Sakrabani, Anthony, & Mandavgane, 2019). Activation temperature of the material varies and range between 400 °C to 800 °C. The time utilised for the activation also varies as fastest as 30 minutes and up to 4 hours. Optimisation of the activation process was attempted by several studies as the best conditions are different between different precursors and highly depended on the nature of the precursors. Some advantages of chemical activation are it produces high yield with more defined development of microporosity (Hernández-Montoya, García-Servin, & Bueno-López, 2012). Contrary to chemical activation, physical activation is a straight forward process where it only needs a single step activation using air, carbon dioxide, steam or combination of these agents at temperature ranging between 700 °C to 1200 °C. Although the physical activation is more environmental friendly and cheaper, however, it leads to problems such as low carbon yield, destruction of pores network, and ash generation (Ukanwa et al., 2019).

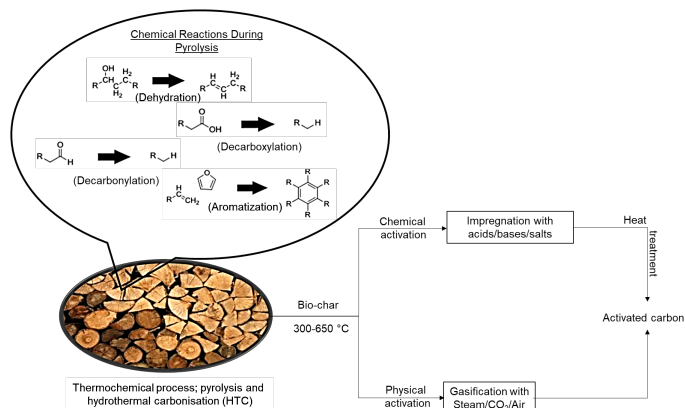


Fig. 3 General synthesis pathway of activated carbon through chemical and physical activation.

Biomass-based adsorbents which were synthesised from biomass such as coconut shell and rice husk are also commercially available and either used directly or undergo further modification such as in several studies (Abiko, Furuse, & Takano, 2010; Adelodun, Ngila, Kim, & Jo, 2016). A study oxidised the commercial activated carbon prior functionalisation it with triethylenetetramine solution (Keramati & Ghoreyshi, 2014). Besides that, amide is also has been used in functionalisation of biomass precursor (Rao et al., 2019). The only difference between amine and amide is that amine has no carbonyl group attached to the nitrogen atom, meanwhile for amide there is a

carbonyl group attached to a nitrogen atom. Above that, modification of activated carbon also has been made through incorporation of metal oxide such as copper oxide, chromium oxide, and nickel oxide. Metal oxide incorporation can be done via simple dissolution of activated

carbon with metal oxide, plating, and post-oxidation method (Jang & Park, 2012; Kim, Cho, & Park, 2010; Somy, Mehrnia, Amrei, Ghanizadeh, & Safari, 2009).

Table 1 Biomass-based carbon dioxide adsorbent.

Carbon precursor	Method	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Adsorption capacity (mmol/g)	References
Vine shoots	Biochar production	374	0.186	1.10	(Manyà, González, Azuara, & Arner, 2018)
Sugarcane bagasse and hickory wood	Biochar production	388	-	1.67	(Creamer, Gao, & Zhang, 2014)
Pine sawdust	Physical activation with CO ₂	788	0.34	0.42	(Durán, Rubiera, & Pevida, 2017)
Olive stones and almond shell	Physical activation with CO ₂	1215	0.51	3.10	(González, Plaza, Rubiera, & Pevida, 2013)
Oil palm empty fruit bunch	Physical activation with CO ₂	548.07	0.2552	2.09	(Joseph, Quek, Daud, & Moh, 2017)
Cherry stones	Physical activation with CO ₂ and steam	1045	0.48	2.69	(Álvarez-Gutiérrez, Gil, Rubiera, & Pevida, 2016)
Giant reed (<i>Arundo donax</i>)	Mixture of giant reed (carbon source) and urea (nitrogen source) was activated with KOH	982	0.62	9.00	(Singh et al., 2018)
Seaweed	Activation with KOH	291	0.24	1.05	(Ding & Liu, 2020)
Rice straw	Activation with KOH	1048	0.64	-	(Rahman & Chin, 2019)
Wood	Activation with H ₃ PO ₄	1215	0.752	4.61	(Botomé et al., 2017)
Jujun grass	Activation with KOH	2753	1.23	4.90	(Coromina et al., 2015)
<i>Camellia japonica</i>	Activation with KOH	2557	1.21	5.00	(Coromina et al., 2015)
Coconut shell	-	824	0.502	-	(Huang, Cheng, & Lin, 2015)
Peanut shell	Activation KOH	956	0.43	5.23	(Deng et al., 2015)
Sunflower seed	Activation with KOH	1790	0.77	7.06	(Deng et al., 2015)
Empty fruit bunch	Activation with KOH	2511	1.06	3.71	(Parshetti, Chowdhury, & Balasubramanian, 2015)
Water chestnut shell	Activation with NaNH ₂	2615	1.59	4.50	(Rao et al., 2019)
Commercial AC	Nickel oxide modification via plating	1053	1.07	2.08	(Jang & Park, 2012)
Commercial AC	Chromium oxide modification via dissolution	814	-	~1.50	(Somy et al., 2009)
Activated carbon	Copper oxide modification via plating and post-oxidation	1510	0.86	~0.51	(Kim et al., 2010)

Characteristics and adsorption mechanism by biomass-based adsorbents

Through thermochemical conversion of biomass to char product, several chemical reactions may take place such as decarboxylation, dehydration, decarbonylation, demethoxylation, condensation, intermolecular derangement, and aromatization as shown in Fig. 3 (Kambo & Dutta, 2015; Wang, Dai, Yang, & Luo, 2017). Differences of physicochemical properties of biochar and hydrochar have been reported previously. The improvement of surface area and porosity can be observed in both biochar and hydrochar at temperature not exceeding 500 °C and 230 °C, respectively. For instance, porous structure was observed in biochar produced from oil palm wastes which may be due to liberation of volatile matter during pyrolysis (Aliyu, Abdullahi, & Sulaiman, 2017). As the HTC process is conducted at

lower temperature, the mass yield of char obtained generally higher around (40-70 %) compared to biochar with yield around (25-35 %) (Dieguez-Alonso et al., 2018). Besides, the presence of water in HTC process involved in hydrochar production enable demineralization of inorganic compositions of biomass resulting in reduction of ash content. Meanwhile, biochar obtained from pyrolysis recorded an increase in the percentage of ash. Although with small correlation, pH of the biochar increases as the ash content increases and this might be an advantage in adsorption of slightly acidic gas of carbon dioxide.

Biomass-based adsorbents are excellent adsorbents for carbon dioxide. Table 1 presented several types of biomass that have been used as carbon precursors and it is proven that biomass can be an excellent carbon dioxide adsorbent with high adsorption capacity. For instance, activated carbon synthesised from sunflower seed has high adsorption

capacity of 7.06 mmol/g. Most of the prepared biomass-based adsorbents exhibit Type I isotherm which indicate that the adsorbents are microporous material. Influence of narrow micropore (< 1 nm) in determination of adsorption capacity has been widely accepted in many studies. Moreover, micropore structure also influenced the specific surface area which is another important parameter in preparation of carbon dioxide adsorbent. What can be clearly seen in this review is the common utilisation of chemical activation especially with potassium hydroxide (KOH) which is not limited to activation of biomass only.

During the activation with KOH, more mesopores and micropores are developed due to the intercalation of potassium into the carbon network (Hui & Zaini, 2015). Therefore, activation with KOH increase the porosity and surface area of the adsorbent which was reported in several literatures (Mopoung, Moonsri, Palas, & Khumpai, 2015; Rahman & Chin, 2019; Rostamian, Heidarpour, Mousavi, & Afyuni, 2015). Good enhancement of porosity governs the efficiency of physical adsorption where the adsorbate weakly interacts with the surface of the adsorbent via weak intermolecular forces as illustrated in Fig. 4. Thus far, no definite conclusion can be made to determine which is the best activating agent of all as it primarily depends on the precursor used and the purpose of the activation. Both physical and chemical activation were proven to enhance the physical properties of the carbon surface. However, it can be seen that the enhancement recorded by physical activation is moderate compare to chemical activation which manifest a greater improvement in general. This explains why chemical activation is more preferred by researchers despite the preparation process is more tedious as illustrated in Fig. 3.

Effect of activation temperature and time were analysed in several studies such as in the production of activated carbon from wood. Activation time was reported to be more pronounced than activation temperature as it controls the characteristics of the adsorbent. As activation time increases, surface area and micropore volume increased, while the yield was reduced (Botomé et al., 2017). The ratio of activating agent and precursor in the activation process also influence the carbon dioxide adsorption capacity. The amount of carbon dioxide adsorbed increased with the increase of mass ratio but up until certain threshold. Increase beyond the optimum ratio will reduce the performance of the activated carbon as the over-intense activation process will cause a microporous structure to collapse (Deng et al., 2015). Notably, the optimise conditions for activation process might be different for different precursors.

Carbon dioxide as a slightly acidic gas has an affinity for basic sites which promote chemisorption to take place. Chemical adsorption involves stronger bond such as covalent bond due to electron sharing as illustrated in Fig 4. Incorporation of several functionalities during pre-treatment, such as pyridinic, pyrrolic, and pyridonic are attributed to the changes in the acidity of the prepared materials. Meanwhile, basic nitride and aromatic amine groups show basic affinity towards carbon dioxide as there are available unpaired electrons and absence of electron-withdrawing elements. Some reactions such as dehydration and decarboxylation during pyrolysis were reported to reduce hydrogen and oxygen-containing functionalities while nitrogenous groups increased (Creamer et al., 2014). As the addition of basic species enhances the adsorption of carbon dioxide, removal of acidic groups such as carboxylic is also favourable in the adsorption process. Chemical activation process by H_3PO_4 was reported to decompose carboxylic groups and resulting in the formation of new C sites which easily adsorb carbon dioxide (Botomé et al., 2017).

Among the distinctive methods applied to incorporate basic sites on the carbon surface is through introduction of metal oxide such as nickel oxide and chromium oxide. A study by Somy had performed modification of commercial activated carbon with chromium oxide reported that the carbon dioxide adsorption capacity increased (Somy et al., 2009). Similarly, a study by Kim had modified activated carbon with copper oxide reported that the metal oxide have base features which definitely will influence the adsorption of this slightly acidic gas through chemisorption (Kim et al., 2010). Through the incorporation of metal oxide, reduction in the average pore size is also predicted. Treatment of activated carbon with nickel oxide in a study concluded that such observation is obtained due to the action of pore filling or blocking behaviours of the metal (Jang & Park, 2012). In authors

opinion, this method is promising to alter the performance of a problematic activated carbon such as the one with relatively low surface area and pore volume. However, the process might increase the production cost of the adsorbent.

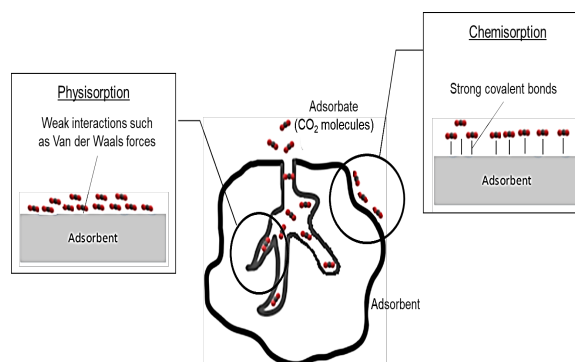


Fig. 4 Schematic illustration of the adsorption of carbon dioxide via physisorption and chemisorption.

Polysaccharide

Polysaccharides are polymeric carbohydrate molecules composed of long chains of monosaccharide units bound together by glycosidic linkage. Examples of polysaccharides are cellulose, chitosan, and sucrose as shown in Fig. 5. Polysaccharides are produced naturally from plants and animals which is known as biopolymer. Meanwhile the artificially produced polymers are called synthetic polymers. For instance, chitosan, a derivative which naturally occurs as chitin is a major waste from shells of the crustaceans (Younes & Rinaudo, 2015). Commercially, polysaccharides were used in industries such as in food packaging and textile (Ferreira, Alves, & Coelho, 2016). Good sorption properties of the biopolymers make it suitable to be used in removal of dye, heavy metals, clean-up of oil and solvent spills and carbon dioxide adsorption (Dassanayake, Acharya, & Abidi, 2018). Previous studies proved that biopolymers can be as good as biomass as shown in Table 2. For instance, to date, a study done by Hu recorded the highest adsorption capacity for polysaccharide-based adsorbent with 4.99 mmol/g (Hu et al., 2016).

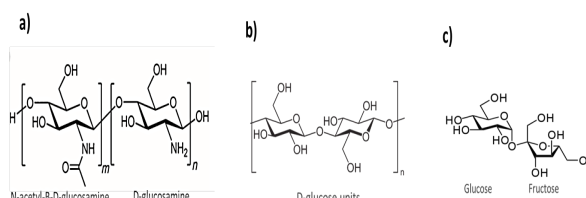


Fig. 5 Chemical structure of some polysaccharides; a) Chitosan; b) Cellulose; c) Sucrose.

Preparation process of polysaccharide-based adsorbents

Previous studies have established three techniques to prepare polysaccharide-based adsorbent as illustrated in Fig. 6. A straight forward and simple route of polysaccharide-based adsorbent preparation is in the usage of usually non-porous polysaccharide as coating material on mesoporous and macroporous solid support. Meanwhile, a common procedure of chemical activation that has been explain in previous section for polysaccharide materials is applied. Furthermore, a more complex method is applied in amino modification approach. Thus far, two methods that have been established for amine functionalisation are freeze drying and hot press method. Freeze drying method is a conventional and the most utilised way to introduce amine groups to carbon material, however, it has several major drawbacks. In general, freeze drying method is not only expensive and energy inefficient but it is also time consuming (Antal, 2015). Therefore, a more recent method which is hot press is introduced. As can be seen from Fig. 6, the coating method is the simplest method, however, chemical activation and amine functionalisation are more preferred probably because it produces adsorbent with higher adsorption capacity.

Table 2 Polysaccharide-based carbon dioxide adsorbents.

Carbon precursor	Method/s	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Adsorption capacity (mmol/g)	References
Chitosan	Chemical activation with K ₂ CO ₃	2567	1.49	3.86	(Fan, Zhang, Zhang, Shu, & Shi, 2013)
Chitosan	Chemical activation with alkali metal carbonate (Na ₂ CO ₃ , K ₂ CO ₃ and etc.)	2145.3	0.99	4.88	(Fujiki & Yogo, 2016)
Chitosan	Amine functionalisation with polyethylenimine	73.29	0.134	2.90	(Fujiki & Yogo, 2014)
Chitosan	Amine functionalisation with 4-formyltriphenylamine	52.78	0.071	0.85	(Kumar, Silva, Wani, Dias, & Sobral, 2015)
Chitosan	Coating material	26.56	0.587	-	(Yoshida, Oehlenschlaeger, Minami, & Terashima, 2002)
Chitosan	Coating material	376	0.56	0.98	(Sneddon, Ganin, & Yiu, 2015)
Chitosan and glucose	Carbonisation	1049	0.72	5.52	(Wu, Zhang, et al., 2019)
Chitosan	Activation under nitrogen	462	0.27	3.23	(Wu, Gao, et al., 2019)
Glucose	Activation with potassium oxalate monohydrate	1270	0.50	4.50	(Sevilla, Al-Jumaily, Fuertes, & Mokaya, 2017)
Cellulose	Nitrogen doping of carbon aerogel	615	0.64	4.99	(Hu et al., 2016)
Cellulose	Amino modification by freeze drying method	7.1	-	1.39	(Gebald, Wurzbacher, Tingaut, Zimmermann, & Steinfeld, 2011)
Cellulose	Amino modification by hot press method	-	-	1.00	(Helmlinger et al., 2017)
Cellulose	Amino modification with freeze drying method	36.4	0.177	1.78	(Liu et al., 2018)
Cellulose	Amino modification at room temperature	2.37	-	2.11	(Valdebenito et al., 2018)
Cellulose	Amino modification at 100 °C	77	0.60	1.68	(Zhang, Zhang, Jiang, & Wang, 2018)
Sucrose	Sucrose as impregnation agent on zeolite template	1254.38	0.945	2.39	(Gunawan, Wijiyanti, & Widiastuti, 2018)
Sucrose and Urea	Chemical activation with KOH	2366	1.16	4.30	(Sivadas, Vijayan, Rajeev, Ninan, & Prabhakaran, 2016)

Table 3 Microorganism-based carbon dioxide adsorbent.

Carbon precursor	Method/s	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Adsorption capacity at 25°C and 1 bar (mmol/g)	References
<i>Saccharomyces cerevisiae</i> (yeast) from brewery	Carbonisation and chemical activation with KOH	Carbonised sample: 2 m ² /g. Activated samples: 415-1348 m ² /g.	Carbonised sample: 0.05 cm ³ /g. Activated samples: 3-0.67 cm ³ /g.	Adsorption capacity of carbonised sample is 1.30 mmol/g. Adsorption capacity of activated samples is between 4.05-4.77 mmol/g. It showed that surface area and pore volume are important in carbon dioxide adsorption. Sample activated at 600°C has more nitrogen content compared to sample activated at 700°C.	(Shen, He, Zhang, Li, & Fan, 2012)
<i>Agaricus</i> (fungi)	Chemical activation with KOH	Carbonised fungi: 2 m ² /g. Activated sample: 2264 m ² /g.	The highest pore volume recorded is 0.92 cm ³ /g.	Adsorption capacity of the activated samples is between 3.1-5.5 mmol/g. Sample with higher micropore volume will have higher adsorption capacity even when the samples compared have quite similar surface area.	(Wang et al., 2012)

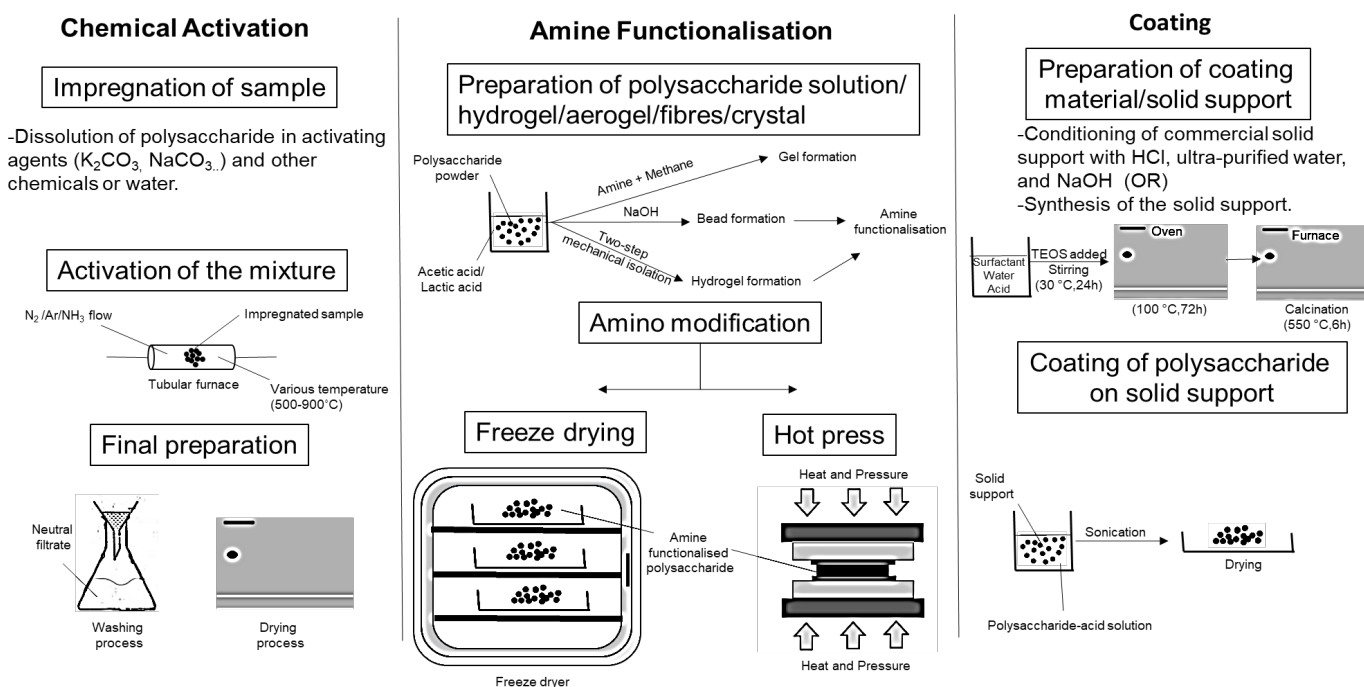


Fig. 6 Different preparation techniques in development of polysaccharide-based adsorbent.

Characteristics and adsorption mechanism by polysaccharide-based adsorbents

Natural chemical structure of some polysaccharide such as chitosan consists free amine groups, which can chemically bind carbon dioxide molecules despite it being non-porous has been studied by Sneddon (Sneddon et al., 2015). Moreover, amino modification which is to introduce amine groups to the carbon-based adsorbent has allows chemisorption to occur. Incorporation of amine groups provides carbon surface with basic sites which will bind carbon dioxide molecules although the observed surface area and pore volume of the modified carbon were greatly reduced or lowered compared to the activated polysaccharide. For instance, a study conducted by Valdebenito observed a reduction in surface area of amino-modified cellulose precursor, but the adsorption capacity was 2.11 mmol/g which was higher compared to non-modified cellulose precursor with only 0.15 mmol/g.

Referring to Table 2, polysaccharide-based adsorbents prepared by chemical activation presented, in general a greater surface property such as high surface area and total pore volume. Hence, chemical activation method is probably more appealing as it recorded a higher adsorption capacity. Previous studies demonstrated that the existence of significant number of pores and nitrogen functional groups enable both physisorption and chemisorption to occur simultaneously on the same medium (Fan et al., 2013; Fujiki & Yogo, 2016; Wu, Zhang, et al., 2019).

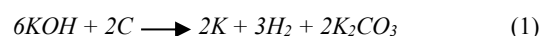
Microorganism

Microorganisms are microscopic living organisms like bacteria, protozoa, and even fungi, which most of it cannot be seen by naked eyes and can be only viewed by viewing aids such as microscopes. These organisms can be found everywhere and anywhere and have several relationships with other living organisms such as in a symbiotic and parasitic relationship. It also has been utilised in many ways such as in food production and bioremediation (Abatenh, Gizaw, Tsegaye, & Wassie, 2017; Caplice & Fitzgerald, 1999). Interestingly, less than a decade ago, organisms such as fungi and yeast, started to be used in a few studies for carbon dioxide capture. To date there are only two studies that used microorganism as carbon precursor to adsorb carbon dioxide.

Preparation process of microorganism-based adsorbents

Microorganism-based carbon dioxide adsorbent also can be prepared through chemical activation, especially KOH. It will start with carbonisation followed by activation. The process is similar to what has been explained in the preparation process of biomass-based adsorbents by chemical activation as discussed in previous section.

A study by Wang in 2012 was the first ever study to use fungi known as *Agaricus* as the carbon precursor in the development of porous adsorbent. The *Agaricus* was dried prior pre-carbonised at 500 °C under argon flow and a product known as char was obtained. Activation of carbon precursor under inert gases such as nitrogen and argon is usually applied to reduce the liberation of carbon by oxidation, hence it will increase the yield obtained after the activation (Indayaningsih, Destyorini, Purawiardi, Insiyanda, & Widodo, 2017). Then, the fungi-based chars were chemically activated by KOH (Wang et al., 2012). Chemical activation of fungi-based chars by KOH, as represented by the stoichiometry equation below, was reported to be successful in enhancement of pore volume and surface area. Prior activation process, the fungi-based char was described as non-porous material with very low specific surface area of only 2 m²/g.



Another study conducted by Shen used yeast, another type of microorganism, to synthesis a carbon dioxide adsorbent (Shen et al., 2012). A budding yeast known as *Saccharomyces cerevisiae* is widely used in food production such as in baking and alcohol production. In the study, a discarded brewery yeast was collected and used as carbon source. Normally, the yeast has about 10.6 % of nitrogen content, which give it an additional advantage as carbon dioxide adsorbent.

Characteristics and adsorption mechanism by microorganism-based adsorbents

Microorganism-based adsorbent is the least utilised type of adsorbent when only a few studies are found. However, microorganisms have proved to have a great potential in development of adsorbents. Table 3 presented few studies that used microorganisms in preparation of carbon dioxide adsorbents with good adsorption capacity. For instance, fungi-based char and yeast-based char produced from both literature mentioned in this review, have a very low surface area of about 2 m²/g which were considered as non-porous material.

However, after activation by using KOH, both types of samples were greatly enhanced. (Wang et al., 2012; Shen, He, Zhang, Li, & Fan, 2012). These results prove that the surface properties of microorganisms are keen for modification. The only difference observed between these two studies are the degree of enhancement.

Fungi-based adsorbent recorded a high surface area of 2264 m²/g, almost double the surface area recorded by the activated yeast with the highest surface area recorded was 1348 m²/g, given that they have a similar starting surface area and used the same activating agent. This observation was observed maybe due to the different amount of KOH used. With the increasing amount of KOH, the specific surface area and micropore volume also increased. Therefore, it is understood that every carbon precursor may have its own optimum char/activating agent ratio in order to avoid over-activation and to have a great adsorption capacity. The prepared porous carbons from fungi and yeast exhibit Type I isotherm which indicates the microporosity of the samples which is the main contribution to the high carbon dioxide uptakes. Moreover, both studies concluded that the adsorption process deviates from Langmuir model which only possible for monolayer adsorption.

The highest carbon dioxide uptake recorded by activated fungi was 3.5 mmol/g under atmospheric condition and these fungi-based carbons were claimed to have comparable or higher carbon dioxide uptakes compared with the most porous polymers and carbons. Meanwhile carbon dioxide adsorption by activated yeast showed a better performance with the highest adsorption capacity recorded was 4.77 mmol/g under atmospheric condition. Synergetic effect of high surface area, pore volume and availability of nitrogen species in this particular sample is believed to contribute to its good performance.

The budding yeast, *S. cerevisiae* originally is a material mainly composed of carbon, oxygen, nitrogen, and oxygen. Nitrogen content available in the yeast is able to serve as basic binding site for slightly acidic gas such as carbon dioxide, even though it is non-porous. The carbonised sample with the highest nitrogen content compared to another sample was reported to have adsorption capacity of 1.30 mmol/g. However, observed in the study, nitrogen content decreased after the activation process due to condensation of oxygen and nitrogen-functional groups, which results in an increase of hydrophobicity.

NON-RENEWABLE SOURCES

Coal

Coal the carbonaceous fossil fuel is a black or brownish-black sedimentary rock which is classified as non-renewable energy because it takes hundreds of millions of years to be formed (Sear, 2009). Fly ash is the main component of the total combustion residues from coal-fired power plants. Approximately, the production of fly ash reaches about 1 billion tonnes annually. The disposal of fly ash to the landfills and ash ponds posed threats especially to the environment. Green and sustainable development involving the use of fly ash can be seen mainly in construction (Association, 2003; Nordin, Abdullah, Tahir, Sandu, & Hussin, 2016).

Fly ash has been used as carbon precursor that can be developed into a different type of adsorbents such as activated carbon, zeolite and mesoporous silica depending on the content of the fly ash. Adsorptive removal of carbon dioxide using fly ash is based on its alkali and alkaline earth metals content. (Dindi, Quang, Vega, Nashef, & Abu-Zahra, 2019). Production of zeolite-based and mesoporous silica from fly ash is not discussed in detail in this review as the authors focusing on the carbon-based adsorbent development.

Preparation process of coal-based adsorbent

Fly ash with high carbon content (14%-60%) has limited usage in construction but it is suitable to be used in the production of activated carbon. Preparation of activated carbon from fly ash started with isolation of carbon content through physically or/and chemically such as sieving and acid digestion respectively. Then, the carbon residual is activated either thermally or chemically. Thermal activation was conducted at 850-900°C in the steam of nitrogen or carbon dioxide. From the activation process, the surface area of the residual carbon is increased but the activated carbon yield is lowered. Therefore, activation can be done chemically such as by using amine like

monoethanolamine (MEA) and diethylamine (DEA) (Sarmah, Baruah, & Khare, 2013).

Other type of adsorbents for carbon dioxide adsorption also can be produced from fly ash. Fly ash with low amounts of unburned carbon and high content of silicon and aluminium compounds is suitable to produce zeolite-based adsorbent through several methods; hydrothermal, fusion-hydrothermal, molten salt, and hollman method (Dindi et al., 2019). General steps in the synthesis of zeolite as described in Table 4 are dissolution, condensation, nucleation, and crystal growth.

Table 4 Description of reactions involved in the formation of zeolites (Dindi et al., 2019).

Steps	Details
Dissolution	Silicates and aluminates are released from fly ash into the solution.
Condensation	The dissolved aluminates and silicates undergo condensation reaction to form polymeric silico-aluminate species. This reaction will stop the dissolution process.
Nucleation	The polymeric formed become nucleation sites for zeolite crystallisation. This reaction will stop the dissolution process
Crystal growth	With increasing time and temperature, zeolite crystals will grow.

It is interesting to note that fly ash has substantial amounts of silica that can be utilised in synthesis of mesoporous silica with pore size between 2-50 nm as illustrated in Fig. 7 which involves alkali fusion, sodium silicate extraction, and thermal treatment (Zhang, Ravi, Lee, Ahn, & Ahn, 2018).

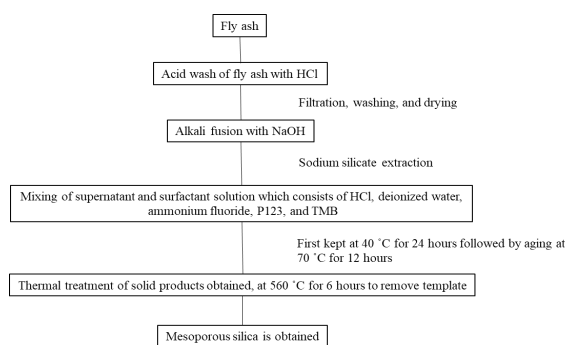


Fig. 7 Synthesis pathway of mesoporous silica from fly ash.

Development study has been carried out by Adelodun as shown in Fig. 8, started back in 2013 to chemically modify the surface of commercially available coal-based activated carbon through various pre-treatment prior application of thermal treatment. Chemically modified carbon surfaces in all his studies successfully enhanced the selectivity of carbon dioxide adsorption compared to the virgin activated carbon. In general, the main objective of his studies is to increase surface oxygen functionalities (SOFs) and surface nitrogen functionalities (SNFs) as illustrated in Fig. 9 and Fig. 10, respectively, as these groups have high affinity toward carbon dioxide.

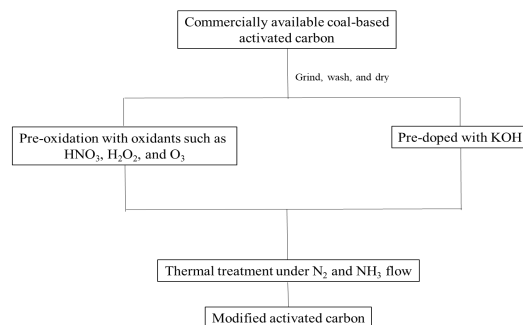


Fig. 8 Chemical modification of coal-based activated carbon conducted by Adelodun .

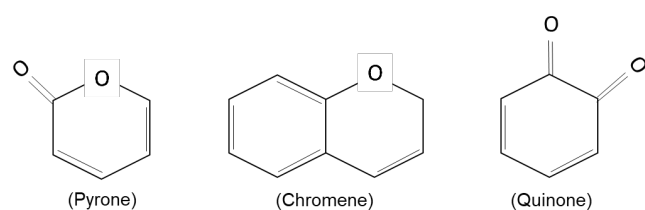


Fig. 9 Basic oxygen functionalities on carbon surface.

Characteristics and adsorption mechanism by coal-based adsorbents

A study conducted by Ariunaa using lignite coal liquefaction found that the residual carbon in lignite (lowest rank of coal) and solubilised in a solvent able to adsorb carbon dioxide, methane and nitrogen. Her study shows that, the surface of the residual carbon mainly dominated by aromatic, aliphatic and aromatic-aliphatic hydrocarbons and has several active adsorption sites which have a higher affinity for carbon

dioxide and methane. Carbon dioxide uptakes were found to be higher compared to other carbon materials such as carbon nanotubes and commercial activated carbon (Ariunaa et al., 2018). Despite the claim made by Ariunaa et al. the adsorption capacity of the adsorbent produced from lowest rank of coal has the lower adsorption capacity compared to other adsorption capacity achieved by several other types of adsorbents as presented in Table 5.

Studies by Adelodun et al., Ariunaa et al., and Dindi et al. shows that carbon dioxide binds to the activated carbon surface in a monolayer pattern which fit Freundlich isotherm. It was also found that physisorption was predominant for carbon dioxide adsorption as concluded in several studies (Adelodun et al., 2016; Ariunaa et al., 2018; Dindi et al., 2019). Physical adsorption to capture carbon dioxide involves weak intermolecular attraction and the kinetic follows pseudo-second order and usually operated at low temperature (Adelodun et al., 2016; Dindi et al., 2019). As mentioned, several treatments were conducted in previous literatures to enable chemisorption to takes place.

Table 5 Coal-based carbon dioxide adsorbent.

Carbon precursor	Method/s	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Adsorption capacity (mmol/g)	References
Fly ash	Functionalisation with amine	481	1.88	4.70	(Zhang et al, 2018)
Fly ash	Fly ash-amine composites	-	-	6.89	(Sarmah et al., 2013)
Commercial coal-based activated carbon	Pre-oxidation with HNO ₃ , Ca(NO ₃) ₂ , and Ca(Et) ₂ followed by thermal treatment	1428.2	0.664	2.50	(Adelodun & Jo, 2013)
Commercial coal-based activated carbon	Pre-oxidation with H ₂ O ₂ and O ₃ followed by thermal treatment	1295.4	0.61	0.26	(Adelodun, Lim, & Jo, 2014a)
Commercial coal-based activated carbon	Pre-doping with KOH follows by thermal treatment	1324	0.561	2.53	(Adelodun, Lim, & Jo, 2014b)
Commercial coal-based activated carbon	Surface modified activated carbon	1324	0.56	2.53	(Adelodun et al., 2016)
Lignite coal	Solvothermal treatment	176	-	1.88	(Ariunaa et al., 2018)

For physisorption, the pores presence on the surface governs the adsorption process. For microporous adsorbents such as coal-based activated carbon and chemically modified activated carbon, they typically exhibit Type I isotherm (Adelodun et al., 2016). Meanwhile, mesoporous adsorbents such as mesoporous silica synthesis in a study conducted by Zhang, they typically exhibit Type IV isotherm. In his study, adsorbent prepared from the extracted sodium silicate has smaller pore volume and pore size compared to the adsorbent prepared using commercial sodium silicate. However, incorporation of TMB as swelling agent is believed to produce adsorbent with larger pore volume and pore size (Zhang et al., 2018). Despite the enlargement of pores, the study was able to achieve good adsorption capacity of 4.7 mmol/g due to development of a structure resembling 'tree branches' which was believed to greatly enhanced the diffusion properties.

Adsorption capacity can be influenced by several factors and in most studies, the researches investigate the factors of temperature and pressure. Study conducted by Ariunaa reported that the selectivity of carbon dioxide over methane and nitrogen gradually increased when the pressure increased. Usually, as temperature increases, the amount of carbon dioxide adsorbed will be decreased. In contrary, the study reported that with PEI-impregnated adsorbent, the amount of carbon dioxide adsorbed increased at higher temperatures up to 75°C as PEI became more flexible and resulting in more carbon dioxide affinity sites. However, at higher temperature (higher than 90°C), desorption is favoured (Zhang et al., 2018).

Petroleum coke or pitch

Petroleum is also a naturally existing fossil fuel in yellowish-black liquid which commonly further refined into various types of fuels such as petrol and diesel. Along the oil refining process, a by-product known

as petroleum coke is generated. Petroleum coke is the non-volatile solid carbon residue material primarily composed of carbon but low levels of inorganic compounds. This by-product of the oil-refining process is a promising low-cost carbon precursor and has been used to make electrodes for steel and aluminium industry (Edwards, 2015). Other than that, petroleum coke is also widely used in several industries such as in cement plants and power plants (Chatziaras, Psomopoulos, & Themelis, 2016). Some advantages of this material are high fixed carbon content, low ash content, low volatile content, and the price of petroleum coke is cheaper by 33 % compared to coal (Yang et al., 2016). Therefore, petroleum coke is suitable to be used as the carbon precursor to produce carbon dioxide adsorbent.

Preparation process of petroleum-based adsorbent

Unlike other carbon precursors, pyrolysis of petroleum coke forms a material known as polycrystalline graphite which is non-porous. Therefore, it is not suitable to be used as carbon dioxide adsorbent. However, the activation process proved to enhance its characteristics. In general, all studies reviewed in this review, had activate the petroleum precursor with KOH. A study has been conducted to activate this pyrolysed material with KOH. Firstly, isotropic pitch precursor, which was obtained via condensation of the pyrolysed fuel oil was heated at 360°C for 5 hours. Then, the sample was activated with an aqueous solution of KOH of several weight ratios. The process of porous carbons preparation was conducted under N₂ environment (Lee et al., 2014). Other than that, a study also used nitrogen-doped activated petroleum coke which is synthesised by combining ammoxidation with KOH activation to adsorb carbon dioxide. Ammoxidation is a process where the sample is treated with ammonia and oxygen to generate surface nitrogen and oxygen groups (Yang et al., 2016). It is said that

as petroleum coke is heated, its porosity increases due to the creation of micro and macroporosity. Low-sulphur petroleum coke as the carbon precursor in the development of activated carbon dioxide adsorbent by KOH also has been done (Zhu et al., 2013).

Characteristics and adsorption mechanism by petroleum-based adsorbents

The untreated pitch precursor was reported to be non-porous material with very low specific surface area and pore volume of 2 m²/g and 0.008 cm³/g respectively. Significant increase in surface area and pore volume were observed for all activated pitch samples. Pore volume and micropore volume increased with an increasing amount of KOH until it reached its threshold. The study confirmed that micropore development occurred mainly in regions where the pore diameter is < 1 nm. The presence of abundant micropores enhanced carbon dioxide trapping and in results facilitate the diffusion of the gas inside the pore channels. Activated samples with the highest specific surface area, total pore volume, and micropore volume of 1442 m²/g, 0.593 cm³/g, and 0.504 cm³/g respectively have the highest carbon dioxide uptake of 11.28 mmol/g, the highest carbon dioxide adsorption capacity that has been reported in literature as shown in Table 6, compared to other types of adsorbents (Lee et al., 2014). Most studies that utilised petroleum-based activated carbon exhibit a typical Type 1 adsorption isotherm, which explain the nature of micropore adsorbent.

Table 6 Petroleum-based carbon dioxide adsorbent.

Carbon precursor	Method/s	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Adsorption capacity (mmol/g)	References
Pitch	Condensation and chemical activation with KOH	950-1442	0.59	11.28	(Lee et al. 2014)
Petroleum coke	Amoxidation and chemical activation with KOH	2329	0.94	4.57	(Yang et al. 2016)
Petroleum coke	Chemical activation with KOH	2413	-	3.45	(Zhu et al. 2013)

Surface area and pore volume of untreated petroleum coke in another study were also reported to be very low at 0.43 m²/g and 0.12 cm³/g respectively. Then, the activation process was again proved to be effective to enhance these characteristics. Activation time of the prepared samples will influence its characteristics and the effects are manifest in the carbon dioxide adsorption capacity of the particular sample. A study by Zhu et al. reported that the optimum activation time is 60 minutes for carbon dioxide uptake ability at atmospheric pressure. Drop in adsorption capacity at atmospheric pressure was observed at a when the activation time was reduced and no further enhancement was recorded when longer activation time was applied. On the other hand, at elevated pressure of 10 bar, it was reported that the carbon dioxide adsorption capacity was enhanced because as the activation time increased, the BET surface area also increased which is consistent with previous studies. Thus, it was concluded that the adsorption capacity at atmospheric pressure mainly depended on micropores structure, meanwhile at higher pressure, the adsorption capacity was controlled by BET surface area (Zhu et al., 2013)

Synthetic Polymer

Polymers are materials which consist of repeated structural units known as monomers. As mentioned in previous section, synthetic polymers are those chemically synthesised. Synthetic polymers are widely used, such as in the production of fabrics and bottles. Other than that, the synthetic polymer also has been widely used in the development of carbon dioxide adsorbent. There are several advanced porous materials which are available; porous organic polymers (POPs), porous aromatic frameworks (PAFs), porous polymer network (PPNs) and metal-organic framework (MOF). Among the polymers mentioned, POPs which can be synthesised from varieties of monomers are widely used in carbon dioxide adsorption. For instance, monomers that can be used are multidentate amines, aldehydes, carboxylic acids, and triazine monomers (Bhanja, Modak, & Bhaumik, 2019).

Amoxidation process was proved to be effective to introduce nitrogen species to the samples as after the process, nitrogen content increased from 0.20% to 8.34%. However, during the activation process, there might be decomposition or reaction of certain nitrogen species resulted in lower nitrogen content. Three types of nitrogen species as illustrated in Fig. 10; pyridinic-N, pyridonic-N, and quaternary-N were identified in all samples. Amount of pyridonic-N was higher compared to other nitrogen species and this nitrogen species has a more significant contribution to carbon dioxide adsorption.

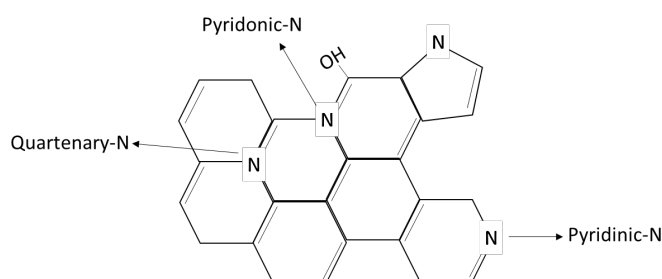


Fig. 10 Chemical structure of three nitrogen species; pyridonic-N, pyridinic-N, and quaternary-N.

Preparation process of synthetic polymer adsorbent

In preparation process of synthetic polymer adsorbents, the methods involved are more complex than other methods as listed in Table 7, compared to preparation methods that have been discussed in previous sections. It can be seen that carbonisation and activation of polymer are considered as a common practise in the preparation of polymer-based adsorbent. A study demonstrated the use of pre-oxidised polymer of polyacrylonitrile fibres (PAN) in preparation of activated carbon to have faster adsorption rate and higher adsorption capacity (Shen, Zhang, He, Li, & Fan, 2011). In another study by Seema, a polymer was produced from reduced-graphene-oxide, which involved several stages. The polymer was synthesised by dissolution of reduced-graphene-oxide with thiophene in chloroform, FeCl₃ and CHCl₃. After that, the polymer was mixed with methanol and after filtration of the mixture, the precipitate was washed with methanol before being treated with acid. Subsequently, chemical activation with KOH was conducted. The precipitates recovered after impregnation was heated in a tube furnace under N₂ atmosphere (Seema et al., 2014).

Furthermore, incorporation of nitrogenous groups into the activated polymer through direct and indirect methods has been conducted in several studies. Examples of indirect methods are impregnation of amine groups, reaction with nitrogen-containing reagents and thermal treatment with NH₃ gas. Meanwhile, in the direct method, it involves the utilisation of nitrogen-rich precursors. For instance, a study conducted by Sevilla has used a polymer known as polypyrrole as carbon precursor in the synthesis of N-doped porous carbon. The polymer which was distilled under N₂ was mixed with FeCl₃ and the precipitate obtained after filtration was activated with KOH as the activating agent (Sevilla, Valle-Vigón, & Fuertes, 2011). In another study by Wan, nitrogen-rich polybenzoxazine was synthesised via a soft-templating method in combination with KOH activation. The obtained benzoxazine monomer together with surfactant F127 was heated stepwise in an oven at a temperature of 120-260°C. Then, the cured polybenzoxazine was carbonised and activated with KOH. Both carbonisation and activation were conducted under nitrogen atmosphere (Wan, Wang, Feng, Sun, & Li, 2015).

Besides that, in another study, the introduction of extra carbon-source to another type of polymer which is porous aromatic framework (PAF) also has been investigated by grafting with sulfonic acid and mixing with furfuryl alcohol (FA). The adsorbed FA was catalysed by the grafted sulfonic acid to polymerise within the pores which successfully reduced the pore size of the adsorbent (Zhang, Li, Williams, Gao, & Ma, 2013). Above that, sulphur polymers, another type of polymers can be produced through several processes known as inverse vulcanizations and direct process at elevated temperatures. Inverse vulcanisation able to produce a stable polymeric material compared to the one produce via direct process. A study produced sulphur polymer by using dicyclopentadiene (DCPD) as the crosslinker and obtained a high surface area of 2200 m²/g. This polymer is not only suitable for carbon dioxide sorption but also H₂ as well as mercury and gold capture from water (Lee, Parker, Cooper, & Hasell, 2017).

Extensive crosslinking which act as stabiliser was included in the preparation of porous polymers to ensure that the structure does not collapse thus retaining its porosity which is important in the adsorption

of carbon dioxide. Among the crosslinker that have been used are diene, dicyclopentadiene, and dichloroxylene. A study by Mane conducted an investigation to determine the influence of crosslinker length to its adsorption performance (Mane et al., 2017). In the study, they concluded that small cross-linker used was able to increase the surface area and textural properties compared to the polymers with the use of long or without the use of crosslinker, which lead to a greater adsorption capacity.

The usual practise in the synthesis of porous organic polymer is the use of cross-linker. A study had developed a new family of POPs which is known as covalent organic polymers (COP); the extended polymer networks without the use of cross-linker to attain the porous structure of the polymer (Patel et al., 2012). Instead, they combine the mono-protic divalent nucleophiles with triazine which has high nitrogen content through rather simple method which only involves dissolution of monomers, washing, and drying process.

Table 7 Synthetic polymer carbon dioxide adsorbent.

Carbon precursor	Method/s	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Adsorption capacity (mmol/g)	References
Phenolic resins	N-doped carbonisation and chemical activation with NaNH ₂	2155	0.83	4.64	(Wang et al. 2018)
Polybenzoxazine	Soft-templating method and chemical activation with KOH	1257	0.63	4.02	(Wan et al., 2015)
Polyacrylonitrile fibre	Carbonisation and chemical activation with KOH	2231	0.76	4.40	(Shen et al., 2011)
Pyrrole	Polymerisation and chemical activation with KOH	3480	0.39	3.90	(Sevilla, Valle-Vigón, & Fuertes, 2011)
Dicyclopentadiene	S-doped polymerisation and chemical activation with KOH	2216	1.21	2.20	(Lee et al., 2017)
Porous aromatic framework	Introduction of new carbon source and carbonisation	1174	NA	4.1	(Zhang, Li, Williams, Gao, & Ma, 2013)
Polyaniline-based porous carbon	Thermal annealing of the polymer hydrogel and chemical activation	4196	2.26	28.30 (30 bar)	(He et al., 2016)
Covalent Organic Polymer (COP)	Dissolution of raw material followed by heat treatment	168	NA	1.36	(Patel et al., 2012)
Chloromethylbenzene (monomer) and diamines	Nucleophilic substitution reaction	99.9	0.073	1.42	(Sun, Kang, Shi, Jiang, & Liu, 2015)
Tris(chloromethyl)-mesitylene (TCM as monomer)	Friedel-craft reaction	1137.6	0.7	4.73	(Mane et al., 2017)
Tris(4-bromophenyl)-1,3,5-triazine-2,4,6-triamine (TPTT as monomer)	Palladium(0)-catalysed cross-coupling polycondensation	736	0.463	3.25	(Yao, Li, Wang, Xu, & Chang, 2018)
1,4-diaminobenzene	Reaction of monomer with phosphate esters in boiling ethanol	213.5	0.32	1.42 (100 °C, 40 bar)	(Satar et al., 2019)

Characteristics and adsorption mechanism by synthetic polymer adsorbents

Carbon dioxide adsorbents synthesised from synthetic polymers have good adsorption capacity as presented in Table 7. Polyacrylonitrile fibres (PAN) contain a large amount of nitrogen-containing groups which increase basic sites for carbon dioxide adsorption. Most synthetic polymer adsorbents exhibit Type I isotherm which indicates the microporosity nature of the adsorbents. Pore size plays a crucial role in carbon dioxide adsorption where the narrow pores can strengthen the interaction between pore walls and carbon dioxide molecules. Carbon dioxide molecules have been identified to be the size of 0.209 nm. Thus only materials with pores less than 1 nm are efficient for adsorption of carbon dioxide at atmospheric pressure (Seema et al., 2014).

Pre-oxidised activated carbon fibres have high selectivity for carbon dioxide than nitrogen, which is good as carbon dioxide adsorbent. From the study, they found out that it is more effective to

pre-oxidise the fibres prior to the activation. Activated carbon fibres produced from pre-oxidised fibres exhibit higher BET surface area and pore volume which are 2231 m²/g and 1.16 cm³/g respectively. The highest adsorption capacity of this adsorbent at 25°C is 4.4 mmol/g (Shen et al., 2011). Study conducted by Seema reported a quite similar observation where she found out that the surface properties of the activated carbon were enhanced and together with the elemental oxidised sulphur, higher adsorption capacity was obtained (Seema et al., 2014).

The polymer of polypyrrole exhibits a sponge-like structure which offers a large interfacial area to react with KOH and ensures the activation process occurred uniformly and resulting in good pore development. As temperature increases, enlargement of pores will occur as proved that at 600°C and 800°, the pore sizes were around 1 nm and 2.7 nm respectively. Therefore, changes in the adsorption isotherms were observed. Besides that, it was reported that the BET surface area and pore volume increased significantly at higher

temperatures and amount of KOH used. In contrary, as temperature and amount of KOH increases, nitrogen content decreased as nitrogen is oxidised and more easily removed during activation process compared to the removal of carbon. To obtain samples with high nitrogen content, the activation needs to be conducted at mild conditions as the basic N species can act as an anchor for carbon dioxide capture. The study proved that the activated samples under mild conditions have higher carbon dioxide uptakes as the samples have narrower porosity and considerably larger nitrogen content (Sevilla, Valle-Vigón, & Fuertes, 2011).

In a comparison of carbonised polybenzoxazine and activated polybenzoxazine, the specific surface area and total/micro-pore volume also greatly increased after KOH activation. It was reported in the study that the polymer can only be activated under 600°C as at higher temperatures over 700°C, K₂CO₃ will decompose into K₂O and CO₂. Results obtained from FTIR revealed the existence of C-N and N-H species in all prepared samples. Contrary to other studies, this study claimed that nitrogen species in the carbon network exhibited excellent thermal stability (Wan et al., 2015). Additionally, it was reported that pyridonic nitrogen is more stable under oxidising conditions such as in the activation process (Sevilla, Valle-Vigón, & Fuertes, 2011; Wan et al., 2015).

CONCLUSION

The diversity of choice in carbon dioxide adsorption is great as it provides researchers and industries to choose the type of adsorbent to be used depending on their particular needs and requirements. Carbon-based adsorbents from both renewable and non-renewable sources provide numerous advantages such as low cost, variety of forms, wide range of porosity, and feasibility of surface chemistry modification. However, utilisation of renewable materials in the development of carbon dioxide adsorbent is interesting as the possibility seems to be countless. Other than that, this practise can turn wastes into value-added products and directly alleviates problems associated with waste production. Furthermore, the availability of renewable sources is not affected by the consumption rate. On the other hand, non-renewable sources are available in limited quantities and consumption rate will disturb its availability in the long term and may pose negative effects especially to the next generation.

From the literature study, it was observed that the characteristics of the adsorbent from both types of materials are comparable and adjustable. Adjustment or modification can be done through several methods of preparation. The most common preparation method of carbon dioxide adsorbent is chemical activation, where the carbon materials are activated. This process is considered as simple and effective to prepare adsorbents with desirable characteristics. General properties to be considered as good adsorbent are high surface area, pore volume, small pore size, and presence of chemical functionalities such as oxygen, nitrogen, and sulphur. In most studies, involvements of both physical and chemical adsorption were reported. Enhancement of properties are proved to contribute to higher adsorption capacity. In conclusion, carbon-based adsorbents for carbon dioxide are numerous and versatile. Therefore, research and sustainable development of carbon dioxide adsorbent from different materials including the one that has never been used in the previous studies are anticipated.

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